An investigation of novel low-temperature carbon monoxide gas sensors

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AN INVESTIGATION OF NOVEL LOW TEMPERATURE CARBON MONOXIDE GAS SENSORS

by

Alison Beech

A Doctoral Thesis

Submitted in partial fulfilment of the requirements for the award of

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CONTENTS

Abstract i

Acknowledgements iii

Chapter 1

INTRODUCTION

1.1 The Poisoning Effect of Carbon Monoxide 1
1.2 Standards for Safety. 3
1.3 Current Methods of Gas Sensing.
   1.3.1 Sensor diversity. 4
   1.3.2 An Introduction to Gas Sensor Technology. 5
   1.3.3 Zirconia Gas Sensors. 6
   1.3.4 Tin Oxide Semiconductor Gas Sensors. 11
   1.3.5 Metal Phthalocyanine Sensors. 14
   1.3.6 Gas Sensors with Liquid Electrolytes. 17
   1.3.7 Colourimetric Methods of Gas Sensing. 20
   1.3.8 Infrared Spectroscopy Gas Detection. 23
   1.3.9 Optical Fibre Gas Sensors. 25
   1.3.10 Surface Acoustic Wave Gas Sensors. 29
   1.3.11 Metal Oxide Semiconducting Gas Sensors. 31
   1.3.12 Biosensor Methods of Gas Sensing. 34
1.4 Sensor Markets. 36

Chapter 2

THE SENSOR FABRICATION

2.1 General. 38
2.2 The Solid Polymer Electrolytes.
   2.2.1 Nafion® as a Solid Polymer Electrolyte. 40
   2.2.2 DAIS as a Solid Polymer Electrolyte. 44
   2.2.3 Deposition of the Electrolyte Layer. 45
2.3 The Deposition of the Electrodes.
   2.3.1 Vacuum Evaporation Deposition. 49
   2.3.2 DC Sputter Coating. 51
   2.3.3 Screen Printing. 51
   2.3.4 Pressing of Catalyst Loaded Cloth Electrodes. 55
2.4 The Electrode and Electrolyte Configurations.
   2.4.1 The Printed Design Configurations. 56
   2.4.2 The Pressed Design Configuration. 57
Chapter 3

ELECTROCHEMICAL CHARACTERISATION OF THE ELECTRODES

3.1 Introduction. 58
  3.1.1 The Study of a Gold Reference Electrode - Experimental. 59
  3.1.2 Results. 61
  3.1.3 The Study of a Silver/Silver Chloride Reference Electrode - Experimental. 63
  3.1.4 Results. 65

3.2 The Electrochemistry at Planar Electrodes. 66
  3.2.1 Experimental 66
  3.2.2 Results. 67

Chapter 4

REQUIREMENTS FOR SENSOR TESTING

4.1 The CO Sensor Test Rig Design 74
4.2 Details of Sensors Tested. 76
4.3 Electrochemical Testing Techniques. 78
  4.3.1 DC Technique (Cyclic Voltammetry). 78
  4.3.2 AC Impedance Spectroscopy Technique. 79
4.4 Electrochemical Testing Procedure. 85

Chapter 5

RESULTS FROM SENSOR TESTING IN CLEAN AIR AND IN ENVIRONMENTS CONTAINING CARBON MONOXIDE

5.1 An Introduction to the Observed Responses of the Sensors to CO. 88
  5.1.1 General Changes Observed in the Open Cell Potential Values. 88
  5.1.2 General Response Observed by the Cyclic Voltammetry Testing Technique. 89
  5.1.3 General Response to the AC Impedance Spectroscopy Testing Technique. 90

5.2 Results Obtained with the Planar Sensor with a Cast DAIS Electrolyte. 91
  5.2.1 Effect of Working Electrode Area. 91
  5.2.2 Effect of Electrolyte Film Thickness. 100
  5.2.3 Effect of Electrode Design - Interdigitated Working and Counter Electrodes. 108
5.2.4 Effect of Electrode Design  
- Interdigitated Working and Reference Electrodes. 118

5.2.5 Effect of Electrode Material  
- Pt/C Working and Counter Electrodes. 124

5.3 Results Obtained with the Planar Sensor with a Cast Nafion® Electrolyte. 130  
5.3.1 Effect of Working Electrode Area. 130  
5.3.2 Effect of Electrolyte Film Thickness. 134

5.4 Results Obtained with a Planar Sensor with a Cast Thermally Activated Nafion® Electrolyte. 143  
5.4.1 The Observed Effects Due to the Thermal Activation Production Method. 144  
5.4.2 Reliability of the Production Method. 147  
5.4.3 Effect of Electrode Design  
- Interdigitated Working and Counter Electrodes. 152

5.5 The Sensor with Catalyst Loaded Cloth Pressed onto Nafion® 115 Electrolyte. 163

5.6 The Sensor with Catalyst Loaded Cloth Pressed onto DAIS Electrolyte. 166

5.7 Summary. 171

Chapter 6

RESULTS FROM SENSOR TESTING IN SIMULATED DOMESTIC ENVIRONMENTS  
- The Effects of Time, Humidity and Other Likely Gases

6.1 Effect of Test Gas Relative Humidity Level on the Sensor’s Response. 172  
6.1.1 Effect of RH Level on the Sensor’s Response in Clean Air. 172  
6.1.2 Effect of RH Level on the Sensor’s Response to CO. 177

6.2 Effect on the Sensor’s Response to Alternative Analyte Gases. 183  
6.2.1 Effect of Methane. 183  
6.2.2 Effect of Hydrogen. 186

6.3 Results from Experiments Studying the Ageing Effect. 191  
6.3.1 Ageing Effect Experiments with Planar Sensors with a Cast DAIS Electrolyte. 192  
6.3.2 Ageing Effect Experiments with Planar Sensors with a Cast Thermally Activated Nafion® Electrolyte. 192  
6.3.3 Ageing Effect Experiments with the Sensors which Possessed Catalyst Loaded Carbon Cloth Electrodes Pressed onto a Commercial Electrolyte Membrane. 202

6.4 Summary. 202
Chapter 7

INTERPRETATION OF THE RESULTS FROM SENSOR TESTING

7.1 Introduction. 204
7.2 Chemisorption of CO on a Supported Platinum Catalyst. 204
7.3 Explanation of the Variation in OCP Value. 206
7.4 Explanation of the Response Obtained by Cyclic Voltammetry. 208
7.5 Explanation of the Response Obtained by AC Impedance Spectroscopy. 211
7.6 Explanation of the Response Obtained when the RH was Varied. 214
7.7 Explanation of the Response Obtained when an Alternative Analyte Gas was Present. 216
7.8 Explanation of the Response Obtained as a Result of Long Term Testing (The Ageing Effect). 217
7.9 Fitting of the AC Impedance Spectroscopy Data. 218
7.10 Calculation of the Resistance and Capacitance Values. 224
7.11 Summary. 231

