Development of Microelectrode Techniques for Analytical Measurements

by

Nafeesa Simjee

Thesis
Submitted to the University of Warwick for the degree of
Doctor of Philosophy

Department of Chemistry
January 2003
To my family without whose support none of this would be possible.
Table of Contents

Acknowledgements .......................................................................................................... vi
Declaration ..................................................................................................................... vii
Abstract ....................................................................................................................... viii
Abbreviations ................................................................................................................ ix

Chapter 1  Introduction............................................................................................. 1
1.1 Dynamic Electrochemistry ............................................................................. 1
1.2 Ultramicroelectrodes ....................................................................................... 4
1.3 Hydrodynamic Ultramicroelectrodes ............................................................ 7
  1.3.1 Fast Flow Tubular UMEs .......................................................................... 8
  1.3.2 Channel UMEs .......................................................................................... 9
  1.3.3 Micro-dropping Mercury Electrode ........................................................ 13
  1.3.4 Microjet Electrode ................................................................................... 15
  1.3.5 Radial Flow Microring Electrode ............................................................ 18
1.4 Hydrodynamic Modulation Voltammetry .................................................. 21
  1.4.1 Electrode Motion Modulation ................................................................. 22
  1.4.1.1 Vibrating Wire and Microband Electrodes ......................................... 22
  1.4.1.2 Hydrodynamically Modulated Radial Flow Microring Electrode ...... 23
  1.4.2 Flow Modulation ..................................................................................... 24
  1.4.2.1 Hydrodynamically Modulated Microjet Electrode .............................. 24
  1.4.2.2 Stopped Flow Channel Electrodes ...................................................... 25
  1.4.2.3 Ultrasound ........................................................................................... 26
1.5 Scanning Electrochemical Microscopy ........................................................ 26
  1.5.1 Basic Principles of SECM ....................................................................... 27
  1.5.2 Modes of Operation ................................................................................. 28
  1.5.2.1 Feedback Mode ................................................................................... 28
  1.5.2.2 Generation / Collection ....................................................................... 31
  1.5.3 Imaging Using SECM ............................................................................. 32
  1.5.3.1 Tip Position Modulation ...................................................................... 34
1.6 Atomic Force Microscopy ............................................................................. 35
1.7 Aims ................................................................................................................ 37
References .................................................................................................................. 40

Chapter 2  Experimental ...................................................................................... 46
2.1 Ultramicroelectrode Fabrication .................................................................. 46
  2.1.1 Fabrication of 25 μm Diameter Pt UME ................................................. 46
  2.1.2 2 and 5 μm Diameter Pt Disc UMEs ....................................................... 48
  2.1.3 Double Barrelled 25 μm – 25 μm Diameter Pt UMEs ......................... 50
2.2 Chopped Flow MJE Instrumentation ......................................................... 51
| 2.2.1 | Electrochemical Detection | 51 |
| 2.2.2 | Optical Detection | 56 |
| 2.3 | SECM Instrumentation and Apparatus | 59 |
| 2.4 | TPM Instrumentation and Apparatus | 62 |
| 2.5 | AFM Instrumentation | 63 |
| 2.6 | Chemicals | 64 |
| 2.7 | Substrates | 65 |
| References | | 68 |

**Chapter 3**

**Scanning Electrochemical Microscopy Coupled With The Microjet Electrode**

| 3.1 | Introduction | 69 |
| 3.2 | Effect of Volume Flow Rate in the MJE System | 71 |
| 3.2.1 | Current Enhancement | 71 |
| 3.2.2 | Temperature Effects | 75 |
| 3.3 | Mass Transfer Imaging | 77 |
| 3.4 | SECM Investigation of the Effects Of Viscosity In The MJE System | 86 |
| 3.5 | Conclusions | 94 |
| References | | 97 |

**Chapter 4**

**Chopped Flow Microjet Electrode**

| 4.1 | Introduction | 98 |
| 4.2 | Electrochemical Detection Reference Signal | 102 |
| 4.2.1 | The Response Of Dual Disc UMEs In A MJE Arrangement | 102 |
| 4.2.2 | Convective Effects Arising From A Rotating Blade | 106 |
| 4.2.3 | Response of the Dual Disc Electrode To A Chopping Blade | 108 |
| 4.2.4 | Implementing Phase Sensitive Detection | 110 |
| 4.2.5 | Facilitating Trace Level Detection | 114 |
| 4.3 | Optical Detection Reference Signal | 117 |
| 4.3.1 | Practical Arrangement Of The Optical Detection System | 117 |
| 4.3.2 | Preliminary Experiments | 119 |
| 4.3.3 | Trace Level Detection Of IrCl$_6^{3-}$ | 122 |
| 4.4 | Conclusion | 126 |
| References | | 128 |

**Chapter 5**

**SECM Tip Position Modulation (TPM)**

| 5.1 | Introduction | 129 |
| 5.2 | Establishing TPM At Conductive and Insulating Surfaces | 131 |
| 5.3 | Applications of TPM | 144 |
| 5.3.1 | Band Electrodes | 144 |
Chapter 6 Carbon:Epoxy Composite Electrodes..............................................161
6.1 Introduction ...........................................................................................161
6.2 Voltammetry and Scanning Electrochemical Microscopy ......................163
   6.2.1 Voltammetry of Carbon:Epoxy Composite Electrodes.........................165
   6.2.2 SECM of Carbon:Epoxy Composite Electrodes ...................................172
6.3 Atomic Force Microscopy .......................................................................183
6.4 Conclusion .............................................................................................190
References ....................................................................................................193

Chapter 7 Overall Conclusions.........................................................................195
References ....................................................................................................199
Acknowledgements

I would like to extend my thanks to both Prof. Patrick Unwin and Dr. Julie Macpherson for supervising my PhD studies, for providing continued support over the past three years and for providing coherent feedback on my work.

I would like to thank all of the diverse members of the Warwick Electrochemistry Group. Thanks to the past members Nicki, Bex, Lou and Chris who helped me through my first and perhaps most challenging year. Thanks to my house/labmates Cat and Isabel, who have really supported me with their friendship over these past few years. Doug, thanks for explaining things to me in simple terms! I would like to extend my sincere thanks to Sue, you’ve been a brilliant friend, and have especially supported me throughout my PhD write-up! Thank-you Anna for your friendship and help with all things complex right from the start of my PhD. Thanks to Mark and Dave, who provided me with a source of non-stop comical entertainment and friendship both in and out of lab!

Thanks to everyone in the Mechanical, Electronic and Glassblowing workshops, all of whom have contributed greatly to the construction of the specially designed apparatus used throughout this project.

Finally, thanks Nick for your never-ending support, and encouragement, you’ve really made my years at Warwick fly by.
Declaration

The work contained in this thesis is entirely original and my own work, except where specifically acknowledged in the text. I confirm that this thesis has not been submitted for a degree at another university. Parts of this thesis have been published or submitted for publication with the following references:


Simjee, N., Macpherson, J. V., Unwin, P. R., Hydrodynamic Modulation Voltammetry with a Dual Disc Chopped Flow - Microjet Electrode, accepted for publication. *Electroanalysis.*
Abstract

This thesis describes the development and application of hydrodynamic modulation voltammetric (HMV) techniques coupled to ultramicroelectrodes (UMEs) that possess intrinsically high mass transport rates in quiescent solutions. This study demonstrates that the well defined convective-diffusive conditions of the microjet electrode (MJE) arrangement allows mass transport to be enhanced by almost two orders of magnitude compared to a 25 μm diameter disc-shaped UME. The MJE comprises a nozzle which is used to deliver solution to a UME surface at high velocity. Scanning electrochemical microscopy (SECM) with small UMEs has been used to image the hydrodynamics of the jet system with high precision. Variations in local mass transport for both IrCl₆³⁻ and Fe(CN)₆⁴⁻ oxidation at a range of flow rates has been observed at various positions within the impinging jet and the stagnation zone has been thoroughly characterised under a variety of experimental conditions. Agreement has been found between experiment and theory for voltammetric data recorded with the nozzle and UME aligned in the stagnation zone, for a range of viscous solutions examined.

By modulating the mass transport rate to the surface of an UME, in the MJE arrangement, by the introduction of a rotating blade between the end of the nozzle and the UME, it was possible to enhance the current sensitivity of the system. Trace level detection, to $2 \times 10^{-7}$ mol dm⁻³ IrCl₆³⁻ solution, was readily facilitated. This type of HMV experiment has utilised two methods to provide the reference signal for phase-sensitive detection of the current signal, involving either a dual-disc electrode or a single UME coupled to an LED detection system. Both HMV methods have been shown to work well.

Tip position modulation (TPM), in which an electrode is modulated vertically above a substrate surface, was used to enhance the resolution of conventional feedback SECM. The basic parameters controlling the TPM system have been investigated and the method has been used to image band electrode structures on insulating glass substrates, carbon:epoxy composite electrodes and of bovine articular cartilage. In all cases the merits of the approach compared to conventional SECM have been noted.

Cyclic voltammetry, SECM, and conducting atomic force microscopy (C-AFM) techniques were used to investigate the surface activity and resistivity of carbon:epoxy electrodes of varying thickness and composition. These electrodes are commercially significant as they are cheap and easy to produce and can be miniaturised readily for a variety of applications. It was shown that the behaviour of the composite depends greatly on their composition and thickness. It was determined that the thinnest electrodes (1 mm) containing the highest carbon content (60 carbon: 40 epoxy), behaved most similarly to macroelectrodes on the voltammetric timescales of interest. Conversely, a 2.5 mm thick 40 carbon: 60 epoxy blend, showed behaviour similar to an array of microelectrodes, and was found by C-AFM to have the greatest resistivity. C-AFM was used to provide images of the topography and conductivity of these samples. It was found that there were far more complete conducting pathways through the 60 carbon: 40 epoxy sample, then the 40 carbon: 60 epoxy. These distinct regions were related specific surface features and their dimensions were readily measured. These microscopic insights have provided information that allows the macroscopic behaviour of these electrodes to be understood readily.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
</tr>
<tr>
<td>AgQRE</td>
<td>Silver quasi reference electrode</td>
</tr>
<tr>
<td>CF-MJE</td>
<td>Chopped flow microjet electrode</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusion coefficient</td>
</tr>
<tr>
<td>DME</td>
<td>Dropping mercury electrode</td>
</tr>
<tr>
<td>DM$\mu$E</td>
<td>Dropping mercury microelectrode</td>
</tr>
<tr>
<td>ET</td>
<td>Electron transfer</td>
</tr>
<tr>
<td>GC</td>
<td>Generation collection</td>
</tr>
<tr>
<td>HA</td>
<td>Weak acid</td>
</tr>
<tr>
<td>HMV</td>
<td>Hydrodynamic modulation voltammetry</td>
</tr>
<tr>
<td>HPLC</td>
<td>High pressure liquid chromatography</td>
</tr>
<tr>
<td>HSCE</td>
<td>High speed channel electrode</td>
</tr>
<tr>
<td>H-UME</td>
<td>Hydrodynamic ultramicroelectrodes</td>
</tr>
<tr>
<td>$i$</td>
<td>Current</td>
</tr>
<tr>
<td>i.d.</td>
<td>Inner diameter</td>
</tr>
<tr>
<td>IDA</td>
<td>Interdigitated array</td>
</tr>
<tr>
<td>$i_{\text{MJE}}$</td>
<td>Limiting current at the MJE</td>
</tr>
<tr>
<td>$i_{\text{rms}}$</td>
<td>Root mean square current</td>
</tr>
<tr>
<td>$i_T$</td>
<td>Tip current</td>
</tr>
<tr>
<td>$i_{T\infty}$</td>
<td>Limiting current in quiescent solution</td>
</tr>
<tr>
<td>$i_{\text{UME}}$</td>
<td>Limiting current at the UME</td>
</tr>
<tr>
<td>$k_e$</td>
<td>Electron transfer rate coefficient</td>
</tr>
<tr>
<td>$k_i$</td>
<td>Mass transfer rate coefficient</td>
</tr>
<tr>
<td>LED</td>
<td>Light emitting diode</td>
</tr>
<tr>
<td>LSV</td>
<td>Linear sweep voltammetry</td>
</tr>
<tr>
<td>MJE</td>
<td>Microjet electrode</td>
</tr>
<tr>
<td>o.d.</td>
<td>Outer diameter</td>
</tr>
<tr>
<td>Ox</td>
<td>Oxidised form of a redox couple</td>
</tr>
<tr>
<td>Pt</td>
<td>Platinum</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------------------</td>
</tr>
<tr>
<td>RDE</td>
<td>Rotating disc electrode</td>
</tr>
<tr>
<td>Red</td>
<td>Reduced form of a redox couple</td>
</tr>
<tr>
<td>RFMRE</td>
<td>Radial flow microring electrode</td>
</tr>
<tr>
<td>RG</td>
<td>Characteristic dimensions of a UME</td>
</tr>
<tr>
<td>SECM</td>
<td>Scanning electrochemical microscope</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SG/TC</td>
<td>Substrate generation/Tip collection</td>
</tr>
<tr>
<td>SPM</td>
<td>Scanned probe microscopy</td>
</tr>
<tr>
<td>TG/SC</td>
<td>Tip generation/Substrate collection</td>
</tr>
<tr>
<td>TPM</td>
<td>Tip position modulation</td>
</tr>
<tr>
<td>UME</td>
<td>Ultramicroelectrode</td>
</tr>
<tr>
<td>$V_f$</td>
<td>Volume flow rate</td>
</tr>
<tr>
<td>WE</td>
<td>Working electrode</td>
</tr>
<tr>
<td>WTE</td>
<td>Wall tube electrode</td>
</tr>
</tbody>
</table>
Chapter 1 Introduction

This chapter outlines briefly the fundamentals of dynamic electrochemistry, and reviews ultramicroelectrodes (UMEs) and their application in hydrodynamic flow systems. An overview of the scanning electrochemical microscope (SECM) system is presented, followed by an introduction to a technique, tip position modulation (TPM), which implements the basic principles of SECM in a novel fashion.

1.1 Dynamic Electrochemistry

A general electrode reaction (Figure 1-1) occurs in a series of steps\(^1,2\) where the electroactive reactant molecule (e.g. in this case Ox) is transferred from the bulk of solution, at a concentration, Ox\(_{\infty}\), to the electrode surface, Ox', whereupon it undergoes electron transfer to produce a surface concentration of species Red'. The product then diffuses away to bulk solution, Red\(_{\infty}\). The overall rate of the electrochemical reaction is controlled by the slowest step in the reaction scheme. Hence, the rate can either be determined by the electron transfer (ET) kinetics, which is a surface limiting step, or by transport of reactants to the electrode surface, a mass transport-limiting step. In general, in order to determine the ET kinetics sufficiently high mass transfer rates are often necessary.
Under conditions where mass transport limits the rate of the reaction \( i.e. k_r \gg k_t \), the current (or electrode reaction rate), \( i \), flowing at the electrode surface (held under potential control) is given by equation 1:1.

\[
i = k_r nFAC^* \tag{1:1}
\]

Where, \( n \) is the number of electrons involved in the electron transfer process, \( F \) is Faraday’s constant, \( A \) is the area of the electrode, and \( c^* \) represents the bulk concentration of the species of interest \( \text{Ox} \).

In theory, mass transport of species to and away from an electrode surface can occur in any or all of the following three manners:

i. Diffusion (the movement of species down a concentration gradient);

ii. Migration (the movement of a charged species under the influence of an electric field gradient);
iii. Convection (the physical movement of fluid or solution).

Diffusion is always present in a dynamic electrode process, as the concentration of species at the surface of the electrode differs to that in bulk solution, resulting in the formation of a concentration gradient within a diffusion or boundary layer of thickness, $\delta$.

Application of a potential difference between two electrodes creates a potential field that extends from the electrode into the solution. The movement of charged species in response to this potential field is called migration. The distance the potential field extends from the electrode surface is controlled by the ionic strength of the solution. In order to minimise migration effects an excess concentration of an inert electrolyte, often called supporting or background electrolyte, is added to the solution. This shrinks the size of the electrical double layer to well within that of the diffusion layer, such that diffusion only mass transport dominates under practical conditions.

Convection is the movement of species due to external mechanical forces. Convection can occur inadvertently within a solution, in the form of vibrations from the laboratory environment, and is generally undesirable in this form as it is very often difficult to predict. It can be induced in a more controlled manner by bubbling gas through the solution or shaking the electrochemical cell concerned, or more precisely by flowing the solution over an electrode at a known rate. Forced convection generally enhances the mass transport process compared to diffusion only conditions. Laboratory experiments are usually carried out under conditions that are most amenable to mathematical description, such as employing an unstirred solution, which contains a large
concentration of supporting electrolyte, ensuring that diffusion is the only form of mass transport. Forced convection is used, but normally only when the hydrodynamics of the system can be well defined.

Mass transport to an electrode surface is most simply described under diffusion-only conditions. Under planar diffusion conditions, the flux of species arriving at an electrode surface, \( j_x \), may be defined by Fick's first law, equation 1.2.

\[
    j_x = -D \left( \frac{d[O]}{dx} \right)
\]

Where \( j_x \) is the flux of the species at position \( x \), \( (d[O]/dx)_x \) is the concentration gradient, and \( D \) is the proportionality constant known as the diffusion coefficient. The value of the diffusion coefficient typically varies between \( 10^{-5} \) and \( 10^{-6} \) cm\(^2\) s\(^{-1}\), and may be extracted from electrochemical current/voltage profiles.

1.2 **Ultramicroelectrodes**

Electrodes with characteristic dimensions in the micrometer or sub-micrometer range are known as ultramicroelectrodes (UMEs).\(^3,4,5,6,7\) The smallest electrode made to date has an estimated radius of ca. 10 Å, formed from the etching and subsequent insulation, of a microwire.\(^8\) UMEs can be fabricated with a variety of geometries including discs, rings, bands, arrays, and cylinders. Due to their small size, UMEs can be used in new environments with particular applications to biological and medicinal sciences.\(^9,10\) UMEs have been used successfully at low temperatures in solutions where the media becomes highly resistive.\(^11\) The small dimensions of UMEs enable electrochemical
measurements in minute volumes, and also allow the observation of discrete spatial events in microscopically small areas. UMEs have also been employed to make measurements in living systems such as recording oxygen gradients in cell tissue.¹²

UMEs are able to probe fast chemical reactions, as the diffusion layer is thin across the surface with a corresponding high concentration gradient. This results in an increased rate of mass transport.¹³ At short timescales, with the electrode held under potential control, biased at a potential sufficient to detect the species of interest at a diffusion controlled rate, the thickness of the diffusion layer is much less than the size of the electrode surface. Hence, the current observed is similar to that expected for planar diffusion. However, on longer timescales, as radial diffusion contributes, the dimensions of the diffusion layer can be much larger than the dimensions of the electrode, and the current approaches a steady-state as there is a large volume from which the molecules diffuse to support the current, and the process is dominated by spherical or radial diffusion⁴,¹⁴,¹⁵ as shown in Figure 1-2.

![Figure 1-2 Schematic to show the diffusion profiles at (a) a macroelectrode and (b) a microdisc electrode.](image-url)
The small area of UMEs results in small measured currents, usually within the nA - pA range. This is a favourable characteristic, as the solution $iR$ ohmic drop is very small. This enables the use of the two-electrode mode for electrochemical measurements and results in negligible ohmic effects, which can then allow solutions containing low concentrations of electrolyte, or poorly conducting media to be analysed. The double layer capacitance is also greatly diminished at UMEs due to the small area of the exposed electrode surface. The electrode potential can thus be varied rapidly, and resulting voltammetric measurements can be monitored on short timescales (micro- to nano-seconds).

The most commonly used geometry for an UME, is the microdisc electrode, due to its ease of construction. Under steady-state conditions, the bulk current, $i_{T\infty}$, flowing at a microdisc is defined by equation 1:3.

$$i_{T\infty} = 4naFDc^*$$  \hspace{1cm} 1:3

where $a$ is the radius of the microdisc electrode, and $D$ is the diffusion coefficient.

Disc-shaped UMEs are typically constructed by sealing the required metal wire, such as platinum or carbon fibre, in either a glass capillary or using epoxy resin. The surface can then be polished flat to expose a disc electrode surrounded by an insulator.
1.3 Hydrodynamic Ultramicroelectrodes

There are several techniques, both conventional and those that have been developed specifically, which are able to deliver high mass transfer rates under defined and controllable conditions. The simplest manner to increase mass transport to an electrode is to shrink the size of the electrode. Since the steady-state diffusion-limited current density at an UME depends on the reciprocal of the electrode radius (for a disc electrode)\(^{16}\) small electrodes promote fast mass transfer rates. In the absence of convection, for a disc microelectrode of radius \(a\), the rate of mass transfer to the electrode is inherently high and can be described by equation 1.4.\(^2\)

\[
k_t = \frac{4D}{\pi a}
\]

There have been several attempts to fabricate electrodes of overall dimension in the nanometer scale range,\(^{17,18,19}\) where the steady-state current response is largely uncomplicated by capacitative and resistive effects. However, there are questions over kinetic data obtained from these electrodes, as the geometry of the tip is difficult to ascertain. In many cases the geometry for nanometer scale electrodes must be assumed, thus voltammetric data can be misinterpreted.\(^{20,21,22}\)

The deployment of UMEs in convective systems to produce hydrodynamic ultramicroelectrodes (H-UMEs) represents an alternative and attractive approach for achieving enhanced and variable mass transfer rates under steady-state conditions.\(^23\)

The basic idea is to use micrometer-scale electrodes that can be reproducibly fabricated and characterised with high precision in well-defined hydrodynamic systems. Solution is either passed over the electrode surface, or the electrode is moved with respect to the solution to allow species to reach the electrode surface by convection and diffusion.
Thus, mass transport can be controlled and varied over a wide dynamic range. Four main systems have resulted to date, which have enabled a broad range of rate constants to be measured\(^\text{24}\): (i) fast-flow tubular and channel microelectrodes\(^\text{25,26,27,28,29,30,31}\); (ii) a micro-dropping mercury electrode \(^\text{32,33,34,35}\); (iii) a microscopic wall-tube electrode, termed the microjet electrode (MJE) \(^\text{36,37,38,39}\) and (iv) a radial flow micro-ring electrode (RFMRE)\(^\text{40,41}\).

### 1.3.1 Fast Flow Tubular UMEs

The fast flow tubular microelectrode was one of the primary techniques employed to achieve high steady-state mass transport rates by using the combination of a microelectrode and a convective flow system.\(^\text{25}\) The experimental apparatus, Figure 1-3, is based on a standard three-electrode configuration, where the working and reference electrodes comprise thin metal rings 100 \(\mu\text{m}\) in width, separated by a gap of 50 \(\mu\text{m}\), in a tubular cell (typical dia. 0.22 cm). In some studies, working electrodes as short as 7 \(\mu\text{m}\) in width have been used.\(^\text{25}\) A recirculating flow system pumps solution from a reservoir into the flow cell, via a tube system, and then back into the reservoir.

The maximum achievable flow rate is 66 cm\(^3\) s\(^{-1}\) and mass transport for this system is characterised by Reynolds numbers up to 2 \(\times\) 10\(^5\), so that flow is turbulent, but quantifiable.\(^\text{27}\) This system has also been used to study reasonably fast heterogeneous electron transfer kinetics, and the rates of homogeneous reactions coupled to heterogeneous electron transfer.\(^\text{25-27}\) The standard rate constant for the ferro-ferricyanide redox couple in 0.5 mol dm\(^{-3}\) aqueous K\(_2\)SO\(_4\) was determined to be 0.12 cm s\(^{-1}\) (assuming a transfer coefficient of 0.5). Investigations of homogeneous kinetics focused on simple model systems of the EC and catalytic-EC' type.
1.3.2 Channel UMEs

The channel flow cell set up consists of an electrode embedded in one wall of a rectangular cell over which electrolyte solution flows (Figure 1-4). The embedded electrode sits flush to its surroundings, so that only the geometry of interest is exposed to the solution flow. The cell can be adapted to fit micro, macro or band electrodes. A typical channel flow cell consists of a base plate and a top plate constructed from an inert substance such as Teflon or resin. The two sections can be joined together producing a distance of normally less than 1 mm, through which the solution flows. The electrode is positioned in the centre of the base plate, allowing a distance of at least 1 mm from each of the sides of the cell, to minimise any “side edge effects”, and to ensure a constant velocity over the width of the cell. Solution is either mechanically pumped through the cell, or flowed through using a gravity feed system. After passing

Figure 1-3 Schematic of a fast-flow tubular microelectrode set-up, where the arrows indicate the direction of flow.
the electrode in the cell, the spent solution flows directly to waste, to avoid stagnant solution building up in the system.

Figure 1-4 Schematic of a typical channel flow cell arrangement, incorporating a band electrode.

The most common channel flow electrode is the band electrode. In this case the channel flow arrangement is defined by the dimensions $x_e$ and $w$ which represent the thickness and the width, respectively. The total width of the channel flow cell is denoted $d$. The distance between the plane bearing the electrode and the roof of the cell is denoted $2h$. These dimensions are illustrated in Figure 1-4.

The practical arrangement of the channel flow set-up is usually set such that $2h<\ll d$, and $w<d$, so that the electrode sees a two-dimensional Poiseuille laminar flow profile. This type of hydrodynamic electrode offers many advantages when applied to analytical systems, given the well-defined flow characteristics of the system. The channel flow electrode can be used when continuous online analysis is required, or for mechanistic investigations of electrode processes. It is also possible to use the channel flow system for spectroelectrochemical studies without modification to the cell, or by irradiating the surface of the electrode photoelectrochemical studies can be performed. Under well defined, laminar flow, steady-state conditions, the transport-limited current
flowing at the channel flow electrode is given by the Levich equation 1:5 where $V_f$ is the volume flow rate.

\[ i = 0.925nF_e \sigma D^{2/3}V_f^{1/3} \left( \frac{h^2d}{3x} \right)^{1/3} \]

Under laminar flow conditions, $V_f$ can be varied easily, which results in the rate of mass transport being controllable over a well-defined range. Variations in the cell depth or the electrode length within the range of microns to millimetres can also control the rate of mass transport. The geometry of the cell can therefore be manipulated to give the optimum rate of mass transport for a given application.

Microband electrodes are often preferred over macroband electrodes in channel flow cells due to the higher mass transport rates, which can be probed with a smaller ohmic drop. Channel microband array electrode systems have recently been used to investigate complex electrochemical reaction kinetics. This method involves a system where up to thirteen electrodes varying in size are placed in order of decreasing length, in a channel flow cell enabling a whole range of mass transport rates to be probed at one flow rate. A gravity feed system was used to flow electrolyte solution through the cell. Under steady-state conditions, the diffusion-controlled current at each electrode, for a given $V_f$, obeyed equation 1:5. This system was used to probe the heterogeneous electron transfer kinetics of electrode processes, including one-electron processes ($E$ reactions), and systems involving coupled homogeneous chemistry of differing time scales. Three-dimensional hydrodynamic voltammograms have been acquired by Chao and Huang using a 32-microband electrode array system, and the system has been successfully employed to detect phenolic compounds, where good linearity was obtained in the concentration range of $10^{-4}$ and $10^{-8}$ mol dm$^{-3}$.52
To further increase the range of timescales accessible to H-UME techniques, a high-speed channel electrode (HSCE) has been developed. This system functions in the same way as normal channel flow experiments except that flow over a narrow microband electrode occurs at high sheer rates (up to $3 \times 10^6 \text{ s}^{-1}$). This is achieved through the use of a specially-designed high-pressure flow system, capable of delivering volume flow rates up to $10 \text{ cm}^3 \text{ s}^{-1}$ through a cell which has dimensions: 2 mm (width), 0.1 mm (height), and 2 mm (length) as shown in Figure 1-5. With these cell dimensions and flow rates, mass transport coefficients approaching $1 \text{ cm s}^{-1}$ can be achieved using a 10 $\mu$m long microband electrode.28

![Figure 1-5 Schematic of the high-speed channel flow cell, in both a (a) perspective view and a (b) cross sectional view.](image-url)
Early experiments utilising the HSCE were conducted on the one-electron oxidation of ferrocene in dimethylformamide, to characterise mass transport. A gold microband electrode, 12 μm in length was used together with solution flow rates up to 3.5 cm$^3$ s$^{-1}$. Steady-state transport-limited currents were found to be dependent on the cube-root of volume flow rate, $V_f$, in agreement with the Levich equation (1:5) for a conventional channel flow cell operating under fully-developed Poiseuille (laminar) flow conditions. Studies of the solid/liquid interface with the high speed channel electrode system have also been conducted, where the rapid dissolution of solid $p$-chloranil, induced by the reaction of hydroxide ions was investigated. The HSCE has been also applied to several redox systems characterised by relatively fast heterogeneous electron transfer kinetics. Studies were typically conducted under steady-state conditions and standard rate constants extracted by conventional mass transport-corrected Tafel plots.

