# DEVELOPMENT OF CONDUCTING POLYMER SENSOR ARRAYS FOR WOUND MONITORING

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## ABSTRACT

## The University of Manchester

Arthur L.P.S. Bailey

Doctor of Philosophy

## **Development of Conducting Polymer Sensor Arrays For Wound**

## Monitoring

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The aim of this research was to develop an array of conducting polymer gas sensors as part of an electronic nose designed for monitoring the metabolites produced from the bacteria present in wounds. The device was designed to be a portable system that could discriminate between relevant bacteria non-invasively using solid phase microextraction and an array of conducting polymers and metal oxide sensors in conjunction with pattern-recognition software.

In order to develop the sensors, GC/MS headspace analysis of a selection of bacterial species that are most commonly found to be present in wounds was first undertaken in order to determine the volatile key markers. The chosen key markers were then used as calibration gases in order to test and develop the sensors. Electrochemical techniques were used to polymerise and study a variety of conducting polymers, focusing on polypyrrole based sensors with differing functionality. The use of different dopant ions was also studied in an effort to optimise the sensitivities of the polymer sensors.

The results of electrochemical development and gas testing were used to elucidate the optimal sensor array in relation to the calibration gases used, which was subsequently used in the hybrid device prototype. Although the conducting polymer sensors did not perform well using solid phase microextraction sampling methods, results using a direct injection method of the headspace showed that the device could discriminate between *Pseudomonas aeruginosa* and *Staphyloccocus aureus*.

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## DEDICATION

For Alfred Henry Arthur Bailey

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"At times our own light goes out and is rekindled by a spark from another person. Each of us has cause to think with deep gratitude of those who have lighted the flame within us."

- Albert Schweitzer

## LIST OF ABBREVIATIONS

AFM	atomic force microscope/microscopy
AMP	adenosine monophosphate
ATP	adenosine triphosphate
$BF_4^-$	tetrafluorophosphate
CIO <sub>4</sub> <sup>-</sup>	perchlorate
CA	chronoamperometry
CP	conducting polymer
C-V	Capacitance (C) vs. (gate) potential (V) diagram
CV	cyclic voltammetry
Ep	peak width (voltammetry, where $E_{p/2}$ = half-wave potential)
GC/MS	gas chromatography/mass spectrometry
IMOS	Intelligent Modulated Multi Sensor
I <sub>pa</sub>	anodic current ( $I_{pc}$ = cathodic current)
IR	infrared
I-V	Current (A) vs. Potential (V) diagram
MOx	metal oxide [sensor]
MRSA	methicillin resistant staphylococcus aureus (MSSA = methicillin sensitive)
NMR	nuclear magnetic resonance
NSA	naphthalenesulfonic acid
OTf⁻	trifluoromethanesulfonate (triflate)
P3HT	poly(3-hexyl)thiophene
PCA	principal components analysis
PCB	printed circuit board
PCR	polymerase chain reaction
PDA	personal digital assistant
PEDOT	poly(3,4-ethylenedioxythiophene)
$PF_6^-$	hexafluorophosphate
PPY	polypyrrole
PTFE	polytetrafluoroethylene
Q	charge passed on oxidation (Qa) / reduction (Qc)
RGB	red, green, blue
sccm	standard cubic centimeters per minute (cm <sup>3</sup> /min, flow rate)
SDS	sodium dodecyl sulfate
SNS	2,5-di(2-thienyl)pyrrole
SPME	solid phase microextraction
TsO⁻	anion of <i>p</i> -toluenesulfonic acid (tosylate)
VOC	volatile organic compound

## CHAPTER 1

## INTRODUCTION

In modern medicine, early detection and qualitative discrimination of bacteria present in infections is decidedly important. Currently, the analysis of wound infections requires expensive analytical instrumentation, which must be operated by skilled technicians. A biopsy, which can prove uncomfortable for the patient, is usually performed to collect tissue samples of a wound. Bacteriological analyses are performed to detect bacteria present using techniques such as PCR and GC/MS. However, these processes require skilled technicians and analysis can take a matter of days to complete, by which time the bacteria in the infection will have advanced.

The subsidiary effect of this is the administration of inappropriate antibiotics, dispensed due to insufficient knowledge regarding the infection. A serious problem of antibiotic resistance has recently occurred due to this and the problem has been coined a "shadow epidemic". [1.1] Antibiotic resistance poses a grave danger to society and rapid, accurate detection of bacteria presence in wound infections is of great urgency. Development of new antibiotics is no longer viable due to the increasing prevalence of antibiotic resistant bacteria. For example, MRSA was treated with the antibiotic, Vancomycin, but this has led to yet another resistant strain. Research is now focused on rapid detection of bacteria and the development of new state-of-the-art technology for this purpose has started to appear. Examples are real-time polymerase chain reaction (PCR) or the use of polymers that will emit light when bound to bacterial cells. Further examples of sensor technologies used are given in the next chapter.

Developments in sensor technology, namely machine olfaction, have facilitated the detection of bacteria and microbial disease successfully. [1.2; 1.3] This technology has been used effectively within the past couple of decades in the medical environment, food and beverage industry, agriculture and environmental monitoring, using research based

instrumentation. More specifically targeted devices are now being presented for commercial applications and such devices, coined "electronic noses", have encouraging potential for the future. [1.4] Advantages of using this technology include the rapid detection times possible (approximately 30 minutes for conclusive results compared to 2 days using today's methods of analysis); accurate diagnosis with no ambiguous results; reliability of the results and the portability of the device.

Numerous studies, particularly those using GC/MS headspace analysis, show that micro organisms produce a range of volatile organic compounds, as detailed in chapter 5. The purpose of this project was to provide a portable instrument that would be capable of analysing, in real-time, the volatiles produced from a superficial wound, sampled non-invasively, and identifying the bacteria present. This would enable medical staff to make a more informed choice as to what treatment should be administered. The work presented in this thesis was done in partnership with the European Commission funded project, Woundmonitor (Sixth Framework Programme IST-2004-027859).

The electronic nose instrument incorporated a hybrid array design, utilising both metal-oxide and conducting polymer sensor technologies. Solid phase microextraction fibres were used to preconcentrate the volatiles emitted and present them to the sensor arrays. The instrument featured online processing of the data received from the sensors to identify the volatile key markers and compare fingerprints of the volatiles with known data sets for the sensors.

The aim of this work was to develop an array of conducting polymer gas sensors suited to the needs of the wound monitoring device. In order to achieve this, a study of commonly used conducting polymers was undertaken to gain insight into their sensing abilities. Research focused on the properties of polypyrrole and various derivatives with different functional groups along the backbone of the polymer. A selection of pyrrole based monomers with differing alkyl chain lengths at the beta position were chemically synthesised that were later polymerised electrochemically. A number of other polymers were also

investigated electrochemically for comparison, such as *N*-substituted polypyrroles and polythiophenes. The effect of using differing dopant ions on the sensing characteristic of the polymer sensors was also studied in order to improve their response magnitudes and sensitivities to the volatiles tested.

After testing the sensors with the calibration volatiles, which were previously decided upon through GC/MS headspace analysis of the most pertinent bacteria present in wounds, the sensor performances, stability and ease of fabrication were used to decide upon an array of eight suitable sensors for implementation into the hybrid device.

Testing of the hybrid device revealed deficiencies in the sampling method with the chosen sensors, however, by using a direct injection method some indication was given of the potential of the ability of the device to discriminate between different bacteria.

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## **CHAPTER 2**

## BACKGROUND

This chapter reviews some of the current literature relevant to this field of study and gives an overview of technologies used at the present time. An introduction to conducting polymers is given and the theories of how they function are discussed. Finally, the operation and advancement of artificial olfaction is explained, focusing on the aspects of this project.

### 2.1 The Electronic Nose

### 2.1.1 Introduction

The first electronic noses were reported in the mid-1960's by Wilkens and Hartman [2.1] and Buck *et al.* [2.2]. The initial goal in this research area was to amplify chemical reactions between sensing materials and the volatile compounds at low concentrations for qualitative differences to be measured.

In 1982, Persaud and Dodd [2.3] reported a device consisting of a sensor array system that was sensitive to a wide variety of *odorants* with partial specificity, rather than multisensors which respond more specifically to individual components of a simple gas mixture; the outputs were processed in a convergent feature detection system. The term "electronic nose" did not arise until the late 1980's during a number of conferences on the subject of artificial olfaction. For the work reviewed here, the definition used is that described in a review by Gardner and Bartlett: [2.5]

"...an instrument, which comprises of an array of electronic chemical sensors with partial specificity and an appropriate pattern recognition system, capable of recognising simple or complex odours".

### 2.1.1.1 Odorants

There are many aspects such as shape and charge distribution that determine a molecule's properties and in turn whether they exist as odorants and their particular scent. Odorants that are typically found in nature tend to be a vast complex mixture of many different chemical species at various concentrations rather than one type of molecule. Varying the concentration of compounds in the aromatic mixture, changing the functional group chemistry or position, altering the stereochemistry or conformation of a molecule, amongst other changes that can be made, all affect the smell of an odorant or odorous mixture. Although there are examples of simple single molecules with distinct aromas, the discovery of the olfactory code is, for the reasons listed, an extremely complicated task.

Odorants must be volatile in order to be able to be carried to the nasal cavity. Therefore the molar mass is typically less than 300g.mol<sup>-1</sup>. Other important factors are charge distribution and polarisability. Non-polar and symmetrical molecules tend to be gaseous at room temperature but not many are classed as odorants. Introduction of one or two functional groups establishes some polarity and better interaction between molecules. Hydrogen bonding is also expected to play an important role in odorants, particularly the interaction of the odorant molecules and the olfactory receptor proteins. These characteristics are typical of odorants and relate to their affinity and interaction with the olfactory receptors. The recognition of an odour also depends on the threshold detection limit, which varies between different people and greatly varies between different animals.

Molecules containing covalently bonded sets of atoms with a delocalised conjugated system of  $\pi$ -orbitals in a coplanar arrangement with one or more rings have a special place in organic chemistry. If the number of delocalised  $\pi$ -electrons is even but not a multiple of 4 (Hückel's rule), the molecule is called "aromatic". Although this term has a precise definition, the name arose from the fact that many of these types of molecules have a distinctive odour.

#### 2.1.2 Artificial Olfaction

Electronic noses fitting the previous definition have notable analogies to human olfaction. In the human olfactory system, the volatile odorant molecules are drawn into the nasal cavity across the epithelium, where there are olfactory cilia containing chemosensory receptors. Receptor cells are coupled to a G-protein, which initiates a multistep intracellular process on interaction with an odorant; the G-protein (G<sub>olf</sub>) activates adenylyl cyclase enzyme which catalyses the conversion of ATP to the secondary messenger, cyclic AMP (cAMP), which in turn binds to an ion channel, allowing the flow of ions into the cell. This reduces the potential across the plasma membrane and an action potential can be generated if cell depolarisation reaches a threshold, which is conducted down the olfactory nerve. Axons converge to glomeruli nodes in the olfactory bulb where olfactory sensor neurons of a specific odour receptor type converge upon a common glomerulus. Patterns across the multiple glomeruli provide the basis for odour discrimination. The information is ultimately transmitted to higher brain centres for processing by the olfactory tract via mitral cells, which "have narrower molecular receptive ranges than olfactory receptor neurons." [2.4;2.5]

Analogously, the electronic nose encompasses sensory materials that convert a chemical input into an electrical signal. Like the olfactory receptor cells, the sensors have partial specificity as this is necessary for the ability to detect numerous odorants as opposed to highly specific gas sensors that respond only to a particular volatile compound. These signals are pre-processed and normalised to give response vectors that may then be analysed using pattern-recognition (PARC) processes.

In industries such as food and beverage, or perfumery, panels of experts are normally used to assess scents. The human nose can be an extremely accurate tool for discriminating complex odours, especially when trained. However, this method is subjective and dependent on ones state of health and age as well as many other factors that vary the sense of smell. There are also problems such as long recovery times and adaptation to

scents, partial or full anosmia, and it is not feasible for toxic or offensive, repugnant odours to be inhaled by a human panel. [2.4] An electronic nose can overcome these difficulties, offering accurate reproducible detection, a round-the-clock operation and the ability to detect odours at very low parts-per-billion (ppb) levels quantitatively. The human nose has a much broader range of odour classification than is currently possible by an electronic nose; therefore electronic noses tend to be produced for a specific purpose with the ability to assess only a number of odorants. [2.6] The success of this technology is evident; many examples of its prevailing use in industry can be found and its potential continues to grow. [2.7]

#### 2.1.3 Sensor Requirements

There are many aspects of a sensor array and its sensors in an electronic nose that are important to observe. The odour of a gas is largely determined by its chemical structure, therefore it is required that the sensors are non-specific and respond to the conformations of these odorants. It would be ideal to select sensors and design a sensor array in accordance with how they function chemically and physically with certain types of odorants, however, the knowledge of this and the workings of the olfactory receptor proteins are not fully understood. Thus the current design of sensors are made via the tailoring of available sensors to a certain application. [2.4]

The most essential requirement of a sensor array in an electronic nose is to produce a pattern of responses that have observable differences for different odours. For this to be realized, the sensors must be non-specific and sensitive to a broad range of volatiles, yet simultaneously their responses must not be highly correlated to one another.

The response time and recovery time should be as short as possible, ideally within a few seconds, although this is not always attainable. Together, the response and recovery time determine the sample throughput time, so a matter of minutes is often acceptable. The response time ( $t_{resp}$ ) is defined as the time taken for a response of a sensor to reach

equilibrium after exposure to a volatile, whereas the recovery time ( $t_{rec}$ ) is defined as the time taken for the sensor measurement to return to the baseline after exposure to a volatile is ceased and a reference or carrier gas, normally clean air, is passed over the sensor (see Figure 2.1) It is necessary for a sensor to be responsive within the appropriate concentration range required for its particular task. However, it is also important that there is enough dynamic range so that the sensor responses do not saturate within the concentration range that they are required to measure.



Fig 2.1 - Dynamic response curve

It would be ideal to have a linear dependency to concentration to allow for linear data processing techniques, however in reality, all sensors saturate at a certain point. At low concentrations, it can be assumed that response is proportional to concentration up to a point.



**Fig 2.2** – Steady state response showing saturation. The detection limit is the concentration at which response is 3 standard deviations above the baseline noise

The baseline noise should also be as low as possible to improve the resolution of the sensors and the resolving power of the electronic nose.

Also of great importance is the reproducibility of sensor responses both over time and between sensors of the same type. Reproducibility over time is advantageous when having to train and calibrate a system. This can be problematic if the sensor responses vary greatly over time due to sensor drift or poisoning. Reproducibility between sensors of the same type is sought after for the ease of replacing a sensor if poisoned, or training a set of instruments using the same parameters. This reproducibility is challenging to achieve in laboratory scale manufacture but is improved as the manufacturing process is more automated and better controlled.

The perfect sensor would also be insensitive to changes in temperature, humidity and flow rate. Realistically this is not possible and these influencing factors must be minimised, or at least compensated for.

Additionally, a small physical size is desired to improve efficiency and reduce manufacturing cost, and a small sample volume should be used in application (~1cm<sup>3</sup>) to increase response time and enhance sensitivity since a large volume will cause sample dilution.

#### 2.1.4 Wound Monitoring

Devices that are often defined as wound monitoring devices fall into two categories:

- Those of a diagnostic nature that aid in the identification and characterisation of bacteria present
- Those that simply monitor the progression of a wound and its healing progress, or are of an indicative nature on the state of healing of the wound.

There are many examples of the second type that monitor the state of a wound's healing process. There are a couple of devices that use advanced imaging techniques for this purpose including a PDA-powered laser digitiser developed by ARANZ medical called

the Silhouette Mobile which is able to extract accurate information about the area, depth and volume of a wound and can store the data, aiding clinical staff catalogue patient data in more detail. [2.8] A number of successful case studies and reports on its accuracy and repeatability are encouraging and make the device a viable tool in chronic wound management. [2.9] Another imaging device is based on patented laser speckle imaging technique to monitor treatment of diabetic wounds. [2.10] The device is non-invasive and allows for viewing the microvasculature, documenting the blood flow velocity accurately and quantitatively. The accuracy remains unaffected by skin pigmentation.

Besides imaging techniques, there are a number of other non-diagnostic wound monitoring technologies that are in development. Research has been conducted into the development of hydration monitoring at the wound-dressing interface. An optimal balance of moisture is very important in the healing process and removal of the dressing can disrupt this. Important information was obtained that highlighted the differences in maintaining the balance of wound exudate between numerous dressings tested. [2.11] Similarly, a European project named BIOTEX lead by CSEM has been in development of a smart textile dressing that integrates biosensors which can monitor two important markers of the healing process; the varying pH and the inflammatory protein, CRP (C-reactive protein). [2.12]

Fast identification and characterisation of bacteria in wounds remains of great importance in administration of the appropriate treatment, hence the withstanding urgency for a diagnostic system fulfilling the requirements.

This project includes the use of metal oxide and mixed oxide thin film sensors and intrinsic conducting polymer sensors within an electronic nose system. A few commercially available electronic nose devices exist that use arrays of extrinsic (see 2.2.3) conducting polymers, such as the Cyranose® 320, which has been shown to be able to detect and discriminate bacteria, for example those found in ear, nose and throat infections. [2.13]

These sensor technologies are amongst the most common in artificial olfaction, however there are numerous other sensor technologies that are in use that could be applied. The following section reviews the technologies available.

### 2.2 Sensor Technologies

Many different technologies are available that can be used as sensors in an electronic nose; the simplest and most commonly used being metal oxide sensors and conducting polymers. This section gives an overview of the principles of each technology and a succinct list of their benefits and drawbacks.

All chemical gas sensors interact with the analyte to induce a physical and/or chemical change, which produces a signal but there are two distinct types; those where the interaction between the analyte and the sensor is reversible and those where it is irreversible. For the reversible type, the analyte separates away from the sensor without change and are analogous to the binding of odorants to the olfactory receptor proteins through attractive forces in biological olfaction. However, in the irreversible type, the analyte undergoes a chemical reaction at the site of the sensor.

### 2.2.1 Metal Oxide Sensors

Metal oxide (MOx) sensors were shown to be sensitive to gas by Seiyama *et al.* [2.14] in 1962 and the first commercially available sensor was available in 1968. [2.15] The initial research into electronic noses used this type of sensor. [2.3; 2.16] Many commercially available electronic noses use this type of sensor from manufacturers such as Airsens GmbH (Germany), EEV Ltd. (UK) and Shimadzu Co. (Japan). Tin dioxide (SnO<sub>2</sub>) is the mostly commonly used sensing material, usually doped with a catalytic metal like platinum or palladium. [2.17] The addition of small amounts of noble metals, such as platinum or palladium, have been shown to improve the responses and sensitivity. Proposed mechanisms for this were discussed by Kolmanov *et al.* [2.18]. Other oxides have also been

utilised including zinc oxide (ZnO) [2.19], titanium dioxide (TiO<sub>2</sub>) [2.20] and tungsten oxide (WO<sub>3</sub>) [2.21], all of which are intrinsically *n*-type semiconductors. The variety of available material was discussed by Eranna *et al.* [2.22].

The essential structure of a metal-oxide sensor remains the same, consisting of a planar substrate with a platinum heater coil. The semi conducting material and catalyst are coated on the outside.

Although metal oxide sensors have been extensively used and studied, the gas sensing mechanisms are not fully understood and remain a controversial topic of ongoing debate. The general mechanism is usually explained in terms of an ionosorption theory where adsorbed oxygen species (free ions) are electrostatically stabilised on the surface without forming chemical bonds. The ionosorption model originates from the boundary layer theory of chemisorption, developed by Hauffe around the 1950s [2.23] and expanded upon to describe gas adsorption on semiconductors by Hauffe and Morrison through to the late 1970s. [2.24] The general mechanism proposed [2.4; 2.25 – 2.28] involves chemisorption of oxygen creating extrinsic surface acceptor states, immobilising conduction band (CB) electrons from the near-surface region and creating an electron-depleted region (space-charge layer) for n-type semiconductors. A potential barrier is formed between the grain boundaries, which limits the flow of electrons, reducing the conductivity (Fig 2.3). An accumulation surface layer occurs for p-type semiconductors.

The presence of reducing or oxidising gases can further affect the density of charge carriers (n-type electrons/p-type holes). For an n-type semiconductor, reducing gases abstract the surface oxygen species, releasing immobilised electrons and decreasing the depletion layer thickness, and thus increasing conductance. Whereas oxidising gases create additional surface acceptor states, further immobilising CB electrons and increasing the depletion layer thickness.



**Fig 2.3** – Potential barrier, eVs, formed between grain boundaries acts as scattering centre for conduction. Potential is lowered when a reducible gas is adsorbed and oxidation occurs – electron flow is easier so conductivity is increased (n-type).

The nature of the oxygen species depends on the operating conditions; they can be molecular  $O_2^-$  (superoxide),  $O^-$  (charged atomic oxygen) or  $O^{2-}$  (peroxide ion), or become part of lattice oxygen. Yamazoe *et al.* [2.29] used temperature programmed desorption (TPD), electron paramagnetic resonance (EPR) and conductivity measurements to study specific types of adsorption on tin dioxide, including water and hydrogen interaction. However, controversy remains regarding the nature and origin of the surface oxygen species. Gurlo [2.30] discussed the lack of convincing spectroscopic evidence for the presence of the ionosorbed oxygen species.

The sensing properties can be tailored to the application by changing the catalytic metal or altering the operating conditions but it remains non-specific, responding to a range of gases. [2.31] The operating temperature greatly affects sensor performance mainly due to the kinetics of the reaction between analyte and sensor material as well as the kinetics of gas diffusion through the sensing layer, for which a model was proposed by Sakai and Yamazoe [2.32]. Barsan *et al.* [2.33] also found that the final annealing temperature influences the concentration of the reactive sites for ionosorption, governing the temperature dependence of the distribution of different oxygen surface species and changing the main reaction route (for CO), thus altering the sensor response and sensitivity.

The usual operating temperature of metal oxide sensors is within the range of 200 - 500°C. Below 200°C the reaction rates are too slow and below 100°C the oxide surfaces are covered by water, inhibiting gas adsorption. Due to the high temperatures required, there is a

large power consumption of around 800mW per sensor. This led to the development of silicon supported, planar metal oxide sensors. Due to the smaller size and being suspended on a thin plate or membrane, the power consumption is considerably lower. The metal oxide layer can be a thin or thick film. Thin films can be deposited by a variety of methods, the most common being physical vapour deposition (PVD). [2.34] Thin films are said to have a greater sensitivity especially towards strongly oxidising gases. [2.35] Thick films are more reproducible and are mainly produced via screen-printing methods. [2.36] In addition, grain size, interconnectivity of grains, the surface-to-volume ratio, material porosity, film thickness, and preparation history all influence the sensing properties. [2.27]

#### 2.2.2 MOSFET

Metal-oxide-semiconductor field effect transistors (MOSFET) have been used as sensors within electronic noses and have been applied to bacteria classification. [2.37; 2.40] MOSFETs are an example of a potentiometric sensor and are sensitive to many organic compounds. Variations of the MOSFET such as ion sensitive, open gate and suspended gate exist, however the MOSFET is most common to electronic nose applications. The use of different metal gates with varying thickness, porosity, and operating temperature is important and has enabled the selectivity of its sensitivity to different gases. [2.38]

The current is established and a potential is applied at the metal gate. At the semiconductor-insulator boundary a channel allows current to flow from the source to the drain. The surface potential governs the drain current and size of the channel and the charge carrier concentration at the surface. The metal gate properties change as it reacts with a gas, causing a change in the drain current. However, the sensor response is normally measured by the change in gate voltage needed to maintain a constant drain current. MOSFET sensors can operate at higher temperatures than MOx sensors and are therefore able to detect volatiles such as hydrocarbons that are difficult to detect with MOx sensors. [2.39]

#### 2.2.3 Conducting Polymer Sensors

Conducting organic polymer sensors are chemiresistors that have rapid adsorption and desorption kinetics at room temperature and have high sensitivities, typically able to detect concentrations from 0.1ppm. Conducting polymer sensors are of the reversible type and no heater elements are required, therefore the sensors operate with low power consumption. Like metal oxide sensors their conductivity changes when exposed to a gas but the mechanism is not fully understood. The proposed mechanism of conductivity, their composition and fabrication is discussed in more detail in section 2.3.

Conducting polymers can be intrinsic or extrinsic. Intrinsic conducting polymers are doped with an electron-donating (*p*-type) or electron-withdrawing (*n*-type) species to enhance the polymer's conductivity. There are many monomers that may be used to make conducting polymers, mainly pyrrole, thiophene, aniline and their derivatives, but they all have in common a conjugated systems of  $\pi$ -electrons along their polymer backbone. They are easy to develop and various methods of manufacture can be used. Specificity of the sensors towards different classes of compounds can be closely tailored by altering the functional group chemistry of the sensors. Furthermore, conducting organic polymer sensors are not subject to poisoning by sulfur containing compounds [2.41], which would normally inactivate inorganic semiconductors. However, conducting polymers sensors are sensitive to humidity and experience sensor drift. [2.42; 2.43]

Extrinsic, or composite, conducting polymers are made by combining conventional, insulating polymers or other additives, such as carbon-black or metal powders, with conducting polymers. [2.44] This type of sensor responds by swelling when interacting with an analyte, which increases in electrical resistance. There are many examples of this type of conducting polymer. [2.45 – 2.47] It has been demonstrated that conducting polymer composites can be made more reproducibly, giving higher sensitivities than intrinsic conducting polymers. [2.42]

#### 2.2.4 Gravimetric Sensors

Gravimetric odour sensors make use of acoustic wave devices, which function by measuring the effect on the acoustic wave propagation after sorption of analytes. Two main types have been used; quartz crystal microbalance (bulk acoustic wave or BAW) and surface acoustic wave (SAW) devices. Both of these use a piezoelectric substance, such as Quartz, with a sorbent coating.

The piezoelectric effect describes the generation of electric dipoles when certain anisotropic crystals are subjected to mechanical stress. [2.48] The opposite effect has also been demonstrated. [2.49]

Quartz crystal microbalance (QCM), also known as thickness shear mode (TSM) devices, use BAWs. They are the simplest of the piezoelectric devices and consist of a crystal, usually AT cut quartz, with gold electrodes evaporated onto the both sides. When alternating current is applied to the electrodes, the crystal oscillates at a characteristic resonant frequency. As long as any layers added to the crystal do not diminish the oscillation, the extra thickness can give a frequency change. Choice coatings on the crystal can be used to extract analytes. The resonant frequency is related to the change in loading mass via the Sauerbrey equation, thus small changes in mass due to analyte adsorption can be measured. [2.50] There are a number of examples of QCM used for odour sensing and electronic nose applications. [2.51; 2.52]

Within the field of bacteria identification, an array of eight QCM sensors coated with different metalloporphyrins was used in the research of possible diagnosis of urinary tract cancer. [2.53] A similar device was also used to analyse breath for the detection of lung cancer. [2.54] A hybrid device featuring both QCM sensors and metal oxide sensors has been used to attempt to discriminate between coliform bacteria, however the discrimination between two strains of *E. coli* under identical conditions was unsuccessful. [2.55]

Surface acoustic wave devices employ a relatively thick piezoelectric material and interdigitated electrodes which encourage oscillation of surface (Rayleigh) waves normal to the crystal surface. When an alternating current is applied to the electrodes, excitation and deformation of the crystal surface occurs. Changes in the crystal's surface properties affect the propagation of the surface acoustic waves. Gas sensors using a SAW device use a duel-delay line configuration where one electrode is coated with a sorbent material and the other is used as a reference to reduce temperature drift effects.

When a polymer is used as a sensing material, it can be tailored to adjust the selectivity. SAW based sensors are more sensitive than BAW based devices but they suffer from long-term instability and are highly sensitive to humidity, however they have been used successfully in electronic nose research. [2.56; 2.57]

A microarray of SAW sensors was devised and implemented into a system that employed solid-phase microextraction (SPME) headspace analysis as a proposed method for VOC monitoring in food quality. The system demonstrated rapid response dynamics and potentially good selectivity. [2.58] The QCM device devised for lung cancer detection [2.54] experienced difficulties in the selection of metalloporphyrins and polymers and the repeatability of the coating process. To improve upon this, a device utilising a pair of SAW sensors, one coated with polyisobutylene, was used in conjunction with GC. [2.59] A number of other GC/SAW devices have also been developed. [2.60, 2.61]

Although the sensitivity of SAW sensors is generally greater than that of BAW sensors, larger noise levels can be problematic. The application of Flexural Plate Wave (FPW) sensors can overcome this, which make use of asymmetric Lamb waves. By decreasing the plate thickness, the mass sensitivity can be increased whilst also decreasing the oscillating frequency. [2.62] Therefore, less complicated electronics can be used, thus reducing the noise levels. In 1999, Cai *et al.* [2.63] demonstrated the first system using polymer coated FPW sensors that were capable of multi-vapour detection.

#### 2.2.5 Amperometric Sensors

Amperometric gas sensors (AGS) are distinguished by their operating temperatures. The two main types include the ambient temperature liquid electrolyte gas sensors that are commonly used within medicine applications and the high temperature solid electrolyte O<sub>2</sub> sensors used within the automotive industry. AGS sensors can operate from very low to high temperatures and their composition can vary greatly.

AGS sensors are a category of the electrochemical gas sensors. Other types of electrochemical gas sensors are the potentiometric and the conductimetric type, based on those techniques respectively. Amperometric sensors measure the current produced as an analyte reacts at an electrode, which can be measured at a constant or a variable electrode potential. When operated at diffusion-limited conditions, the rate of reaction is proportional to the concentration of analyte and is a linear relationship. The open-circuit potential between two electrodes can be monitored, whose relationship to analyte concentration is typically expressed by the Nernst equation.

Concentrations can be measured over a wide range and high sensitivity is accurately achievable (ppm to ppb). Sensitivity and selectivity can be adjusted by the geometry of the device, choice of electrolytic and other design materials such as choice of gas membrane, electrode material, as well as the electrochemical parameters. [2.64]

The earliest example of a functional AGS is the Clark sensor that was used to measure oxygen content in blood highly selectively. [2.65] Modern Clark sensors are fitted with porous PTFE membranes. Whilst aiding selectivity, the membranes can increase response times. However, gas-diffusion electrodes, first developed by Niedrach, can transfer analyte to the working electrode faster, shortening response times. [2.66]

Aqueous electrolytes can limit specificity and the operating and potential ranges. Extensive research led to the development of non-aqueous [2.67] and solid polymer electrolytes. [2.68] With the advent of microfabrication and the development of mircroelectromechanical systems (MEMS), microelectrodes for AGS technologies allowed for faster response times, higher sensitivities and could be used with small sample volumes. Recently, electrodes using carbon nanotubes have been reported leading to improved sensitivities with low signal-to noise ratios. [2.69, 2.70] AGS sensors have also been used in sensor array devices and were shown to improve electronic nose technologies, adding complementary information and enhancing sensitivity and selectivity. [2.71]

### 2.2.6 Optical Sensors

Optical sensors have some advantages over the electrochemical sensors: they are free from electromagnetic interference, there is no need for a reference sensor, they are safe in flammable gases and they have the capabilities of transferring a greater amount of data using multiwavelength transmission. Amongst the first gas sensing optical sensors are those developed by Wolfbeis [2.72] and the first implementation of optical sensors into an electronic nose device was described by Walt [2.73]. Optical sensing can employ a vast range of techniques such as absorbance, reflectance, fluorescence, and refractive index.

Fluorescence techniques remain the most popular. They often use optical fibres as a means of directing light source to a sensing element immobilised at the distal tip. The first electronic nose to use optical sensors had individual fibre optic strands whose tips were coated with polymer-immobilised fluorescent dyes that would give different fluorescent response patterns. [2.74] Many fluorescence type optical sensors consist of optical fibres that are deposited with fluorescent solvatochromatic dyes in polymer matrices with varying properties such as polarity, hydrophobicity, elasticity, pore size and swelling abilities. [2.75] Many alternative methods employed in fluorescence optical sensors exist, such as the multi-analyte fibre optic chemosensor described by Bernard *et. al.* [2.76], where the appropriate

dye was photopolymerised onto the fibre surface. Dickinson *et al.* [2.77] and Johnson *et al.* [2.78] described the use of optical sensors in electronic nose applications with improvements in dynamics, ease of preparation, sensitivity, cost and reproducibility.

Other optical sensors make use of the intrinsic evanescent waves of the light travelling along the fibre optics. When totally internally reflected at the interface between fibre core and surrounding medium, the field can penetrate the interface. The magnitude of the field decreases exponentially with distance from the fibre. Fluorophores close to the fibre can be excited by the evanescent wave and emit light. This principle has been used in total internal reflection fluorescence (TIRF) and fibre optic evanescent wave (FOEW) sensors. [2.79; 2.80] FOEW have been proven to be accurate and fast. [2.81]

Absorbance techniques are also popular in a number of optical gas sensing systems, particularly those incorporating porphyrin based materials. Porphyrins and related macrocycles possess appealing properties due to their ability to form highly stable complexes with metals (metalloporphyrins) with chromogenic attributes, making them useful as optical sensors. Due to  $\pi$ - $\pi$  interactions between the macrocycles, splitting and shifts of bands occur with respect to the solution spectra. [2.82] Interaction with VOCs alter these interactions causing identifiable changes in spectra, which have been shown to be useful in gas sensing applications. [2.83]

Surface plasmon resonance (SPR) has also been used to monitor the coupling of photons to surface plasmons at the metal-active layer interface. Nylander *et al.* [2.84] first demonstrated the application of SPR to gas sensing by using a thin film of silicon-glycol copolymer to detect halothane anaesthetic gas. The most common method of matching light waves to the surface plasmon for observation of the resonance is by using a prism for coupling the light into the metal film via the Kretschmann configuration. [2.85] Other methods use the perturbation of light and plasma wave via surface roughness or a grating, such as

that employed by Challener *et al.* [2.86] Since the coupling conditions and the resonance depth are highly sensitive to the dielectric properties of any additional layer placed on the metal surface, it makes the technique very suitable for gas sensing purposes.

Other techniques that have been applied to the field of gas sensing include reflectometric interference spectroscopy (RIfS) using arrays of different polymer coatings [2.87, 2.88] or cyclohexapeptides [2.89], and colorimetric techniques, using porphyrin based materials due to their intense colour changes induced upon ligand binding. Rakow and Suslick [2.90] spotted various solutions of metalated tetraphenylporphyrins onto reverse phase silica TLC plates and colour-channel differences (RGB values) were used to quantify responses. Good linear responses to single analytes and interpretable results to mixtures were achieved with concentrations below 2ppm. Another example is described by Akrajas *et al.* [2.91]

#### 2.2.7 Biosensors

Biosensors are analytical devices that can convert a biological response into an electrical signal. They incorporate one of the following properties:

- biological material
- biologically derived material
- a biomimic

It is also necessary that a recognition element should be closely associated with a physicochemical transducer or transducing microsystem, be it electrochemical, optical, piezoelectric, thermometric, magnetic or micromechanical. The electronic signal produced can usually be related to the concentration of a specific analyte.
Biosensors can be separated into two main categories: direct, where the biospecific reaction is determined directly in real time by measuring the physical changes, and indirect (labelled), where a biochemical reaction occurs and the products are detected by a sensor.

Direct biosensors often make use of enzymes as the biologically responsive material but other biological systems can be used such as whole cell metabolism, ligand binding and antibody-antigen reactions. [2.92] Immobilised enzymes have a number of advantages that make them useful in biosensor systems. They are reusable and the immobilisation process often stabilises the enzyme. An important category of enzyme based biosensors are those that function in an electrochemical nature, which are subdivided into amperometric, potentiometric [2.92] and conductimetric/impedimetric [2.95] type sensors.

Biosensors can be labelled as one of three generations. The first generation describes biosensors that give an electrical responses when the normal product of the reaction diffuses to the transducer, such as the glucose biosensor which can determine glucose concentration using an immobilised glucose oxidase. Second generation biosensors employ the use of a "mediator" between the reaction and the transducer for improved responses. The mediator should react rapidly with the reduced enzyme, be sufficiently soluble in both oxidised and reduced forms, and its reduced form should not react readily with oxygen. [2.93] Biosensors whose response is the product of the reaction itself are described as third generation biosensors. [2.94]

Optical biosensors function by detecting tiny changes in the refractive index or the thickness as cells bind to receptors immobilised on the transducer. Many optical techniques have also been used in biosensing for detection of bacteria including SPR [2.96], ellipsometry [2.97], evanescent waves; resonant mirror [2.98]; interferometric measurements [2.99] and leaky waveguide sensors. [2.100]

Where natural fluorescent components are present, bacteria may be examined directly. Glazier and Weetal [2.101] were able to directly detect *E. coli* using silver membrane filters. The technique is rapid, cheap and simple. The main limitation is that the bacteria under examination must have or produce some suitable fluorophore.

Bioluminescence sensors can be used to detect the presence and physiological conditions of cells and have been used to detect a wide range of microorganisms such as *Mycobacterium paratuberculosis* and *Mycobacterium avium* [2.102], *M. segmantis* [2.103] and *Listeria* strains. [2.104] *Salmonella newport* and *E. coli* were detected with a sensitive and specific method in which bacteriophages were used to lyse bacteria and the cell content was measurable by ATP bioluminescence. [2.105] These methods are appealing due to their high specificity, but long assay times are required and there is a lack of sensitivity to low numbers of bacteria.

A number of indirect (labelled) methods of biosensor detection exist. Since microorganisms are immunogenic, containing proteins and polysaccharides in their outer coats, the use of immunoassay techniques are available for use in detection of bacteria. Fluorescent immunoassay (FIA) techniques makes use of the high degree of specificity inherent in immunological reactions. Other examples of indirect bacteria identification are seen with techniques such as microbial metabolism, where oxidoreductase reaction and mediators transduce the metabolic redox reactions of microorganisms into quantifiable electrical signals. A great amount of research has also been conducted into electrochemical immunodetection of bacteria. Modern techniques offer very low detection limits, achievable with small volumes of samples. [2.106] The attributes of the electrochemical techniques described in section 2.2.5 can all be applied. Amperometric immunosensors in particular are well suited for bacterial assay due to the linear concentration dependence, high sensitivities, rapid responses and low cost.

#### 2.3 Conducting Polymers

#### 2.3.1 Development and Use

In 1862, Henry Letheby [2.107] showed that oxidation of aniline in dilute acids produced a blue-black powder at an anode's surface, which later became known as aniline black, or polyaniline; the first synthesized conducting polymer. 100 years later, Shirakawa and coworkers [2.108; 2.109] demonstrated high levels of conductivity in doped polyacetylene, the simplest of conducting polymers, for which they received the 2000 Nobel prize in chemistry. A couple of years later, Diaz *et al.* [2.110] studied the conduction properties of polyaniline. Diaz also successfully electrochemically synthesised and studied a thin film of polypyrrole [2.111], as did Weiss *et al.* some twenty years earlier. [2.112 – 2.114]

Polypyrrole, as prepared in 1968 by Dall'Olio *et al.* [2.115], showed a conductivity of 8 Scm<sup>-1</sup>. Doping of the polymer with a charge transfer agent (dopant) through chemical oxidation or reduction essentially converts an insulating polymer to a conductive one. [2.116] Doped polymers have a conductivity of around 100 Scm<sup>-1</sup>. The optimal structure of polypyrrole is planar and bonded at the 2 and 5 positions of the pyrrole. [2.117]



Fig 2.4 – Optimal structure of polypyrrole

A conjugated system of  $\pi$ -electrons typically adopt a planar configuration to maximize  $\pi$ -orbital overlap and this planarity should be maintained for high electrical conductivity. [2.118] Realistically, coupling also occurs at 2,3-positions since the energy required for this is not substantially higher than for 2,5-position coupling. Hence, deviation from the ideal linearity occurs through such "defects" and conjugation is reduced, lowering the conductivity. Hydrogenation of the double bonds can also occur, further reducing the conjugation and conductivity of the polymer. Structural evidence of doped polyacetylene

indicate they are effectively ionic compounds, so the doping process can be regarded a redox reaction. [2.119]

Conducting polymers can show low ionisation potentials, the energy required to remove an electron (easily oxidized), and high electron affinities, the energy gained from the addition of an electron (easily reduced). Hence, conducting polymers can be more easily oxidised or reduced than conventional polymers. These electronic parameters are related to the band theory of orbitals as shown in Figure 2.5. A large band width correlates to a high intrachain carrier mobility indicating a high conductivity. [2.116]



Fig 2.5 – Band structure

## 2.3.2 Theory

The doping of conducting polymers is mainly performed chemically or electrochemically; this review concentrates on the electrochemical method.

A dopant is required to have a sufficient oxidising or reducing ability. Oxidative doping is called *p*-type and reductive doping, *n*-type. The redox reactions can be generalized as follows, where CH is a monomeric unit of a polymer [2.120]

 $(CH)_n$  + oxidant  $\longrightarrow$   $(CH)_n^+$  + oxidant derivative  $(CH)_n$  + reductant  $\longrightarrow$   $(CH)_n^-$  + reductant derivative Doping is mostly performed using electrochemical techniques where the electrons of the electrodes are the oxidising or reducing agents. Electrochemical oxidation of polypyrrole involves the removal of an electron resulting in a conjugated radical ion which is delocalised over a section of the polymer. The defect is called a *polaron* and has a positive charge and a spin of ½. The polaron achieves stability by polarising the surrounding environment. The polaron may be further oxidised to form a *bipolaron*, or oxidation may occur on another neutral polymer unit to form another polaron, but it is more energetically favourable for bipolaron formation. Polarons and bipolarons are mobile across the polymer chain via rearrangement. [2.121]



Fig 2.6 – Polaron/Bipolaron formation for polypyrrole

The positive charges are considered the mobile charge carriers and their concentration and mobility determine the polymer's conductivity,  $\sigma$ , as defined in the following equation:

$$\sigma = e n \mu$$

where  $e = charge of an electron = 1.6022 \times 10^{-19} C$ 

n = charge carrier concentration (cm<sup>-3</sup>)

 $\mu$  = carrier mobility (cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>) = *limiting factor of conductivity* 

When a polymer has two equivalent resonance forms (degenerate ground states) such as polyacetylene, the bipolaron dissociates into two spinless cations called *solitons*. [2.122]

In a conventional semiconductor, electrons can be promoted from the valence band to the conduction band; for conducting polymers excitation is accompanied by structural deformation and defects in the lattice via polaron/bipolaron/soliton formation. The mechanism of conduction in conducting polymers, how the conductivity changes on adsorption/desorption of chemical species and the distribution of dopants within the lattice is not fully understood but a number of explanations have been put forward. The need for qualitative data on the dopant distribution and conduction is required for a better understanding on the mechanisms involved. This information is difficult to achieve due to the complexity of the morphology and the carrier mobility is influenced by interchain transport and contact as well as intramolecular mobility.

Although not yet fully understood, a number of explanations have been proposed as to why the conductivity of conducting polymers is changed by organic vapours. Janata and Josowicz reported that several possible locations of a chemiresistor can account for the signal modulation that occurs on interaction with a gaseous analyte. [2.123] Thus, it is not always known what takes place in the conducting polymer during interaction. It was supposed that electrically neutral "inert" analyte gases act as a secondary dopant, inducing changes in the properties of the polymer as reported by MacDiarmid *et al.* [2.124] These changes are based primarily on the change in molecular conformation of the polymer from compact to expanded coils during the secondary doping process. The amount of charge and its distribution are governed by the electroaffinity of the analyte, or Mulliken, scale [2.125] and the electron affinity of the polymer, which is given by its work function. The various sites of interaction and the processes discussed are summarised here.

A charge transfer can occur between secondary dopant (gas) and conducting polymer, which can act as a Lewis acid or base, altering the number of charge carriers in the polymer and hence its conductivity. A change in the bulk mobility of carriers can also occur, usually as a result of conformational changes of the polymer backbone. [2.126] Due to the slow penetration of gases into the conducting polymer, the responses occurring from change in bulk mobility create long response times which is often accompanied by hysteresis.

At the electrode-polymer interface, modulation of the Schottky barrier height can cause changes in conductivity. The value of the contact barrier is determined by the

difference in work function of the polymer and metal. A space-charge region is formed at the interface meaning that the effective resistance depends on bias voltage applied during measurement. [2.123]

Interpretation of conductivity changes at the polymer surface are even more difficult to interpret due to the complexity of the surface morphology. Adsorption isotherms can describe the primary interaction but the effects are more difficult to interpret. The interface between polymer and substrate may also contribute to the overall conductivity of the polymer.

Due to the variety of interfaces in a chemiresistor that can contribute to the overall conductivity of the polymer, interpretation of signal modulation on exposure to an analyte is rendered more difficult.

The responses of conducting polymers are often dependent on humidity, so it may mean that water absorbed by polymer plays an important role in the mechanism. [2.4] The response of the polymer to differing vapour concentrations have been investigated and show a Langmuirian-type response [2.127], explained further in section 5.1.2.1. This response is characteristic of binding sites on the polymer for the volatile compounds to bind to, typified by the binding constant, *K*, in the following relationship:

$$\frac{1}{\Delta R_v} = (1 + \frac{c_v}{K})/(R_{sat} - R_0)$$

where  $\Delta R_v$  is the change in resistance when exposed to vapour,  $c_v$  is the vapour concentration and  $R_{sat}$  and  $R_0$  are the resistances in saturated vapour and in vapours absence respectively. The affinity of a conducting polymer sensor to a gaseous analyte has also been increased by introducing specific binding sites. [2.123]

A number of sensing mechanisms have been proposed in an effort to understand the processes which alter the conductivity of CP sensors. These are discussed further in the introductory sections of chapter 5.

### 2.3.3 Methods of Synthesis

The main method used to polymerise and deposit a conducting polymer film is through electrochemical techniques, but there are various other methods of polymer deposition.