Chapter 8

ELECTRODE AND ELECTROLYTE SURFACE ANALYSIS STUDIES

8.1 Scanning Tunnelling Microscopy Theory and Experimental Details. 234
8.2 Atomic Force Microscopy Theory and Experimental Details. 235
8.3 STM Imaging of Sputter Coated and Screen Printed Platinum and Gold Electrodes. 236
8.4 AFM Imaging of Cast Films of DAIS and Nafton®. 241
8.5 Summary. 244

Chapter 9

GENERAL DISCUSSION AND CONCLUSIONS

9.1 Reiteration of the Original Objectives. 245
9.2 Review of the General Findings and Conclusions. 246
9.3 Recommendation of Further Work. 253
   9.3.1 Catalytic Additions to the Working Electrode Material. 253
   9.3.2 Further Long-term Testing. 254
   9.3.3 Further Variation of the Electrode and Electrolyte Parameters. 254
   9.3.4 Single DC and AC Measurements. 255
ABSTRACT

Carbon monoxide (CO) is a colourless and highly toxic gas. The detection of CO is a key requirement for safety and control in combustion processes. A number of sensors are currently available but all have drawbacks with most if not all having questions raised about their effective detection of CO over other gases such as hydrogen and methane.

The power consumption of some methods of gas sensing is high as the active material must be heated to 400-600 °C in order to function. The aim of this project was to attempt to eliminate this high power requirement and to study the design, fabrication and testing of CO sensors which function at room temperature, based on a supported platinum electrode in combination with a solid polymer electrolyte. It is therefore conceivable that the power source of such a sensor could be a battery, which could power a microcontroller and the relatively simple diagnostic testing equipment in a final commercial product.

The study presented describes how both re-cast and commercial films of Nafion® (Du Pont) and DAIS (DAIS Corporation) have been employed as proton conducting solid polymer electrolytes. The feasibility of utilising catalyst loaded carbon cloth electrode material (ETEK) and of various methods of depositing platinum and gold electrodes on an alumina substrate have also been studied. Protons and water are transported within the polymer electrolyte layer, while CO, CO₂ and O₂ gases diffuse through the layer to the electrode/electrolyte interface. The surface analysis techniques of SEM, STM and AFM have been used to provide an insight into the methods of electrode deposition and the pre-treatment of electrolyte materials. Also, the potential of these electrodes to be produced from more inexpensive materials has been identified.

The development and commissioning of a satisfactory testing rig, which could provide a desired relative humidity and allowed accurate gas concentration control, was carried out. The use of a DC conditioning process, in combination with AC
impedance spectroscopy as an appropriate testing technique to monitor the presence of CO was studied.

CO has been successfully detected, indicating a decrease in the resistance with gas concentration. A small response to hydrogen was observed and methane was not detected. Finally, a proposed model for the mechanism of CO detection has been given, and future sensor design modifications, such as electrode and electrolyte materials, and microelectronic technology requirements have been considered, with the view of producing a commercial sensor unit.
ACKNOWLEDGEMENTS

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I wish to express my gratitude to the technical staff from the Chemistry Department at Loughborough University, in particular Alan Stevens, John Spray and Dave Wilson, and also many thanks to Roger Tomlinson in the Electrical Engineering Department for his invaluable assistance regarding the deposition of metals.

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I would like to thank all my friends throughout my time at Loughborough University. Finally, I would like to thank John, Margaret and Stan Weightman, Christine, Nigel and my Parents for their support and encouragement throughout my studies.
CHAPTER 1

INTRODUCTION

1.1 The Poisoning Effect of Carbon Monoxide.

Carbon monoxide is a colourless, odourless and highly toxic gas. CO poisoning is a common cause of death which results from the faulty combustion of fuel or exhaust fumes from motor vehicles.\(^1\) The toxicity of CO results from its ability to bind strongly to the iron atom of haemoglobin (Hb) to form carboxyhaemoglobin (COHb). Carboxyhaemoglobin is more stable than oxyhaemoglobin (O\(_2\)Hb), although the processes of absorption and desorption of CO are much slower.

\[
O_2\text{Hb} + \text{CO} \rightleftharpoons \text{COHb} + O_2 \quad \text{(1.1)}
\]

Although CO binds one hundred times more strongly to Hb than does oxygen, the above reaction can be reversed by administering pure oxygen to force the equilibrium to the right in equation 1.2.\(^2\)

\[
\begin{align*}
\text{Fe-C} & \quad + \quad \text{O}_2 \\
\text{(in haemoglobin)} & \quad \rightleftharpoons \quad \text{Fe-O} \\
\text{(in haemoglobin)} & \quad + \quad \text{CO}
\end{align*} \quad \text{(1.2)}
\]

Therefore, like oxygen, CO absorbs into the blood through the lungs, and desorbs from the body by the same route. This accumulation of COHb in the blood, not only reduces its oxygen carrying capacity, but also the ability of the remaining O\(_2\)Hb to release oxygen to the tissues. The level of COHb in the blood will approach a well defined equilibrium if the CO level in the inspired air is constant. However, the rate at which that equilibrium is reached depends on many factors, including lung ventilation rate (i.e. the level of physical activity), blood volume, lung health, atmospheric pressure, and the oxygen concentration in the air.\(^3,4\) The typical effects of different levels of COHb in the blood of an average, healthy adult are illustrated in table 1.1 and in figure 1.1 below.
Table 1.1 The Effects of Carboxyhaemoglobin in the Blood.

<table>
<thead>
<tr>
<th>%COHb</th>
<th>Health Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1-1</td>
<td>Normal background level.</td>
</tr>
<tr>
<td>1-5</td>
<td>Selective increase in blood flow to vital organs to compensate for reduced O₂-carrying capacity of blood</td>
</tr>
<tr>
<td>5-10</td>
<td>Visual light threshold increases, no subjective effects.</td>
</tr>
<tr>
<td>10-20</td>
<td>Tightness across forehead, mild headache.</td>
</tr>
<tr>
<td>20-30</td>
<td>Headache, nausea; fine manual dexterity impaired.</td>
</tr>
<tr>
<td>30-40</td>
<td>Severe headache, dizziness, nausea and vomiting.</td>
</tr>
<tr>
<td>40-50</td>
<td>Collapse, increased pulse and respiration rate.</td>
</tr>
<tr>
<td>50-60</td>
<td>Coma, intermittent convulsions.</td>
</tr>
<tr>
<td>60-70</td>
<td>Depresses heart action, death possible.</td>
</tr>
<tr>
<td>70-80</td>
<td>Weak pulse, slow respiration, death likely.</td>
</tr>
</tbody>
</table>

Figure 1.1 The Effect of CO Concentration in the Atmosphere on COHb Levels.
1.2 Standards for Safety.