1.3.3 Micro-dropping Mercury Electrode

The dropping mercury microelectrode (DMμE) technique evolved from "conventional" dropping mercury electrode (DME) experiments carried out with a deliberately damaged capillary, which was found to produce microdrops (typical radius 50 μm). The apparatus for DMμE experiments is akin to the DME, with the working electrode comprising mercury microdrops that are expanded up to a final radius in the range 40-80 μm, along with a mercury pool auxiliary electrode and a reference electrode. Experiments are carried out in a temperature-controlled environment. The $V_f$ of mercury can be calculated from the weight of mercury collected over a certain time period, while the drop time (typically 2 - 5 ms) is measured using an oscilloscope, from
Chapter 1

the working electrode current output. The fast drop times inherent in the DMµE allow the use of more rapid potential scan rates than for the conventional DME. It is possible to study fast kinetics using this system due to the short time scales involved, resulting in high concentration gradients within the thin diffusion layer adjacent to the electrode.33

Two methods have been suggested for preparing capillaries suitable for the production of microdrops.32 The exploded capillary method involves the use of a standard DME capillary and a pool of mercury. These are placed in a conducting electrolyte solution, typically 1 M aqueous potassium chloride, and a voltage pulse of 50 - 200 V is applied for one second or less. As the mercury heats up in the capillary tube, an orifice on the side of the capillary (near the tip) is produced by explosion. The explosion method can be repeated until the optimum drop size is produced. The second method involves grinding a blunt capillary at an oblique angle, typically less than 45° between the polishing plane and the longitudinal axis of the capillary. By varying the internal diameter of the capillary, and the polishing angle, it is possible to manipulate the drop time and size down to 2 ms and 40 μm radius, respectively.34

The main applications of the DMµE are the study of kinetic parameters of reactions and probing surface charge densities at these electrodes, as the short drop times lead to much higher charging current densities than at the conventional DME which serves to minimise errors from the presence of electro-reducible or -oxidisable impurities. A consequent drawback of the DMµE is its ineffectiveness to measure concentrations below 10⁻⁴ M, because of the high charging current.33
Mass transport to the DMµE is complex, however, the mean Faradaic current has been shown to be similar to that of a normal DME, so that established methods can be used to analyse data. Due to the high mass-transfer coefficients attainable, it has been estimated that standard rate constants up to 0.5 cm s\(^{-1}\) can be measured, which are twenty times higher than with a conventional DME.\(^1\)

1.3.4 **Microjet Electrode**

The microjet electrode (MJE) (Figure 1-6) consists of a high velocity jet of electroactive solution, which is fired from a capillary (nozzle) onto the surface of a disc UME (typical dia. 25 µm or less).\(^{36,38}\) Mercury hemisphere UMEs, which are formed by depositing mercury onto conventional disc UMEs have also been used in the MJE.\(^{39}\) The nozzle for the MJE is produced by pulling a borosilicate glass capillary to a fine point using a micropipette puller, and then polishing the end flat to expose the desired internal diameter (typically 25 – 100 µm).

![Figure 1-6 Photomicrograph of a typical MJE arrangement.](image-url)
Depending on the flow rate required, either a syringe pump, HPLC pump\textsuperscript{37,38} or a gravity feed system\textsuperscript{36} is used to fire solution through the nozzle onto the electrode surface at predetermined rates. The nozzle is held in a custom built holder, and can be translated above the UME, which is fixed in position to the cell base, to achieve the highest possible mass transport limited current. Alignment can be achieved by either using a simple manually controlled $x,y,z$ micropositioning stage or a higher resolution piezo controlled positioning stage. This latter approach has been used to image the fluid flow profile of the impinging jet,\textsuperscript{37,39} using scanning electrochemical microscopy (SECM), although these measurements were limited as a 25 $\mu$m diameter electrode was used.\textsuperscript{54,55}

A characteristic of the MJE arrangement is that the nozzle diameter is significantly greater than that of the UME, thus resembling a miniature wall-tube electrode (WTE),\textsuperscript{56,57} rather than a wall jet electrode.\textsuperscript{1} The hydrodynamics of the MJE system are based on an impinging jet electrode. This comprises a submerged circular jet of electrolyte solution which flows incident onto a flat surface. For the purpose of the MJE experiments the flat surface comprises a metal disc surrounded by glass insulator. The flow profiles of a jet colliding with a surface can be characterised by four flow regimes (Figure 1-7).

The first distinct region, 1, occurs when the solution leaves the capillary and the flow profile changes from pipe flow to free flow. The flow is then able to mix with the surrounding solution, and this zone extends in the downstream direction to give a distinct conical potential core. The established flow section is region 2, where the velocity profile is well established. This leads to region 3, which is a layer of fluid from
the jet that moves from the axial region to radial flow. This is known as the stagnation region, where it is assumed that the mass transport rate is constant, similar to that found in rotating disc experiments. Homann was first to describe a mathematical solution to the boundary layer flow in this region. The fourth region is the wall-jet region where the radial velocity of the solution starts to decay and the boundary layer increases with radial position from the centre of symmetry.

![Diagram of an impinging jet on a planar surface]

**Figure 1-7 Schematic to show the flow profile for an impinging jet on a planar surface.**

It has been demonstrated that the steady-state mass transport rate to the surface of a 25 μm diameter platinum disc UME can be enhanced by two orders of magnitude using the MJE configuration. This is an ideal characteristic for the study of fast reaction kinetics. The MJE has been used to measure the standard rate constant for the ferro/ferrocyanide redox couple, and has been applied to study CE processes, specifically the electro-reduction of weak acids (HA) in aqueous solution.
For the MJE the transport-limited current has been found to depend on the square root of the solution flow rate, and under laminar flow conditions it can be defined by the following (1:6):

\[
\frac{i_{MJE}}{i_{UME}} = \beta \left[ \frac{H}{d} \right]^{0.054} \left( \frac{\pi}{4} \right)^{1/2} a D^{-1/3} v^{-1/6} d^{-1/2}
\]

where \( i_{MJE} \) is the limiting current at the MJE, \( i_{UME} \) is the limiting current recorded in a quiescent solution at the UME, \( v \) is the kinematic viscosity, \( H \) is the distance between the electrode and the capillary nozzle, \( d \) is the internal diameter of the capillary nozzle, \( \beta \) is a constant, and \( \bar{U} \) is the mean solution velocity, which may be determined from the volume flow rate, \( V_f \), by application of equation 1:7:

\[
V_f = \pi \left( \frac{d}{2} \right)^2 \bar{U}
\]

High solution flow rates can be attained with relatively small volumes of solution, when using MJE's, by simply varying the nozzle diameter. This is a considerable advantage over the channel flow geometry, which requires high-pressure systems with large solution reservoirs. Contamination of the electrode surface in the form of products building up is prevented, as the jet serves to continuously wash the electrode surface during measurement.\(^{37}\)

1.3.5 Radial Flow Microring Electrode

The radial flow microring electrode (RFMRE) is a novel H-UME that can attain steady state mass transport coefficients in excess of 2 cm s\(^{-1}\), with low volume flow rates.\(^{40}\)

The arrangement of the electrochemical cell, depicted in Figure 1-8, consists of a nozzle
(typical i.d. 100 µm) through which solution flows, positioned 5 – 40 µm away from an inert planar substrate using micropositioners. There are two different arrangements that are commonly used, either with the microring electrode on the capillary or with the ring positioned on the substrate underneath the capillary. Effectively, a thin layer radial flow cell is achieved, as the solution flowing out of the capillary nozzle is forced radially into the gap. Solution is flowed through the cell using either a syringe pump or HPLC pump. Thin ring electrodes have approximately 100 times more effective diffusional areas than disc electrodes, thus intrinsically high mass transport rates, which help to lower the detection limit in analytical applications.41

Figure 1-8 Schematic of the RFMRE in a configuration where the ring is on the capillary.

Platinum ring electrodes are fabricated by painting a platinum organometallic paint on the outside of a borosilicate glass capillary that has been pulled to a fine point, and then firing to leave a thin film of Pt adhered to the glass surface. The sides of the ring electrode are then insulated using a resin, and a flat surface exposed by polishing. Different ring thicknesses can be attained by varying the number of coats of paint applied to the capillary. Typically, one coat results in an approximate ring thickness of ca. 200 nm, and three coats result in ca. 500 nm thick ring.23,40
The geometry of a microring is desirable as an electrode, as mass transport in quiescent solution is governed by its thickness, whereas its circumference controls the magnitude of the current. Thus, a thin, large diameter ring is preferred to maximise both of these factors. Mass transport to the RFMRE is similar to that of a channel flow cell operating under laminar flow conditions, with $2h$ as the distance between the glass substrate and ring capillary electrode, $x_e$ is equivalent to $(b-a)$, the exterior-interior radius of the ring, and $w$ is equivalent to $d$, the channel width. However, importantly, the nozzle height can be manipulated \textit{in-situ}, as well as the flow rate, in order to vary the rate of mass transport.

A series of steady-state voltammograms were obtained from experiments performed at a constant flow rate, and the nozzle / electrode distance, $h$, varied between 5.8 and 17.8 $\mu$m. It was determined that as $h$ was decreased, the solution was forced radially across the electrode at increased velocities, resulting in a larger flux of electroactive material at the surface of the electrode. The increases in limiting current measured indicate that mass transfer coefficients up to a maximum of 2.3 cm s$^{-1}$ could be achieved. A rotating disc electrode would have to rotate at speeds in excess of $3.7 \times 10^6$ Hz, to achieve similar mass transfer rates. This value is almost five orders of magnitude larger than the maximum speed in commercially available rotating disc electrode systems.

Owing to the high mass transfer rates attainable, RFMRE voltammetry has been used to investigate rapid heterogeneous electron transfer processes, where it was estimated that standard rate constants up to 20 cm s$^{-1}$ could be distinguished from reversible redox processes through steady-state measurements.
1.4 Hydrodynamic Modulation Voltammetry

In hydrodynamic modulation voltammetry (HMV),\textsuperscript{60,61,62,63,64} the mass transport rate to an electrode surface is periodically oscillated. This general approach enables the mass transport controlled component of a current signal to be separated from the background component, which is usually associated with surface processes, as well as double-layer charging. This can be achieved by either varying the flow rate over the electrode surface or by modulating the electrode with respect to the solution.\textsuperscript{60} HMV is thus recognised as an attractive option for extending detection limits and increasing the potential window of a solvent.\textsuperscript{65} The use of high modulation frequencies in HMV reduces the detection time and enhances sensitivity. The manner in which HMV enables trace level measurements, where the signal would usually have been masked by background processes, can be understood from the following equations (1.8).

\begin{align*}
    i_{\text{high}} &= i_{MT,\text{high}} + i_{bg} \\
    i_{\text{low}} &= i_{MT,\text{low}} + i_{bg} \\
    \Delta i &= i_{MT,\text{high}} - i_{MT,\text{low}} \tag{1.8}
\end{align*}

Here, $i_{\text{high}}$ and $i_{\text{low}}$ are the currents observed at high and low mass transport rates respectively, e.g. a switch between flow and no flow conditions. $i_{MT,\text{high}}$ and $i_{MT,\text{low}}$ are the mass transport components of the signal at high and low transport rates, and $i_{bg}$ is the summation of the current attributed to the background processes. This is assumed to be mass transport independent and is constant. $\Delta i$ is the difference between the high and low mass transfer currents, and the overall equation shows that $\Delta i$ is independent of background processes. In practice, higher sensitivity is achieved by using phase sensitive detection methods to extract the current at the frequency of perturbation of mass transport, rather than dc methods.
The hydrodynamic ($\tau_H$) and diffusional ($\tau_D$) relaxation times play an integral role in HMV, and control the maximum frequency rate of the current modulation. Typically, the hydrodynamic relaxation time is much shorter than that of diffusion, \(^{59,60}\) thus experimentally the overall relaxation time can be related directly to the rate of diffusion across the concentration boundary layer. This relaxation time is controlled by $D$ for the electroactive species and the mass transport properties of the system. By employing smaller electrodes and higher mass transport rates it is possible to decrease $\tau_D$. Hence, diffusion coefficients can also be determined using HMV.\(^{60}\)

### 1.4.1 Electrode Motion Modulation

Classical HMV methodology developed around the rotating disc electrode (RDE). Here, the rotation rate of the electrode is periodically modulated between two well-defined extremes.\(^{66,67,68,69}\) This has enabled the measurement of low detection limits such as $4 \times 10^{-8}$ mol dm\(^{-3}\) for ascorbic acid,\(^{70}\) and $1 \times 10^{-8}$ for ferrocyanide,\(^{66}\) in an aqueous phosphate buffer. However, advances in this technique have been hampered by the low modulation frequency and poor response time of the motor used.

#### 1.4.1.1 Vibrating Wire and Microband Electrodes

Vibrating a wire,\(^{71,72}\) or a microband\(^{75}\) electrode has proved to offer low detection limits in amperometric measurement. Vibrating a wire electrode produces a very simple hydrodynamic system, with detection limits achieved as low as $1 \times 10^{-8}$ mol dm\(^{-3}\) for ferrocene.\(^{73}\) The arrangement used in this case was a 25 µm diameter platinum wire (3 mm length), vibrated at a high modulation frequency in the range of 80 – 160 Hz. The higher frequencies lead to better discrimination against electronic background
noise. The effect of varying the geometry of the wire, on the modulation efficiency and the hydrodynamic profile close to the electrode, has also been investigated.\textsuperscript{73,74}

Vibrating microband electrodes have been employed for the detection of chlorine in water, with detection limits in the range of $3 \times 10^{-7}$ mol dm\textsuperscript{-3}. The electrodes are simple to construct and can be fabricated with a high degree of reproducibility.\textsuperscript{75} The microband electrodes show similar enhancements in signal to the vibrating microwire electrodes, and the system has been found to be less sensitive to background vibrations.

1.4.1.2 Hydrodynamically Modulated Radial Flow Microring Electrode

The mass transport properties of the RFMRE were described earlier, where the mass transport-limited current could be enhanced by decreasing $h$ (at constant volume flow rate), and was shown to be defined by the Levich equation. A schematic of the RFMRE arrangement is shown in Figure 1-8. For a given ring electrode thickness, mass transport at the RFMRE surface can be modulated in two ways, by either (i) varying $h$, which involves modulating the position of the capillary nozzle using a piezoelectric positioner at constant $V_f$, or (ii) by varying $V_f$ at a given $h$. It was determined to be experimentally easier to periodically modulate $h$ (typically $\pm 2 - 9 \ \mu m$) perpendicular to the substrate, about a central position, at a constant flow rate. By coupling this system to in-phase detection, it was possible to detect $\text{Ru(bipy)}_3^{3+}$ in 0.1 mol dm\textsuperscript{-3} KNO\textsubscript{3} solution, at a concentration of $1 \times 10^{-5}$ mol dm\textsuperscript{-3}, whereas the dc current signal in either quiescent or flow conditions was masked by electrolysis of the electrolyte solution\textsuperscript{59,60}
1.4.2 Flow Modulation

Modulating the flow of solution to, or over, an electrode surface has been used successfully in HMV. This has considerable advantages over other non-flow HMV techniques including low sample consumption, and the ability to facilitate on-line detection. Initial studies were based upon pulsing the flow of solution through either a channel-shaped or tubular electrode, where measurements were made based on the difference in steady state current between flow and stopped flow. Typical detection limits of $1 \times 10^{-7}$ mol dm$^{-3}$ were attained. Although these detection levels are reasonable, mass transport rates were found to be low, as it was necessary to employ lengthy cycling times to attain the maximum steady-state current-difference signal. Thin layer cells were developed to shorten relaxation times. These thin layer cells were used in conjunction with pulsed flow techniques, but were only found to function well between pulse rates of 0.5 and 2 Hz. Outside this range the current signal was attenuated.

1.4.2.1 Hydrodynamically Modulated Microjet Electrode

The microjet electrode can also be employed as a hydrodynamically modulated technique. This arrangement offers high mass transport rates, and fast diffusional response times. Modulations are achieved by oscillating a jet of solution, over the surface of a microdisc electrode. The capillary is modulated parallel to the electrode surface (Figure 1-9). When the jet is aligned directly over the surface of the electrode, high mass transport rates are acquired through convective-diffusion. The jet is then moved away from the electrode until the jet stream completely (although experimentally this is almost) misses the electrode, and mass transport is then largely dependent on diffusion alone. By modulating the jet between the two extremities of mass transport, it is possible to discriminate against non-mass transport processes. Experimental detection
limits as low as $5 \times 10^{-8}$ mol dm$^{-3}$ for Ir(Cl)$_6^{2-}$ have been achieved, by modulating the position of the nozzle by ± 30 µm, at a frequency of 1 Hz.$^{78,62}$

![Figure 1-9 Schematic of the hydrodynamically modulated MJE arrangement.](image)

1.4.2.2 Stopped Flow Channel Electrodes

Stopped channel flow is a technique, first developed in the 70's,$^{76}$ in which the flow is suddenly halted and the resulting current-time profile is measured for the electroactive mediator present in the solution. The diffusion coefficient of the solution species can then be determined without prior knowledge of the concentration of the test solution. The system has been characterised for a channel microband electrode with electrochemical detection and shown to support theory for the diffusion-controlled oxidation of a test solution of ferrocyanide.$^{79}$
1.4.2.3 Ultrasound

Ultrasound can be used in electrochemistry as a means of increasing the rate of mass transport, by introducing convection to the system.\(^8^0\) Early methods involved pulsed ultrasonic agitation of the solution under investigation, which results in acoustic streaming. An ultrasonic probe was located typically 1 cm above the working electrode, and the limiting current with and without the pulse was recorded.\(^8^1\) Tiny microjets of solution are produced by ultrasound, by the formation and collapse of bubbles. This is known as transient cavitation, and can lead to an increase in mass transport rates. Transient cavitations can, however, erode electrode surfaces, and this phenomenon can be difficult to model mathematically.\(^8^2\)

1.5 Scanning Electrochemical Microscopy

The scanning electrochemical microscope (SECM) is a scanned probe microscope (SPM)\(^8^3,8^4,8^5\) technique. The probe is an UME, and the resulting image attained using this technique is dependent upon the electrochemical response between the electrode and the substrate of interest.\(^5^4,8^6,8^7,8^8,8^9\) Images of the substrate, which contain topographical, chemical and electrochemical information, are obtained by recording the tip current as a function of position. Thus, SECM has been used to investigate a variety of interfacial processes such as electron transfer rates at metallic electrode surfaces,\(^9^0\) etching of semiconductor substrates,\(^9^1\) creating polymer modified electrodes,\(^9^2,9^3\) imaging biological materials,\(^9^4,9^5\) and measuring electron transfer rates across liquid/liquid interfaces.\(^9^6,9^7\) In each case, the resolution of the image acquired is limited by the diameter of the UME used.
1.5.1 **Basic Principles of SECM**

SECM images are obtained by immersing the tip, which acts as the working electrode, into an electroactive solution together with a reference and auxiliary electrode. The tip is typically an UME, and is more commonly an amperometric\(^\text{86-88}\) rather than potentiometric\(^\text{19,54}\) probe. For imaging purposes the probe is brought close to the substrate (typically \(d \approx a\)), where it is then moved at a fixed height in a raster fashion, over the sample surface, and the current flow is measured as a function of the tip position. The position of the UME is controlled by piezo positioners that facilitate movement across the surface with sub-micrometer resolution, in the \(x, y,\) and \(z\) axes. A method to construct an UME was described briefly earlier, and a more detailed description is given in Chapter 2. For SECM investigations it is important to ensure the tip is flat, so that it is possible to hold the tip close to the substrate\(^2\) and the \(RG\), defined as the ratio of the radius of the overall probe to the radius of the electrode, is approximately ten for modelling purposes. If the substrate is a metal or semi-conductor, it may form part of a bipotentiostat circuit and function as an electrode, alternatively insulating or biological substrates are often fixed to the base of the electrochemical cell (Figure 1-10).\(^{86}\)

![Figure 1-10 Schematic of a typical SECM arrangement.](image-url)
1.5.2 **Modes of Operation**

Amperometric UMEs are usually used for SECM investigations, typically a disc UME is placed in solution at a large distance away from the substrate surface (Figure 1-11), and is held at a potential sufficient to either oxidise or reduce the electroactive species of interest present in the solution at a diffusion controlled rate. Thus, hemispherical diffusion is observed to the electrode, as described earlier for diffusion to UMEs. A steady-state current flow in bulk solution, $i_{T_\infty}$ is observed, the magnitude of which is described by equation 1.3.16,98

![Figure 1-11 Hemispherical diffusion to an UME, when the electrode is positioned in solution far from the substrate surface. The case where an oxidised species, Ox, is reduced at the electrode is depicted.](image)

1.5.2.1 **Feedback Mode**

SECM can be used to obtain information about the activity and topography of a substrate surface. This can be achieved by using “feedback mode”, where the tip is located within a few radii of the surface. 86,99,100
When an electrode is held at a potential sufficient to induce diffusion of the species in solution, and it is moved close to an inert substrate surface (Figure 1-12a), the hemispherical diffusion to the electrode becomes hindered. The resulting tip current, $i_T$, decreases. This phenomenon is known as “negative feedback” where $i_T < i_{T,\infty}$ and at very small tip-substrate separations $i_T$ tends to zero. When the tip is scanned over the insulating substrate, in feedback mode, any changes in the tip current can be related to changes in the distance between the tip and substrate, $d$, and therefore, information about the sample topography can be deduced.¹⁰¹

When a conductive sample is to be investigated using SECM, an increase in tip current is observed as the tip approaches the substrate surface, i.e. $i_T > i_{T,\infty}$. The smaller $d$ becomes, the larger the observed tip current. This is termed “positive feedback” (Figure 1-12b), and is observed because the conducting substrate is biased at a potential governed by the redox species present in solution, to enable conversion of the reduced species back to its oxidised form. This results in an increase in the flux of oxidised species reaching the electrode surface, and subsequently an increase in current.¹⁰²

![Figure 1-12 Schematic diagram to show the different feedback modes of operation of the SECM.](image)

(a) Demonstrates negative feedback mode, where diffusion is hindered to the electrode, and (b) positive feedback mode, where there is increased flux of the oxidised species at the electrode, due to the conductive or redox active substrate.
From the two distinct types of feedback in SECM, it can be seen that the magnitude of the tip current response is directly governed by the nature of the substrate, and the distance between the tip and substrate.\textsuperscript{54} This response was first modelled by Kwak and Bard\textsuperscript{99} over a range of $d$ values for disc shaped UMEs, although this model has been extended to other electrode geometries, such as conical or spherical tips.\textsuperscript{2}

More recently, there have been further developments of this model to examine the effects on the SECM system for finite electron transfer kinetics of the surface of the electrode.\textsuperscript{90,103,104,105} It is, therefore, possible to determine the nature of a substrate by plotting $i_T$ as a function of the tip position. For any electrode this is achieved by measuring an "approach curve", which simply involves recording $i_{T\infty}$ and then moving the tip, at a steady rate, closer to the substrate surface, until it touches the surface. The experimental data can be compared to theory to determine both the nature of the substrate, and the distance of closest approach of the tip.

Figure 1-13 illustrates the theoretical steady-state approach curves to an insulating and a conducting substrate, where the distance has been normalised by the electrode radius, $a$, and the current response has been normalised by $i_{T\infty}$. 
Feedback mode has been applied to a range of applications including the high resolution etching of and corrosion of metal surfaces and semiconductors where the tip induces local dissolution.

1.5.2.2 Generation / Collection

Generation / Collection (GC) is an alternative mode of use of the SECM depicted in Figure 1-14. The most commonly used method is known as substrate generation/tip collection (SG / TC). Here, a UME is held at a potential sufficient to monitor the flux of a species generated by or near the substrate surface, thus producing a concentration map of the electroactive species in solution. The first reported use of electrodes to monitor surface reactivity at macroscopic electrodes was by Engstrom et al. The SG/TC mode has been used to investigate differences between diffusion coefficients for the oxidised and reduced forms of a redox couple, and to study EC-type
mechanisms. It is also possible to generate short-lived intermediates at the tip and collect the generated species at a substrate (TG/SC).
activity or surface information, respectively. Usually, a second electroactive species is added to the solution, which does not interfere with the surface processes. Recent advances in SECM imaging have included the use of smaller electrodes, digital image processing, shear force, and constant current imaging to improve resolution. Constant current mode operates using a closed loop electronic circuit and a mechanical servosystem, to maintain a constant tip current, by adjusting the substrate/tip distance. This has a distinct advantage over constant height imaging mode, as the tip is less liable to crash into the sample surface when held at small separation distances, should there be a large change in the topography of the sample, or a sample tilt. Where a uniformly active substrate is investigated, the technique is simple to implement, however, if a sample has heterogeneous surface activity i.e. it has both conducting and insulating regions, the tip is liable to crash into the surface as it moves from one region of surface activity to the other.

Another derivation on the original scheme of SECM, is a technique which uses the hydrodynamic forces which are created between a vibrating tip and substrate, to control the distance between the two, whilst imaging the surface. Here, the vibration of the amperometric tip is monitored using a photodiode that detects a laser beam shining at the tip. The tip height above the sample can be adjusted according to the diffraction signal recorded, thus enabling a form of SECM constant current imaging mode. Non-amperometric probes have been used in SECM which were operated in a shear force based constant-distance mode.

The simplest method by which to address topographical resolution issues is by the fabrication of small SECM probes. There have been several attempts to miniaturise
SECM tips, however, as the probes become smaller the fabrication of the tips becomes more difficult,\textsuperscript{130} as does characterisation of their geometry, as already mentioned briefly.\textsuperscript{131} These tips were implemented in order to improve current resolution, and to measure the surface topography independently using a force sensing cantilever. Initial atomic force microscopy (AFM) and SECM imaging experiments were conducted by using platinum coated AFM tips. These probes were used to provide high resolution topographical and electrochemical images of solution filled track etched membranes.\textsuperscript{132} Unique SECM-AFM probes have been recently designed and characterised by Macpherson \textit{et al}.,\textsuperscript{133} which are based on etched wires, the fabrication of which is described in Chapter 2 (section 2.5).\textsuperscript{19,134} These probes enable high-resolution topographical AFM images to be recorded simultaneously alongside electrochemical activity of a substrate surface. One disadvantage of this method is the sensitive fabrication procedure, which affects the ability to manufacture reproducible probes. However, these probes are extremely versatile, and have been used to electrochemically induce dissolution at the surface of a single crystal, map the surface of an UME, and probe diffusion through micropores.\textsuperscript{135}

1.5.3.1 Tip Position Modulation

The ability to simultaneously resolve the topography and reactivity of a substrate surface is a fundamental conundrum of SECM, as discussed earlier. Wipf \textit{et al.} proposed a new variant on SECM imaging, tip position modulation (TPM),\textsuperscript{136} in order to differentiate between insulating and conducting regions of a surface, showing variations in surface topography. In TPM, the tip was sinusoidally modulated, at a specific amplitude about a mean position, and the resulting current signal analysed using a lock-in amplifier. As the tip was moved towards a conducting surface an
increase $i_T$ would be observed, however over an insulating region, $i_T$ would decrease. Thus, the phase of the recorded signal shifts by $180^\circ$ depending on the conducting nature of the surface. By simply recording the in-phase component of the signal at the modulation frequency, it is possible to extract information about the nature of the surface.\textsuperscript{136}

TPM has been used to image the surface of an interdigitated array (IDA) electrode, where the insulating regions were found to be significantly more resolved when compared to SECM images of an identical area.\textsuperscript{136} TPM has also been coupled to a constant current imaging mode of SECM with an auto-switching circuit.\textsuperscript{126} This has provided information about the different regions of gold, both the electrically connected and isolated regions, that make up a composite electrode.\textsuperscript{137}

1.6 Atomic Force Microscopy

AFM\textsuperscript{138} (Figure 1-15) is a modern technique that has enabled the study of surfaces, irrespective of sample conductivity, at an atomic level. This procedure was primarily developed to improve upon scanning tunnelling microscopy (STM), which is limited to conducting or semi-conducting surfaces, as it relies on a tunnelling current between the sample and the probe. Similarities do exist between the two techniques, in that a sharp probe is used to scan the sample surface. However, in AFM a cantilever is used to sense the forces between the sharp probe and the surface. The deflection of the cantilever is monitored using a laser that is focused on its mirrored beam, which is detected by a position sensing diode.\textsuperscript{139} Thus, the tip/substrate separation distance can be maintained at a constant distance through a feedback mechanism. To achieve atomic scale resolution it is crucial to perform experiments using a sharp tip. Commercial probes are
available that are made of silicon or silicon nitride, however, it is possible to fabricate home-made tips, as described in Chapter 2 (section 2.5).

The main mode of use in AFM is the contact mode, and this is typically operated with the tip in constant contact with the sample surface. The tip is firstly lowered towards the surface of the sample, until a pre-determined repulsive-force is reached, whereupon an image of the sample is acquired whilst maintaining a constant force via a feedback mechanism.

For biological or other types of fragile samples, tapping mode was developed. Here, the tip is scanned at a constant height, whilst vibrated over small amplitudes at its resonance frequency. As the probe is scanned across a surface, changes in the tip/substrate separation distance cause a change in frequency and phase of the vibration. This mode has been used to image many types of sample including cartilage, DNA and biological cells.
1.7 Aims

The goals of this work are to extend the analytical applications of UMEs in both flow systems and SECM, primarily through the development of new modulation methods and the extension of existing methods. After a description of the general experimental details in Chapter 2, Chapters 3 and 4 consider the microjet electrode, while Chapters 5 and 6 discuss applications of SECM.

It has been demonstrated, earlier in the introduction, that the ability to increase mass transport rates to an electrode surface is of significant importance. In Chapter 3 the investigation of mass transfer from an impinging jet, containing an electroactive species, onto the surface of various UMEs is described. The system used is the microjet electrode. This is followed by an investigation of jet hydrodynamics using the scanning electrochemical microscope. In contrast to earlier studies, small UMEs are utilised to provide finer information on local mass transport rates. These results are compared to a recent finite element model, which aims to extend the description of mass transport beyond the empirical treatment embodied in equation 1:6. The effects of varying the temperature and viscosity of the mediator solution on the diffusion coefficient, and jet flow are investigated experimentally and compared to theoretical models.