- Electrochemical techniques: the main advantage of electrochemical deposition is that parameters can be closely managed and the film thickness controlled with reproducible results. When deposited over interdigitated electrodes (IDEs), the covering film can be used for chemiresistor applications as used in this project.
   [2.128]
- Dip-coating involves the submersion of a substrate into a solution of the polymer. The film thickness is controlled by the amount of time the substrate is dipped for. Alternatively, the substrate can be dipped into a solution of the monomer and dopant. Polymerisation occurs on the substrate's surface.
- Spin-coating is a simple process for soluble conducting polymers. The solution is spread on a rotating substrate. The film is formed after the solvent is evaporated. The film thickness can be controlled by varying the concentration of the solution and the rate of rotation of the substrate.
- Drop-coating is similar to dip and spin-coating; a polymer solution or monomer/dopant solution is drop dried on the substrate. The problem with this technique is that the film is not uniformly thick.
- Vapour deposition polymerisation first involves the preparation of an oxidant film which is then exposed to the vapour of the monomer. The monomer is diffused onto the film and polymerised. The deposition occurs rapidly and the film is very pure.
- Langmuir-Blodgett technique can produce a ultra-thin film of polymer and surfactant. The monomer and the dopant are deposited and polymerisation occurs on the substrate. Thicker films are produced by repeating the process.
   Other techniques include layer-by-layer self-assembly, thermal evaporation, and inkjet printing methods.

#### 2.3.4 Substituent Effect

A variety of substituents have been attached to pyrroles, thiophenes and different copolymers in order to investigate their effects on the resulting polymer films and how the use of different substituents along the polymer backbone effect the processability of the polymer, its electrical properties and their stability. The majority of studies into the chemical tailoring of polymers by using various side-chains have been focused on the heterocyclic polymers of pyrrole and thiophene.

Substitution at the nitrogen of pyrrole has been extensively studied with a variety of substituents. In general, the degree of oxidation, density and conductivity of *N*-substituted polymers are lower than those of polypyrrole. [2.129]

Cross *et al.* [2.130] demonstrated that the phenyl and  $-CH_2CH_2OH$  substituents formed visible films that inhibited any further electrochemistry being performed. It was postulated that this was due to steric effects that would disturb the coplanarity of the polymer and blocking of the  $\alpha$ -positions could also be a factor. The *N*-pyridyl substituent also suppressed electrochemistry, which was attributed to the pyridine basicity. The results concurred with the extensive studies carried out by Diaz *et al.* [2.129]; steric effects were investigated using substituents with progressively increasing sizes, but which possessed similar electronic effects. It was found that conductivity tended to decrease with the size of the substituent, mostly due to the steric effect disturbing coplanarity. However, the electronic effect of the group can oppose the steric effects, as with the unsaturated phenyl substituent.

Substitution at other positions of the pyrrole ring have also been studied, especially at the  $\beta$ , or 3-position. Pfluger and Street [2.131] conducted X-ray photoelectron spectra (XPS) studies to characterise the properties of polypyrrole and polybithiophene where they found that XPS data was more consistent with a molecular solid model than the one-dimensional linear metallic chain model. It was shown that substitution at the  $\beta$ -sites ensured

 $\alpha, \alpha'$  bonding, creating more structurally ordered polymers and polybithiophene was significantly more ordered than polypyrrole.

Sensitivities of the substituted pyrroles differ from those of polypyrrole. In general, the 3-substituted pyrrole polymers displayed greater sensitivity to non-polar vapours than those of polypyrrole alone, which increased with the length of the alkyl chain of the substituent. [2.132] It was also shown that the 3-substituted ester derivatives displayed greater sensitivity than their corresponding acid derivatives, especially to non-polar vapours such as toluene and hexane. Additionally, as the substituent alkyl chain length increased, the resultant polymer conductivity and stability in air decreased.

The effects of substituents on the properties of polythiophene have also received a significant amount of attention, if not more so than for polypyrrole. Electron-withdrawing groups such as NO<sub>2</sub><sup>-</sup> or COOH create unstable radical cation intermediates that can impede, or even halt the polymerisation reaction. Electron-donating groups, however, can help stabilise the radical intermediate, lowering the oxidation potential and help facilitate polymerisation. [2.133] In fact, the stability of the radical intermediate is an important parameter in determining the likelihood that a given monomer will polymerise. [2.134] Alkoxythiophenes show even lower oxidation potentials due to the electron-donating characteristics of the alkoxy group, and alkoxythiophenes variants have been shown to be more stable than their corresponding alkylthiophenes. [2.133]

3-substituted alkylthiophenes have an asymmetric structure that can lead to a number of regioisomers; head-to-tail (HT, 2-5'), head-to-head (HH, 2-2') and tail-to-tail (TT, 5-5') configurations. HT couplings yield highly regioregular, crystalline structures with the least steric hindrance from side chains. [2.135]

Poly-3-methylthiophene was reported to be environmentally stable and highly conductive when doped. [2.136] In contrast to polypyrroles, substitution at the 3-position was found to enhance the conductivity of polythiophenes. Elsenbaumer *et al.* [2.137] found that

alkyl substituents that were equal to or greater in size than butyl significantly improved the solubility of the polymer in organic solvents, which increased with the length of the alkyl chain. Hotta *et al.* [2.138] confirmed the results and showed via IR spectroscopy that the the straight-chain macromolecules are dominant from the well-defined chemical structures prevalent. Interestingly, the length of the alkyl chain has little effect on the polymerisation process but does affect the structure and properties of the results film. [2.137; 2.139] It was also found that the optimal mean conjugation length and electrochemical reversibility can be achieved when the number of carbons in the alkyl chain is between 8-9. [2.139] In the same study, steric effects were investigated by using the isopropyl group. Studies showed that the steric hindrance of the branched alkyl was sufficient enough to completely inhibit polymerisation, although the effect was neutralised when the branched chain was separated from the thiophene ring by two methylene groups.

#### 2.3.5 Multilayer Sensors

The sensors fabricated for this project were multilayered as opposed to monolayer polymeric films. Bilayers of conducting polymers have been used for a variety of applications and studied for their potential rectifying properties and substitution of inorganic semiconductors in the field of molecular electronics. [2.140] Schottky barriers and heterojunctions have been fashioned from the superposition of two discrete organic polymer layers. The work was pioneered using redox polymers, which in contrast to conducting polymers, are characterised by highly localised electrochemically active sites; typically where a redox-active transition metal based pendant group is covalently bonded to some sort of polymer backbone. The bilayers are chosen to have distinct redox potentials so that electron transfer is forced to mediate through the inner layer catalytically for electron transfer to occur between the electrode and the outer layer. [2.141] If the inner layer has a higher redox potential than the outer layer then charge becomes trapped on the outer layer. Charge trapping can occur in a similar way with conducting polymer bilayers if the outer layer is impervious to counterions that are required for charge compensation of the inner layer. [2.142]

As with redox polymers, oxidation or reduction of the outer film is mediated by the inner film. The following diagram demonstrates the energy bands for a polymer bilayer system that can serve as a rectifying devices or charge-trapping systems.



Fig 2.7 – Energy bands for a polymer bilayer

The outer layer can be oxidised only when the electrode potential (E) is greater than the formal potential  $E_F$  (Ox1) and can only be reduced when below the formal potential  $E_F$ (Red1). However, the formal potentials are distributed within a potential range, represented by the dashed lines, because mixtures of oligomers and polymers with differing chain lengths are formed during electropolymerisation.

The redox processes of the bilayers are also dependent on the permeability of the outer layer to the electrolyte ions. Maksymiuk *et al.* [2.142] describe three possible mechanisms of the redox processes:

- Oxidation or reduction of the inner layer alone can occur when the oxidation potential of the outer layer is markedly higher and has high permeability to the electrolyte ions of the surrounding solution.
- ii) When the inner layer is in a reduced state and its oxidation potential is much lower than the outer layer, the outer layer can be oxidised/reduced. This is due to free polarons and/or bipolarons in the inner layer which can form a mediation current, controlling the rate of reaction.

iii) When the permeability of the outer layer to ion species is low, the system depends on the state of the inner layer. When oxidised, the polymer will be highly conductive and the bilayer properties are exhibited only in the response of the outer layer. When reduced, the current of the bilayer is controlled via a mediation current through the inner layer.

Pickup *et al.* [2.143] found that the rate limiting step of the redox processes was electron diffusion through the inner layer and not interfacial electron transfer between the two layers. Hillman *et al.* [2.144] used poly(2,2'-bithiophene) as the inner layer and reached the same conclusion. In conducting polymers, the electron diffusion occurred by the movement of counterions. Additionally, the charge transfer resistances for bilayers and monolayers investigated by Bobacka *et al.* [2.145] were similar and indicated that the interface between the layers did not contribute significantly. The charge-trapping and rectifying characteristics of various conducting polymer bilayers have been investigated electrochemically whilst immersed in an electrolyte solution. [2.145 – 2.147]

The overall properties of the bilayer structure are fundamentally dependent on the spatial separation of the layers. [2.143] Interpretation of results can be complicated by the possibility of outer layer growing through the inner layer, making direct contact with the electrode. Torres *et al.* [2.146] added that it is imperative for an effective rectifying bilayer that the electrode and the outer layer do not make direct contact.

Studies with polythiophene, poly(bithiophene), polypyrrole and polyxylylviologen carried out by Hillman *et al.* [2.144] also demonstrated that the broadening of energy levels, which is shown in particular for conducting polymers, can result in energy level overlap of both polymer layers. This can be detrimental to the current characteristics of the bilayer due to charge leakage. A stable outer film charge storage required non-overlapping energy bands, which was not found for polythiophene/bithiophene or polypyrrole due to their broad energy level distributions.

The effects of polymer regioregularity and of electron-withdrawing/donating substituents on the junction properties of Schottky diodes based on polythiophene have been reported [2.148; 2.149]. It was found that better performance resulted from regioregular polymers with short alkyl chain substituents or the presence of electron-withdrawing groups. Steric effects on the junction properties were also studied by Saxena *et al.* [2.150]

The use of gas sensitive conducting polymer bilayers should allow interesting sensing properties as the polymer matrix constituting the inner layer has a work function different from that of the metal electrode. Multilayer conducting polymer chemoresistive gas sensors have been demonstrated to have advantages over monolayer sensors. [2.151, 2.152]

The gas sensing properties of bilayer conducting polymer Schottky diodes have been reported with poly(3-alkylthiophenes). Ohmori *et al.* [2.153] used poly(3-dodecylthiophene) sandwiched between Au-Sn and Al electrodes to investigate the I-V and C-V characteristics in air, water vapour, chloroform and ethanol. The reverse bias current increased in air by a factor of two, which was caused by doping of impurities into the film. The impurity level decreased the effective Schottky barrier height. The reverse current also increased for water vapour but decreased in chloroform gas and ethanol. Similar effects had been observed for P3HT. The decreased reverse current was explained by a modification of the energy level of the polymer whereby the top of the valence band was shifted to a lower energy level. C-V measurements confirmed that the barrier heights were altered on exposure to gases and was deemed a suitable explanation for the changes that were observed in the reverse bias current. These changes were also found to be reversible, but the recovery times were relatively slow.

Assadi *et al.* [2.154] also investigated the gas sensing properties of a poly(3-octylthiophene) Schottky diode, sandwiched between aluminium as the rectifying contact and gold as the ohmic contact. Water vapour, ammonia, ethanol and nitric oxide were used in conjunction with I-V measurements to study the effects. All of the gases increased the

forward current, except for ammonia which decreased the current. Nitric oxide also changed the reverse current. The results were also explained by changes in the Schottky barrier height and this was confirmed through C-V measurements. The gases also induced a change in the series resistances of the polymer; decreasing for ammonia and increasing for water and ethanol.

### 2.4 Electrochemical Principles

#### 2.4.1 Purpose and Principles

Electrochemistry is concerned with the effects of charge separation and the relation of chemical and electrical effects of reactions. Electrochemical cells encompass the system of electrochemical study. Two types of electrochemical cells exist; galvanic and electrolytic cells. A vast amount of electrochemical study is concerned with galvanic cells where reactions occur spontaneously at the electrodes as an external conductor forms their connection. This process converts chemical energy into electrical energy and is the basis of the functioning of batteries and fuel cells. Conversely, electrolytic cells involve chemical changes and reactions via the passage of electrical current. Here the electrical energy applied is converted to chemical energy and is the basis of electroplating and electrolytic synthesis. Electrolytic cells are of sole interest in this project as polymerisation is achieved by applying a variety of potentials across electrodes to induce electropolymerisation and deposition on the working electrode.

The electrode/electrolyte solution interface and the charge transfers that occur in this region is of most interest in electrochemical experiments. In the simplest case, transfer of electrons (e) can be represented in terms of an oxidised (O) and a reduced species (R):

O + *ne*<sup>-</sup> ≓ R

#### 2.4.2 Electrode Potentials and Transition State Theory

In a typical electrochemical cell, a potential difference can be measured between the electrodes called the cell potential. This value indicates the amount of energy available for driving charge transfer processes. The magnitude of the cell potential controls the direction and rate of charge transfer since it affects the relative energies of the carriers in both phases. Therefore, cell potential measurement and its control is of vital importance in electrochemical experiments and analysis.

When a metal wire (electrode) is immersed in an ionic solution (electrolyte), electrons are exchanged between the electrode and the electrolyte via oxidative and reductive processes. Eventually, equilibrium is attained at the electrode surface and a charge separation, or potential difference, will exist between the phases. This is called the electrode potential. The number of electrons transferred across this interface is measured in terms of total charge passed, which is proportional to the concentration of electroactive species close to the electrode surface, which in turn governs the magnitude and sign of the electrode potential. [2.155]

Faraday's law relates the amount of product formed (or reactant used) and the charge passed. At equilibrium, Nernst showed that the potential established at the electrode is given by the following, assuming that O and R activities are unity:

$$E_{eq} = E^{\Theta} + \frac{RT}{nF} \ln \frac{[O]}{[R]}$$

The concentrations of O and R at the electrode surface are the same as those in the bulk solution at equilibrium. Many thermodynamic parameters can be readily obtained from equilibrium electrochemical measurements since it is sufficient to describe electron transfer processes using the transition state model to understand the rates of reaction: a reaction path is followed whereby reactants overcome an energy barrier, where the maximum equates to the transition state, in order to become the products. The transition state is highly

sensitive to the potential drop between the metal and solution and for many reaction the transition coefficient ( $\alpha$ ) is approximately  $\frac{1}{2}$ , meaning that the transition state has intermediate behaviour. [2.156] The sensitivity of electrochemical rates to changes in electrode potential can be derived from the changes in the absolute and relative values of free energy of activation.

#### 2.4.3 Redox Processes

When the applied potential is the same as the equilibrium potential, no current flows through the cell, but when any other potential is applied, electrolysis becomes thermodynamically viable. Although, the flow of current is dependent on the kinetics of the particular electrode reaction. The deviation from the the equilibrium potential is called the overpotential ( $\eta$ ):

$$E - E_{eq} = \eta$$

The electronic structure of a metal is often described by a "sea of electrons" since the electrons occupy an effective continuum of energy levels whereby the conducting electrons are able to move freely through the solid. The energy levels are filled to a maximum known as the Fermi level ( $E_F$ ). Contrastingly, the electrons of the electrolytic ions occupy discrete energy levels. The Fermi level is influenced by the applied potential. By applying a negative potential, the Fermi level is raised. When the level is raised higher than the lowest unoccupied molecular orbital (LUMO) of the electrolytic ion in solution, reduction becomes favourable and electrons can transfer from the metal to the electroactive species in solution. This is termed the reductive or cathodic current. As the negative potential applied becomes more negative, the free energy of activation becomes smaller and the rate of reduction ( $k_{red}$ ) increases. Thus, as the magnitude of overpotential increases, the rate of reaction increases, which is associated with a shift in the Fermi level of the electrode. The converse process occurs when the applied potential is positive, lowering the Fermi level, enabling electrons from the highest occupied molecular orbital (HOMO) to transfer to the electrode. This is termed the oxidative or anodic current.



Fig 2.8 Charge transfer processes

#### 2.4.4 Faradaic and Nonfaradaic Processes

The number of electrons that cross the electrode/solution interface is measured in terms of total charge passed (Q) and can be related to the amount of product generated (or reactant used) by Faraday's law: 96485.4C of charge equates to 1mol of product generated or reactant used in a one-electron reaction. Since processes occur almost exclusively at the electrode surface, it is heterogeneous, therefore the rates of reaction are described in terms of moles per second per unit area as follows:

$$Rate(mol.s^{-1}.cm^{-2}) = \frac{i}{nFA} = \frac{j}{nF}$$

where j = current density and n = stoichiometric number of electrons used

Such processes are called faradaic processes owing to the fact that they obey Faraday's law, however a range of potentials where charge-transfer does not occur exist yet adsoptive or desorptive effects can alter the electrode/solution composition with potential. These are known as nonfaradaic processes and must be taken into account when interpreting electrochemical data. Many factors can affect the reaction rates of the electrochemical process. In the simplest case, mass transfer occurs, transporting the electroactive species to and from the electrode surface, and heterogeneous electron transfer occurs with the nonabsorbed species. However, more complex pathways commonly occur, which involve chemical reactions before and after electron transfer, and adsorption/desorption or crystallisation at the electrode surface.

#### 2.4.5 The Electrochemical Cell

Even though it is usually only one particular interface or electrode that is of interest in an electrochemical experiment, it is impossible to study one interface in isolation. Therefore experiments are performed in an electrochemical cell that consists of, at the very least, a working electrode of interest, a reference electrode and a separating electrolyte phase. [2.157]

An ideal nonpolarisable electrode is an electrode whose potential does not change with current; its potential is fixed. It would be characterised by a vertical line on an I-V plot. Reference electrodes approach this ideal nonpolarisability. If two ideal nonpolarisable electrodes were used to make up a cell, the characteristic I-V plot would demonstrate pure resistance, i.e. the resistance of the solution. By using a reference electrode that retains a constant composition and fixed potential, changes in the cell are attributable to the working electrode. However, a potential drop ( $iR_s$ ) always occurs during the passage of current, where  $R_s$  is the resistance of the solution phase Thus:

$$E_{app}(vs R E) = E(vs R E) - iR_s = E_{eq}(vs R E) + \eta - iR_s$$

The system described is that of a two-electrode electrochemical cell and can be used when the ohmic drop is less than a couple of millivolts. When nonaqueous solutions with a higher solution resistance are used, the electrode must be very small for the process to be feasible and reduce the risk of affecting the reference electrode potential. Otherwise, a three-electrode electrochemical cell is preferred and commonly used for controlled-potential measurements. The current is passed between a working electrode of interest and a counter electrode. The counter (auxiliary) electrode is usually made from an inert material such as gold, platinum or a carbon rod, that will not affect the reaction at the working electrode. It is also recommended that the surface area of the counter electrode is substantially greater than that of the working electrode in order to avoid passivation or deactivation which may affect the current measurement. [2.158] The current drawn through the reference electrode is negligible thus its potential remains constant. Even in a three-electrode cell, not all of the voltage drop is removed.

However, many modern potentiometers use a combination of operational-amplifiers and feedback loops in order to minimise errors from the voltage drop; analysers are capable of providing a polarising potential to the cell whilst simultaneously monitoring the current flow through the cell. [2.159]

The working electrode can be composed of a variety of different materials depending on the situation. Platinum, gold or carbon remain a common choice because they can be utilised over a wide range of positive and negative potentials in aprotic solvents, and in aqueous solvents they can be used in the positive potential range in which they are partially oxidised. The inert nature of the electrode is important since polymer films are usually formed via an oxidative process therefore the electrode must not oxidise in competition with the polymer. [2.159] A variety of semi-conducting materials, such as silicon, gallium phosphide, cadmium sulfide and cadmium selenide have also been studied as electrode materials but smoother, more adherent films are generally achieved on metal. [2.160]

The traditional reference electrodes, such as the saturated calomel electrode or silver-silver chloride, can always be used but they should remain separated from the electrolyte of the analysed cell in order to prevent contamination of either electrolyte. When the precision of the voltammetric half-wave potential is not so important, or when the electrolyte has a very low ionic strength, a quasi-reference electrode can be used. Normally platinum foil is used for the purpose.

#### 2.4.6 Parameters Of Electrochemistry

There are many variables that can affect the overall process of an electrochemical reaction; electrode material, surface area, geometry and condition; mass-transfer variables; external variables such as temperature and pressure and applied potential time/scan rate; the concentration of species in the electrolyte and the choice of solution, as well as the electrical parameters. It is important for repeatability and for obtaining reliable results that as many of these parameters are controlled.

In relation to electropolymerisation, the variables of most importance include the solvent choice, the monomer and the electrolyte salt concentrations, temperature, and electrode choice. Solvents should have high dielectric constants, poor nucelophilicity and decent dissolving capabilities in relation to the monomer and electrolyte salt used. The electrolyte choice can greatly influence the electropolymerisation and the resultant film. The solubility, degree of dissociation and nucelophilicity/reactivity of the ions are important factors to bear in mind when choosing a suitable electrolyte. The electrical parameters used are of the utmost importance in forming a polymer with desirable properties. The electrochemical methods applied to polymerisation have been studied as well as the morphology, adherence to electrode and conductivities. [2.161 – 2.163] Wood *et al.* [2.164] found that the amount of polypyrrole formed increases as the following factors are increased: monomer and electrolyte concentration, the applied voltage and the reaction time. Of these, the electrolyte concentration and applied voltage exerted the greatest impact. Montemayor *et al.* [2.165] showed that films grown at lower current densities have more considerable chain-oriented morphology and longer chain lengths.

## 2.5 Application of Technology

## 2.5.1 Sampling

Sampling techniques are of great importance in gas sensing application; a device may contain a perfect sensor and excellent data processing facilities, but if impure samples are presented to the instrument, its purpose is undermined. Effective sampling procedures enhance the instruments reliability and the most appropriate sampling technique should be chosen for the application. The three main types of sampling procedures are sample flow systems, static systems and the use of preconcentration.

Sample flow systems place the sensor in the vapour flow of the analyte; they are the most popular of techniques because they are convenient and easy to handle. [2.166] Systems include headspace sampling, diffusion, permeation and bubblers. Headspace sampling systems employ a carrier gas such as dry air to deliver the analyte present in the headspace above a liquid sample to the sensor. Solenoid valves can be used to switch between a flow of pure carrier gas and the sample giving a distinct difference in sensor output. However, the sampling time must be sufficiently small yet still be appropriate with respect to the sensor's response/recovery time, because the vapour concentration in the headspace is not certain and changes with time until liquid-vapour equilibrium is reached.

In the diffusion method, vapour is diffused from a tube of known dimensions. The sample liquid is placed in a reservoir and allowed to diffuse through the diffusion tube to a carrier gas with a constant flow rate. As long as the temperature of the system is kept constant, the diffusion rate can be calculated and thus the concentration can be known. The permeation method employs the same principle but uses a permeation tube instead. A liquefied gas in the tube permeates at a known, regular rate and the concentration can be calculated. Bubbling systems use a bottle of the liquid sample where the carrier gas is bubbled through the sample to generate a vapour. [2.166]

Static systems measure the steady-state response to a vapour at constant concentration and temperature. A very small amount of liquid sample is injected into a vessel containing the sample. The sample is allowed to evaporate and the sensor response is measured when equilibrium is reached. This technique is slow due to the time needed to allow the sample to evaporate, but automation is simple to implement into the design.

Preconcentration is used to improve the sensitivity and can be selective in concentration of analytes. The technique can be used to measure very low concentration, for example, employing SPME fibres which are used in this project.

### 2.5.2 Data processing

Before any processing of data from sensor sets is performed, it is beneficial for the sensor signals to be conditioned and preprocessed beforehand to ensure the data is reliable and the best results are obtainable. A range of hardware and software methods are used but only a selection of signal preprocessing techniques are discussed here.

The purpose of signal preprocessing is to extract the most relevant information from the sensor data in preparation for multivariate pattern recognition. The first stage is baseline processing which preprocesses sensor responses with respect to its baseline to compensate for sensor drift and to give good contrast between signals. There are three baseline processing techniques that are used depending on the application; differential, relative, and fractional. [2.25] Differential processing can remove noise and drift by subtracting the baseline from the sensor response. Relative processing removes multiplicative drift and gives a dimensionless response by dividing the sensor response by the baseline. Fractional measurements are normalised and dimensionless; the baseline is subtracted and divided by the sensor response. Compression of the responses follows this. The purpose is to reduce the responses to generate a fingerprint normally by extracting a single feature from each sensor, disregarding the initial transience from a dynamic response. Recently, however, transient analysis has received more attention since it can give improved performance. The

information that can be obtained from dynamic responses can give a comprehensive insight and can improve selectivity, reduce the data acquisition time and so increase the sensor's lifetime.

The final stage of preprocessing is the normalisation of the data. The two classes of normalisation used are local methods, which work on a sensor's individual response and correct variations between samples and drift, and global methods that are applied to the entire history of responses for a sensor and are used to correct sensor scaling.

After these signals are pre-processed and normalised to give response vectors, they may be analysed using pattern-recognition (PARC) processes. Techniques include supervised systems such as discriminant function analysis (DFA), or unsupervised multivariate techniques, such as cluster analysis. Principal component analysis (PCA) is a prominent method of visualising large data sets and fingerprinting. It is a linear unsupervised process that is widely used. Response vectors are conveyed by linear combinations of orthogonal vectors (principal components) against a fresh set of coordinates. The multivariate data may be represented in two or three dimensions. The displayed components show the variance in data. However, if sensor output parameters are not linear, PCA plots can be difficult to interpret. [2.4; 2.25]

Cluster analysis is an unsupervised technique that separates data into clusters based on the correlation. Since the technique is non parametric is can be used in artificial neural networks and expert systems.

Neural networking techniques have recently become part of the process since they can handle non-linear data and tolerate sensor drift and noise. Artificial neural networks and the use of fuzzy logic are being used as they mimic more closely the olfactory system for odour classification. [2.25; 2.167]

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## **CHAPTER 3**

# **MONOMER SYNTHESIS**

This chapter presents the processes that were used to synthesise and polymerise the conducting polymers for testing and use throughout the project. Whilst many of the polymers used were developed from readily available monomers, a study was carried out to freshly synthesise a selection of pyrrole monomers with differing alkyl chain lengths at the beta position. This was carried out in order to compare the gas sensing properties of their respective conducting polymers, as well as having assuredly pure monomers with which to work from. Although not all of the monomers were successfully synthesised, the experience gained from this study gave insight into their feasibility as sensing materials based upon their ease of manufacture.

The polymers used throughout this project were all polymerised and deposited onto substrates electrochemically due to the ease with which this could be done and the amount of control afforded over the methods employed. Chapter 4 continues the discussion on the techniques used and the results obtained, as well as the individual studies into the factors affecting the electrical properties of the conducting polymers.

### 3.1 Monomer Synthesis

There exists an abundance of research into conducting polymer materials as gas sensors, discussed previously in chapter 2. In order to develop an array of sensors for wound monitoring in a systematic way, it was decided to limit the study by focusing mainly on polypyrrole and its derivatives.

Polyacetylene is the simplest conductive polymer but it is unstable under ambient conditions, so characterisation can be difficult. [3.1] Therefore polypyrrole was chosen for study owing to the fact that it is one of the most studied conducting polymer materials due to

its ease of preparation, its mechanical strength and, while it retains a fully conjugated chain of  $\pi$ -electrons, it is chemically stable to a wide range of chemicals. In addition, polypyrrole is readily oxidised and shows high electrical conductivity. [3.1] Another factor of polypyrrole is its electrochemical reversibility; it can be oxidised and reduced (see section 2.4). [3.2]

The synthesis of a selection of 3-substituted pyrrole derivatives was attempted. This study was undertaken in order to gain experience in making the monomers, helping to evaluate how cost effective their production would be. More importantly though, the main aim of this study was to evaluate and compare their gas sensing properties. The polymers were chosen in order to investigate the differences in alkyl chain length and functional group at the 3-position. 3-substituted polypyrroles have been shown to exhibit higher conductivities than those of *N*-substituted pyrrole due to the more planar nature of the final polymer. [3.3] It has also been shown that alkyl chains substituted at the 3-position increase the conducting polymer's sensitivity to non-polar species [3.4], especially with increasing alkyl chain length. [3.5 - 3.7] It was decided to conduct original research into whether these properties are still exhibited or even enhanced when deposited as a top-layer onto a polypyrrole base-layer, since it has been observed that polymers that are deposited onto a supporting layer display different electrical properties than when they are deposited as a stand-alone film (see 2.3.5).

The monomers chosen for investigation were 3-ethyl, 3-butyl, 3-hexyl, 3-dodecyl and 3-docosylpyrrole. Since the ketone equivalents of these (3-ethanoyl, 3-butanoyl etc.) are synthesised in the process, these were also retained and used. It has also been shown that 3-substitution of carboxylic acid groups produce a hydrophilic polymer [3.8], thus it was intended to see how the ketone equivalents compared.

Unfortunately, the synthesis of all the monomers was not wholly successful, as detailed in the results and the discussion in Appendix 1. Only 3-dodecanoyl, 3-hexanoyl, and 3-hexyl, 3-dodecyl pyrrole were successfully synthesised. The others were too difficult to purify or isolate within the time frame designated to this study. Of these monomers, 3-hexanoylpyrrole, 3-dodecanoylpyrrole, 3-hexylpyrrole and 3-dodecylpyrrole were later

electropolymerised and tested as gas sensors. Chapter 5 elaborates and discusses their results.

## 3.1.1 Reason for general synthetic route chosen

The high reactivity of the  $\alpha$  (2-position) protons compared to the  $\beta$  (3-position) protons of the pyrrole ring results in electrophilic substitution directed almost exclusively to the  $\alpha$ -position. However, there are of couple of methods that can promote substitution at the  $\beta$ -position. [3.4]

One method is to use removable blocking groups at the  $\alpha$ -position. [3.9] Although, for this study, an electron-withdrawing group, such as 1-phenylsulphonate, was used at the *N*-position to promote substitution at the  $\beta$ -position since the removal of the phenylsulfonyl group can be easily done through basic hydrolysis under mild conditions. [3.10] It is also the most common method used in conjunction with the Friedel-Crafts acylation reaction for attaching the acyl group regioselectivly at the  $\beta$ -position on a pyrrole ring with near quantitative results. Although there is no definitive explanation as to why this reaction is so regiospecific, a number of hypotheses have been provided by Kakushima *et al.* [3.10] One compelling explanation is based on electronic factors: Complete Neglect of Differential Overlap (CNDO) calculations revealed that the electron density of 1-phenylsulfonylpyrrole was largest at the 3-position. Also, <sup>13</sup>C NMR showed that the carbonyl carbon of the acetyl chloride was notably deshielded by AlCl<sub>3</sub> and thus charge control is supposed whereby the polarised complex, RCOCI-AlCl<sub>3</sub>, prefers to attack the C-3 carbon of the pyrrole ring. [3.10] Steric factors are believed to play an important role as well. As Ruhe stated:

"The importance of the steric effect is demonstrated by the increasing yield with increasing size of the substituent. Accordingly the yields of the 2-isomers formed as by-products are rather low (5 - 10%)". [3.11]

Since all of the products desired for the experiment rely on the preliminary reactant 1-phenylsulfonylpyrrole, it was imperative to have a reliable method for its synthesis and a guarantee of sufficient purity for continued use in the experiments. A number of methods were tried. The first method tried was that described by Papadopoulos *et al.* [3.12] involving the formation of a pyrrole-potassium salt. The second method attempted was a Clauson-Kaas reaction with benzenesulfonamide and 2,5-dimethoxytetrahydrofuran as described by Wasley *et al.* [3.14] An alternative route using sodium hydroxide, as detailed by Zelikin *et al.* [3.13], was also followed. These last two methods were preferred over the first because they circumvented the hazards of using large quantities of potassium metal.

All of these methods produced good yields of product. Since the production and purity of the precursor was of vital importance to the rest of the reactions carried out, all three methods were studied in order to decide which to use for regular synthesis. Problems with purity were also encountered, therefore, by trying all three methods it could be ensured that the purity of the product was justified. The method described by Zelikin was preferred due the ease of preparation and the need for only two reactants as well as the short reaction time.

## 3.1.2 Clauson-Kaas reaction

The procedure followed to produce 1-phenylsulfonylpyrrole via the reaction of 2,5dimethoxytetrahydrofuran and benzenesulfonamide was first reported by Wasley *et al.* [3.14]. The reaction method employed the use of the Clauson-Kaas reaction. In 1952, Clauson-Kaas *et al.* [3.15; 3.16] reported a method of transforming 2,5-dialkoxy substituted tetrahydrofurans into *N*-substituted pyrroles using primary amines or ammonia. It was suggested that the 2,5-dialkoxytetrahydrofuran hydrolyses to the corresponding 1,4dicarbonyl compound, which then undergoes a Paal-Knorr pyrrole synthesis with the amine to produce the *N*-substituted pyrrole.

Gourley *et al.* [3.17] showed that acidic conditions are not necessary for the hydrolysis of the tetrahydrofuran but is required for the reaction to progress to the formation of pyrrole. It was also stipulated that the product of hydrolysis (succinaldehyde) exists as the 2,5-dihydroxytetrahydrofuran in aqueous environments (see Fig 3.1).


In the Paal-Knorr reaction, the amine adds to one of the carbonyl groups of the diketone to form a hemiaminal. A number of mechanistic routes have been suggested. Katritzky *et al.* [3.18] proposed that the hemiaminal dehydrates to form the imine, which can form the enamine that then cyclises to produce the 5-hydroxy-2-pyrroline. This can then dehydrate to form the pyrrole. However, this mechanism was ruled out by Amarath *et al.* [3.19]. They showed that whilst the imine is formed, it does not lead to pyrrole formation directly. The imine is formed and reaches a maximum before tautomerising back to the hemiaminal and diketone. The cyclised diol intermediate has been shown to exist and its cyclisation is considered the rate determining step. [3.20] The paper discusses the mechanistic details of the intermediates involved in much more detail. Figure 3.2 shows an overview of the possible mechanistic route involved in Paal-Knorr pyrrole synthesis



Fig 3.2 Paal-Knorr pyrrole synthesis

#### 3.1.3 Friedel-Crafts acylation

The Friedel-Crafts reaction is used as a means of attaching an acyl group to an aromatic ring. The procedure has been reliably used to attach an acyl group at the 3-position of pyrrole. The reaction occurs via an electrophilic substitution reaction between the acyl group and the aryl compound in the presence of an aluminium catalyst. Aluminium chloride reacts with the acyl group to form the electrophile,  $RC^+O$ , and an  $AlCl_4^-$  ion. Depending on the conditions, the acyl group can either complex with aluminium chloride to form a polarised complex or it can form the ion pair (Fig 3.3). Either way, the electrophile attacks the aryl compound. The  $AlCl_4^-$  ion completes the reaction by removing the hydrogen. Aluminium chloride is regenerated and hydrogen chloride is formed as a by-product. Figure 3.4 demonstrates the viable processes of Friedel-Crafts acylation. Polyacylation does not occur due to the reactivity of the product being much less than that of the starting material. [3.21]



Polarised Complex

Fig 3.3 Friedel-Crafts electrophile formation



Fig 3.4 Addition of acyl substituent

#### 3.1.4 Reduction (Deoxygenation Of The Ketone)

The reduction scheme used in these experiments followed the procedure according to Ruhe *et al.* [3.11] Other methods of reduction are the Clemmensen reduction and the Wolf-Kishner reduction. The Clemmensen route uses a zinc catalyst and is performed in a strong acid. However, if the substrate is acid-labile the Wolf-Kishner route should be used. This route involves the condensation of the carbonyl compound with hydrazine to form the hydrazone. Treatment with base then induces the reduction of the carbon, coupled with the oxidation of the hydrazine to gaseous nitrogen yields the corresponding alkane.

# 3.2 Methodology

The Friedel-Crafts acylation process appeared to be a common method of producing 3-substituted pyrroles with reliable results and has been reported in a number of papers. Facile deprotection of the product of acylation is achieved by hydrolysis with a suitable base and reduction of the ketone products was achieved using NaAlH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub> (Red-Al) as reported by Ruhe *et al.* [3.11] The chosen synthetic route is shown in Figure 3.5.



Fig 3.5 Synthetic route

- 1)  $R = CH_3$  (3-ethylpyrrole)
- 2)  $R = (CH_2)_2CH_3$  (3-butylpyrrole)
- 3)  $R = (CH_2)_4 CH_3$  (3-hexylpyrrole)
- 4)  $R = (CH_2)_{10}CH_3$  (3-dodecylpyrrole)

The precursor, 1-phenylsulfonylpyrrole, was used in the synthesis of all these monomers. The general synthetic route was:

- i) Friedel-Crafts acylation
- ii) Deprotection of the product (hydrolysis) product refluxed with NaOH
- iii) Reduction using NaAlH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub> (Red-Al)

# 3.2.1 Materials

The chemical reagents used were either readily available or purchased from Sigma-Aldrich or Fluka. The chemicals purchased were benzenesulfonamide (Cat. no. 108146, CAS 98-10-2), 2,5-dimethoxytetrahydrofuran (Cat. no. 38821, CAS 696-59-3), butyryl chloride (Cat. no. 236349, CAS 141-75-3), hexanoyl chloride (Cat. no. 294659, CAS 142-61-0) and Red-Al® (Cat. no. 71495, CAS 22722-98-1).

#### 3.2.2 General Procedure

# 3.2.2.1 1-phenylsulfonylpyrrole

Benzenesulfonamide (7.86g, 0.05mol), 2,5-dimethoxytetrahydrofuran (7.9g, 0.06mol) and glacial acetic acid (50ml) were combined and heated under reflux for 2 h. The mixture was then cooled to 20°C, poured into ice-water (600ml) and allowed to stir for 30 min. The solidified product was collected by filtration and recrystallised from ethanol (85%). The alternative methods used were as described by Papadopoulos *et al.* [3.12] and Wasley *et al.* [3.14]

# 3.2.2.2 Friedel-Crafts acylation

A solution of acyl chloride (11.2 mmol – amounts listed in Table 3.1) in dry dichloroethane (5cm<sup>3</sup>) was slowly added at room temperature to a stirred suspension of anhydrous AlCl<sub>3</sub> (1.60g, 12 mmol) in the same solvent (20cm<sup>3</sup>). The resulting solution was stirred for 10 min, during which a solution of 1-benzylsulfonylpyrrole (2.07g, 10mmol) in dry dichloroethane (20cm<sup>3</sup>) was added drop wise at room temperature. The mixture was then stirred for a further 30 min. The reaction was quenched with ice-water and the product extracted with chloroform (3x80cm<sup>3</sup>). The collected extracts were washed with 5% aqueous sodium hydrogen carbonate (2x50cm<sup>3</sup>) and water (50cm<sup>3</sup>), dried, and evaporated. Chromatography on a short silica gel column with light petroleum-diethyl ether (2:3) as the eluent was used to purify the crude product.

Reactant	Amount (g) [mmol]
Acetic anhydride	7.65g [75 mmol]
Butyryl chloride	1.19g [11.2 mmol]
Hexanoyl chloride	1.51g [11.2 mmol]
Dodecanoyl chloride	2.45g [11.2 mmol]
Docosanoyl chloride	4.02g [11.2 mmol]

Table 3.1 Friedel-Crafts acylation reactant amounts

In the case of 3-acetyl-1-phenylsulfonylpyrrole production, the procedure described by Kakushima *et al.* [3.10] was followed, where acetic anhydride was used as the reactant. This method did not successfully produce any 3-substituted acetyl pyrrole. Andersen *et al.* [3.22] described the successful preparation of 3-acetyl pyrrole by first introducing an electron-withdrawing group, such as a nitrile group, at the 2-position before attaching the acetyl group at the 4-position. The final removal of the nitrile group involved reduction to the aldehyde and then decarbonylation. However, time constraints did not permit investigation of this method.

## 3.2.2.3 Deprotection (Hydrolysis)

Into 120ml of 1,4-dioxane, 3-acetyl-1-phenylsulfonyl pyrrole (4.99g, 20mmol) was dissolved. An equal volume of 5M sodium hydroxide was added and the solution refluxed for 24 h. The phases were separated and the aqueous layer was extracted with diethyl ether. Combined organic layers were washed with saturated sodium chloride solution and dried over sodium sulfate. The solvent was evaporated and the product recrystallised from hexane.

The same procedure was used for the other pyrrole derivatives using the following amounts (Table 3.2). Due to difficulties in purifying 3-docosanoyl-1-phenylsulfonyl pyrrole, it was omitted from further study.

Table 3.2 ⊦	lydrolysis	reactant	amounts
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Reactant	Amount (g) [mmol]
3-acetyl-1-phenylsulfonyl pyrrole	4.99g [20 mmol]
3-butyryl-1-phenylsulfonyl pyrrole	5.55g [20 mmol]
3-hexanoyl-1-phenylsulfonyl pyrrole	6.11g [20 mmol]
3-dedecanoy1-phenylsulfonyl pyrrole	7.79g [20 mmol]

#### 3.2.2.4 Reduction of 3-acylpyrroles to 3-alkylpyrrole

Into 30ml of dry THF, red-Al (12ml, 19.5mmol) was suspended under nitrogen. 3acylpyrrole (6.5mmol – amounts listed in Table 3.3) was added in small portions while cooling with ice-water. The resulting mixture was stirred for 3h at room temperature and then heated for an additional hour at 50°C. After cooling to ambient temperature, the solution was cautiously hydrolysed with water (10ml) and extracted with diethyl ether. The organic extracts were dried over sodium sulphate and the solvent was distilled off.

#### Table 3.3 Reduction reactant amounts

Reactant	Amount (g) [mmol]
3-butyryl pyrrole	0.89g [6.5 mmol]
3-hexanoyl pyrrole	1.07g [6.5 mmol]
3-dedecanoyl pyrrole	1.62g [6.5 mmol]

# 3.2 Results

#### 3.2.1 Summary of achievements

Firstly, the preliminary reactants were made, namely 1-phenylsulfonyl pyrrole, via a Clausson-Clark reaction with 2,5-dimethoxytetrahydrofuran and docosanoyl chloride. After the purity of the precursor was initially disputed due to NMR results (see discussion in Appendix 1), two alternative synthetic routes (discussed earlier) were investigated. After satisfaction that the precursor had sufficient purity, it was used with the corresponding acyl chloride in a Friedel-Crafts reaction to produce the 3-acyl-1-phenylsulfonyl pyrrole products. These were subsequently deprotected by hydrolysis in sodium hydroxide. Although 3-acetyl pyrrole and 3-docosanoyl pyrrole were not successfully obtained and omitted from further study, a portion of the successfully synthesised 3-acyl pyrroles were reduced to their 3-alkyl (reasons given in section 3.4.2).

The following data is a summary of the results obtained from <sup>1</sup>H-NMR analysis of the compounds achieved from this study. Mass spectrometry was performed for 1-phenylsulfonyl pyrrole due to the need for absolute confirmation of purity. IR spectrometry was utilised for the 3-acyl-1-phenylsulfonylpyrroles and the 3-acylpyrroles. Literature sources for the compounds were sourced as listed in table 3.4

Table 3.4 Literature	sources for co	mpounds made
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Compound	Ref.	Analytical data available
phenylsulfonyl pyrrole	[3.13]	<sup>1</sup> H-NMR, IR, elemental composition, mp
3-butyryl-1-phenylsulfonyl pyrrole	[3.23]	<sup>1</sup> H-NMR, <sup>13</sup> C-NMR, IR, elemental composition
3-hexanoyl-1-phenylsulfonyl pyrrole	[3.23]	<sup>1</sup> H-NMR, <sup>13</sup> C-NMR, IR
3-dodecanoyl-1-phenylsulfonyl	[3.24]	<sup>1</sup> H-NMR, <sup>13</sup> C-NMR, IR, MS, mp
pyrrole		
3-butyryl pyrrole	[3.25]	<sup>1</sup> H-NMR, <sup>13</sup> C-NMR, MS
3-hexanoyl pyrrole	[3.25]	<sup>13</sup> C-NMR, MS, elemental composition, mp
3-dodecanoyl pyrrole	[3.26]	IR, mp
3-butyl pyrrole	[3.25]	<sup>13</sup> C-NMR, MS, elemental composition, bp
3-hexyl pyrrole	[3.25]	<sup>13</sup> C-NMR, MS, bp
3-dodecyl pyrrole	[3.24]	<sup>1</sup> H-NMR, <sup>13</sup> C-NMR, IR, MS

# 1-phenylsulfonyl pyrrole

37.3g (90%) Papadopoulos method [Lit: 97%]; 88% Zelikin method
[Lit: 91%]; 87% Wasley
$\delta$ 6.2 (2H, t); 7.18 (2H, t); 7.52 (1H, t); 7.62 (1H, t); 7.88 (2H, m)
m/z 77 (M⁺), 207 (39), 143 (8), 141 (31), 115 (8), 51 (25)
$85^{\circ}$ C (confirmed through DSC) Literature value = $88 - 89^{\circ}$ C [10]

# 3-butyryl-1-phenylsulfonyl pyrrole

Yield:	2.1g (74%) [Lit: 94%]
<sup>1</sup> H-NMR (CDCl <sub>3</sub> ):	$\delta$ 0.98 (t, 3H); 1.75 (tq, 2H); 2.75 (t, 2H); 6.73 (d, 1H); 7.17 (d, 1H);
	7.49 – 7.79 (2H, m); 7.74 (1H, t); 7.95 (1H, s)
IR (KBr):	1681, 1545, 1176, 1136, 1072, 686 cm <sup>-1</sup>

# 3-hexanoyl-1-phenylsulfonyl pyrrole

Yield:	1.8g (60%) [Lit: Quant.]
¹H-NMR (CDCl₃):	δ 0.95 (t, 4H); 1.30 – 1.40 (m, 3H); 1.60 – 1.75 (m, 2H); 2.75 (t, 2H);
	6.72 (d, 1H); 7.19 (d, 1H); 7.50 – 7.72 (2H, m); 7.77 (1H, t); 7.95
	(1H, s)
IR (KBr):	3128, 1672, 1546, 1063, 760 cm <sup>-1</sup>

# 3-dodecanoyl-1-phenylsulfonyl pyrrole

Yield:	3.1g (79%) [Lit: 82%]
¹H-NMR (CDCl₃):	$\delta$ 0.92 (t, 3H); 1.25 – 1.35 (m, 18H); 1.59 (q, 2H); 2.75 (t, 2H); 6.72
	(d, 1H); 7.19 (d, 1H);7.70 (t, 2H); 7.75 (1H, s); 7.95 (1H, t)
IR (KBr):	3141, 1680, 1548, 1071, 756 cm <sup>-1</sup>
m.p.	48°C (lit value 49 – 50°C)

# 3-butyryl pyrrole

Yield:	0.3g (10%) [Lit: 75%]
<sup>1</sup> H-NMR (CDCl₃):	$\delta$ 0.97 (t, 3H); 1.70 – 1.80 (m, 2H); 2.73 (t, 2H); 6.30 (1H, s); 6.72
	(1H, s); 7.19 (d, 2H); 7.50 – 7.70 (m, 3H); 7.88 (d, 2H); 7.95 (d, 2H)

# 3-hexanoyl pyrrole

Yield:	1.9g (59%) [Lit: 78%]
¹H-NMR (CDCl₃):	δ 0.92 (t, 2H); 1.29 – 1.38 (m, 3H); 2.75 (t, 2H); 6.32 (s, 1H); 6.7 (s,
	2H); 7.17 (s, 2H); 7.50 – 7.62 (m, 2H); 7.68 (t, 1H); 7.75 (s, 1H);
	7.82 (d, 2H)

### **3-dodecanoyl pyrrole**

Yield:	3.4g (68%) [Lit: 80%]
<sup>1</sup> H-NMR (CDCl <sub>3</sub> ):	$\delta$ 0.92 (t, 3H); 1.32 (m, 18H); 2.75 (t, 2H); 6.32 (s, 1H); 6.72 (s, 1H);
	7.17 (d, 2H); 7.45 – 7.70 (m, 3H); 7.75 (s, 1H); 7.95 (s, 2H)

# 3-hexyl pyrrole

Yield:	0.2g (23%) [Lit: 44%]
<sup>1</sup> H-NMR (CDCl <sub>3</sub> ):	$\delta$ 0.90 (t, 2H); 1.23 (m, 3H); 2.60 (t, 1H); 6.60 (s, 1H); 6.79 (s, 1H);
	7.38 (s, 1H); 7.45 (s, 1H)
IR (KBr):	3212, 1150, 992 cm <sup>-1</sup>

# 3-dodecyl pyrrole

Yield:	0.9g (60%) [Lit: 68%]
¹H-NMR (CDCl₃):	δ 0.90 (t, 3H); 1.20 – 1.40 (m, 20H); 1.70 (t, 2H); 2.75 (t, 1H); 6.69
	(s, 1H); 6.80 (s, 1H); 7.28 (s, 1H); 7.45 (s, 1H)
IR (KBr):	3210 (broad), 1628, 1164, 921 cm <sup>-1</sup>

# 3.3 Discussion of results

# 3.4.1 Precursor

Three different methods of synthesising 1-phenylsulfonylpyrrole were tried (see section 3.2.2.1). All methods yielded similar amounts of product however a singlet peak at  $\delta$ 1.6 in the <sup>1</sup>H-NMR spectra was unaccounted for. The melting point of the product remained close to that of the literature value (c. 88°C) and was confirmed through differential scanning calorimetry experiments. The peak remained after numerous purification steps. After being certain that the methods used were controlled and the product was purified sufficiently, the

deuterated solvent used (CDCI<sub>3</sub>) was tested and found to be contaminated, yielding the singlet at  $\delta$ 1.6. Therefore this peak was disregarded and it was assumed that the product was sufficiently pure. Furthermore, this was confirmed through MS analysis, with an exact match being given via the NIST library.