COHb in the range 10-20% may cause headaches in the average person, but is unlikely to cause a fatality or irreversible harm. Levels higher than 50% COHb are found in fatal incidents, and yet complete recovery from coma induced by such levels is not unknown. A CO alarm should, therefore, aim to limit the COHb in the blood of the room occupant to less than 20% under the worst conditions, and less than 10% under typical conditions.

An extreme case of a hazardous combustion build-up in domestic premises is a case of a natural gas fire, operating at full rate (6.5 kW) with a totally blocked flue, for a period of several hours. For an average person this would produce a COHb level of 20% within two hours, with a continual rise to dangerous levels of over 50% COHb. In such a situation an alarm triggered by 150 ppm CO within fifteen minutes would provide ample time for corrective action to avoid a poisoning incident.

The possibility of false alarms, i.e. an alarm response to safe (low) levels of CO and responses to other non-hazardous gases should be taken into account. Indoor sources of CO are also common in domestic premises. For example, short-term emissions are often observed following the ignition of a cooker burner, and the triggering of an alarm in this circumstance would be considered to be a false alarm. As a result it may be useful to specify a long response time before the triggering of an alarm at relatively low CO concentrations.

As a consequence, the British Standard Institution (BSI) has produced a specification for electrical apparatus designed to detect carbon monoxide in domestic premises. It states that a detector must be triggered either within thirty minutes when exposed to 150 ppm CO, or within six minutes when exposed to 350 ppm CO. It must, however, not respond to 45 ppm CO within sixty minutes. When triggered, such electrically operated detectors must sound an alarm of at least 85 dB (at three metres) and a visual signal may also be appropriate of at least
ten millicandelas. The apparatus should then recover from the alarm state within five minutes in clean air.

As discussed above, the cross-sensitivity of a CO sensor to other gases is an important factor. Hydrogen is present with CO in combustion products, usually at about half the CO concentration. It may also be evolved from food during cooking. Therefore, the response to hydrogen should preferably be less than that for CO. Also, an electrically operated detector should not respond to a concentration of 500 ppm methane. Ethanol vapour may be produced in kitchens during cooking; to avoid false alarms, the device should be immune to ethanol up to 1000 ppm. This has been achieved in one commercially available sensor by the use of an internal charcoal filter.

The BSI standards also state that the detection of CO can be used as an early warning system for fires, as CO is emitted during the early stages of a fire, often well before the production of smoke. However, it is envisaged that the CO sensor within domestic premises will not remove the requirement for a smoke detector.

1.3 Current Methods of Gas Sensing.

1.3.1 Sensor diversity.

A chemical sensor may be defined as a simple-to-use, robust device that is capable of chemical recognition and transduction, i.e. the conversion of the chemical step into an optical or electrical signal. The sensor industry is extremely diverse, with commercially available sensors responding to one of over a hundred physical, chemical and biological variables (measurands). Some examples of these variables are given in table 1.2 below.
Table 1.2 Physical, Chemical and Biological Variables.

<table>
<thead>
<tr>
<th>Physical variables</th>
<th>Radiant</th>
<th>UV, IR and visible light, ionising radiation, microwaves</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Thermal</td>
<td>Temperature, heat flow, thermal conductivity</td>
</tr>
<tr>
<td></td>
<td>Magnetic</td>
<td>Field strength, flux density</td>
</tr>
<tr>
<td></td>
<td>Mechanical</td>
<td>Flow, pressure, torque, load, strain, force, weight</td>
</tr>
<tr>
<td></td>
<td>Electrical</td>
<td>Current, voltage, power</td>
</tr>
<tr>
<td>Chemical Variables</td>
<td>Gas phase</td>
<td>Oxygen, combustible and toxic gases, organic vapours</td>
</tr>
<tr>
<td></td>
<td>Liquid phase</td>
<td>pH, glucose, nitrates, metals, dissolved oxygen</td>
</tr>
<tr>
<td></td>
<td>Solids</td>
<td>Airborne biochemicals, metals, soil contaminants</td>
</tr>
<tr>
<td>Biological variables</td>
<td>Liquid phase</td>
<td>Bacterial numbers, individual species of micro-organism</td>
</tr>
</tbody>
</table>

Sensor technologists have utilised a great range of effects and phenomena in order to detect certain variables. For example, piezoresistance for the variables of pressure, acceleration and strain\(^8,9\); the Hall effect for speed, current and magnetic flux\(^10\); the Doppler effect for flow velocity; enzyme reactions for the detection of phenols, glucose\(^11\) and organophosphorous pesticides; and electrochemical effects for the detection of gases and dissolved metals.

1.3.2 An Introduction to Gas Sensor Technology.

The development of sensors for CO has received a great deal of attention in recent years. A practical sensing device must be robust, relatively easy to make and inexpensive. The effect of the gas on the sensor must be reversible, so that when the gas is removed the measured parameter must return to its original value, with false readings and triggered alarms kept to a minimum.
The majority of CO sensors described in the literature are of the electrochemical semiconduction type. It has been known for a long time that the presence of different gases in the atmosphere surrounding a semiconducting material can affect the electrical conductivity of the metal oxide. They usually have low selectivity and must be heated to a suitable temperature, generally higher than 50° C.\(^\text{12}\)

Other kinds of sensors, both potentiometric or amperometric, are based on solid electrolyte technology. The temperature at which these sensors operate depends on the electrolyte used. The \(\text{O}^2\) conductors, like zirconia,\(^\text{13,14}\) possess a sufficient conductivity only at temperatures higher than 300 °C, while, conducting polymers can be employed at a lower temperature range, usually room temperature to 100 °C.\(^\text{15-17}\)

Many other methods are discussed in the literature which are commercially well established. The most developed detecting methods for gases in domestic premises and industrial applications, as well as remote sensing methods for the detection of toxic gas clouds in the atmosphere, are described in the following sections.

1.3.3 Zirconia Gas Sensors.

In 1961, Wiessbert and Ruca\(^\text{18}\) reported the first solid state oxygen sensor using a zirconia (zirconium oxide) solid electrolyte. As a result, oxygen sensors incorporating a zirconia-based electrolyte and platinum electrodes have been commercially available since about 1965. They are used predominantly to monitor oxygen in high temperature applications. Millions of sensors have been produced and their fields of application are numerous, including metallurgical production, combustion in boilers and air/fuel ratio control in internal combustion engines. More recently the same concept has been adopted by the automotive industry where these devices are used as feedback elements to the engine management systems in vehicles fitted with catalytic converters. Indeed, this application of zirconia sensors currently constitutes the largest sector of the global sensor market.\(^\text{19}\)
(a) Operating Principles.