With a knowledge of the hydrodynamics, Chapter 4 describes a novel hydrodynamically modulated technique, the chopped flow microjet electrode (CF-MJE). This is a device that has specifically been developed to vary mass transport to the surface of an UME at periodic intervals, using a thin rotating semi-circular blade, positioned between the nozzle and the electrode in the MJE system. The use of the CF-MJE device enables detection of electroactive species at trace levels, by discrimination of background
processes that normally obscure small current signals. Two detection systems were
developed to monitor the frequency of modulation. The first to be tested was an
electrochemical detection method, employing a dual-disc UME, where one electrode
was used to detect the electroactive species in solution, and the other to monitor the
modulation frequency. A second, optical detection system was found to be far simpler
to use. Again an UME was used to detect the electroactive species in solution, but an
LED and photodiode were used to monitor the frequency of the rotating blade. Trace
level detection has been facilitated using both of these systems, and the relative merits
are discussed later.

Tip position modulation, a technique that further increases the resolution of SECM, is
discussed in Chapter 5. The implementation and characterisation of the technique is
first discussed, where experimental results are modelled to ensure that these
observations correlate to those of Wipf et al. who pioneered this technique. It is
shown that the response is quantitative for positive feedback and even negative
feedback, provided that modulation frequencies are not too high in the latter case. TPM
is finally used to investigate different substrates, including band electrodes and
cartilage, the results of which are compared to images recorded using conventional
SECM.

Chapter 6 is an investigation of novel carbon:epoxy composite electrodes. These
carbon based devices are cheap, easy to fabricate and have easily renewed surfaces, thus
are suitable for a diverse range of applications where robust electrochemical sensors are
required. The voltammetry of different blends and thicknesses of the electrodes are
initially investigated. This is followed by a thorough investigation of the different
electrodes, using SECM, TPM, AFM, and SEM techniques to characterise their surface activity and topography. These microscopic measurements are used to provide a greater insight into the origin of macroscopic cyclic voltammetric measurements carried out with these electrodes. These studies serve to demonstrate the capabilities of UMEs, in particular, in characterising electrodes of practical importance.
References


Chapter I

Chapter I

79 Evans, N. J., Martin, R. D., Unwin, P. R., paper in preparation.


Chapter 2 Experimental

This chapter describes the experimental methods developed and employed in the work described in this thesis. The fabrication of ultramicroelectrodes (UMEs) is described, followed by a description of the apparatus used for the chopped flow microjet electrode (CF-MJE); the scanning electrochemical microscope (SECM); tip position modulation (TPM), and atomic force microscopy (AFM) studies.

2.1 Ultramicroelectrode Fabrication

2.1.1 Fabrication of 25 µm Diameter Pt UME

The fabrication of UMEs was based on procedures first reported by Wightman and Wipf, and Bard and co-workers. To fabricate a 25 µm Pt UME, a borosilicate glass capillary (o.d. 2 mm, i.d. 1.16 mm, Harvard Apparatus, Kent, U.K.) was pulled to a fine point using a vertically mounted, gravity operated pipette puller (Narishige, Japan). The tip of the capillary was trimmed using a knife for glass cutting and sealed by melting, using a Bunsen burner flame.

A length (approx. 10 mm) of platinum wire (dia. 25 µm Goodfellow, Cambridge) was positioned inside the capillary, such that it rested against the sealed tip. Air was evacuated from the capillary, by placing it under vacuum for 20 minutes. Whilst still under vacuum, the tip of the capillary was lowered into a resistively heated nichrome wire coil (annealed Ni80Cr20, 0.75 mm diameter wire, Goodfellow, Cambridge) to seal the glass around the microwire. By removing air from the capillary it was possible to melt the glass around the wire without the introduction of bubbles at the
glass/microwire interface, which may otherwise have hindered the performance of the electrode.

An electrical connection was made to the sealed microwire by placing a slug of solder (length approx. 10 mm, 60:40 tin:lead alloy, R.S. Components, Corby) into the capillary, followed by a length of stripped, tinned copper wire (length approx. 100 mm, R.S. Components). The solder was then melted to form an electrical connection between the two wires. The open end of the capillary was sealed using Araldite Rapid (Ciba-Geigy, Cambridge), to stabilise and protect the copper electrical connection.

The surface of the electrode was exposed by polishing the sealed end on a coarse Carbimet paper disc (600 grit, Buehler, Coventry). The dimensions of the exposed electrode surface (platinum and glass) were measured using an optical microscope (Olympus BH2 light microscope with Nomarski differential contrast interference objectives, range × 50 to × 1000 magnification). A finer grit Carbimet disc (240 grit, Buehler) was used to further polish the surface of the electrode, followed by a succession of diamond impregnated pads (between the range of 1 and 6 μm, Buehler) to produce a mirror-like finish to the surface. To ensure a flat surface, the pads were adhered to a home-built polishing wheel, and the electrode position, with respect to the pad, controlled using micropositioners. The electrode surface was finally polished gently on a microcloth polishing pad (Buehler) coated with a slurry of alumina (0.05 μm gamma alumina, Buehler).

After polishing, the glass around the electrode surface was “coned” on a 600 grit pad to produce the desired disc-shaped tip as shown in Figure 2-1, where the \( RG \) of the
electrode was 10. The $RG$ of an electrode is defined as the ratio of the radius of the overall probe (electrode plus surrounding glass), $r_{\text{probe}}$, to the radius of the electrode, $a$, i.e. $RG = r_{\text{probe}}/a$.

![Diagram of a typical 25 μm diameter Pt disc UME.](image)

Figure 2-1 Schematic of a typical 25 μm diameter Pt disc UME.

2.1.2 **2 and 5 μm Diameter Pt Disc UMEs**

The construction method for 2 and 5 μm diameter Pt UMEs was similar to that described previously for the larger UMEs. However, microwires of this size are only available in the form of Wollaston wire (Goodfellow, Cambridge). In this form, the Pt was surrounded by a sheath of silver that had to be removed prior to forming a seal between the Pt and glass. This was achieved by cutting a length (15 mm) of the Wollaston wire, and folding one end over into a hook shape. This was then pushed to the bottom of an open-ended borosilicate glass capillary (Harvard, Kent), which had been pulled to a fine point. The hook worked simply to stop the microwire from falling from the bottom of the capillary. Nitric acid (≈ 69% conc., BDH) was then used to
dissolve the coating from the bottom section of the microwire. This was accomplished by drawing the acid up into the capillary to just below the level of the hook, and then, after a few seconds, removing the solution out by dabbing the open end of the capillary on a tissue. After each nitric acid treatment, distilled water was used in the same manner to clean the microwire. After at least twenty successive nitric acid/water treatments, the state of the microwire was checked under a light microscope (Olympus BH2). The treatment was continued until all of the Ag coating had been removed from the surface, and the Pt microwire was fully exposed. Acetone was drawn into and expelled from the capillary several times to remove any traces of residue, and the capillary was left to dry in an oven (60 °C, 20 min). The tip of the capillary was sealed in a Bunsen burner flame, after which air was evacuated from the capillary using a vacuum pump. Whilst under vacuum, the tip was lowered into a heated coil, so that the glass melted to form a bubble-free seal around the microwire. A connection was made to the microwire, and the surface was polished flat, and coned to an $RG$ of 10, as described in section 2.1.1. A typical optical micrograph of a 5 μm diameter Pt UME is shown in Figure 2-2.

Figure 2-2 Schematic of typical 5 μm diameter Pt UME, and optical light micrograph of the surface of a 5 μm diameter Pt UME.
2.1.3 **Double Barrelled 25 μm – 25 μm Diameter Pt UMEs**

The dual disc UME (see Figure 2-3) was constructed by sealing two 25 μm diameter platinum wires (Goodfellow, Cambridge) in a "theta" glass capillary (i.d. 0.75 mm / half section, overall o.d. 2.0 mm, Harvard Apparatus), using a similar method to that described elsewhere\(^3\)\(^4\) and in section 2.1.1 for single disc UMEs. Here, two pieces of Pt microwire were required for the construction of each double-barrelled electrode, and these were placed in separate compartments of the glass capillary. On completion, the electrodes were typically 200 μm apart (centre to centre), which ensured negligible overlap of the diffusion fields for steady-state amperometric detection under quiescent conditions and convective-diffusion control.\(^1\) The insulating glass surrounding the two electrodes was polished so that both electrodes lay equidistant from the outside edge of the glass sheath. This was achieved by carefully polishing the insulator on a 600 grit pad (Carbimet paper discs, Buehler) until the overall probe diameter was 450 - 500 μm. The dimensions of the probe were measured accurately (± 1 μm) using an optical microscope.

![Figure 2-3 Optical micrograph (a) of the surface and schematic (b) of a double barrelled 25 μm diameter Pt-Pt disc UME.](image)
2.2 Chopped Flow MJE Instrumentation

2.2.1 Electrochemical Detection

The apparatus shown in Figure 2-4 was developed specifically for the CF - MJE experiments. The main additional features of the device, compared to the original MJE system,\textsuperscript{5,6,7,8} are a rotating blade that is situated between the nozzle (i.d. 100 μm) and electrode assembly. The latter was either a double-barrelled dual-disc Pt (dia. 25 μm) - Pt (dia. 25 μm) UME or a single UME, bearing an optical detection system (described later). The rotating blade was used to modulate mass transport to either a single or dual Pt disc UME, in order to facilitate trace level measurements of analyte species, using in-phase detection.

![Diagram of apparatus with labels](image-url)

\textsuperscript{5} Ag-Quasi Reference Electrode
\textsuperscript{6} Pt-Gauze Counter Electrode
\textsuperscript{7} Bi-Potentiostat
\textsuperscript{8} Personal Computer
\textsuperscript{9} Lock-In Detector
\textsuperscript{10} Motor
\textsuperscript{11} Solution
\textsuperscript{12} x y z micropositioning stages
\textsuperscript{13} Nozzle
\textsuperscript{14} Blade
\textsuperscript{15} Video Microscope
\textsuperscript{16} 25 μm Diameter Pt Dual Working Electrode

(a)
The semi-circular blade (36 mm dia.) used in this investigation (Figure 2-5(a)) was laser cut from stainless steel (0.5 mm thickness, Goodfellow, Cambridge, U.K.), and attached to a drive shaft which was positioned through the base of the cell, using a stainless steel screw. The edges were polished to a mirror finish using a range of polishing abrasives (Buehler, Coventry, U.K). A series of different blade sizes were tested during the course of these investigations and they are also depicted in Figure 2-5.
Figure 2-5 A photograph of the different blade sizes that were employed to modulate flow to the surface of the UMEs. Blade (c) was determined to possess the optimum geometry and thickness for these investigations. Each of the blades tested was 0.5 mm thick, and either (a) = 72 mm, (b) and (c) = 36 mm, or (d) = 18 mm in diameter.

The nozzle was produced by drawing a borosilicate glass capillary (1.16 mm i.d., 2.0 mm o.d., Harvard Apparatus, Kent, U.K.) to a fine point using a vertical micropipette puller (Narishige PB7, Tokyo, Japan). The tip of the nozzle was polished flat as described for the UME construction, in section 2.1.1. Views of a typical nozzle are shown in Figure 2-6. Construction of the dual disc UME was described in section 2.1.3.

Figure 2-6 Optical micrographs of a typical borosilicate nozzle (100 µm i.d., 120 µm o.d.), where (a) is an end on view of the nozzle outlet, and (b) is a side view.
For the MJE measurements, the nozzle was supported in a home-built capillary holder mounted on a 3-axis translation stage (3 x model 461 stages in an x, y, z configuration, Newport Corp., Newbury, U.K.). A differential micrometer (model DM-13) controlled the movement of the nozzle in the z-direction, normal to the electrode surface, whilst x and y movement was regulated using AJS-1 fine adjustment screws.

The chopped flow cell, shown in Figure 2-4(a), and in further detail in Figure 2-7, consisted of a fully detachable Teflon base, and a cylindrical glass body with a total volume of 25 cm³. The glass body contained an overflow pipe through which excess solution drained into a waste vessel. An optical window (1.5 cm dia.), incorporated within the glass cell allowed use of a zoom video microscope with a CCD camera attachment (on screen resolution of 2.2 μm per pixel) to aid the alignment of the nozzle above the dual UME. The cell base contained a small hole (2 mm dia., located 5 mm away from the wall of the glass body) to allow the probe containing the working electrodes to be securely fixed in position below the blade. A larger, centrally-located hole accommodated the drive shaft for the rotating blade.

The entire experimental assembly was placed on a Newport CSD series breadboard positioned inside a home-built Faraday cage. This apparatus was located on a granite block with vibration isolation incorporated.
All voltammetric measurements were made in a four-electrode arrangement, with a silver wire serving as a quasi-reference electrode (Ag-QRE), a platinum-gauze auxiliary electrode, and the dual Pt-Pt disc probe as two working electrodes. Electrochemical measurements were made using either an Oxford Electrodes bipotentiostat (Oxford, UK) and voltage scan generator or a model EI-400 bipotentiostat (Cypress Systems, Lawrence, Kansas, USA) with a high gain preamplifier. The latter was used specifically when picoampere-level currents were detected. In-phase detection of the amperometric signal for the analyte of interest was accomplished using a Stanford Research Systems lock-in amplifier (model SR810 DSP, California, USA), with the reference signal obtained from the second amperometric UME, in the dual Pt-Pt probe. The voltammetric data were recorded using QuickBasic software written in-house on a Lab-PC-1200 data acquisition card (National Instruments, Austin, Texas).
A hybrid 1.8° step angle size model 17 stepper motor (RS Components, U.K.) controlled by a Unipolar, 2A stepper motor controller (Astrosyn, U.K.) connected to the shaft via a drive belt (Figure 2-4) was used to turn the blade at controlled speeds. The blade was used to interrupt electrolyte flow from the nozzle to the surface of the working electrodes, so producing a defined change in mass transfer simultaneously to each electrode. Flow of the electrolyte solution was delivered at a constant volume flow rate using a precision dual drive syringe pump (model no. U-74900-15, Cole-Palmer Instrument Company). All measurements were made in an air-conditioned laboratory (23 ± 0.5 °C).

2.2.2 Optical Detection

Optical detection was developed specifically for CF-MJE experiments, as an alternative method to the dual-disc electrochemical detection system, to monitor the blade rotation frequency. In this case, a simple LED, located in the Teflon base of cell, was used in combination with a homebuilt photodiode detector, that was suspended above it. As illustrated in Chapter 4, this provided a stable reference signal for the location of the rotating blade, used to facilitate phase sensitive detection. Detection of the analyte of interest was accomplished using a single 25 μm diameter Pt disc UME as the working electrode. The CF-MJE cell, described in 2.2.1, was adapted to accommodate the unique optical detection device and is depicted in Figure 2-8.
The flow cell base for these measurements, shown in Figure 2-9, incorporated a hole through which the UME could be inserted into the cell, as described in section 2.2.1. A larger, centrally located hole accommodated the drive shaft for the rotating blade, and a LED (dia. 5 mm, Farnell Components) was set alongside the electrode opening using black epoxy (potting compound, RS Components, UK). Black epoxy resin was used specifically to focus the light from the LED to the detector. A photodiode detector (Farnell Components) was clamped directly above the LED (100 mm separation), and the alignment verified, using an oscilloscope (Tektronix TDS 210 oscilloscope, RS Components) to detect the position at which a maximum light intensity was recorded.
A 25 μm diameter Pt UME and a 100 μm i.d. nozzle were used in these studies. The fabrication of both have been described in sections 2.1.1 and 2.2.1, respectively.

![Figure 2-9 Photograph (top view) of the cell base used for the optical detection set-up.](image)

The entire experimental assembly was placed on a Newport CSD series breadboard within a home-built Faraday cage. This apparatus was located on a home-built vibration isolation table. All voltammetric measurements were made using a simple triangle wave pulse generator (Colburn Instruments, Coventry, U.K.), with the addition of a patch clamp amplifier (PC-501A, Warner Instruments Corporation), modified for voltammetry to facilitate low current detection for trace level analysis. A simple two-electrode system was used with a silver wire serving as a quasi-reference electrode (Ag-QRE) and a disc UME as the working electrode. In-phase detection of the amperometric signal for the analyte was accomplished using a Stanford Research Systems lock-in amplifier (model SR810 DSP, California, USA), with the reference signal obtained from the photodiode. Voltammetric data were acquired using a PC.
Chapter 2

equipped with a National Instruments Lab-PC board (Austin, Texas) and software written in-house.

2.3 SECM Instrumentation and Apparatus

Conventional SECM\textsuperscript{9,10,11,12} involves the movement of a probe UME close (typically within \(\mu\)m) to the surface of the substrate of interest. This methodology is well established and both feedback and substrate generation / tip collection modes\textsuperscript{13,14} were used to investigate the surface activity of carbon/epoxy composite electrodes, described in Chapter 6. For mass transfer imaging measurements of the MJE profile (Chapter 3), a SECM was used to scan the jet nozzle at a constant height, over the surface of a fixed UME, as shown in Figure 2-10. The nozzle was supported in a home-built capillary holder, attached to a piezoelectric positioner (model no. P-843.30, Physik Instrumente, Waldbronn, Germany) which was used to control movement of the nozzle in the \(z\)-direction (normal to the UME) over a maximum expansion of 45 \(\mu\)m. The piezoelectric positioner was mounted on a translational stage (M-015.00, Physik Instrumente), controlled by a differential micrometer (model DM-13). This facilitated a larger range of movement in the \(z\)-axis (25 mm) with micrometer resolution. Movement of the \(x\) and \(y\) stages, to which the nozzle was also connected, was achieved using DC-mike drives (M223.21 Physik Instrumente), controlled via a signal processor (C-852, Physik Instrumente) and 2-axis DC motor controller cards (C-842.20, Physik Instrumente). The positions of each axis were determined by digital encoders (MT25, Heidenhain, Germany) with a resolution of 0.1 \(\mu\)m. The entire experimental assembly was placed on a Newport CSD series breadboard within a home-built Faraday cage. This apparatus was located on a home-built vibration isolation table.
Two electrochemical cells of different dimensions were employed to facilitate SECM mass transfer imaging. Preliminary studies used a cell similar to that developed for chopped flow studies, described in section 2.2, where the total volume of the cell was 25 cm$^3$. Later, a larger custom built experimental cell (Figure 2-11) was developed in
order to minimise possible convection effects from the walls of the cell that might contribute to the current images, of the MJE flow profile. The large cell comprised of a fully detachable Teflon base, which was attached to a cylindrical glass body (diameter 10.4 cm). The total volume of the cell was approximately 380 cm$^3$.

A zoom video microscope with a CCD camera attachment (on screen resolution of 2.2 $\mu$m per pixel) was used to aid the alignment of the nozzle above the UME. The UME was positioned through a small hole (2 mm dia.) in the base of the cell, so that it protruded approximately 1.5 cm above the bottom of the cell, but was submerged below the level of the solution. The cell could be drained by simply removing excess solution using a syringe (50 cm$^3$, BDH Laboratory Supplies, UK), prior to each experiment.

![Figure 2-11 Photographs of the large cell used for SECM imaging experiments: (a) Teflon cell base and (b) the glass body.](image)

For SECM mass transfer imaging, measurements were made in a two-electrode arrangement, with a silver wire serving as a quasi-reference electrode (Ag-QRE), and a Pt disc UME as the working electrode. Electrochemical measurements were made
using a triangle wave-pulse generator (Colburn Electronics, Coventry), and a home-built current follower (gains of $10^{-5}$ to $10^{-9}$ A/V). Data were recorded using a Lab-PC-1200 data acquisition card (National Instruments, Austin, Texas).

For SECM studies of carbon:epoxy composite electrodes SECM, it was necessary to apply a bias to both the 2 µm diameter Pt UME used for imaging and to the substrate electrode, in order to obtain feedback and substrate generation / tip collection data. Measurements were made using a bipotentiostat (model CH1730A, CH Instruments Inc., USA) functioning in a four-electrode arrangement. The Pt UME served as the working electrode, the carbon:epoxy composite electrode functioned as a second working electrode, a silver wire served as an Ag-QRE and a Pt gauze was used as a counter electrode.

2.4 TPM Instrumentation and Apparatus

The apparatus used for TPM, shown in Figure 2-12, was similar to that described in section 2.3 for the SECM, in that TPM is simply a different implementation of SECM. The reference voltage output of a lock-in amplifier was used to modulate the UME probe in a direction perpendicular to the sample surface, by application to the z-axis piezoelectric positioner. The output current signal for electrolysis of the analyte of interest from the working electrode was recorded on an oscilloscope (Tektronix TDS 210, Tektronix Inc, USA), connected to a laptop, and by the lock-in detector.

All voltammetric measurements were performed as described earlier for SECM investigations. Depending on the nature of the substrate investigated, either a two
electrode set-up was used, or a bipotentiostat was used to facilitate measurements using a four electrode arrangement.

![Schematic of the SECM tip position modulation set-up.](image)

**Figure 2-12 Schematic of the SECM tip position modulation set-up.**

### 2.5 AFM Instrumentation

Conducting AFM was performed in order to correlate and quantify the local conducting nature of carbon:epoxy composite electrodes, together with sample topography, at high spatial resolution. A hand-fabricated conducting AFM probe,\(^5\) made according to the scheme in Figure 2-13, was employed for these studies. In brief, a 50 μm diameter Pt microwire electrode was (a) initially compressed to create the cantilever portion of the probe (b), and then electrochemically etched to a fine point (c). The resulting device was then mounted onto the underside of a commercial AFM probe body (Digital Instruments) (d).
Figure 2-13 Schematic of the steps involved in the fabrication of SECM-AFM tips.

2.6 Chemicals

A complete list of the source and grades of the chemicals used in the investigations covered herein is given in Table 2-1. All the solutions were prepared with Milli-Q reagent water (Millipore Corp., 18.2 MΩ resistivity), using volumetric flasks to dilute stock solutions where necessary.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Source</th>
<th>Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>BDH</td>
<td>GPR</td>
</tr>
<tr>
<td>Ethanol</td>
<td>BDH</td>
<td>A.R. (95 % v/v)</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>BDH</td>
<td>GPR (≈ 69 %)</td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>BDH</td>
<td>A. R.</td>
</tr>
</tbody>
</table>
Potassium hexacyanoferrate (II)  
Fisher Scientific  
A. R.

Potassium hexacyanoruthenate (II) hydrate  
Strem Chemicals  
A. R.

Potassium hexachloroiridate (III)  
Aldrich  
A. R.

Potassium nitrate  
Fisher Scientific  
99.5 % purity

Sulfuric acid  
BDH  
GPR (~ 98 %)

Sucrose  
Aldrich  
GPR

Table 2-1 A list of the chemicals used in these investigations. A.R. is analytical reagent grade, and GPR is general-purpose reagent grade.

2.7 Substrates

The carbon: epoxy composites were prepared by mixing fine graphite powder (Ultra F, Union Carbide) and epoxy resin ("Araldite" CY1300+Hy1301, Ciba-Geigy, Duxford, UK) in predetermined ratios, as required. The mixtures were allowed to set hard in casts, and then cut into thin slices using a diamond saw, which produced discs of diameter 4.5 mm, of various thickness (1 - 2.5 mm). Prior to experimentation, it was necessary to first clean the outer surfaces of the discs using a slurry of alumina, followed by copious rinsing and sonication (Ultrasonic bath, model Decon F52006, Decon Labs., East Sussex, U.K.) in deionised water, for 15 minutes. After this the substrate surfaces were rinsed with ethanol, and allowed to dry. An electrical connection was made using silver loaded epoxy resin (Acheson Eletrodag 1415M, Agar Scientific LTD, Essex, UK) and a length of tinned copper wire (RS Components) to one surface of each of the substrates. The remaining exposed surface was flat and clean, as verified using an optical microscope.
The gold band electrode structures that were investigated in TPM studies were prepared using photolithography at the University of Glasgow, courtesy of Dr. P. S. Dobson, with a thiol adhesion layer. The band electrode consisted of a series of parallel lengths of gold that were connected together at the vertices, where each band was 168 μm thick, and the gold bands were separated by 168 μm of glass. For all of the imaging experiments, the conductive areas (gold bands) of the substrate were not externally biased.

Bovine articular cartilage was investigated using both conventional SECM and TPM methodologies. Full depth plugs of cartilage (dia. 5 mm) were obtained from fresh joints, sliced into 50 μm thick sections on a microtome (Leica, Milton Keynes, UK), whereupon the sections were immediately frozen using solid carbon dioxide. Prior to experimentation, the required section was thawed and equilibrated in a solution of phosphate buffer (pH 7.0 ± 0.2). The section was then fixed to a glass disc, by carefully laying it flat onto the disc, removing any excess buffer solution using a lens tissue (Whatman International Ltd, Maidstone, England), and finally dabbing a mixture of nail-varnish and cyanoacrylate glue (1:1) around the circumference of the section. When the glue had dried, optical micrographs were taken of the section, before mounting the disc into the recess of a custom made Teflon cell. SECM and TPM imaging experiments were conducted in a solution containing potassium hexacyanoruthenate (II) hydrate (5 mM), and potassium chloride (0.2 M), which was phosphate buffered to pH 7.0 ± 0.2, in which the section had been allowed to equilibrate, prior to experimentation.
For SECM and TPM investigations, it was necessary to quantify the distance of closest approach of the UME to a substrate surface, and for these studies a glass disc or a sputter coated Pt covered glass disc (optically flat, dia. 1.2 cm) was used as the substrate. The discs were cleaned using acetone and dried using a nitrogen source, prior to use.
References

Chapter 3  **Scanning Electrochemical Microscopy Coupled With The Microjet Electrode**

This chapter describes work undertaken to further understand the hydrodynamics of jet flow, emerging from a nozzle onto the surface of an UME, in the MJE arrangement. The studies, herein, illustrate that it is possible to obtain information on the nature of local mass transfer in the impinging jet through both imaging experiments and voltammetric measurements. These experiments were carried out on the oxidation of two different electroactive species, IrCl$_6^{3-}$ and Fe(CN)$_6^{4-}$, in aqueous solution, at a range of solution viscosities. To support and enhance the experimental measurements, simulations have been developed elsewhere (Prof. R. G. Compton's group, Oxford University) that use a finite element modelling package. The computational approach provides clarification of the experimental data and is able to highlight important features of mass transport in the MJE system that are difficult to obtain experimentally.

3.1 **Introduction**

The MJE,$^{1,2}$ described in detail in Chapter 1, has proven attractive for investigating electron transfer kinetics,$^{2}$ coupled solution reactions,$^{3}$ and for flow analysis.$^{4}$ In the latter case, trace-level detection has been facilitated by coupling the MJE with hydrodynamic modulation voltammetry,$^{5}$ as discussed in detail in Chapter 4. Many of these studies utilised an empirical treatment of mass transport to the wall tube electrode,$^{6}$ but recently a comprehensive model for mass transport in the MJE configuration has been developed,$^{7}$ which is more generally applicable.
The basic set-up of the MJE consists of a high velocity jet of solution that is fired from a nozzle onto the surface of a disc UME. This resembles a wall-tube electrode arrangement,\(^6\) rather than a wall jet electrode,\(^8\) and is shown schematically in Figure 3-1. The hydrodynamics of the MJE system are based on an impinging jet electrode.\(^3,9\) This comprises of a submerged circular jet of electrolyte solution flowing perpendicular to a flat surface. The flow profiles of a jet colliding with a surface can be characterised by four flow regimes, which were described in detail and shown schematically in section 1.3.4, Chapter 1. The profiles from the impinging jet will be investigated using SECM, to further elucidate the local variation of mass transport in MJE arrangement. Previous studies have made such measurements but with a 25 \(\mu\text{m}\) dia. Pt UME,\(^3\) which has limited the spatial resolution.

![Figure 3-1 Schematic to show the basic MJE set-up.](image)

Under steady-state conditions, mass transport to the surface of the electrode is enhanced by more than or by several orders of magnitudes, depending on variables which include
the velocity of the solution, electrode-nozzle separation,\(^3\) and the diameter of the electrode.\(^10\)

Under laminar flow conditions, the dependence of the transport-limited current, measured at wall-tube electrodes on the volume flow rate can be defined by equation 1.6, which was described empirically by Chin and Tsang,\(^6\) and introduced in Chapter 1, section 1.3.4. \(\beta\) is a parameter determined by Chin and Tsang to be 1.51 for wall tube electrode configurations.

In this chapter, the volume flow rate effects on mass transport for the MJE will be investigated, in particular to identify when, and if, equation 1-6 applies to the MJE.

### 3.2 Effect of Volume Flow Rate in the MJE System

#### 3.2.1 Current Enhancement

Previous attempts to examine the effect of varying the volume flow rate to an electrode in a wall tube arrangement on the current response was defined earlier by equation 1-6. Prior to the mass transport imaging experiments, it was imperative to establish whether the MJE arrangement used for the imaging experiments satisfied this equation. Thus, initially, simple experiments were performed to vary the volume flow rate over a wide range, by use of assorted nozzle inner diameters (i.d.), onto the surface of two differently sized UMEs, whilst the mass transport limited current was recorded. The electrode and nozzle were aligned by the use of a zoom video microscope with a CCD camera attachment (on screen resolution of 2.2 \(\mu\)m per pixel), and by monitoring the mass-transport limited current, as the nozzle (with flow initiated) was moved over the
electrode surface, until a maximum current enhancement was achieved. In this configuration the nozzle sits slightly off centre with respect to the electrode (*vide supra*).