Methods of purification attempted included:

- slow and fast recrystallisation from methanol, ethanol, isopropanol and acetonitrile
- liquid-liquid extractions with hexane and methanol, and hexane and acetonitrile
- hot filtration with methanol

# 3.4.2 Friedel-Crafts

Having a satisfactorily pure precursor to work with, Friedel-Crafts acylation was performed using the acyl chlorides. The reaction was monitored using TLC to compare the products with the starting materials and gauge the purity of the products. 3-butyryl-1-phenylsulfonylpyrrole and 3-hexanoyl-1-phenylsulfonylpyrrole were obtained as oils that solidified over time. TLC showed that the 3-butyryl, 3-hexanoyl and 3-dodecanoyl products were different from their starting materials although impurities were present. The acylation with acetic anhydride was deemed unsuccessful because the product collected did not show any differences from 1-phenylsulfonylpyrrole. The experiment was repeated but the same results were found.

## 3.4.3 Hydrolysis

The Friedel-Crafts acylation process was repeated for the butanoyl, hexanoyl and dodecanoyl variants. In order to afford more control, the reaction was carried out at 0°C under a nitrogen atmosphere. Friedel-Crafts acylation and subsequent hydrolysis was later performed without interruption in order to optimise the yield. NMR was used to characterise the products retrieved. Successful synthesis of the products was justified by the presence of the downfield peaks for the alkyl hydrogens: the triplet at 0.9 and 2.75 is present in all of the spectra representing the CH<sub>3</sub> hydrogens at the end of the alkyl chain and the CH<sub>2</sub> hydrogens

nearest the carbonyl carbon respectively. The peaks around 1.25 – 1.4 represent the hydrogens along the alkyl chain and the integral value increases as the length of the alkyl chain increases for each product. The multiple peaks above 6ppm represent the aromatic hydrogen of the pyrrole ring. Although, more aromaticity is evident in these regions than would be expected for the products themselves. This would indicate that the product is not sufficiently pure and some starting material still remained after the reaction.

#### 3.4.4 Reduction

Despite some impurities in the 3-acyl pyrroles produced that were not improved via recrystallisation, it was decided to retain some of the products made and use the remainder in an effort to reduce the carbonyl group. 3-butyl pyrrole was not successfully purified since NMR spectra indicated the presence of the phenylsulfonate substituent. It was not know why this was unsuccessful. However, 3-hexyl pyrrole and 3-dodecyl pyrrole were reduced and purified sufficiently. The NMR spectra was uncomplicated, displaying clear peaks for the alkyl hydrogens and the hydrogens of the pyrrole ring and the IR spectra demonstrated absorption peaks around 3200 cm<sup>-1</sup> corresponding to the N-H bond of the pyrrole ring and the absence/reduction of the peak at 1690cm<sup>-1</sup> of the C=O bond as evidence of the successful deoxygenation of the carbonyl derivative.

#### 3.5 Conclusion

In summary, after achieving a sufficiently pure yield of 1-phenylsulfonyl pyrrole, Friedel-Crafts acylation produced all of the desired products except 3-acetyl-1phenylsulfonylpyrrole. The investigation was continued without any further study of this product. Friedel-Crafts acylation and hydrolysis were repeated without interruption and under a more controlled environment, producing compounds of reasonable purity, although NMR data suggested that some unreacted starting material remained. Due to difficulties in purification, the reduction of these products was continued. Whilst 3-butyryl pyrrole remained unchanged, 3-hexyl pyrrole and 3-dodecyl pyrrole were successfully synthesised as

evidenced by their clear NMR results and IR absorption peaks corresponding to the presence of the N-H bond and the reduction of the C=O bond.

The successfully isolated products of hydrolysis and reduction were retained for polymerisation and gas testing. This is described further in the following chapters.

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# **CHAPTER 4**

# SENSOR FABRICATION: ELECTROCHEMICAL AND MORPHOLOGY STUDIES

In the following chapter, the electrochemical analysis and investigations into polymerisation of different conducting polymers will be described together with the study of surface topology using AFM. Electrochemical techniques were used to deposit and study a variety of polymers throughout the project.

Chemical polymerisation yields polymers with good conductivity and crystallinity but the methods are time consuming and film thickness is difficult to control. Although polymers prepared electrochemically are more amorphous and less crystalline, their thickness and electrical properties are easier to observe and control. Thus the reproducibility of polymers produced electrochemically is better than that of chemically prepared polymers. The electrical parameters and control gained from electrochemical analysis were more suited to the needs of the project, hence all of the polymers studied were deposited electrochemically.

The aims of the electrochemical analysis performed were to gain an understanding of the feasibility of the conducting polymers as sensors for use in the wound monitoring device, that is, their ease of polymerisation, stability and reproducibility. Analysis involved cyclic voltammetry measurements to deduce redox potentials and polymer deposition, which was also studied using chronoamperometry.

Initially, polymers were studied in terms of the potential range in which polymerisation was achieved and the ease of deposition onto the substrate in order to gain experience in sensor array fabrication and obtain an appreciation of their sensing properties through gas testing. Further study then ensued with attempts to gain an overview of the properties of the various polymers and methods into which their electrical properties could be optimised.

The preliminary goal for investigation was to improve the ease of polymerisation, which in turn would enhance the polymer stability. The factors that were used to monitor this were the redox and polymerisation potentials and efforts to bring these into a stable range involved the study of different dopants and the use of different reference electrodes. The base resistances of the polymer sensors were also an important factor that was monitored. Optimisation of the resistance was necessary for use in the woundmonitoring device. The repeatability and reproducibility of the polymers studied was also taken into account. AFM images were taken of the polymers as a means of comparing the surface morphologies and monitoring the deposition of polymers as top-layers, since the majority of sensor made were multi-layered sensors with polypyrrole used as a base layer.

# 4.1 Limits Of Investigation

The following points describe the limits of investigation together with the reasons why they were not studied:

Chemical polymerisation

- due to the successes achieved and the amount of control afforded using electrochemical methods

Use of different solvent systems

- the poor nucleophilicity and aprotic nature of acetonitrile was suited for all of the polymers fabricated for this project. Also, all of the monomers studied were soluble in the solvent system used.

Electrolyte concentrations were mostly kept constant

- as explained in section 2.4.6 of chapter 2, the electrolyte concentration and the applied voltage exert the greatest impact on polypyrrole formed. By keeping the electrolyte concentration constant, the focus of investigation could be kept to the different electrochemical parameter and their effects could be correlated to

polymer properties in the knowledge that other experimental parameters were not influential.

• The dopants used were limited to organic anionic dopants

- these dopants produced p-type conducting polymer films and were readily soluble in acetonitrile. These dopants worked well and further explanation on the dopants used are given in section 4.7.2

Different substrate materials were not used

- the main reason different substrates were not used was due to the practicality of the polyimide substrates and their compatibility with the devices that were used in the laboratory, such as the electronics employed for sensor resistance interrogation.

• The research only employed the use of intrinsic conducting polymers (ICP)

- ICPs are amongst the most studied type of conducting polymers, so there was a wealth of information available with which to begin investigations. Additionally, despite the limitation, a huge array of different possible conducting polymer sensor materials exist.

Although chemical polymerisation yields polymers with more crystalline structures and has been reliably deposited across electrodes to effectively bridge the gaps, it was decided to use electropolymerisation exclusively for this project. By dip-coating the electrodes in P3HT first, lateral polymer growth bridged the electrode gaps reliably and the uniform film achieved was reproducibly made and easily controlled. It is supposed that hydrophobic interactions of P3HT concentrates the pyrrole in the hexyl chains in a similar fashion to that observed by Ye *et al.* [4.1] with Nafion treated electrodes on silanized glass. Therefore, due to the reliability and reproducibility afforded by this method, chemical polymerisation of base layers was not investigated and research was focused on the polymers deposited as top-layers on polypyrrole.

Electrochemical experiments are generally performed in organic solvents rather than aqueous media. Organic solvents have a number of advantages; they are more difficult to oxidise or reduce and no solvation or hydration occurs, so there is little to no complication of the oxidation peaks observed. Unfortunately, many organic solvents have lower dielectric constants than aqueous solutions and so they are a less conductive media. However, this may be overcome by using a high concentration of salt.

The choice of solvent used for the electrolyte can greatly affect the properties of the polymer film grown. The most important consideration is the nucleophilicity of the solvent. Since the polymerisation process involves the formation of radical cation intermediates, regions near the electrode surfaces are sensitive to nucleophilic attack and it is therefore important to use solvents that have poor nucleophilicity. Typically, aprotic solvents such as acetonitrile are used, as was employed in the experiments performed for this project. Polypyrrole films formed in acetonitrile with a small percentage of water formed smoother films that adhered to the substrate better than films formed in anhydrous acetonitrile, as reported by Diaz *et al.* [4.2]. However, as the concentration of water in the electrolyte is increased, the conductivity of films produced becomes substantially less. Polypyrrole has been reported to grow in aqueous media [4.3; 4.4], but for the purposes of control over the many parameters that affect polymer formation, the solvent system used for electrolytes was confined to acetonitrile-water with 99:1 ratio, as utilised by Diaz *et al.* and others.

Electrolyte salt choice can also greatly affect the film produced. Throughout the course of this project, a number of dopant ions have been investigated but they have mainly been limited to tetraalkylammonium salts. Important considerations for the choice of dopant ion are its solubility, nucleophilicity and degree of dissociation. Iodine and ferrous chloride have been commonly used as dopants for polyaniline, polypyrrole and polythiophene. Although, nucleophilic anions such as halides, alkoxides and hydroxides, which can be easily oxidised, do not produce good films. [4.5] Anionic surfactants have often been used as dopants, particularly tetraalkylammonium salts, which are readily soluble in acetonitrile and are highly dissociated. The long alkyl chains of the surfactant have been shown to contribute to the increase in conducting polymer solubility. [4.6]

# 4.2 Instrumentation

Electrochemical experiments performed using a microAutolab Type III potentiostat/galvanostat in conjunction with the data acquisition software, General Purpose Electrochemical Software (GPES), Version 4.9 from Ecochemie<sup>®</sup>. AFM images were taken with an Explorer<sup>™</sup> AFM from Veeco Instruments. Data was acquired with SPMLab v5.01 from ThermoMicroscopes<sup>®</sup>. AFM tips used were SuperSharp non-contact AFM tips from µMasch<sup>®</sup>.

#### 4.3 Methodology

The substrates used throughout this project consisted of eight gold interdigitated electrodes (IDE) supported on a flexible polyimide sheet (Kapton®) that was 125  $\mu$ m thick. These substrates were used as supplied from Biomedical Microsensors Laboratory (BMMSL), NC State University. Chemical vapour deposition had been used to deposit the gold and a layer of chromium was used to promote adhesion of the gold to the polyimide surface. A thin film (15  $\mu$ m) was patterned across the substrate in order to insulate the gold tracks outside of the sensor area. The gold tracks were patterned at one end so as to conveniently connect to devices using 1.25mm pitch connections. The dimensions of the substrate are shown in Figure 4.1.



Fig 4.1 Polyimide substrate with interdigitated electrodes

This substrate was used due to its practical, robust design that allows it to be implemented into a device very conveniently. It was also the same design used for the smart fire detection system described by Scorsone *et al.* [4.7] It proved to be an efficient substrate and so it was used for the entirety of this project.

After electrochemical polymerisation and deposition, sensors were exposed to temperatures of 115 – 120°C for up to 30 minutes and then left overnight to dry in a dessicator prior to any gas testing. This process removed any residual moisture and helped to bring most of the sensors into a resistance range more suitable for gas testing, presumable by dedoping the polymers and annealing them, making them more stable. The heat treatment process is discussed further in section 4.10.1.

### 4.3.1 Electrochemical Setup

A three electrode electrochemical cell setup was used for all of the measurements. The electrodes and the electrolyte solution were held in a purpose built well made from a Teflon block. The substrate described in the previous section was used as the working electrode (anode). A sheet of gold was used as the counter (auxiliary) electrode, the surface area of which was much greater than that of the working electrode. As with the working electrode, it is important that the material is electrochemically inert and gold was shown to be suitable for the experiments performed.

The reference electrode used for the majority of measurements was that of a platinum quasi reference electrode ( $\Phi = 1$  mm). A small study was carried out that investigated the use of other reference electrodes, namely Ag/AgCl and the calomel electrodes, but otherwise the platinum reference electrode was used.

In order to maintain a consistency in the results obtained, it was endeavoured to control as many of the parameters affecting polymerisation as possible. Fresh monomer/electrolyte solutions were made prior to electrochemical experimentation. In

particular, polypyrrole solution degraded fairly quickly over time and had to be remade quite regularly. Additionally, pyrrole was always distilled prior to preparing an electrolyte solution.

The polyimide substrate was cleaned and prepared before any polymerisation was attempted. This was achieved by cleaning the gold electrodes on the substrate with chromic acid and washing with deionised water and isopropanol. The substrate was then allowed to dry overnight at 40°C. As mentioned previously, the substrate was dip-coated with P3HT in order to encourage the lateral growth of polypyrrole films across the interdigitated electrodes. This was done was submerging the electrode area of the substrate into a solution of P3HT in *p*-xylene (0.2 mg.L<sup>-1</sup>) for ten minutes. The substrate was then allowed to dry at 40°C for 30 minutes. Evaporation of the solvent left a thin film of P3HT that was barely visible.

It has been shown that the temperature at which the polymer is formed has a substantial effect on the morphology of the film, its crystallinity and conductivity. [4.8; 4.9] The electrolyte solutions used were stored in a fridge at 5°C when not used. So electrochemical experiments were performed between  $5^{\circ}C - 20^{\circ}C$ . However, it would have been more beneficial if the solutions had been maintained at a more constant, lower temperature.

During the course of this project it was observed that the resistance of the polymers formed was also dependent on the position at which it was deposited on the substrate. Higher resistances were found for polymers that were deposited further into the solution of the electrochemical cell than those formed nearer the surface. This observation was later taken advantage of in deciding the optimal position of the different conducting polymer sensors on the sensor array. The distance of the working electrode (substrate) from the counter electrode was also maintained at a distance of  $7mm \pm 2mm$ .

Before polymerisation was attempted onto the substrate, the polymers were first characterised through cyclic voltammetry in order to estimate the range of the polymerisation and redox potentials and judge the feasibility of polymerisation. Resistances were measured

using either a multimeter or by calculating the gradient of a linear sweep voltammogram of the sensor measured across the two electrodes of the corresponding IDE.

#### 4.4 Polypyrrole and Derivatives

It was previously noted that polypyrrole is one of the most studied conducting polymer materials owing to its chemical and mechanical stability, ease of preparation and high electrical conductivity. For these reasons and its availability, it was decided to focus most attention on polypyrrole and some of the derivatives in order to study their suitability as sensing materials for wound monitoring.

An early example of polypyrrole used in an electronic nose device was described by Nylander *et al.* [4.10] and Shurmer *et al.* [4.11]. Polypyrrole has since been one of the most used conducting polymers in gas sensing applications from environmental and industrial analysis [4.12] to clinical applications [4.13], as well as having received a great amount of attention in the design of bioanalytical sensors. [4.14]

The sensitivities of conducting polymers can be tailored by attaching various side chains to the polymer backbone as has been described in the background chapter. The inclusion of a variety of polypyrroles containing numerous different substituents was included in the study to observe their differences and compare which polymers could be combined to produce a suitably orthogonal sensor array for the purposes of this project.

The success of conducting polymer materials as non-specific gas sensors aided the commercialisation of numerous electronic nose devices, such as those by AromaScan/Osmetech®, BloodhoundTM and Cyranose® of Cyrano Sciences that have been widely used to successfully detect odours including metabolites of various bacteria. [4.15 – 4.18]

#### 4.4.1 Polypyrrole Base Layer

The majority of the polymer sensors fabricated and used in this project were duallayered, whereby a polypyrrole film, doped with naphthalene sulfonic acid (NSA), was used as a baselayer and a different polymeric top layer was deposited onto this, which consisted of the functionalised conducting polymer of interest. The effects of conducting polymer bilayers were discussed in the chapter 2, section 2.3.5 on Multilayer Sensors.

By using a base layer of conducting polypyrrole doped with naphthalenesulfonic acid (NSA), the top layer polymers deposited onto a surface with a different work function to that of the gold electrode and function via a mediated current through the polypyrrole inner/base layer. Such conducting polymer base layers are typically deposited onto substrates via chemical methods such as chemical oxidation with the use of oxidative transition metal ions or metallic salts (most commonly ferric salts) [4.19], through the use of metal catalysed condensation reactions [4.20] or by chemical vapour deposition [4.21] or by electrospinning [4.22]. Polymer layers formed this way are stable and highly crystalline.

Although polymers formed electrochemically are more amorphous, the technique is preferred due to the ability to control the conductivity, adherence, morphology and processability of the polymer through the choice of counter ions, the nature of the electrolyte, monomer/dopant concentrations, the solvent used, the nature of the electrode and the temperature. Electrochemical polypyrrole growth tends to be confined to the electrode tracks and it is difficult to grow film between the electrodes. Therefore, when fabricating conducting polymer bilayer sensors, the base layer is normally deposited chemically in order to form a uniform layer that covers the gap between electrodes. By dip-coating the substrate in P3HT prior to electropolymerisation, it was found that polypyrrole could be grown across the electrode sensing area, including the gaps between the electrodes, reliably and repeatably.

Linear sweep voltammetry was applied to the polypyrrole-NSA baselayers from a batch of four sensor arrays, each using eight sensors with a polypyrrole baselayer. The

linear sweep voltammograms for all of these are superimposed in Fig 4.2. The degree of variation is greater between different sensor arrays, which could be attributable to differences in electrode distances during setup, however the sensor-to-sensor variation was encouragingly small.



Fig 4.2 Linear Sweep Voltammograms of polypyrrole baselayers

The curves shown are symmetric and follow a non-ohmic relation. This is attributable to the formation of polarons and bipolarons as the voltage increases, contributing to the higher currents exhibited. [4.23]

The resistance of the polypyrrole baselayers were noted for a number of sensor arrays and their average values are listed in Table 4.1 (based on 10 measurements for Set-A and 3 measurements for Set-B). The main set, Set-A, consisted of sensor arrays of polypyrrole sensors with low resistances which were used for the majority of experiments. Set-B consisted of arrays with polypyrrole baselayers whose thickness's were increased and had slightly higher resistances. In some cases, the resistances found were uncharacteristically high but this was usually due to lack of control over factors such as the nature of the electrolyte solution and the temperature.

Array Set	Mean Resistance (Ω)	S.D.(σ)
Set-A	360 ± 7.1	80.3
Set-B	688 ± 15.3	140.2

Table 4.1 Base layer resistances

It can be observed that as the average resistance of the base layers increases, the variance increases which implies that the precision or repeatability of sensor fabrication decreases with resistance.

AFM imaging of the polymer showed a globular-shaped "cauliflower" surface (see Fig. 4.3), as described in literature. [4.24] The surface seems to mostly comprise of small globules with an average height of  $152.8 \pm 43.6$ nm and average diameter of  $0.79 \pm 0.18$ nm, between less frequent but evenly spaced larger globules of average height 771.9 ± 181.9nm and diameter 1.93 ± 0.37nm. The root-mean-square average roughness is 0.8919µm and arithmetic roughness average, 0.705µm.

Polypyrrole doped with *p*-toluenesulfonic acid (tosylate ion, TsO<sup>-</sup>) was also made. According to literature, polypyrrole-TsO<sup>-</sup> films were slightly more conductive than when doped with NSA although the arylsulfonic acid counter ions behave similarly. [4.25] However, in some instances when using tosylate as the counter ion, the polymer would grow to areas beyond the IDEs and sometime partially cover adjacent IDEs on the substrate. The reasons for this were not investigated further since using pyrrole-NSA provided a reliable and repeatable method of deposition and was used for the remainder of the project.



Fig 4.3 Topological representations of polypyrrole surface

# 4.4.2 Polypyrrole Derivatives

The polymers used in this project were primarily those of polypyrrole. Studies were focused on polypyrrole and a range of pyrrole based monomers that were available for use, which were chosen to highlight the differences between pyrrole derivatives, such as alkyl chain length, the functional group, positional influences and steric factors. The following monomers were studied in terms of their polymerisation, electrical properties and, most importantly, their gas sensing abilities. The monomers chosen for study were *N*-methylpyrrole, *N*-hexylpyrrole, *N*-dodecylpyrrole, 3-hexylpyrrole, 3-dodecylpyrrole, 3-hexanoylpyrrole, 3-dodecanoylpyrrole, *N*-pentafluorobenzylpyrrole, and *N*-phenylpyrrole. The chemical structures of these are displayed below.

(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>  $(CH_2)_5CH_3$ *N*-methylpyrrole *N*-hexylpyrrole *N*-dodecylpyrrole CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub> CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub> 3-hexylpyrrole 3-dodecylpyrrole (CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub> (CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub> 3-dodecanoylpyrrole 3-hexanoylpyrrole F F *N*-phenylpyrrole N-pentafluorobenzylpyrrole

*N*-hexylpyrrole and *N*-dodecylpyrrole were chosen for comparison with their 3-alkyl isomers, 3-hexylpyrrole and 3-dodecylpyrrole respectively. Monomers were also chosen for the comparison of the increasing alkyl chain lengths of their substituents. As mentioned in the previous chapter, the increase in alkyl chain length has been shown to allow for more sensitivity towards non-polar species. Although the *N*-substituted pyrroles have been shown to have much lower conductivities compared to 3-substituted pyrroles due to a lack of ring planarity [3.3], their inclusion in these studies remained in order to evaluate their performances when deposited onto a polypyrrole baselayer.

3-hexylpyrrole, 3-hexanoylpyrrole, 3-dodecylpyrrole, and 3-dodecanoylpyrrole were chosen to compare the differences between straight alkyl chain substituents and their acyl equivalent, where the carbonyl carbon is attached to the pyrrole ring. *N*-pentafluorobenzylpyrrole and *N*-phenylpyrrole were chosen in order to observe steric effects. Steric effects could also be a factor for the *N*-substituted pyrroles.

#### 4.4.3 Results of electrochemical analysis and electropolymerisation

The electrochemical data is presented here for the pyrrole derivatives described that were tested. Sample averages are listed in the following tables together with the standard deviation for the sample (in brackets), which shows the amount of repeatability in the measurements performed. The majority of monomers tested involve redox processes. The counter ions used in each case acted as a supporting electrolyte for initial polymerisation and polymers formed were in a conducting state. In some cases the monomer oxidation and polymer growth coincided with the same potential range thus making conclusions on the electrochemical process more difficult to interpret.

The potential of polymerisation and the redox potentials have been listed together with the current and charge passed during the redox processes. The half-wave potentials ( $E_p - E_p/2$ , where  $E_p$  = peak width) have also been listed in order to estimate the ratio of electrons involved in the process.

The reversibility of the processes were evaluated by calculating the ratios based on both the amount of current ( $I_{pa}$  /  $I_{pc}$ , i.e. anodic current / cathodic current) and the charge passed (Qa / Qc, i.e. charge passed on oxidation / charge passed on reduction). Quasireversible systems were more apparent than truly reversible processes; oxidation was often more defined whereas reduction kinetics were slower.

#### 4.4.3.1 N-methylpyrrole

<b>Polymerisation Potential</b>			
(V)	0.748 (0.023)		
Oxidation potential (V)	0.270 (0.016)	Reduction potential (V)	0.191 (0.007)
Anodic current (mA)	0.0468 (0.0119)	Cathodic current (mA)	0.0577 (0.0160)
Integrated anodic charge		Integrated cathodic	
(mC)	0.2436 (0.0679)	charge (mC)	0.2590 (0.0616)
Anodic half-wave		Cathodic half-wave	
potential Ep-Ep/2	0.276 (0.021)	potential Ep-Ep/2	0.355 (0.031)
No electrons involved	0.21 (0.02)	No electrons involved	0.16 (0.02)
Reversibility based on		•	
current (lpa/lpc)	0.82 (0.02)		
Coulombic reversibility			
(Qa/Qc)	0.93 (0.07)		

**Table 4.2** Electrochemical results for N-methylpyrrole/PF<sub>6</sub><sup>-</sup>

The results generally showed a good degree of reversibility and as can be seen in Table 4.2 above, the parameters for the oxidative and reductive processes are comparably similar. The polymerisation potential was in a reasonable range for reliable deposition.

## 4.4.3.2 N-hexylpyrrole

Results for *N*-hexylpyrrole polymerisation with  $BF_4^-$  are presented in Table 4.3. The oxidation potential often coincided with the polymerisation potential and the peak was not identifiable. The greater current shown in the forward scan in comparison with the reduction in the reverse scan means that the reversibility estimations were far from unity, suggesting that the process was less reversible. There were some cases in which the oxidation potentials shifted to more potentials and the processes were more quasi-reversible in nature.

However, as mentioned, the oxidation potentials were quite high and the maxima of the peaks were never observed. However, the shape of the waveforms of the forward sweep suggested that the process may have had a reversible nature. This idea is demonstrated in Fig 4.4.

Polymerisation Potential			
(V)	0.784 (0.096) initial		
Oxidation potential (V)	0.904 (0.095)	Reduction potential (V)	0.387 (0.057)
Anodic current (mA)	0.2779 (0.0606)	Cathodic current (mA)	0.1006 (0.0523)
			· · · ·
Integrated anodic charge		Integrated cathodic	
(mC)	0.6032 (0.2766)	charge (mC)	0.4472 (0.2522)
Anadia halfwaya		Cathadia halfwaya	
Anodic nall-wave		Cathodic nan-wave	
potential Ep-Ep/2	0.167 (0.039)	potential Ep-Ep/2	0.229 (0.035)
No electrons involved	0.36 (0.09)	No electrons involved	0.25 (0.05)
Reversibility based on			
current (lpa/lpc)	2.95 (1.07)		
Coulombic reversibility			
(Qa/Qc)	1.44 (0.43)		

**Table 4.3** Electrochemical results for N-hexylpyrrole/BF<sub>4</sub><sup>-</sup>



Fig 4.4 Illustration of oxidation peak beyond potential scan range

Fig 4.4 demonstrates the assumption made with regard to the measurements performed. It is thought that the oxidation peak lies beyond the potential range that was scanned during cyclic voltammetry; reversing the direction of the potential sweep at 1.0V (dashed line). If the potential was allowed to continue and the electrode surface did not degenerate, it is thought that the oxidation peak would eventually be attained, as represented in the diagram.

Polymerisation Potential (V)	0.925 (0.040)		
Oxidation potential 1		Reduction potential 1	
(V)	0.551 (0.049)	(V)	0.451 (0.033)
Anodic current at 50mV/s (mA)	0.0510 (0.1030)	Cathodic current at 50mV/s (1 <sup>st</sup> peak)	0.0547 (0.1001)
Anodic charge at 50mV/s (mC)	0.2119 (0.1110)	Cathodic charge at 50mV/s (1 <sup>st</sup> peak)	0.1878 (0.1119)
Oxidation potential 2 (V)	0.867 (0.034)	Reduction potential 2 (V)	-0.634 (0.053)
Reversibility based on	0.93 (1.03)		
Coulombic reversibility (Qa/Qc)	1.13 (0.99)		

**Table 4.4** Electrochemical results for N-hexylpyrrole/PF<sub>6</sub><sup>-</sup>

The use of other dopant ions was investigated in cases where the conductivity and/or base resistance needed adjustment. Although decent results were obtained with *N*-hexylpyrrole using the tetrafluoroborate anion as dopant, hexafluorophosphate was also studied with the same system. However, extra peaks were found that could not be explained for the reaction. These peaks only appeared at scan rates below 25 mV/s. Their presence was not significant compared to the current involved for the other peaks, which show a reversible process. Thus the potentials of the extra peaks are listed in Table 4.4 but they may be due to some impurity and disregarded with respect to the polymerisation of *N*-hexylpyrrole/PF<sub>6</sub><sup>-</sup>.

# 4.4.3.3 N-dodecylpyrrole

Results for *N*-dodecylpyrrole polymerisation with  $PF_6^-$  are presented in Table 4.5. Oxidation and reduction peaks were clear. The anodic current was considerably larger than the cathodic current. The higher oxidation potentials compared with *N*-hexylpyrrole demonstrate the steric effects of the longer alkyl chain present on the nitrogen. Reversibility for *N*-dodecylpyrrole/PF<sub>6</sub><sup>--</sup> was poor, although in some cases the peaks coincided and were difficult to resolve. This may be due to a catalytic effect of the oxidised polymer, which can extract electrons from the monomer. This has been described in papers by Tang *et al.* [4.26] and Geun Gi Min *et al.* [4.27]

Polymerisation Potential			
(V)	0.823 (0.037)		
Oxidation potential (V)	0.747 (0.036)	Reduction potential (V)	0.442 (0.039)
Anodic current (mA)	0.2655 (0.0220)	Cathodic current (mA)	0.1065 (0.0105)
Integrated anodic charge		Integrated cathodic	
(mC)	0.7184 (0.0853)	charge (mC)	0.5158 (0.0633)
Anodic half-wave		Cathodic half-wave	
potential Ep-Ep/2	0.107 (0.033)	potential Ep-Ep/2	0.342 (0.022)
No electrons involved	0.57 (0.16)	No electrons involved	0.17 (0.01)
Reversibility based on			
current (lpa/lpc)	2.52 (0.37)		
Coulombic reversibility			
(Qa/Qc)	1.39 (0.04)		

Table 4.5 Electrochemical results for N-dodecylpyrrole/PF<sub>6</sub><sup>-</sup>

# 4.4.3.4 N-pentafluorobenzylpyrrole

Dolymorization Dotontial	•	• • •	
Folymensation Folentia	4 000 (0 007)		
(V)	1.399 (0.027)		
Oxidation potential 1 (V)	-0.0022 (0.00491)	Reduction potential (V)	-0.385 (0.033)
Anodic current (mA)	0.1638 (0.0404)	Cathodic current (mA)	0.1416 (0.0444)
Integrated anodic charge		Integrated cathodic	
(mC)	0.5251 (0.1992)	charge (mC)	0.6019 (0.2574)
Anodic half-wave		Cathodic half-wave	
potential Ep-Ep/2	0.172 (0.031)	potential Ep-Ep/2	0.202 (0.037)
No electrons involved	0.34 (0.059)	No electrons involved	0.29 (0.05)
Oxidation potential 2 (V)	0.889 (0.107)		
Anodic current (mA)	0.0376 (0.0213)		
Integrated anodic charge			
(mC)	0.3732 (0.1359)		
Anodic half-wave			
potential Ep-Ep/2	0.236 (0.038)		
No electrons involved	0.25 (0.04)		
Reversibility based on			
current (lpa/lpc)	1.18 (0.15)		
Coulombic reversibility			
(Qa/Qc)	0.97 (0.27)		

Table 4.6 Electrochemical Results for N-pentafluorobenzylpyrrole/TsO

## 4.4.3.5 *N*-phenylpyrrole

*N*-phenylpyrrole and *N*-pentafluorobenzylpyrrole possess interesting properties due to their enhanced electronic stability from the phenyl ring conjugation with the pyrrole ring. *N*-pentafluorobenzylpyrrole has received considerable attention in literature. [4.28 – 4.30] Diaw reports that *N*-phenylpyrrole exhibits two oxidation peaks and one reduction peak. The first (lower) oxidation peak occurs due to pyrrole oxidation, which is reversible, and the second oxidation peak occurs due to oxidation of the benzene ring which is an irreversible process.

The results reported in tables 4.6 and 4.7 confirm these processes. It was anticipated that the oxidation and polymerisation potentials for *N*-pentafluorobenzylpyrrole would be lower than those for *N*-phenylpyrrole due to the fluorine atoms around the benzene rings imparting greater stability of the radical intermediate through conjugative effects from the electron donating properties of fluorine. However, the steric effects have a greater influence and the potentials are slightly higher than for *N*-phenylpyrrole, yet they are still comparable.

Polymerisation Potential	·		
(V)	1.342 (0.026)		
		Reduction potential 1	
Oxidation potential 1 (V)	-0.0317 (0.0492)	(V)	-0.139 (0.200)
Anodic current (mA)	0.0214 (0.0153)	Cathodic current (mA)	0.0156 (0.0123)
Integrated anodic charge		Integrated cathodic	
(mC)	0.0944 (0.0702)	charge (mC)	0.0917 (0.0745)
Anodic half-wave		Cathodic half-wave	
potential Ep-Ep/2	0.189 (0.104)	potential Ep-Ep/2	0.241 (0.073)
No electrons involved	0.38 (0.16)	No electrons involved	0.25 (0.07)
		Reduction potential 2	
Oxidation potential 2 (V)	0.856 (0.022)	(V)	0.114 (0.082)
Anodic current (mA)	0.0075 (0.0041)	Cathodic current 2 (mA)	0.0049 (0.0024)
Integrated anodic charge		Integrated cathodic	
(mC)	0.0564 (0.0337)	charge 2 (mC)	0.0493 (0.0237)
Anodic half-wave		Cathodic half-wave	
potential Ep-Ep/2	0.159 (0.023)	potential Ep-Ep/2	0.148 (0.038)
No electrons involved	0.36 (0.05)	No electrons involved	0.40 (0.08)
		Reversibility based on	
Reversibility based on		current [benzene]	
current [pyrrole] (lpa/lpc)	1.40 (0.44)	(lpa/lpc)	2.66 (0.81)
Coulombic reversibility		Coulombic reversibility	
[pyrrole] (Qa/Qc)	1.05 (0.16)	[benzene] (Qa/Qc)	1.47 (0.30)

Table 4.7 Electrochemical Results for N-phenylpyrrole/TsO<sup>-</sup>

In light of the high potentials for *N*-pentafluorobenzylpyrrole and *N*-phenylpyrrole, the same testing was performed using  $PF_6^-$  as the counter ion so as to try to lower the polymerisation potential. Encouraging results were found as shown in Tables 4.8 and 4.9.

Polymerisation			
Potential (V)	1.002 (0.032)		
Oxidation potential (V)	0.768 (0.008)	Reduction potential (V)	0.458 (0.004)
Anodic current (mA)	0.1571 (0.0215)	Cathodic current (mA)	0.1446 (0.007)
Integrated anodic		Integrated cathodic	
charge (mC)	0.6001 (0.0712)	charge (mC)	0.5764 (0.0738)
Anodic half-wave		Cathodic half-wave	
potential Ep-Ep/2	0.221 (0.033)	potential Ep-Ep/2	0.239 (0.011)
No electrons involved	0.26 (0.04)	No electrons involved	0.24 (0.01)
Reversibility based on			
current (Ipa/Ipc)	1.08 (0.11)		
Coulombic reversibility			
(Qa/Qc)	1.04 (0.04)		

 Table 4.8 Electrochemical Results for N-pentafluorobenzylpyrrole/PF<sub>6</sub><sup>-</sup>

 Table 4.9 Electrochemical Results for N-phenylpyrrole/PF<sub>6</sub>

Polymerisation			
Potential (V)	0.992 (0.016)		
Oxidation potential (V)	0.863 (0.036)	Reduction potential (V)	0.332 (0.057)
Anodic current (mA)	0.0777 (0.0178)	Cathodic current (mA)	0.0704 (0.0023)
Integrated anodic		Integrated cathodic	
charge (mC)	0.2452 (0.0269)	charge (mC)	0.2477 (0.0246)
Anodic half-wave		Cathodic half-wave	
potential Ep-Ep/2	0.176 (0.023)	potential Ep-Ep/2	0.204 (0.017)
No electrons involved	0.33 (0.05)	No electrons involved	0.28 (0.02)
Reversibility based on			
current (lpa/lpc)	1.10 (0.26)		
Coulombic reversibility			
(Qa/Qc)	0.99 (0.04)		

#### 4.4.3.6 3-hexylpyrrole

3-hexylpyrrole/PF<sub>6</sub><sup>-</sup> polymerisation results are listed in Table 4.10. Weak redox peaks in the cyclic voltammograms were found and polymerisation was slow, requiring a number of cycles before polymer films formed with any significant thickness. However, polymerisation was slightly more forthcoming when  $BF_4^-$  was used as the counter ion instead of  $PF_6^-$  due to the lower polymerisation potential (Table 4.11). Redox peaks were not observed for  $BF_4^-$  though. The peaks observed for 3-hexylpyrrole/PF<sub>6</sub><sup>-</sup> may have simply occurred due to movement of the counter ions in and out of the polypyrrole matrix.

Polymerisation Potential			
(V)	0.758 (0.080)		
Oxidation potential (V)	0.209 (0.030)	Reduction potential (V)	-0.019 (0.013)
Anodic current (mA)	0.0021 (0.0008)	Cathodic current (mA)	0.0015 (0.0005)
Integrated anodic charge		Integrated cathodic	
(mC)	0.0095 (0.0042)	charge (mC)	0.0046 (0.0018)
Anodic half-wave		Cathodic half-wave	
potential Ep-Ep/2	0.225 (0.020)	potential Ep-Ep/2	0.262 (0.026)
No electrons involved	0.25 (0.02)	No electrons involved	0.22 (0.02)
Reversibility based on		•	
current (lpa/lpc)	1.41 (0.16)		
Coulombic reversibility			
(Qa/Qc)	2.08 (0.52)		

 Table 4.10 Electrochemical Results for 3-hexylpyrrole/PF<sub>6</sub>

Table 4.11 3-hexylpyrrole/BF<sub>4</sub>

	-
Polymerisation	
Potential (V)	0.522 (0.039)

# 4.4.3.7 3-dodecylpyrrole

Polymerisation Potential		Initial Polymerisation	
(V)	0.493 (0.010)	Potential (V)	0.710 (0.005)
Oxidation potential (V)	0.216 (0.016)	Reduction potential (V)	0.004 (0.007)
Anodic current (mA)	0.0372 (0.0171)	Cathodic current (mA)	0.0306 (0.0077)
Integrated anodic charge		Integrated cathodic	
(mC)	0.1274 (0.0291)	charge (mC)	0.1040 (0.0241)
Anodic half-wave		Cathodic half-wave	
potential Ep-Ep/2	0.032 (0.009)	potential Ep-Ep/2	0.168 (0.011)
No electrons involved	1.96 (0.71)	No electrons involved	0.34 (0.02)
Reversibility based on			
current (lpa/lpc)	1.17 (0.28)		
Coulombic reversibility			
(Qa/Qc)	1.26 (0.31)		

Table 4.12 Electrochemical Results for 3-dodecylpyrrole/PF<sub>6</sub>

The results for 3-dodecylpyrrole polymerisation with  $PF_6^-$  are given in Table 4.12. The redox potentials found were similar to 3-hexylpyrrole; polymerisation was wholly successful and facile in comparison. A decent level of reversibility was also displayed. Polymerisation with 3-dodecylpyrrole/ $BF_4^-$  was equally successful, however the redox potentials were more varied and quite broad (Table 4.13). The anodic current was greater than cathodic current yet the charge passed for each process was similar.

		7	
Polymerisation			
Potential (V)	0.644 (0.105)		
Oxidation potential (V)	0.362 (0.086)	Reduction potential (V)	-0.050 (0.034)
Anodic current (mA)	0.8561 (0.3139)	Cathodic current (mA)	0.05098 (0.1246)
Integrated anodic		Integrated cathodic	
charge (mC)	0.3135 (0.1139)	charge (mC)	0.3229 (0.1083)
Anodic half-wave		Cathodic half-wave	
potential Ep-Ep/2	0.757 (0.254)	potential Ep-Ep/2	0.322 (0.024)
No electrons involved	-	No electrons involved	-
Reversibility based on			
current (lpa/lpc)	1.62 (0.30)		
Coulombic reversibility			
(Qa/Qc)	0.96 (0.08)		

Table 4 1	13 Electrochemic	al Results for ?	3-dodecv/nvrrole/	RF -
			J-uouecyipyiioie/	

# 4.4.3.8 3-hexanoylpyrrole

Table 4.14 Electrochemica	al Results for 3-hexanoylpyrrole/PF
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Polymerisation Potential			
(V)	0.801 (0.020)		
Oxidation potential (V)	-0.246 (0.067)	Reduction potential (V)	-0.597 (0.037)
Anodic current (mA)	0.0737 (0.0358)	Cathodic current (mA)	0.0425 (0.0157)
Integrated anodic charge		Integrated cathodic	
(mC)	0.2499 (0.0792)	charge (mC)	0.2031 (0.0685)
Anodic half-wave		Cathodic half-wave	
potential Ep-Ep/2	0.177 (0.020)	potential Ep-Ep/2	0.201 (0.026)
No electrons involved	0.32 (0.04)	No electrons involved	0.29 (0.04)
Reversibility based on			
current (lpa/lpc)	1.62 (0.37)		
Coulombic reversibility			
(Qa/Qc)	1.04 (0.06)		

Table 4.15         Electrochemical         Results         for         3-hexanoylpyrrole/BF <sub>4</sub> 3	-
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Polymerisation			
Potential (V)	0.934 (0.035)		
Oxidation potential (V)	0.659 (0.054)	Reduction potential (V)	-0.127 (0.052)
Anodic current (mA)	0.0793 (0.0600)	Cathodic current (mA)	0.0503 (0.0352)
Integrated anodic		Integrated cathodic	
charge (mC)	0.1976 (0.0866)	charge (mC)	0.1398 (0.0363)
Anodic half-wave		Cathodic half-wave	
potential Ep-Ep/2	0.324 (0.047)	potential Ep-Ep/2	0.320 (0.056)
No electrons involved	0.18 (0.02)	No electrons involved	0.18 (0.02)
Reversibility based on			
current (lpa/lpc)	1.51 (0.16)		
Coulombic reversibility			
(Qa/Qc)	1.34 (0.31)		
Results for the polymerisation of 3-hexanoylpyrrole with  $PF_6^-$  and  $BF_4^-$  are listed in Tables 4.14 and 4.15 respectively. Polymerisation was repeatable and the reversibility of the systems tested were considered reasonable based on calculation of the charge passed on oxidation/reduction. However, the currents for the process showed a large difference due to high anodic current and a shallow, broad cathodic peak. The anodic currents were also varied for different cycles. Thus, although polymerisation was achievable, it was difficult to control its oxidation level.

## 4.4.3.9 3-dodecanoylpyrrole

Polymerisation Potential		· · · · ·	
(V)	1.014 (0.015)		
Oxidation potential (V)	0.829 (0.062)	Reduction potential (V)	0.667 (0.022)
Anodic current (mA)	0.0540 (0.0172)	Cathodic current (mA)	0.0392 (0.0074)
Integrated anodic charge		Integrated cathodic	
(mC)	0.2960 (0.3275)	charge (mC)	0.3790 (0.3844)
Anodic half-wave		Cathodic half-wave	
potential Ep-Ep/2	0.150 (0.027)	potential Ep-Ep/2	0.200 (0.015)
No electrons involved	0.39 (0.09)	No electrons involved	0.28 (0.02)
Reversibility based on			
current (lpa/lpc)	1.33 (0.23)		
Coulombic reversibility			
(Qa/Qc)	0.99 (0.02)		

 Table 4.16 Electrochemical Results for 3-dodecanoylpyrrole/PF<sub>6</sub>

Table 4.17	Electrochemical	Results for	<sup>-</sup> 3-dodecanoylpyrrole/BF <sub>4</sub> <sup>-</sup>
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Polymerisation			
Potential (V)	0.904 (0.021)		
Oxidation potential (V)	0.674 (0.059)	Reduction potential (V)	-0.105 (0.049)
Anodic current (mA)	0.0432 (0.0054)	Cathodic current (mA)	0.0323 (0.0030)
Integrated anodic		Integrated cathodic	
charge (mC)	0.2174 (0.0215)	charge (mC)	0.1321 (0.0210)
Anodic half-wave		Cathodic half-wave	
potential Ep-Ep/2	0.351 (0.038)	potential Ep-Ep/2	0.356 (0.022)
No electrons involved	0.16 (0.02)	No electrons involved	0.16 (0.01)
Reversibility based on		·	
current (lpa/lpc)	1.34 (0.07)		
Coulombic reversibility			
(Qa/Qc)	1.68 (0.27)		

Electrochemical results for the polymerisation 3-dodecanoylpyrrole with  $PF_6^-$  and  $BF_4^-$  are listed in Tables 4.16 and 4.17 respectively. Polymerisation was achievable with 3-dodecanoylpyrrole/ $BF_4^-$  although redox processes were not observed during the

polymerisation process. When cyclic voltammetry was applied using an electrolyte solution of the counter ion only (no monomer), reversible redox processes were observed but the results were varied and experimental control was difficult; Table 4.17 represents only a selection of the more reliable results.