Zirconia, ZrO\(_2\), undergoes transition changes at elevated temperatures, as shown in scheme 1.1.

**Scheme 1.1 The Phase Transitions of ZrO\(_2\).**

\[ 1170 \, ^\circ C \quad 2730 \, ^\circ C \quad 2680 \, ^\circ C \]

Monoclinic $\longleftrightarrow$ Tetragonal $\longleftrightarrow$ Cubic $\longleftrightarrow$ Liquid

The addition of oxides of rare earths such as CaO, MgO and Y\(_2\)O\(_3\) tend to stabilise the high temperature phases, and are referred to as stabilisers. Most authors now agree on the main steps of oxygen interaction at platinum electrodes on stabilised zirconia: adsorption and dissociation of oxygen at the platinum surface, transport along the platinum surface and charge transfer of electrons.

The stabilisers possess a lower valency than the Zr atom in ZrO\(_2\), as a consequence, a high concentration of oxygen ion vacancies (V\(_{\text{O}}\)) are generated. Adjacent oxygen ions (O\(_{2^-}\)) are able to move into the vacancies (equation 1.3). Equations (1.4 and 1.5) outline the generation of electronic carriers.

\[
\text{CaO} \rightarrow \text{Ca}_{\text{Zr}} + \text{O}_{2^-} + \text{V}_{\text{O}} \quad (1.3)
\]

\[
\text{O}_{2^-} \leftrightarrow \frac{1}{2}\text{O}_2 + \text{V}_{\text{O}} + 2\text{e}^- \quad (1.4)
\]

\[
\text{V}_{\text{O}} + \frac{1}{2}\text{O}_2 \leftrightarrow \text{O}_{2^-} + 2 \text{ holes} \quad (1.5)
\]

As they operate on electrochemical principles, they may be based on a variety of electrochemical phenomena, both amperometric and potentiometric.

(b) Potentiometric Zirconia Sensors.

Potentiometric oxygen sensors consist of stabilised zirconia in contact by a reference electrode with a constant oxygen activity, this is usually in air, and a
porous platinum measuring electrode according to the sequence $\text{Pt,air/zirconia/Pt}, p_{O_2}$, where the zirconia electrolyte is physically impervious to the gas. The platinum/zirconia interface is the critical part of these oxygen sensors. All of the characteristic sensor properties are determined by the electrical conditions, chemical reactions and equilibria at that interface.

Providing that the electronic partial conductivity (equation 1.4) is very low, then the EMF ($E$) of the cell is indicated in equation 1.6.

$$E = \frac{RT}{4F} \ln \frac{p_{\text{air}}}{p_{O_2}} \quad (1.6)$$

Where

$R =$ the molar gas constant,

$T =$ temperature,

$F =$ Faraday constant,

$p =$ partial pressure of the gas in question.

Workers in this field have coated one of the electrodes on the surface of a yttria-stabilised zirconia (YSZ) electrolyte with an oxide catalyst layer of CuO/ZnO/Al$_2$O$_3$. \textsuperscript{20-23} They carried out their experiments at 350-450 °C and discovered that this oxide mixture catalysed the oxidation of CO resulting in a lower oxygen concentration at the surface of the underlying electrode, compared with the uncoated electrode, and an EMF was induced.

One approach, suggested by Okamoto \textit{et al}, for the measurement of CO in vehicle exhaust has one electrode which only encounters oxygen in a pseudo-reference atmosphere; this was achieved by the incorporation of a catalytic coating ensuring that the gaseous analyte does not reach the electrode.\textsuperscript{24} The second electrode is exposed to the full concentration of CO present in the atmosphere and the output of the sensor would provide an indication of the CO concentration. A schematic diagram of Okamoto’s sensor design is illustrated in figure 1.2.\textsuperscript{23}
As well as following the change in EMF, Lukacs et al. utilised AC impedance spectroscopy as a testing technique. They observed a change in the impedance characteristics of the electrochemical sensor system when CO was introduced to the analyte gas. Figure 1.3 indicates the basic response of their sensor design to a 10 mV AC amplitude input over the frequency range 10 kHz to 0.01 Hz. Technical details of this testing technique are discussed in chapter 4 and the implications of Lukacs’ observations are discussed in greater detail in chapter 5.

(c) Amperometric Zirconia Sensors.

In this application, oxygen is pumped from the cathode to the anode with the electrode processes as outlined in equation 1.7. A porous barrier is positioned in front of the cathode to restrict the transport of oxygen to the electrode as indicated in scheme 1.2 below.

\[
O_2 + 2\bar{v} + 4e^- \rightleftharpoons 2\bar{O}_2\tag{1.7}
\]

Scheme 1.2 Schematic Diagram of an Amperometric Zirconia Sensor.
The partial pressure of oxygen at the cathode is reduced to zero when a sufficient potential is applied between the anode and cathode. This situation creates a current limited condition, $I_{\text{lim}}$, where the rate of diffusion of oxygen through the porous barrier controls the device, which in turn is determined according to an adaptation of Fick's First Law.

\[ I_{\text{lim}} = \frac{4FDQ}{L} C_{O_2} \]  

(1.8)

Where

\( D \) = the diffusion coefficient of oxygen,

\( Q \) = the sum of the cross-section of the pores,

\( L \) = the effective length of the pores,

\( C_{O_2} \) = the concentration of oxygen in the sample gas.

Hence, the limited current is directly proportional to the concentration of oxygen, thus enabling the sensing of the gas with a rapid response time.26

Dietz used mixtures of oxygen and carbon monoxide in an amperometric device with platinum electrodes at 500 °C.25 A chemical reaction occurred and the sensor measured the equilibrium oxygen value, although it was not apparent whether the platinum electrode or the diffusion barrier had catalysed the reaction.

(d) **Coulometric Zirconia Sensors.**

Coulometry describes a method in which a volume of gas is quantitatively converted by electrolysis. The charge passed as a result, provides the partial pressure of the gas. In 1976, Heyne27 used a coulometric device similar to the schematic illustrated in figure 1.4. It is comprised of an electrochemical pump and a leak into an enclosed volume.28 Initially, the oxygen is pumped out of the cavity by applying a constant current. The voltage of the pump rises sharply when almost all of the oxygen has been removed. Oxygen is then allowed to leak into the enclosed volume until the inner and outer gases closely equilibrate.
The cycle is repeated by reapplying the pump current and the oxygen partial pressure can be obtained by the use of Faraday’s Law.

\[ p_1 = \frac{RTq}{4FV_1} \] (1.9)

where,

- \( q \) = the charge passed,
- \( V_1 \) = the enclosed volume.

If the applied current, \( I \), remains constant then \( p_1 \) is given by:

\[ p_1 = \frac{RTI_l}{4FV_1} \] (1.10)

where,

- \( t_1 \) = the time over which the current was applied.