Figure 3-2 shows a typical set of LSVs, recorded in an aqueous solution for the oxidation of $5.0 \times 10^{-4}$ mol dm$^{-3}$ IrCl$_6^{3-}$ (0.5 mol dm$^{-3}$ KNO$_3$ background electrolyte) at a 25 µm diameter Pt UME, with a nozzle of 100 µm i.d. The volume flow rate, $V_f$, was randomly varied between 0.05 and 10 mL min$^{-1}$. The electrode and nozzle separation, $H$, was 300 µm.

![Figure 3-2 A set of LSVs recorded at a 25 µm diameter Pt UME, with a 100 µm diameter nozzle, in the MJE arrangement. The volume flow rate was varied and had values of (○) = 0, (●) = 0.05, (●) = 0.1, (●) = 0.2, (●) = 0.5, (●) = 1, (●) = 2, (●) = 4, (●) = 6, (●) = 8, (●) = 10 mL min$^{-1}$.

The current recorded at the UME was found to be significantly enhanced with an increase in the volume flow rate. The mass transport limited current in quiescent solution (bulk current, $i_{UME}$) was determined typically to be 1.8 nA, of the order expected from equation 1.3, Chapter 1. The diffusion coefficient, $D$, of IrCl$_6^{3-}$ was
determined to be $7.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, which is in good agreement with literature values.\textsuperscript{11} At the maximum $V_f$ ($10 \text{ mL min}^{-1}$) the limiting current observed under steady-state mass transport limited conditions was 110 nA, an enhancement of almost two orders of magnitude, on the bulk current. The $V_f$ was limited to a maximum of 10 mL min$^{-1}$ when using an HPLC pump, due to the high back pressures generated to force solution through the small sized nozzle exit.

To determine whether the results shown in Figure 3-2 analysed well in terms of equation 1.7, Figure 3-3 was constructed. Here, the ratio of the mass transport limited current recorded during the MJE experiments to the bulk quiescent current i.e. the normalised current ($i_{UME}/i_{MJE}$) was plotted versus the mean solution velocity, $\bar{U}^{1/2}$, defined by equation 1.7 (Chapter 1, section 1.3.4). As shown in Figure 3-3, a linear relationship between normalised current and the square root of the flow rate holds for most flow rates of interest. However, there is a region at the lowest flow rates where the current is essentially independent of flow rate. This is due to the inherently high rates of diffusion to UMEs in quiescent solution, which will be explored further in studies with small electrodes, discussed later. For this arrangement, in the flow rate region where the convective effect was strong, the normalised current was closely proportional to $\bar{U}^{1/2}$, and $\beta$ was determined to be 1.41.
Figure 3-3 A plot of normalised current versus $U^{1/2}$, for a 25 $\mu$m diameter Pt UME, and a 100 $\mu$m (i.d.) nozzle, for the oxidation of IrCl$_6^{3-}$ in aqueous solution, at a concentration of $5 \times 10^{-4}$ mol dm$^{-3}$.

Experiments were conducted for different combinations of nozzle and UME, where the diameters of each were varied. In each case, the current was closely proportional to $U^{1/2}$ and $\beta$ was calculated for each set of conditions from the gradient of the plots. The results of the measurements are summarised in Table 3-1.

<table>
<thead>
<tr>
<th>Diameter of Disc UME ($\mu$m)</th>
<th>I.D. of Nozzle ($\mu$m)</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>100</td>
<td>1.41</td>
</tr>
<tr>
<td>25</td>
<td>125</td>
<td>1.22</td>
</tr>
<tr>
<td>50</td>
<td>100</td>
<td>1.12</td>
</tr>
<tr>
<td>50</td>
<td>200</td>
<td>1.11</td>
</tr>
<tr>
<td>50</td>
<td>125</td>
<td>0.96</td>
</tr>
</tbody>
</table>

Table 3-1 A summary of the results of experiments performed with various electrode and nozzle dimensions and the $\beta$ values obtained.
From the results summarised in Table 3-1 it is possible to see that the set of conditions that most closely satisfies the Chin and Tsang model, for a wall tube electrode configuration, occurs when the disc UME is 25 μm in diameter, and when the i.d. of the nozzle is 100 μm, where a value of 1.41 was obtained. Under other conditions, although the current was proportional to $U^{1/2}$ over most of the flow rates of interest, smaller $\beta$ values were obtained compared to that expected from the empirical model. These initial results suggest that a more rigorous treatment of mass transport is needed and this is the subject of later studies in this chapter. By probing the nature of mass transport locally using SECM, it may be possible to understand why the value of $\beta$ varies over the range tested.

The mass transport rates attainable in this system can be calculated using equation 3:1.\textsuperscript{12}

The largest transport-limited current obtained from the data shown in Figure 3-2 corresponds to a mass transport coefficient, $k_t$, of approximately 0.5 cm s\textsuperscript{-1}.\textsuperscript{9}

$$k_t = \left( \frac{4D}{\pi a} \right) \frac{i_{\text{MJE}}}{i_{\text{UME}}}$$ \hspace{1cm} 3:1

3.2.2 Temperature Effects

The simulations are sensitive to temperature, which affects the solution viscosity and diffusion coefficient of the redox-active species. Consequently, prior to mass transfer imaging experiments, it was necessary to determine the effect of temperature on the diffusion coefficient of IrCl\textsubscript{6}\textsuperscript{3-}. Typically, solutions that were held in the laboratory environment were found to be at a temperature of 23 ± 0.5 °C.
A solution of $5 \times 10^{-3} \text{ mol dm}^{-3} \text{IrCl}_6^{3-}$ (0.1 mol dm$^{-3}$ KNO$_3$, supporting electrolyte), was placed in a double layered glass cell (total volume 50 cm$^3$), that enabled water at a specific temperature provided by a water-bath, to run completely around the sides and base of the cell, thus acting as a thermostated jacket. The outside of the cell and the tubing carrying water to the cell, were thoroughly insulated to avoid heat loss. By varying the temperature of the water-bath and allowing time for equilibration, it was possible to successfully manipulate the temperature of the test solution, and thus record the mass transport limited current at a 5 μm dia. Pt UME, as a function of temperature, Figure 3-4. The temperature was measured directly in the cell.

![Figure 3-4 A plot of $D$ versus $T/\eta$ recorded at temperatures between 10 - 30 °C using a 5 μm dia. Pt UME, for the oxidation of $1 \times 10^{-3}$ mol dm$^{-3}$ IrCl$_6^{3-}$.](image)

From these results it was possible to determine the diffusion coefficient of the IrCl$_6^{3-}$ at the laboratory temperature at which the imaging experiments were to be performed, which was found to be $7.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. This value is very close to that cited earlier. From Figure 3-4 an increase of $D$ with temperature between 10 and 30 °C is observed.
This is predicted by the Stokes-Einstein equation 3.2, where $D$ and temperature are proportional to one another.

$$D = \frac{k_B T}{6\pi \eta r}$$  \hspace{1cm} \text{Eq 3.2}

Where, $k_B$ is the Boltzmann Constant, $\eta$ is the solvent viscosity and $r$ is the radius of the solvated ion. Since the gradient in Figure 3-4 from equation 3.2 is $k_B/6\pi r$, $r$ was calculated to be $2.4 \times 10^{-10}$ m, which is in good agreement with that expected for the naked ion.

### 3.3 Mass Transfer Imaging

It has been shown that mass transfer to the surface of an electrode can be enhanced considerably when placed in the MJE arrangement. SECM experiments were conducted to further characterise the nature of mass transport directly at the UME surface, with the prospect of observing the two main flow regimes near the surface. Previous studies have suggested that a stagnation region exists directly under the nozzle exit,\textsuperscript{13,14} where the purely axial flow becomes radial, and that there is a second region at larger radial displacements, where the radial flow velocity begins to decay,\textsuperscript{15} across the electrode surface, as shown in Figure 3-5. These early experiments utilised a 25 µm diameter Pt UME, which had limited spatial resolution. In contrast, the measurements herein utilised a 5 µm diameter Pt electrode, and explored a much wider range of conditions.
For all imaging experiments, the UME was held at a potential sufficient to oxidise the analyte of interest, either Fe(CN)₆⁴⁻ or IrCl₆³⁻, at a mass-transport controlled rate. Initial experiments were performed in a 1 × 10⁻³ mol dm⁻³ IrCl₆³⁻ solution, with 0.5 mol dm⁻³ of potassium nitrate serving as background electrolyte. Experiments were conducted by initially aligning the nozzle, with mediator solution flowing onto the electrode surface, so that the current for the transport-controlled oxidation of analyte of interest was at its maximum value. Images were acquired over a typical scan area of approximately 400 μm square and, where possible, the position where the jet and electrode were coaxial appeared at a co-ordinate of approximately (200 μm, 200 μm) on the x, y axes. A step size of 5 μm was used between each successive unidirectional line, and data were acquired at points every 2 μm across a line. Using a scan speed of 10 μm s⁻¹, it typically took 90 minutes to acquire a complete image.

Figure 3-5 Schematic of the flow profile in the stagnation region of an impinging jet.¹
Chapter 3

There were two main reasons for the choice of a small UME for these studies. Firstly, it is well established that in quiescent solution, mass transport to UMEs increases with decreasing electrode size\textsuperscript{16} and it is interesting to examine the effect of fast flow under such conditions. Secondly, it should be possible to obtain higher resolution images by carrying out such measurements with smaller electrodes. The ratio of the electrode diameter to that of the surrounding insulator was 1:220, so that the 5 \( \mu \text{m} \) diameter Pt electrode could be considered to sit in an infinite insulating plane.

To ensure that the nozzle was at the same separation from the electrode for each experiment, the end of the nozzle was gently contacted on the surface of the electrode and then retracted from it a specified distance (500 \( \mu \text{m} \)) using the micrometer controlled z-stage, as described for the MJE voltammetric experiments.

For the initial scan in each set of experiments, a flow rate of 1 mL min\(^{-1}\) was used to ensure that the nozzle / UME alignment was satisfactory and that a mass transport image of the region of interest could be obtained. When this alignment process was complete, it was possible to acquire successive images of mass transfer at a range of volume flow rates (0.1 - 1.5 mL min\(^{-1}\)), as the nozzle was scanned across the electrode.

A typical mass transfer image recorded at the UME, as a function of nozzle position is shown in Figure 3-6. This figure clearly displays the significant enhancements of current that can be achieved using the MJE arrangement, with a relatively low volume flow rate. The mass transport limited current recorded in quiescent solution was found to be 0.74 nA, and was determined prior to, and after, each experiment to ensure that the electrode functioned satisfactorily throughout the scan.
It is possible to see in Figure 3-6 that in the centre of the impinging jet, represented by a light blue colour, we observe a small area of enhanced transport-limited current, but this is encompassed by a ring of the more greatly enhanced current (pink/purple). This observation is consistent with predictions which have established that the effect of a submerged jet close to the surface of a planar surface creates a stagnation zone, directly under the nozzle. This zone is created, as the flow of solution emerging from the jet, is purely axial in the centre. Moving a small distance, laterally away from this point leads to both axial and radial flow regimes that contribute to the overall current, which is thus increased.

The appearance of the stagnation zone was observed at a variety of flow rates and with a different mediator solution. This point is illustrated, for example, in Figure 3-7 where an image is shown of the mass transport limited current at the UME, recorded for a $1 \times 10^{-2}$ mol dm$^{-3}$ Fe(CN)$_6^{4-}$ solution (background electrolyte 0.5 mol dm$^{-3}$ KNO$_3$) at a
volume flow rate of 1 mL min\(^{-1}\), where \(H\) was 500 \(\mu\text{m}\). The image shown in Figure 3-7 is a selection of the total scan which was recorded over an area of 500 \(\times\) 500 \(\mu\text{m}^2\). By cropping the image, it is possible to clearly observe the feature of interest, the stagnation zone. Prior to and after experimentation, the limiting current was measured in quiescent solution and was determined to be 6.4 nA.

![Image](image.png)

**Figure 3-7** Variation of the transport limited current at the MJE, recorded at a 5 \(\mu\text{m}\) dia. Pt UME, for the oxidation of 1 \(\times\) 10\(^{-2}\) mol dm\(^{-3}\) Fe(CN)\(_6\)\(^{4-}\) solution.

The stagnation region in Figure 3-7, appears in light blue/green, surrounded by an area where the current reaches its maximum value (pink). Cross sections of this image are shown in Figure 3-8, where the stagnation zone appears more clearly, as a series of current dips in the centre of the image. By analysis, the minimum current in the stagnation region was determined to be 27.7 nA, for this particular case.
Figure 3-8 A cross sectional image, of current versus nozzle position on the x-axis, for various positions on the y-axis. The data used were extracted from the image shown in Figure 3-7.

From Figure 3-8 it is possible to see that mass transport varies with radial position in the stagnation region. As the nozzle is moved radially, the current is observed to increase with distance away from the position where the jet and electrode are co-axial. The stagnation region extends over a radial distance of approximately 50 μm in the images shown for both mediator solutions. At displacements greater than this the wall-jet region is encountered, the features of which are highlighted below, but essentially involves a decrease in the local rate of interfacial mass transport.

The next step of the investigation was to obtain sufficient data to allow comparison with models to verify the hydrodynamics. Voltammograms were recorded to investigate the mass transport limited current at different volume flow rates, when the nozzle and electrode were aligned co-axially, which was the simplest case to treat as it represented an axisymmetric cylindrical geometry. The symmetrical nature of the current response when the jet is scanned in a line through the centre of the electrode is shown in Figure 3-9. These single cross-sectional line scans were obtained using a 5 μm diameter Pt
UME, in a $1 \times 10^{-3}$ mol dm$^{-3}$ IrCl$_6^{3-}$ solution (oxidation process), at volume flow rates between 0.5 - 2 mL min$^{-1}$. The stagnation zones at each volume flow rate can be seen clearly.

![Graph showing y-axis position vs. normalised current at different volume flow rates.](image)

**Figure 3-9** A series of cross sections acquired from mass transfer images showing the y-axis position vs. normalised current, at an x position that bisected the electrode. The data were obtained at different volume flow rates, where ($\times$) = 0.5, (o) = 0.75, (e) = 1 ($\circ$) = 1.5, and ($\ast$) = 2 mL min$^{-1}$.

It is evident that the central current minimum, corresponding to the stagnation zone (centred at ca. y position = 175 µm), is flanked by two peaks of much enhanced current, that are of similar magnitude, and shape. Moving away from the stagnation zone results in a drop in the mass transport limited current, which is a consequence of the solution flow velocity radially across the surface on which it impinges, and mixes with the bulk solution. As expected, the normalised current is enhanced as the volume flow rate increases.

Owing to the lengthy nature of the imaging scans, recording a complete image of mass transfer for several different flow rates was eventually determined to be nonessential. In
order to investigate the flow rate dependence of the limiting current it was only necessary to fix the nozzle and electrode in a desired position. For the reasons outlined earlier, the simplest scenario is where the nozzle and electrode are co-axial. The procedure was thus shortened by conducting one initial imaging scan at a flow rate of 1 mL min⁻¹, to locate the minimum current in the stagnation zone, moving the nozzle, so that its axis coincided with that of the electrode, and then proceeding to record voltammograms at various flow rates at this position. These experiments were conducted using a 5 μm diameter Pt UME and for both redox mediator solutions. In each case, the mass transport limited current was determined at each volume flow rate by recording a full voltammogram at a scan rate of 10 mV s⁻¹, so that the steady-state response was obtained. A $1 \times 10^{-3}$ mol dm⁻³ IrCl₆³⁻ solution (oxidation thereof) was used to produce the results shown in Figure 3-10, and Figure 3-11 shows the results from experiments (*) conducted in a $1 \times 10^{-2}$ mol dm⁻³ Fe(CN)₆⁴⁻ solution, which was again subject to a one-electron process. In each case, 0.5 mol dm⁻³ KNO₃ was added to the solutions, as supporting electrolyte.

Figure 3-10 and Figure 3-11 clearly indicate, for both analyte solutions, that as the volume flow rate is increased a corresponding current enhancement is observed. It is important to note that great care was taken to ensure that the same experimental conditions were adopted for these experiments, so that the concentration and type of analyte remained the only difference.
Figure 3-10 A comparison of experimental (*) and simulated (□) data recorded at a 5 μm diameter Pt UME, for the one-electron oxidation of a $1 \times 10^{-3}$ mol dm$^{-3}$ IrCl$_6^{2-}$ solution, over a range of volume flow rates.

Numerical simulations (□) were carried out (Prof. R. G. Compton's group, University of Oxford) to support and enhance the voltammetric measurements, using a finite element modelling package, FIDAP$^\text{TM}$ (version 8.52, Fluent Europe Ltd.) to solve the Navier-
Stokes equation. This provided the velocity field and the resulting convection-diffusion problem was then solved. The general approach adopted to carry out simulations has been described fully elsewhere.\textsuperscript{17}

As can be seen, there is excellent agreement between the experimental (\textbullet) and simulated (□) results for measurements recorded for the one electron oxidation of IrCl\textsubscript{6}\textsuperscript{3-} (Figure 3-10). On the other hand, in some Fe(CN)\textsubscript{6}\textsuperscript{4-} experiments (Figure 3-11), transport-limited currents were sometimes larger than expected, which is consistent with the slight misalignment of the nozzle and UME, as already discussed. In terms of the future application of the MJE for voltammetric studies, there would be advantages to working in the position of maximum current. This would be easier to achieve practically, as well as delivering higher mass transfer rates, enabling the study of faster kinetics. However, mass transport in this configuration is necessarily three-dimensional and more complicated to treat computationally.

3.4 SECM Investigation of the Effects of Viscosity in the MJE System

The stagnation region has been probed and found to be consistent with a model. The following investigations were conducted to elucidate the effect, if any, of an increase in the viscosity of the solution at ambient temperature (296 K). This increase was simply achieved by using a sucrose solution of predetermined concentration. For the experiments described herein, the oxidation of 1 × 10\textsuperscript{-2} mol dm\textsuperscript{-3} Fe(CN)\textsubscript{6}\textsuperscript{4-} (0.5 mol dm\textsuperscript{-3} KNO\textsubscript{3} supporting electrolyte) was performed. The effects of solution viscosity on enhanced mass transfer for an impinging jet have not been examined previously.
Complete images of transport-limited current, as a function of nozzle position, were recorded at each viscosity, at a flow rate of 1 cm\(^3\) min\(^{-1}\), at three different solution viscosities, which required the addition of 114.7, 170.2, and 239.8 g L\(^{-1}\) of sucrose. These were chosen from a range of viscosities that were investigated initially by linear sweep voltammetry (LSV) in quiescent solution and viscometry. Voltammograms were then obtained at different volume flow rates, with the nozzle and electrode closely co-aligned.

LSVs were measured in \(1 \times 10^{-2}\) mol dm\(^{-3}\) Fe(CN)\(_6^{4-}\) solutions, with sucrose added at a specified level. The experiments were repeated three times at each concentration level and were conducted in a thermostated cell so that the temperature could be maintained at 23 ± 0.5 °C. The diffusion coefficient was extracted from each LSV, by use of equation 1:3, Chapter 1, where, as expected, \(D\) was found to decrease as the solution viscosity increased. The relative viscosity of each of these solutions was determined at 23 ± 0.5 °C using a simple glass viscometer. The relative viscosity (\(\eta/\eta_0\)) is given for each solution and is defined by the ratio of the viscosity of the Fe(CN)\(_6^{4-}\) sucrose-containing solutions to the viscosity of a Fe(CN)\(_6^{4-}\) solution without sucrose added. The viscosities and diffusion coefficients, derived from viscometry and steady-state limiting current measurements are given in Table 3-2, along with the measured solution densities, \(\rho\).
Table 3-2 A summary of results for LSV and viscometry experiments which were conducted on a range of Fe(CN)$_6^{4-}$/sucrose solutions, in which the concentration of sucrose was varied.

<table>
<thead>
<tr>
<th>Sucrose Conc./ g L$^{-1}$</th>
<th>$\rho$ / g cm$^{-3}$</th>
<th>$D$ / ($10^{-6}$ / cm$^2$ s$^{-1}$)</th>
<th>Relative Viscosity $\eta/\eta_0$</th>
<th>$\mu$ / g cm$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.00</td>
<td>6.74</td>
<td>1.00</td>
<td>0.0093</td>
</tr>
<tr>
<td>114.7</td>
<td>1.08</td>
<td>4.87</td>
<td>1.36</td>
<td>0.0127</td>
</tr>
<tr>
<td>170.2</td>
<td>1.10</td>
<td>4.30</td>
<td>1.60</td>
<td>0.0149</td>
</tr>
<tr>
<td>239.8</td>
<td>1.12</td>
<td>3.21</td>
<td>2.07</td>
<td>0.0193</td>
</tr>
</tbody>
</table>

A plot of log $D$ versus log $\eta/\eta_0$ is shown in Figure 3-12. Based on the Stokes-Einstein equation (Eq. 3:2), the radius of the solvated ion was calculated to be $3.5 \times 10^{-10}$ m, which is close to that determined for the temperature-dependent measurements reported earlier in this Chapter.

Figure 3-12 Plot of log $D$ versus log $\eta/\eta_0$ for experiments conducted in Fe(CN)$_6^{4-}$/sucrose solutions, in which the sucrose concentration was varied.
Having established the viscosities and diffusion coefficients in the Fe(CN)$_6^{4-/}$ sucrose solutions, the effects of viscosity on the local mass transfer limited current in the MJE, was next investigated.

Complete images of the mass transfer limited current were recorded at each of the sucrose concentrations at a flow rate of 1 mL min$^{-1}$, and voltammograms at different volume flow rates were recorded with the nozzle and electrode arranged axially. A typical steady-state mass transfer limited current image for the oxidation of $1 \times 10^{-2}$ mol dm$^{-3}$ Fe(CN)$_6^{4-}$ (0.5 mol dm$^{-3}$ KNO$_3$) in a solution containing 114.7 g L$^{-1}$ sucrose is shown in Figure 3-13. The mass transfer limited current enhancements are less impressive, when compared to those recorded in sucrose free solutions (e.g. Figure 3-7).

![Figure 3-13](image)

**Figure 3-13** A mass transfer limited current image of normalised current at the MJE, recorded at a 5 $\mu$m diameter Pt UME, for the one-electron oxidation of $1 \times 10^{-2}$ mol dm$^{-3}$ Fe(CN)$_6^{4-}$ solution, with 114.7 g L$^{-1}$ sucrose.

Figure 3-14 depicts a mass transfer image recorded for the oxidation of $1 \times 10^{-2}$ mol dm$^{-3}$ Fe(CN)$_6^{4-}$ solution, containing 170.2 g L$^{-1}$ of sucrose. As in previous cases, the
The normalised currents in the image shown in Figure 3-14 are of a smaller magnitude compared to the data acquired from the sucrose free solutions (Figure 3-7), and with a lower concentration of sucrose (Figure 3-13). The normalised current ratio recorded at this sucrose concentration (170.2 g L$^{-1}$) at the minima in the centre of the image is 3.6.

Figure 3-15 depicts an image of local mass transfer recorded at a sucrose concentration of 239.8 g L$^{-1}$. This corresponded to a dynamic viscosity of 0.0221 g cm$^{-1}$ s$^{-1}$ and was the most viscous solution examined in these investigations.
Figure 3-15 Variation of local mass transfer at a MJE, where the solution examined comprised $1 \times 10^{-2}$ mol dm$^{-3}$ Fe(CN)$_6^{4-}$, 0.5 mol dm$^{-3}$ KNO$_3$, and 239.8 g L$^{-1}$ sucrose.

Here, the viscosity of the solution severely diminishes mass transfer to the electrode surface. This is reflected by the normalised currents that are far smaller than those observed in the previous images, and indeed much smaller absolute currents. At higher concentrations of sucrose than those presented here, it was difficult to acquire a complete mass transfer image, because small particles of sucrose were found to precipitate out and accumulate in the nozzle aperture.

Further experiments involved steady-state current-voltage measurements to investigate the effect of viscosity on transport-limited currents. Typical experimental results (*) at a series of solution viscosities are shown below, where Figure 3-16 depicts the data recorded with a concentration of 114.7 g L$^{-1}$ of sucrose present, Figure 3-17 with 170.2 g L$^{-1}$ of sucrose, and Figure 3-18 with 239.8 g L$^{-1}$ of sucrose. From these results it can clearly be seen that there is a significant effect of solution viscosity on mass transport under both quiescent and convective-diffusion conditions.
Figure 3-16 A comparison of experimental (•) and simulated (□) data recorded at a 5 μm diameter Pt UME, using a $1 \times 10^{-2}$ mol dm$^{-3}$ Fe(CN)$_6^{4-}$ in 114.7 g L$^{-1}$ sucrose solution, over a range of $V_f$ between 0.1 and 1.5 mL min$^{-1}$.

Figure 3-17 A comparison of experimental (•) and simulated (□) data recorded at a 5 μm diameter Pt UME, using a $1 \times 10^{-2}$ mol dm$^{-3}$ Fe(CN)$_6^{4-}$ in 170.2 g L$^{-1}$ sucrose solution, over a range of volume flow rates.
Although there is some disagreement between the experimental and theoretical data, which may arise from even a small misalignment of the nozzle and electrode in the case of Figure 3-16, Figure 3-17, and Figure 3-18, the importance of viscosity is clear. The theoretical simulations, carried out at Oxford, to investigate the effects of viscosity on the current-flow rate response, chose different values of viscosity and diffusion coefficient to obey “Walden’s Rule”: the product of viscosity and conductivity is approximately a constant for the same ions in different solvents. Hence the product of viscosity and diffusion coefficient should also be a constant. Values of viscosity and diffusion coefficient were chosen so that

$$\mu D = 6.00 \times 10^{-8} \text{ g cm s}^{-2}$$  \hspace{1cm} \text{Eq 3:3}$$

where $\mu$ is the dynamic viscosity (in g cm$^{-1}$ s$^{-1}$) and $D$ is the diffusion coefficient (in cm$^2$ s$^{-1}$). This resulted in a dynamic viscosity of 0.010 g cm$^{-1}$ s$^{-1}$ when the diffusion
coefficient was $6.00 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$. It can be seen from Table 3-2 that this is fairly typical of the values for an aqueous solution containing $\text{Fe(CN)}_6^{4-3-}$ under the experimental conditions. For each viscosity, a series of limiting currents at the MJE was simulated for a 10 mM solution of $\text{Fe(CN)}_6^{4+}$ at ten different flow rates, between 0.1 and 1.5 mL min$^{-1}$. The results for each simulated viscosity are represented as (□) in Figure 3-16, Figure 3-17, Figure 3-18. As would be expected, an increase in viscosity and the commensurate decrease in diffusion coefficient reduces the current at all flow rates.

The experimental data in Figure 3-17 fit theory reasonably well, particularly at low volume flow rates (0.1 – 0.75 mL min$^{-1}$). For the most viscous solution used (298.8 g L$^{-1}$ of sucrose), the observed experimental currents (Figure 3-18) are much smaller than predicted, particularly above 1 mL min$^{-1}$ where the experimental current is observed to be fairly constant. This observation was general and requires further study to elucidate the variation between experiment and the idealised model represented elsewhere.$^7$

### 3.5 Conclusions

The results in this chapter have shown that the microjet electrode provides a method through which mass transfer to an UME can be substantially enhanced. These enhancements have been investigated using scanning electrochemical microscopy. Modelling and experiment for both $\text{IrCl}_6^{3-}$ and $\text{Fe(CN)}_6^{4+}$ oxidation at a range of different flow rates, have allowed variations in mass transport to be investigated and the stagnation zone to be characterised. With the nozzle and disc-shaped UME coaxially...
aligned, so that the MJE system is axisymmetric, experimental limiting current measurements for IrCl₆³⁻ oxidation are in good agreement with simulation. Under these conditions, increasing the viscosity of the solution results in a significant decrease in mass transfer rate, mainly through a reduction in the diffusion coefficient of the redox probe molecule.

SECM images of local mass transfer were also recorded for more viscous solutions, in which different concentrations of sucrose were added to solutions containing 1 × 10⁻² mol dm⁻³ Fe(CN)₆⁴⁻ and 0.5 mol dm⁻³ KNO₃. Overall, as the sucrose concentration was increased, the magnitude of the currents recorded in quiescent solution decreased as suggested by the Stokes-Einstein equation. Current enhancements were observed, in the sucrose solutions, as the volume flow rate of the impinging jet was increased, although the effect was less than observed in sucrose free solutions. Voltammetric data were recorded with the nozzle and UME aligned, in the stagnation zone for each of the viscous solutions. Qualitative agreement between experiment and the simulated results was found. Both viscosity and the diffusion coefficient are important in determining the mass transport limiting current in a MJE, under typical experimental conditions.