## 4.4.4 Summary Of Electrochemical Results

#### Long vs. short chain

The *N*-substituted pyrrole derivatives ranged from a methyl group to a dodecyl alkyl chain, whereas the 3-alkylpyrroles had a hexyl group and a dodecyl group. For either substitutions it can be seen that the polymerisation potential increases with alkyl chain length, as would be expected with the increasing size of the substituent creating more steric effects and more strain on the polymer formed.

For the *N*-substituted pyrroles, *N*-methylpyrrole has the lowest polymerisation potential as well as the lowest redox potentials. The system also displays quite a good level of reversibility based on both the current and the charge ratios of the oxidative and reductive processes. The oxidation and polymerisation potentials increase considerably when the substituent is a hexyl chain. Good reversibility is retained but it is lost when the substituent is a dodecyl group and polymerisation was not possible within the potential range tested.

The trend continues for the 3-substituted pyrroles. Although polymerisation was difficult for 3-hexylpyrrole with  $PF_6^-$ , it was successful using  $BF_4^-$  and the polymerisation potentials were lower for 3-hexylpyrrole than for 3-dodecylpyrrole. Similarly, lower potentials were observed for 3-hexanoylpyrrole than for 3-dodecanoylpyrrole. although the redox processes were more troublesome to control.

### N-substituted vs. 3-substituted equivalents

In general, the *N*-substituted pyrroles exhibited higher polymerisation and oxidation potentials than the 3-substituted isomers, as expected from the results of Delabouglise [3.3] and Diaz [2.111]. 3-dodecylpyrrole was easily polymerised whereas *N*-dodecylpyrrole was not. However, the reversibility of the *N*-substituted pyrroles was generally better.

### Alkyl vs acyl

Comparisons cannot be drawn between 3-hexyl and 3-hexanoyl pyrrole derivatives since polymerisation was not successful for 3-hexylpyrrole, but polymerisation was more easily achieved for 3-dodecylpyrrole than for 3-dodecanoylpyrrole. It was thought that the presence of the carbonyl group of the ketone substituents would stabilise the radical intermediate and lower the oxidation potential but it was found that the redox potentials were variable, especially for 3-dodecanoylpyrrole, and were difficult to control.

#### Steric effects

The steric effects of the pentafluorobenzylpyrrole and phenylpyrrole were very evident from the high polymerisation potentials. Waveform shapes of the voltammograms were comparable to literature [4.28 - 4.30], yet the potentials were lower than expected. The deposition onto a conducting polymer base layer rather than as a monolayer onto a metal electrode will have facilitated this, although the potentials still remained impractical for use with the substrates used for this project.

### 4.4.5 AFM Results

A great deal of research has been carried out to investigate the charge mobility and conductivity of organic thin film transistors, such as pentacene, and correlate the influence of grain boundaries and surface roughness. It is known that charge traps are concentrated at grain boundaries in polycrystalline materials and models have been proposed to describe this. [4.31] Grain morphology and size have been discussed in relation to this and the surface roughness of the material. [4.32]

Charge mobility has been interpreted using grain-boundary potential barriers, potential wells and localised gap state trapping. There is some debate as to whether grain boundaries models, such as the Levinson [4.33] model are able to appropriately describe transport properties. Street *et al.* [4.34] and others [4.35] argue that this does not accurately describe the transport mechanism. However, Verlaak [4.31] argued that trap-controlled transport assumed spatially homogeneous trap distribution whereas in polycrystalline materials, charge traps were concentrated at grain-boundaries and thus the grain-boundary models apply. The observed difference between dopant concentration dependences of the mobility were explained by noting that grains can be depleted by barriers in films with very low doping and small grains, and in these cases a homogeneous trap distribution can be assumed.

The root-mean-squared (RMS) roughness and the arithmetic (average) roughness was recorded for a selection of the polymer films formed to see how they compared. The average globule height and diameter were also estimated. These results are presented in Table 4.18.

		Mean Roughness	Globule/Grain Height	Globule/Grain
	RMS (µm)	(µm)	(nm)	Diameter (nm)
N-hexylpyrrole/PF <sub>6</sub> <sup>-</sup>	0.654	0.491	704.33 (238.94)	2.70 (0.51)
N-pentafluorobenzylpyrrole/PF6	0.473	0.365	91.64 (28.42)	2.85 (0.58)
N-phenylpyrrole/PF <sub>6</sub> <sup>-</sup>	0.905	0.719	413.64 (208.73)	1.16 (0.37)
3-hexylpyrrole/BF <sub>4</sub> <sup>-</sup>	0.066	0.053	157.94 (49.72)	0.80 (0.19)
3-dodecylpyrrole/PF <sub>6</sub> <sup>-</sup>	0.103	0.081	71.22 (21.64)	0.48 (0.10)
3-hexanoylpyrrole/PF <sub>6</sub> <sup>-</sup>	0.801	0.640	171.00 (54.34)	1.02 (0.23)
3-dodecanoylpyrrole/PF <sub>6</sub> <sup>-</sup>	0.427	0.322	131.53 (36.23)	0.47 (0.10)

Table 4.18 AFM Results of pyrrole derivatives

With the exception of *N*-pentafluorobenzylpyrrole and 3-dodecanoylpyrrole, the grain height increases as the diameter of the grain/globular sphere becomes larger, although not proportionally due to the variety of interactions and potential coupling defects possible between the monomers. The smaller grain sizes were found for the polymers whose substituents were more bulky; namely *N*-pentafluorobenzylpyrrole, 3-dodecyl and 3-decanoyl

pyrroles. This could be due to the limited number of monomers coupled due to steric hindrance, although this is not seen for *N*-phenylpyrrole, perhaps due to the availability of the 3 and 4 positions, as well as the 2 and 5 positions. However, this was not confirmed and the polymerisation of *N*-phenylpyrrole remained difficult and conductive polymers films were rarely stable. Most of the films had a similar globular appearance to the polypyrrole base layer but with varying degrees of regularity. However, other than 3-hexanoylpyrrole/PF<sub>6</sub><sup>-</sup>, the roughness and globule/grain dimensions are significantly different from the polypyrrole base layer. Although *N*-phenylpyrrole/PF<sub>6</sub><sup>-</sup> has a similar RMS to polypyrrole, the grains are much more irregular with a much larger grain size. Table 4.18 includes results of *N*-phentafluorobenzylpyrrole and *N*-phenylpyrrole with PF<sub>6</sub><sup>-</sup>. The electrochemical results previously described these monomers as having too high a polymerisation potential with TsO<sup>-</sup>, however it was found that using PF<sub>6</sub><sup>-</sup> lowered the polymerisation whilst maintaining reversibility. The polymerisation potential of *N*-pentafluorobenzylpyrrole/PF<sub>6</sub><sup>-</sup> was found to be 0.94 ± 0.06V and *N*-phenylpyrrole/PF<sub>6</sub><sup>-</sup>, 0.99 ± 0.02V (95% confidence interval).

3-hexanoylpyrrole/ $PF_6^-$  had very similar morphological properties to the pyrrole base layer and its polymerisation onto the base layer was dubious. It is possible that any deposited material may have been over-oxidised since the anodic current was large relative to the cathodic current and the charge passed on oxidation was slightly larger than expected, although this was attributed to the polymerisation growth process.

The morphology of *N*-pentafluorobenzylpyrrole and *N*-phenylpyrrole films had a much more irregular and more cauliflower-like appearance than the regular globular spheres found for the other polymer films. The grains were more irregular in shape and size.

## 4.4.6 Summary

N-substituted pyrroles were generally more difficult to polymerise than 3-substituted pyrroles.

- Longer alkyl chain substituents rendered polymerisation more difficult than shorter chain substituents.
- Acyl equivalent substituents were more difficult to control in terms of doping level than alkyl substituted pyrroles due to the variability in oxidation/reduction current/charge found.
- Steric effects dominate over electron-donating stability of *N*-pentafluorobenzylpyrrole and *N*-phenylpyrrole; their polymerisation potentials were too high for use with the substrate.
- BF<sub>4</sub><sup>-</sup> aided polymerisation where PF<sub>6</sub><sup>-</sup> was unsuccessful, however redox processes were generally better controlled and more apparent with PF<sub>6</sub><sup>-</sup>.
- Except for 3-hexanoylpyrrole/PF<sub>6</sub><sup>-</sup>, the 3-substituted pyrroles tended to have a smoother surface with smaller grains than the *N*-substituted pyrroles.

## 4.5 Repeatability

The repeatability of polypyrrole as a base layer has already been discussed. It was found to be reliably deposited electrochemically with little variation in its electrical properties, both between different sensors and between different sensor arrays.

However, this repeatability was lost when depositing various polymers as top layers onto the polypyrrole and it was found to be very difficult to reliably control the properties of the top layer polymers between different sensor arrays. These difficulties arose from the number of different parameters that could influence the polymerisation process. The factors deemed to have the most influence on the variability of the polymers were the temperature at which the electrochemical experiments were conducted, the concentration of the monomers and counter ions in the electrolyte solutions used, the relative distances of the electrodes to one another, and possible mass transport effects during electropolymerisation.

Some improvements were found by exerting a certain amount of control over some of these parameters. The temperature was not maintained constant however a greater amount of control was possible by storing electrolyte solutions in a fridge between measurements. Measurements were performed immediately after removing a solution from the fridge and were not repeated before replacing the solution in the fridge. Temperatures could be maintained between  $5 - 15^{\circ}$ C this way.

Electrodes were always attempted to be placed in the same configuration and could be controlled to within 3 – 5mm within the Teflon block that contained the electrochemical cell.

Concentrations of the monomer and counter ion used in solution are known to greatly influence the properties of electrochemically polymerised films. Over time, the concentration of monomer in solution changes as polymerisation occurs slowly, and oligomers formed. This was controlled by not using solutions older than 4 – 6 weeks and fresh solutions were made using purified chemicals as often as possible. Other parameters could also have influenced the variability of the polymerisation process, such as mass transport effects.

			Resistance range	Variability	Variability of				
			for sensors	of sensors	sensors on			Average	Average
	Typical	Estimated	tested (2 s.d. of	between	the same	Oxidation	Anodic	reversibility	reversibility
	Resistance	conductivity	overall average	arrays	array (RSD	potential	current	(based on	(based on
	(Ω)	(S/m)	resistance) kΩ	(RSD %)	%)	RSD	RSD	current ratio)	charge ratio)
N-methylpyrrole / PF <sub>6</sub>	710.65	400	0.088	6.2%	5.2%	5.9%	25.5%	0.82	0.93
N-hexylpyrrole / PF <sub>6</sub>	94563.18	3	566.53	45.3%	12.1%	8.9%	21.8%	0.93	1.13
N-dodecylpyrrole / PF <sub>6</sub>	73791.31	4	363.49	38.6%	6.7%	4.8%	8.3%	2.52	1.39
N-pentafluorobenzylpyrrole									
TsO <sup>-</sup>	143283.89	2	403.58	140.8%	87.0%	223.2%	24.7%	1.18	0.97
N-pentafluorobenzylpyrrole									
PF <sub>6</sub>	15747.5	18	39.92	73.0%	1.5%	1.0%	13.7%	1.08	1.04
N-phenylpyrrole / TsO	126620.44	3	399.23	157.6%	49.4%	155.2%	71.5%	1.40	1.05
N-phenylpyrrole / PF <sub>6</sub>	6880.86	42	13.36	23.5%	4.2%	4.2%	22.9%	1.10	0.99
3-hexylpyrrole / PF <sub>6</sub>	2670.07	107	3.82	39.4%	10.5%	14.4%	38.1%	1.41	2.08
3-dodecylpyrrole / PF <sub>6</sub>	111727.54	3	223.11	13.6%	4.9%	7.4%	46.0%	1.17	1.26
3-dodecylpyrrole / BF <sub>4</sub>	344.7	820	2.97	N/A*	0.4%	23.8%	37.4%	1.62	0.96
3-hexanoylpyrrole / PF <sub>6</sub>	12069.51	24	25.39	105.2%	29.6%	27.2%	48.6%	1.62	1.04
3-hexanoylpyrrole / BF <sub>4</sub>	3428.19	84	5.48	71.8%	37.1%	8.2%	75.7%	1.51	1.34
3-dodecanoylpyrrole / PF <sub>6</sub>	3721.11	78	9.87	49.0%	16.0%	7.5%	31.9%	1.33	0.99

Table 4.19 Sensor Variability

\* only tested once on one sensor array

Resistance variabilities are listed in Table 4.19 for the polymers studied together with the variation found in the electrochemical parameters observed, such as oxidation potential/current variability and reversibility. These properties are studied and compared with each other more thoroughly in chapter 5, section 5.7. The range in resistances found for the tested sensors generally became larger the greater the typical base resistance of the polymer. In general, this would mean a greater variability in resistance of sensors between different arrays for higher resistance sensors, as shown in Fig 4.5. However, the outliers in red do not fit this trend. This is most likely due to the difficulties found in controlling the level of oxidation for the 3-acyl substituted pyrrole polymers, as well as the large differences in resistance variability and oxidation potential variation between *N*-phenylpyrrole and *N*-pentafluorobenzylpyrrole polymers made using TsO<sup>-</sup> and PF<sub>6</sub><sup>-</sup>



Fig 4.5 Influence of resistance magnitude on batch (resistance) variation

This does not always hold true however. Sensors such as *N*-hexylpyrrole/PF<sub>6</sub><sup>-</sup> and *N*-dodecylpyrrole/PF<sub>6</sub><sup>-</sup> have high resistances but relatively low variation across different arrays, demonstrating a good repeatability. Other sensors, such as 3-hexanoylpyrrole/BF<sub>4</sub><sup>-</sup> have a low typical resistance but a very large amount of variation between sensor arrays.

The large variability of polymers such as those of 3-dodecylpyrrole, 3hexanoylpyrrole, and *N*-pentafluorobenzylpyrrole/TsO<sup>-</sup> and *N*-phenylpyrrole/TsO<sup>-</sup> can be seen to arise from the amount of variation, or instability, of their oxidation potentials and anodic currents. This variation may arise from steric effects of the bulky substituents of *N*pentafluorobenzylpyrrole and *N*-phenylpyrrole, and the long alkyl chain of 3-dodecylpyrrole. 3-hexanoylpyrrole variation was later reduced after further investigation with different dopants was conducted (see section 4.7.2). When variation in these electrochemical parameters were so large, the control over the amount of oxidation of the polymer became remarkably difficult. Thus variation and a lack of repeatability were inevitable in these circumstances.

However, it can also be seen that although variations between arrays could be discouragingly large, the variation between sensors deposited onto the same array were significantly lower in all cases. Resistances varied between sensors of the same type deposited onto the same substrate, such that those which were more submerged in the electrolyte solution exhibited larger resistances that polymers deposited at positions closer to the surface of solution.

The results described above were for sets of sensor array in which the methodology was kept the same so as to evaluate the repeatability in a consistent way. For sensor optimisation, the electrical properties of the sensors could be altered by controlling the amount of oxidation through cyclic voltammetry. For reversible processes, cyclic voltammetry could be used to dope or dedope (oxidise or reduce) the polymer by cycling through the oxidation potential range or reduction potential range respectively. Oxidation control could also be achieved by changing the potential at which the voltammetric measurement was stopped. Otero *et al.* [2.161] described how the electrochemical methodology applied, such as limiting the potential sweep, can greatly influence the results polymer films. Ceasing the measurement at more positive potentials gave more conductive polymer films, whilst stopping the measurement at more negative potentials gave less conductive polymers.

Since the polymer films were grown from a solution of the monomer together with the counter ion, they were produced in their conductive state. Further voltammetric cycling with the counter ion enabled control the oxidation level as well as stabilising the polymer via the process of successive doping-dedoping. Although, for polymers such as *N*-dodecylpyrrole/PF<sub>6</sub><sup>-</sup> where the reversibility was poor, control over the oxidation level was more difficult.

### 4.6 Sensor Stability Over Time

Due to the high volume of sensors that were tested throughout this project and the number of sensors that did not perform successfully, measuring the stability of sensors over a long period was not achieved. A series of stable sensor arrays that were used for testing over a period of two months were monitored periodically and their base resistances were noted. Figure 4.6 displays the resistances found over a 63 day period.



Fig 4.6 Change in base resistance over time

This data was collected from a batch of sensor arrays that were simultaneously used for gas testing, thus the data represents the stability of operational sensors, which can account for some non-linearity.

The most dramatic changes in resistance would occur within the first few days of fabrication of a sensor and sensors with a higher initial base resistance would change more over time than ones with lower resistances.

As part of the fabrication process, once the polymers had been successfully deposited onto the substrate and optimised with the desired amount of oxidation, they would be subjected to heat treatment. This involved baking the sensors for 30 minutes at 115°C. This was to anneal the freshly prepared polymer sensors, remove any residual moisture and

solvents and generally stabilise the sensors. Since the resistances of the polymers would change as a result of this, all of the base resistances reported here are those found after heat treatment. Sensors prepared in this manner also had improved stability and less drift when used for gas sensing than sensors that had not been subjected to heat treatment.

## 4.7 Study Of Different Dopant lons

#### 4.7.1 Relevance Of Study

Some of the conducting polymer sensors studied did not display high sensitivities or were unstable during gas testing but their results were promising enough to justify an investigation into improving their electrical properties and ease of fabrication. Namely by electropolymerising and doping these polymers with different counter ions.

A tremendous amout of literature exists reporting the various parameters that can influence and be used to improve the properties of conducting polymers as was discussed previously. Of these, many have described the dramatic effect of employing different dopant ions [4.36; 4.37]. The conducting polymers formed in this project were doped using large organic anions (*p*-doped) since they are readily soluble in acetonitrile and are highly dissociated in solution.

The anion concentration in the polymer films is governed by the degree of oxidation of the polymer (distribution in the polymer), which is characteristic of each film, and the nature of the dopant. The means with which this process was controlled was described in the previous section. Since the polymer films are prepared from an electrolytic solution containing the anion, which is incorporated in the process, the investigation of different dopants was easily carried out by simply changing the electrolyte salt.

The oxidation level of polypyrrole is between 0.25 - 0.32 per pyrrole unit, which translates as approximately one anion for every 3 - 4 pyrrole units [4.37]. This was

confirmed through XPS measurements by Pfluger and Street [2.131] for polypyrrole doped with  $BF_4^-$  and  $CIO_4^-$  anions. This level of oxidation is confirmed by the electrochemical results presented in Tables 4.2 – 4.17, therefore no modification of the method used was necessary. The level of oxidation is an intrinsic property of the polymer, however the anion can influence the structural properties and electroactivity of the polymers. [4.39] The anions can also act as specific binding sites in the interaction between the conducting polymer and the analyte. [4.40]

The electrochemical results presented for the pyrrole derivatives includes polymers that were studied with an alternative dopant ion.  $BF_4^-$  often enabled polymerisation of polymers which were difficult to polymerise with  $PF_6^-$  but the level of oxidation obtainable was generally found to be more difficult to control.

### 4.7.2 Dopant Anions Studied

At the time that 3-hexanoylpyrrole was initially investigated, the deposition was difficult and oxidation potentials were generally not observed well. Whilst improvements were later made through purification of the chemicals used and using a fresh solution, these initial difficulties prompted the first study into using other dopant ions to improve the deposition and final resistances of polymer sensors.

In addition to  $PF_6^-$  and  $BF_4^-$ , 3-hexanoylpyrrole was also studied using the  $CIO_4^$ and  $TsO^-$  ions. The use of the perchlorate ion as a dopant is a common practice, thus it was included in the study for comparative purposes. Melato *et al.* [4.38] have also reported that poly(3,4-ethylenedioxythiophene) (PEDOT) films formed from lithium perchlorate have more compact structures with increased electroactivity and crystallinity in comparison with the more porous films formed from  $PF_6^-$ . However, it has been reported [4.4; 4.41] that the tosylate ion shows marked improvement over the aforementioned dopant ions in terms of oxidation level, percentage void volume and conductivity. [4.4]

Although, in the case of *N*-pentafluorobenzylpyrrole and *N*-phenylpyrrole polymers, the results were contrary to this, perhaps due to the size of the tosylate ion and the steric effects observed with the bulky substituents of these two monomers – the suitable incorporation of tosylate may have been more demanding sterically. So, in addition to TsO<sup>-</sup> and PF<sub>6</sub><sup>-</sup>, the *N*-pentafluorobenzylpyrrole and *N*-phenylpyrrole monomers were also studied using the BF<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup> and triflate (trifluoromethanesulfonate, or OTf<sup>-</sup>) ions. Warren *et al.* [4.3] also studied the use of large space-filling dopant anions such as tosylate and dodecylbenzenesulfonate and found that the conductivity and stability of the polymer films produced was improved. These findings prompted Walker *et al.* to use these larger dopants to chemically prepare polypyrrole films from Fe<sup>3+</sup> based oxidants. [4.42] They found that the triflate-doped polymer showed the highest conductivities.

After testing various conducting polymers, one of the key difficulties in their optimisation was increasing the base resistance of the polymer to an ideal range without over-oxidising, or dedoping, or increasing the thickness too much, whilst maintaining a sufficient amount of conductivity for gas sensing purposes. The main difficulty lie in the lack of control over the oxidation of polymer films; the sensors were either good conductors but had low resistances, and thus quite low sensitivities to the vapours tested, or the resistances were so high and had little to no conductivity.

Naphthalenesulfonic acid (NSA) had been successfully used to deposit the base layer of polypyrrole electrochemically and the stability of the films was shown to be consistent. The use of NSA for other polymer films grown as top layers was tested. In order to control the doping-dedoping process with more success, and yield higher resistance polymers, sodium dodecyl sulfate (SDS) was also used due its surfactant properties. It was hoped that the long alkyl chain would help offer more overall control.

### 4.7.3 Control Measures And Limits Of Investigation

The particular control measures implemented in the study of different dopant ions were to use 0.1M solutions of the all the dopant salts tested. All of the other control parameters described for electropolymerisation were maintained and the same solvent system was used throughout.

Although the variation in electrolyte concentration would offer a greater scope of information for sensor optimisation, this parameter was kept constant since the ultimate purpose of this study was to compare the efficiency of the dopant ions with regard to the electrochemical polymerisation and deposition. Therefore, as many of the influencing factors on the process were kept the same so that dopant anions could be compared without complication from any other attributes.

### 4.7.4 Results

### Poly(3-hexanoylpyrrole)

Polymerisation was possible with perchlorate, however the polymerisation potential was found to be  $1.026V \pm 0.007$ ; higher than films formed with  $PF_6^-$  or  $BF_4^-$ . The oxidation potential was  $0.531V \pm 0.083$  and the average anodic current,  $0.038V \pm 0.009$ . However, the reversibility was poor; a small reduction peak was only noted at high scan rates, indicative of a quasi-reversible redox process. Additionally, the oxidation potentials were found to shift anodically with subsequent voltammetric cycles. This anodic shift was explained by Novák *et al.* [4.43] and Tsuchiya *et al.* [4.44] as occurring from a change in the rate of electron transfer, which could be caused by a degradation of the polymer. It is possible that due to the lack of reversibility, the polymer was over-oxidised in the process and degraded as a result.

Polymerisation was not achievable using the tosylate anion. Redox potentials similar to those reported for *N*-pentafluorobenzylpyrrole/TsO<sup>-</sup> and *N*-phenylpyrrole/TsO<sup>-</sup> were found, but polymerisation was not noticeable within the potential range scanned.

## Poly(N-pentafluorobenzylpyrrole)

•

Although polymerisation was achieved for *N*-pentafluorobenzylpyrrole/ $BF_4^-$  and coherent redox potentials were observed, the polymerisation potential was found to be very high and polymer degradation ensued.

Both perchlorate and triflate counter ions enabled polymerisation at lower potentials within a reasonable range and, although only one set of redox potentials were observed, their reversibility was shown to be excellent. Triflate lowered the potentials the most and successful deposition was achieved most easily with triflate compared to all of the other dopant anions tested.

Electrochemical results are presented below in Tables 4.20 – 4.22 where the figures in brackets are the values for sample standard deviation. Good repeatability/amount of variation between sensors was also demonstrated.

Polymerisation Potential (V)	1.368 (0.019)		
Oxidation potential 1 (V)	0.817 (0.002)	Oxidation potential 2 (V)	0.977 (0.004)
Anodic current (mA)	0.0764 (0.0053)	Anodic current (mA)	0.0038 (0.0019)
Integrated anodic charge		Integrated anodic charge	
(mC)	0.1282 (0.0173)	(mC)	0.1659 (0.0194)
No electrons involved	0.342 (0.013)	No electrons involved	0.278 (0.010)
Reduction potential (V)	0.802 (0.002)		
Cathodic current (mA)	0.0759 (0.0051)		
Integrated cathodic charge			
(mC)	0.1417 (0.0083)		
Reversibility based on			
current (lpa/lpc)	1.01 (0.04)		
Coulombic reversibility			
(Qa/Qc)	0.90 (0.07)		

 Table 4.20 Electrochemical Results for N-pentafluorobenzylpyrrole/BF<sub>4</sub><sup>-</sup>

Polymerisation Potential (V)	1.068 (0.079)		
Oxidation potential (V)	0.701 (0.019)	Reduction potential (V)	0.436 (0.006)
Anodic current (mA)	0.01439 (0.0096)	Cathodic current (mA)	0.1423 (0.0124)
Integrated anodic charge		Integrated cathodic charge	
(mC)	0.4629 (0.0241)	(mC)	0.4485 (0.0307)
No electrons involved	0.30 (0.02)	No electrons involved	0.30 (0.01)
Reversibility based on			
current (lpa/lpc)	1.01 (0.02)		
Coulombic reversibility			
(Qa/Qc)	1.01 (0.02)		

Table 4.21 Electrochemical Results for N-pentafluorobenzylpyrrole/ClO<sub>4</sub><sup>-</sup>

 Table 4.22 Electrochemical Results for N-pentafluorobenzylpyrrole/OTF

Polymerisation Potential (V)	0.863 (0.042)		
Oxidation potential (V)	0.516 (0.035)	Reduction potential (V)	0.279 (0.007)
Anodic current (mA)	0.0676 (0.0048)	Cathodic current (mA)	0.0647 (0.0042)
Integrated anodic charge		Integrated cathodic charge	
(mC)	0.1618 (0.0061)	(mC)	0.1639 (0.0084)
No electrons involved	0.33 (0.01)	No electrons involved	0.22 (0.00)
Reversibility based on			
current (lpa/lpc)	1.05 (0.02)		
Coulombic reversibility			
(Qa/Qc)	1.00 (0.03)		

# • Poly(*N*-phenylpyrrole)

Polymerisation of *N*-phenylpyrrole with  $BF_4^-$  did not occur until potentials of +1.45V to +1.57V were reached, which is well beyond ca. +1.2V, where the gold working electrode begins to degrade. With  $CIO_4^-$ , however, polymerisation was achievable just within the limits of the potential scan range. One set of redox potentials were observed with reversible characteristics. Results are given in Table 4.23. Polymerisation with  $OTf^-$  was achieved at even lower potentials, however the redox peaks were very weak, only appearing on the first few cycles. Polymerisation occurred between +0.75V to +0.88V. The weak peaks were noted to occur at around +0.39V for oxidation and -0.15V for reduction.

Polymerisation Potential (V)	1.052 (0.034)		
Oxidation potential (V)	0.606 (0.018)	Reduction potential (V)	0.383 (0.005)
Anodic current (mA)	0.0849 (0.018)	Cathodic current (mA)	0.0804 (0.0061)
Integrated anodic charge		Integrated cathodic charge	
(mC)	0.0849 (0.0056)	(mC)	0.2423 (0.0506)
No electrons involved	0.24 (0.02)	No electrons involved	0.24 (0.01)
Reversibility based on			
current (lpa/lpc)	1.06 (0.03)		
Coulombic reversibility			
(Qa/Qc)	0.97 (0.02)		

 Table 4.23 Electrochemical Results for N-phenylpyrrole/ClO<sub>4</sub><sup>-</sup>

# 4.7.5 AFM Results



**Fig 4.7** RMS roughness of N-pentafluorobenzylpyrrole (N6) and N-phenylpyrrole (N7) polymers with perchlorate and triflate





Fig 4.9 AFM images at 20x20um a) N-phenylpyrrole/ClO<sub>4</sub><sup>-</sup>b) N-phenylpyrrole/OTf<sup>-</sup>

Fig 4.7 shows that surface roughness is greater for N-phenylpyrrole than for N-pentafluorobenzylpyrrole and films formed with triflate as the dopant ion have a rougher surface than those of perchlorate. This is clearly visible in the images presented in Figs 4.8 and 4.9. It can be seen in the images that the surface of N-pentafluorobenzylpyrrole/CIO4<sup>-</sup> consists of relatively large grains that have a rough texture. All of the surfaces have quite a regular distribution of grains with a rough appearance. As the grain size increases, the roughness increases, with N-phenylpyrrole/OTf<sup>-</sup> possessing the roughest surface. The typical resistances of the films were about the same (ca. 1 k $\Omega$ ) with N-phenylpyrrole/OTf<sup>-</sup> exhibiting slightly higher resistances.

### Naphthalenesulfonic Acid (NSA) and Sodium Dodecyl Sulfate (SDS)

*N*-hexylpyrrole, *N*-dodecylpyrrole, 3-dodecylpyrrole and 2,2'-bithiophene were deposited as top layers onto polypyrrole and tested using dopants NSA and SDS. NSA results showed a lack a redox potentials and polymerisation onto the polypyrrole baselayers could not be elucidated. However, interesting results were found when using SDS to dopededope the polymer films. Wernet *et al.* [4.45] reported that the properties of polypyrrole were improved by using SDS and many have reported on the various properties of polypyrrole-SDS films [4.3; 4.46 - 4.48].

For all of the monomers that were polymerised with SDS, the polymerisation potentials was lowered, in comparison with the smaller dopant anions reported previously. However, after the first scan (polymerisation and deposition) the shape of the voltammograms changed. Further polymerisation with subsequent scans diminished and, from the shifts in the redox potentials, it was assumed that degradation started to occur. Therefore, the polymer films were deposited using cyclic voltammetry for only 2 - 5 scans, after which the amount of oxidation was controlled through cyclic voltammetry using only a solution of SDS.

*N*-hexylpyrrole and *N*-dodecylpyrrole showed very broad redox potentials. Their initial scans with the monomer showed oxidation potentials at first, but no reduction potential. After deposition, the sensors were dedoped using cyclic voltammetry within a negative range until appreciable base resistances were achieved. However, 2,2'-bithiophene showed large redox potentials at negative potentials. 3-dodecylpyrrole displayed a large, broad oxidation wave. Although a reduction peak was not observed, the cathodic current decreased with each scan by amounts proportional to the anodic current increase. The reduction potential may have been at voltages lower than the scan range used (< -1V). In both cases, conductive polymer films with high resistances were obtainable.

Typical resistances were considerably higher for bithiophene films, thus the repeatability was worse. However, sensor-to-sensor variation on the same array was decent in both cases. The results are summarised in Tables 4.24 and 4.25

Table 4.24 Results for 3-dode	ecylpyrrole/SDS		
Typical Resistance ( $\Omega$ )	1214.46 (391.4)		
Variability of sensors between arrays (RSD %)	32.2%		
Variability of sensors on the same array (RSD %)	8.8%		
Polymerisation Potential (V)	0.445 (0.036)		
Oxidation potential (V)	0.022 (0.055)	Reduction potential (V)	-
Anodic current (mA)	0.0263 (0.0285)	Cathodic current (mA)	-
Integrated anodic charge (mC)	0.0854 (0.0721)	Integrated cathodic charge (mC)	-
Reversibility based on current (lpa/lpc)	_		

### Table 4.25 Results for 2,2'-bithiophene/SDS

Coulombic reversibility (Qa/Qc)

<u> </u>			
Typical Resistance ( $\Omega$ )	69653.13 (110661.43)		
Variability of sensors			
between arrays (RSD %)	158 9%		
	100.070		
variability of sensors on the			
same array (RSD %)	18.9%		
Polymerisation Potential (V)	0.750 (0.020)		
Oxidation potential (V)	-0.487 (0.027)	Reduction potential (V)	-0.912 (0.017)
Anodic current (mA)	0.0294 (0.0030)	Cathodic current (mA)	0.0322 (0.0026)
Integrated anodic charge		Integrated cathodic charge	
(mC)	0.1063 (0.0165)	(mC)	0.1134 (0.0115)
Reversibility based on			
current (lpa/lpc)	0.92 (0.15)		
Coulombic reversibility			
(Qa/Qc)	0.93 (0.06)		

AFM images showed that the polymers formed with SDS gave rougher surfaces than those formed with  $PF_6^-$  (or  $CIO_4^-$  in the case of bithiophene). Large, smooth, donut-like grains were found for *N*-hexylpyrrole; spherical, globular surfaces were found for the other polymers with decreasing globule/grain size in the order *N*-dodecylpyrrole > 3-dodecylpyrrole > 2,2'-bithiophene.



Fig 4.10 AFM images of polymers doped with SDS

### 4.8 Reference Electrode Investigations

### 4.8.1 Relevance Of Study

The reference electrode represent a non-polarisable electrode that provides a stable and reproducible potential reference against which the working electrode potential is compared. In the 3-electrode cell, as used in the experiments performed in this project, a fixed potential difference is applied between the working and the reference electrode, which drives the electrochemical reaction at the working electrode.

The current that is produced as a result is buffered by an opposing current at the counter electrode. The reference electrode provides the stable potential reference point by which the oxidation/reduction processes at the working electrode are measured. This arbitrary potential axis is set by the reference electrode. So, due to the different nature of different reference electrodes, this potential axis is offset relative to the standard potential; applied potentials will be different for different reference electrodes. This is why it is imperative to address the reference electrode used when quoting any electrochemical results obtained and why the proper selection of a reference electrode is critical for optimal use in electrochemical experiments. [4.5; 4.49]

The standard hydrogen electrode (SHE) is the most familiar reference electrode since most of the standard half-reaction redox potentials were obtained against the SHE. However, it is too impractical for routine use. Common alternatives include the calomel (mercury/mercurous chloride) electrode and the silver/silver chloride electrode, which are examples of a "wet" electrode comprising of a metal and an insoluble salt. Both of these and the platinum electrode were used for comparison. Cyclic voltammetry was performed with a variety of monomer/electrolyte solutions. The same 3-electrode cell as used for the entirety of this project was employed with all the same parameters maintained. The only variables of interest in this study were the reference electrodes and the monomer/electrolyte in order to assess which reference electrode was best for the fabrication and study of the polymers used in this project.

### 4.8.2 Results

As can be seen in Fig 4.11, the polymerisation potentials differ for the different reference electrodes tested. The lowest potentials are found with the platinum electrode and the highest were found when using the silver-silver chloride electrode. Polymer deposition was generally found to be much easier when using the platinum reference electrode, therefore its use was justified for the investigations carried out.

For 2,2'-bithiophene/SDS, *N*-hexylpyrrole/SDS and 3-dodecylpyrrole/SDS, deposition was achievable with all of the reference electrodes, but the best films were produced most easily with the platinum reference electrode. 3-hexanoylpyrrole/BF<sub>4</sub><sup>-</sup> was also attempted with all of the reference electrodes due to its high polymerisation potential. Deposition was not possible using cyclic voltammetry within an acceptable scan range, but deposition was achieved when a potential step of 1.8V was applied for no more than 10 seconds.

Poly(3,4-ethylenedioxythiophene) (PEDOT) doped with  $PF_6^-$  was tested with the reference electrodes, but polymerisation was only achieved with the platinum reference electrode.

Similar oxidation potentials were found for *N*-hexylpyrrole/SDS and 3dodecylpyrrole/SDS. Both of these were polymerised and deposited reliably with all of the reference electrodes tested – especially 3-dodecylpyrrole/SDS, which had a particularly low polymerisation potential. The oxidation current was less when the calomel reference electrode was used. Therefore, it was decided to use the calomel electrode over the platinum for control of the doping amount of these polymers and avoid the risk of overoxidation.



Fig 4.11 Polymerisation potentials with different reference electrodes

## 4.9 Other Conducting Polymers

Aside from polypyrrole, the most studied conducting polymer materials include polythiophenes, polyanilines, polyphenylenes and polyselenophenes. Although the majority of research carried out for this project focused on polypyrrole and its derivatives, some attention was turned to polythiophene derivatives, polyaniline and some pyrrole-thiophene copolymers.

## 4.9.1 Polythiophenes

Polythiophenes offer a high stability in both oxidised and neutral states, they are capable of forming highly regular polymer films and can have a reversible doping level between 25 – 50%. [4.50; 4.51] Also, according to Street *et al.* and Tourillon *et al.* [4.52] polythiophenes are more stable in their undoped state than polypyrrole. A diverse range of thiophene-based structures are possible since they have been functionalised at the  $\alpha$  and  $\beta$  positions, as well as at the sulfur atom. So a variety of polythiophene derivatives are available. [4.53]

Thiophene was found to be difficult to polymerise electrochemically; the oxidation potential increases with the electronegativity of the heteroatom so the oxidation potential was too high for practical use. Literature has often stated that polythiophene is not stable at the potentials used for its synthesis, yet polymers using the thiophene monomer have been achieved. Krische *et al.* [4.54] dubbed this occurrence as the "thiophene paradox". By comparing the UV/Vis and IR spectra of doped and undoped polythiophene and bithiophene, they argued that the product of electropolymerisation was not the simple poly(2,5-thienylene) but a composite of polythiophene and its over-oxidised product. Nevertheless, substituted thiophenes and thiophene oligomers have a lower oxidation potential and have been widely used in conducting polymer research. The substituent effects of polythiophenes were already discussed previously.

The thiophenes tested were 2,2-bithiophene, 3-methyl and 3-decylthiophene, and 3,4-ethylenedioxythiophene, which were chosen as examples of thiophene oligomers, 3-alkylthiophenes and 3-substituted alkyloxythiophenes.

2,2'-bithiophene exhibits a much lower oxidation potential and since the thiophene rings are  $\alpha$ -  $\alpha$ ' linked, less  $\alpha$ -  $\beta$ ' defects are expected. [4.55] 3-methyl and 3-decylthiophene also present lower oxidation potentials. The conductivity decreases with alkyl chain length but remains at a high level. The dopant initially used was perchlorate.

Although limited success was found when using the perchlorate anion as a dopant with the polypyrroles, the role of the anion has been said not to be determining in the case of polythiophenes; the i-V characteristics show no difference when different anions are substituted. [4.56] Despite this, the choice of solvent used does have significant impact on the electrochemical properties of polythiophenes. [4.1] The solvent system used for the study of thiophenes was the same as that for the polypyrroles studied; 99% acetonitrile:1% deionised water.

## 4.9.1.1 Results

Thiophene monomer was measured electrochemically using a gold contact as the working electrode, Ag/AgCl reference electrode and a gold counter electrode. 0.1M Lithium perchlorate and 0.1M thiophene monomer solution in acetonitrile:water was used as a quiescent medium. Polymerisation did not occur until around +1.4V. Three oxidation peaks and three reduction peaks were observed in a cyclic voltammogram scanned from -1V to +2V. The experiment was repeated using a gold interdigitated electrode substrate with a deposited polypyrrole baselayer as the working electrode and scanning only to +1.5V. The polymerisation potential was not demonstrably affected by the different work function of the polypyrrole base layer and, as expected, polymerisation did not occur before the base layer and the electrode degraded.

The polymerisation of 3-methylthiophene and 3-decylthiophene were not possible due to the high polymerisation potentials. By using a larger gold electrode as the working electrode it was found that 3-methylthiophene polymerised around 1.3 – 1.4V. Although polymerisation was not possible within the scan range and with the substrate used, oxidoreduction peaks were present in the cyclic voltammograms (See Tables 4.26 and 4.27). Those for 3-methylthiophene were found to be reversible where as 3-decylthiophene displayed a much more defined oxidation peak than the reduction peak, which was shallow and broad. The redox potentials were substantially greater for 3-decylthiophene than for 3-methylthiophene, indicating that the oxidation potentials are greater for thiophenes with longer alkyl chain substituents and they are more difficult to polymerise. This is analogous to the results found for the alkyl chain length of substituents on pyrrole.

Polymerisation Potential (V)	1.360 (0.060)		
Oxidation potential (V)	0.653 (0.031)	Reduction potential (V)	0.423 (0.132)
Anodic current (mA)	0.0752 (0.0148)	Cathodic current (mA)	0.0723 (0.0091)
Integrated anodic charge (mC)	0.3922 (0.0137)	Integrated cathodic charge (mC)	0.4074 (0.0078)
Reversibility based on current (lpa/lpc)	1.03 (0.07)		
Coulombic reversibility (Qa/ Qc)	0.96 (0.02)		

Table 4.26 Results for 3-methylthiophene/CIO<sub>4</sub><sup>-</sup>

Polymerisation Potential (V)	-		
Oxidation potential (V)	1.050 (0.046)	Reduction potential (V)	0.823 (0.005)
Anodic current (mA)	0.0340 (0.0135)	Cathodic current (mA)	0.0193 (0.0072)
Integrated anodic charge (mC)	0.1152 (0.0367)	Integrated cathodic charge (mC)	0.0091 (0.0048)
Reversibility based on current (lpa/lpc)	1.73 (0.19)		
Coulombic reversibility (Qa/ Qc)	18.65 (13.02)		

Table 4.27 Results for	<sup>-</sup> 3-decylthiophene/ClO <sub>4</sub> <sup>-</sup>
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Lower polymerisation potentials and easier deposition was achieved for 2,2'bithiophene and 3,4-ethylenedioxythiophene (PEDOT). The polymerisation and oxidation potentials for 2,2'-bithiophene coincided. The polymerisation potential reported in Table 4.28 is the average potential at which polymer deposition first became visible during measurement. The oxidation potential reported is the maximum of the peak identified on the forward cycle of the voltammogram.

Typical Resistance ( $\Omega$ )	6533.3		
Variability of sensors between arrays (RSD %)	48.5%		
Variability of sensors on the same array (RSD %)	9.6%		
Polymerisation Potential (V)	0.661 (0.080)		
Oxidation potential (V)	0.896 (0.054)	Reduction potential (V)	0.334 (0.045)
Anodic current (mA)	0.2934 (0.0554)	Cathodic current (mA)	0.1141 (0.0122)
Integrated anodic charge (mC)	0.7540 (0.0301)	Integrated cathodic charge (mC)	0.5122 (0.0305)
Reversibility based on current (lpa/lpc)	2.66 (0.84)		
Coulombic reversibility (Qa/ Qc)	1.48 (0.13)		

Table 4.28 Results for 2,2'-thiophene/CIO,

The data presented for  $PEDOT/PF_6^-$  in Table 4.29 is split into two parts: the average electrochemical data found on the initial cycle and the data found for all the subsequent

cycles (post deposition). It is usual for the voltammetric peaks to alter after the initial scan in most of the tests performed, however for PEDOT the differences were quite substantial.

After the first cycle, the redox peaks shifted anodically and the peak separation became very small. Although, the reversibility found was excellent. Typical resistances were larger for 2,2'-bithiophene, hence the variabilities found were greater than for PEDOT.

Typical Resistance ( $\Omega$ )	3205		
Variability of sensors between arrays (RSD %)	17.6%		
Variability of sensors on the same array (RSD %)	6.6%		
Initial Polymerisation Potential (V)	0.837 (0.030)		
Initial Oxidation potential (V)	-0.217 (0.009)	Initial Reduction potential (V)	-0.596 (0.011)
Initial Anodic current (mA)	0.0332 (0.0175)	Initial Cathodic current (mA)	0.1237 (0.1628)
Polymerisation Potential (V)	0.766 (0.009)		
Oxidation potential (V)	0.145 (0.055)	Reduction potential (V)	0.132 (0.149)
Anodic current (mA)	0.1560 (0.0072)	Cathodic current (mA)	0.1575 (0.0092)
Integrated anodic charge (mC)	1.1733 (0.0713)	Integrated cathodic charge (mC)	1.2132 (0.0470)
Reversibility based on current (lpa/lpc)	0.99 (0.01)		
Coulombic reversibility (Qa/ Qc)	0.97 (0.02)		

Table 4.29 Results for PEDOT/PF<sub>6</sub><sup>-</sup>

## 4.9.2 Polyaniline

Polyaniline was successfully deposited electrochemically onto one of the substrates. A solution of 0.1M aniline and sodium sulfate in 2M hydrochloric acid was used with cyclic voltammetry, scanning potentials from -0.2V to 1.2V at a scan rate of 10mV/s. It was found that higher scan rates did not produce a polymer film. A complex series of voltammograms were obtained with multiple peaks which looked similar to the voltammograms found in literature, displaying the various oxidation states of polyaniline (Fig 4.12). The mechanism of polyaniline growth is not fully understood but a number of viable explanations have been proposed. [4.57]



Fig 4.12 Cyclic voltammogram of aniline/sodium sulfate in 2M HCI

Although polyaniline was deposited without much difficulty, it was not used in gas testing due to damaged substrates (explained in 5.9.1). However, commercially synthesised Panipol®, designed for use as a printable ink, was purchased and a 2:1 solution with deioinised water was used to drop-coat onto the interdigitated electrode of the substrate with a microlitre pipette. The drop was left to dry for an hour at 40°C, after which the deposition was durable enough for immediate use in gas sensing applications.

The main disadvantage of this method was the lack of control in the amount of polymer deposited and the electrode coverage. Although large sensor variability was inevitable, this method was chosen due to the high resistances and sensitivities achievable. Despite the variations between sensors, their ease of preparation and use in gas sensing was preferred. Another printable conducting polymer material was also used in the same fashion: Poly(thiophene-3-[2-(2-methoxyethoxy)ethoxy]-2,5-diyl), sulfonated solution – 2% in 1,2-propanediol/isopropanol (Plexcore® OC1100). This was used as purchased and deposited onto the substrate in the same manner.