Therefore, the measured value \( t_1 \) is directly proportional to the partial pressure of oxygen. This is opposed to a logarithmic response as obtained in a potentiometric device, (equation 1.6).

1.3.4 Tin Oxide Semiconductor Gas Sensors.

Another very important family of gas sensors are based on semiconducting metal oxides. In 1991, nearly five million semiconducting metal oxide sensors were marketed for detecting inflammable gases. The majority of semiconductor gas sensors now in service use tin oxide (SnO₂) as the reactive element. A typical sensor which utilises this technology is shown schematically in figure 1.5.
The archetypal device is the Japanese "Tugachi" sensor. These tend to suffer from insufficient gas selectivity, however, they are sold in very large numbers, particularly for domestic applications.

Figure 1.5 Schematic Diagram of a Semiconductor Gas Sensor.

(a) Operating principles.

Tin(IV) oxide is a n-type semiconductor with a wide band gap of about 3.5 eV. The predominant charge transfer is by conduction band electrons resulting from the non-stoichiometry of SnO$_{2-x}$.\textsuperscript{30,31} The mechanism most frequently proposed to account for the response characteristics of a semiconductor gas sensor, is that oxygen adsorbed at the gas-solid interface abstracts electrons from the bulk of the solid to form surface oxygen ions as shown in figure 1.6.

Figure 1.6 The Chemisorption of Oxygen at a Semiconductor Surface.
The oxygen ions can be considered to be surface traps for electrons from the bulk. As the surface charge is developed, the adsorption of further oxygen is inhibited. The resistance of the material is dominated by the depletion layers, or Schottky Barriers, which exist at the junctions between the grains of the porous material. As a consequence, the overall resistance is sensitive to the coverage of adsorbed oxygen at the surface and any factor which disturbs this will alter the resistance. If carbon monoxide, a reducing gas, was to be present at the surface, the level of adsorbed oxygen may be reduced due to a catalysed oxidation process, releasing electrons into the conduction band, leading to a measurable decrease in resistance.

In the case of a p-type semiconductor, such as Ti_{0.9}Cr_{0.1}O_{2}, adsorbed oxygen gives rise to an increase in charge-carrier (hole) concentration at the interface. Hence the removal of adsorbed oxygen at the surface would lead to a decrease in the charge-carrier density and a resistance increase would be expected. The changes in conductivity are summarised in Table 1.3.

<table>
<thead>
<tr>
<th>Semiconductor type</th>
<th>Oxidising conditions</th>
<th>Reducing conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-type</td>
<td>Resistance increase</td>
<td>Resistance decrease</td>
</tr>
<tr>
<td>p-type</td>
<td>Resistance decrease</td>
<td>Resistance increase</td>
</tr>
</tbody>
</table>

(b) Improving the Selectivity.

There has been a significant amount of work carried out in an attempt to improve the selectivity and sensitivity of the sensor by catalytic additions of Pt, Rh, Pd, Mn, Al, Cu, CuO, and CaO/NbO_{2} to the SnO_{2} layer, and by varying the operating temperature of the sensor system. Figure 1.7 shows the variation in sensitivity to CO and CH_{4} with temperature of SnO_{2}, indicating that the maximum sensitivity occurs at different temperatures for different gases.
1.3.5 Metal Phthalocyanine Sensors.

A class of organic molecules known as phthalocyanines have semiconductor rather than insulating properties. Sensors based on metal-substituted phthalocyanines have been the topic of research for many years and are now enjoying a limited degree of commercialisation. The structure of the metal-free phthalocyanine (H$_2$Pc) is shown in figure 1.8 below.$^{42}$
(a) Operating Principles.

The central hydrogen atoms can be replaced by any of the metallic elements to provide a reasonable conductivity in the temperature range 100-300 °C. They are usually p-type (hole-carrier) semiconductors which are thermally stable up to 400-500 °C.

The exact way in which gases react with the phthalocyanines is still unclear. It is thought that the overlap of π-electron orbitals may provide the charge transfer, whereas, in others, the overlap of the d-electron system associated with the metal atom may occur.

Most of the metal phthalocyanines are planar molecules with the metal atom in the plane of the ring structure, such as CuPc. An exception to this is PbPc, in which the lead atom is positioned out of plane due to its size and forms a saucer-shape, as indicated in figure 1.9 below.

Figure 1.9 The Crystal Structure of PbPc.

PbPc has been found to possess a high conductivity, possibly due to the crystal structure of PbPc giving rise to a linear chain of Pb\(^{2+}\) ions with a distance of 0.373 nm between them, only slightly greater than in metallic lead.

Sensors based on PbPc have been shown to be particularly sensitive to NO\(_2\), with useful sensitivity to Cl\(_2\). The delocalised π-electrons of phthalocyanine are
transferred to the adsorbed electrophilic NO$_2$, increasing the p-type semiconductivity. Van Ewyk \textit{et al.} and Jones and Bott$^{47,48}$ tested films of PbPc which were a few microns thick in the presence of NO$_2$, at an operating temperature between 150$^\circ$ C and 200$^\circ$ C. They compared the response of PbPc and H$_2$Pc to 1 ppm NO$_2$, as indicated in figure 1.10.$^{49}$

Figure 1.10 Conductance versus NO$_2$ Concentration on PbPc and H$_2$Pc at 150$^\circ$C.

![Conductance versus NO$_2$ Concentration](image)

(b) Selectivity and Reversibility.

The advantages of these devices are high sensitivity to some gases, low cost and ease of use. The major disadvantage is an almost total lack of selectivity. Limited success in this area has been achieved by the incorporation of additives. For example, Jeffery and Burr$^{50}$ have studied silicon and germanium phthalocyanine polymers of the type (PcMO)$_n$, (M=Si, Ge; n=10-100), in the presence of NO$_2$ and Cl$_2$. They discovered that these materials were good candidates for gas sensing because they possess good thermal stability, and as a consequence are better suited to operation at higher temperatures (>200$^\circ$C). They also indicated a very small response on the variation of relative humidity.

The slow reversibility of some metal phthalocyanines with the analyte has always been problematic when attempting to develop practical sensor devices. The
response to step changes in gas concentrations are slow and the return to clean air even slower. The response time can be reduced by operating the material at higher temperatures, however, this can dramatically shorten the lifetime of the sensors.\textsuperscript{51} Another method to improve the selectivity and reversibility of these sensors is to chemically synthesise substituted phthalocyanines. Roisin \textit{et al}\textsuperscript{52} have achieved rapid reversible detection of \textsuperscript{5}NO\textsubscript{2} by substituting the phthalocyanines by long chain alkoxy groups or crown ether rings.

(c) Deposition Techniques.