Electrochemical imaging experiments highlight the very high precision with which the nozzle and electrode have to be aligned in order that the experimental configuration conforms to the axisymmetric model. As the nozzle is displaced laterally from this position, mass transport to the electrode, from the action of the impinging jet, increases up to a distance of about one nozzle radius displacement. While more difficult to treat computationally, this configuration could be attractive for practical measurements with the MJE. First, this arrangement would be easier to configure in the position of
maximum current, for example simple manual micrometer-driven stages could be utilised. Second, since the mass transport rate in this position can be almost twice as large as for the axisymmetric configuration, this arrangement is potentially more sensitive for analytical and kinetic measurements. Future work should consider the quantitative treatment of mass transport under these conditions.
References

5 Simjee, N., Macpherson, J. V., Unwin, P. R., Electroanalysis, accepted for publication.
14 Strand, T., AIAA Paper No. 64-424.
Chapter 4  Chopped Flow Microjet Electrode

This Chapter describes a novel form of hydrodynamic modulation voltammetry (HMV), based on the periodic modulation of mass transport in a microjet electrode system, and used in combination with phase-sensitive detection techniques. In the configuration developed a jet containing electroactive solution is fired from a nozzle on to the surface of either a dual disc or single disc UME. A thin rotating blade positioned between the nozzle and the electrode is used to periodically interrupt flow to the UME, thus modulating the rate of mass transfer to the UME between two well-defined extremes. Two methods have been developed to detect the rotation frequency of the blade, which generates a reference signal that reflects the variation in the mass transport, and enables extraction of the current component of the analyte signal at this frequency. The purely electrochemical method functions by employing a dual disc UME with one electrode detecting the analyte of interest, and the other detecting a reference analyte present in the solution (oxygen). The optical detection system utilises a single disc UME to monitor the analyte of interest, whilst a simple light emitting diode (LED) positioned below the blade and a photodiode detector placed above the blade, were employed to monitor the rotation frequency of the blade. Both of these systems were successfully used to facilitate trace level detection of analyte species.

4.1 Introduction

Hydrodynamic modulation voltammetry involves the periodic modulation of mass transport to an electrode surface\(^1\), and can be combined with phase-sensitive detection methods to extract the current component at the frequency of the perturbation of mass transport. This general approach enables the transport-controlled component of a
current signal to be separated from background processes, which can include solvent decomposition and electrode surface reactions, among other factors. HMV is thus recognised as an attractive option for extending detection limits and increasing the potential window of a solvent.$^{1,2,3}$

Classical HMV methodology was developed around the rotating disc electrode (RDE).$^{2,3,4,5,6}$ Initially, studies involved variation of the rotation rate of the electrode between two well-separated speeds (for stopped rotation voltammetry, the lower speed was zero), and the steady-state current difference, largely free from background processes, measured in dc mode only.$^2$ This approach facilitated concentration detection down to $1 \times 10^{-8}$ mol dm$^{-3}$ for Fe(CN)$_6^{4-}$, in an aqueous phosphate buffer.$^3$ Phase-sensitive detection was subsequently employed to measure the in-phase current component of the signal from an RDE, which was modulated sinusoidally about a fixed central rotation frequency.

Vibration of a wire or a band electrode has also proved effective for modulating mass transport and measuring low concentrations.$^{1,3,7}$ By vibrating a wire electrode (dia. 25 μm) at frequencies in the range of 80 - 160 Hz, detection limits down to $1 \times 10^{-8}$ mol dm$^{-3}$ for ferrocene have been achieved.$^8$ More recently, vibrating microband electrodes have been employed for the detection of chlorine in water,$^9$ where a detection limit of approximately $3 \times 10^{-7}$ mol dm$^{-3}$ was achieved.

Flow-through electrochemical cells offer many desirable features such as low sample consumption, the possibility of rapid multi-sample analysis, and on-line detection.$^{10}$ Modulation of the solution flow rate has improved concentration detection limits, and
enhanced the stability of the electrode response in flow systems.\textsuperscript{1,3} Initial measurements in channel or tubular electrodes, involved measuring the steady-state current difference between a maximum and a minimum (in some cases zero) flow rate.\textsuperscript{11,12} Typical detection limits of $1 \times 10^{-7}$ mol dm\textsuperscript{-3} were reported, although in order to attain the maximum steady-state current difference signal, it was necessary to employ lengthy cycling times due to the inherently low mass transport rates in these systems. Improvements in cycling times (up to a maximum of 2 Hz) were made by the employment of thin layer flow cell geometries.\textsuperscript{13,14}

There has recently been interest in the combination of hydrodynamic ultramicroelectrode (H-UMEs)\textsuperscript{15,16} with HMV methodology.\textsuperscript{17,18} H-UMEs are micrometer-sized electrodes coupled with high velocity convective systems. Given the high mass transport rates associated with these systems (up to 2 cm s\textsuperscript{-1} for some H-UME geometries\textsuperscript{19}), and the short diffusional relaxation times, it is possible to employ relatively high modulation frequencies, without serious attenuation of the current signal. This enables greater detection sensitivity and much reduced analysis times,\textsuperscript{20} and has been discussed in more detail in Chapter 1.

As discussed in Chapters 1 and 3, the microjet electrode (MJE)\textsuperscript{21,22} is an H-UME technique, based on a wall-tube arrangement,\textsuperscript{23} in which solution is fired at high velocities from a nozzle (typical nozzle diameter $\approx 100 \mu$m) onto the surface of a disc UME. Modulation of the mass transfer rate in the MJE has been achieved by oscillating the nozzle in a plane parallel to the electrode surface between two different coordinates, one where the jet impinges directly on the electrode surface, the other where the flowing stream largely misses the electrode.\textsuperscript{17} With this technique, coupled with in-
phase detection, the measurement of trace levels of electroactive species, to a detection limit of $5 \times 10^{-9}$ mol dm$^{-3}$, was possible. However, oscillation of the nozzle position required the use of piezoelectric positioners, which could limit the practical use of this methodology.

In this chapter we introduce a new variant on the MJE-HMV system which could be easily adapted for practical flow analysis systems. The experimental configuration is based on the MJE, but with the addition of a thin rotating blade, positioned between the nozzle and the electrode, which is employed to periodically interrupt (or chop) flow to the surface of the electrode. In this manner, mass transport to the electrode is modulated between a maximum due to convective-diffusion from the impinging jet, and a lower limit when the blade interrupts the flow. We call this new device a chopped flow (CF) – MJE. A simple schematic of the instrumentation was shown in Figure 2-4 (a) and a detailed description of the apparatus, including photographs of the electrochemical cell can be found in section 2.2, Chapter 2.

Two methods have been developed to generate a reference signal which reflects the variation in the mass transport rate (and determines the perturbation frequency), and thus enables extraction of the current component of the analyte signal at this frequency. Initially, this reference signal was provided by employing a dual disc UME with one electrode detecting the analyte of interest, and the other detecting a reference analyte present in the solution. For the studies described herein, carried out in aerated solution, the current for the reduction of O$_2$ is shown to provide a suitable reference signal. An alternative method was developed later, in which a simple LED positioned below the blade, and a photodiode detector placed above the blade were employed to monitor the
frequency of modulation of the blade, and hence provide an optical reference signal. Here, a single disc UME was used to detect the analyte of interest present in the solution.

4.2 Electrochemical Detection Reference Signal

4.2.1 The Response Of Dual Disc UMEs In A MJE Arrangement

The chopped flow experiments were conducted by initially aligning the nozzle, with mediator solution flowing over the dual disc UME, so that the current for the transport-controlled electrolysis of the reference mediator (O₂ reduction) was at its maximum value, over both electrodes. This task was greatly aided by the use of video microscopy.

Careful alignment of the dual disc working electrode probe under the blade was essential to ensure that flow of solution to the surface of both electrodes would be chopped simultaneously by the rotating blade, and also that mass transport to each electrode would be as similar as possible. This was achieved by placing the electrodes in the cell such that they lay adjacent to one another, parallel to the leading edge of the rotating blade. In this way, the two electrodes were exposed to the same chopped flow profile.

For all experiments, the mass-transfer limited reduction of oxygen at one UME served as the reference signal for phase sensitive detection and the potential of this electrode was held at an appropriate value. The other electrode was either scanned linearly, or held at a value sufficient to detect the analyte of interest, ultimately at a mass-transport
controlled rate. Prior to commencing each experiment, it was essential to test the voltammetric response of the electrodes, aligned under the nozzle outlet, but in quiescent solution. Linear sweep voltammetric (LSV) curves were recorded at each of the dual disc UMEs, for both the oxidation of the analyte of interest and for the reduction of oxygen naturally present in the aerated solutions. In each case, the diffusion limited currents were compared to those predicted by theory and defined by equation 1.3, section 1.2, Chapter 1. It was determined that, under both experimental conditions, the electrodes behaved in a similar fashion to one another with limiting currents typically differing by a maximum of ca. 10%. Thus, either electrode could be used to monitor the analyte signal or act as reference signal generator, in the dual Pt-Pt UME arrangement.

With the experimental arrangement adopted, the position of the working electrode could be moved manually normal to the face of the blade, while the nozzle, attached to a micrometer-driven stage, could be adjusted with greater precision. To ensure that the nozzle was at the same separation from the blade for each CF-MJE experiment, the nozzle was gently contacted on the surface of the blade and then retracted a specified distance in the range 450 - 550 µm. The separation between the face of the electrode and the underside of the blade was 2 mm for all of the studies described herein, and the thickness of the blade used was 500 µm. This distance was established as optimal, based on preliminary experiments that are discussed later.

MJE experiments were initially carried out to determine whether solution was delivered from the nozzle, to the two Pt-Pt UMEs incorporated in one probe, with similar mass transfer rates, with the arrangement described above. These experiments did not
Chapter 4

involve a rotating blade; rather, solution was delivered from the nozzle to the two electrodes, at a range of flow rates. These measurements represent an extension of earlier work with single electrodes, which is described in Chapter 3. Figure 4-1 displays typical steady-state limiting current responses, recorded simultaneously at the two disc UMEs for the oxidation of $1 \times 10^{-2}$ mol dm$^{-3}$ Fe(CN)$_6^{4-}$ (0.5 mol dm$^{-3}$ KNO$_3$), as a function of the mean solution velocity, $\bar{U}$. These measurements were derived from LSVs recorded at 10 mV s$^{-1}$ from 0 to +0.9 V (vs. AgQRE). A 100 μm diameter nozzle was employed, which was positioned 3 mm from the dual 25 μm diameter Pt-Pt UME probe. This separation is larger than employed in previous MJE experiments, but was necessary for the CF-MJE experiments that follow.

![Figure 4-1 Normalised current versus (mean solution velocity)$^{1/2}$ response recorded simultaneously at both electrodes (A: •) and (B: △) in the dual Pt-Pt disc UME, for the oxidation of $1 \times 10^{-2}$ mol dm$^{-3}$ Fe(CN)$_6^{4-}$ in 0.5 mol dm$^{-3}$ KNO$_3$.](image)

As Figure 4-1 demonstrates, over the range of flow rates investigated, both electrodes experience similar mass transfer rates, as evident from the close similarity of the transport-limited currents. The currents measured in the impinging jet arrangement

104
have been normalised by the current measured in quiescent solution at each electrode, which has been defined earlier by equation 4-1. Values of $i_{UME}$ of 34.3 and 32.6 nA were obtained for each electrode, suggesting an average diffusion coefficient for ferrocyanide of $6.95 \times 10^6$ cm$^2$ s$^{-1}$, in agreement with literature values.$^{19}$

The volume flow rate dependence of the current enhancement was found to correlate well with the empirical response expected for the MJE, defined by equation 1.6, section 1.3.4, Chapter 1.$^{21,25}$

The ratio $i_{MJE}/i_{UME}$ is the normalised current (as in Figure 4-1), where $i_{MJE}$ is the steady-state limiting current at the MJE, $v$ is the kinematic viscosity, $H$ is the distance between the electrode and nozzle, $d$ is the inner diameter of the nozzle, and $\beta$ is a constant (usually assumed to be 1.51). The latter parameter is related to the experimental volume flow rate, $V_f$, via equation 1.7, section 1.3.4, Chapter 1.

A closely linear relationship between the limiting current and the (mean solution velocity)$^{1/2}$ is clearly evident from Figure 4-1. The slopes of the best lines through the data yield $\beta = 1.19$ (●), and $\beta = 1.20$ (▲). The intercept is non-zero on the current axis because equation 4:2 ignores diffusional edge effects, which are important at slow flow rates. A full numerical treatment considering such effects has recently been developed and was discussed in Chapter 3.$^{26}$
4.2.2 Convective Effects Arising From A Rotating Blade

With the CF-MJE system, a rotating blade was used to modulate the flow of analyte solution to the surface of the UME. For low concentration detection applications it was both important that the CF-MJE technique was quantitative, to enable ready analysis of the current response, and that the current oscillation (signal) was as large as possible. In the absence of jet flow, experimental parameters needed to be established such that the rotating blade had a minimal effect on the transport-limited current response of the UME.

Initial experiments examined the effect of the UME-blade separation on mass transport to the electrode under conditions of no jet flow, with various blade rotation speeds (0.5 - 5 Hz). For these experiments, the working UME was attached to a micropositioner and the distance with respect to the blade surface was varied, whilst the diffusion-limited current for the oxidation of $5 \times 10^{-4} \text{ mol dm}^{-3} \text{ IrCl}_6^{3-}$ was recorded at each position. As expected, current enhancements were most pronounced at the smallest electrode-blade separations examined (40 - 60 µm) and at the maximum rotation frequency employed (5 Hz). Under these experimental conditions the mass transport limited current was approximately three times the magnitude of the diffusion-limited current in quiescent solution. This current enhancement arises from convective flow, due to the movement of the rotating blade.

For separation distances of 0.1 – 1.5 mm the transport-limited current was still found to be enhanced at all blade rotation rates, but decreased with increasing separation between the blade and electrode. At an electrode-blade separation of 2.0 mm, the maximum current enhancement observed at the highest rotation frequency (5 Hz) was no more
than 5% above the diffusion-limited current measured under quiescent conditions. Thus, to minimise convective effects arising from rotation of blade, the separation between the underside of the blade and the electrode surface was maintained at 2 mm for subsequent experiments with the CF-MJE system. Increasing the electrode-blade separation, further reduced the magnitude of the maximum current signal recorded with the jet flow on. The results of this investigation for blade-UME separation distances examined in the range of 0.5 - 2 mm are illustrated in Figure 4-2, which depicts a plot of normalised current versus the separation distance between the UME and the blade. The potential applied to the UME was scanned between 0 and +0.6 V, at a rate of 10 mV s\(^{-1}\), whilst a voltammogram was recorded at each of the different blade rotation frequencies (1 (•), 2 (○), 3 (●), 4 (×), 5 (▲) rev sec\(^{-1}\)) and separation distances.

![Figure 4-2 A plot of the normalised current versus electrode-blade separation distances (between 0.5 and 2.5 mm) recorded at a 25 μm diameter Pt UME, for the transport limited oxidation of a 5 × 10\(^{-4}\) mol dm\(^{-3}\) IrCl\(_6\)^{3-} solution. The blade rotation frequency was varied between 1 and 5 Hz (1 (●), 2 (○), 3 (●), 4 (×), 5 (▲)). The normalised current is the values measured with the blade rotating divided by the diffusion limited quiescent value.](image)
4.2.3 **Response of the Dual Disc Electrode To A Chopping Blade**

It was imperative that the two electrodes of the dual disc UME responded to the modulated flow from the nozzle simultaneously. Figure 4-3 displays the current-time responses for a dual 25 μm diameter Pt-Pt UME probe, operating in the CF-MJE arrangement, in an aerated analyte solution containing $5 \times 10^{-4}$ mol dm$^{-3}$ FeCN$_6^{4-}$ and 0.1 mol dm$^{-3}$ KNO$_3$, where $H = 3$ mm. One working electrode was held at a potential of +0.45 V (vs. AgQRE) sufficient to oxidise FeCN$_6^{4-}$ at a diffusion-controlled rate (●). The second electrode was held at -0.7 V, sufficient to reduce O$_2$ (●), naturally present in the aerated solution at a concentration of ca. $2.5 \times 10^{-4}$ mol dm$^{-3}$ at a diffusion-controlled rate. A volume flow rate of 2 mL min$^{-1}$ (nozzle diameter, $d = 100$ μm) was employed for this particular case with a blade rotation rate of 0.67 Hz, and the current was sampled at 500 μs intervals.

![Figure 4-3 Mass transport controlled current responses, recorded simultaneously at a dual disc UME. One disc UME was used to facilitate the oxidation of Fe(CN)$_6^{4-}$ (●) present in the solution, whilst the reduction of oxygen (●) occurred at the other UME. A blade rotation frequency of 0.67 Hz was employed.](image)
As Figure 4-3 clearly shows, no attenuation of the current signal was observed in the frequency range employed for the experiments (0.5 - 2Hz). The steady-state current can be seen to oscillate between two extremes in Figure 4-3. The maximum current plateau corresponds to convective-diffusion mass transfer, resulting from solution impinging from the nozzle directly on the surface of the electrode. In contrast, when the blade interrupts flow, the current falls to a value largely dominated by diffusion-only mass transport to the UMEs. It can be seen that the switch between the two extremes in limiting current occurs quite rapidly. However, the change in current and attainment of the steady-state occurs most rapidly (several millisecond timescale) when the flow switches on. In this situation, the diffusion layer at the UME, which is essentially hemispherical, is suddenly compressed by the action of the impinging jet. The time taken for the electrode to be fully exposed to the jet is of the order of $dl/(2\pi fr)$, where $f (= 0.67 \text{ Hz})$ is the frequency of the rotation and $r (= 15 \text{ mm})$ is the radial displacement of the nozzle from the centre of the blade. The resulting time of ca. 1.6 ms correlates well with the sharp rise times evident in Figure 4-3.

The decrease in the magnitude of the current when the blade interrupts the flow occurs more slowly. This corresponds to flow from the impinging jet effectively being shut off by the blade moving between the nozzle and the electrode. In the absence of convection, the concentration boundary at the UME expands until a new steady-state is established due to hemispherical diffusion. This switch in mass transport is rather similar to that experienced by an UME in potential step chronoamperometry, where diffusion is essentially planar at short times (thin diffusion layer) and increases to a hemispherical field at longer times. The associated timescale is of the order of $a^2/D$, 

109
yielding a time of ca. 0.15 s for \( a = 12.5 \, \mu m \) and \( D = 10^{-5} \, cm^2 \, s^{-1} \), consistent with the timescale for the flow on to off transient.

### 4.2.4 Implementing Phase Sensitive Detection

As expected, the modulated absolute current signals for oxygen reduction and Fe(CN)\(_6\)\(^{4-}\) oxidation are in phase, which is crucial as the oxygen current response is to be used as a reference signal for subsequent phase sensitive detection. Following this result, Figure 4-4 shows, respectively, the raw (——) and in-phase current (*) (root-mean-square current amplitude, \( i_{rms} \), of the modulated signal) versus potential for the oxidation of \( 5 \times 10^{-4} \, mol \, dm^{-3} \) IrCl\(_6\)^{3-} (0.2 mol dm\(^{-3}\) KNO\(_3\) supporting electrolyte) in a CF-MJE system. A volume flow rate and blade rotation rate of 2 mL min\(^{-1}\) and 1.27 Hz, were employed, respectively, while \( H \) was 3 mm. For these measurements, the potential of one electrode was held at a value of -0.7 V to maintain oxygen reduction at a transport-controlled rate, while the potential of the other electrode was scanned from +0.4 to +0.8 V to promote the oxidation of IrCl\(_6\)^{3-}.

![Figure 4-4 CF-MJE voltammetric data for the oxidation of a 5 × 10^{-4} mol dm^{-3} solution of IrCl_{6}^{3-} (0.2 mol dm^{-3} KNO_{3} supporting electrolyte), V_{f} = 2 mL min^{-1}, blade rotation rate = 1.27 Hz. The raw data (—) and the in-phase rms voltammetric response (*) are plotted.](image)
At a potential where oxidation of the IrCl₆³⁻ analyte approaches the maximum transport-controlled rate (+ 0.7 V and higher), a significant modulation in the raw current is evident, from an upper convective-diffusion value of ca. 22 nA to a lower limit of 2.0 nA. Thus, mass transport to the UME is modulated by an order of magnitude on a rapid timescale. Values for the upper and lower mass transfer coefficients, \( k_t \), in the CF-MJE system, are readily calculated using:

\[
k_t = \frac{\text{i}_{\text{lim}}}{nAFc^*}
\]

where \( \text{i}_{\text{lim}} \) is the transport-limited current and \( A \) is the area of the electrode. Thus, \( k_t \) varies between \( 8.9 \times 10^{-2} \) cm s\(^{-1} \) (flow on) and \( 8.2 \times 10^{-3} \) cm s\(^{-1} \) (flow interrupted). For diffusion-only conditions, with \( D = 8 \times 10^{-6} \) cm\(^2\) s\(^{-1} \), \( k_t = 4D/(\pi a) = 8.1 \times 10^{-3} \) cm s\(^{-1} \), which is very close to the flow interrupted value determined experimentally. The limiting current value for \( i_{\text{rms,lim}} \) measured by phase sensitive detection, was 7.6 nA (as shown in Figure 4-4). This value is in quantitative agreement, with the data presented, where \( i_{\text{rms,lim}} = \Delta \text{i}_{\text{lim}} / (2\sqrt{2}) \), again providing evidence for the in-phase nature of the reference signal and the analyte signal during chopped flow.

To attempt trace level detection it was necessary to use current recording equipment capable low current detection (pA and lower). Thus, an EI400 bipotentiostat system combined with sensitive pre-amplification heads was used. It was possible to vary different parameters, including sensitivity, and time constant settings, on the phase sensitive detector to optimise the detection of analyte species. Typically, the time constant setting used to record the phase sensitive voltammetry was maintained at values between 30 and 300 ms.
The CF-MJE arrangement with in phase detection was initially used to facilitate detection of $5.02 \times 10^{-5}$ mol dm$^{-3}$ IrCl$_6^{3-}$, with $5 \times 10^{-2}$ mol dm$^{-3}$ KNO$_3$ serving as background electrolyte, to establish that the system was functioning appropriately. The effect of varying the blade frequency between 0.67 – 2.68 Hz, and changing the volume flow rate, was investigated, to determine the optimum conditions required for subsequent trace-level analysis studies.

Figure 4-5 shows $i_{rms}$ versus potential recorded at a dual disc UME, at $V_f = 2$ mL min$^{-1}$, at different blade rotation frequencies, 0.67 (●), 1.34 (●), and 2.68 (●) Hz. The time constant of the lock-in detector was set at 100 ms. All of the signals are all well-defined, and a mass-transport limited in-phase rms current of 0.66 ± 0.1 nA is observed which is of the magnitude expected for this concentration level i.e. a factor of 10 lower than that recorded for the $5.02 \times 10^{-4}$ mol dm$^{-3}$ IrCl$_6^{3-}$. For comparison, the current recorded in quiescent solution would be 0.18 nA, and would not have any of the benefits of phase-sensitive current detection. It is clear from Figure 4-5 that there is little effect when varying the frequency of the blade rotation on the magnitude of the in-phase current, though there is a slight shift in the wave towards positive potentials as the chopping frequency decreases. This is simply a consequence of the time constant of the lock-in detector compared to the chopping frequency and the finite scan rate of 5 mV s$^{-1}$ utilised.

At this concentration level the effect of varying the flow rate to the electrode surface was also investigated, whilst maintaining the frequency of the blade rotation at a constant rate. Figure 4-6 depicts in-phase rms current versus potential plots, recorded at
$V_f$ of 0.5 (●), 1 (●), 1.5 (●) and 2 (●) mL min$^{-1}$, with a blade rotation frequency of 1.34 Hz.

Figure 4-5 In-phase rms current vs. potential plots, recorded at a scan rate of 5 mV s$^{-1}$, using the electrochemical detection CF-MJE. A dual-disc UME was used to facilitate detection in a $5.02 \times 10^{-5}$ mol dm$^{-3}$ IrCl$_6^{3-}$ solution, at a range of blade rotation frequencies, 0.67 (●), 1.34 (●), and 2.68 (●) Hz, and at a volume flow rate of 2 mL min$^{-1}$. The time constant was set at 100 ms.

Figure 4-6 A series of in-phase rms current versus potential plots recorded using the CF-MJE system, coupled to electrochemical detection. A 25 µm diameter Pt-Pt dual disc UME was used to facilitate detection in $5 \times 10^{-5}$ mol dm$^{-3}$ IrCl$_6^{3-}$ solution. The volume flow rate was varied, 0.5 (●), 1 (●), 1.5 (●) or 2 (●) mL min$^{-1}$, and the blade rotation kept constant at a frequency of 1.34 Hz.
Figure 4-7 depicts a plot of $i_{\text{rms}}$ versus $V_f^{1/2}$, for the data shown in Figure 4-6. As expected from earlier studies in this chapter, $i_{\text{rms}}$ is observed to increase linearly as the volume flow rate to the electrode surface is increased. The overall enhancement in current, tested here, at the highest flow rate is almost four times larger than that recorded in quiescent solution.

![Figure 4-7 In-phase rms current versus $V_f^{1/2}$ response for the data depicted in Figure 4-6, which were recorded at a 25 μm diameter Pt UME, for the oxidation of $5 \times 10^{-5}$ mol dm$^{-3}$ IrCl$_6^{3-}$ solution.](image)

4.2.5 Facilitating Trace Level Detection

Having shown that mass transport modulation and phase sensitive detection is possible with the dual-disc MJE method, the next stage was to demonstrate that low concentrations of analyte could readily be determined. One of the main advantages of HMV is the ability to discriminate against background processes, which may hamper conventional voltammetric measurements, when employed to detect analytes at low concentration.
To illustrate that the CF-MJE system could be used for trace level detection, an attempt was made to detect Fe(CN)$_6^{4-}$ at a concentration of $5 \times 10^{-6}$ mol dm$^{-3}$. Figure 4-8 shows typical in-phase rms current versus potential plots, recorded at a dual disc UME, at a volume flow rate of 3 mL min$^{-1}$ and a blade rotation frequency of either 0.67 (●) or 2.68 (●) Hz. The in-phase rms current response at this volume flow rate yields mass transport limited currents of approximately 0.12 nA. Different settings of the time constant for the lock-in detector were used to record the data shown, with a time constant of 300 ms used for the blade rotation rate of 0.67 Hz, whereas at 2.68 Hz the time constant was set at 30 ms.

![Figure 4-8 In-phase rms current versus potential recorded in a solution of Fe(CN)$_6^{4-}$ 5 x 10$^{-6}$ mol dm$^{-3}$. Vf was 3 mL min$^{-1}$ and the blade rotation frequency was either 0.67 (●) or 2.68 (●) Hz.](image)

Figure 4-9 shows the in-phase rms voltammetric response for the oxidation of IrCl$_6^{3-}$ present in solution at a concentration of $5 \times 10^{-7}$ mol dm$^{-3}$, with $5 \times 10^{-2}$ mol dm$^{-3}$ KNO$_3$ background electrolyte. These results were acquired using the experimental set-up described for the data in Figure 4-3. A potential scan rate of 2 mV s$^{-1}$ was employed for
detection of the analyte. The maximum current recorded at an analyte (IrCl$_6^{3-}$) concentration of $5 \times 10^{-7}$ mol dm$^{-3}$ was around 6 pA. Even at this low concentration and current, the signal to noise ratio is sufficiently good for an accurate measurement of the limiting current.

![Graph](image)

**Figure 4-9** In-phase rms voltammetric behaviour for the oxidation of IrCl$_6^{3-}$ at a concentration of $5 \times 10^{-7}$ mol dm$^{-3}$ utilising a Pt-Pt dual disc UME. $V_f = 1.0$ mL min$^{-1}$, scan rate = 2 mV s$^{-1}$ and blade rotation frequency = 1.27 Hz.

Figure 4-10, is a summary of the rms limiting current - concentration behaviour obtained over a wide concentration range, with blade rotation frequencies in the range 1.27 ± 0.40 Hz and a flow rate of 1 mL min$^{-1}$, for IrCl$_6^{3-}$ detection. The excellent linear correlation of this calibration plot (slope of the log-log plot is 0.98; correlation coefficient of 0.99) serves to demonstrate the quantitative nature of the CF-MJE voltammetric method, when coupled to the electrochemical detection technique.
4.3 Optical Detection Reference Signal

The use of oxygen reduction as a reference signal for phase sensitive detection has been shown to work well, however, instances arise where this form of reference signal for in-phase HMV detection may not be suitable, e.g. when analyte oxidation / reduction occurs at a similar potential to the reference signal. Thus an optical detection system has been developed to provide a non-electrochemical reference signal for phase-sensitive detection.

4.3.1 Practical Arrangement Of The Optical Detection System

The arrangement resembled the CF-MJE set-up shown in Figure 2.4 (a) Chapter 2, however, a single Pt UME (dia. 25 µm) was used to facilitate electrochemical measurement of the analyte under investigation, and an LED-photodiode detector system provided a reference signal. The LED was fixed at the base of the cell in a
position close to the electrode (4 mm separation), a schematic of the arrangement was given in Figure 2.8, Chapter 2. The alignment of the LED and the photodiode detector prior to each experiment was essential as it was imperative that a constant reference signal was provided to the lock-in detector. This was accomplished, initially without solution in the cell; by adjusting the position of the detector, above the LED (between 5 -7 cm), until a maximum light intensity response was recorded at the photodiode detector measured using an oscilloscope. As the blade was rotated at frequencies, the light intensity was observed to modulate in the form of square waves, between a maximum (on) and a minimum (off) response, corresponding to the blade interrupting the signal to the detector.