## 4.9.3 Poly(2,5-di-(2-dithienyl)pyrrole) [SNS]

Poly(heteroaromatic) copolymers, or "substitutional alloys" of organic conducting polymers, have received considerable attention due to their processability and useful optical, electrical and electrochemical properties. The presence of heteroatoms theoretically presents one more degree of freedom in the tailoring of conducting polymer materials but this parameter is yet to be fully comprehended. [4.58] Their beneficial properties have been exploited in a variety of applications including field-effect transistors, batteries, non-linear fast-response optical devices, and heterojunction and Schottky diodes.

Poly(2,5-di-(2-dithienyl)pyrrole), or poly(SNS), has been extensively researched and was used as a conducting polymer gas sensor this project. Its preparation, growth characteristics and various electrochemical and morphological properties, of both its oxidised and reduced forms have been reported in numerous papers. [4.59 – 4.63]

A polymer film of poly(SNS) doped with NSA was deposited onto the substrate by using a potential step method with a solution of 0.01M SNS and 0.2M NSA in a 50:50 solution of acetonitrile and water. With the same electrochemical cell setup used as before, a potential of +0.75V was applied for 10s. The substrate and newly deposited film was washed with deionised water and left to dry for up to one hour. The process could be repeated to build up a thicker layer of polymer, but no more than two to three times was ever necessary. Cyclic voltammetry experiments showed reversible redox peaks at ca.+0.87V (oxidative) and ca. +0.05V (reductive). Post-deposition doping-dedoping with NSA,  $PF_6^-$  and OTf<sup>-</sup> were tried. All of the anions produced similar results; a single set of redox peaks that were reversible, enabling good control of the degree of oxidation of the polymer. Triflate showed the lowest potentials for the process, but all of the oxidoreduction peaks of the anion were within a reasonable range (between 0 and +1V). Controlled sensor variability was 13.3% based on the standard deviation of all sensor arrays made which incorporated the poly(SNS)-NSA polymer, fabricated chronoamperometrically as described above.

### 4.10 Sensor Optimisation

During the course of electrochemical investigations, sensors arrays that were produced were tested on a gas rig (described in the following chapter). Studies on sensor optimisation through electrochemical and gas testing experiments were run concurrently. Typically, the sensitivities of a sensor were identified and electrochemical experiments followed in an effort to improve the performance of a sensor.

Besides the investigations that have already been mentioned (use of different dopants, reference electrodes and alternate conducting polymer materials), a couple of findings helped in the optimisation of sensor fabrication, its electrical properties and stability.

## 4.10.1 Heat Treatment

After electropolymerisation and deposition onto the substrate, the sensors were exposed to 115 – 120°C for up to 30 minutes. This was applied as a final step immediately after deposition, prior to any gas testing experiments. This step expelled most of the moisture and any solvent remaining within the polymer and it also helped stabilise the sensors; "annealing" them through exposure to heat. Sensors that were not subjected to heat treatment were found to display more varied sensor responses to the tested gases and base line drift was more prominent for higher resistance sensors. Resistances would usually change and conductivity normally reduced after heat treatment, but were ultimately more stable.

Heat treatment was briefly attempted on the polypyrrole base layers prior to deposition of the different conducting polymer top layers. However, it was found that the conductivity reduced too much so that top layer polymer deposition was rendered more difficult.



Fig 4.13 Percentage changes in resistance after heat treatment

Fig 4.13 show the average percentage changes in resistance after sensors were subjected to heat treatment. For the majority of sensor, resistances were positively increased or experienced little change. In a couple of cases the resistance actually decreased, such as for 3-dodecylpyrrole and *N*-dodecylpyrrole sensors.

AFM images were taken of a sensor array to examine the effect of heat treatment on the surface morphology of the sensors. Figure 4.14 show the comparative RMS roughness found. PEDOT/PF<sub>6</sub><sup>-</sup> displayed the greatest change and increased in roughness after heating. The appearance changed from a typical globular structure with a regular grain distribution to a seemingly smooth surface of undulating contours which comprised of much smaller grains. 3-dodecylpyrrole/SDS and 2,2'-bithiophene/SDS did not show any significant differences to the globular appearance. *N*-hexylpyrrole/SDS surfaces became smoother after heat treatment and grain size became notably smaller. SNS/NSA surfaces also changed from the globular structure usually found to a smoother surface with shiny surfaces.



Fig 4.14 RMS surface roughness before and after heat treatment

## 4.10.2 Potential Sweeping P3HT Layer With PF<sub>6</sub><sup>-</sup>

In an effort to improve the stability, reproducibility and sensitivity of the sensors, the sensors were cycled through potentials -1V to +1V with a solution of 0.1M hexafluorophosphate anion in acetonitrile, analogous to the dope-dedope procedure used to stabilise the polymer sensors after deposition.

The slope of the i-V curve of the linear sweep voltammograms were used to measure the resistance of each sensor before and after cyclic voltammetry was applied with  $PF_6^-$ . The resistances were found to be extremely high, indicating that the gap between the electrodes was not sufficiently bridged by the thin layer of P3HT. This finding, in turn, revealed that a more consistent, thicker layer was required so subsequent sensors were dip-coated for longer periods (10 minutes – twice applied).

Nevertheless, the percentage variation in resistances prior to  $PF_6^-$  potential sweeping was 51.1%. After cycling, the resistances of the sensors were brought into more similar ranges and the linear sweep voltammograms were more defined with less variation. The percentage variation was lowered to 27.1%. Fig 4.15 exemplifies this by comparing the resistances found. However, no substantial differences were found between the final

conducting polymer sensors that were grown on substrates which underwent this procedure and those that did not.



Fig 4.15 Resistance measured before and after PF<sub>6</sub><sup>-</sup> cycling of P3HT layer

## 4.10.3 Cyclic Voltammetry Vs. Chronoamperometry

The initial set of sensors made at the start of this project were deposited by applying a potential step for various lengths of time. The applied potential was decided by observing the polymerisation potential found through voltammetric measurements and using a potential that was slightly greater than the value found to accommodate for any variation in potential during measurement. Chronoamperometric methods were shown to be reliable for polypyrrole base layer deposition. However, potential step methods were not always found to achieve top layer deposition for some of the polymers. Cyclic voltammetry was much more reliable and was subsequently used as the preferred method of polymer growth and deposition.

Otero *et al.* [4.64] provide insight into the differences displayed. Investigations were carried out into the growth, morphology and adherence of polypyrrole electrogenerated by potentiostatic, galvanostatic and potentiodynamic methods. It was found that chronoamperometric measurements indicated a nucleation step in the polymer growth

process, as proposed by Genies *et al.* [4.56] and explained by Pletcher *et al.* [4.65] The polymer films obtained were dendritic and adherence to the electrode surface was poor. However, polymer films obtained through cyclic voltammetry exhibited smooth, shiny surfaces and adherence was markedly improved.

Finally, AFM was used to observe surface morphology of sensors that were in their oxidised and reduced forms. Fig 4.16 clearly shows that surface roughness was increased upon reduction. Although grain size or typical structures were unchanged, reduced forms exhibited more hollow troughs and holes in the surfaces than found for oxidised species. This would indicate an expulsion of dopant ions from the film on reduction. Gas testing results showed that this produced larger signal responses, with significant improvements for PEDOT/PF<sub>6</sub><sup>-</sup> sensors, but it was found that the more reduced, more resistive sensors were noisier and less stable than their oxidised forms, especially for polybithiophene.



Fig 4.16 RMS surface roughness of oxidised and reduced forms of polymers

## 4.11 Concluding Remarks

- Electrochemical polymerisation used rather than chemical polymerisation due to ease of use, repeatability and greater amount of control over electrical properties of the polymer sensors.
- Polypyrrole base layer deposited chronoamperometrically with repeatable results and good conductivity. Naphthalenesulfonic acid proved to be a more effective counter ion than tosylate for polypyrrole base layer deposition.
- A range of pyrrole derivatives were chosen and studied as top layer polymers. They
  were chosen for comparison of substituent functionalisation, positional influence and
  steric effects.
- The polymerisation potentials were found to increase with increasing substituent alkyl chain length. Higher potentials were generally found for *N*-substituted pyrroles compared to 3-substituted derivatives. Potentials were also greater for alkoxysubstituted pyrroles than alkyl derivatives and less control over oxidation level was possible. Steric effects dominated over the electron-donating stabilising effect of phenylpyrrole and pentafluorobenzylpyrrole.
- Smoother surfaces were generally found for 3-substituted pyrrole than N-substituted pyrrole.
- The repeatability of sensor fabrication was interrogated in terms of batch variation and sensor-to-sensor variability. Sensor variability was greater for higher resistance sensors and polymers in which the oxidation level was difficult to control. Higher resistance sensors also showed more drift in base resistance over a two month period.
- Polymers were investigated with different dopant anions. 3-hexanoylpyrrole was best with PF6; *N*-pentafluorobenzylpyrrole and *N*-phenylpyrrole potentials were lowered to reasonable range with triflate. Surface roughness was altered with different dopants. NSA and SDS were also tried. NSA results were inconclusive but SDS provided lower polymerisation potentials and greater control for 3-dodecylpyrrole and 2,2'-bithiophene

- Ag/AgCl and calomel electrodes were compared to the platinum electrode. Platinum
  electrode generally gave the lowest polymerisation potentials and easier polymer
  growth. *N*-hexylpyrrole/SDS and 3-dodecylpyrrole/SDS sensors were grown using
  calomel electrode due to the greater control afforded over redox processes.
- Polythiophenes 2,2'-bithiophene, 3-methylthiophene and 3-decylthiophene, and 3,4ethylenedioxythiophene were studied. 3-alkylthiophenes polymerisation was not achieved but 2,2'-bithiophene and 3,4-ethylenedioxythiophene polymer growth and deposition were facile.
- Polyaniline and SNS were also successfully grown and deposited electrochemically.
- · Heat treatment generally lowered sensor conductivity but improved stability.
- PF<sub>6</sub><sup>-</sup> cycling of P3HT layer prior to electrochemical methods reduced sensor variability but had no appreciable affect on the final sensors.
- Cyclic voltammetry produced polymer films more reliably than films grown using potential step methods
- Reduced polymer films had rougher surfaces with less grain regularity (holes/troughs)
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# **CHAPTER 5**

# SENSOR CHARACTERISATION

This chapter presents the results of the gas testing experiments of the successful conducting polymer sensor arrays fabricated. Prior to implementation in the wound monitoring hybrid device prototype, the sensors that were investigated and discussed in the preceding chapter were tested on a purpose built gas rig. The results were used to elucidate the sensitivity of the sensors to the volatile chemicals of interest and the cross-selectivity, or orthogonality, of the sensor arrays made.

Besides monitoring the sensitivities of the sensors and discerning which sensors had the most potential for the purposes of the project, the effect of the different polymer substituents and various dopants used were observed in terms of their gas sensing abilities.

The results presented in this chapter cover a range of polypyrrole derivative sensors, polythiophene based sensors, 2,5-di-(2-dithienyl)pyrrole, and two commercially available conducting polymer materials. The sensitivities of these conducting polymer sensors are collated, the repeatability of the sensors are discussed and the discriminatory ability of the different sensor arrays constructed is examined through the use of principal component analysis (PCA).

#### 5.1 Background

# 5.1.1 Conducting Polymer Sensing Mechanisms

In chapter two it was recounted that the mechanism of conduction of conducting polymers and the way in which they interact with organic vapours is currently not well established. Despite the amount of comprehensive research conducted on the elucidation of the sensing mechanisms of conducting polymers and their interaction with analytes, the

processes by which conduction is altered are not fully known. The main difficulty lies in the ability to trace the path of the charge carriers through the polymer matrix and the variety of polymer interface locations that can affect the overall conductivity in a chemiresistor [2.123].

In chapter 2, the initial discoveries of conductive polymers were reported up to the development of halogen doped polyacetylene by Shirakawa *et al.* [2.108]. One of the key discoveries was made in 1973 when polysulfur nitride was formed with a conductivity approaching that of copper [5.1], which lead to the subsequent surge in interest to develop highly conducting and processable polymers. A year after Shirakawa and coworkers found that polyacetylene could be doped with halogens to produce near metallic conductivity, analogous effects were observed by using electron donors (alkali metals) [5.2]. The vast amount of research conducted was driven by the technological possibilities of such materials and the role of solitons in the charge-transfer doping mechanism [2.122]. The theory of conduction via polarons and bipolarons soon followed.

The electropolymerisation of conducting polypyrrole films by Diaz *et al.* [2.162] and electrochemical control over the doping process was the breakthrough that initiated the voluminous amount of research devoted to the understanding of conducting polymers and their applications to technology. There have been many applications where conducting polymers have been researched. Their use as a processable conducting material, or synthetic metal, has been exploited in areas such as electronic and electromechanical devices. However, as pointed out by Janata and Josowicz [2.123], the success of these applications depends on the environmental stability of the conducting polymers used, which accounts for the varying degrees of success. In other applications, the electroactive properties of conducting polymers are taken advantage of, and have been used in the development of a multitude of devices including various sensing technologies, batteries and solid electrolytes, actuators, and molecular electronics.

As research of conducting polymers progressed into various fields and applications, the need to gain a deeper understanding of their properties and how they function in order to

optimise their use in technology lead to the formulation of a number of theories and sensing mechanisms. The following sections summarise the main sensing mechanisms that have been proposed.

The mechanisms of interaction can be categorised into two main classes: i) chemical interaction between the conducting polymer and analyte, and ii) physical interaction/adsorption between the sensing material and analyte.

# 5.1.1.1 Redox Electron Transfer

Chemical interaction has been reported to occur with many volatiles at room temperature. Redox active gases are reportedly able to cause oxidation or reduction of the polymer, thereby changing the doping level or charge carrier concentration, providing a simple technique for the detection of analytes. Electron acceptor gases such as nitrogen dioxide and iodine can remove electrons from the polymer units, increasing the doping level in p-type conducting polymers, whereas electron donating gases like ammonia and hydrogen sulfide have the opposite effect, dedoping the polymer and increasing its resistance.

Xie *et al.* [5.3] prepared polyaniline-based ultra-thin film gas sensors and studied their sensitivity to NO<sub>2</sub>. Since NO<sub>2</sub> is a known oxidising gas, it was suggested that on contact with the sensing material it was likely that electron transfer from polymer to gas would occur, resulting in a positively charged polymer. The charge carriers created from this process would increase the conductivity of the film. However, they also found that polyaniline-PSSA (polystyrene sulfonic acid) self-assembled films increased in resistance with NO<sub>2</sub> concentration due to a dedoping effect, which was confirmed by comparing the results of the film when it was treated with an oxidant,  $(NH_4)_2S_2O_8$ .

Mohammad [5.4] reported on the compensation behaviour, or electron transfer, of thin films of polythiophene and polypyrrole with gaseous and aqueous ammonia, explaining that the compensation may be viewed as n-type doping of a p-type doped polymer or vice

versa. Mohammad proposed reaction mechanisms between the dopant ions and ammonia which comprised of four stages:

- i) compensation of the counter ions on the outer layer of the polymer;
- ii) the affected outer monolayer extends into the polymer matrix which may occur via diffusion of the compensant through various percolation paths, steadily decreasing the conductivity;
- iii) complete disconnection of the percolation path resulting in a dramatic decrease in electrical conductivity;
- iv) complete homogenisation of the polymer into an insulator.

However, electronic interaction was proposed at the heteroatom of polypyrrole forming a hydrogen bond.

# 5.1.1.2 Partial Charge Transfer

Besides the pure redox reactions mentioned, partial charge/electron transfer can occur, altering the conductivity of the conducting polymer material. A relationship between the partial pressure of a gas and conducting polymer was proposed by Janata [5.5], whereby the charge-transfer complex formed altered the work function. Blackwood and Josowicz [5.6] investigated the mechanism of interaction of polypyrrole and p-polyphenylene films on exposure to a number of organic vapours. UV-visible spectroscopy was used to follow changes in polaron and bipolaron concentration, and the Kelvin probe technique was used to monitor changes in the work function of the polymer. Since polyphenylene was shown to be sensitive to organic vapours, a mechanistic explanation was required that was not dependent on the presence of heteroatoms or permanent dipoles. Adsorbed molecules can donate or accept electron density to or from the conducting polymer and optical measurements suggested that partial electron transfer took place between analyte and sensing layer. It was concluded that the relative magnitude of the electronegativity of the vapour and work function of the sensing material governed the amount and direction of electron transfer. By adjusting the initial work function of the conducting polymer, it was shown that the selectivity towards different gases could be tuned [2.123].

Charge transfer was also suggested as the mechanism of interaction between a polyaniline blend and carbon monoxide gas by Watcharaphalakorn *et al.* [5.7] FTIR measurements were made *in situ* during carbon monoxide (CO) exposure and showed no discernible differences from measurements made prior to exposure, suggesting that the CO molecules did not chemically bond with the polymer. XRD analysis also suggested that no structural changes occurred as a result of CO. A mechanism was proposed whereby a stable resonance of  $^+C\equiv O^-$  coexisted or replaced the counter ion, withdrawing a lone pair of electrons at the amine nitrogen, neutralising the carbon atom so that the nitrogen possessed a positive charge, thus increasing the charge carrier concentration and consequently increasing the electrical conductivity of the polymer.

# 5.1.1.3 Grain Boundaries Model

An alternative mechanism of interaction between carbon monoxide and polyaniline was proposed by Dixit *et al.* [5.8] Polyaniline films were vacuum deposited onto glass substrates in both their doped and undoped forms. Using Fe-Al as a dopant seemingly made the polymer sensor more specific towards carbon monoxide. The proposed mechanism involved a decrease of adsorbed oxygen ions and electrical resistance as oxidation occurred at the interface of CO and polymer. This was thought to occur as a result of the reduction in the surface potential, barrier height and the depletion length.

Similarly, Torsi *et al.* [5.9] studied the sensitivity of alkoxy-substituted polyterthiophenes to alcohol vapours. Since no swelling of the polymer took place and responses were fast and reversible, it was proposed that analyte adsorption on the polymer surface enhanced the potential barrier at the boundaries between grains, which reduced the current flow in the channel region of the thin-film-transistors.

# 5.1.1.4 Proton Transfer

Additionally, chemical interaction involving proton transfer has also been proposed. Gustafsson *et al.* [5.10] offered an alternative to the compensation effect of ammonia as described by Mohammad. A reversible interaction was observed between ammonia and polypyrrole at low concentrations, which could be interpreted as a reduction in bipolaron concentration and consequent dedoping, increasing the resistance of the polymer. As an alternative to the compensation reaction, proton transfer between ammonia and polypyrrole was proposed as follows:

$$Polymer^{+}A^{-} + NH_{3} \rightleftharpoons Polymer(-H) + NH_{4}^{+}A^{-}$$

This process could only occur where polymers had acidic protons. However, the elucidation of which compensation reaction caused the reversible interaction was difficult. If a large concentration of ammonia, or wet ammonia, was exposed to the polymer for long periods of time, the process became irreversible. Degradation of the polymer could result from irreversible nucleophilic attacks and the ammonium-anion complex formed from deprotonation could result in the formation of salt-crystals over a longer period of time. Additional attack could occur from the hydroxide ion produced from NH<sub>3</sub> + H<sub>2</sub>O  $\rightleftharpoons$  NH<sub>4</sub><sup>+</sup> + OH<sup>-</sup> which is an even stronger nucleophile. These nucleophilic attacks could be reduced by preparing longer chain conducting polymers with less defects.

This proton transfer model was further supported by work reported by Guernion *et al.* [5.11] who tested the responses of polypyrrole sensors to a variety of amines of differing basicity. The order of sensitivity was shown to follow the order of p*K*a of the amines and deprotonation was better with stronger bases such as methylamine and dimethylamine, and at low concentrations the process was reversible.

Reemst *et al.* [5.12] and Kemp *et al.* [5.13] studied the temperature dependence of conductivity changes induced by ammonia and also supported the proton transfer mechanism. Reemts argued that bulk chemical redox interaction was less likely to occur and

the strong decrease in conductivity of polyaniline when exposed to ammonia indicated deprotonation of the polymer, neutralising the oxidised monomer units. Also, the reversibility of the process further supported the interaction mechanism since mobility changes resulted from local morphology, which is otherwise often irreversibly affected.

Verji *et al.* [5.14] examined a number of response mechanisms by using novel polyaniline nanofiber gas sensors with organic vapours; hydrochloric acid, ammonia, hydrazine, chloroform, and methanol, to investigate protonation, deprotonation, reduction, swelling and conformational alignment mechanism respectively. Due to the reversible acid/base doping, polyaniline is a unique polymer; its conductive and insulating forms are interconverted via acids/bases and it can exist in a number of intermediate oxidation states. When exposed to hydrochloric acid, polyaniline is doped via protonation of the imine nitrogen, forming polarons and rapidly increasing the conductivity. Deprotonation can occur when the conducting emeraldine salt form is exposed to ammonia, decreasing the conductivity and forming the insulating emeraldine base form of polyaniline. The mechanism for this dedoping accounted for the slower response times and smaller changes in resistance. Resistance increases were also found when exposed to hydrazine and the colour change observed indicated that the formation of the fully reduced leucoemeraldine form was generated.

However, exceptions have been shown; Kriván et al. [5.15] demonstrated that hydrogen sulfide, a reducing gas, significantly increased the conductivity of polypyrrole films. The reasons for this were explained as a result of hydrogen sulfide dissociation within the polymer and proton transfer to the polymer. The compensation of HS<sup>-</sup> anions and proton transfer to the polymeric chain lead to conductance being increased since the cation mobility was larger than the ionic conduction of the partially oxidised film.

#### 5.1.1.5 Physical Interaction

Not all organic vapours necessarily react with conducting polymers; changes in conductivity may occur through various physical interactions. Physisorption can occur through weak van der Waals interactions such as dipole-dipole or dipole induced interactions or London dispersion forces, and via hydrophobic or hydrophilic interactions.

Ruangchuay *et al.* [5.16] studied the conductivity responses of polypyrrole to acetone and discussed the interaction mechanism. Responses were found to be smaller than those of alcohol due to lower polarity of acetone. X-ray photoelectron spectroscopy (XPS) was used to characterise imine-nitrogens defects (=N-), polaron species (-NH<sup>+</sup>-) and bipolaron species (=NH<sup>+</sup>-). Thermogravimetric analysis (TGA) suggested that chemisorption took place during prolonged exposure of polypyrrole to acetone, which was confirmed by FTIR measurements; the stretching vibration observed for C=O was lower than that in acetone vapour and was accounted as a hydrogen-bond between the carbonyl group of acetone and the amine group of pyrrole, formed using the lone pair of electrons of the oxygen atom.

Alcohol interactions were studied by Virji *et al.* [5.14] and Athawale *et al.* [5.17]. Both reported that the size of the alcohol molecules governed the efficiency of interaction and diffusion into the polymer. It is supposed that small alcohol molecules interact differently from halogenated solvents due to their polar nature and high dielectric constant, sorbing into the polymer film causing expansion of the compact polymer chains into a linear form, increasing the crystallinity and conductivity of the polymer. Athawale *et al.* confirmed this with X-ray diffraction patterns before and after exposure to the analytes. It was also reported that the larger size of butanol and heptanol impeded their efficiency of diffusion; they acted as strong barriers due to their long chain lengths and non-polar nature, which accounts for the observed loss of conductivity.

The physical swelling of the polymer is a known phenomenon which has been used to aid some understanding of the interactions that occur between analyte and conducting polymer. Lee *et al.* [5.18] developed a polyaniline based optical sensor that operated on the principle of the swelling of the polymer on exposure to ammonia. A repulsive force was said to be generated between the polyaniline chains which induces the swelling, changing the volume of the film, consequently changing its transmittance.

However, Segal *et al.* [5.19] in studying the sensitivity of polystyrene/polyaniline nanoblends to aliphatic alcohols concluded that significant conductivity changes were not likely to occur as a result of swelling since low sorption levels were expected and slower, more gradual resistance changes would occur had a swelling-controlled mechanism been the case. Instead it was proposed that the sorbed molecules enabled conduction via the insulating moieties by reducing the "potential barrier for hopping/tunnelling processes, or by increasing interchain and interparticle charge mobility." [5.19]

Physical interactions between analyte gas and conducting polymer were discussed by Vercelli *et al.* [5.20] It was shown that responses in low level doped polymers were governed by the relative permittivity of the solvent ( $\varepsilon$ s) and of the polymer ( $\varepsilon$ p); conductivity increased for  $\varepsilon$ s >  $\varepsilon$ p and decreased for  $\varepsilon$ s <  $\varepsilon$ p. It was assumed that weak van der Waals interactions existed between the polymer chains and the oxidative charges moved through the polymer matrix according to a hopping mechanism – experimental results were shown to follow Mott's variable-range hopping conductivity model. Moreover, it was reported that heavily doped systems gave very little response to the tested vapours unless exposed to saturated vapour pressures. This observation was explained as occurring due to the delocalisation of electronic states and the formation of well-packed, highly conducting domains, so any solvation may occur at the substituents without any arbitration of the conduction. Therefore responses would only become appreciable if the swelling was enough for the polymer grains to separate into large insulated domains. [5.20]

#### 5.1.2 Adsorption Processes

Sorption is a term used to collectively describe the processes of absorption and adsorption. Chemical absorption is the process in which a substance in one state is taken up and permeates into another substance, usually of a different state. Adsorption describes the adhesion of substances onto the surface of another substance through physical attractive forces or through chemical bonding.

Adsorption can be divided into two classes; physical adsorption via van der Waals interactions (physisorption) and chemical adsorption, where chemical bonds (ionic or covalent) are formed between the gaseous molecules and the solid surface (chemisorption). Physical adsorption equilibrium is attained rapidly and is reversible (except when limited by mass diffusion rates), whereas chemical adsorption can be rapid or slow and is expected by its nature to be limited to a monolayer.

The fractional coverage of the surface ( $\theta$ ) is described by the following ratio and is often described in terms of volume of adsorbate absorbed

# $\theta = \frac{number \ of \ occupied \ adsorption \ sites}{total \ number \ of \ adsorption \ sites}$

Adsorption is normally described in terms of an empirical adsorption function n = f(P, T) where *n* is the amount adsorbed. Adsorption isotherms describe the relationship between the amount of adsorbed gas and its partial pressure at a fixed temperature in terms of the variation in fractional coverage. They are the most convenient form in which to obtain and plot experimental data and develop theoretical treatments. [5.21]

Numerous isotherm models exist and are regularly used to explain experimental results and support theoretical calculations. Two of the most common adsorption isotherms are explained here since they are frequently used to describe the adsorption and sensing process between volatile analytes and conducting polymer gas sensors.

# 5.1.2.1 Langmuir Isotherm

According to the Langmuir isotherm, dynamic equilibrium is established between the gas (G) and solid surface (S) thus

$$G + S \xrightarrow{k_a} G - S$$

where  $k_a$  is the rate constant of adsorption and  $k_d$ , the rate constant of desorption

The following assumptions are made: [5.22]

- i) adsorption limited to a monolayer coverage
- ii) all adsorption sites are equivalent (energetically homogeneous)
- iii) the solid surface is perfectly uniform
- iv) the adsorption of a molecule is independent of the occupancy of neighbouring sites

The rate of change of fractional coverage due to adsorption is described as:

$$\frac{d\theta}{dt} = k_a p N (1-\theta)$$

where *p* is the partial pressure and  $N(1 - \theta)$ , the number of vacant sites and *N*, the total number of sites.

The rate of change due to desorption is proportional to the number of adsorbed species,  $N\theta$ 

$$\frac{d\theta}{dt} = k_d N \theta$$

At equilibrium, the rate constants are equal (no net change), so the Langmuir isotherm is found by solving for  $\theta$ 

$$\theta = \frac{Kp}{1 + Kp}$$
 where  $K = \frac{k_a}{k_d}$ 

This expression can be rearranged for Kp

$$Kp = \frac{\theta}{1 - \theta}$$

Therefore a plot of log(K) against log(p) will be linear when  $\theta$  is constant.

The Langmuir adsorption isotherm can be easily adapted for dissociative adsorption since the adsorption rate is proportional to the square of the number of vacant sites and so the desorption rate is proportional to the square of the number of adsorbed species. Therefore the isotherm is described as for non-dissociative adsorption but with the square root of the *Kp* terms, meaning that the surface coverage is less dependent on pressure. Figure 5.1 shows the typical shape of the Langmuir isotherm; a constant increase in uptake up to a certain value, after which a plateau is reached.



Fig 5.1 Langmuir isotherm for different values of K (0.1, red; 1.0, blue; 10.0, yellow)

# 5.1.2.2 BET Isotherm

The most commonly used isotherm describing multilayer adsorption was derived by Stephen Brunauer, Paul Emmett, and Edward Teller, and is named the BET isotherm (an abbreviation of the names of the respective authors). [5.23]

The Langmuir isotherm is limited to monolayer adsorption, however physisorption allows for multilayer adsorption where an initial adsorption layer can act as a substrate for further adsorption. Thus, instead of a plateau of saturation being reached, the isotherm can continue to rise, giving a shape that is convex towards the x axis. The following assumptions are made:

- i) physisorption can occur in infinite layers
- ii) no interaction between adsorbed layers
- iii) Langmuir isotherm can be applied to each layer

The expression describing the isotherm is:

$$\frac{V}{V_{mon}} = \frac{n}{n_{mon}} = \frac{cz}{(1-z)[1-z(1-c)]} \quad \text{where} \quad z = \frac{p}{p_0}$$

 $V/V_{mon}$  is the ratio of the volume of adsorbed molecules (*V*) and the volume of molecules adsorbed in the monolayer ( $V_{mon}$ );  $n/n_{mon}$  is the ratio of the number of moles of adsorbed molecules (*n*) to the number of moles adsorbed in a single monolayer ( $n_{mon}$ ); *c* is a constant of the relative strength of surface adsorption and condensation of pure adsorbate; *p* is the equilibrium pressure of the adsorbate and  $p_0$  is the vapour pressure of the pure condensed adsorbate.

The BET isotherm is characteristic of a weak interaction between gas and solid and is normally exhibited by non-porous or macroscopic solids.

# 5.1.2.3 Adsorption Processes In Conducting Polymer Sensors

Adsorption is integral to the understanding of sensing mechanisms of gas sensors since it is regarded as the first step in all sensing techniques, especially QCM sensors.

Bartlett *et al.* [5.24] presented diffusion and adsorption equations in terms of several fundamental dimensionless parameters so as to describe the processes involved in conducting polymer gas sensing. The adsorption process was described using the Langmuir isotherm where it was assumed that the polymer film consisted of a uniform distribution of immobile adsorption sites. Two equations were derived; a dimensionless diffusion equation and an equation relating the sorption kinetics of gases bound/released from the diffusion process. The solution of these two nonlinear partial differential equations with appropriate boundaries would yield the adsorption/desorption concentration and site occupancy profiles.

However, these equations have not been analytically solved. Nevertheless, the authors derived approximations for six limiting cases: pure diffusion, slow diffusion, unsaturated and saturated (linear) reaction kinetics, saturated (nonlinear) reaction kinetics, and a mixed diffusion reaction process. Experimental agreement was found by constructing a simple conductance model where conductivity was linearly related to the site occupancy, and a steady-state response was found to follow a Langmuir isotherm.

Hwang *et al.* [5.25] proposed a simpler model based on the Langmuir isotherm using equilibrium state as opposed to dynamic cases. By assuming that the total resistance of the film was composed of n resistances of R in parallel, where each R was composed of m resistances in series, the authors were able to explain their experimental results with the sensing equation they derived.

In contrast to these Langmuirian observations, Charlesworth *et al.* [5.26] considered both the mass uptake and resistance changes of polypyrrole and observed a BET isotherm. Using a piezoelectric mircrobalance to measure mass uptake and a resistance probe with similar conducting polypyrrole films, a linear variation was observed below circa 5% mass uptake. They assumed the film behaved as a uniform sheet and described the rate of mass uptake using Fick's equation of diffusion. Experimental results were analysed by plotting fractional mass uptake against  $t^{1/2}$  and the diffusion coefficient was determined by least-squares fitting the rising part of the adsorption curve. The model worked well for methanol but the goodness of fit became poorer for larger alcohol molecules. Other models gave an even poorer fit. Thus it was suggested that the polymer was either relatively porous or had sufficient mobility to enable chain relaxation during the diffusion. A positive correlation was found with the dielectric constant of the analyte, which the authors explained by holding the variable range electron hopping process responsible for the conductivity as an electron-hopping transfer mechanism. [5.26]

A VOC partition model has been used to describe the effects in neutral polymers and polymer composites. [5.27; 5.28] Bissell *et al.* [5.29] sort to investigate whether such a

model could be applied to the responses of conducting polymer gas sensors, which are charged, porous materials whose resistances change through complex transduction processes. If conformation to the model was found, it was expected that, for a homologous series of analytes, a double reciprocal plot of  $C_g$  against  $p_2$  would be linear, where  $C_g$  is the concentration required to generate a fixed amplitude of response. If the ratio of the transduction constant (describing the efficacy of signal translation by adsorbed analyte) and the vapour activity coefficient was constant across a series, the gradient of the plot would be unity.

The data collected demonstrated that molecular partitioning of the analyte was the initial stage of the sensing process, with partition predominantly governed by analyte volatility, and the conducting polymers were non-selective across homologous groups of analytes.

For alcohols, close correlation was observed between branched primary, secondary and tertiary species and the homologous straight chain series, suggesting that there was little selectivity for molecular shape or size. Additionally, the responses to aromatic compounds containing heteroatoms did not closely correlate with hydrocarbon aromatics for polyalkylthiophene sensors, which indicated the occurrence of specific  $\pi$ - $\pi$  interactions. Overall, sensitivity was consistent with broad trends in analyte polarity. The following order was observed: alcohols>esters>aromatics  $\approx$  alkanes.

# 5.2 Calibration Gases

# 5.2.1 Microorganisms Studied

Wound colonisation is often polymicrobial, predominantly supplied from the normal microflora of the gut, the oral cavity, gastrointestinal mucosae, or the genitourinary tract [5.30], with close correlation found between wound flora and the normal flora of the sites mentioned that are in close proximity to the wound. [5.31] A significant amount of anaerobes

were expected in the microflora of acute and chronic wounds since an average proportion of up to 50% of anaerobes in infected wounds have been reported in literature. [5.30, 5.32; 5.33]

The most common strains of bacteria found in wounds are *Staphylococcus aureus* (representing over 75 % of the pathogens found in burn wounds), *Pseudomonas aeruginosa*, *Streptococcus pyogenes* and *Bacteroides fragilis*. Other streptococci, anaerobic organisms and fungi can also cause infection. [5.34] Table 5.1 lists the mircroorganisms used for the project. GC/MS headspace analysis was performed with the listed strains to determine the volatile key markers.

	Microorganism	Strain	Medium
1	Staphylococcus aureus subsp aureus	ATCC-12600	Tryptic Soy Agar
2	Staphylococcus aureus subsp aureus	ATCC-25923	Tryptic Soy Agar
3	Staphylococcus aureus subsp aureus MRSA	ATCC-43300	Tryptic Soy Agar
4	Staphylococcus aureus subsp aureus	ATCC-27659	Tryptic Soy Agar
5	Staphylococcus aureus subsp aureus	ATCC-29247	Tryptic Soy Agar
6	Staphylococcus aureus subsp aureus	ATCC-12598	Tryptic Soy Agar
7	Staphylococcus aureus MRSA	DSMZ-11729	Tryptic Soy Agar
8	Pseudomonas aeruginosa	ATCC-10145	Brain Heart Agar
9	Pseudomonas aeruginosa	ATCC-27853	Brain Heart Agar
10	Pseudomonas aeruginosa	ATCC-27315	Brain Heart Agar
11	Pseudomonas aeruginosa	ATCC-35032	Brain Heart Agar
12	Streptococcus pyogenes	ATCC-14289	Brain Heart Agar
13	Streptococcus pyogenes QC A62	ATCC-49399	Brain Heart Agar
14	Bacteroides fragilis	ATCC-23745	Chopped Meat Agar

Table 5.1 List of microorganisms used in the woundmonitor project

A selection of volatiles was used to begin development of a suitable sensor array. The identification of the volatile key markers for each bacterial species studied was of great importance in the design of the woundmonitor device. The sensor design and calibration was based upon these chosen volatiles markers, which would ultimately govern the efficiency of bacterial detection. Large amounts of literature exist that have expounded the knowledge of volatiles produced from various bacteria. Table 5.2 lists the common volatile compounds reported in literature. The most ubiquitous volatiles reported were selected and used to develop a reliable preliminary sensor array.

	Staphylococcus aureus	Pseudomonas aeruginosa	Bacteroides fragilis
Acetaldehyde	[5.35]	[5.35]	
Acetic acid	[5.43]	[5.35]	[5.38];[5.39]
Ethanol	[5.35]	[5.35]	[5.44]
Acetone	[5.35]	[5.35]	
Ammonia	[5.35]	[5.35]	
Hydrogen sulfide	[5.35]	[5.35]	
Methanethiol	[5.35]	[5.35]	
Dimethyl sulfide	[5.35]	[5.35]	
Dimethyl disulfide	[5.35]	[5.35]	
Trimethylamine	[5.35]		
Indole	[5.35]		
Aminoacetophenone	[5.35]	[5.41]	
Hexanal	[5.35]		
Isovaleric acid	[5.43]		[5.38];[5.39]
Hydrogen cyanide		[5.36]	
Acetonitrile		[5.36]	
2-nonanone		[5.41]	
2-undecanone		[5.41]	
Dimethyl trisulfide		[5.41]	
2-butanone		[5.41]	
1-undecene		[5.41]	
Isopentanol		[5.41]	
Propionic acid			[5.38]
Isobutyric acid			[5.38]
Heptanoic acid			[5.40]
Propanol			[5.39]
n-Butanol			[5.39]
n-Amyl alcohol			[5.39]
Butyric acid			[5.39]
Valeric acid			[5.39]
Isocaproic acid			[5.39]
Caproic acid			[5.39]

Table 5.2 Volatiles produced from microorganisms as reported in literature

Allardyce *et al* [5.35] used selected ion flow tube mass spectrometry (SIFT-MS) to measure the metabolites produced in the headspace of bacteria grown in BacT/ALERT<sup>®</sup> blood culture media. They were able to characterise *pseudomonas aeruginosa* by elevated levels of acetic acid and acetone, whilst *staphylococcus aureus* produced acetaldehyde, ethanol, ammonia, methanethiol (methyl mercaptan), and dimethyl sulfide. Carroll *et al.* [5.36] also employed SIFT-MS. Using blood agar and Pseudomonas-selective media to culture bacteria, they found that although volatile compounds were found in the headspace of both sterile and inoculated media, higher concentrations were present above bacteria cultures; particularly for ammonia. Bacterial growth did not affect the concentrations of acetic acid, butanone, methanol, and dimethylsulfide. However, quantities of hydrogen cyanide were found which was not identified when using GC/MS.

GC techniques have been compared by a number of authors. Gardini *et al.* [5.37] argued the usefulness of headspace analysis and the periodical monitoring of microorganism activity. Van den Bogaard *et al.* [5.38] concluded that headspace analysis was unsuitable for quantitative analysis. They found that headspace analysis of volatile fatty acids (VFA) produced larger peaks for the isoacids, compared to their straight-chain analogues, due to their greater volatility. This result confirms the findings of Larsson *et al.* [5.39] Also, the recovery of larger acids was lower due to their higher boiling points. Concentrations of VFAs were also analysed by gas-liquid chromatography by Wiggins *et al.* [5.40]

GC/MS headspace analysis was used by Labows *et al.* [5.41] to investigate the metabolites produced by *Pseudomonas aeruginosa* and related species, grown on tryptic soy agar. The presence of 2-aminoacetophenone, the volatile responsible for the grape-like odour found when *Pseudomonas aeruginosa* was grown in culture [5.42], was confirmed for *Pseudomonas aeruginosa* but not for other pseudomonas.

VFA production from a variety of bacteria were investigated by Julák *et al.* [5.43] Their evaluation of blood cultures via the analysis of VFAs by GC showed that all the species they tested, except *Pseudomonas aeruginosa*, produced acetic acid which was generally a dominant component. Anaerobic bacteria were found to produce greater amounts of acetic/propionic/isovaleric acid and usually one of the higher molecular weight acids; the presence of isobutyric acid, butyric, valeric, isocaproic, or caproic acid was reported to be indicative of anaerobe presence. In another paper by Julák *et al.* [5.44], it was shown that preliminary detection of bacteria in clinical samples can be rapidly performed using solid phase microextraction (SPME) with GC analysis, which is described in detail by Zhang *et al.* [5.45] Analysing VFA patterns of the exudates they found staphylococci produced higher amounts of acetic and isovaleric acid and that negligible amounts were produced by common bacteria (pseudomonas/streptococci).

# 5.2.2 SPME Headspace GC/MS Analysis Of Bacteria

SPME headspace analysis using GC/MS was performed on the selected bacteria, cultured on both brain heart agar and tryptic soy agar, and chopped meat agar for *bacteroides fragilis*. SPME fibres were exposed to cultures for 30 minutes at 37°C and samples were analysed at intervals of 24h and 48h after culturing. Standard microbiological analysis and polymerase chain reaction (PCR) was used to identify the bacteria strains.

This work was performed by Dr. Anna-Maria Pisanelli in conjunction with Partner 5 (Biodiversity) as part of the first work package for the Woundmonitor project. The results were searched against Wiley275, NIST and Saturn libraries. The types of volatiles produced by bacteria were dependent on the growth stage of the cultures, as well as the medium. Therefore, it was necessary to carry out GC/MS measurements at specific times after inoculation.

It was shown that dimethylsulfide was present in all strains of bacteria analysed in differing amounts. In the headspace of *Pseudomonas aeruginosa*, mostly ketones (nonanone, octanone, and undecanone) and alcohols (heptanol, dodecanol, undecanol) were present. Fatty acids (acetic, propionic, isovaleric acid) were prevalent in the headspace of *Streptococcus aureus*, as well as aldehydes, but no ketones were present. Table 5.3 summarises the identified biomarkers of each strain investigated after 24 – 48 hours incubation. Results for *Bacteroides fragilis* were not obtained due to the difficulties involved in culturing anaerobic bacteria.

Bacteria	Strain	24h Markers	48h Markers	
Staphylococcus aureus	ATCC-12600	Butyric acid	lsovaleric acid	
Staphylococcus aureus	ATCC-25923	Butyric acid	Butyric acid	
Staphylococcus aureus	ATCC-43300	Isovaleric acid	Butanal	
		Butyric acid	Benzaldehyde	
Staphylococcus aureus	ATCC-27659	Isovaleric acid	Isovaleric acid	
			Butyric acid	
Staphylococcus aureus	ATCC-29247	Isovaleric acid	Isovaleric acid	
Staphylococcus aureus	ATCC-12598	Isovaleric acid	Isovaleric acid	
			Butyric acid	
Staphylococcus aureus	DSMZ-11729	Valeraldehyde	Isovaleric acid	
		Acetic acid	Butyric acid	
Pseudomonas aeruginosa	ATCC-10145	Ethylhexanol	2-nonanone	
		Undecanol	2-undecanone	
		2-nonanone		
Pseudomonas aeruginosa	ATCC-27853	Hexanol	Hexanol	
		2-nonanone	2-nonanone	
Pseudomonas aeruginosa	ATCC-27315	Dodecanol	2-nonanone	
		2-nonanone	2-undecanone	
		Undecanone		
Pseudomonas aeruginosa	ATCC-35032	Dodecanol	Heptanone	
		Heptanol	Octanone	
		1-tridecanol	2-nonanone	
		Undecanol	Undecanone	
		Octanone		
		2-nonanone		
Streptococcus pyogenes	ATCC-14289	Acetic acid	Acetic acid	
		Butanoic acid	Butanoic acid	
		Propionic acid	Propionic acid	
Streptococcus pyogenes	ATCC-49399	Acetic acid		
		Butanal		

# 5.2.3 Volatile Key Markers

The volatile key markers chosen for the calibration of the device were initially ethanol, ammonia, 2-butanone, butyric acid, acetic acid, and acetone. These were chosen as the most ubiquitous biomarkers reported in the literature surveyed and from discussions with the clinical partners involved in the project. From the results of GC/MS headspace analysis of bacteria, it was decided to include acetaldehyde to the list of calibration gases used for sensor array development.

	Ethanol	Ammonia	2-butanone	Butyric acid	Acetic acid	Acetone	Acetaldehyde
Molecular formula	$C_{2}H_{6}O$	NH <sub>3</sub>	C₄H <sub>8</sub> O	$C_4H_8O_2$	$C_2H_4O_2$	C₃H₀O	C <sub>2</sub> H <sub>4</sub> O
Molar mass (g/mol)	46.07	17.03	72.11	88.11	60.05	58.08	44.05
pK <sub>a</sub>	15.5	34	14.7	4.83	4.76	19.3	13.57
Dipole moment (D)	1.69	1.47	2.78	1.65	1.7	2.88	2.75
Dielectric constant	25.3	16.5	18.56	2.98	6.2	21.01	21
Log <i>K</i> <sub>ow</sub> [5.45]	-0.3	0.23*	0.29	0.79	-0.17	-0.24	0.45
Log P <sub>hxd</sub> [5.46]	-2.19	-2.47	-0.43	-1.83	-3.16	-1.09	-1.34
Log <i>L</i> <sup>16</sup> [5.46]	1.49	0.68	2.29	2.83	1.75	1.7	1.23
Molecular radius <sup>†</sup> (nm)	0.033	0.025	0.037	0.040	0.035	0.035	0.038
[5.47]	0.033	0.025	0.037	0.040	0.035	0.035	0.038

Table 5.4 Properties of the calibration gases used

Values taken from the CRC Handbook of Chemistry And Physics 89<sup>th</sup> Edition [5.44] unless otherwise referenced

\* estimated value

The parameters listed in Table 5.4 pertain to the concepts in the mechanism of gas sensing and changes in conductivity. The acid dissociation constants ( $pK_a$ ) are provided since Guernion *et al.* [5.11] found that the sensitivity of polypyrrole sensors followed the order of  $pK_a$  of the various amines they tested. Proton transfer mechanisms may be involved in the gas-sensor interaction especially for stronger acids and bases. Acid/base interaction is a potential factor which could determine the sensitivity of polymers with acidic protons, especially polyaniline.