Two methods exist for the deposition of metal phthalocyanine films, both of which act as a further purification step. Vacuum sublimation is a convenient and widely used method of depositing these films. Rigby \textit{et al}\textsuperscript{53} utilised vacuum sublimation for the deposition of 20,000 Å thick PbPc films at a pressure of 5x10\textsuperscript{-5} mbar. This deposited the film at a rate of 2 Å/s onto polycrystalline alumina substrates, which were fitted with a printed Pt heater coil on the reverse side. Unfortunately, not all metal phthalocyanines will undergo vacuum sublimation.

The Langmuir-Blodgett (LB) technique is a method which can produce one monolayer at a time, and can therefore give rise to ordered films of metal phthalocyanines and substituted phthalocyanines.\textsuperscript{54} This technique provides a smooth, uniform and better defined film than the vacuum sublimation method. Only a small number of workers have studied the effect of gases on the electrical conductivity of LB-prepared phthalocyanine films.

1.3.6 Gas Sensors with Liquid Electrolytes.

Electrochemical sensors which incorporate a liquid electrolyte have been outstandingly successful in the gas sensing market. They are used universally to detect oxygen and an extensive range of toxic gases such as CO, NO, NO\textsubscript{2}, NH\textsubscript{3}, Cl\textsubscript{2}, Br\textsubscript{2}, H\textsubscript{2}S, SO\textsubscript{2}, and O\textsubscript{3}.\textsuperscript{55,56} These sensors can function over a temperature range of -50° C to +50° C and therefore eliminate the requirement for external heating, whilst being reliable, compact and inexpensive to produce.
One of the important advantages of electrochemical sensors with a liquid electrolyte is that the electrical output of the device is directly related to the gas concentration being measured. They also offer a high sensitivity, being able to detect gases from a concentration of 20% (200000 ppm) down to a few tenths of a part of a million.\textsuperscript{57}

(a) Operating Principles.

They operate on fuel cell principles with an aqueous electrolyte. A schematic of a basic fuel cell sensor is shown in figure 1.11.

![Figure 1.11: Schematic Diagram of a Liquid Electrolyte Gas Sensor](image):

An electrochemical sensor consists of:

- A diffusion barrier to control the diffusion of the reactant gas to the working electrode.
- A working electrode situated such that external gases have easy access, the working potentials are normally in the range 0.7-1.4V vs. the SHE, i.e. between the oxygen reduction and evolution potentials.
- A counter electrode which is positioned where the reactant gas access is severely restricted.
- A concentrated, ionically conducting aqueous electrolyte, e.g. sulphuric acid or sodium hydroxide solution, separating the two electrodes.
- A low impedance external circuit to measure the current output of the cell.
An 'air rest potential' is set up when the sensor is placed in a clean atmosphere, this is due to the diffusion of oxygen through the barrier followed by the adsorption of oxygen onto both the electrodes, and no current passes. If a reducing gas is present in the atmosphere, such as CO, it will initially diffuse through to the working electrode and cause a cathodic shift in potential. This potential difference will cause a current to flow in the external circuit. An equivalent amount of oxygen reduction will occur at the counter electrode.

If an acidic electrolyte is utilised, the following reactions shown in the equations below will occur;

**Working Electrode:** \[2\text{CO} + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \quad (1.11)\]

**Counter Electrode:** \[\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \quad (1.12)\]

**Cell Reaction:** \[2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2 \quad (1.13)\]

Essentially, CO is oxidised to CO₂ and protons, consuming water and releasing electrons into the external circuit. The resulting protons migrate via the acidic electrolyte to the counter electrode, where with oxygen and electrons (from the external circuit), water is formed. If suitable electrodes are chosen, this principle can be applied to any gas, some examples include;

**Nitric oxide:** \[\text{NO} + \text{H}_2\text{O} \rightarrow \text{NO}_2 + 2\text{H}^+ + 2\text{e}^- \quad (1.14)\]

**Sulphur dioxide:** \[\text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 2\text{H}^+ + 2\text{e}^- \quad (1.15)\]

**Hydrogen sulphide:** \[\text{H}_2\text{S} + 4\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 8\text{H}^+ + 8\text{e}^- \quad (1.16)\]

The oxidation of hydrogen can also occur at the electrode and the reduction reaction occurs at the counter electrode (equation 1.12). Some oxidising gases can also be detected, in this case they are reduced at the working electrode;
Oxygen: \[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \]  
(1.17)

Nitrogen dioxide: \[ \text{NO}_3^- + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{NO} + \text{H}_2\text{O} \]  
(1.18)

Chlorine: \[ \text{Cl}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{HCl} \]  
(1.19)

The counter electrode reactions in this case would be water oxidation leading to oxygen evolution or possibly a metal corrosion reaction, for example, the oxidation of lead which is often used in combination with an alkaline electrolyte.

Water oxidation: \[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \]  
(1.20)

Metal corrosion: \[ \text{Pb} + 2\text{OH}^- \rightarrow \text{Pb(OH)}_2 + 2\text{e}^- \]  
(1.21)

(b) Factors Affecting the Life-time of Liquid Electrolyte Gas Sensors.

In theory, these sensors have unlimited life. In practice, however, the catalysts become poisoned, and as a consequence the active surface area is reduced. The acid electrolyte can attack the seals and casing, and there is the possibility of solution-recrystallisation reactions occurring. In a normal temperate environment these processes are slow, however, in extremes of humidity, or strongly adsorbing chemical species, the working life of these sensors is drastically reduced.

1.3.7 Colourimetric Methods of Gas Sensing.

In 1955, the Health and Safety Executive published a series of booklets entitled ‘Methods for the Detection of Toxic Substances in Air’. It described the detection of gases by chemical methods involving colour changes. Examples are given, such as a test-paper moistened with palladium chloride which when suspended in an atmosphere of CO for five minutes will develop stains of metallic palladium. Some of these techniques have been developed into commercial instruments which are currently used for a variety of applications; Drager and Gastec have developed detector tube technology and Seiger and MDA have promoted paper tape systems. In many cases the intensity of the colour is related to the concentration of the species being analysed. The actual concentration can be
obtained by comparing the colour change to a colour comparator chart, or more accurately, by the use of a spectrophotometer.

(a) Detector Tube Technology.

This method can provide a rapid spot measurement of toxic gases that may be present in the atmosphere. It requires a sample of air that is drawn through a tube containing a chemical which is sensitive to the gas or vapour in question. The change in colour of the chemicals can be observed through the glass wall, while the length of the colour change along the tube provides an indication of the concentration of the gaseous analyte. The operator of the tube can observe the colour generation and can take preventative action, although no audible alarm is given.