When analyte solution was added to the electrochemical cell, it was necessary to focus the relatively diffuse light emitted from the LED, in order to enhance the modulating signal recorded at the detector, and thus provide a stable reference signal. Focusing was achieved by simply fastening a small circle of Teflon (dia. 10 mm, 2 mm thickness) with a pinhole (dia. 2 mm) drilled through it, over the LED using black epoxy resin. As a result, an overall increase in light intensity detected was noted, and the detector could be positioned up to 10-15 cm away from the LED, with little loss of signal intensity. In order to facilitate phase sensitive detection for the experiments herein, the response at the detector as the blade passed over the LED, was used to generate a reference signal, whilst the working electrode was scanned (or held) at a potential sufficient to detect the analyte of interest, ultimately at a mass transport controlled rate.
4.3.2 Preliminary Experiments

Experiments were initially conducted to establish the performance of the optical detection system over a range of blade frequencies, and to ensure that the modulated optical signal was in-phase with the electrochemical signal at the UME. Figure 4-11 depicts the typical simultaneous current-time response for the modulated LED signal, and the associated transport-limited current response of a 25 μm diameter Pt UME operating in the CF-MJE arrangement. The responses were recorded over 2.5 seconds, in an aerated analyte solution containing \(2.5 \times 10^{-4} \text{ mol dm}^{-3} \text{IrCl}_6^{3-}\) and 0.2 mol dm\(^{-3}\) KNO\(_3\), with the MJE characterised by \(H = 3 \text{ mm}, V_f = 2 \text{ mL min}^{-1}\), \(d = 100 \mu\text{m}\). The UME was biased at a potential of +0.9 V (vs. AgQRE) sufficient to perform the one electron oxidation of the analyte at a transport-controlled rate. The blade was rotated at a frequency of 0.67 Hz.

![Figure 4-11](image)

Figure 4-11 The modulated photodiode (optical) voltage (●) and mass-transport controlled current (○) responses, were recorded simultaneously by an oscilloscope. The disc UME was used to facilitate the oxidation of IrCl\(_6^{3-}\) present in the solution. A blade rotation frequency of 0.67 Hz and \(V_f = 2 \text{ mL min}^{-1}\) were employed.
From the typical result shown in Figure 4-11, it is possible to see that both the current and optical signals modulate between two extremes. The maximum current plateau corresponds to convective-diffusion mass transfer, resulting from solution impinging from the nozzle directly on the surface of the electrode. When the blade blocks flow, a sharp drop in the current response is observed, similar to that previously seen for the electrochemical detection results in section 4.2.3. The optical signal is also modulated between two extremes, where the blade either blocks or allows the signal from the LED to the photodiode. It can be seen that the two signals are closely in-phase, though from further similar experiments it was determined that above 2 Hz, the optical signal became severely distorted. This meant that a clean square wave corresponding to the blade rotation rate was not observed, and so frequencies of less than 2 Hz were used for subsequent experiments.

Since the overall experimental parameters, such as the maximum blade rotation frequency and the nozzle electrode separation distance (2.5 - 3 mm), had been optimised for the electrochemical detection experiments (described earlier), and the response of the optical detection system had been characterised, it was possible to conduct experiments using the optical detection arrangement, without need for further testing.

The first set of experiments conducted with the optical detection set-up were performed using a solution of $5 \times 10^{-4}$ mol dm$^{-3}$ IrCl$_6^{3-}$ with 0.5 mol dm$^{-3}$ KNO$_3$ acting as background electrolyte. Figure 4-12 shows the raw ($\bullet$) and rms in-phase (−) voltammetric response, versus potential recorded using a 25 μm diameter Pt UME, at a blade frequency of 1.35 Hz, with a volume flow rate of 2 mL min$^{-1}$. The UME potential was scanned between 0 and +1 V, at 2 mV s$^{-1}$. 

120
Figure 4-12 The raw (+) and rms (−) in-phase voltammetric response recorded at a 25 μm diameter Pt UME, in a solution of $5 \times 10^{-4}$ mol dm$^{-3}$ IrCl$_6^{3-}$, with a blade rotation frequency of 1.35 Hz.

From this result it can be seen that the current modulates between two well-defined extremes, corresponding to the situations where the flow reaches the electrode (high current) and where it is blocked (low current). The magnitude of the rms in-phase current was found to be 8.6 nA, which is in agreement to the expected value given that $i_{rms, lim} = \frac{\Delta i_{lim}}{\sqrt{2}}$, and $\Delta i_{lim}$ in this case is 21 nA.

Figure 4-13 shows the raw (+), and rms in-phase (•) voltammetric response recorded using similar conditions to those described above, but with the blade rotation frequency decreased to 0.67 Hz. The limiting current data acquired is of a similar magnitude to that recorded in Figure 4-12. The time constant for both experiments was 300 ms. Thus, it may be concluded that it is possible to use both frequencies and those within this range for further experiments to facilitate trace level detection.
4.3.3 Trace Level Detection Of IrCl₆³⁻

The optical CF-MJE was used to facilitate the detection of IrCl₆³⁻ over a range of concentrations from $5 \times 10^{-4} - 2 \times 10^{-7}$ mol dm⁻³. In each case the test solution was freshly diluted from a stock solution prior to use, and a selection of the data acquired is presented below in Figure 4-14 to Figure 4-17.

Figure 4-14 shows the rms in-phase current versus potential recorded in a solution of $5 \times 10^{-5}$ mol dm⁻³ IrCl₆³⁻. The data were acquired using a blade rotation rate of 1.36 Hz, at three different volume flow rates, 0.5 (−), 0.75 (−) and 1 (−) mL min⁻¹. As expected from earlier studies, the rms in-phase current is closely dependent on the $V_f^{1/2}$. As mentioned earlier in the Chapter, the in-phase currents measured are significantly larger than the dc current that would be expected in quiescent solution. A key observation is
that all three voltammetric responses are relatively noise free, and in each case a well-defined plateau is observed, as the current response becomes limited by mass transport. There is some shift in the position of the waves, associated with the filter frequency utilised in the lock-in detector.

![Figure 4-14 RMS in-phase current vs. voltage plots recorded at a 25 \( \mu \)m diameter Pt UME, in a 5 \( \times \) \( 10^{-5} \) mol dm\(^{-3} \) solution of IrCl\(_6^{2-}\), at a series of volume flow rates, 0.5 (-), 0.75 (-), 1 (-) mL min\(^{-1} \).](image)

Experiments investigating the effects of volume flow rate and blade rotation frequency were conducted for the oxidation of a 5 \( \times \) \( 10^{-6} \) mol dm\(^{-3} \) IrCl\(_6^{3-}\) solution (0.05 mol dm\(^{-3} \) KNO\(_3\), background electrolyte). Figure 4-15 depicts a typical set of results acquired at this concentration. For these experiments, the blade was rotated at a frequency of either 0.67 (●) or 1.36 (○) Hz for \( V_f = 1 \) mL min\(^{-1} \), and 0.67 Hz for \( V_f = 0.5 \) mL min\(^{-1} \) (●). The potential applied to the UME was scanned at 2 mV s\(^{-1} \), between +0.3 and +0.85 V, whilst the rms in-phase current was recorded. The voltammetric data attained at this level of concentration level are noise free and, in each case, the mass transport limited current is well defined. At \( V_f = 1 \) mL min\(^{-1} \) the in-phase rms limiting current is determined to be 0.1 nA, which is of the order of magnitude expected. The small
glitches in the current response that appears in this image are due to occasional variations in the blade rotation frequency, which influences the measurement of frequency by the optical phase sensitive detector.

![A set of in-phase rms current vs. potential plots recorded at a 25 μm diameter Pt UME, in a 5 x 10^{-6} mol dm^{-3} IrCl₆^{3-} solution. The plots show data recorded using the following conditions: \( V_f = 1 \text{ mL min}^{-1} \) and a blade rotation frequency of 0.67 (●) or 1.36 (○) Hz; \( V_f = 0.5 \text{ mL min}^{-1} \), and a blade rotation frequency of 0.67 Hz (●).](image)

It was evident from the quality of the results shown above, which were obtained at relatively weak concentrations of analyte solution, that it would be possible to further extend the limits of the optical detection CF-MJE technique. For the following experiments modified patch clamp instrumentation combined with high gain preamplifiers were used to facilitate detection of low current signals.

Figure 4-16 depicts a typical result recorded at a 25 μm diameter Pt UME, for the oxidation of 1 x 10^{-6} mol dm^{-3} IrCl₆^{3-} solution, containing 5 x 10^{-2} mol dm^{-3} KNO₃, serving as background electrolyte. As the limits of this detection technique are reached
the signal becomes noisier, although it is still possible to see a clear limiting current plateau, where the rms in-phase current becomes mass transfer limited at potentials between +0.7 and +0.9 V. The rms in-phase current is approximately 16 pA with ±1 pA of noise, which is close to a fifth of that observed at the previous concentration level.

![Graph](image)

Figure 4-16 In-phase rms current versus potential plot recorded at a 25 μm diameter Pt UME in a solution of $\text{IrCl}_6^{3-}$, flowed on to the electrode surface at 2 mL min$^{-1}$, whilst the blade was rotated at 1.35 Hz.

The concentration of $\text{IrCl}_6^{3-}$ in the test solution was decreased to $2 \times 10^{-7}$ mol dm$^{-3}$ (0.01 mol dm$^{-3}$ KNO$_3$, serving as background electrolyte), which was below the limit of detection for the CF-MJE coupled to the purely electrochemical detection technique. A volume flow rate of 1 mL min$^{-1}$ was flowed on to the surface of the electrode to obtain the data shown in Figure 4-17, whilst the potential was scanned between +0.3 to +1.0 V, at a rate of 2 mV s$^{-1}$. The blade was rotated at a frequency of 1.36 Hz. The rms in-phase current signal is approximately 1.6 pA, which is close to the expected value of 2 pA, based on the in-phase current recorded under similar experimental conditions for the oxidation of $5 \times 10^{-6}$ mol dm$^{-3}$ $\text{IrCl}_6^{3-}$. The quality of the signal recorded indicates
that the limits of detection are close to being reached using this technique. A final experiment was conducted in a $1 \times 10^{-7}$ mol dm$^{-3}$ IrCl$_6^{3-}$ solution, however, the lock-in detector was unable to aid the identification of the mass transport controlled current signal.

![Graph showing in-phase rms current versus potential](image)

**Figure 4-17** In-phase rms current versus potential recorded at a 25 μm diameter Pt UME in a solution of $2 \times 10^{-7}$ mol dm$^{-3}$, with a blade rotation frequency of 1.36 Hz and $V_r = 1$ mL min$^{-1}$.

### 4.4 Conclusion

The CF-MJE, coupled with two phase-sensitive detection techniques, has been introduced as a novel HMV technique. This new arrangement is a development of the original MJE-HMV system that employed a piezoelectric positioning apparatus, but allows the modulation of mass transport more readily, by the simple action of a rotating blade positioned between the nozzle, from which solution was flowed, and the electrode probe. In both cases, the blade has been shown to interrupt flow to the detector (working) electrode in a well-defined periodic fashion, such that the rate of mass
transfer, as manifested in the current, was modulated between high (flow on) and low (flow blocked) values. The modulation frequencies employed (0.5 - 2 Hz) compare favourably with those employed in the best pulsed-flow methodologies. By careful arrangement of the electrode, blade and nozzle, it is possible to obtain flow-on current signals, as experienced by a free flowing jet, and flow-off current values close to the expectations for a quiescent solution. This makes both of the techniques quantitative and allows ready analysis of current signals. The use of a dual-disc microelectrode probe enables the current for two electroactive solutes to be recorded simultaneously, so providing both a reference signal (reduction of oxygen), and a signal for the analyte of interest, thereby permitting the use of phase sensitive detection. These techniques have been utilised for the detection of a low concentration of analyte (sub-micromolar), where background processes would normally have obscured the small current signal. A further advance of the methodology has been the employment of a LED and photodiode detector to provide an optical reference signal for determination of the mass transfer switching frequency. This negated the use of a second electroactive mediator whose potential window may overlap with the analyte of interest. It has been shown in this chapter that the optical detection system works over a wider range of concentrations for the detection of IrCl₆³⁻ in solution.
References

Chapter 5  SECM Tip Position Modulation (TPM)

This chapter describes the use of tip position modulation (TPM) which functions in SECM as a means of identifying and enhancing the contrast in regions of varying surface activity. A set-up for this technique has been established and the basic parameters controlling the TPM response are identified for studies of inert and conducting samples and compared to earlier work.¹ This method is extended to the investigation of heterogeneous substrates, namely conducting band electrode structures on glass, and bovine articular cartilage.

5.1 Introduction

Scanning an UME, usually in a raster fashion or in a series of unidirectional lines, over either a conductive or insulating surface is a well-established technique and forms the basis for SECM imaging experiments.²,³,⁴ The UME is typically biased at a potential sufficient to either oxidise or reduce the species present in solution, and the corresponding current response is measured. In feedback SECM, movement of the probe toward a conducting surface results in an increase in the observed current, whereas the current decreases as the probe approaches an insulating surface.⁵ A fundamental problem with conventional SECM measurements, carried out at a constant height, is the inability to extract topographical information about a substrate that comprises both conductive and insulating regions, as a change in surface activity could be misconstrued for a change in topography.⁶,⁷

To overcome this problem, Wipf and Bard introduced TPM,¹ in which the UME is modulated vertically about a position, at predetermined peak-peak amplitudes, ±δ.
whilst being scanned over the substrate (Figure 5-1). As mentioned in section 1.5.3.1, Chapter 1, and highlighted briefly above, a movement of the UME away from a substrate surface results in a decrease in tip current \( (i_T) \) over a conductive area but an increase in \( i_T \) is observed over an insulating area. Thus, the two \( i_T \) responses are 180° out of phase with one another, and by recording the in-phase component of the modulated current response it is possible to highlight the activity of a substrate surface. Typically, SECM image resolution can be improved by using smaller tips, however, as the currents decrease the signal can become masked by noise. In TPM, this problem is overcome by modulating the tip, which removes the dc offset from the signal and therefore, the low frequency noise. The TPM technique was first used to characterise the surface of an interdigitated array (IDA) electrode, with a high degree of spatial resolution, but it has found surprisingly little application since.

![Figure 5-1 Schematic to show the modulation of the UME in TPM experiments, and the idealised current, \( i \), responses over a homogeneous conducting or insulating surface.](image)
The preliminary experiments described in this chapter were conducted to verify the set-up and establish the nature of the TPM current response over different surfaces. This is followed by a comparison of SECM and TPM images recorded at various substrate surfaces, including a band electrode structure on a glass substrate, and bovine articular cartilage. TPM has also been used as part of an investigation of graphite/epoxy composite electrodes; the results of the investigations are described in Chapter 6. One of the general aims of this work was to determine whether TPM data could be combined with the conventional fixed height imaging response to obtain both the topography and activity of a surface, as this has not previously been realised.

5.2 Establishing TPM At Conductive and Insulating Surfaces

Initial experiments were conducted to establish the parameters that influence the TPM response. There were a number of variants that could be manipulated whilst the tip was not in imaging mode, to optimise the tip response for subsequent imaging studies. These variants include the tip-substrate separation distance, the amplitude of tip modulation and the frequency of modulation.

The apparatus used for these experiments has been described in detail in Chapter 2. For these initial experiments, the x- and y-axis stepper motors were used to hold the tip in a fixed position parallel to the substrate surface, whilst the axial position of the electrode (normal to the surface) was manipulated using a piezo positioner. The output of the modulated current signal, recorded at the tip, was passed into both a lock-in detector (model SR810 DSP, California, USA), and an oscilloscope (Tektronix TDS 210, Tektronix Inc, USA) that was connected to a laptop computer that was used to record the response. Modulation of the tip was achieved by applying a voltage from the lock-
in detector to the piezo positioner, which caused it to move about a fixed point, over specific amplitudes and at defined frequencies.

In order to enhance the spatial resolution of the TPM method, a small Pt electrode of 5 \( \mu \text{m} \) diameter was utilised, and the \( RG \) of the electrode was 10. The fabrication of platinum electrodes\(^8\) was described in detail in section 2.1.2, Chapter 2. To acquire high-resolution images, it was also necessary to scan the tip close to the surface of the substrate. An UME of these dimensions, enables the tip to approach the surface at close distances, hence changes in topography and activity can be monitored with more detail than possible with a larger tip. Approach curves to both conductive and insulating surfaces were recorded with the 5 \( \mu \text{m} \) diameter Pt tip. A typical approach curve to a conducting surface, for the one electron oxidation of a solution containing \( 1 \times 10^{-2} \) mol dm\(^{-3}\) Fe(CN)\(_6\)^{4-} with 0.5 mol dm\(^{-3}\) KNO\(_3\) serving as background electrolyte, is shown in Figure 5-2. The conductive surface was a glass disc coated with a thin layer of platinum. After matching the experimental approach data to theory,\(^6\) it can be seen, from Figure 5-2, that the UME used for all of the TPM experiments described later, was able to reach within 0.6 \( \mu \text{m} \) of the conductive surface. An approach curve was recorded prior to all of the imaging experiments described herein, as it was deemed to be the most accurate way of interpreting the tip-substrate.
The modulated current signal, $i_{\text{rms}}$, was recorded at conductive and insulating surfaces, with the tip positioned above the substrate surface of interest. The majority of the experiments performed at the conductive substrate involved a solution containing $1 \times 10^{-2}$ mol dm$^{-3}$ ruthenium hexammine (III) chloride, and 0.5 mol dm$^{-3}$ potassium nitrate serving as background electrolyte. A steady state LSV was recorded, at a scan rate of 10 mV s$^{-1}$, to determine initially the potential required to perform a one-electron reduction of the mediator species present in solution (Figure 5-3). A potential of -0.45 V was found to be suitable to reduce the species at a diffusion-controlled rate, which resulted in a bulk tip current of ca. 8.6 nA.
Figure 5-3 A current-voltage plot recorded at a 5 μm dia. Pt UME, at a scan rate of 10 mV s⁻¹, for the reduction of 1 × 10⁻² mol dm⁻³ ruthenium hexammine chloride in a quiescent solution.

Initial experiments were performed with the 5 μm diameter UME biased at a potential sufficient to oxidise a solution of 1 × 10⁻² mol dm⁻³ Fe(CN)₆⁴⁻ with 0.5 mol dm⁻³ KNO₃ serving as background electrolyte, at a diffusion controlled rate. The UME was modulated over ± 0.25 μm, at a frequency of 30 Hz above both a conducting and insulating substrate surface, to investigate the phase of the signal generated, which was recorded directly by an oscilloscope. A comparison of the applied voltage signal (•), to the tip current response above each substrate was made and is shown in Figure 5-4. The initial separation between the tip and substrate surface was 1.5 μm. From Figure 5-4 it can be clearly seen, that the applied signal and tip response are reasonably in phase above the insulating substrate (•), although there is a small lag in the current response which is associated with the inherent diffusional time constant in electrochemical signal. In contrast the current signals recorded above the conducting substrate surface (•) is completely out of phase with the applied perturbation. The phase angle was
calculated by modelling the applied tip modulation signal to a sine wave. From these calculations, it was determined that the insulator and conductor current signal were 190° out of phase with one another, comparable to the expected value determined from previous studies, described earlier.

Figure 5-4 Current-time transients to demonstrate the effect of an applied tip position modulation (•) on the current signal, over a conducting (●) and insulating (*) substrate surface.

The next stage of the investigations focussed on optimising and quantifying the current signal for imaging purposes. For these experiments the current signal generated at the tip was passed into a phase sensitive detector, to facilitate the detection of the in-phase current component of the modulated signal.

Current-time signals were recorded using an oscilloscope, with the tip held in a fixed position away from the conducting substrate surface, and the amplitude of the modulation varied. Figure 5-5 shows a series of current-time signals that were recorded at an electrode-substrate separation distance of 0.9 µm, whilst the amplitude of the
modulation was varied between ± 0.05 and ± 0.25 µm at a fixed frequency of 10 Hz, about a fixed point. As expected, the magnitude of the resulting current can be seen to increase with an increase in the amplitude of the oscillation of the probe position. It was imperative that the tip, whilst modulating, did not touch the surface of the substrate, thus smaller amplitudes than the initial tip-substrate distance were used. The amplitude of modulation was also kept to relatively small values, to enable the piezo expansion to occur readily over the range of interest, with the possibility of using high frequencies when required. It is also important to emphasise that since a balance exists between the need to reach the steady-state current response at the two extremes of expansion (in order to treat the response in the simplest ways), and the ability to image a sample on a reasonable time scale. The first effect will place a maximum value on the oscillation frequency and amplitude that can be used.

![Figure 5-5 Current-time plots recorded at an electrode-substrate separation distance of 0.67 µm, for the oxidation of 1 x 10^-2 mol dm^-3 ruthenium hexamine (III) chloride (0.5 mol dm^-3 potassium nitrate, background electrolyte) above a conducting substrate surface. The tip was modulated at a frequency of 10 Hz, over different amplitudes (-) ± 0.05, (-) ± 0.1, and (-) ± 0.25 µm.](image-url)
The effect of a change in frequency on the locked in current can be seen in the plot shown in Figure 5-6, where the amplitude of modulation of the electrode was held at a fixed value, and the modulation frequency varied between 5 and 10 Hz. For these two extreme values, it can be seen in Figure 5-6 that a change in the frequency of modulation causes little affect on the amplitude of the tip current response, over the selected range. It is possible to conclude that at these relatively low piezo positioner frequencies and modulation amplitudes, the tip current response is well-defined and free from the possible convective effects or transient effects above a conducting substrate. Similar conclusions were previously made by Wipf and Bard, who carried out a much more comprehensive analysis.

Figure 5-6 Current-time plots for the oxidation of $1 \times 10^{-2}$ mol dm$^{-3}$ ruthenium hexamine (III) chloride (0.5 mol dm$^{-3}$ potassium nitrate, background electrolyte) to show the effect of varying the frequency on the tip response for a z-position modulation of $\pm$ 0.1 µm. The initial tip position was at a separation of 0.5 µm from the substrate surface.
The experiments described above were repeated at 20 Hz over the conductive surface, for the one-electron oxidation of $1 \times 10^{-2}$ mol dm$^{-3}$ Fe(CN)$_6^{4-}$ solution, containing 0.5 mol dm$^{-3}$ KNO$_3$ serving as background electrolyte, to determine whether the modulated signal generated at the UME would be attenuated by the use of a higher frequency. The in-phase root mean square current at the UME was recorded over a range of amplitudes between ± 0.05 and ± 0.25 μm. Figure 5-7 depicts the results for the experimental investigation. The in-phase tip current, $i_{\text{rms}}$, is normalised with respect to the tip steady-state current recorded in quiescent solution, $i_{\text{Tss}}$, far from the substrate surface. The electrode was held at three different separations from the surface, where $d$ was 1.6 (○), 2 (○), 2.5 (○) μm.

Figure 5-7 Normalised current recorded when modulating an UME at different amplitudes and various distances above a conducting surface; 1.6 (○), 2.5 (○), 3 (○) μm. The tip modulation frequency was maintained at 20 Hz.

These results are consistent with those shown earlier where, as the total amplitude of modulation is increased, a rise in $i_{\text{rms}}/i_{\text{Tss}}$ is seen.
Previous studies of TPM,\textsuperscript{1} have quantified $i_{rms}$ for small values of $\delta$, by considering the in-phase TPM signal to be the derivative of the theoretical feedback response at conducting or insulating substrates.\textsuperscript{1} Thus, theoretically for each value of $i_{rms}$ the tip-substrate separation could be realised. The derivatives of the feedback equations at conducting and insulating substrates are given by equations 5:1 and 5:2 respectively, and are plotted in the form of $\Delta i/\Delta d$, in Figure 5-8.

\[ \frac{\Delta i_{\text{cond}}}{\Delta d} = -1.96 + 0.89 \frac{-2.69}{d^2} \]

\[ \Delta i_{\text{insulator}} = \frac{0.98(d - 15.75)}{d^2} \exp \left( \frac{0.98}{d^2} \right) \]

\[ \Delta i_{\text{insulator}} = - \left[ - \frac{3.84}{d^2} + 1.65 \frac{-2.85}{d^2} + 0.09 \left( \frac{0.98(d - 15.75)}{d^2} \right) \exp \left( \frac{0.98(d - 15.75)}{d^2} \right) \right] \]

Figure 5-8 A plot of the theoretical $\Delta i/\Delta d$ TPM response versus distance at a conducting (-) and insulating (-) substrates, calculated from equation 5:1 and 5:2.
Chapter 5

The experimental TPM data acquired for the conductive substrate were compared to equation 5:1 and the tip-substrate separation distances were calculated from the in-phase $i_{ms}$ currents. For the data presented in Figure 5-7 the tip-substrate separation distances from steady-state feedback responses were determined to be 1.6 (●), 2 (●), 2.5 (●) μm, and those calculated from the derivative curves, $\Delta i/\Delta d$, the average separations were found to be 1.7 ± 0.15, 2.1 ± 0.05, and 2.4 ± 0.1 μm, respectively. This comparison and further studies demonstrate that TPM gives reliable information on tip-substrate separations.

Having successfully investigated SECM-TPM responses over a conductive surface, similar experiments were performed over an insulating glass surface. Figure 5-9a, b, and c depict a selection of the data recorded to investigate the effect of moving the 5 μm diameter Pt UME at amplitudes ranging between ± 0.05 and ± 0.25 μm, over an insulating surface at two different frequencies, 5 or 10 Hz. The experiments were conducted in a solution of $1 \times 10^{-2}$ mol dm$^{-3}$ ruthenium hexammine (III) chloride, with 0.5 mol dm$^{-3}$ KNO$_3$ serving as background electrolyte. The electrode was positioned so that it was 0.75 μm away from the substrate surface. This was estimated by moving the electrode towards the surface using a piezo controller, whilst monitoring the tip current, until it dropped to approximately 1/3 of the current recorded in quiescent solution. By comparison of the ratio of the tip current to the current recorded in quiescent solution, it is possible to determine the tip-substrate separation, as described theoretically by Kwak and Bard.$^6$
Figure 5-9 A series of current-time data recorded at a 5 μm diameter Pt UME above an insulating glass substrate, at an initial tip-substrate separation of 0.75 μm, at different amplitudes and frequencies: (●) ± 0.05 μm, at a frequency of 10 Hz (●) ± 0.1 μm at a frequency of 10 Hz and (●) ± 0.25 μm at a frequency of 5 Hz.

From Figure 5-9 it can clearly be seen that as the amplitude of tip oscillation is increased, there is a corresponding enhancement in current. For the largest amplitude displacement tested the observed current is seen to vary by 0.2 nA. The frequency at which the tip modulation occurs has little effect upon the amplitude of the signal recorded. These frequencies were deemed to be suitable for use in later imaging experiments. It can also be seen that the magnitude of the currents recorded at each displacement, are much smaller than those recorded at the conducting surface. This is as expected based on the negative feedback distance responses.

To quantify the magnitude of the TPM currents observed above the insulating substrate further experiments were conducted at a different tip modulation frequencies and amplitudes. A 5 μm diameter Pt UME was used for these investigations, for the one-
electron oxidation of $1 \times 10^{-2}$ mol dm$^{-3}$ Fe(CN)$_6^{4-}$, in a solution also containing 0.5 mol dm$^{-3}$ KNO$_3$ serving as background electrolyte. The tip was maintained at a constant separation of 1.5 µm above the insulating substrate surface. This distance was determined by biasing the UME at a potential, sufficient to oxidise Fe(CN)$_6^{4-}$ at a diffusion controlled rate, typically +0.6 V, and performing an approach curve to the insulating surface, and comparing the experimental approach curve to theory. Having established the tip-substrate separation distance, TPM experiments were conducted where the UME position was modulated at frequencies between 10 - 20 Hz, over amplitudes between $\pm 0.0125$ and $\pm 0.25$ µm. The results of this investigation are shown in Figure 5-10, where the ratio of the in-phase current signal to the current recorded prior to tip modulation in quiescent solution ($i_{rms}/i_{\infty}$) versus log of the modulation frequency is plotted. As for the conductor TPM experiments, the theoretical TPM responses above an insulating substrate can be calculated for small values of $\delta$ from equation 5:2, a derivative of the theoretical dc SECM response, and have been plotted as a function of tip-substrate separation distance, $d$ in Figure 5-8.

From Figure 5-10 it is evident that as the frequency is increased $i_{rms}/i_{\infty}$ remains reasonably constant (showing a small increase) at all amplitudes, indicating that it is possible to modulate the tip at frequencies up to 20 Hz without serious effect on the signal. Again, as the total modulation amplitude was increased, the $i_{rms}/i_{\infty}$ current recorded also increased. It was possible to calculate the tip-substrate separation distances for each of the results depicted in Figure 5-9, by comparison of the experimental results to the derived theory (Figure 5-8). The actual tip-substrate separation distance was 1.5 µm, from the dc hindered diffusion response and the mean
of the TPM responses yielded a separation distance of $1.4 \pm 0.1 \mu m$. It should be mentioned that at closer tip-substrate distances, the TPM data did not give as good agreement with the $dc$ response at this range of frequencies. This is most probably because the inherent diffusional time becomes longer the closer the separation in hindered diffusion mode, which introduces a timelag in the current response following TPM perturbation.

Figure 5-10 Plot of $i_{rms}/i_{m0}$ versus Log frequency, recorded for the one-electron oxidation of a solution of $1 \times 10^{-2}$ mol dm$^{-3}$ Fe(CN)$_6^{4-}$ at a 5 $\mu$m diameter Pt UME. A variety of modulation amplitudes were used, where $\delta$ was 0.0125 (•), 0.025 (+), 0.05 (•), 0.075 (+), 0.1 (•), and 0.25 (+) $\mu$m.