Odorant properties were discussed in the chapter 2, where it was mentioned that the shape, charge distribution and polarisability were important properties that determined whether a molecule was an odorant or not. The charge distribution, or polarity, can be represented on a number of scales. The molecular dipole moment can be used to indicate

<sup>&</sup>lt;sup>†</sup> based on spherical molecule calculation using van der Waals molality (b) constant

how polar a molecule is. All of the calibration gases used possess a molecular separation of charge and thus a permanent dipole moment, the magnitude of which is given by its dipole moment ( $\mu$ ) measured in Debye (D). Polarity and the variation in electronegativity of a vapour was said to govern the magnitude and direction of electron transfer in relation to gassensor charge transfer mechanisms. Greater responses were also reported for more polar analytes in terms of physical interactions with the sensing material. The permittivity, or dielectric constant, is the ratio of electric displacement in a medium to the electric field strength. [5.46] The dielectric constant can similarly be used to represent the polarity of a molecule. Vercelli *et al.* [5.20] demonstrated that sensor responses were influenced by the relative permittivity of the analyte.

Hydrophobic or hydrophilic interactions between gases and the sensing materials are also thought to have a significant role in sensing processes. As was discussed in previous chapters, it was generally found that the longer alkyl chain length polymer substituents produced sensors with greater sensitivity to non-polar organic compounds. This could indicate the importance of such interactions. The degree of hydrophobicity of a compound can be qualitatively described via its solubility in water. However, there are a number of scales that have been used to describe the hydrophobicity of a molecule, or its lipophilicity. The octanol-water partition coefficient ( $K_{ow}$ ) has been extensively used in relation to quantitative structure-activity relationships (QSAR) and the relationship between chemical structure and biological activity, especially in the field of drug design. This work was pioneered by Corwin Hansch. [5.47; 5.48] For a solute added to a combination of two solvents that are immiscible with each other, at equilibrium, a concentration (mole fraction) ratio is attained. This distribution ratio is the partition coefficient for the given solute. For consistency, Nernst [5.49] defined the value to refer to same molecular species in both solvents. The work of Abraham et al. [5.50] is perhaps more applicable to the studies of this project. They discussed the solubility of gases in polymers and the gas-polymer interaction. They utilised the hexadencane-water and hexadencane-gas partition coefficients (Lhxd and L<sup>16</sup> respectively) which were found to be inherently useful parameters.

#### 5.3 Instrumentation

# 5.3.1 Gas Testing Rig

The following section describes the experimental setup that was used to test the sensor substrates that were discussed in the previous chapter. The design of the gas rig was developed over the course of the project to make testing procedures simple and results reliable and consistent.

The gold connectors of the sensor substrate were a standard 1.25mm pitch, enabling them to be quickly connected to integrated circuitry via standard flat flexible cable connectors. The sampling unit consisted of a Teflon gas testing chamber with a volume of about 1cm<sup>3</sup>, microcontrollers for real-time data collection from resistance interrogation circuitry and component control, a small 2-way rotary pump, and filters to protect the pump. Data was transferred via a RS232 serial communication protocol to a host PC on which custom software could record and store the data for immediate analysis. The preprocessed data was recorded as percentage response, i.e. percentage of resistance change over base resistance (%AR/R). Sensor responses were normalised across the sensor array by dividing the sensor responses ( $\Delta$ R/R) by the sum of all the sensor responses of the array ( $\Sigma$ AR/R).

The volatile organic compounds were provided to the system from permeation tubes. The permeation tubes of each of the calibration gases were obtained from Fine, Nuova Grangiara, Italy.

The use of permeation tubes as a sampling method was discussed in the chapter 2, section 2.5.1. The principles are the same as the diffusion method. An inert polymeric material contains the pure compound in a gas-liquid phase equilibrium and at a constant temperature, it emits the compound through a permeable membrane at a constant rate (see Fig 5.2).





VOC concentration was controlled by means of a series of mass flow controllers. By varying the flow of dilutant carrier gas (clean dry air) across the permeation tube at a known rate, the concentration could be calculated using the following:

Concentration, C (ppm) =  $\rho$  (ng/min) x K

where K = 24.46/molar mass

24.46 is the molar volume in litres (at 25°C, 760mmHg), i.e. the volume occupied by one mole of ideal gas, which is calculated from the idea gas law: pV = nRT

The relevant values of  $\rho$  and K used are listed in Table 5.5.

VOC	Calibration temperature (°C)	Permeation Rate (ρ) ±5% (ng/min)	<i>K</i> (at 298.15K, 101.3kPa)
Ethanol	25	3776	0.531
Ammonia	25	1352	1.439
2-butanone	25	6138	0.339
Butyric acid	25	4935	0.278
Acetic acid	25	6034	0.407
Acetone	25	6243	0.421
Acetaldehyde	25	4766	0.556

Table 5.5 Permeation tube parameters

The mass flow controllers were calibrated using a bubble flow meter for larger flow rates and a digital flow meter for rates below 200 sccm.

Initially the setup consisted of a mass flow controller dedicated to the generation of sample gas from the permeation tubes. The permeation tubes were thermostatted at 25°C using a water bath and were equilibrated for 12 hours before use. A check valve was used to ensure continuous ventilation on this line. Another mass flow controller was used to dilute the gas to the desired concentration. Prior to the gas sensing chamber, both lines were directed to a Teflon mixing block with two chambers; gas input lines entered the first chamber and sampled gas was output from the second chamber which was extracted at a constant rate with the integrated pump of the sensor testing device. All plumbing was connected using PTFE tubing since it was inexpensive, flexible and connections could be swiftly made and maintained. Stainless steel Swagelok<sup>®</sup> fittings were used for connecting tubing and Omnifit adaptors and connectors were used for connection to and from the Teflon sensing and mixing chambers. Compressed air was used as the carrier gas for experiments. Prior to introduction to the system, the air was dried through a filter of activated carbon and cleaned via a molecular sieve.

Over a period of initial testing, the experimental setup was amended to improve consistency, its ease of use and general maintenance. The following modifications were made, all of which significantly improved the results obtained:

 3-way ball valve switch inserted between mixing chamber/tube and gas sensing chamber

This enabled instantaneous switching between a continuous stream of air for base line response and sample measurement. Equilibration dynamics in the gas sensing chamber were minimised and response/recovery times were clearer to distinguish.

A temperature and humidity cabinet was used in place of the water bath

Permeation tubes could all be stored in a constant environment, unaffected by laboratory conditions. This eliminated the need for long equilibration times for each permeation tube and gas concentrations could be obtained more reliably.

Glass Schott bottles/tubes replaced the Teflon mixing chamber

The Teflon block used was suspected of holding residual traces of gases and contaminating subsequent experiments. The Teflon also deformed over time so glass was used since it is more durable and inert.

The implementation of a sparge system for a "wet" line was also carried out for some humidity tests (as shown in Fig 5.3) but otherwise both sample line and dilution line were dry. Also, although the diagram shows all of the permeation tubes connected to the line, only one valve was open at a time so as to ensure there was no cross contamination.



Fig 5.3 Gas testing rig configuration

#### 5.3.2 Experimental control

A number of controls were performed prior to any gas sensing measurements. The sensors were first monitored whilst a continuous stream of dry air was passed over the sensors at a constant rate. No measurements would be taken until a stable base line was achieved. Normally a duration of between 10 - 60 minutes was allowed. This process was repeated between each measurement taken. Once the system was stable after initial activation, equilibration was possible with 2 - 5 minutes.

To ensure that a constant flow rate was achieved across the sensors, the signal was monitored for both the continuous air stream and the dilution line from the sampling chamber. It was always ensured that switching between the two lines did not affect the signal produced and measurements could be made in the knowledge that dynamic effects of different flow rates were not present. Changes in sensor response upon switching were usually indicative of poor ventilation in the mixing chambers and pressure build-ups. These were easily remedied. Additionally, the output flow rate from the gas sensing chamber was monitored with a digital flow meter to ensure that there was a constant flow rate and that the pump was working satisfactorily.

Before any measurements were recorded, the system calibrated its baseline by measuring the initial sensor resistances for a short period. It was always ensured that the constant air flow used for equilibration was passed over the sensors during this period.

In order to reduce variability in the concentrations emitted from the permeation tubes, the setup involved using a constant flow rate over the permeation tubes whilst the dilution line would be altered as appropriate to deliver the required concentration for measurement.

#### 5.3.3 Limits of investigation

The purpose of these experiments was to quickly test the sensor substrates made and evaluate their potential as gas sensors for the wound monitor device. This involved measuring the sensor responses to the calibration gases and making comparisons as to which performed better and which combinations showed the most potential in discriminating between the calibration gases used. Clinical testing with complex odours was reserved for the final wound monitor hybrid device. Results obtained using the gas rig were for an overview of performance and quick evaluation.

For these reasons, only individual gases were measured at a time; mixtures of VOCs were not studied. This enabled a facile overlap of the results obtained for each sensor array with each of the separate VOCs without complication and sensor performance could therefore be comprehensively compared.

Furthermore, concentrations of the gases studied were limited to between 1 – 10ppm. This was decided upon by the partners involved in the Woundmonitor project since it was expected that most of the volatiles emitted by the bacteria studied resided within this range. Saturated vapours were occasionally tested but only when the performance of a sensor was suspect. The concentrations used were applicable to the concentrations of wound exudates and were decided as the appropriate range for the scope of this project.

Although some humidity tests were performed for a selection of sensors, an intensive investigation of the effects of water vapour on sensor performance was not carried out. Since it was known that the wound monitor device would sample headspace gases using SPME, the effects of water would be negligible in the hybrid system. Thus humidity tests were deemed superfluous for the purposes of this investigation.

#### 5.4 Results

The results are presented in a number of sections. First, the results obtained from gas testing during sensor optimisation are presented in terms of the concentration-response profiles. The sensitivities calculated from these results are then presented and discussed in terms of the properties of the sensing materials and the volatile organic compounds used for testing. Fig 5.4 illustrates the data obtained from an array of 4 functioning sensors to measurements of 2, 4, 6, 8, and 10ppm ethanol concentrations. The sensor responses were calculated by averaging the response value ( $\Delta R/R_0$ ) for the last 30s of the asymptote achieved before measurements were stopped and air was passed over the sensor (seen in Fig 5.4 as the responses return to baseline).



Fig. 5.4 Example of raw data sensor responses to 2 – 10 ppm ethanol concentrations

These values were collated and averaged for repeated measurements and subsequently used to generate the concentration-response profiles presented here (Section 5.4.1) for each sensor. The error bars represent the sample standard deviation ( $\pm$  1 s.d.) for each of the calculated average responses. Between 5 – 8 measurements were taken for each of the sensors.

Repeatability of the sensors in terms of their performance during gas testing and how similar sensors of the same type behave is discussed in the following section. The results of sensor optimisation, in particular the extensive investigations into the use of different dopant ions, is also presented.

In the final section, the PCA results of the sensor arrays developed is discussed and reasons for sensor choice in the final design are given.

#### 5.4.1 Pyrrole Based Sensors

# 5.4.1.1 Poly-(N-methyl)pyrrole

*N*-methylpyrrole was only made with  $PF_6^-$ . Electrochemical deposition was facile and the polymerisation and redox potentials were the lowest of all the *N*-substituted pyrrole sensors made. In section 4.4.3.1 of chapter 4, the reversibility was shown to be good and conductive films were successfully deposited onto polypyrrole baselayers.



Fig 5.5 Concentration-response profiles for N-methylpyrrole/PF<sub>6</sub><sup>-</sup>

Figure 5.5 displayed the concentration-response profiles generated for *N*-methylpyrrole/PF<sub>6</sub><sup>-</sup> sensors. Sensitivities towards different volatiles change with increasing concentrations. For example, the sensor shows little sensitivity towards acetaldehyde and greatest sensitivity to butyric acid at 2ppm. However, at greater concentrations the sensitivity of the sensors to acetaldehyde is comparatively much greater than for butyric acid. Such differences between sensitivities at different concentrations may indicate the occurrence of different interaction mechanisms between volatiles and sensor material, as well as possible competing factors between these interactions.

# 5.4.1.2 Poly-(N-hexyl)pyrrole

Although *N*-hexylpyrrole was successfully prepared with  $PF_6^-$  electrochemically, a full set of results was unavailable due to breakages in the substrate contacts. Hence, only results obtained for *N*-hexylpyrrole/BF<sub>4</sub><sup>-</sup> are presented, of which the polymerisation potential was lower than for *N*-hexylpyrrole/PF<sub>6</sub><sup>-</sup>. As reported in section 4.4.3.2, the oxidation potential was not clear, but by limiting the cycling potential to lower than 1V, over-oxidation was avoided.



Fig 5.6 Concentration-response profiles for N-hexylpyrrole/BF<sub>4</sub><sup>-</sup>

The concentration-response profiles for *N*-hexylpyrrole/ $BF_4^-$  are presented in Figure 5.6. The three-dimensional ribbon plot is ordered in overall increasing sensor response for clarity. However, the colour coding is kept constant in all figures presented in this section (5.4) for ease of identification.

Butyric acid yielded the greatest sensor responses overall except at 2ppm, where ammonia and butanone showed the greatest responses. Again, the responses were not linear. A general increase was observed but with varying amounts for the different volatiles and significant changes in sensor response were not observed until ca. 6ppm. Of all the volatiles tested, *N*-hexylpyrrole/ $BF_4^-$  was least sensitive to ethanol at all concentrations.

# 5.4.1.3 Poly-(N-dodecyl)pyrrole

In section 4.4.3.3, higher oxidation potentials were observed for *N*-dodecylpyrrole than for *N*-hexylpyrrole and reversibility was poor due to the anodic (oxidising) current always remaining much greater than the cathodic (reducing) current. Despite this, working sensors were achieved and tested with the calibration gases. Low responses were observed; due to the poor reversibility, higher resistance sensors were difficult to manufacture and sensor variability was greater.

The response profiles for each volatile (shown in Figure 5.7) were all similar with the greatest change in response from 2ppm to 4ppm and smaller increments in sensor response with each higher concentration tested. Only responses to ethanol progressed from 4ppm in a linear fashion to give the greatest response at 10ppm.



Fig 5.7 Concentration-response profiles for N-dodecylpyrrole/PF<sub>6</sub><sup>-</sup>
### 5.4.1.4 Poly-(N-pentafluorobenzyl)pyrrole

*N*-pentafluorobenzylpyrrole was initially investigated using TsO<sup>-</sup> as the dopant. Some gas testing results were obtained but since the polymerisation potential was too high and generally yielded sensors that produced noisy signals,  $PF_6^-$  was used as a dopant. Although separate dopant investigations were conducted later, as reported in the previous chapter (section 4.7), gas testing was not performed due to faulty substrates. Therefore the results of *N*-pentafluorobenzylpyrrole/TsO<sup>-</sup> and *N*-pentafluorobenzylpyrrole/PF<sub>6</sub><sup>-</sup> are presented here.

In order to electrochemically deposit *N*-pentafluorobenzylpyrrole using TsO<sup>-</sup> as the counter ion, a potential step method was used with small time intervals (no greater than 5s) in order to avoid degeneration of the base layer and electrodes. Appreciable sensor responses resulted from gas testing and are presented in Fig. 5.8. The sensor was most sensitive to butanone and least sensitive to acetic acid, acetone and acetaldehyde. Although using  $PF_6^-$  produced more reliable *N*-pentafluorobenzylpyrrole sensors, the gas testing results, shown in Figure 5.9, are comparable to those obtained with the *N*-pentafluorobenzylpyrrole/TsO<sup>-</sup> sensors with only slightly higher responses.



Fig 5.8 Concentration-response profiles of N-pentafluorobenzylpyrrole/TsO<sup>-</sup>



Fig 5.9 Concentration-response profiles for N-pentafluorobenzylpyrrole/PF<sub>6</sub><sup>-</sup>

# 5.4.1.5 Poly-(N-phenyl)pyrrole

The combined sensor responses obtained for *N*-phenylpyrrole sensors made with a variety of counter ions is reported later in this chapter in section 5.8.3. In summary, butyric acid generally produced the largest responses and acetone the lowest. *N*-phenylpyrrole/TsO- produced the greatest responses but the concentration-response curve for different volatiles were quite similar to each other with little variation.

### 5.4.1.6 Poly-(3-hexyl)pyrrole

3-hexylpyrrole sensors were successfully made with  $PF_6^-$  as the dopant. Although weak redox potentials were found, resistances of ca.  $2k\Omega$  were achieved and working sensors were tested with the calibration gases. 3-hexylpyrrole sensors were made with  $BF_4^-$ , however no clear redox potentials were obtained and sensors were mostly over-oxidised as reported in section 4.4.3.6. Therefore 3-hexylpyrrole/ $BF_4^-$  sensors were not tested.

The concentration-response profiles are shown in Figure 5.10. The sensors were most responsive to butanone and least responsive to acetone. The sensing range was also found to be quite varied; significant increases in sensor response were found for butyric acid, butanone and ammonia over all concentrations, whereas acetone and acetic acid did not produce significant responses below 6ppm.



Fig 5.10 Concentration-response profiles for 3-hexylpyrrole/PF<sub>6</sub><sup>-</sup>

### 5.4.1.7 Poly-(3-dodecyl)pyrrole

3-dodecylpyrrole sensors were successfully made with  $PF_6^-$  dopant but not with  $BF_4^-$ ; the redox potentials were too varied and a reliable set sensors for testing was not achieved (see section 4.4.3.7).

Facile deposition and decent reversibility using  $PF_6^-$  as a dopant meant that sensors could be reliably fabricated and their dopant level could be well controlled. Due to the decent amount of electrochemical control afforded by the reversibility, the sensors were able to be dedoped enough to produce working high resistance sensors, which yielded relatively large signal responses. However, it was found that saturation occurred too readily the higher the

resistances of the sensors. Therefore, more conductive sensors were employed in order to maximise the dynamic range.

Concentration-response profiles are shown in Figure 5.11. 3-dodecylpyrrole/ $PF_6^-$  sensors were most sensitive to butyric acid and acetic acid, and least sensitive to acetone. Measurement repeatability and sensor reproducibility was also found to be good as discussed in sections 4.5 and 5.6.



Fig 5.11 Concentration-response profiles for 3-dodecylpyrrole/PF<sub>6</sub><sup>-</sup>

# 5.4.1.8 Poly-(3-hexanoyl)pyrrole

Initial investigation of 3-hexanoylpyrrole sensors showed variable redox potentials and poor reversibility, which prompted a further study of the polymer with different dopants. So, as with *N*-phenylpyrrole, the gas testing results are not presented here since they are discussed later in section 5.8.2. In general, it was found that sensors were most responsive to butyric acid and butanone, and least responsive to acetone.

### 5.4.1.9 Poly-(3-dodecanoyl)pyrrole

3-dodecanoylpyrrole sensors were made using  $PF_6^-$  dopant and tested. In section 4.4.3.9, it was reported that the redox potentials were varied and polymer oxidation level was consequently difficult to control. Due to this the gas testing results obtained were quite variable and sensor repeatability was poor in comparison to the other sensors described here.

 $BF_4^-$  was also used as a counter ion but no redox potentials were observed during polymerisation and deposition, so the sensors produced were often over-oxidised and were often of such low resistance that they were not fully tested with the calibration gases.

Despite the variability of sensor responses, 3-dodecanoylpyrrole/ $PF_6^-$  sensors were generally most responsive to butyric acid and least responsive to acetone, as can be seen in Figure 5.12. The shapes of the concentration-response profiles were also similar for all of the volatiles tested.



Fig 5.12 Concentration-response profiles for 3-dodecanoylpyrrole/PF<sub>6</sub><sup>-</sup>

#### 5.4.2 Polythiophene Sensors

### 5.4.2.1 Poly-(3-methyl)thiophene

The polymerisation potential of 3-methylthiophene/ClO<sub>4</sub><sup>-</sup> was too high (1.3 - 1.4V) to use cyclic voltammetry for polymer deposition (see section 4.9.1.1). A set of sensors were made in an attempt to deposit 3-methylthiophene/ClO<sub>4</sub><sup>-</sup> as a top layer onto a polypyrrole base layer by using a potential step method with small time intervals, as was performed for *N*-pentafluorobenzylpyrrole deposition where the polymerisation potential was also too high for reliable deposition via voltammetric methods.

The effectiveness of polymerisation and deposition was not clarified but the sensors produced were tested nonetheless. Concentration-response profiles are shown in Figure 5.13. Relatively low sensor responses were found and most of the volatiles tested did not produce a significant change in response below 6ppm. As was found for the majority of polypyrrole based sensors, the highest sensitivity was towards butyric acid and the lowest towards acetone.



Fig 5.13 Concentration-response profiles for poly-3-methylthiophene/CIO<sub>4</sub><sup>-</sup>

#### 5.4.2.2 Poly-2,2'-bithiophene

As for 3-hexanoylpyrrole and *N*-phenylpyrrole sensors, sensors of 2,2'-bithiophene were investigated using a different dopants, reported later in section 5.8.4. Hence the results are not presented here. In summary, sensors of 2,2'-bithiophene/ClO<sub>4</sub><sup>-</sup> showed largest responses towards butyric acid and lowest to acetone, as was common for most of the polypyrrole based sensors. However, responses to acetic acid and ethanol were comparatively greater than those found with polypyrrole sensors. Overall, sensor responses were low, thus an investigation into the use of other dopants was undertaken to improve the magnitude of response.

# 5.4.2.3 Poly-3,4-ethylenedioxythiophene [PEDOT]

PEDOT sensors were made with  $PF_6^-$  as the dopant ion. Polymerisation potentials were found to be lower than for 2,2'-bithiophene/ClO<sub>4</sub><sup>-</sup> and the reversibility was excellent (see section 4.9.1.1, Table 4.29). Thus oxidation levels could be controlled better and there was less variability between sensors.



Fig 5.14 Concentration-response profiles for PEDOT/PF<sub>6</sub><sup>-</sup>

 $PEDOT/PF_6^-$  sensors were investigated more exhaustively using the hybrid device; few results were obtained using the gas testing rig. A couple of sensors were briefly tested using the gas rig at concentrations of 2ppm, 5ppm, and 10ppm. The results presented in Fig 5.14 show the results found using the gas rig. Since less data was gained for analysis at a limited set of concentrations, the results were cubically interpolated for graphical presentation.

Reversibility of  $PEDOT/PF_6^-$  was found to be excellent and only small variations were observed between sensors. Although sensor responses were low, the separation of signals produced from the different volatiles was encouraging. The sensors were least sensitive to acetic acid and most sensitive to butanone and ethanol (above 5ppm).

# 5.4.3 Other Sensor Types

# 5.4.3.1 SNS/NSA

SNS polymer sensors were made using NSA as the counter ion and were deposited using chronoamperometry as reported in section 4.9.3. The concentration-response profiles are shown in Figure 5.15. The sensors demonstrated very high sensitivity to ammonia and



Fig 5.15 Concentration-response profiles for SNS/NSA

were least sensitive to butanone and acetic/butyric acid. The low sensitivity to these volatiles contrasts the pyrrole based sensors and the sensitivity to ammonia was an attractive feature for incorporation into the final sensor array for prototype testing.

The responses could be easily improved by increasing the film thickness, however, it was found that in doing so, the recovery time of sensor responses to ammonia were substantially increased from minutes to a matter of hours. Higher resistance sensors were tested later using the hybrid device since it was assumed that the increased operating temperatures would reduce overall recovery times and the concentrations of ammonia vapour produced from samples tested would be significantly less than those tested using the gas rig.

### 5.4.3.2 Plexcore<sup>™</sup>

The concentration-response profiles generated from gas-testing of the printable ink polymer, Plexcore, is presented in Figure 5.16.



Fig 5.16 Concentration-response profiles for Plexcore

#### 5.4.3.3 Panipol<sup>™</sup>

The concentration-response profiles generated from gas-testing of the printable ink polymer, Panipol, is presented in Figure 5.17.



Fig 5.17 Concentration-response profiles for Panipol

### 5.5 Sensitivities To The Calibration Gases

# 5.5.1 Definition of "Sensitivity"

The definition of the term "sensitivity" has itself been under scrutiny within the scientific community and controversy over its precise meaning and its use has arisen, particularly in relation to response-dose profiles. Some organisations, such as the International Federation of Clinical Chemistry and Laboratory Medicine (IFCC) and Clinical and Laboratory Standards Institute (CLSI), define sensitivity in terms of the detection limit achievable, i.e. the smallest response resolvable within a given confidence interval. Alternatively, institutions such as the International Union of Pure and Applied Chemistry

(IUPAC) specifically define sensitivity as the rate of change of response for a small change in stimulus (eg. concentration); the gradient of the response-dose calibration curve. [5.51]

Ekins and Edwards vehemently argued in favour of the detection limit interpretation of sensitivity, describing the "slope" definition as "untenable" and leading to "many absurdities and confusion". [5.52] The authors, in their work on ligand assay design and optimisation, constrained the meaning of sensitivity to the "resolving power at zero dose". They proposed that the maximal sensitivity is achieved when the imprecision of zero dose is least and that this value represents the most appropriate identifier of the ability of a system to respond to small stimulus.

In the article following this, Pardue presented a counterargument in support of the slope definition and justifies its use on the basis of its consistency with the formal definition, its historical precedence, and the amount of information that is afforded over the detection limit definition. [5.53] The quotient of measurement error and sensitivity (described as the quantitative resolution) represents the uncertainty in sensitivity and can be calculated for different values, and is independent of the coordinate frame in which the response-dose curve is plotted. The principles can be applied to nonlinear systems, where both values can offer valuable information that can be used in the design of an analytical method.

### 5.5.2 Data Presentation

The concentration-response profiles presented in the preceding pages showed that the curves were not linear, generally tending towards saturation at concentrations above 8 ppm. Therefore the use of the gradient of a linear trend line through all the data points would not be comprehensively representative of the sensitivities of sensors for the entire range tested. More informative sensitivity curves and their corresponding qualitative resolution plots are presented in Appendix 2 for each of the calibration gases used. Where sensors with more than one dopant were tested, only those of  $PF_6^-$  are compared in order to eliminate any influence of different dopants on the sensitivities of sensors and focus on the

inherent gas sensing properties of the sensor series. Results are also separated into four categories of *N*-substituted polypyrrole sensors, 3-substituted polypyrrole sensors, polythiophene based sensors and other sensors (copolymer and commercial printing conducting polymers). This is done so as to make visual comparison easier overall and between different sensor types.

# 5.5.3 General Observations From Sensitivities

In general, the sensitivities decrease with concentration and the qualitative resolutions tend to be lower for more sensitive sensors. This is apparent from the fact that the measurement errors tend to be larger for the more responsive sensors and increase with concentration.

For the *N*-substituted polypyrrole sensors, *N*-pentafluorobenzylpyrrole can be seen to be most sensitive. Although *N*-hexylpyrrole sensitivities were not as high as for *N*pentafluorobenzylpyrrole, their qualitative resolutions were mostly greater.

The results of the 3-substituted polypyrrole sensors were more consistent across the range of volatiles tested and sensors were generally more sensitive and responses more resolvable. The order of sensitivity was 3-dodecylpyrrole>3-hexanoylpyrrole>3-dodecanoylpyrrole>3-hexylpyrrole, with sensitivities decreasing with concentration except for 3-hexylpyrrole which increased with concentrations above 4ppm. This indicates that the longer alkyl chain substituents increased the overall sensitivities.

The polythiophene based sensors demonstrated the least sensitivities whereas the commercial printing polymers showed some of the highest sensitivities. Panipol (polyaniline) is an n-type polymer therefore its responses were negative. Plexcore and Panipol exhibited similar curves for the volatiles tested, yet they seem to contrast each other well; sensitivity to acetic acid, acetone, and butanone was greater for Plexcore whereas Panipol was more sensitive to acetaldehyde and ammonia than Plexcore. Although the sensitivities of SNS

were lower in comparison, its linear concentration dependent responses are evident from the little variation shown in the curves.

In order to compare the sensitivities of all the sensors in relation to each other, the gradient of a linear fit through the data points up to 6ppm were calculated to give a single numerical index of sensitivity (linear dynamic range sensitivity). This represents the dynamic range for the majority of the sensors before responses tended towards saturation. However, some of the response curves do not increase linearly within this range. For example *N*-hexylpyrrole, 3-hexylpyrrole and 3-methylthiophene responses did not substantially increase with concentration until above 4 – 6ppm and indicated more of a BET adsorption isotherm than the typical Langmuir isotherm asymptote at high concentrations (further investigated in section 5.6). Also, Plexcore and Panipol, although highly sensitive, tended towards saturation at concentrations over 4ppm. For these reasons, the correlation coefficient of the linear fit for data within the limited range (6ppm and below) are quite poor.

In an effort to encompass the entire range of concentrations tested and to overcome the shortcomings of the sensitivities calculated using the linear dynamic range, the slopes of the semi-log plot (response vs. log concentration) were calculated and compared, however, results were less correlated due to the varied nature of the response curves across the entire range of sensors tested.

Since the linear trend at lower concentrations was common to most of the sensors and represented the concentration range of most interest to the application intended, the linear dynamic range sensitivities are used in subsequent analyses and discussions, plotted in Figures 5.18 – 5.24 for each of the volatiles tested. The correlation coefficients are plotted as the dashed line and labelled on each graph; sensitivities are represented as blue column bars.



Fig 5.18 Linear dynamic range sensitivities to acetaldehyde



Fig 5.19 Linear dynamic range sensitivities to acetic acid



Fig 5.20 Linear dynamic range sensitivities to acetone



Fig 5.21 Linear dynamic range sensitivities to ammonia



Fig 5.22 Linear dynamic range sensitivities to butanone



Fig 5.23 Linear dynamic range sensitivities to butyric acid



Fig 5.24 Linear dynamic range sensitivities to ethanol

Overall, the 3-substituted polypyrrole sensors displayed much greater sensitivities to the volatiles tested than the *N*-substituted polypyrrole sensors. This is most likely due to the lower conductivities of the *N*-substituted polypyrroles, arising from the lack of ring planarity, as mentioned previously. [3.3]

Although the polymerisation potentials for pyrroles with shorter alkyl chain substituents were lower than for those with longer alkyl chains, the general sensitivity to the volatiles tested is seen to improve with alkyl chain length: the sensitivities of *N*-methylpyrrole and 3-hexylpyrrole are much lower compared to those of *N*-hexylpyrrole, *N*-dodecylpyrrole and 3-dodecylpyrrole, respectively. This trend is also observable between *N*-hexylpyrrole and *N*-dodecylpyrrole for acetic acid, acetone, and ethanol. However, *N*-hexylpyrrole sensitivity was greater than *N*-dodecylpyrrole for the other volatiles, displaying more selectivity, especially towards butyric acid. It is possible that as the substituent becomes more bulky, steric hindrance becomes a greater factor and impedes the formation of crystalline polymer chains, which can be seen with the increase in polymerisation potential. This in turn reduces the conductivity and the effects are more pronounced for *N*-substituted polypyrroles due to the lack of ring planarity. Thus, despite *N*-hexylpyrrole possessing

shorter alkyl chain substituents than *N*-dodecylpyrrole, its sensitivity to more non-polar volatiles was greater – the steric effects the larger substituent of *N*-dodecylpyrrole made polymerisation more difficult and reversibility poorer, as reported in chapter 4.

Comparison of the sensitivities also reveals that the 3-alkyl substituted polypyrroles were generally less sensitive than their equivalent 3-acyl polypyrroles, more so for the hexyl and hexanoyl substituents than for the larger dodecyl and dodecanoyl substituents. The difference in sensitivity may be due to the added stability that the acyl group imparts to the aromatic pyrrole ring. The results of the polypyrrole sensors tested echoed the results reported by de Lacy Costello [3.4, 3.5, 3.7] with respect to the increasing alkyl chain length and 3-substituted polypyrroles.

The sensitivities of the polythiophene based sensors were all lower than the polypyrrole sensors te ed, especially for PEDOT, which exhibited the lowest sensitivities to all of the volatiles tested. The high polymerisation potential of 3-methylthiophene meant that film fabrication was difficult, therefore it was expected that responses and subsequent sensitivities would be low due to poor film quality. However, sensitivities for poly-2,2'-bithiophene were generally also low despite a lower polymerisation potential and the capability to produce good quality, uniform films repeatably. Although, as discussed in his review [4.53], Roncali pointed out that, contrary to expectation, the use of conjugated precursors, such as 2,2'-bithiophene, does not lead to the same polymers produced using monomeric structures and are also found to be less conductive and less conjugated. [5.54; 5.55] Due to its selectivity towards acetaldehyde and butyric acid, poly-2,2'-bithiophene films were investigated further using dodecyl sulfate as an alternative counter ion in order to increase responses and sensitivities. This is discussed in section 5.9.4.

Despite the low sensitivities of PEDOT, its selectivity towards ethanol was of interest and attempts to improve its responses were made by dedoping electrochemically and through heat treatment. The alkoxy substituent may contribute to its affinity to more polar

compounds as well as the stability of the polymer through delocalisation of the lone pair on the oxygen.

The varied sensitivities found towards the different volatiles tested illustrates the non-specificity of the sensors, which was desirable in the context of electronic nose applications. The following sections compare the various properties of the calibration gases used for testing the sensitivities of the sensors studied.

#### 5.5.4 Influence Of Polarity

The following graphs display the sensitivities plotted against some of the analyte properties that were listed in Table 5.4. The sensitivities of different polymer series are plotted separately for visual clarity and easier comparison.

Figures 5.25 and 5.26 display the sensitivities against the dipole moment (D) and dielectric constant, respectively, for each of the sensor series tested. The dipole moment is a measure of the polarity of a compound, that is, its separation of charge. A dipole moment is a vector in the direction of positive charge and is defined as the charge magnitude times the distance between the two opposite charges. Many compounds possess a permanent dipole and conducting polymer sensors are generally more sensitive to these polar compounds, but can be functionalised with various substituents that can increase sensitivity towards non-polar compounds.

The calibration gases used to test the sensors do not vary dramatically in terms of polarity; acetaldehyde, butanone, and acetone possess similar dipole moments between 2.75D - 2.88D; butyric acid, ethanol, and acetic acid also possess very similar dipole moments between 1.65D - 1.7D. Between these two groups of volatiles, it is generally observed that the sensitivities were greater for more polar compounds (high dipole moments), and in the case of *N*-dodecylpyrrole, *N*-pentafluorobenzylpyrrole, and 3-dodecylpyrrole, an increase in sensitivity was observed between butyric acid, ethanol, and acetic acid.



Fig 5.25 Sensitivities vs. dipole moment (D)

The dipole moments of ethanol and acetic acid, and acetaldehyde and butanone were virtually the same. Consequently, the majority of sensors displayed very similar sensitivities between these volatiles, indicating that the polarity played a notable role in the sensing process, albeit it was not the sole determinant of a sensing mechanism – ammonia sensitivities were comparatively high despite it possessing the lowest dipole moment of the calibration gases used. The higher sensitivity of ammonia could be due to the lone pair, which may aid in a partial charge transfer process with the sensor.

Another common measure of polarity is the relative permittivity of a compound, or dielectric constant. Most of the calibration gases have dielectric constants between 15 - 25 and are considered semi-polar. Acetic acid and butyric acid are considered to be less polar, however, their protic nature may mean that proton transfer processes could occur and comparisons based solely between polar and non-polar species would not conclusive.



Fig 5.26 Sensitivities vs. dielectric constant

With the exception of ethanol ( $\varepsilon = 25.3$ ) some of the sensors demonstrated a correlation between their sensitivities and the increasing dielectric constants of ammonia, 2-butanone, acetaldehyde, and acetone. Although the sensitivities of the *N*-substituted polypyrrole sensors were generally greater for more polar species, the sensitivity towards non-polar species could be increased in the case of 3-hexylpyrrole/PF<sub>6</sub><sup>-</sup> due to the longer alkyl chain substituent. However, the same was not observed for longer chain substituents such as 3-dodecylpyrrole, perhaps due to steric effects or other competing factors regarding its sensing mechanism. Comparison of the 3-substituted polypyrroles showed that the sensitivity towards more polar species was generally higher for the 3-acyl substituted polypyrrole sensors than their equivalent 3-alkyl substituted polypyrroles, as expected in light of the research reported by Delabouglise *et al.* [3.8]

Greater sensitivity towards less polar compounds (lower dielectric constants) were also observed for 3-methylthiophene. As was observed for sensitivities to volatiles with similar dipole moments, the sensitivities of most sensors were very similar for acetaldehyde and acetone, which have nearly the same dielectric constant. Many other scales of polarity have been developed, usually to correlate a more specific model or to better describe solvation processes in chemical reactions [5.56; 5.57] Using the common descriptors of polarity (dipole moment and dielectric constant), although no stark correlations were evident across the series of sensors tested, the above observations indicate that there was some reliance on the polarity of an analyte vapour. Assuming physisorption takes places in the sensing process, it is reasonable to assume that the polarity of an analyte does have a bearing on a sensors affinity to its adsorption, however it is not the determining factor of sensitivity.

#### 5.5.5 Influence Of Hydrophobicity

Related to the polarity of an organic compound is its hydrophobicity/hydrophilicity. With the occurrence of physical adsorption, it is expected that hydrophobic, non-polar volatiles would preferentially interact with sensors that possessed more hydrophobic polymer substituents, and vice versa.

As mentioned in section 5.2.3, a number of systems have been developed for the purpose of quantifying the hydrophobicity of a compound. A common scale utilises the octanol-water partition coefficient ( $K_{OW}$ ) and sensitivities are plotted against these values in Figure 5.27.

According to the log  $K_{ow}$  values, acetone and acetic acid are less hydrophobic than ammonia, butanone, and acetaldehyde; and butyric acid is the most hydrophobic volatile of the calibration gases.

Sensitivities seemingly increased for more hydrophobic volatiles with alkyl chain length in the case of *N*-substituted polypyrroles, but the same trend was not evident amongst the 3-substituted polypyrroles.



Fig 5.27 Sensitivities vs. Log Kow (octanol-water partition coefficient)

There was a slight general increase in sensitivity towards the more hydrophobic ammonia, butanone, and acetaldehye for *N*-methylpyrrole, but a decrease in sensitivity for butyric acid. The sensitivities of *N*-methylpyrrole were all quite small however, and did not vary considerably. The strongest correlation was found for *N*-hexylpyrrole, where sensitivity greatly increased with hydrophobicity according to the log  $K_{ow}$  values. Apart from acetone and butanone, which have lower sensitivities than expected, there was almost a linear trend. The sensitivity towards acetone and butanone, which possess the highest dipole moments, could be due to the hydrophobic character of the alkyl chain substituent along the polymer chain.

Likewise, there was an increase in sensitivity with log  $K_{ow}$  for *N*-dodecylpyrrole, except for butyric acid, for which the lowest sensitivity was found (similar to *N*-methylpyrrole). No correlation was apparent for *N*-pentafluorobenzylpyrrole; the sensitivities were varied. However, *N*-phenylpyrrole showed some increase in sensitivity with log  $K_{ow}$  if one ignores the higher sensitivities of acetone and acetic acid.

The same trends were not found for the 3-substituted polypyrroles, except that butyric acid yielded the lowest sensitivity for all sensors except 3-hexylpyrrole, which was most sensitive to butyric acid. The acidity and large molecular size could account for the disparities observed.

Again, no obvious correlation was observed for polythiophene based sensors but a similarity in relative sensitivities was found between poly(3-methylthiophene) and poly(2,2'-bithiophene), except where poly(2,2'-bithiophene) showed a selectivity towards acetaldehyde. PEDOT was generally more sensitive to the more hydrophilic ethanol, acetone, and acetic acid. Similarly, Plexcore was generally more sensitive to more hydrophilic volatiles, except for ethanol.

Log  $L^{16}$  is another measure of hydrophobicity and is a measure of the partition coefficient between hexadecane and the vapour;  $L^{16}$  is the solute Ostwald solubility coefficient in n-hexadecane at 25°C. Since the model is based on liquid phase separation, it was thought that it would be more applicable to the gas-solid interactions between analyte and sensor material. The log  $L^{16}$  scale itself presented a more even spread than the log  $K_{ow}$ scale and the hydrophobicity of the volatiles used was representatively more dispersed, with acetone and acetic acid having the closest values. In fact, most of the sensitivities were very similar for these volatiles, akin to the similarities found between acetaldehyde and acetone, which have similar dielectric constants. However, besides *N*-methylpyrrole and 3hexylpyrrole exhibiting a slight decrease, and *N*-phenylpyrrole an increase, in sensitivity with log  $L^{16}$ , no obvious correlations were observed for any of the other sensors using this scale.

It would be more comprehensive to describe solubility properties of the gaseous analytes in the polymers via a collection of coefficients such as solute dipolarity, polarisability correction terms, hydrogen-bond acidity and basicity, rather than relying on one descriptor (eg. L16). As utilised by Abraham *et al.* [5.50], a general equation that encompasses these various attributes can be used to describe polymer-solute interactions more completely, however this would be a matter for further research.

#### 5.5.6 Influence Of Acidity

Of the calibration gases tested, only acetic acid and butyric acid possess protic hydrogens and they are considered only to be weakly acidic. Conversely, ammonia is the only volatile tested that has an appreciable basicity. The other volatiles are considered to be aprotic.

If proton transfer processes were the predominant mechanism of interaction, it would be expected that the sensitivities of butyric acid, acetic acid, and/or ammonia would be higher than for the aprotic compounds. This was not observed for any of the sensors tested, except for SNS which displayed a degree of selectivity towards ammonia. This particular sensitivity towards ammonia may be due to the nucleophilicity imparted on the pyrrole nitrogen during the oxidation/doping process.

Even Panipol (polyaniline), which has been shown to be sensitive to acids and bases [5.14], did not display increased sensitivity towards the more acidic/basic volatiles used.

On average, the sensitivities were much greater for butyric acid than acetic acid. If proton transfer processes were a contributory factor in the sensitivity of the sensors, greater similarity between butyric acid and acetic acid would be expected – this was not observed.

#### 5.5.7 Influence Of Molecule Size

Sensing processes involving physical interaction and incorporation of the analytes within the polymer matrix have been reported to be correlated to the size of the analyte molecules. [5.14; 5.17] Certainly, where swelling phenomena have been proposed as mechanisms of polymer sensing, the importance of molecular size cannot be overlooked; the efficacy of analyte diffusion into the polymer matrix would intuitively be governed by size and shape as well polarity/hydrophobicity.

Zeng *et al.* [5.58] also reported their conducting polymer composite gas sensors as having discrimination capabilities governed by molecular size for low permittivity vapours. This behaviour was accounted for in terms of size/shape fit between analyte-polymer, as well as the hydrophobic cavities of the  $\beta$ -cyclodextrin composite material.

The sensitivities were plotted against the molecular radius of the tested analyte (Figure 5.2). With the exception of ammonia and butyric acid, to which sensors displayed varied sensitivities, a general increase in sensitivity with molecular radius was noticed for the polypyrrole based sensors. Very similar sensitivities were also observed between acetic acid and acetone, which have the same molecular radius, except for 3-dodecylpyrrole. The exception of 3-dodecylpyrrole can be explained by its sensitivity to differences in polarity, discussed earlier.

The polythiophene based polymers, Plexcore, and Panipol do not correlate with molecular radius, but SNS sensitivities decreased for larger molecules, except in the case of butyric acid.



Fig 5.28 Sensitivities vs. Molecular radius (nm)

The AFM results of the polypyrrole sensors reported in section 4.4.5 were compared with their corresponding sensitivities, however correlations were not generally observed. With the exception of 3-hexanoylpyrrole and 3-dodecanoylpyrrole, which displayed relatively high sensitivity, the sensitivity decreased with surface roughness, contrary to expectation. Additionally, with the exception of *N*-phenylpyrrole, sensitivities decreased with grain diameter. This could be due to a reduction in grain boundaries.

However, the combined effects of the different sensitivities to polarity and hydrophobicity, as well as the different degrees of oxidation achievable, means that comparisons cannot be based solely upon surface morphology. A more thorough investigation into surface morphology between the same series sensors would be more informative.

### 5.6 BET Isotherm Fit

In section 5.5.3 it was observed that the profiles of *N*-hexylpyrrole, 3-hexylpyrrole, and 3-methylthiophene displayed responses that were more characteristic of a BET adsorption isotherm. In order to evaluate this, the data is fitted here using a BET plot. The BET adsorption expression was given in section 5.1.2.2. It can be reorganised into the following form [5.22]:

$$\frac{z}{(1-z)V} = \frac{1}{cV_{mon}} + \frac{(c-1)z}{cV_{mon}}$$

Thus, a plot of the left hand expression, z/(1 - z)V, against *z* should give a straight line with a slope of  $(c - 1)/cV_{mon}$  and intercept  $cV_{mon}$ . The results can then be combined to give the BET constant, *c*, and the volume of monolayer coverage,  $V_{mon}$ . In order to use the BET plot for evaluation with the data obtained from gas testing, the relative saturation term, *z*, was equated to the concentration of the analyte and the volume of adsorbed molecules, *V*, was equated to the percentage response found (%dR/R<sub>0</sub>). An example BET plot of 3-methylthiophene/ClO<sub>4</sub><sup>-</sup> responses to acetaldehyde is shown in Figure 5.29.



Fig 5.29 BET plot for 3-methylthiophene/ClO<sub>4</sub> responses to acetaldehyde

Table 5.6 lists the results found from the BET plot with a linear least squares fit applied through the data points. 3-methylthiophene/ $CIO_4^-$  results demonstrated the best fit, but butyric acid responses did not fit a BET isotherm for any of the sensors tested.

Table 5.6 BET Plot results

	Correlation coefficient [R <sup>2</sup> ]	(c – 1)/cV [gradient]	cV [intercept]
	N-hexylpyrrole/BF <sub>4</sub>		
Acetaldehvde	0.884	61.94	-1.63
Acetic Acid	0.857	3.03	-4.60
Acetone	0.866	75.51	-7.70
Ammonia	0.875	1054.00	-2.99
Butanone	0.903	6.37	-1.60
Butyric Acid	0.555	1.75	-7.50
Ethanol	0.881	4.34	-2.07
	3-hexylpyrrole/PF <sub>6</sub>		
Acetaldehyde	0.897	90.35	-2.41
Acetic Acid	0.888	1.78	-2.92
Acetone	0.957	28.80	-3.19
Ammonia	0.863	1108.00	-3.09
Butanone	0.902	8.02	-1.93
Butyric Acid	0.665	0.42	-2.00
Ethanol	0.860	8.01	-3.41
	3-methylthiophene/ClO <sub>4</sub> <sup>-</sup>		
Acetaldehyde	0.961	221.00	-6.56
Acetic Acid	0.917	2.94	-5.49
Acetone	0.955	61.75	-7.84
Ammonia	0.929	2376.00	-7.40
Butanone	0.920	27.68	-6.94
Butyric Acid	0.791	1.41	-6.81
Ethanol	0.941	17.52	-7.93

#### 5.7 Measurement Repeatability and Sensor Reproducibility

In section 4.5 on sensor variability, a general trend between the typical base resistance of sensors and the amount of variation found between sensors of the same type was observed. Although there were some exceptions to this observation, the assumption mostly held true throughout the course of investigation. The variation that occurred was explained as arising from the stability of the oxidation process during electrochemical polymerisation and doping.