One of the Drager tube designs can be used for monitoring CO. Iodine pentoxide and fuming sulphuric acid are dispersed on an inert carrier within the tube. When CO is introduced into the tube, CO₂ and iodine are formed. The green colouration of the iodine is used to indicate the presence of CO. A similar arrangement uses N,N’diphenylbenzidine to monitor the presence of nitrogen dioxide, as a blue-grey colouration develops. Unfortunately, this has a drawback, with the effects of cross-sensitivity of other oxidising gases such as ozone or chlorine.

In general, the detector tube devices have a shelf-life of only two years due to degradation of the active reagents.

(b) Diffusion and Permeation Devices.

These devices provide a simple and cost-effective method of monitoring toxic gases over long periods of exposure. A gas sample is taken from the atmosphere, it is made to either migrate along a fixed path or to diffuse through a membrane, where it is then adsorbed. The solid adsorbent is generally charcoal or a colour-generating reagent. Such diffusion tubes are available for hydrogen sulphide,
hydrochloric acid vapour, ammonia and formaldehyde. In the case of formaldehyde, 2-hydrazinbenzothiazole is used as the colour-generating reagent.\textsuperscript{60}

Permeation devices are commonly found in the form of a badge where the sorbent is kept in place by a gas diffusion membrane. In general, these devices are worn on a workers clothing. After a period of time the device is capped and analysed in the laboratory, where desorption and concentration is carried out. A gas chromatograph and mass spectrometer can then be used to identify the chemicals, providing a time-weighted average over the shift.

(c) Paper Tape Monitors.

These are particularly effective for the continuous monitoring of toxic gases. A gas sensitive reagent is impregnated into a paper tape, whereby a colour change is immediately visible in the presence of the toxic gas, this is a similar response as obtained with detector tubes (section 1.3.7(a)). The paper tape can be wound onto a spool so that the sensitive area is drawn past the sample inlet. If a reaction occurs a stain will appear which will alter the reflectance characteristics of the paper on that spot. The intensity of the stain indicates the fluctuations in the concentration of the gas and a corresponding change in reflectance can be monitored. Figure 1.12 outlines the set up of a paper-tape monitoring device.

Figure 1.12 Schematic Diagram of a Paper-tape Monitoring Device.
In 1969, Reilly\textsuperscript{61} patented the use of a tape impregnated with Brenthol AG to detect toluene di-isocyanate. This method, which produces a pink colour change, gained popularity on a large scale in the polyurethane industry where toluene di-isocyanate is used as a starting material.

A choice of paper-tape types are available with an operational life between one week and one month, with the possibility of detecting as many as forty gases or vapours on one instrument with the correct software and paper-tape samples.

1.3.8 Infrared Spectroscopy Gas Detection.

The identification of flammable and toxic gaseous species by infrared spectroscopy relies on the ability of the species to absorb infrared radiation at wavelengths that are characteristic of the chemical structure of the molecule. Recent advances in infrared technology has led to the construction of detectors for flammable gases. The C-H stretch of most hydrocarbons exhibit intense absorptions in the 3.4 $\mu$m region.

(a) Toxic Gas Monitoring.

Most toxic gases and vapours can be detected in the parts per million range using ultraviolet-visible-infrared wavelengths. Infrared spectroscopy is the preferred technique for carbon dioxide and chlorofluorocarbon vapours. The most common infrared source consists of a heated incandescent filament. Gas correlation spectroscopy is an infrared technique commonly used to detect toxic gases.\textsuperscript{62} This method uses a reference cell that contains a non-infrared absorbing gas such as nitrogen. The beam alternately passes through the sample cell and the reference cell. The ratio of the two intensity values can be used to determine the concentration of the analyte in the sample gas. Figure 1.13 shows the basic design of an analyser using gas correlation spectroscopy.
However, depending on their structure, not all gases will absorb strongly in the infrared region. Table 1.4 below indicates the required absorption wavelengths for a range of toxic gases.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Absorption Wavelength/ μm</th>
<th>Lowest range (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>4.6</td>
<td>0-30</td>
</tr>
<tr>
<td>CO₂</td>
<td>4.2</td>
<td>0-20</td>
</tr>
<tr>
<td>NH₃</td>
<td>6.1</td>
<td>0-200</td>
</tr>
<tr>
<td>NO</td>
<td>5.3</td>
<td>0-125</td>
</tr>
<tr>
<td>SO₂</td>
<td>7.3</td>
<td>0-200</td>
</tr>
<tr>
<td>SF₆</td>
<td>10.6</td>
<td>0-200</td>
</tr>
<tr>
<td>C₆H₅CH₃</td>
<td>3.3</td>
<td>0-500</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>7.8</td>
<td>0-500</td>
</tr>
</tbody>
</table>

(b) Remote Sensing of Toxic Gases.

If a very short pulse of light is transmitted through a scattering medium and a receiver detects the light scattered from that medium, then the processing of the return signal can lead to information about the medium. A powerful source, such
as lasers are required to provide enough energy, for light detection and ranging (LIDAR)\textsuperscript{63,64} The pulsed gas laser must operate at the resonant wavelength of the gas being detected.\textsuperscript{65} The analyte gas absorbs the infrared energy and back-scattered light from the aerosol particles in the atmosphere are received by a highly sensitive photodetector. Range information is obtained from the time delay between the transmitted and the received signals. A typical range can be between 1-5 km. Figure 1.14 indicates the arrangement of receiver and transmitter used in the LIDAR technique.

![Figure 1.14 The Arrangement of Equipment used in the LIDAR Technique.](image)

LIDAR systems have been successfully used to detect carbon monoxide, carbon dioxide and nitrous oxide.\textsuperscript{66} However, LIDAR gas detection systems represent the extreme high cost end of the market and a reduction in cost is required to fully exploit the technique.

1.3.9 Optical Fibre Gas Sensors.

The development of inexpensive high-quality optical fibres for the communications industry has provided the technology for optical fibre sensors. They have been shown to be a viable technology for the detection of gases. Fibre optic sensors can be classified as either extrinsic or intrinsic. Extrinsic sensors merely behave as a light guide between the measurement point and the analyser, whereas, intrinsic sensors use the fibre as a sensing transducer.
Further classification can than be made depending on which parameter is measured:

*Species-species specific sensors:* consist of remote spectrometry, i.e. the change in an optical property of an immobilised reagent which is affected by the analyte.

*Non-species-species sensors:* the direct measurement of some optical property, such as refractive index, which is perturbed by the analyte.

*Indirect techniques:* the direct measurement of some non-optical property, e.g. temperature, which is related to the presence of the analyte.

Some of these classifications and their adaptations will be discussed in further detail.