In summary, TPM experiments at the conducting and insulating substrate surfaces have demonstrated that a change of phase of the experimental $i_{rms}$ was observed compared to the applied modulation. The $i_{rms}$ currents recorded under each set of conditions were compared to theory derived from the original feedback equations. By comparison of the experimental results to the derived theory it was determined that at low tip modulation frequencies ($5 - 20$ Hz), above conducting substrates, the $i_{rms}$ data could provide an
accurate tip-substrate separation distances. However, for the parameters tested, above the insulating substrate, the experimental tip-substrate separation distances were not always comparable to those determined prior to TPM experimentation, from SECM feedback responses, if the tip-substrate distance was too close or modulation frequency too high. This is in agreement with earlier work.¹

5.3 Applications of TPM

5.3.1 Band Electrodes

Since suitable parameters for the modulation frequency and amplitude had been determined at the uniform test substrate surfaces, with the tip fixed in the x-y plane, the next stage of the investigation was to examine a system where TPM imaging could be used to map the activity of a surface. Both conventional feedback SECM and TPM were used to allow a comparison of the two methods.

A simple band electrode structure on a glass slide was selected as a test substrate. The band electrode consisted of a series of parallel lengths of gold, which were all connected together at the vertices, as shown in the optical micrograph, Figure 5-11. Each regular band was 168 μm wide and the bands were separated by 168 μm of glass. The pattern had been placed on the slide using a photolithographical method (courtesy of Dr. P. Dobson, Electronic Engineering, Glasgow University). Prior to the imaging experiments, a biased 5 μm diameter Pt UME was moved towards the insulating region of the substrate surface, whilst the current was monitored, to record an approach curve for the one-electron oxidation of $1 \times 10^{-2}$ mol dm$^{-3}$ Fe(CN)$_6^{3-}$ containing 0.5 mol dm$^{-3}$
KNO₃ which served as background electrolyte. This information was used to determine the overall tip/substrate separation distance⁶ for the course of the SECM and TPM imaging experiments. For each imaging experiment, a scan size of 1000 (y) × 30 (x) µm was used, so that a large variation between areas of activity would be observed. The electrode was scanned in a series of unidirectional lines across the surface at a rate of 5 µm s⁻¹, and the corresponding tip current was monitored, as a function of tip position.

Figure 5-11 An optical micrograph of the band electrode structure investigated using both SECM and TPM. The co-ordinates for the x-y imaging scan are indicated.

Figure 5-12 depicts a typical SECM image recorded at a 5 µm diameter Pt UME, biased at +0.6 V, sufficient to oxidise Fe(CN)₆³⁻ (1 × 10⁻² mol dm⁻³, with 0.5 mol dm⁻³ KNO₃ serving as background electrolyte) at a mass transport limited rate. The tip was maintained at 2.5 µm from the surface of the substrate, with a step size of 2 µm in the x-axis and 5 µm in the y-axis. The currents shown on this image have been normalised by the steady-state diffusion-limited current recorded, prior to imaging, in a quiescent solution. The colour key, which relates to the normalised currents, is shown in Figure
5-13. From this image it is possible to observe that the pink/purple regions are related directly to an enhanced region of current, i.e. an active/conductive region of band electrode structure. Conversely, the red/orange areas relate to areas where the surface of the structure is non-conducting, which we may assume is the exposed insulating glass slide.

![Figure 5-12 A 2-D SECM plot of normalised current versus tip position, recorded at a 5 µm diameter Pt UME, biased at +0.6 V, in a solution of 1 x 10^-2 mol dm^-3 Fe(CN)_6^{3-}, with 0.5 mol dm^-3 KNO_3 background electrolyte. The current data correspond to the key shown in Figure 5-13.](image)

**Figure 5-12** A 2-D SECM plot of normalised current versus tip position, recorded at a 5 µm diameter Pt UME, biased at +0.6 V, in a solution of 1 x 10^-2 mol dm^-3 Fe(CN)_6^{3-}, with 0.5 mol dm^-3 KNO_3 background electrolyte. The current data correspond to the key shown in Figure 5-13.

![Figure 5-13 A 3-D plot of normalised current vs. x and y position of the UME, for data recorded over a band electrode structure, using a 5 µm diameter Pt UME.](image)

**Figure 5-13** A 3-D plot of normalised current vs. x and y position of the UME, for data recorded over a band electrode structure, using a 5 µm diameter Pt UME.
By plotting the data shown in Figure 5-13 in 3-D format, the conducting regions can be seen to be well defined, and appear at regular intervals. Each conductive area is flanked by a thin stripe of blue/green (approx. 10 \( \mu \)m thick), which represents the rapid change between the conducting and insulating regions. The areas of activity correlate closely with the dimensions of the bands observed by optical microscopy.

A series of TPM experiments were carried out to compare with the conventional feedback SECM experiment described above. These experiments utilised an identical initial tip-substrate separation distance, scan size, scan rate and step size. The electrode was modulated over amplitudes of either \( \pm 0.25 \) or \( \pm 0.1 \) \( \mu \)m, at a frequency of 20 Hz. The modulated current signal was fed into both an oscilloscope and a lock-in detector, in order that the in-phase imaging signal, \( i_{\text{rms}} \), could be extracted.

Figure 5-14 depicts a typical TPM image of the gold band substrate recorded at a 5 \( \mu \)m diameter Pt UME, where the lock-in current, \( i_{\text{rms}} \), has been normalised with respect to the current recorded at the tip in quiescent solution, \( i_{\text{T,0}} \). In this experiment the tip was modulated over an amplitude of \( \pm 0.25 \) \( \mu \)m and the tip was biased at a potential of +0.6 V throughout the course of the experiment, to promote the diffusion-limited electrolysis of \( 1 \times 10^{-2} \) mol dm\(^{-3}\) Fe(CN)\(_6\)\(^{3-}\).
Figure 5-14 A plot of $i_{\text{rms}}/i_{\text{dc}}$ vs. $x$ and $y$ position recorded at a 5 μm dia. Pt UME during a TPM experiment. The tip was modulated over an amplitude of ± 0.25 μm, at a frequency of 20 Hz.

The most notable aspect of the image in Figure 5-14 is that both positive and negative signals are observed, corresponding to different areas of the image. This result indicates that a change of phase of the tip current, with respect to the applied modulation, is seen in different areas of the substrate surface. In comparison to the conventional SECM image (Figure 5-13), the purple regions in Figure 5-14 (positive currents, in phase with the applied modulation) now correspond to regions of glass insulator, and the orange areas (negative currents, out of phase with the applied modulation) represent the gold bands. The TPM set-up is responding in the manner expected from preliminary experiments that investigated the phase change at conducting and insulating substrates.
The TPM image resembles the SECM image shown in Figure 5-13, in that the image consists of a series of bands. However, there is a noticeable difference in resolution between the images of the bands. In the 3-D TPM image, the current response over a particular region within a band appears to be less uniform than in the conventional feedback SECM image. It is important to note that in the TPM image a sharp peak (pink band) in the current is seen before each region of positive current, i.e. when the probe moves from the conducting to the insulating region. This peak may be explained as an artefact of the phase-sensitive detection process, where there is a sudden change of phase between the two regions, which occurs in a short period of time.

Figure 5-15 shows the TPM data acquired at a tip modulation of ± 0.1 µm, a modulation frequency of 20 Hz, where the ratio of in-phase tip current to the current recorded in quiescent solution, prior to tip modulation, versus the tip x-y position is plotted. From the TPM images in Figure 5-15, it is possible to see that as the magnitude of the overall tip position modulation was decreased a corresponding decrease in the magnitude of the currents was observed, by the phase sensitive detection method. This observation correlates well with the preliminary experiments in section 5.2, conducted at the planar conducting and insulating glass substrates. A thin band of increased normalised current also appears in this image, as it did for the larger modulation amplitude, suggesting that it is a true artefact of the interface between the conducting and insulating regions. Again, the various regions of the band structure appear less uniform than in a conventional feedback SECM image; this illustrates the ability of TPM to highlight variations in activity and/or topography.
Figure 5-15 TPM images of the band electrode structure, recorded at a 5 µm diameter Pt UME, modulated over an amplitude of ± 0.1 µm, at a frequency of 20 Hz.

5.3.2 SECM and TPM Imaging of Bovine Articular Cartilage

The previous studies were carried out on a substrate where the topography was relatively uniform and the activity changed between two extremes in well-defined domains. The following investigations probe a substrate of non-uniform activity and topography, namely bovine articular cartilage, a substance that has been examined using conventional feedback SECM. These earlier studies involved the use of SECM to investigate the permeability of oxygen in cartilage. The experiments involved probing the topography and permeability of the substrate by recording an SECM image at a fixed height using two mediators; one that permeated the cartilage (oxygen) and one that was impermeable (Ru(CN)$_6^{4-}$). The latter responded to topographical changes in the substrate. A mathematical model was developed to relate the two images, resulting
in oxygen permeability maps of the cartilage surface.\textsuperscript{9} In the studies described herein, the idea is to use TPM to simultaneously image both topography and activity of the cartilage substrates, with the use of only one mediator solution, by recording the in-phase current component of the signal generated, and the mean current (or dc response).

The experimental arrangement and preparation of the sample was described in detail in Chapter 2. Briefly, the cartilage used for these investigations was acquired from a fresh joint, from which plugs had been removed, sliced into thin sections (approx. 50 µm thick, 5 mm diameter) and frozen. Prior to experimentation, the required section was defrosted in phosphate buffer solution. Figure 5-16 shows an optical micrograph taken of a typical section of cartilage.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{cartilage_section.png}
\caption{An optical micrograph of a section (50 µm thick) of bovine articular cartilage.}
\end{figure}
Cartilage is composed of an extracellular matrix, which is made up of negatively charged proteoglycan molecules, and chondrocyte cells, that are supported by a network of collagen fibres. It is possible to see some of these structures in Figure 5-16. The chondrocyte cells appear as oval pit-like shapes approximately 15 – 25 µm in diameter and are typically located in small groups distributed throughout the matrix. Other features are too small to be visualised under a light microscope and have been studied previously using SEM\textsuperscript{10} and more recently using atomic force microscopy,\textsuperscript{11} where the structural nature of collagen fibres was elucidated.\textsuperscript{12}

For the experiments described herein, both dc SECM images and TPM images of the cartilage surface were recorded. Prior to experimentation to establish the tip-substrate separation distance, an approach curve was recorded to the surface of the cartilage, where, the tip current, $i_T$, for the oxidation of $5 \times 10^{-3}$ mol dm$^{-3}$ Ru(CN)$_6^{4-}$ solution was monitored as the UME was slowly approached to the substrate until the limiting current fell to approximately three quarters of the value recorded when the electrode was placed in bulk solution, i.e. $i_T/i_{T_{\infty}} = 0.35$. For an inactive surface, SECM negative feedback theory predicts a tip-substrate separation of 1.5 µm.\textsuperscript{6} This method assumes that the surface of the substrate is planar with respect the UME.

A series of TPM and conventional SECM experiments were carried out over the cartilage substrates, and only a small selection of the resulting images is presented here. These images show the different modes of imaging for the same sample area. A typical 2-D contour plot is shown in Figure 5-17, representing SECM data recorded at a 5 µm
diameter Pt UME for the one-electron oxidation of $5 \times 10^{-3}$ mol dm$^{-3}$ Ru(CN)$_6^{4-}$ in solution containing 0.5 mol dm$^{-3}$ KNO$_3$ serving as background electrolyte. The total area scanned was $100 \times 100$ µm ($x \times y$), at a scan rate of 5 µm s$^{-1}$. The tip was biased at +1.2 V which was determined to be the potential required to facilitate mass transport-limited detection. The tip currents recorded have been normalised by the current recorded in quiescent solution, $i_{T_{dc}}$, which was determined to be 3.1 nA. The pink areas represent high-normalised currents, though a more detailed key to the image can be found in Figure 5-17.

Figure 5-17 A typical SECM image of cartilage recorded at a 5 µm diameter Pt UME, for the one-electron oxidation of $5 \times 10^{-3}$ mol dm$^{-3}$ Ru(CN)$_6^{4-}$ at a diffusion controlled rate, over a scan area of $100$ µm $\times$ $100$ µm ($x \times y$).

This SECM image is typical of the results acquired over larger scan areas and at different tip-substrate separation distances. As the mediator used was impermeable to the cartilage, this image represents the topography of the cartilage surface. The most notable features of this image are the appearances of small circular areas (generally
represented as pink/blue areas), which have higher values of normalised current, than the surrounding cartilage matrix. The increase in current in the localised areas can only be due to an increase in the tip-substrate distance, which highlights that the surface contains a series of reasonably well-defined pits, as found previously.\(^9\)

TPM experiments were performed with both the impermeable and permeable mediators, in order to improve the resolution of the SECM images acquired and to attempt to highlight clearly the surface activity of the cartilage.

The experimental data presented relates to an identical scan area to that described and shown in Figure 5-17, and the tip was initially maintained at the same tip-substrate separation distance. Figure 5-18 shows a contour plot representing data recorded during a TPM experiment with a 5 µm diameter Pt UME, for the oxidation of \(5 \times 10^{-3}\) mol dm\(^{-3}\) \(\text{Ru(CN)}_6^{4-}\) solution containing 0.5 mol dm\(^{-3}\) \(\text{KNO}_3\) serving as background electrolyte. The total area scanned was 100 µm \(\times\) 100 µm \((x \times y)\), at a scan rate of 5 µm s\(^{-1}\). The tip was modulated over an amplitude of \(\pm 0.5\) µm at a frequency of 20 Hz. For the image shown \(i_{\text{rms}}/i_{\text{Tao}}\) versus the lateral tip position is plotted.
The image shown in Figure 5-18 is significantly better resolved than the image acquired for the same mediator using conventional SECM methodologies. Here, it is possible to distinguish well-defined oval pit areas, which are likely to correspond to chondrocyte cells, as seen in the optical micrograph image (Figure 5-16). In this TPM image, the pits appear to be approximately between 20-25 μm in diameter. This corresponds well to the sizes defined earlier by optical micrography. Moreover, the current response is higher at the closer tip-substrate separations, which agrees with the approach curve for hindered diffusion.

A series of oxygen reduction SECM images were recorded for the identical area to that described above and a typical image is shown in Figure 5-19. Here, the UME was biased at a potential sufficient to reduce oxygen at a diffusion-controlled rate, -0.6 V.\textsuperscript{13}
The tip was maintained at the same separation distance away from the substrate, and scanned across the sample at the same rate. For the image shown the ratio between $i_T$ and $i_{T_{0}}$ versus the UME position has been plotted. The normalised currents are all much higher than for the Ru(CN)$_6^{4-}$ oxidation experiment and this is due to the ability of oxygen to permeate the majority of the cartilage matrix.\textsuperscript{14} However, it can be seen that there are definite regions of high and low current, which can be compared to the topographical Ru(CN)$_6^{4-}$ scan. This oxygen reduction data contains information on both topography and permeability.

![Figure 5-19 A contour map of the cartilage surface, imaged using conventional SECM for the diffusion controlled reduction of oxygen.](image)

TPM experiments were repeated using oxygen as a mediator, a typical result, recorded over an identical area to that described above, is shown in Figure 5-20. The electrode-substrate separation distance was maintained at that used for the previous experiments. The electrode was modulated at a frequency of 20 Hz, over an amplitude of ± 0.5 μm. The UME was scanned over the identical area to that investigated using SECM, where the total scan area was 100 × 100 μm.
There is a noticeable difference when comparing the SECM (Figure 5-19) and TPM (Figure 5-20) images recorded for the diffusion-controlled reduction of oxygen. It is evident that there is a marked improvement in the resolution of cartilage activity when using TPM. From the TPM image, it is possible to see individual circular areas that are thought to correspond to the chondrocyte cells, which cannot be distinguished from the SECM image. These cellular areas appear to be of equivalent size to those observed in both the Ru(CN)$_6^{4-}$ SECM and TPM images. The magnitude of the currents differs across the scan, in that the smallest currents appear as red regions, which correspond to areas of the image containing pits. The majority of the cartilage matrix is coloured in pink/purple and the normalised currents in these areas vary between 0.05 – 0.07. It is important to note, however, that the normalised TPM currents for O$_2$ reduction are generally lower than for Ru(CN)$_6^{4+}$ oxidation. This indicates that O$_2$ is drawn from the sample by the scanning tip which decreases the magnitude of the in-phase current, based
on approach curves from SECM induced transfer. In principle, it should be possible to analyse a dc image such as that in Figure 5-19 and a TPM image such as that in Figure 5-20 to obtain both topography and permeability (activity) information, since the dc and TPM current responses are expected to have different dependence on tip-substrate separation and activity. However, this procedure would require that the tip current response to be extremely stable.

5.4 Conclusions

Experiments have been undertaken at planar surfaces, to quantify and optimise the parameters under which TPM is performed. The current response at the conductive substrate surface was found to fit well to the theory, however, the response at the insulating substrate surface did not always correlate well over the entire range of amplitudes and frequencies tested, but there were conditions where reasonable agreement was found.

As established previously, the TPM imaging technique has considerably better resolution capability than dc SECM. The results of the TPM imaging experiments over a regular band electrode showed that it was also possible to highlight small variations in activity of the conducting bands, which were not observed in a conventional feedback SECM imaging scan of the corresponding area. The ability of TPM to distinguish between variations in surface activity has been demonstrated, in particular, by the investigation of bovine articular cartilage. It has been shown that it is possible to
differentiate between pit-like chondrocyte cells and the remaining cartilage matrix, by imaging with either a permeable or impermeable mediator.

Although the results obtained for TPM cartilage imaging are purely qualitative at this time, it should ultimately be possible to relate the modulated tip and $dc$ (or mean) currents recorded to the topography and activity of a substrate surface, without the need for SECM imaging with two mediators.
References


Chapter 6 Carbon:Epoxy Composite Electrodes

This chapter describes electrochemical and electrical investigations of the local surface activity of carbon:epoxy composite electrodes, using a variety of techniques, namely SECM, TPM, and C-AFM. The composite electrodes vary in thickness and comprise conducting graphite particles mixed with an insulating epoxy resin in a variety of ratios. This study investigates variations in the electrical and electrochemical activity as the thickness and carbon:epoxy mass ratio is changed. The electrochemical behaviour of the composite electrodes will be compared to arrays of microelectrodes and macroelectrodes.

6.1 Introduction

The fabrication and use of composite electrodes, where a conducting material is embedded in an insulator, is well established. Carbon based composite electrodes have considerable advantages over other more conventional electrodes such as those made from platinum or gold, in that they are cheap and easy to produce, miniaturised easily where required, and can been used for a variety of applications. These include composites where biological receptor phases, such as catalysts or enzyme cofactors, are added to improve the response of the electrochemical biosensors. Carbon black filled polymers have also been used for a variety of industrial applications where anti-static conducting materials or semi-conducting materials are required.

The amount of conductive material in a composite can be varied to change its electrical properties. For low quantities of conductive material, the distance between conducting particles is large, therefore, the conductance is limited by the insulating matrix. At a
critical content of conducting material, the conductive particles get closer and form conductive paths through the material, thus the composite undergoes a transition from insulating to conducting behaviour.\textsuperscript{2} The point at which this transition occurs is known as the percolation threshold.\textsuperscript{6,7} The percolation theory is dependent upon the existence of clusters of connected sites (bonds). An infinite number of clusters are said to exist above the percolation threshold.\textsuperscript{4} The percolation behaviour of different types of composites has been well studied,\textsuperscript{2} including those that incorporate conductive carbon fibres and carbon nanotubes.

Previous studies of the behaviour of different ratios of the carbon (in the form of graphite):epoxy composite electrodes,\textsuperscript{8} using conducting atomic force microscopy (C-AFM)\textsuperscript{9,10,11} and cyclic voltammetry (CV), found that 1 mm thick composite slices, comprising a 60 carbon:40 epoxy (ratio by weight) mixture, behaved as a bulk macroscopic conductor, with isolated islands of insulator.

The investigations described herein focus on high resolution surface activity and topography measurements of 60:40 and 40:60 carbon:epoxy composite electrodes of 1 mm and 2.5 mm thickness. These measurements are performed using scanning electrochemical microscopy (SECM)\textsuperscript{12} in both feedback\textsuperscript{13} and substrate generation / tip collection modes (SG/TC)\textsuperscript{14} and C-AFM. In the latter case the C-AFM tip is held in constant contact with the surface of the composite electrode, while SECM measurements are made in solution as the tip is scanned just above the surface.\textsuperscript{15}

Preliminary AFM topographical imaging experiments were conducted using a silicon-nitride probe tip (Nanoprobes, Inc.). A typical topographical and deflection image, of a
40 carbon: 60 epoxy blend, over a 10 × 10 μm scan area, is shown in Figure 6-1. The variations of the surface structure are clearly visible in the topographical image (a). Surfaces edges, corners and steps are highlighted by the deflection image (b), which is generated by recording every deflection made by the cantilever, as it is scanned across the surface, in response to changes in the surface topography. It is clear that over the region investigated the height of the surface varies up to a maximum of 1.5 μm, this is significant when determining the scan height for SECM imaging described in section 6.2.2.

![Figure 6-1 Topographical (a) and deflection (b) AFM images of the surface of a typical 40 carbon: 60 epoxy composite electrode.](image)

### 6.2 Voltammetry and Scanning Electrochemical Microscopy

The construction of the composite electrodes was described in detail in section 2.7, Chapter 2. Briefly, fine graphite powder was mixed in different ratios with epoxy resin, and cast in plastic tubes. The required thickness of each electrode (either 1 or 2.5 mm) was sectioned off, and an electrical connection made to the entire base using silver loaded epoxy resin. In each case, the diameter of the exposed electrode surface was 4.5 mm. The blends tested here were of a carbon mass ratio that is above the lower percolation limit,\(^4\) where the transition from an insulator to conductor occurs.
The composite electrodes were mounted on the Teflon base of an electrochemical cell, using epoxy resin to insulate the exposed sides of the electrode. Epoxy was also used to fix the composite sample to the cell base so that mediator solution would not reach the electrical contacts. A photographic image and schematic of the experimental arrangement that was used for both voltammetric and SECM imaging measurements is shown in Figure 6-2.

![Figure 6-2 A photograph and schematic of a composite electrode mounted onto a cell base.](image)

All voltammetric measurements made with the composite electrodes utilised a three-electrode arrangement. Here, the composite electrode served as the working electrode, a silver wire served as the reference electrode and Pt gauze was used as a counter electrode. For SECM feedback and SG/TC imaging experiments a 2 μm diameter Pt UME tip was utilised.
6.2.1 Voltammetry of Carbon: Epoxy Composite Electrodes

Cyclic voltammetry was used to understand the behaviour of the composite electrodes in quiescent solution. Prior to experimentation, all of the composite electrodes were prepared in the same manner, in which they were first polished on a slurry of alumina, sonicated in distilled water (15 min.), and finally wiped clean with ethanol. The polishing process was conducted in an attempt to remove any traces of contamination at the exposed test surface. CV experiments were performed on each type of electrode, in a test solution of $1 \times 10^{-2}$ mol dm$^{-3}$ IrCl$_6^{3-}$ with 0.5 mol dm$^{-3}$ KNO$_3$ serving as a background electrolyte. The potential at the electrodes was swept between 0 and +1.2 V, at a scan rate of either 10 or 100 mV s$^{-1}$. The results shown in this chapter are representative of many experiments performed at the different composite electrodes.

Figure 6-3 depicts five successive CVs that were performed at the 1 mm thick, 40 carbon: 60 epoxy sample at 100 mV s$^{-1}$. Each successive cyclic voltammogram is shown in a different colour, where the dark blue CV was recorded first, followed by the green, red, orange, and light blue CV last.

Figure 6-3 A set of successive CVs recorded in a solution of $1 \times 10^{-2}$ mol dm$^{-3}$ IrCl$_6^{3-}$ containing 0.5 mol dm$^{-3}$ KNO$_3$, at the 1 mm thick, 40:60 composite electrode, at a scan rate of 100 mV s$^{-1}$. 
As shown, electrochemical activity in the region between +0.4 and +1.0 V, where the oxidation of IrCl₆³⁻ typically occurs, is ill defined. However, it is known that the rate and potential range where redox activity is observed on a carbon surface may differ to that for a noble metal electrode, eg. Pt or Au, as electron transfer is dependent on the structure and preparation of the surface.¹⁶ For the investigations described herein, the electrodes comprise a graphitic carbon surface, mixed with epoxy resin. Also, as carbon has a higher surface activity than conventional metallic electrodes,¹⁶ it is therefore, susceptible to contamination by organic compounds present in solution. Thus, it was deemed necessary to "electrochemically clean" the surface of the electrodes. This process, termed herein as surface activation, was achieved by performing a series of CVs (typically 10) in a solution of 0.5 mol dm⁻³ H₂SO₄. The potential at the composite electrode was swept between 0 and +2.5 V, at a scan rate of 10 or 100 mV s⁻¹, to oxidise or desorb any contaminating organic products from the surface.

Once the activation process was complete, the composite surface was washed with distilled water before a series of CVs were recorded in a solution containing 1 × 10⁻² mol dm⁻³ IrCl₆³⁻ and 0.5 mol dm⁻³ KNO₃. The potential was again swept between 0 and +1.4 V, at a scan rate of 10 (a) and 100 (b) mV s⁻¹. Typical voltammetric results are shown in Figure 6-4 (a) and (b), and each successive CV is represented as a different colour.
Chapter 6

Figure 6-4 A series of successive CV scans recorded at a 1 mm thick, 40 carbon:60 epoxy composite electrode, after activation treatment. Two different scan rates were used, where (a) was recorded at 10 mV s⁻¹, and (b) at 100 mV s⁻¹.

The effect of activating the composite electrode surface on the current response for oxidation of IrCl₆³⁻ and reduction of IrCl₆²⁻, is clearly evident by comparing Figure 6-3 and Figure 6-4 a and b. The CVs of the activated electrode appear peak shaped, with
considerable hysteresis, suggesting linear diffusion to the composite surface. This may be due to diffusional field overlap from closely spaced small islands of graphite embedded in the insulating epoxy resin,\(^1\) and/or by the intrinsic ohmic resistance of the composite electrode material.\(^2\)

By comparison of the peak potentials for the oxidative \((E_{p}^{\text{ox}})\) and reductive \((E_{p}^{\text{red}})\) sweeps of the CV it is possible to investigate the reversibility of the redox system, for the electrode/electrolyte system under test. For Nernstian electron transfer at a macroscopic electrode/electrode interface subject to minimal \(iR\) drop distortion, at 298 K, the difference between the two peak potentials is 59/n mV, such that \((E_{p}^{\text{ox}} - E_{p}^{\text{red}}) = 59/n \text{ mV}.\) From the CVs performed for the \(\text{IrCl}_6^{3-}\) oxidation and \(\text{IrCl}_6^{2-}\) reduction \((n = 1)\), recorded at a scan rate of 10 mV s\(^{-1}\), at the 1 mm thick 40 carbon:60 epoxy composite electrode (Figure 6-4a) the peak separation was found to be 170 mV, and at a scan rate of 100 mV s\(^{-1}\), 198 mV. At both scan rates, the difference between the peak potentials are much larger than expected for reversible electron transfer at a macroscopic electrode. This could be attributed to either the intrinsic resistance of the composite electrode or the existence of discrete metallic zones in the insulating matrix (the theory holds under conditions where the whole surface is uniformly active). SECM and C-AFM imaging experiments were later conducted to locally probe the surface activity of the carbon:epoxy composites and provide microscopic information (section 6.3) on the macroscopic voltammetric data presented here.
Chapter 6

CV experiments were repeated at a 2.5 mm thick, 40 carbon:60 epoxy blend composite electrode. As above, it was necessary to first activate the surface of the electrode. A series of CVs were recorded in quiescent solution for the oxidation of $1 \times 10^{-2}$ mol dm$^{-3}$ IrCl$_6^{3-}$ and subsequent reduction of IrCl$_6^{2-}$ ($0.5$ mol dm$^{-3}$ KNO$_3$, background electrolyte), at a scan rate of 10 mV s$^{-1}$ (Figure 6-5) and 100 mV s$^{-1}$ (Figure 6-6). Each successive CV is represented as a different colour to demonstrate the reproducibility of the results acquired on short (Figure 6-6) and long (Figure 6-5) time scales.

![Graph showing CVs](image)

Figure 6-5 Five successive CVs recorded in a solution containing $1 \times 10^{-2}$ mol dm$^{-3}$ IrCl$_6^{3-}$ and $0.5$ mol dm$^{-3}$ KNO$_3$ serving as background electrolyte, at a 2.5 mm thick, 40:60 composite electrode, at a scan rate of 10 mV s$^{-1}$. 
In contrast to the $i-V$ data presented in Figure 6-4, the current in Figure 6-5 and Figure 6-6 reaches a plateau as opposed to being peak-shaped. This suggests a switch in the mass transport mechanism of redox mediator to the electrode surface, from planar to hemispherical diffusion. This behaviour may be due to the increased thickness of the electrode, reducing the number of complete conducting pathways from the bottom of the electrode to the surface. This results in fewer connected surface sites, which are likely to be spaced further apart and therefore the diffusion fields are likely to be non-interacting.\textsuperscript{20} This switch in behaviour may also be due to increases in the resistance of the composite material with the increase in thickness of the composite. This hypothesis will be tested further using SECM C-AFM (section 6.3).

The last blend of carbon:epoxy composite to be voltammetrically investigated, was a 1 mm thick slice, of composition 60 carbon:40 epoxy. The electrode was again activated
as described previously, and successive CVs were recorded in a solution containing $1 \times 10^{-2}$ mol dm$^{-3}$ IrCl$_6^{3-}$ and 0.5 mol dm$^{-3}$ KNO$_3$ serving as background electrolyte, at scan rates of both 10 (a) and 100 (b) mV s$^{-1}$, shown in Figure 6-7.