The following section parallels the findings reported in chapter 4 on sensor variability and further demonstrates the correlations between base resistance of a sensor, its measurement reproducibility and electrochemical parameters. The variations were measured between sensors of the same type, on both the same array (sensor-to-sensor repeatability) and different arrays (sensor array reproducibility). The measurements involved calculating the mean values and standard deviation of measurement for every volatile tested at each concentration. The collated values were used to find the average sensor response variation and the coefficient of correlation, or relative standard deviation (RSD expressed as a percentage), was used for comparison with the values reported in Table 4.19 of chapter 4.



Fig 5.30 Resistance vs. sensor response variations between different arrays

Figure 5.30 is a plot of the variability of same-type sensors between different arrays against the variation in sensor response between those sensors. The linear trend line shows that the greater the variation in base resistance, the greater the variation in sensor response. From the general trend stated in section 4.5, it can be assumed that, in the main, higher resistance sensors will have less measurement repeatability.

3-dodecylpyrrole/PF<sub>6</sub><sup>-</sup> (marked in Fig 5.30) is an outlier with a high sensor response variability but low resistance variability. Although clear redox potentials and a decent reversibility were found, large resistances were achievable, which could be repeatably achieved through controlled deposition (section 4.4.3.7). Due to high resistances, the sensitivity of the sensor was greater and responses were more variable. The value was excluded for the purposes of curve fitting.

As stated in section 4.5, sensor variability was much less when sensors were made as duplicates on the same array. The many parameters that affect the properties of a sensor during fabrication remained much more constant whilst using the same array during an experiment than between different arrays, made at different times for later experiments. This same observation applies for sensor response variability as is clearly demonstrated in the following plots.



Fig 5.31 Resistance vs. sensor response sensor to sensor variation (same array)

The highlighted markers in Figure 5.31 represent the polymer sensors of 3dodecylpyrrole, 2,2'-bithiophene and *N*-hexylpyrrole doped with SDS. These were excluded for curve fitting. It was explained in section 4.7.2 that SDS was studied as a counter ion and its use enabled a decent amount of control over the doping of the polymer sensors. Sensors with reasonably high resistances and sensitivities were produced and could be made reproducibly. Therefore, despite the large resistance variation, particularly for *N*-hexylpyrrole/ SDS, the sensors performed reliably with decent repeatability in terms of measurement.

The oxidation potential and currents of 3-dodecylpyrrole/SDS varied substantially, however over-oxidation did not result and resistances were relatively low and repeatable.



Fig 5.32 Variability of sensor response and oxidation potentials

The right hand plot of Figure 5.32 displays the plot of oxidation potential variation vs. variation of the sensor responses. The sensors 3-dodecylpyrrole/PF6 and 3-dodecanoylpyrrole/PF<sub>6</sub><sup>-</sup> are highlighted as outliers and were excluded for curve fitting the linear trend line. Although the variability in oxidation potential was low for 3-dodecylpyrrole/PF<sub>6</sub><sup>-</sup> sensors, the variability in anodic current was high. This reduces the amount of control afforded over the oxidation process and therefore the response variation

was found to be high. Similarly, the anodic current variability was high for 3dodecanoylpyrrole/ $PF_6^-$  despite its low variation in oxidation potential.

The relationship between the variation in anodic current and sensor response variability is shown in Fig 5.33, which also displays a linear trend as for oxidation potential variation. It is clear from Figure 5.33 that the variability of anodic current affects the repeatability of sensor responses in the same manner as variability of oxidation potential. In the left hand plot, which displays the anodic current variation against the sensor response variation, three outliers are highlighted: N-dodecylpyrrole/PF<sub>6</sub><sup>-</sup>, 3-hexanoylpyrrole/CIO<sub>4</sub><sup>-</sup>, and 3-hexylpyrrole/PF<sub>6</sub><sup>-</sup>. Despite *N*-dodecylpyrrole/PF<sub>6</sub><sup>-</sup> having little variation in anodic current, the reversibility based upon the current ratio and the charge ratio was very poor. No matter how stable the redox potentials, the lack of reversibility made repeatable deposition of sensors with little variation difficult via voltammetric methods. For 3-hexylpyrrole/PF<sub>6</sub><sup>-</sup>, the reversibility based on charge ratio was also very high, causing a high variation in sensor properties. Similarly, 3-hexanoylpyrrole/CIO<sub>4</sub><sup>-</sup> showed varied oxidation potentials and current, and was an irreversible system, therefore sensor reproducibility was poor.



Fig 5.33 Variability of sensor response and anodic current



Fig 5.34 Variability of sensor response and reversibility based on current ratio

In light of these relationships it is apparent that the reversibility of the electrochemical process used to fabricate the sensors fundamentally governs the reproducibility of sensors and the variation in responses. Figures 5.33 and 5.34 demonstrate this.

*N-d*odecylpyrrole/PF<sub>6</sub><sup>-</sup> and 3-dodecylpyrrole/PF<sub>6</sub><sup>-</sup> are treated as outliers in the left hand plot of current ratio against response variation in Figure 5.34, and in the right hand analogous plot for duplicate sensors, 3-hexylpyrrole/PF<sub>6</sub><sup>-</sup> and 2,2'-bithiophene/CIO<sub>4</sub><sup>-</sup> are excluded. It was explained earlier that the anodic current variability was large for 3dodecylpyrrole/PF<sub>6</sub><sup>-</sup> and its typical resistance was high, so sensor responses were quite varied. *N*-dodecylpyrrole/PF<sub>6</sub><sup>-</sup> was reported to have a poor reversibility, however, in section 4.4.3.3 it was explained that since the potentials of polymerisation and oxidation coincided, the peaks were difficult to distinguish. Therefore the reversibility may have been better than the values reported, hence the lower response variation. Although the reversibility based on the current ratio was low for 3-hexylpyrrole/ $PF_6^-$ , its reversibility based on charge ratio was very large (see Figure 5.35), thus repeatability of sensor response was poor. It is not known why the variability of 2,2'-bithiophene/ $ClO_4^-$  was so low. Nevertheless, the value was treated as an anomaly and disregarded for curve fitting.



Fig 5.35 Variability of sensor response and reversibility based on charge ratio

### 5.8 Dopant Investigation

### 5.8.1 PF<sub>6</sub> vs BF<sub>4</sub>

The majority of sensors made using  $BF_4^-$  as the counter ion did not function. The reason for this may be due to over-oxidation. 3-hexylpyrrole/ $BF_4^-$  had a lack of any redox peaks; 3-dodecylpyrrole/ $BF_4^-$  redox peaks were broader and more varied than for PF6 and oxidation levels were consequently difficult to control. Similarly, 3-dodecanoylpyrrole/ $BF_4^-$  redox peaks were difficult to observe and control.

Also, sensor substrates were relatively fragile and damage often occurred during use which prevented the measurement of some sensors. Although the substrates themselves were flexible and robust, and the polymer depositions usually adhered well to the substrate, the gold tracks used to connect the sensors to the circuitry of the sampling unit were prone to hairline fissures which prevented continuity. This occurrence was problematic, especially with a certain batch of substrates, and many efforts to create a fully functional series of eight sensors on an array were in vain. Therefore, the majority of sensors made with  $BF_4^-$  described in the previous chapter were not tested and not enough results were gained from the few functional sensors to justify any comparisons. Thus, in anticipation of such problems, multiple sensor arrays were later made and tested as a fail-safe and also as a means of evaluating the reproducibility and repeatability of the sensors.

### 5.8.2 3-hexanoylpyrrole with different dopants

Due to initial difficulties in polymerisation and oxidation control, 3-hexanoylpyrrole sensors were fabricated with  $PF_6^-$ ,  $BF_4^-$ ,  $CIO_4^-$  and  $TsO^-$  counter ions and tested with the calibration gases. Concentration-response profiles are presented in Figure 5.36 and the sensitivities calculated from these are plotted in Figure 5.37.

It was reported in chapter 4 that 3-hexanoylpyrrole deposition was not possible with TsO<sup>-</sup> dopant, however the sensor continued to function after electrochemical attempts to deposit 3-hexanoylpyrrole/TsO<sup>-</sup>. Although it is unclear whether deposition was successful, the sensor was tested regardless and results are presented here for comparison. Polymerisation with  $PF_6^-$  and  $BF_4^-$  was easiest and it can be seen that 3-hexanoylpyrrole sensors made with these dopants exhibited the greatest overall sensitivity to the tested volatiles. For sensors made using  $CIO_4^-$  counter ion, the reversibility was poor and the polymerisation potential high. Consequently, the sensitivity was lower in comparison with the 3-hexanoylpyrrole/PF\_6^- and 3-hexanoylpyrrole/BF\_4^-, sensors. Also, the concentration-response profiles of 3-hexanoylpyrrole/CIO\_4^- sensors were very similar for all the tested volatiles.



**Fig 5.36** Concentration-response profiles for 3-hexanoylpyrrole with different dopants. Sensor responses are averaged from 5 repeated measurements and the error bars represent  $\pm$  1 s.d.

With the exception of 3-hexanoylpyrrole/TsO<sup>-</sup> for which successful deposition was dubious, the sensors displayed relatively similar sensitivities to the tested volatiles, which corroborates with a fact that has been stated in a number of conducting polymer sensor reviews:

"Changing the dopant ion in the conducting polymer has a large effect on absolute sensor sensitivity but does not markedly affect the relative sensitivity toward different analyte functional groups." [5.59; 5.60]

The greatest sensitivity was found for acetaldehyde, acetone, and butanone and least sensitivity to butyric acid. These sensitivities correlate well with the dipole moment of the volatiles.



Fig 5.37 Linear slope sensitivities for 3-hexanoylpyrrole with different dopants
## 5.8.3 N-phenylpyrrole

Polymerisation potentials for *N*-pentafluorobenzylpyrrole and *N*-phenylpyrrole were initially too high for reliable deposition using cyclic voltammetry, most likely due to steric effects of the bulky substituents on the nitrogen. So it was decided to investigate the polymerisation and sensing properties of these pyrroles with different dopant ions in an effort to reduce their polymerisation potential and improve responses to the volatiles.

Although *N*-pentafluorobenzylpyrrole polymer sensors were made using a variety of different dopants, breakages in the substrate prevented the array from being tested on the gas rig. Fabrication of the sensors were not repeated for testing due to the difficulties in polymerisation and it was decided to focus attention on other polymer sensors which showed more promise.

An array of *N*-phenylpyrrole sensors was successfully made with different dopants and subsequently tested on the gas rig with the chosen calibration gases. Highest responses and sensitivities were observed for *N*-phenylpyrrole/TsO<sup>-</sup> despite the high polymerisation potentials found. In order to deposit the polymer, it was necessary to use a number of potential steps at high potentials (ca. 1.4V) for brief periods of time (<5s). Although a polymer film was achieved via this method, the sensor soon degraded and signals were generally quite noisy in comparison with *N*-phenylpyrrole sensors made with the other dopants. Concentration-response profiles for the sensors are shown in Figure 5.38.

Contrary to the results of 3-hexanoylpyrrole with different dopants, the relative sensitivities of the *N*-phenylpyrrole sensors with different dopants were vastly different to each other. This is thought to be due to a difference in film quality arising from the different polymerisation potentials achievable with the various dopants investigated, rather than inherent gas sensing properties of the polymer sensors themselves.



**Fig 5.38** Concentration-response profiles for N-phenylpyrrole with different dopants. Sensor responses are averaged from 5 repeated measurements and the error bars represent  $\pm 1$  s.d.

Figure 5.39 displays the sensitivities calculated for the sensors with each tested volatile. Due to the large difference in sensitivities and responses between *N*-phenylpyrrole/TsO<sup>-</sup> sensors and the other *N*-phenylpyrrole sensors, Fig 5.40 presents the same data without *N*-phenylpyrrole/TsO<sup>-</sup> results for clearer comparison.

The relative sensitivities for sensors made with OTf and  $CIO_4^-$  dopants displayed the closest similarity except for acetaldehyde, to which *N*-phenylpyrrole/ $CIO_4^-$  was least sensitive. The sensitivities of sensors made using these dopants also reflected some correlation to hydrophobicity in terms of the log  $K_{OW}$  scale; the sensitivities were generally greater for more hydrophobic volatiles.

Sensors other than *N*-phenylpyrrole/TsO<sup>-</sup> all displayed a selectivity towards butyric acid. This was not thought to be due to acidity because sensitivities to acetic acid were comparatively much lower. Other than the sensitivity to hydrophobicity, it is not clear why such selectivity towards butyric acid occurred and a more thorough investigation would be required to gain insight into the mechanisms responsible for this behaviour.



**Fig 5.39** Linear slope sensitivities below 6ppm for N-phenylpyrrole sensors with different dopants



phenylpyrrole/TsO<sup>-</sup> data omitted

# 5.8.4 SDS dopant investigations

Figure 5.41 displays the averaged response curves for each of the sensors investigated with SDS; left hand plots represent the sensors initially studied and right hand plots are the corresponding response-concentration profiles for the sensor made using the SDS counter ion.

Note that response axes differ for 3-dodecylpyrrole and 2,2'-bithiophene in order to demonstrate the measurement errors clearer.

In the case of *N*-hexylpyrrole, using SDS enabled a more conductive polymer. In contrast to *N*-hexylpyrrole/BF<sub>4</sub><sup>-</sup>, *N*-hexylpyrrole/SDS sensors gave lower responses over the entire concentration range tested but significant changes in response occurred at lower concentrations and tended towards saturation above 6ppm.

*N*-dodecylpyrrole responses were improved by using SDS. Although similar response curves were obtained, the difference in response to different volatiles was greater than for *N*-dodecylpyrrole/PF<sub>6</sub><sup>-</sup>. This was possibly due to the ability to control the oxidation level better with the larger SDS counter ion than  $PF_6^-$ , thus higher resistances and more stable sensors were achievable. The improved stability also increased the quantitative resolution of the sensitivities of the sensors.

As for *N*-hexylpyrrole, responses for 3-dodecylpyrrole were reduced using SDS due to an increased conductivity. This allowed for a more stable signal without too much reduction in response, since the typical resistances of 3-dodecylpyrrole/ $PF_6^-$  were relatively large. In Figures 5.42 – 5.45, the sensitivities for each of the sensors made using SDS are compared with the sensitivities previously calculated with the dopant they were originally made with.



Fig 5.41 Concentration-response curves for sensors studied with SDS as dopant



*Fig 5.42 Relative sensitivities of N-hexylpyrrole/BF*<sup>4</sup> *and N-hexylpyrrole/SDS* 



Fig 5.43 Relative sensitivities of N-dodecylpyrrole/PF<sub>6</sub><sup>-</sup> and N-dodecylpyrrole/SDS



Fig 5.44 Relative sensitivities of 3-dodecylpyrrole/PF<sub>6</sub><sup>-</sup> and 3-dodecylpyrrole/SDS



**Fig 5.45** Relative sensitivities of 2,2'-bithiophene/CIO<sub>4</sub><sup>-</sup> and 2,2'-bithiophene/SDS

The responses of 2,2'-bithiophene were significantly improved using SDS in comparison with  $CIO_4^-$ . Remarkably stable, high resistance sensors were achievable and significant response changes were observed for lower concentrations.

With the exception of 3-dodecylpyrrole/SDS, the use of SDS as a dopant ion considerably increased the overall sensitivities of the polymers studied. 3-dodecylpyrrole/SDS sensitivities were slightly lower than for 3-dodecylpyrrole/ $PF_6^-$ , except in the case of acetic acid, to which it was most sensitive.

In contrast to the previous studies using different dopants, the relative sensitivities of the sensors differed when using SDS. Whilst the inherent sensing properties of the conducting polymers remained the same, the extent to which they were more or less sensitive to properties such as polarity, hydrophobicity, or molecular size/shape could be enhanced (or diminished) by using a much larger, surfactant dopant. Due to the extensive charge transfer between polymer and dopant, the amount of dopant used, and the fact the dopant is not incorporated into the molecular structure of the polymer chains, the structure and geometry of the polymers may be significantly altered, as can be seen in the AFM images presented in Figure 4.9 of section 4.7.5.

The difference in sensitivity is also more apparent due to the differences between the responses found. Using SDS, the dedoping process could be controlled better and higher resistance sensors were achievable. The response curves show that higher responses and greater changes in response were achieved at lower potentials.

# 5.9 Relative Sensitivities

As an overview of the relative sensitivities, Table 5.7 displays a qualitative summary of the sensitivities found and displayed in the previous graphs of this chapter for all of the sensors successfully tested with the calibration gases.