![Graphs showing CVs](image)

Figure 6-7 CVs recorded in a solution containing $1 \times 10^{-2}$ mol dm$^{-3}$ IrCl$_6^{3-}$ (0.5 mol dm$^{-3}$ KNO$_3$, background electrolyte) at a 1 mm thick, 60 carbon:40 epoxy composite, at a scan rate of 10 (a) and 100 (b) mV s$^{-1}$. 
In agreement with Figure 6-4, the CVs performed at the 1 mm thick 60 carbon: 40 epoxy (Figure 6-7) shows peak shaped voltammetry again indicative of planar diffusion being the prominent mass transport mechanism. In contrast to Figure 6-4, the peak separation is smaller, 84.4 mV at a scan rate of 10 mV s\(^{-1}\) and 96 mV at 100 mV s\(^{-1}\) and considerably larger currents were recorded overall for approximately the same area of composite exposed to solution. This tentatively indicates decreased intrinsic composite resistance. There are likely to be more complete low resistance conducting pathways through the material (compared with the 40 carbon: 60 epoxy, 1 mm thick section) given the electrode possesses a higher carbon content. This also accounts for the larger currents recorded. Thus, this blend of composite behaves most closely like a macroelectrode, with a higher degree of surface activity than the other blends tested herein. Again, these hypotheses will be further tested using both C-AFM and SECM techniques.

6.2.2 SECM of Carbon:Epoxy Composite Electrodes

SECM\(^{12}\) images were acquired of each of the composite electrodes, in a solution of 1 \(\times\) 10\(^{-2}\) mol dm\(^{-3}\) IrCl\(_6\)^{3-} (0.5 mol dm\(^{-3}\) KNO\(_3\) background electrolyte), using two well-established imaging modes, feedback\(^{13}\) and SG/TC.\(^{14}\) For all of the SECM imaging experiments a 2 \(\mu\)m dia. Pt UME was scanned in a series of unilateral lines, over the surface of the composite electrode. For feedback SECM, the microelectrode was held at a bias (typically +0.9 V) sufficient to promote the one electron oxidation of IrCl\(_6\)^{3-} at a diffusion controlled rate, whilst the composite was biased at +0.2 V sufficient to reduce the tip generated species IrCl\(_6\)^{2-} at a transport limited rate, as indicated by the CV data recorded at the composites, shown in the previous section. Thus, at the UME the
feedback current, $i_F$, with a contribution from hindered diffusion ($i_{hind}$) was recorded, as shown schematically in Figure 6-8.

For SG/TC imaging experiments, the UME was biased at + 0.2 V, whilst the potential at the composite electrode was varied between + 0.5 and + 0.9 V (diffusion controlled substrate generation of IrCl$_6^{3-}$). Thus, the UME was used to monitor the flux of species generated by the composite, by reducing the substrate produced IrCl$_6^{2-}$, $i_{act}$. This form of generation/collection is described in greater detail in Chapter 1 (section 1.5.2.2) and is shown schematically in Figure 6-9. It is important to note that in this arrangement the UME also served to provide a feedback supply of IrCl$_6^{3-}$ to the composite.

Figure 6-8 Schematic of feedback processes in the SECM geometry.

Figure 6-9 Schematic of the substrate generation / tip collection mode of the SECM.
The SECM initial imaging distance was established in the test \( \text{IrCl}_6^{3-} \) solutions, with the substrate unbiased, and the UME biased at a potential sufficient to oxidise \( \text{IrCl}_6^{3-} \) at a diffusion-controlled rate (typically +0.9 V). The tip current was monitored as the UME was slowly approached to the substrate until the limiting current fell to half the value recorded when the electrode was placed in bulk solution, i.e. \( \frac{i_T}{i_{T,\infty}} = 0.5 \). For a relatively inactive surface, SECM negative feedback theory predicts a tip-substrate separation of \( 1 \ \mu m \).\(^2\) This assumes that the electrode is positioned over an insulating section of the matrix or the size of the graphite zone is sufficiently large to promote electron transfer.\(^2\) Given the domain size of conducting particles measured by C-AFM (see section 6.3) it is believed that this method can only serve as a qualitative approach to measuring the initial tip-substrate separation. Moreover, this theory assumes that the surface of the substrate is planar with respect the UME. From topographical AFM scans (Figure 6-1) variations on the sub-micron/micron scale are known to exist.

In each case, the tip current was normalised with respect to the steady-state current \( i_{T,\infty} \) measured for either the diffusion-limited oxidation of \( \text{IrCl}_6^{3+} \) or reduction of \( \text{IrCl}_6^{2-} \). This was taken to be the value for the diffusion-limited electrolysis of the bulk species given the values of \( D \) for the redox couple \( \text{IrCl}_6^{3+/2-} \) are known to be extremely similar.\(^2\) Typically, the bulk current recorded at the 2 \( \mu \)m diameter Pt UME, was determined to be 2.7 nA, which was close to the expected value, 2.89 nA, calculated from equation 1:3, section 1.2, Chapter 1, using the literature value for \( D \) of \( 7.45 \times 10^{-6} \) \( \text{cm}^2 \text{s}^{-1} \).\(^3\)

Three different areas (50 \( \times \) 50 \( \mu \)m) of each composite electrode were investigated, and both types of SECM technique were employed in each of these areas. The UME was
scanned above the composite at a rate of 5 μm s⁻¹, in 2 μm steps across the y-axis, and 5 μm steps on the x-axis.

The first composite electrode investigated using feedback and SG/TC SECM, was the 1 mm thick, 40 carbon:60 epoxy blend. Figure 6-10 depicts a typical feedback image of the composite electrode, recorded at the UME which was biased at +0.9 V, whilst the composite was maintained at a bias of +0.2 V, as mentioned above.

![Figure 6-10 A feedback SECM image recorded at a 2 μm dia. Pt UME for the oxidation of 1 x 10⁻³ mol dm⁻³ IrCl₆³⁻ (0.5 mol dm⁻³ KNO₃ background electrolyte), above a 1 mm thick, 40:60 carbon:epoxy composite electrode.](image)

From Figure 6-10 it is possible to see that, over the image, $i_T/i_{T\infty}$ varies between 0.8 and 0.96, but in general is below 1. Given the estimated tip current separation these values suggest a partially active surface. However, three distinct zones of lower current are observed in the image, each ca. 5 - 10 μm in diameter, where the normalised current drops to 0.6. Given this value, it is most likely that the lower current regions correspond to areas of relative inactivity. To further elucidate the nature of localised surface activity, SG/TC experiments were performed over an identical scan area. Here,
the UME was biased at a potential of +0.2 V to collect IrCl$_6^{2-}$ by reduction, and the composite electrode was held at +0.9 V to generate IrCl$_6^{3-}$. For SG/TC imaging experiments, the UME essentially served to probe the concentration profiles within the diffusion field of the composite electrode, close to its surface. A typical SG/TC image acquired is shown in Figure 6-11, where the currents, as previously, have been normalised with respect to the current recorded in quiescent solution.

![Figure 6-11 SECM generation/collection image acquired of the 1 mm thick, 40:60 carbon:epoxy composite electrode, which was held at a bias of +0.9 V.](image)

From the SG/TC SECM image, shown in Figure 6-11, it is possible to observe distinct areas of decreased current of the same magnitude to those seen in the feedback image. The SG/TC experiments highlight the activity of the composite, and zones in which the current decreases can almost certainly be related to inactive areas of the composite. Otherwise, the two modes of SECM used have shown that for the 1 mm thick, 40 carbon: 60 composite the surface examined appears relatively uniform in activity. The current values are, however, lower than for positive feedback which suggests that this uniformly active area may be comprised of many small active sites that are closely spaced, on a scale that cannot be probed by SECM.
An alternative SECM technique that has been used to highlight variations in the activity of a sample is TPM, which was used successfully to enhance the contrast in studies of both topography and permeability of cartilage, as described in Chapter 5. For one of the composites investigated, TPM was used in order to provide greater contrast in images of activity of the electrode surface, as discussed later.

Thicker composite electrodes were imaged using conventional SECM methodology. The studies presented here relate to a composite electrode that was 2.5 mm thick, but the composition remained at a blend of 40 carbon: 60 epoxy. Both feedback and SG/TC experiments were performed, with no difference to the experimental arrangement described earlier. Three different scan areas, each of 50 x 50 μm, were probed by a 2 μm diameter Pt UME. A typical feedback image of this composite electrode is shown in Figure 6-12. The feedback image can be compared to the corresponding series of SG/TC images of the same area depicted in Figure 6-13. Complete SG/TC images were acquired by changing the potential bias to the composite, in 0.1 V increments per scan, between +0.8 and +0.5 V, whilst maintaining the bias at the UME at +0.2 V. This variation in potential bias to the composite was conducted to investigate the effect, if any, on the switching on or off the active sites that might be present on the surface of composite. The potential range used was selected from CV data shown earlier (Figure 6-5), where a current maximum was observed when the composite was biased at +0.8 V, conversely little substrate current was noted at a potential of +0.5 V.
Figure 6-12 A 2D feedback SECM feedback image of a 2.5 mm thick, 40 carbon : 60 epoxy composite electrode held at a bias of +0.2 V, recorded at a 2 μm dia. Pt UME, biased at +0.9 V.

Figure 6-13 A SG/TC SECM image of a 2.5 mm thick, 40 carbon: 60 epoxy composite electrode maintained at a bias of +0.8 V. Tip collection was achieved using 2 μm dia. Pt UME, held at a bias of +0.2 V.
The two types of SECM images shown in Figure 6-12 and Figure 6-13, recorded at the maximum limits of feedback and SG/TC, are similar. In the feedback image $i_T/i_{T\infty}$ varies over a range from 0.3 to 0.9. Given the roughness of the sample compared to the size of the tip, it is not possible to identify whether this is due to changes in activity or topography for the upper range of current values. However, a zone of decreased current is observed in both images where $i_T/i_{T\infty}$ drops to a value of approximately 0.25, clearly indicating an inactive site. Small sites of increased current can be seen in both images (pink colour), surrounded by large areas of inactivity. The fact that these are seen in the SG/TC as well as the feedback images provides the information needed to prove that these are indeed active sites. Furthermore, these regions can be seen to switch from active to inactive areas as the potential applied to the composite is decreased from $+0.8$ V to $+0.5$ V, in the following SG/TC images of the same area (Figure 6-14 and Figure 6-15).

Figure 6-14 A SG/TC SECM image of a 2.5 mm thick, 40 carbon: 60 epoxy composite electrode maintained at a bias of $+0.7$ V. Tip collection was achieved using 2 μm diameter Pt UME, held at a bias of $+0.2$ V.
Figure 6-15 A SG/TC SECM image of a 2.5 mm thick, 40 carbon: 60 epoxy composite electrode maintained at a bias of 0.6 V. Tip collection, of the flux of species generated at the composite surface, was achieved using 2 μm diameter Pt UME, held at a bias of +0.2 V.

The SG/TC images demonstrate that the magnitude of $i_T/i_{T\infty}$ varies, such that between bias potentials of +0.7 and +0.8 V, the current that flows is due to the presence of both high and low activity zones on the composite surface. As the potential bias is decreased the magnitude of $i_T/i_{T\infty}$ decreases across the composite surface, as the sites of activity are switched off. At a potential bias of +0.5 V no sites of activity were seen, as the flux of IrCl$_6^{2-}$ to the UME was terminated. No image is shown for this case.

The fact that wide variations in activity were seen, even in a small area, is consistent with the voltammetric results reported earlier. Although clear boundaries between completely active and completely inactive sites were not seen, which might be due to the limited spatial resolution of SECM in this particular case.
Feedback and SG/TC images were recorded at the 1 mm thick, 60 carbon: 40 epoxy composite electrode. The UME was scanned above the composite surface, at separation distance of approximately 1 \( \mu m \). The feedback image is shown in Figure 6-16, where the UME was held at a bias of +0.9 V, whilst the composite was biased at +0.2 V. Figure 6-17 shows the SG/TC image for the same area, where the potential at the UME was held at a bias of +0.2 V and the composite at +0.9 V.

![Figure 6-16 A SECM image of a 1 mm thick, 60 carbon: 40 epoxy composite electrode, recorded in feedback mode at a 2 \( \mu m \) diameter Pt UME.]

![Figure 6-17 A SECM image of a 1 mm thick, 60 carbon: 40 epoxy composite electrode, recorded in SG/TC mode at a 2 \( \mu m \) diameter Pt UME.]

181
The SECM images shown have large varieties of features. Three areas can be observed (red colour) where the normalised current drops to 0.8, and two zones where the current is larger than 1.0 (pink colour) also appear in the image. The SG/TC image contains similar shaped features, however, these appear to cover slightly smaller areas. From CV data described earlier it was determined that this composite behaves most like a macroelectrode, with the closest separation of peak potentials to 59 mV expected for complete reversibility of the redox couple IrCl₆⁴⁻⁻ at an electrode. The SECM results support this in that the overall current at this type of electrode is much higher than for the previous case. The variations in composite activity may be linked to the higher carbon content and thickness of this blend, resulting in many more conducting pathways through the electrode to the underlying contact, and thus creating well-defined regions of activity over most of the electrode.

To qualitatively increase the resolution of the composite surface described above, a series of TPM²⁵ experiments were conducted immediately after the SECM imaging experiments. The results for the TPM experiments are not presented here, however they were found to be in good agreement to the SG/TC images recorded for the same scan area.

Although, feedback and SG/TC SECM has provided valuable information about the surface activity of the composite electrodes, it is important to note that the spatial resolution is limited, particularly in the SG/TC mode. Even in the feedback mode, above a completely conducting site, a 2 µm diameter electrode probes a domain of similar size.²⁶ Consequently, domains smaller than this and more closely spaced are not resolvable. An alternative imaging methodology to those described is AFM, which has
proven to dramatically improve the resolution of localised imaging of surfaces.\textsuperscript{27,28} Here, we use conducting-AFM\textsuperscript{9,10,11} to uncover the different conductive pathways in the composite electrodes and to measure the associated resistivity.

6.3 Atomic Force Microscopy

Conducting AFM, was used to image the conductivity of 1 mm thick samples, of both 40 carbon: 60 epoxy and 60 carbon: 40 epoxy composites. Current-voltage ($i$-$V$) curves were obtained at fixed positions on both samples, to provide further insight into the actual resistance of the sample. Experiments were executed using hand fabricated SECM-AFM probes, the construction of which is described in section 2.5, Chapter 2.

For C-AFM imaging experiments a potential bias of -0.5 V was applied between the tip and the composite electrodes. A 1 M$\Omega$ resistor was connected in series to limit the flow of current through the circuit, and thus prevent damage to the metal tip. The tip was initially used to image areas of $10 \times 10 \ \mu m$ of each of the electrode surfaces, after which a conducting area was identified and a smaller scan size used to provide higher resolution images of the area of interest. By decreasing the scan size to $0 \ \text{nm}^2$, the tip was effectively held stationary in order to perform $i$-$V$ experiments. Where possible, images of larger scan areas of approximately $50 \times 50 \ \mu m$ that incorporated the area used for $i$-$V$ investigations, were acquired. The C-AFM images provide vital information about the number of conducting pathways that run through the composite electrodes, and the variation in the local resistance of the sample.
Figure 6-18 shows height (a), deflection (b), and conductivity (c) images of the same 50 × 50 μm area of the 40 carbon: 60 epoxy composite electrode. The red circle on the conductivity map correlates to the zone where i-V curves were recorded. This area is shown in more detail in Figure 6-19, where a scan area of 3.5 × 3.5 μm was investigated. From these images it is possible to see the structurally diverse regions of carbon and epoxy. The conducting zone in the conductivity image corresponds directly to a feature of similar dimensions in the deflection image (both are circled in red). From the deflection image it is also possible to see that the surface of the carbon and epoxy differs, where the carbon appears to be banded and rough, conversely, the epoxy appears to be made up of bulbous areas.

Figure 6-18 Height (a), deflection (b) and conductivity (c) AFM images of a 50 × 50 μm area of the 1 mm thick 40:60 carbon:epoxy composite, recorded with a 1 MΩ resistor connected in series.
Figure 6-19 Height (a), deflection (b) and conductivity (c) AFM images recorded with a 1 MΩ resistor connected in series. The image was recorded over a 3.5 × 3.5 μm area that was selected, from the image shown in Figure 6-18, for i-V investigations. The areas circled in red on the deflection and conductivity image correspond to a conducting zone of graphite.
The height, deflection and conducting AFM imaging experiments were repeated for the 60 carbon:40 epoxy blend of composite. A $50 \times 50$ μm area was initially imaged, shown in Figure 6-20, from which a conducting feature was selected and further investigated by imaging a $6 \times 6$ μm area shown in Figure 6-21, and an area was selected in which $i-V$ experiments were performed (circled).

![Figure 6-20 Height (a), deflection (b) and conductivity (c) AFM images of a 50 x 50 μm area of a 1 mm thick 60 carbon:40 epoxy composite electrode surface, recorded with a 1 MΩ resistor connected in series.](image-url)
From Figure 6-20 it is possible to see that a higher density of condensation sites are present in this image. Figure 6-21 shows a comparison between the two composite images of 3-3 μm in resolution. As the surface height was not measured, the resolution of the images could provide useful information. For i-V experiments, it was possible to identify the three distinct peaks in each of the images. Figure 6-22 shows a more detailed view of the current data. The zone selected for the i-V investigations was [1.87].

Figure 6-21 Height (a), deflection (b) and conductivity (c) AFM images recorded with a 1 MΩ resistor connected in series, over a 6 × 6 μm area. The zone selected for the i-V investigations is circled.
From Figure 6-20 it is possible to see that a larger density of conducting sites are present in this image, than for a similarly sized scan area of the 40 carbon:60 epoxy electrode (Figure 6-18). A variation in surface height was also observed between the two composite blends. For the 60 carbon:40 epoxy composite a surface height variation of 3.3 μm was recorded and for a similarly sized area of the 40 carbon:60 epoxy sample the surface height was found to vary by 2 μm. These phenomena are as expected considering the increased quantity of carbon in the 60 carbon:40 epoxy composite.

For $i-V$ experiments on each sample the AFM tip was positioned in one of the areas identified as the most conducting, from cross sectional line analysis of individual images. Figure 6-22 demonstrates the wide variation in conductivity over a typical cross sectional line scan (a) of the 1 mm thick 40 carbon:60 epoxy composite electrode from the image shown (b) in Figure 6-18. From this line scan it is possible to see that there are three distinct regions of varying current, as well as regions of insulator, where no current is recorded. The current measured in these three regions, at points highlighted in the figure, are ($\nabla$) 0.46, ($\nabla$) 0.133, and ($\nabla$) 0.433 μA. It may be assumed that the variations in current are directly related to the length and complexity of conduction paths through the electrode, where regions of high current are related to paths of least resistance through the composite electrode. This hypothesis will be further tested by the $i-V$ experiments performed and described herein.
Chapter 6

In each conducting zone an $i-V$ curve was recorded (between -1.5 and +1.5 V) at a scan rate of 10 mV s$^{-1}$, for a range of different resistance values between 1 MΩ and 1 kΩ connected in series. Calibration $i-V$ curves for each resistor were also recorded by applying the voltage directly across the specified resistor (the composite electrode and conducting tip were removed from the circuit).

The resistance of each of the composites ($R_{\text{comp}}$) was then calculated by subtracting the gradient of the calibration $i-V$ curves ($R_{\text{ext}}$) for a particular resistor in series with the circuit, from the gradient of the experimental data ($R_{\text{meas}}$), i.e. $R_{\text{meas}} = R_{\text{composite}} + R_{\text{ext}}$.
By averaging the results acquired, the resistance of the 40 carbon: 60 epoxy composite electrode in one of the most conducting zones was found to be 47.2 kΩ and 2.9 kΩ for the 60 carbon: 40 epoxy blend. From these results it is possible to see that the local resistance of the 60 carbon: 40 epoxy blend is lower than that of the 40 carbon: 60 epoxy composite electrode. The resistances for the 40 carbon: 60 epoxy composite appear to be of the same order of magnitude to that measured previously using time constant experiments. The differing resistances of the composites may account for the peak broadening as observed for the CV data shown in section 6.2, owing to variations in the number and resistance of active sites on the electrode surface. The 40 carbon: 60 epoxy (1 mm thick) composite showed peak shaped CVs, where the peak separation indicated that the reaction at the electrode was not reversible. Conversely the 60 carbon: 40 epoxy composite electrode had less broad peaks with a far smaller peak separation, thus more closely resembling classical reversibility, at a macroscopic planar metal electrode.

6.4 Conclusion

A variety of techniques, namely CV, SECM, and C-AFM have been used to investigate different blends of carbon composite electrodes, and have shown that the behaviour of the composite depends greatly on the composition and thickness.

Voltammetric studies have indicated that the behaviour of the three composites investigated varies depending upon the quantity of graphite in the composite. From the CV of the 2.5 mm thick 40 carbon: 60 epoxy composite, it was determined that this blend behaved as an array of microelectrodes at the fastest scan rates investigated (100 mV s$^{-1}$). This behaviour is expected, owing to the low graphite content, and
thicker dimensions, which signifies that it is less likely for complete conducting pathways to occur from the base to the top surface of the electrode. However, at slower scan rates (10 mV s\(^{-1}\)) the behaviour resembled that of macroelectrodes, which was a result of diffusional field overlap.

The 1 mm thick 40 carbon: 60 epoxy composite electrode provided peak shaped cyclic voltammetric data at the scan rates investigated indicating diffusional field overlap so that the electrode behaved more like a macroelectrode with some resistive contribution. The 1 mm thick, 60 carbon: 40 epoxy blend composite electrode had the highest graphite content of electrodes tested, and this was reflected by the acquisition of peak shaped cyclic voltammograms, at both scan rates, with voltammetric behaviour most closely resembling reversibility.

The SECM data were obtained with a 2 \(\mu\)m diameter Pt UME, to enhance the spatial resolution in imaging the surface activity of the composite electrodes. Both feedback and SG/TC measurements were used to provide data about the surface activity for each of the composites. Though SECM probed the diffusion field approximately 1 \(\mu\)m above the surface of the composites, it was possible to see a difference between the images for the various composites, consistent with the voltammetric data.

C-AFM was used to obtain \(i/V\) curves and to provide images of the topography, and conductivity of the 1 mm thick samples, of both blends of composites of interest. From the images obtained, it was observed that there were far more complete conducting pathways through the 60 carbon: 40 epoxy sample, than the 40 carbon: 60 epoxy. It was also possible to relate specific features in the deflection images to either conducting
Chapter 6

graphite particles or to insulating epoxy resin. Current-voltage curves determined that the 40 carbon: 60 epoxy blend was far more resistive than the 60 carbon: 40 epoxy electrode.

The nature of surface activity and topography has been elucidated for the different blends of the carbon:epoxy composite electrode, using a variety of electrochemical and scanned probe techniques. The results of the different investigations appear to be in good agreement with one another, with the 1 mm thick 60 carbon: 40 epoxy composite the voltammetric behaviour most closely resembled a macroelectrode, and a large number of conducting and active sites were observed, thus lowering the resistance. The 1 mm thick, 40 carbon: 60 epoxy blend showed quasi-reversible cyclic voltammetry, and this observation was supported by C-AFM which showed a smaller quantity of complete conducting pathways from the surface of the electrode through to the electrical connection. The 2.5 mm thick 40 carbon: 60 epoxy composite electrode, contained the fewest number of conductive pathways through the electrode, and this was reflected by both the CV data, which were plateau-shaped, resembling those expected for microelectrode-like behaviour, and also by less activity in the SECM images.
References


Chapter 7 Overall Conclusions

This thesis has described the development of various microelectrode techniques, which have been used to facilitate analytical measurements in both solution and at interfaces. The work presented has covered flowing systems and electrochemical imaging, notable scanning electrochemical microscopy. A significant aspect of the studies described has been the implementation and assessment of modulation methods, coupled to phase sensitive detection.

In Chapter 3 the microjet electrode was used to dramatically increase the rates of mass transport to the surface of UMEs. SECM was used to investigate the nature of these enhancements on a local scale using small UMEs to enhance the spatial resolution. The SECM measurements allowed the stagnation zone to be characterised as a small region of decreased current, that extended over an area typically 100 µm in diameter, for the arrangement used. The stagnation region was observed to be surrounded by a zone where maximum current enhancements were recorded. Voltammetric data were recorded in the stagnation region, when the nozzle and electrode were aligned co-axially, which was the simplest case to treat theoretically as it represented an axisymmetric cylindrical geometry at the point of minimum current. Good agreement between the experimental and simulated results for measurements recorded for the one electron oxidation of either IrCl$_6^{3-}$ and Fe(CN)$_6^{4+}$ were found. SECM was used to analyse the effects of viscosity on the stagnation zone, and it was found that an increase of viscosity of the test solution significantly diminished mass transfer to the electrode surface. Voltammetric data were recorded with the nozzle and UME aligned, in the
stagnation zone for each of the viscous solutions, and qualitative agreement in the trends between experiment and the simulated results was noted.

A novel hydrodynamic modulation voltammetric technique was introduced in Chapter 4, namely the chopped flow microjet electrode. This system was coupled to phase sensitive detection, to facilitate the measurement of low concentrations of analytes in solution. The chopped flow set-up consisted of a thin rotating blade, located between the nozzle and UME in the MJE arrangement, which was used to modulate the rate of mass transport to the UME, between two well-defined extremes. Two detection methods were used to monitor the frequency of the rotating blade and provide a reference signal for the phase sensitive detector. The electrochemical detection system consisted of a dual disc microelectrode probe that enabled the current for two electroactive solutes to be recorded simultaneously, so providing both a reference signal (reduction of oxygen), and a signal for the analyte of interest, thereby permitting the use of phase sensitive detection. The optical detection system employed a photodiode detector and simple LED arrangement. These were coaxially aligned above and below the blade, respectively, to provide a non-electrochemical reference signal. This negated the need for a second electroactive mediator whose potential window, in principle, might overlap with the analyte of interest. Trace level detection to a limit of $2 \times 10^{-7}$ mol dm$^{-3}$ IrCl$_6^{3-}$ was facilitated using the optical detection system and a limit of $5 \times 10^{-7}$ mol dm$^{-3}$ IrCl$_6^{3-}$ was reached with the purely electrochemical system.

The studies described in Chapter 5, tip position modulation$^2$ was implemented to increase the imaging resolution of conventional SECM. In TPM, the UME is modulated vertically above a surface at a fixed amplitude and frequency.
Simultaneously, the tip is scanned across a substrate surface in a series of unidirectional lines, and the resulting modulated current passed into a phase-sensitive detector, where the in-phase current component of the signal is extracted. The polarity of the resulting current is dependent on the surface activity of the substrate. From preliminary experiments it was possible to relate the in-phase current to the derivative of Kwak and Bard feedback theory,\(^3\) over a conducting and insulating surface to extract a tip-substrate separation distance. Complete TPM images of the surface of a band electrode structure, and cartilage were recorded, and were found to provide increased resolution when compared to conventional SECM images of the same area.

The investigations of the properties of carbon:epoxy composite electrodes were described in Chapter 6. A range of techniques including CV, SECM, C-AFM and TPM were used to characterise the surface activity of the composite electrodes. Different blends of composite electrode were tested, 1 and 2.5 mm thick 40 carbon: 60 epoxy electrode and a 1 mm thick 60 carbon: 40 epoxy electrode. From the CV data recorded, after the surface of the electrodes were electrochemically activated, it was determined that the 60 carbon: 40 epoxy composite most closely resembled the behaviour of a planar macroelectrode and the 2.5 mm thick 40 carbon: 60 epoxy blend behaved similarly to an array of microelectrodes on the voltammetric timescales of interest.

SECM images of the composite electrodes were recorded with a 2 \(\mu\)m diameter Pt UME using both the feedback and substrate generation/tip collection modes. Although SECM probed the diffusion field approximately 1 \(\mu\)m above the surface of the composites, it was possible to see a difference between the images acquired, particularly for the 1 mm thick, 60 carbon: 40 epoxy composite. In this case, individual sites of activity and
inactivity at the surface were readily seen. TPM was used to image this electrode to
further distinguish between surface activity and topography without the need for the two
modes of SECM imaging.

C-AFM was used to obtain current-voltage curves and to provide images of the
topography, and conductivity of the 1 mm thick samples, of both blends of composites.
From the images obtained it was observed that there were more complete conducting
pathways through the 60 carbon: 40 epoxy sample, than in the 40 carbon: 60 epoxy
sample. It was also possible to relate specific surface features in the AFM deflection
images to either conducting graphite particles or to insulating epoxy resin.
Current/voltage curves determined that the 40 carbon: 60 epoxy blend was far more
resistive than the 60 carbon: 40 epoxy electrode, and quantitative values were obtained.

Although microelectrochemistry and SECM are becoming mature fields, as evidenced
by the wide body of literature, some of which was cited in Chapter 1, this thesis has
shown that there is scope to further develop and improve ultramicroelectrode methods
for both analysis in solution and at interfaces. Notable achievements of the work
presented include providing a better understanding of impinging jet mass transport and
the demonstration of the superior attributes of phase sensitive detection methods. The
studies of cartilage and the carbon:epoxy samples show that some of the methods
considered have significant practical applications and there are tremendous possibilities
for further studies in these directions.
References