Table 5.7 Relative sei	nsitivities
------------------------	-------------

Polymer	Dopant	Acetaldehyde	Acetic Acid	Acetone	Ammonia	Butanone	Butyric Acid
N-methylpyrrole	$PF_6^-$	0	о	о	0	0	О
N-hexylpyrrole	$BF_4^-$	000	00	0	000	00	0000
N-hexylpyrrole	SDS	0000	0000	0000	000	000	000
N-dodecylpyrrole	$PF_6^-$	00	00	00	00	00	0
N-dodecylpyrrole	SDS	0000	0000	000	000	000	000
N-pentafluorobenzylpy	$PF_6^-$	000	000	000	000	000	00
N-phenylpyrrole]	PF <sub>6</sub>	о	о	о	0	o	00
N-phenylpyrrole]	TsO <sup>-</sup>	х	Х	Х	XX	Х	0000
N-phenylpyrrole]	OTf	0	0	0	0	0	000
N-phenylpyrrole]		0	ο	0	0	0	00
3-hexylpyrrole	$PF_6^-$	000	000	000	000	000	000
3-dodecylpyrrole	PF <sub>6</sub>	0000	x	x	0000	x	0000
3-dodecylpyrrole	SDS	0000	X	0000	0000	0000	000
3-hexanoylpyrrole	$PF_6^-$	x	0000	0000	0000	x	0000
3-hexanoylpyrrole	$BF_4^-$	XX	ХХ	XX	X	XX	0000
3-hexanoylpyrrole	TsO <sup>-</sup>	00	00	00	00	00	00
3-hexanoylpyrrole		000	00	000	00	00	0
3-dodecanoylpyrrole	$PF_6^-$	0000	х	0000	х	x	0000
3-methylthiophene		0	ο	o	0	0	00
2,2'-bithiophene		0000	ο	0	0	0	0000
2,2'-bithiophene	SDS	XXX	XXXX	ххх	ХХХ	XX	XX
PEDOT	$PF_6^-$	о	о	o	0	o	0
SNS	NSA	0	0	0	000	0	00
Plexcore		Х	XX	XX	000	000	00
PaniPol		Х	000	000	000	00	00
I EGEND.		SYMBOL	SENSITIVITY	KEY	PF6	0/X	1
LEGEND.		0	0.00 - 0.15		BF4	0/X	
		00	0.15 - 0.30		SDS	0 / X	
		000	0.30 - 0.60		CIO4	<b>O / X</b>	
		0000	0.60 - 1.00		Other	0 / X	J
		X	1.00 - 1.50				
			1.50 - 2.00				
		~~~	2.00 - <del>1</del> .00	1			

>4.00

XXXX

#### 5.10 Humidity Effects

The effects of humidity were not investigated as extensively as other attributes since it was know in advance of sensor design and optimisation that the woundmonitor device was to use SPME sampling and elevated operating temperatures; therefore, the effects of humidity would be minimised in the final device. However, a small investigation was carried out with a selection of sensors to observe the relative amount by which humidity affected the sensor responses, stability and sensitivity.

At 20% relative humidity, it was generally found that all sensitivities to the volatiles tested were reduced between 30 - 50%, and significant baseline drift occurred, especially for higher resistance sensors. These effects became more apparent at greater humidity levels.

# 5.11 Sensor Array Design

#### 5.11.1 Principal Components Analysis (PCA)

Multivariate data analysis is employed in order to help determine any underlying relationships between a set of independent variables (eg. sensor array outputs) and a set of dependent variables (eg. concentrations). Chemometrics is applied in the data analysis of many fields of scientific investigation, thus many techniques are available. However, it is important to select the appropriate technique for the application, so an understanding of the nature of the data acquired and the investigative problem is required. [5.61]

The sensors used are preprocessed and presented as a percentage of response using the fractional difference model ( $\Delta R/R_0$ ). For the most part, time-slices of the response signal were collected after initial transient response – reaching the asymptotic value – so the response vectors represent this time window. Occasionally, time-slices were averaged to give a time-independent collection of vectors however, it will be specifically addressed in the results when this was done.

PCA was used to analyse the data recorded and was used in the wound monitor electronic nose device as part of the pattern recognition technique. Therefore, PCA was used to evaluate the orthogonality of the conducting polymer sensors in terms of the calibration gases tested, i.e. the degree of discrimination achievable between the VOCs.

# 5.11.1.1 Principles of PCA

PCA is a powerful non-parametric, unsupervised technique – a multivariate statistical model using the Karhunen-Loéve transform, which qualitatively displays the correlation between data points as well as reducing the dimensionality.

As a non-parametric technique, a probability density function is not assumed and any data set can be used without the requirements of any parameter alteration or knowledge of how data was recorded. [5.62]

A few stringent assumptions are made in order for this to be accomplished. Firstly, data sets are assumed to be *linear* and the new coordinate basis is expressed as a linear combination of *orthogonal* vectors (principal components) that account for the amount of variance in the data in order of importance. This simplification conveniently allows for linear algebra decomposition techniques. The other assumption is that large variances in the data account for interesting features and correlation.

Since sensor outputs from electronic nose applications often have a high degree of co-linearity, the dimensionality reduction, or vector decomposition, of PCA is very useful as a tool for visually displaying the majority of information with a small number of principal components (2D/3D plots) and helping to determine the linear separability of responses, i.e. the amount of discrimination possible between tested gases from an array of non-specific gas sensors.

#### 5.11.1.3 Method

The first stage of PCA is subtraction of the mean from each data dimension, which produces a data set with a mean of zero. A covariance matrix is then generated from the original data. The covariance is a measure of the amount with which dimensions vary from the mean with respect to one another, that is, the correlation between two measurement types. A large positive value indicates positively correlated data (dimensions increase together), whilst a large negative value indicates negatively correlated data (as one dimension increases, the other decreases). A value of zero means that there is no correlation between the data sets. Its absolute magnitude denotes the degree of data redundancy. Since covariance can only be measured between pairs of dimensions, a covariance matrix encompasses all of the possible (n!/2(n-2)!) paired measurements for n-dimensions.

The covariance matrix is a diagonal matrix and, by assumption, large values in the diagonal terms signify interesting features and large values in the off-diagonal terms is consistent with high redundancy. [5.62]

So the objective is to maximise the variance and minimise the redundancy. This is normally accomplished by calculating the eigenvectors and eigenvalues of the covariance matrix in order to generate a feature matrix. Dimensionality reduction and minimisation of redundancy is achieved by ordering the eigenvectors in terms of their eigenvalues, from highest to lowest. The eigenvector with the highest eigenvalue corresponds to data dimensions with the most notable correlation. This is the principal component of the data set. Less significant components can be omitted from the feature matrix, thereby reducing dimensionality and redundancy.

The final data set, re-expressed in terms of its principal components, is then found by multiplying the transpose of the feature matrix on the left of the transposed, meanadjusted original matrix of response vectors. This new matrix presents the data in columns

with the chosen dimensions in rows. Since it is generated using eigenvectors, the data is now presented along the perpendicular axes of the principal components – the axes along which the most significant correlations are found.

# 5.11.2 Sensor Choices For Final Array

The following criteria formed the basis on which sensors were chosen for incorporation into the final sensor array for the wound monitor device:

- choose sensors of differing relative sensitivity (orthogonal)
- · varying selectivity to different volatiles but with overlapping sensitivities
- sensitive at low concentrations
- high enough resistance for appreciable signal but not so high that noise and stability of base line are adversely affected
- repeatable signal (small measurement error/large qualitative resolution)
- sensor reproducibility (easy deposition and good redox control low variability)

Initial investigation lead to the formation of a sensor array consisting of a variety of *N*-substituted and 3-substituted polypyrrole based sensors, labelled "C4". All of the sensor arrays successfully fabricated and tested for the project were labelled alphanumerically as <letter>, representing the nature of the experiment or investigation, and <number> for the experiment number. This array featured 5 working sensors: *N*-dodecylpyrrole/PF<sub>6</sub><sup>-</sup>, *N*-pentafluorobenzylpyrrole/PF<sub>6</sub><sup>-</sup>, *N*-phenylpyrrole/PF<sub>6</sub><sup>-</sup>, 3-hexanoylpyrrole/PF<sub>6</sub><sup>-</sup>, and 3-dodecanoylpyrrole/PF<sub>6</sub><sup>-</sup>.

PCA plots presented here were calculated using time slices of the asymptote of the responses found. The data points for the time slices are shown as multiple data points for each class in the PCA plots and are used to gauge the dynamics and repeatability of the responses. All of the following PCA results are for responses at 2ppm analyte concentration. Figure 5.46 shows the 2D and 3D PCA plots for sensor array, "C4"



Fig 5.46 PCA for C4 sensor array

The PCA results demonstrate a clear separation of butyric acid responses and between butanone/ethanol and the other volatiles. In contrast, the data for acetaldehyde, acetic acid, and ammonia are grouped together relatively closely.

The reasons for these results can be understood in terms of the relative sensitivities of the sensors used for the array. Except for *N*-phenylpyrrole/ $PF_6^-$ , all of the sensors had lowest sensitivity to butyric acid. 3-hexanoylpyrrole and 3-dodecanoylpyrrole sensors were also relatively more sensitive to butanone and ethanol than the *N*-substituted polypyrrole sensors due to the more hydrophilic/polar acyl substituents. These contrasting relative

sensitivities explain the clear separation of PCA plots for butyric acid, butanone, and ethanol. The close grouping of acetaldehyde, acetic acid, and ammonia in the PCA plot can similarly be explained since all the sensors displayed relatively similar sensitivities to these volatiles.

The arrays developed following these results investigated the properties of the polypyrroles in terms of substitution. "N1" array consisted of the *N*-substituted polypyrrole sensors and "P2" consisted of the 3-substituted polypyrrole sensors. The PCA results for both of these are displayed in Figures 5.47 and 5.48.

Both of the sensor arrays display clear separations between the various volatiles tested. Greater differences were observed with the N1 array due to the greater variety of substituted polypyrroles; substituents varied from a simple methyl group to longer alkyl chains, to bulky aromatic groups. Although the sensitivities of the *N*-substituted polypyrroles sensors were generally lower than those of the 3-substituted variants, the greater relative differences in sensitivity enabled more differentiation between the tested volatiles.



PCA

Fig 5.47 PCA for N1 array



# Fig 5.48 PCA for P2 array

Again, the PCA for "P2" can be understood in terms of the relative sensitivities of the sensors used. The largest differences were between the 3-alkyl substituted polypyrroles, which were more sensitive to hydrophobic analytes, and the 3-acyl substituted polypyrrole, which had greater sensitivity to more polar analytes. Differences in sensitivity to butyric acid were greatest and the particular sensitivity of 3-dodecylpyrrole towards acetone accounts for its differentiation in the PCA. However, the sensitivities of acetaldehyde and acetic were similar, as were the sensitivities towards ammonia, butanone, and ethanol. Hence little separation between the data points for these analytes was observed.

Sensor arrays developed to investigate the use of different dopants also showed how the difference in relative sensitivity to the volatiles determined the discriminatory ability of a set of sensors. Since the use of a different dopant tended to affect the sensor response magnitude and not its relative sensitivity to different analytes, these arrays had little to no separation of the data collected.

Due to the contradistinctive sensitivities of Plexcore and Panipol, PCA results of a sensor array consisting only of these sensors yielded excellent separation of analyte responses as shown in Figure 5.49.



Fig 5.49 PCA for Plexcore and Panipol array

The following sensor choices were made based on the criteria specified previously, with reasons listed:

• Plexcore and Panipol

- due to their contradistinctive sensitivities and ease of deposition onto substrate

SNS/NSA

- due to its selectivity towards ammonia

• PEDOT/PF<sub>6</sub><sup>-</sup>

- despite its low sensitivity, its deposition was reliable and it was the only sensor to have a particular sensitivity to ethanol

• 2,2'-bithiophene/SDS

- displayed the highest sensitivity of all the sensors, it was easy to deposit electrochemically and its relative sensitivity to acetic acid and acetone was different to the polypyrrole based sensors

N-hexylpyrrole/BF<sub>4</sub><sup>-</sup>

- although not as sensitive as *N*-pentafluorobenzylpyrrole, its polymerisation potential was considerably lower, thus its fabrication was more reliable and reproducible. Measurements were more repeatable and its baseline signal was more

stable. It was also the most sensitive of the *N*-substituted polypyrrole based sensors to butyric acid.

3-dodecylpyrrole/SDS

- demonstrated reliable and repeatable fabrication. Its high sensitivity to acetic acid was also in contrast (with SDS as dopant) to the other sensors.

3-hexanoylpyrrole/BF<sub>4</sub><sup>-</sup>

- sensitivity to more polar analytes complemented the other 3-substituted polypyrrole sensor used (3-dodecylpyrrole).

The resulting sensor array demonstrated good discriminatory abilities to the volatiles tested on the gas rig, as shown in the PCA plots in Figure 5.50, and it was subsequently used in the hybrid wound monitoring device, which is the subject of the next chapter.



Fig 5.50 PCA for final array featuring chosen sensors

# 5.12 Summary

The stages in which sensor testing was developed and carried out in this project were detailed. In summary, the volatile key markers were deduced through GC/MS headspace analysis of the selected bacterial cultures; a gas testing rig was designed and

constructed which utilised mass flow controllers, permeation tubes of the calibration gases, and clean, dry air as a carrier gas to deliver known concentrations to the sensors; changes in sensor resistances were monitored and recorded using in-house electronics and software. This data was then used to generate the concentration-response profiles for each of the sensors tested and their sensitivities were analysed on the basis of this data. PCA was then used to observe the orthogonality of the sensor arrays made and judge which sensors were most suited for use in the woundmonitoring device.

Generally, the dynamic ranges were varied but most sensors tended towards saturation at concentrations above 6ppm. Responses for concentrations below this were used to estimate the corresponding sensitivities. Greater sensitivities and stability were generally found for the 3-substituted polypyrrole sensors compared to their N-substituted analogues, likely due to the loss of ring planarity with N-substituents, especially for larger, more bulky groups that increase steric effects. It was also found that the longer alkyl chain substituents increased sensitivity towards most of the volatiles tested. Additionally, the 3alkyl substituted polypyrroles were generally less sensitive than their equivalent 3-acyl polypyrroles. The polythiophene based sensors yielded lower sensitivities whereas the commercial printing polymers displayed relatively large sensitivities, which contrasted one another. SNS was shown to be quite selective towards ammonia and, although PEDOT exhibited very low sensitivities, it was the only sensor that had selectivity towards ethanol. However, all of the sensors tested were non-specific, which was observable from comparison of their sensitivities to the various attributes of the volatiles used for testing. Some expected trends were observed, as detailed in section 5.5, but the non-specificity of the sensors meant that no one mechanism was responsible for the behaviour of a sensor, which was desirable for the purposes of the electronic nose.

In section 5.7, the sensors and their measurement reproducibility were evaluated and shown to be correlated to the stability of the sensor and the amount of electrochemical control that was possible during the doping/dedoping process.

In order to optimise the sensors made by increasing their response magnitudes, a study into the use of different counter ions was undertaken, as described in chapter 4. The gas testing results showed that dramatic differences were achieved by using different dopants and that by using the dodecyl sulfate ion, responses could be significantly increased through dedoping without affecting the stability of the sensors too much.

PCA was used to evaluate some of the optimised sensor arrays developed and discrimination between the volatiles tested was shown at 2ppm. Improved separation between the volatiles was achievable by using sensors with differing relative sensitivities to the volatiles; the amount of separation possible was explainable by comparing the relative sensitivities. These observations, and the ease of fabrication and stability of sensors reported in chapter 4, were used to select the most appropriate conducting polymer sensors. This sensor array was tested and shown to give excellent separation, especially between acetone, acetaldehyde, and ethanol.

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# **CHAPTER 6**

# **HYBRID DEVICE TESTING**

It was the aim of the Woundmonitor project to produce a portable system capable of using integrated gas sensing technologies to provide a diagnostic aid in monitoring the bacteria present in wounds within the clinical environment. The realisation of the complexity of the project required the optimal use of cross-selectivity and a powerful array of orthogonal sensors. Thus, it was desired to use a combination of metal oxide sensors and conducting polymer sensors in one system, which was constructed in collaboration with partners involved in the Woundmonitor project

## 6.1 Hybrid Device Assembly

The device consisted of a similar construction to the sampling unit used for testing the sensor arrays with the gas rig/permeation tubes, but with a few essential differences. Namely, a SPME loading chamber and automated driving mechanism, the heated SPME desorption chamber connected to the gas chamber containing the gas sensors in a threedimensional array, and resistance interrogation circuitry for collection, conversion, and communication of the resistance changes of both the MOx and CP sensors. Figure 6.1 displays part of the hybrid prototype used. Components are listed beneath.



Fig 6.1 Hybrid Device Prototype

- 1) Metal oxide (MOx) gas sensing chamber
- 2) MOx sensor buffer and mounting PCB (printed circuit board)
- Conducting polymer sensing chamber (underneath MOx sensing chamber)
- SPME desorption chamber, encapsulated between heating plates/AD595 thermocouple
- 5) SPME loading chamber
- 6) Main PCB with two sister PCBs attached; one capable of interrogating 4 MOx sensors (less than 10MΩ resistance) and 8 conducting polymer sensors, another capable of interrogating 4 high resistance MOx sensors for compatibility with those produced from Partner 4 (INFM-CNR) of the Woundmonitor project.
- 7) Air filter
- 8) Pump

Due to the low concentrations of the chemicals present in the headspace above bacterial samples, a preconcentration step was required. Solid Phase Microextraction (SPME) was used for sampling due to its ease of use and applicability to infield deployment, meeting the needs of the device in terms of portability. Fibres were supplied by Supelco®.

SPME is a technique that utilises a fibre of fused silica coated with an adsorbent or absorbent phase, allowing preconcentration of organic compounds. The sampling is a multiphase equilibration process where analytes are transported into the coating of the SPME fibre on exposure. These analytes can then be thermally desorbed. Commercially, the SPME fibre comes encased in a protective needle sheath from which it can be extended and retracted (see Fig 6.2). Sampling involves exposure of the central fibre for an appropriate period of time (determined through experimentation) and retracted for protection. A SPME fibre can reduce effects of background odour interference and be reused several hundred times provided that low concentrations are sampled.



**Fig 6.2** SPME fibre with protective needle sheath and plunger (above) and protective cartridge encapsulating SPME fibre for use with device (below)

A custom built sampler was used to contain and expose the fibres via a plunger and locking system. To aid tracking of the fibres and their frequency of use, RFID chips are embedded into the fibre which can be read by the RFID reader mounted inside the lid of the SPME loading chamber. The sample delivery system is shown in Fig 6.3 and comprises of the SPME loading chamber, desorption chamber and gas sensor header (MOx only in diagram). The SPME cartridge is placed into the channel where a driving mechanism pushes the needle sheath into the desorption chamber and depresses the plunger, exposing the fibre and forming an air-tight seal between the chamber entrance and o-ring seal on the barrel of the SPME cartridge. The desorption chamber is heated to the order of 250°C and a filtered air line is attached which delivers air into the system as a carrier gas (dynamic flow) and for sensor cleaning/equilibration between measurements.



Fig 6.3 3D representation of sample delivery system

The sensor header system designed and used for the hybrid device comprised of the following components, shown in Figs 6.4 - 6.7

- 1) SPME desorption chamber tube
- 2) Stainless-steel MOx sensor header
- 3) Heating Plates
- 4) Ceramic spacer between MOx sensor header chamber and CP chamber
- 5) Upper conducting polymer sensor chamber header
- 6) Lower conducting polymer sensor chamber header/platform



Fig 6.4 Hybrid system header assembly



Fig 6.5 Hybrid system header components

The conducting polymer sensor array lies face-up on the lower CP chamber header (6) where the sample flows through the circular aperture shown, and up into the CP gas sensing chamber which is formed when the components are assembled together and compressed. The Viton® seals on the ends of both parts of the CP chamber header helped create an air-tight seal, although in practise it was found that leakages still occurred and PTFE tape had to be used to seal the system. The metal oxide gas sensor chamber (2) was affixed vertically to the CP gas chamber with a ceramic spacer in between (4) to help reduce heat transfer from the MOx sensor chamber to the CP chamber since the metal oxide sensors function at elevated temperatures typically between 200 – 400°C. The aperture at the top of the MOx sensor chamber enabled an exhaust line to be fitted (visible in Fig 6.4).

Real time data acquisition was achieved using a microcontroller based system. Each input channel was sampled sequentially via a multiplexer switch, setting the gain of the amplifier to unity so as to measure the base resistance of each sensor in clean air at the start of a measurement. The digitised values were stored in memory and were used individually as the input to an offset amplifier via a digital to analog converter (DAC). The output from the offset amplifier was essentially an autozeroed output. This signal was then amplified via a programmable gain amplifiler before being digitised using a 24-bit analog to digital converter (ADC). The microcontroller handled the control of data sampling at regular intervals that were user defined, and sent data to an external host computer via a serial link (RS232 protocol). Default parameters for heater settings, gain settings and time intervals could be stored in permanent memory (EEPROM) for initialisation of the system when powered on.

Essentially the same software used for gas testing of the conducting polymers in the previous chapter was used to collect, store, and analyse the acquired data from the hybrid device. The software was updated to be fully compatible with the device and some added functions were implemented allowing for a number of covariates to be recorded for the purpose of recording/tracking data collected throughout the course of testing and for

exploratory data analysis, developed by Partner 4 of the Woundmonitor project, to be performed on the data acquired.

### 6.2 Metal oxide sensor testing

Before implementation of the conducting polymer sensors into the system, the metal oxide sensors were tested and calibrated for use in the device. This was done in conjunction with conducting polymer design and optimisation. The Woundmonitor project primarily focused on the use of a series of devices using an array of only metal oxide sensors for clinical testing and development whilst the hybrid device underwent construction, modification and optimisation.

Initially an array of 4 commercially available metal oxide sensors and 4 sensors provided by CNR-INFM, who developed mixed metal oxide (MMO) sensors with thin film technology, were tested. The configuration was as follows:

Sensors 01, 02: CAP05-Z Capteur sensor from City Technologies Sensors 03, 04: TGS 2620 Taguchi Figaro sensor Sensor 05: WO3A from CNR (Tungsten oxide) Sensor 06: WO3B from CNR Sensor 07: SN02A from CNR (Tin oxide) Sensor 08: SN03B from CNR

This array was tested with the hybrid device without the conducting polymer sensors. 0.02g.L<sup>-1</sup> solutions were made and used to produce the headspace concentrations of the calibration gases (listed in Table 6.1). Sampling was performed using SPME.

Acetaldehyde	2.2x10 <sup>-2</sup> ppm	
Acetic acid	2.8x10 <sup>-5</sup> ppm	
Acetone	9.1x10 <sup>-3</sup> ppm	
Ammonia	7.0x10⁻³ ppm	
Butyric acid	8.4x10⁻⁵ ppm	
Ethanol	1.6x10⁻³ ppm	

Table 6.1 0.02g.L <sup>-1</sup>	solution	headspace	concentrations
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The PCA results of these tests did not demonstrate satisfactory volatile discrimination. Measurements with saturated vapours of the compounds improved results. Testing was achieved with a batch a clinical samples, however, discriminatory ability remained poor.

The Capteur and Figaro sensors performed well consistently. The use of two of the same type of sensors displayed repeatable results with both pairs exhibiting very similar behaviours. They also gave the largest responses to the gases and samples tested. The CNR sensor worked intermittently and gave comparatively small signals which were noisy due to their high resistances. These sensors eventually ceased to function and were replaced with other sensors provided by CNR including chromium oxide sensors. These were also found to be problematic. Eventually, two other CNR tin oxide sensors were used; one doped with platinum, another doped with gold. These performed more reliably

Sensors provided by partner 2, Puslaidininkiu Fizikos Institutas (PFI), Lithuania, were also supplied and tested with the device. Sensors developed by PFI were SnO<sub>2</sub> based thin film gas sensors made using reactive magnetron sputtering technique. Initially, there were problems with the mechanical strength of the sensor fixing which was affected after prolonged exposure (about 2 months) to high temperatures and sensors tended to be damaged in transit. These issues were overcome after partner 2 investigated and modified the original sensor technology, developing an interfacial layer which improved the morphology of the active sensing layer, its stability, reproducibility and mechanical stability. These sensors were successfully tested and performed consistently with the hybrid device. Due to the Capteur sensors becoming obsolete, they were replaced with a set of Taguchi Figaro metal oxide sensors: TGS 2602, TGS 2610, TGS 2611, and TGS 2620.

The updated configuration performed more reliably and calibration gases were able to be discriminated through PCA as shown in Figure 6.6. The PCA plot shows the dynamics of the response curves obtained for the calibration volatiles, sampled using SPME with 2ppm

headspace concentrations above solutions of each compound (see Appendix 3 for calculation). Measurements were replicated three times.

Apart from the variation in ammonia responses, measurement repeatability can be seen to be excellent and discrimination between all of the volatiles was achieved. 2butanone was tested at a later stage of development.



PCA1 (75.70%)

**Fig 6.6** Optimised, updated metal oxide sensor PCA results – striations occur from the use of time-slices over a section of a response profile. 5 repeated measurements for each tested VOC are shown.

#### 6.3 Metal Oxide Sensor Optimisation

#### 6.3.1 Heater Voltage Study

Some of the sensors received from the partners that were implemented into the prototype were tested and their variation at different heater settings was studied. These sensors were tested using SPME sampling of 2ppm ethanol with dynamic flow (see following section) over a range of different heater voltages. The CrO<sub>2</sub> sensor did not function above 3.3V. The change in baseline resistance with heater voltage and the change in sensor response to 2ppm ethanol for each of the sensors was mapped. A typical response curve set at different heater voltages is demonstrated in Figure 6.7.



Fig 6.7 SnrPt sensor responses to 2ppm ethanol with different heater voltages



PCA1 (94.57%)

Fig 6.8 PCA of 2ppm ethanol responses across range of heater voltages tested

The closest grouping of responses in the PCA (Figure 6.8) and Sammon map (Figure 6.9), and hence the optimal range, was found to be between 3.4 – 4.0V. Sammon mapping is an alternative technique of dimensionality reduction which iteratively attempts to represent the interpoint distances of a data set in a low dimensional projection as close as possible to the Euclidean distance between corresponding points in the higher dimensional space. [6.1]

Inspection of the response curves to 2ppm ethanol from each of the sensors showed that the optimal heater voltage for the sensors from CNR-INFM was at least 0.3V higher than the specified default values. The sensor SN30KA\_LA was set at a default 2.9V which was found to be optimal. The optimal heater voltages found for the sensors tested are listed in Table 6.2.



Fig 6.9 Sammon map of 2ppm ethanol responses across range of heater voltages tested

Partner	Sensor type	Label	Optimal Heater Voltage
CNR-INFM	SnO <sub>2</sub> doped with Pt	SnrPt C14	3.9V
CNR-INFM	CrO <sub>2</sub>	CrO2_55	3.3V
CNR-INFM	SnO <sub>2</sub> doped with Au	SnrAu C3	4.4V
PFI	SnO <sub>2</sub> based MOx sensor	Sn30KA_LA	2.9V

Table 6.2 Optimal heater voltages

Unfortunately, after deciding on these sensors it was found that the SnrPt and the  $CrO_2$  sensors showed poor dynamic response and stability over time – while they did respond, the kinetics of their responses were rather slow as the vapour from thermal desorption of the SPME fibre appeared as a bolus. It was decided to replace these with commercial metal oxide sensors from Applied Sensors Gmbh – MLX and MLC.

## 6.3.2 Dynamic Flow and SPME Fibre Study

A study was undertaken to show the differences in sensor responses when a dynamic flow of air was used to carry the desorbed volatiles from the SPME fibre to the gas sensing chamber as opposed to free expansion of the gases. Partner 2 instigated the study of the methods of sample delivery from the desorption of volatiles from the SPME to the gas sensors. They found that when using a static system relying on the free expansion of the volatiles, the volatile compounds were less detectable than in the case of constant injection of the gas sample. It was supposed that the expansion of comparatively heavy molecules of the gas was weak and direction dependent. Figures 6.10 and 6.11 below show the different sensor response curves found when using static and dynamic flow respectively.



Fig 6.10 Example of sensor responses with free expansion of gas



Fig 6.11 Example of sensor responses when dynamic flow used

When dynamic flow was employed the sensor responses were more rapid, however, as the carrier gas continued to flow through the system, the responses diminished with time due to the cooling of the sensors.







The optimal flow rate was first decided upon by testing the system at different flow rates using 2ppm ethanol. The PCA of the results (Fig 6.12) shows the progression of the responses and the optimal range towards the right of the PCA plot. The legend shows the hexidecimal code used to set the flow rate on the instrument. The values correspond to a range of 2.9 (07) to 137 sccm (10). As would be expected, the sensor responses reduce with increasing flow rate. An ideal flow rate of 6 sccm was decided.

At the same time, the differences between the use of black SPME fibre of Supelco®, Carboxen/polydimethylsiloxane (CAR/PDMS), and their polydimethylsiloxane/ divinylbenzene (PDMS/DVB) 65 µm Bonded Blue fibre were investigated since it was shown during GC/MS analysis that the blue fibre was more selective to the volatiles of interest to this project.

Both array configurations were tested using a static and dynamic flow with both the black and the blue SPME fibres. The updated sensor array gave better discrimination between the calibration gases and much improved measurement repeatability overall. The PCA results for this array using both fibres in both static and dynamic modes are presented in Figures 6.13 - 6.16.



Fig 6.13 PCA results with free expansion of volatiles from black SPME fibre

An appreciable separation is observed between the data sets for ethanol, acetic acid, butyric acid and ammonia, but separation was poorer between acetaldehyde, acetone and butanone. From the three-dimensional representation, it can be seen that the data sets for acetic acid and butyric acid, although clearly separate, are relatively close together. Therefore, it would seem that the selectivity of these sensors is determined by the functional group of the volatile analytes with less discrimination achieved between volatiles of a similar functional series, i.e. ketones (acetone, butanone) and carboxylic acid (acetic acid, butyric acid). In fact, these trends are noticeable in the PCA results for the other tests reported here. Reasonable measurement repeatability can also be seen for acetic acid, butyric acid, and ethanol; greatest variability was found for ammonia measurements.



Fig 6.14 PCA results with free expansion of volatiles from blue SPME fibre
A greater degree of separation was observed when the blue SPME fibre was used for sampling (Figure 6.14) in comparison with the black SPME fibre (Figure 6.13), especially between data sets for acetone and butanone.

Figures 6.15 - 6.16 show the PCA results for the same tests using a dynamic flow of 6sccm where the carrier gas was filtered air.



Fig 6.15 PCA results with dynamic flow using black SPME fibre



Fig 6.16 PCA results with dynamic flow using blue SPME fibre

Similar to the results using static flow, the black SPME demonstrated poorer discrimination between acetone and butanone. However, when a dynamic flow was used to carry the desorbed volatiles, slightly better separation between these volatiles was found than for the static flow. Much better discriminatory ability was shown when the blue SPME fibre was used. Although the sensor responses were smaller, the measurement repeatability was also seen to improve when a dynamic flow was employed, particularly in the reduction of variability between measurements of ammonia. In summary, measurement repeatability and volatile discrimination improved when a dynamic flow mode was used. Results were further improved by using the blue SPME fibre.

#### 6.4 Metal Oxide Sensor Array Initial Testing With Clinical Samples

Initial tests were performed on the headspace volatiles from bacteria grown on culture. Preliminary results showed that the instrument was capable of separating the volatiles from bacteria and distinguishing between *Pseudomonas aeruginosa* (triangles) and *Staphylococcus aureus* (squares) cultures as shown in the PCA results in Figure 6.17.





**Fig 6.17** PCA scores from responses to headspace of volatiles produced from Pseudomonas (triangles) and Staphylococcus (squares) species

Swabs and dressings were collected from 150 patients at Wythenshawe Hospital, Manchester (in collaboration with Partner 7), where the same dressing applied to wounds were applied to different parts of the patient's body that were without wounds in order to determine the influence of body odour. All of the patients were diagnosed using microbial laboratory analysis. Results demonstrated that it was possible to discriminate infected samples even where different dressings were used (Figure 6.18).



PCA1 (79.31%) Fig 6.18 PCA results of data obtained from MOx only device with patient samples

Testing with clinical samples was limited on the hybrid device due to ongoing maintenance and optimisation. Problems were encountered with pneumatic leaks due to the sensor header design, and also with the operation of the conducting polymers at high temperatures, once they were incorporated into the device. However, tests were performed in conjunction with the other prototype devices when the hybrid instrument was fully functional. Although the conducting polymer sensors did not respond sufficiently at these times, the metal oxide sensor arrays provided results that indicated the potential for discrimination between infected and uninfected samples, particularly between *Pseudomonas aeruginosa* and *Staphylococcus aureus*.

#### 6.5 Conducting Polymer Sensor Incorporation

The conducting polymer sensors decided upon in the previous chapter were deposited onto a batch of arrays using the same methodology as described for the individual sensors in chapter 4. A number of the sensor arrays that were studied on the gas rig in the last chapter were transferred to the hybrid device after they had been fully tested. These arrays were used to monitor their stability and functionality in the hybrid instrument at the elevated temperatures for prolonged periods. In general, it was found that sensors with high resistances due to extensive dedoping (>50k $\Omega$ ) and sensors that were suspected of having been over-oxidised, degenerated quite quickly and ceased to work. The base resistances increased due to the high temperatures dedoping the sensors further, but they tended to stabilise after a number of days.

Numerous tests were performed with the conducting polymer sensor arrays developed, but it was found that responses were negligibly small and left little to no impact on the overall discriminatory ability of the device overall. It was found that the reason for the dramatic decrease in sensitivity of the conducting polymer sensors was the delivery of the volatiles using SPME.

The essential difference between the delivery of the volatiles to the sensors using the gas rig and the hybrid device was that only a finite volume of volatiles could be adsorbed by the SPME fibre coating; a volume that was insufficient for the same level of response achieved using the gas rig. Since a dynamic flow using air as a carrier gas was chosen as the ideal mode for the metal oxide sensors, the volatile concentrations were further diluted and only presented to the conducting polymer sensors for a short time whereas the gas rig provided an invariable concentration of gas to the sensors until a sufficient equilibrium between gas-sensor interactions was achieved.

In order to overcome these problems and test the potential sensing abilities of the hybrid device it was decided to use a 20cm<sup>3</sup> syringe with a stop-valve to extract an ample volume (20cm<sup>3</sup>) of the headspace of samples and inject the samples directly into the gas sensing chamber.

Naturally, a number of disadvantages were anticipated by adopting this method of sample delivery. Firstly, the effects of humidity could not be circumscribed as they would using SPME. Also, despite efforts made to ensure an air-tight seal remained around the point of injection, leaks and external contaminants could not be eradicated. This was circumvented by using the static mode whereby a constant stream of air would flow over the sensors except during measurement and injections were made at the very moment that measurements commenced. Lastly, and most significantly, the injections were performed manually since modifications to the instrument design could not be implemented at the stage when testing was performed. Therefore, the flow rate of injection was subject to human error even though every effort was made to ensure injections were made steadily (at 1cm<sup>3</sup> per second, i.e. 60sccm).

#### 6.5.1 Hybrid Device Results: Calibration Gases

As anticipated, the results showed more variation due to the nature of sample delivery being prone to human error. The sensitivities of the sensors also seemed to yield

similar results for the volatiles tested due to the presence of humidity; even the metal oxide sensors showed less discrimination between the tested volatiles. However, some distinction was noticeable and attempts were made to improve the clarity of the results obtained. This was accomplished by performing 30 tests for each of the calibration gases so that response averages could be used and a greater representation of sensor behaviour could be gained by having a larger sample population to analyse.

The responses of the conducting polymer sensors were relatively small in comparison with the metal oxide sensors, even using the injection method. Therefore the responses were amplified by a factor of 15, bringing them into the same range as the metal oxide sensors and then a local regression using weighted linear least squares and a 1<sup>st</sup> degree polynomial model (using locally weighted scatterplot smoothing ("lowess") through Matlab – 10% data points) was applied to reduce the noise. This produced a response curve that was most similar to the original response without loosing too much information and ensured similar relative sensitivities were maintained between the responses of the different conducting polymer sensors.

The features extracted for each measurement were the maximum responses of the conducting polymers after the modifications described above, and the averages of the response curves between 50s and 100s for the metal oxide sensors. This information was collated and obvious outliers occurring from experimental error were identified using boxplot diagrams for each of the sensors. Any measurement containing an outlier was discounted. This was justified since all outliers found occurred for the same measurements.

The degree of normality of the sensor responses were judged by observing the normal distribution probability plot for each of the sensors and using the Shapiro-Wilks W test. [6.2] From these observations, it was decided that the measurements were adequately represented by a normal distribution. Therefore, it was deemed justifiable to remove additional outliers using Grubb's test with a 5% significance level. [6.3] The test detects one outlier at a time based on the difference of the sample mean and the maximum/minimum of

the data considering the standard deviation. After an outlier is expunded, the test can be iterated until there are no more outliers.

The PCA results using just the metal oxide sensor responses (Fig. 6.19) showed good discrimination between acetic acid, ammonia, butanone, and butyric acid but less discriminatory power is displayed for acetaldehyde, acetone, and ethanol. However, the PCA results using just the conducting polymer sensor responses show that discrimination was achieved between these volatiles (Figure 6.20).



Fig 6.19 PCA of calibration gases with metal oxide sensors only



Fig 6.20 PCA of calibration gases with conducting polymer sensors only

Figure 6.21 shows the PCA results of the hybrid device with all the sensors to the calibration gases and a blank sample. A clear difference is seen between the blank sample so it can be assumed that the different responses of the sensors are not attributed solely to humidity variation. Due to the difference in response to the blank from the volatiles tested, the discrimination between the volatiles cannot be seen clearly, however Figure 6.22 shows the same results in a three-dimensional representation where the distinction between the groups of volatiles can be clearly seen.



Fig 6.21 PCA of calibration gases and blank sample with all sensors



Fig. 6.22 – PCA of calibration gases and blank sample with all sensors – 3D plot

#### 6.5.2 Hybrid Device Results: Headspace Of Cultured Bacteria

Using the injection method, the sensor responses to the headspace volatiles of the cultured bacteria were generally larger than for the tests performed using the calibration gases. This was most likely due to the presence of volatiles at concentrations greater than 2ppm. Therefore, the initial PCA scores were plotted using time slices of the dynamic response curves generated without the CP sensor optimisation described in the preceeding section. Results for 24h and 48h cultures are shown in Figures 6.23 and 6.24 respectively.



**Fig 6.23** PCA of cultured bacteria after 24h – without CP optimisation



**PCA1** (77.52%) **Fig. 6.24** – PCA of cultured bacteria after 48h – without CP optimisation



Fig 6.25 3D PCA of cultured bacteria after 48h – without CP optimisation

Grouping of the volatiles obtained for the bacteria cultures were maintained, as can be seen in the 3-dimensional representation in Figure 6.25. However, *S. aureus* subspecies 12598 and 43300 can be seen to be more separate from the other subspecies. It was noticed that, although the responses were generally larger for the bacterial samples, the conducting polymers still gave comparatively small responses. Therefore, the responses were augmented and averages were taken, as done for the calibration gases, in order to see whether the conducting polymer responses offered improved discrimination between the samples tested.

Figures 6.26 and 6.27 show the results obtained after 24 and 48 hours incubation respectively. After 24h, the PCA results show separation of all the data collected, including all the *S. aureus* subspecies, however the results of *P. aeruginosa* are similar to those obtained for *S. aureus* subspecies 11729 and *S. pyogenes* 49399.



**PCA1** (71.84%) **Fig 6.27** PCA of cultured bacteria after 48h – with CP optimisation

The results after 48 hours (Figure 6.27) are more familiar (from the MOx sensor testing), with the responses for *P. aeruginosa* similar and separate from those of *S. aureus* and the subspecies 12598, again, displayed as markedly different from the rest of the results. These results only give an indication of the ability of the instrument to discriminate between different bacteria. Due to the shortcomings of the sample delivery method and limited number of tests performed with bacterial samples, no definite conclusions can be made without more exhaustive testing.

#### 6.6 Conclusion

The construction of a hybrid device incorporating both metal oxide and conducting polymers was undertaken in collaboration with the project partners in response to the desire of the consortium to build a device with a powerful array of orthogonal sensors for the discrimination of different bacteria.

Device optimisation began with testing of the metal oxide sensors with the calibration gases, which were sampled from the headspace of the appropriate solution using SPME. Optimisation involved the study of different heater voltages, different modes of delivery of the desorbed volatiles with different flow rates for the dynamic delivery method, as well as the use of an alternative SPME fibre. It was found that using a constant flow of air to carry the desorbed volatiles to the sensors gave more rapid and more repeatable results in comparison to results obtained when the volatiles were allowed to diffuse from the desorption chamber to the gas sensing chamber. Different flow rates were investigated and an optimal rate of 6sccm was found and subsequently used. It was also found that results using bonded blue SPME fibre enabled a greater degree of separation between the tested volatiles than when using the black fibre, however the black fibre was more robust and used in preference to the blue fibre for the hybrid device. Initial tests of the system using only the metal oxide sensors with clinical samples and bacterial culture samples showed that infected and uninfected samples could be distinguished and discrimination was achieved between *Staphylococcus aureus* and *Pseudomonas aeruginosa*.

Conducting polymer sensor arrays were later incorporated into the system. In general, it was found that high resistance sensors (> $50k\Omega$ ) would be rendered unusable due to the elevated temperatures dedoping, and possibly denaturing, the polymer sensors. Tests using the SPME sampling method showed that conducting polymer response kinetics were slower than for the metal oxide sensors and the finite volume of volatiles sorbed by the SPME fibre was insufficient to yield an appreciable response. Responses were even worse

when a dynamic flow method was used due to further dilution of the volatiles presented to the sensors.

Sampling and sample delivery was therefore performed using direct manual extraction and injection of headspace volatiles with a syringe. This method was prone to human error and inconsistencies arising from humidity and other environmental contaminants, however, testing with the calibration gases and bacterial culture samples was possible. By optimising the conducting polymer sensor responses and eliminating outliers, the discriminating potential of the system was shown.

The difficulties in implementing both metal oxide and conducting polymer sensor technologies into a hybrid device arose from the differences between their different kinetic response behaviour and dynamics. The main difficulty encountered in this project was the slow response kinetics of the conducting polymers to the desorbed volatiles from the SPME fibre. Furthermore, the improved performance of the metal oxide sensors using a dynamic delivery method conflicted with the response behaviour of the conducting polymers. The difference in operating temperatures also presented a number of difficulties. Although the conducting polymers could handle the elevated temperatures, their stability was adversely affected and the higher resistance sensors, which offered the greatest response magnitudes at room temperature, tended to be further dedoped at higher temperatures and were not usable. Also, the high operating temperatures of the metal oxide sensors minimises any effects of humidity whereas the conducting polymers, which operate at ambient temperatures, are highly sensitive to moisture.

The advantage of the conducting polymer sensors was the variability in their sensitivity towards different volatiles. This is due to various different conducting polymer materials available and the degrees with which they can be tailored to alter their gas sensing properties. The metal oxide sensor were less selective, responding similarly to a broad range of volatiles. It was shown that the degree of separation between the tested volatiles was broader for more of the volatiles with the conducting polymers, whereas the metal oxide

sensors exhibited poorer discrimination between acetaldehyde, acetone, and ethanol. However, the combination of both of the sensor technologies ensured an overlap of sensitivities and excellent discrimination was possible from the range of cross-selectivities when used together.

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# **CHAPTER 7**

# **CONCLUSION AND FUTURE DEVELOPMENTS**

The original aim of the project was to develop an array of conducting polymer gas sensors for use in a portable electronic nose device capable of analysing the volatiles produced from wounds and identifying the bacteria present. An array of sensors was successfully developed and implemented into a hybrid device utilising both the conducting polymer array and an array of metal oxide sensors. Using SPME to preconcentrate the headspace volatiles of calibration gases and bacterial samples did not afford results with which adequate discrimination could be achieved. However, by using a method of direct injection of the headspace volatiles, the device demonstrated good discrimination of the tested calibration gases and showed potential for bacteria discrimination.

In order to develop an appropriate array of conducting polymers for the application, it was first necessary to elucidate the volatile key markers of the bacterial species chosen for study by the project consortium, namely *Staphylococcus aureus*, *Pseudomonas aeruginosa*, and *Streptococcus pyogenes*. GC/MS headspace analysis was performed using SPME to preconcentrate the volatiles. Based on these results and on discussions with clinical partners of the Woundmonitor project, as well as a literature review, the volatile key markers used to calibrate the sensors developed were acetaldehyde, acetic acid, acetone, ammonia, 2-butanone, butyric acid, and ethanol.

The stages of development of the conducting polymers included the chemical synthesis of a series of 3-substituted pyrrole monomers, investigation into the electropolymerisation and deposition of a variety of heterocyclic polymers and their optimisation, and the concurrent testing of successfully polymerised polymers on a gas rig with the chosen calibration gases, at concentrations between 1 – 10ppm. Their electrochemical properties, stabilities, and gas sensing behaviour were compared and a series of optimal sensors were chosen for use in the hybrid device. The hybrid device was calibrated and optimised, then testing with the bacterial samples was performed.

Monomers of 3-substituted pyrroles with substituents of differing alkyl chain length and functionality were successfully synthesised, however, those with shorter alkyl chains were problematic. Purification of the acyl derivatives was also difficult. Since carboxylic acid groups as substituents have been shown to yield more hydrophilic polymers [3.8] it would have been beneficial to the project if these polymers were studied and tested, as well as a greater variety of acyl derivatives, since these demonstrated more hydrophilic properties and increased sensitivity to polar analytes. An alternative method of acylation of the pyrroles was described by Andersen *et al.* [3.22], which may have more reliably produced the desired products due to the protection of the alpha position on the pyrrole and greater possibility of producing larger, purer yields of the 3-substituted acyl pyrroles.

A variety of polypyrroles and polythiophenes were then successfully polymerised and deposited onto a substrate of interdigitated gold electrodes for gas sensing purposes. The polymers chosen for investigation focused on a narrow range of the materials available. However, there is a vast amount of research into other conducting polymer materials that could have been used as chemiresistive gas sensors for this project. Plenty of reviews and articles covering their advances can be found in literature [7.1 – 7.3]. Examples include redox polymers incorporating transition metal complexes, or self-doped conducting polymers, which can aid the processability in aqueous media, or the many co-polymers that may be constructed. [7.3; 7.4]

As explained in chapters 2 and 4, there are many electrochemical parameters that can affect the properties of the polymer films produced. These parameters were also correlated to the stability of the polymers produced, which in turn governed their success in gas sensing applications. A number of investigations were carried out identifying how optimisation could be achieved through the use of different counter ions for polymer doping, the use of different reference electrodes and different methods of deposition (potential step method vs. cyclic voltammetry). Research could be extended to gain further insights into the effects of other parameters, such as the effect of different solvent systems; the use of a dynamic, stirred electrolyte system for greater control/less variability by reducing the

diffusion layer and minimising migration effects of electroactive species; and the effect of using different scan rates in order to calculate the pseudo-capacitance and acquire more knowledge regarding the diffusion rates involved in electropolymerisation and a greater understanding of the kinetics and transport processes involved. It was found that the polymer films were more conductive when polymerised at lower temperatures, although, a controlled temperature environment was not used for the electrochemical cell. Repeatability could have been improved by employing a constant temperature environment and a more robust means of setting up the electrochemical experimental apparatus in order to minimise electrode distances, thereby improving consistency. Different electroanalytical techniques could also be employed to gain better understanding of the processes involved, such as differential pulse volammetry or impedimetric techniques. [2.142; 7.5]

The gas sensing properties of the sensors were also compared to the properties of the volatiles tested, such as the polarity and hydrophobicity. The non-specificity of the sensors were evident, although, trends relating to the expected behaviour of the different polymers were shown. Based on all of the obtained results, an array of eight different conducting polymer sensors were chosen and tested. Using PCA to evaluate their discriminatory ability, the array showed good separation of all the calibration gases, whereupon it was incorporated into the hybrid device.

Although the sensors were stable even at the elevated temperature in the hybrid device, low signal responses occurred when sampling and delivery via the SPME fibre was used. This was due to the small, finite volume of volatile that the fibre was capable of holding and the residence time of such a small volume was too short for the polymers to respond. Further research would therefore be concentrated on improving the response times of the sensors. It was generally observed that larger response times were found for higher resistance sensors, however, the elevated temperatures of the gas sensing chamber tended to alter the resistances so that they were out of range or irreversibly degenerated the sensors themselves. Therefore, either a change in device design or the improvement of high

resistance sensor stability at higher temperatures would be required for the SPME sampling method to be feasible.

This setback was circumvented by using a direct injection method of the headspace volatiles, thus testing was achieved with a set of bacteria cultured in the laboratory. Results indicated that the discrimination between different bacteria was possible, particularly for *Staphylococcus aureus* and *Pseudomonas aeruginosa*. The greater potential for discrimination by using the combined technologies of metal oxide sensors and conducting polymer sensors was also demonstrated. With improved sensor technologies and consistency, it would be desirable to further study the ability of the device to discriminate between different strains of bacteria and to investigate whether it would be possible to use the device to distinguish between MRSA and MSSA, as well as extend the testing of the device with clinical samples in order to gain a greater awareness of the its applicability to wound monitoring and to judge how well it works towards its intended purpose.

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# **APPENDIX 1**

# SELECTED SPECTRA OF SOME PRODUCTS FROM MONOMER SYNTHESIS

This appendix presents a selection of spectra that demonstrate the progression of the synthesis of monomers attempted in Chapter 4. The spectra given here are as follows:

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- 274 Mass spectum of 1-phenylsulfonylpyrrole
- 275 Peak matched spectrum of 1-phenylsulfonylpyrrole
- 276 <sup>1</sup>H-NMR spectrum of 1-phenylsulfonylpyrrole
- 277 Expansion of <sup>1</sup>H-NMR spectrum of 1-phenylsulfonylpyrrole
- 278 <sup>1</sup>H-NMR spectrum of 3-dodecanoyl-1-phenylsulfonylpyrrole
- 279 IR spectrum 3-dodecanoyl-1-phenylsulfonylpyrrole
- 280 <sup>1</sup>H-NMR spectrum of 3-butyryl pyrrole
- 281 <sup>1</sup>H-NMR spectrum of 3-dodecyl pyrrole
- 282 IR spectrum of 3-dodecyl pyrrole



Fig A1.1 Mass spectum of 1-phenylsulfonylpyrrole



Fig A1.2 Peak matched spectrum of 1-phenylsulfonylpyrrole



Fig A1.3 <sup>1</sup>H-NMR spectrum of 1-phenylsulfonylpyrrole



Fig A1.4 Expansion of <sup>1</sup>H-NMR spectrum of 1-phenylsulfonylpyrrole



Fig A1.5 <sup>1</sup>H-NMR spectrum of 3-dodecanoyl-1-phenylsulfonylpyrrole



Fig A1.6 IR spectrum of 3-dodecanoyl-1-phenylsulfonylpyrrole



Fig A1.7 <sup>1</sup>H-NMR spectrum of product from 3-butyryl-1-phenylsulfonylpyrrole hydrolysis



Fig A1.8 <sup>1</sup>H-NMR spectrum of 3-dodecyl pyrrole



Fig A1.9 IR spectrum of 3-dodecyl pyrrole

#### **Discussion on spectra**

The mass spectrum presented shows that the main components detected are those that would be expected of 1-pheylsulfonylpyrrole, namely M<sup>+</sup> at 207, the phenylsulfonyl cation at 141 and the benzene ring cation at 77. The peak matched spectrum is also given here showing how the peaks found correspond to those found with the NIST library for 1-phenylsulfonylpyrrole.

Other than the small peak that occurs at 1.6, the peaks found in the <sup>1</sup>H-NMR spectrum correspond to those of 1-phenylsulfonylpyrrole and are comparable to those given by Zelikin *et al.* Other than a small singlet peak at 7.28, which was discounted from the results, the peaks accurately reproduce the results that are cited in literature. The peaks upfield, above 7.3, represent the hydrogens located around the phenyl ring. The triplet at 6.2 corresponds to the two equivalent hydrogens on the pyrrole ring furthest from the nitrogen whereas the triplet at 7.18 correspond to the other two equivalent hydrogens are found on the phenyl ring; those at the position ortho to that directly attached to the sulfur atom of the sulfonyl group (multi at 7.88) and those in the meta position (triplet at 7.52). The triplet at 7.62 corresponds to the one hydrogen on the phenyl ring that is positioned para to the sulfonyl group attachment. The integral of this peak is half that of the others as would be expected due it not having any equivalent hydrogens.

The <sup>1</sup>H-NMR spectrum provided for 3-dodecanoyl-1-phenylsulfonyl shows the peaks corresponding to the aromatic hydrogens of the phenyl group, as explained above. However, a number of peaks appear around 6.7 – 7.3 that differ from 1-phenylsulfonylpyrrole. This is because of the dodecanoyl group attached at the 3-position of the pyrrole ring, which means that the hydrogens of the pyrrole ring are no longer equivalent. The doublets at 6.72 and 7.19 correspond to the pyrrole hydrogen at the 4 and 5 positions respectively. A singlet should appear that represents the pyrrole hydrogen nearest the nitrogen and the dodecanoyl group. A singlet appears at 7.75, which is lower than expected

but this is taken to account for this hydrogen. The large peak around 1.3 represents the hydrogens along the alkyl chain of the dodecanoyl group. The triplet at 0.92 represent the three equivalent hydrogens at the end of the alkyl chain and the triplet at 2.75 represents the two equivalent hydrogens of the alkyl chain that are next to the carbonyl carbon. The quartet at 1.59 represents the two equivalent hydrogens of the alkyl chain that are next to the carbonyl carbon. The quartet at 1.59 represents the two equivalent hydrogens of the carbon next but one to the carbonyl group. The peak at 1.6 is discounted from results as for the NMR spectra of 1-phenylsulfonylpyrrole – this was an impurities found in the deuterated chloroform used. Similar results were obtained for the other products of Friedel-Crafts acylation (except for acetyl variant), with differing peak intensities for the 1.3 peak of the alkyl chain hydrogen chains.

The IR spectrum of 3-dodecanoyl-1-phenylsulfonylpyrrole is also given. The spectra was made using Nujol, whose peaks are ignored (2950-2800, 1465-1450, and 1380-1370 cm<sup>-1</sup>). The absorption peak of most note is 1672cm<sup>-1</sup> corresponding to the ketone C=O stretch of the carbonyl group. Some lower peaks show the presence of the phenyl ring overtones and ring torsion.

The <sup>1</sup>H-NMR of the product from the 3-butyryl-1-phenylsulfonylpyrrole hydrolysis reaction is given simply to demonstrate that the hydrolysis was not successful as the peaks for the aromatic hydrogens of the phenyl group are still present. The spectrum is mostly the same as that for 3-butyryl-1-phenylsulfonylpyrrole

The <sup>1</sup>H-NMR spectrum for 3-dodecyl pyrrole is given. The peaks occuring below 3ppm are very similar to those described for 3-dodecanoyl-1-phenylsulfonyl pyrrole; they represent the hydrogens of the alkyl chain at the 3-position. Despite the loss of the carbonyl group, the peak shifts do not change considerably. The peaks above 6ppm represent the aromatic hydrogens of the pyrrole ring. Due to the lack of the phenylsulfonyl group and the substituted dodecyl group, none of the hydrogens are equivalent.

The IR spectrum for the compound shows a small absorption peak around 3210cm<sup>-1</sup> indicative of the N-H stretch and also the absence of the carbonyl stretch around 1670cm<sup>-1</sup> and a reduction of the aromatic peaks below this.

# **APPENDIX 2**

# SENSITIVITY CURVES AND QUALITATIVE RESOLUTION PLOTS FOR SENSORS WITH EACH CALIBRATION GAS

The following plots present the evolution of sensitivity over each concentration of every volatile organic compound for all of the sensors tested. Their accompanying plots of the quantitative resolution are presented on the right hand side.

The sensitivity (S) was calculated:

$$S = \Delta R / \Delta C$$

= change in response / change in concentration

The quantitative resolution (QR) was calculated:

$$QR = \sigma / S$$

= measurement error / sensitivity

The plots are separated into four categories for ease of comparison between homologous series of sensors; *N*-substituted polypyrrole sensors, 3-substituted polypyrrole sensors, polythiophene based sensors, and other sensor types (the copolymer SNS, and the commercial printing polymers, Plexcore<sup>®</sup> and PaniPol<sup>®</sup>)

The range of the axes are constant for all plots except those of the other sensor types, due to PaniPol responses being negative. However, the scale of the axes has been maintained for facile visual comparison.

ACETALDEHYDE



Fig A2.1 Sensitivities and Quantitative Resolution Plots for Acetaldehyde



Fig A2.2 Sensitivities and Quantitative Resolution Plots for Acetic Acid


Fig A2.3 Sensitivities and Quantitative Resolution Plots for Acetone



Fig A2.4 Sensitivities and Quantitative Resolution Plots for Ammonia



Fig A2.5 Sensitivities and Quantitative Resolution Plots for Butanone



Fig A2.6 Sensitivities and Quantitative Resolution Plots for Butyric Acid



Fig A2.7 Sensitivities and Quantitative Resolution Plots for Ethanol

# **APPENDIX 3**

# CALCULATION OF HEADSPACE CONCENTRATIONS

Due to the low concentrations used, Henry's law constants were used for the calculation of the headspace concentrations. The following explanation is taken from the theoretical development section of a paper by Robbins *et al.*<sup>1</sup>

Henry's law applies when chemical and thermal equilibrium are achieved within an enclosed sampling vessel when the solutes present are at low concentrations. The vapour-liquid system can then be described thus:

$$P_i = k_H \times x_{i(1)}$$

where  $P_i$  is the partial pressure of *i* in the vapour phase,  $x_{i(l)}$  is the mole fraction of *i* in the aqueous phase, and  $k_H$  is the Henry's law constant for *i* at a given temperature and pressure (in atm).

Under ideal gas behaviour, the partial pressure is the mole fraction of *i* multiplied by the total vapour pressure, which is the sum of partial pressures of all components. Since the partial pressures are sufficiently small due to low concentration in the aqueous phase, Dalton's law can be used to express the system thus:

$$P_i = \frac{n_{i(g)}RT}{V_{(g)}}$$

where  $n_{i(g)}$  is the number of moles of *i* in the headspace,  $V_{(g)}$  is the headspace volume, and *R* is the gas constant expressed as 0.08205 atm.L/mol.K.

The total number of moles of *i* in the system is the sum of the number of moles in the aqueous phase at equilibrium and the number of moles in the headspace. The concentration balance equation is obtained by dividing by the volume of the aqueous phase,  $V_{(aq)}$ .

<sup>1</sup> Robbins, G.; Wang, S.; Stuart, J. Using the Static Headspace Method To Determine Henry's Law Constants. *Anal. Chem.* **1993**, 65, 3113 – 3118.

$$C_{i(aq)}^{0} = C_{i(aq)}^{eq} + \frac{n_{i(g)}}{V_{(aq)}}$$

where  $C_{i(aq)}^{0}$  and  $C_{i(aq)}^{eq}$  are the concentrations of *i* in the aqueous phase initially and at equilibrium respectively.

Multiplying the second right hand term by  $V_{(g)}/V_{(aq)}$  gives

$$C_{i(aq)}^{0} = C_{i(aq)}^{eq} + C_{i(g)}^{eq} (\frac{V_{(g)}}{V_{(aq)}})$$

where  $C_{i(g)}^{eq}$  is the equilibrium concentration of *i* in the headspace in molar gaseous units.

Henry's law constant in terms of atmospheres can be converted to a dimensionless form using a conversion factor. This dimensionless form can be expressed as the ratio of concentrations of component *i* in the headspace and in the aqueous phase at equilibrium:

$$k_{\rm H,dim} = \frac{C_{\rm i(g)}}{C_{\rm i(aq)}}$$

Substituting back gives the following equation for the initial concentration of *i* in the aqueous phase:

$$C_{i(aq)}^{0} = C_{i(g)}^{eq} \left( \frac{1}{k_{H,dim}} + \frac{V_{(g)}}{V_{(aq)}} \right)$$

However, since the headspace volume and aqueous solution volume were maintained the same in experimentation (5ml solution in a 10ml headspace vial), the equation simplifies to

$$C_{i(aq)}^{0} = \frac{C_{i(g)}}{k_{H,dim}}$$

which is simply a rearrangement of the expression of the Henry's law dimensionless constant.

Henry's law constants were obtained from experimental values reported in Sander's online source.<sup>2</sup> The values were also checked against the references cited.

<sup>2</sup> R. Sander (1999) Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry (Version 3) http://www.henrys-law.org

# **APPENDIX 4**

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# Development of conducting polymer sensor arrays for wound monitoring

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#### Abstract

A study of conducting polymer sensors for use in monitoring the headspace of metabolites produced from superficial wounds and burns is in progress. Gas chromatography–mass spectrometry (GC–MS) headspace analysis of the most common bacterial species found to be present in wounds has been achieved to determine the key volatile markers for sensor detection.

A preliminary study of sensor arrays using seven pure volatiles known to be produced from the bacteria studied is reported [R.A. Allardyce, V.S. Langford, A.L. Hill, D.R. Murdoch, Detection of volatile metabolites produced by bacterial growth in blood culture media by selected ion flow tube mass spectrometry (SIFT-MS), J. Microbiol. Methods 65 (2) (2006) 361–365; R.J. Wiggins, M. Wilks, S. Tabaqchali, Analysis by gas liquid chromatography of production of volatile fatty acids by anaerobic bacteria growth on solid medium, J. Clin. Pathol. 38 (1985) 933–936]. The sensors used were based on an existing sensor array, previously used in a smart fire detection system [E. Scorsone, A.M. Pisanelli, K.C. Persaud, Development of an electronic nose for fire detection, Sens. Actuators B: Chem. 116 (2006) 55–61], and a sensor array developed from the same design and configuration has given stable results, especially towards butyric acid and ethanol. © 2008 Elsevier B.V. All rights reserved.

Keywords: Electronic nose; Conducting polymers; Wound monitoring; MRSA

### 1. Introduction

In modern medicine, early detection and qualitative discrimination of bacteria present in infections is decidedly important. The methods currently used in medicine such as PCR are expensive, require skilled technicians and, most importantly, results typically take a matter of days to be returned by which time the infection can be quite advanced. As a consequence of this, inappropriate antibiotics have been administered, which in turn has given rise to antibiotic-resistant strains of bacteria such as methicillin-resistant *Staphylococcus aureus* (MRSA) [4], which has received a lot of attention in the media. Due to the seriousness of this dilemma there is a great need for rapid and accurate detection of bacteria. Developments in sensor technology, namely machine olfaction, have facilitated the successful detection of bacteria and microbial disease quickly and reliably [5].

Conducting organic polymer sensors are chemiresistors that have rapid adsorption and desorption kinetics at room temperature and have high sensitivities, typically from 0.1 ppm. Responses are reversible and no heater elements are required, thus allowing operation with a low power consumption. They are easy to develop and various methods of manufacture can be used. Specificity of the sensors towards different classes of compounds can be closely tailored by altering the functional group chemistry of the sensors [3].

A literature review [6,7] indicated that the most common strains of bacteria present in wounds are *S. aureus*, *Pseudomonas aeruginosa*, *Streptococcus pyogenes* and *Bacteroides fragilis*. The threat of antibiotic resistance, in particular MRSA, makes the importance of discriminating between MRSA and MSSA an imperative task.

The metabolites generated from a wound are produced by the bacteria acting upon the wound, not simply by the bacteria themselves. Thus, different metabolites are found when bacteria grown on different media. There exists a vast literature base that describes the range of volatiles that are produced from various bacteria [1,2]. The strategy adopted was to develop a preliminary array that would discriminate the volatiles that were most ubiquitous. The seven volatiles chosen as key markers for this purpose were ethanol, acetic acid, ammonia, acetone, acetaldehyde, 2-butanone and butyric acid.

The final electronic nose device will ultimately employ the use of solid phase microextraction (SPME) to pre-concentrate

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the complex metabolite matrix and present the analytes to the sensor arrays. A hybrid array system of metal oxide sensors and conducting polymer sensors will be used in parallel to offer a good overlap of sensitivities and orthogonality. Online processing of data received from sensors will then be performed using modern neural network techniques.

### 2. Experimental

## 2.1. Identification of volatile key markers

Gas chromatography–mass spectrometry analysis of the headspace of the chosen bacteria was performed on a Varian Saturn GC/MS with SPME fibres supplied from Supelco (Bellefonte, PA). The SPME fibres have a 65-µm thick stationary phase made of polydimethylsiloxane/divinylbenzene (PDMS/DVB).

Headspace analysis was performed on the selected bacteria, cultured on both brain heart agar and tryptic soy agar, and chopped meat agar for *B. fragilis*. The results were searched against Wiley275, NIST and Saturn libraries.

## 2.2. Sensor fabrication

The substrate for the sensor array was made of  $125 \,\mu$ m polyimide strip with deposited gold interdigitated electrodes (IDEs), upon which the conducting polymer was deposited. Conducting polymer films were electrochemically deposited onto the substrate using chronoamperometry with a platinum reference electrode, a gold plate as the counter electrode and the substrate as the working electrode within a custom-made Teflon well. A  $\mu$ Autolab Type III potentiostat was used in conjunction with general purpose electrochemical system (GPES) software for all electrochemical measurements and techniques, which enabled controlled deposition and valuable information from *I/V* curves.



Fig. 1. Sensor array configuration and layout of interdigitated electrodes.

Chronoamperometric polymerisation was performed by immersing the substrate in a quiescent solution of the pyrrole monomer and organic dopant, and applying a constant potential at or above the monomer's oxidation potential for a certain amount of time. After deposition the polymer films were stabilised by reiteratively doping and dedoping the polymers via cyclic voltammetry. It was possible to alter the resistance of the film by stopping the cyclic voltammetric process at different potentials.

The substrates were prepared by cleaning with chromic acid and then depositing a thin film of poly-3-hexylthiophene by dipcoating in a regioregular solution in xylene. This helped the lateral growth of a uniform film in later polymerisations.

A base layer of polypyrrole was used for many of the sensors and has been shown to give stable results in previous work.

The sensor arrays were then subject to heat treatment to further stabilise the films and increase the final polymer resistance. Fig. 1 shows the arrangement of a successfully developed sensor array.



Fig. 2. Setup of sensor testing gas rig used with permeation tubes.

#### 2.3. Sensor testing and data acquisition

Permeation tubes (Fine Permeation Tubes, Nuova Grangiara, Italy) for each of these volatiles were used to generate known concentrations (1-10 ppm) of the pure volatile compound at a constant temperature of 25 °C. A temperature/humidity cabinet was used to control conditions of the permeation tubes. At a constant temperature, the permeation tubes release a volatile gas at a steady rate; mass flow controllers were used to vary the flow rate of a carrier gas (clean air) over the permeation tube to produce a range of known concentrations. Concentrations in the range of 1–10 ppm were achievable by using a dilution stream of air and a mixing chamber.

Additionally, a sparging system was used to control the humidity and the integration of a valve switch before the sensor input improved the contrast between the signal response and the base line resistance, and also allowed instant sampling of the volatile. Fig. 2 shows the setup of the system used for sensor testing.

The analytes were presented to the sensor array dynamically; a miniature rotary vane pump pulled the gas mixture in the mixing chamber across the sensor array at a constant flow rate. The sample volume was 1 cm<sup>3</sup> and the gold electrodes of the sensor array were connected to resistance interrogation circuitry. Real-time data were transferred to a PC via an RS232 serial communication protocol and custom software was used for storage and analysis of the data.

# 3. Results and discussion

#### 3.1. Volatile key markers found

GC/MS analysis showed that dimethylsulfide was present in all strains of bacteria analysed in differing amounts. Mostly ketones (nonanone, octanone, and undecanone) and alcohols (heptanol, dodecanol, and undecanol) were present in the headspace of *P. aeruginosa*. Fatty acids (acetic, propionic, and isovaleric acid) were prevalent in the headspace of *Streptococcus aureus*, as well as aldehydes, but no ketones were present.

#### 3.2. Sensor responses to pure volatiles

A sensor array that was initially used demonstrated a good response to ammonia, especially from S1/NSA (shown in Fig. 3 with the largest sensor responses).

Another sensor array was developed after these results and tested at 1–10 ppm for all seven volatiles. It responded to butyric acid and ethanol well and also gave large responses to ammonia. S1/NSA and P2/PF6 showed the largest signal response (Fig. 4).

More convincing changes in sensor response were shown for concentrations above 5–6 ppm overall. Below this range, it would appear that the responses were not proportional to the concentration of volatile, or at least negligible. Signal responses above 5–6 ppm showed concentration dependence with a gradual increase in resistance change with increasing concentration.



Fig. 3. Responses to ammonia pulsed at 1-5 ppm from left to right. Response and recovery time within 3-10 s.

Ammonia yielded very high responses from S1/NSA, which increased at a fast rate and had very long and impractical recovery times, hence the reason for a plot of only three different concentrations at present. Some sensor drifts became apparent towards the end of each test, especially as sensor responses became greater with higher concentrations. The amount of drift present in this study was not detrimental to the results and disregarded for the most part.

The base line resistance of the sensors were kept fairly low to avoid too much signal noise created using the sensor/signal processing apparatus; however the resistances were too low particularly for P4/PF6. It is apparent that the higher the base resistance of the sensor, the greater its potential sensitivity but too high a resistance gives rise to noise and substantial drift. Therefore, it will be necessary to find the balance between the resistance and conductivity to give the optimal signal response before sensors can be selected.

In the sensor array, the conducting polymer sensors were made in duplicate. They had very similar base line resistances thus allowing the results to be more coherent and valid. It also



Fig. 4. Individual sensor responses of array to the pure volatiles tested. A linear increase in response to concentration can be seen, especially above 5 ppm.



Fig. 5. Sensor responses to saturated ethanol vapour showing a poor return to base line resistance.

gives an indication of the reproducibility and ease of manufacture. The sensor array used for this study had a few predecessors that were also functional.

The low response levels of some of the sensors may also be adjusted by changing the concentrations of the monomer and dopant used in the electrolyte and the electrochemical techniques and parameters. A thicker film would allow for more of the volatile being sensed to be adsorbed and thus give a larger sensor response. In turn, this would give a larger recovery time.

Saturated vapours gave responses from 20% to around 40% (Fig. 5). The results also show that all the sensors except for S1/NSA (shown with the two largest responses in Fig. 5) do not return to base line resistance after exposure to the saturated vapour. Knowledge of the sensors dynamic range before they saturate would be advantageous since any further design could be more closely adapted for the project requirements.

Another sensor array was designed and developed to investigate effects between pyrroles with different substitutions, functional groups and steric factors.

It has been shown that alkyl chains of varying lengths substituted at the 3-position increase the conducting polymer's sensitivity to non-polar species, especially with increasing alkyl chain length [8]. Conversely, it has also been shown that substitution of carboxylic acid groups at the 3-position produce a hydrophilic polymer [9].

It was decided to conduct original research into whether these properties are still exhibited or even enhanced when deposited as a top-layer onto a polypyrrole base layer. Preliminary results show improved stability, a slightly larger sensor response and broad sensitivities indicating a decent potential for use but more investigative work with different volatiles is required before conclusive feature selections can be made.

#### 3.3. Electropolymerisation

The monomers were polymerised electrochemically. Cyclic voltammetry was used to study each of their oxidation and reduction potentials both on their own, using a gold electrode, and as a top-layer deposited on a polypyrrole base layer. The deposition of the polypyrrole base layer was carried out by using chronoamperometry, applying 1.1 V for 5 s or cyclic voltammetry between 0.1 and 0.9 V at a constant rate of 50 mV/s for three cycles. Either method gives a good uniform film across the electrodes with a resistance of  $330-370 \Omega$  and results are very reproducible. Cycling through these potentials back and forth after deposition so as to dope–dedope the polymers was studied, varying the potential at which the cycling was stopped. Vastly different resistances were found depending on the range at which cyclic voltammetry was used and the potential stopped.

Similarities were noted between the voltammograms of polymers deposited on gold and on a polypyrrole base layer, which proved useful for deciding the potential range required for oxidation or reduction (Fig. 6).

Not all of the voltammograms show a Nernstian reversibility. A common feature for some of the monomers is the first cycle markedly different than subsequent cycles, and some peaks disappear after the first cycle indicating a rearrangement of the structure. A more careful and extensive study into this should reveal a clearer mechanistic understanding that will prove useful.

#### 3.4. Base resistances and humidity effects

The low response signifies that these sensors need optimising to be sensitive for a greater dynamic range. The resistances for the sensor range from  $\approx 300 \Omega$  to  $30 k\Omega$ . It is apparent that resistances below  $1 k\Omega$  do not give adequate responses at all, resistances between 1 and  $10 k\Omega$  give a small response, and good responses are observed for resistances within the



Fig. 6. Cyclic voltammograms for an alkylated polypyrrole on gold, between 0 and 1 V (top), and on PPY base layer, between -1 and 1 V (bottom). The similarity between the curves and the oxidation potential can be seen at around 0.75 V.

range  $10-50 \,\mathrm{k\Omega}$ . As the resistance increases beyond this, noise becomes more noticeable. If cyclic voltammetry was stopped at a negative potential beyond the reduction potential, around  $-1 \,\mathrm{V}$ , resistances of  $14 \,\mathrm{k\Omega}$  for N4,  $20 \,\mathrm{k\Omega}$  for N7 and  $40 \,\mathrm{k\Omega}$  for N6 were achieved in tests conducted so far. However, the conductivities were very low and after heat treatment and time the base line resistances increased to over  $50 \,\mathrm{k\Omega}$  and too much signal noise was generated when testing the sensors. Conversely, if stopped at positive potentials above the oxidation potential, very low resistances were found which gave little or no sensor response. Optimal performance was demonstrated when final resistances were in between these two extremes at around  $10-50 \,\mathrm{k\Omega}$ .

A general comparison between sensors responses at 0 and 20% RH show that humidity diminishes the signal response and more drift occurs between measurements.

#### 4. Conclusions

The sensors tested have been shown to work satisfactorily but resistance changes needs to be greater and a broader range of overlapping sensitivities to all the volatile key markers is required before an efficient array can be chosen and optimised for use in a prototype. S1/NSA proves to be good for ammonia detection, and investigation into pyrrole-based sensors with differing functionality on pyrrole base layers is currently still in progress, the results of which should satisfy response to less polar volatiles and an orthogonality to the key markers chosen.

Some short studies into the effects of varying the electrochemical parameters and film thickness were conducted, showing that resistances in the range of  $10-50 \text{ k}\Omega$  were optimal for use in this system. Further investigation is needed to find a balance between a sensor's resistance, conductivity, ease of manufacture/reproducibility and long-term stability for optimal performance.

The synthesis of the three substituted alkyl pyrroles is still in progress and comparisons drawn from the results against the current knowledge of alkyl chain length effects on sensor sensitivity should provide insightful information.

Comprehensive knowledge is expected to be gained from a systematic study of the various effects from different monomers and dopants and electrochemical parameters. This will also enable the selection of conditions necessary for an optimised sensor array, with justification that the sensors are calibrated to their best performance for the application. Attention has only been focused on one type of material (i.e. polypyrole) at the moment, but it would be valuable to have the same knowledge gained from the above methods for different conducting polymer materials, such as thiophene and derivatives.

The successful design and manufacture of an appropriate sensor array can then be further tested to judge its specificity and power of volatile discrimination using PCA techniques. Once an adequate library of sensor's selectivity is built, testing of actual bacterial samples and swabs will be needed to deem its suitability to the wound monitor device.

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