(a) **Extrinsic Species-specific Gas Sensors.**

This method uses the optical fibre as a light guide which measures the level of light absorbed by the analyte. Methane has been detected in this manner, figure 1.15 shows the basic arrangement for the detection of methane by a remote absorption technique.\(^{67}\)

![Figure 1.15 Schematic Diagram of the Remote Absorption Technique for the Detection of Methane](image)

The peak wavelength of light from the light emitting diodes lie closely to one of the absorption bands of methane, i.e. 1.66 µm. The light is passed through the glass cell where it is guided to a monochromator and detector. Chan et al discovered that 700 ppm of methane could be detected using two 1 km fibre links.\(^{68}\)
One of the major applications of this system is for the detection of gases in hazardous locations, as the operator, light source and detection system can be placed a suitable distance away. For example, over the last five years a system has been installed in operational coal mines in Australia.\textsuperscript{69,70} The system, called Fibre Optic Rapid Gas Analysis System (FORGAS), can provide up to ten points of underground measurement in order to produce multi-point methane analysis. The detection sensitivity of 0.1% CH\textsubscript{4} is achieved, which is sufficient for this application.

Kirkbright \textit{et al} have described the immobilisation of pH indicator reagents which undergo a colour change on the introduction of gases such as sulphur dioxide, NO\textsubscript{x}, hydrogen chloride, carbon dioxide and ammonia.\textsuperscript{71} For the pH range 7-9, bromothymol blue indicator can be used. It undergoes a yellow (acid) to blue (basic) colour change. Figure 1.16 illustrates the arrangement of such a probe.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig16.png}
\caption{A cross-section of an Extrinsic Species-species Specific pH probe.}
\end{figure}

In this design, the presence of the analyte creates a change in the optical properties of the input signal, for example a modulation of the wavelength, amplitude or phase with respect to the input signal. Depending on the pH of the system being studied, a variety of indicators can be immobilised in this system. In this way, Woods \textit{et al} has successfully adapted this design to study the concentration of dissolved acidic pollutant gases in rain water.\textsuperscript{72}
(b) Intrinsic Species-specific Gas Sensors.

In this arrangement, a change in a parameter occurs whilst the light is guided through an optical fibre. In such a case, it must be possible for the analyte to penetrate into the system with the use of pores and channels. The use of a thymol-blue doped polymethacrylate fibre has been shown to detect changes in pH. In such a way, ammonia at 10 ppm and hydrogen chloride at 5 ppm have been detected. However, the incorporation of pores can reduce the quality of the light intensity due to scattering losses.

A better method utilises a change in a parameter in close proximity to the optical fibre. This is known as an evanescent wave interaction. A typical example incorporates a sensitive coating of tungsten oxide, $\text{WO}_3$, and palladium on one arm of the waveguide. Hydrogen reduces the $\text{WO}_3$ and causes a yellow to blue colour change allowing the detection of hydrogen gas. Figure 1.17 illustrates the basic layout of an optical evanescent wave hydrogen sensor.

Figure 1.17 An Intrinsic Species-specific Gas Sensor for Hydrogen.

(c) Indirect Techniques of Gas Sensing.

This title describes a technique which utilises a non-optical change, such as strain on the optical fibre. Butler showed that the application of a thin coating of palladium on a fibre could be used to detect hydrogen. This is due to the production of palladium hydride in the presence of hydrogen, resulting in a slight increase in fibre length. This increase in path length of the optical fibre will
modulate the wavelength or phase of the interrogating light, relative to the reference light. Alternatively, an increase in temperature can also be used as a viable parameter. In this case, catalytic coatings have been used to catalyse the oxidation of combustible gases, hence small increases in temperature are observed.

1.3.10 Surface Acoustic Wave Gas Sensors.

At the end of the 19th century, Lord Rayleigh described the surface acoustic wave (SAW) that propagates along the surface of the earth in response to an earthquake. On a smaller scale, devices which use periodic displacements that occur normal to a surface, have been employed in electronic applications, however, the realisation of their potential as gas sensors is relatively recent.

Surface Acoustic Wave devices are generated by metal interdigitated electrodes, generally evaporated, sputtered or photolithographically etched onto a piezoelectric substrate, usually quartz or lithium niobate. Electrical excitation of the electrodes at a given frequency cause a SAW to propagate along a path on the substrate. These deformations transverse across the piezoelectric substrate where the receiver interdigital transducers convert the mechanical energy of the wave into an output R.F. voltage. The wave propagation can be reversibly altered by the adsorption and desorption of gaseous analyte molecules on a suitable catalyst or sorbent material on the surface of the substrate. A simplified diagram of a SAW device is shown in figure 1.18.

Figure 1.18 Schematic Diagram of a SAW Device.
It is found that the shift in resonant frequency of the SAW device due to the mass of adsorbed gas is directly proportional to the mass added. This factor makes it a suitable monitor of gas concentration.\textsuperscript{76,77} In 1959, Sauerbrey developed an equation relating the mass of the adsorbed matter to the change in the fundamental frequency of the piezoelectric material (equation 1.22).

$$\Delta f = \frac{-\Delta M r^2}{A \rho N}$$  \hspace{1cm} (1.22)

where,

$\Delta f$ = the frequency change / Hz

$\Delta M$ = the mass of the coating / kg

$A$ = the surface area of the crystal / m$^2$

$\rho$ = the surface density of the coating / kgm$^{-2}$

$N$ = a frequency constant / Hz

$f$ = the fundamental frequency / Hz

(a) SAW Detection of Inorganic Gaseous Species.

A number of research groups have incorporated phthalocyanines in SAW devices (section 1.3.5). The majority of conductivity investigations have been carried out on vacuum sublimed films of CuPe and PbPe\textsuperscript{78}, with more limited studies of other metal phthalocyanines, such as Mg, Fe, Co and Ni.\textsuperscript{48,79} Work on Langmuir-Blodgett films has concentrated on ring-substituted materials.\textsuperscript{80,81}

In 1986, Vanema \textit{et al} studied the sensitivity of metal-free and various metal phthalocyanine films on quartz crystal as SAW detectors towards NO$_2$, and compared the response with possible interferent gases, such as CO, CO$_2$, CH$_4$, NH$_3$, SO$_2$ and water vapour at 150 °C. The interferents were shown to be far less sensitive than NO$_2$ at this temperature.\textsuperscript{82}
In the same year as Vanema, Nieuwenhuizen et al published work on the use of various metal phthalocyanine films (MgPc, FePc, PbPc, CoPc, NiPc and CuPc) on a quartz crystal SAW device. They succeeded in determining the presence of a number of gases, with concentrations of 1200 ppm CO, 200 ppm SO₂, 100 ppm NO₂ and 200 ppm NH₃ detectable at 150 °C.  

A SAW device which does not utilise a phthalocyanine film was used for the detection of hydrogen by d'Amico et al. It consisted of a palladium coating on a lithium niobate crystal. They varied the thickness of the palladium film and produced coatings of 190, 328 and 760 nm. Although the sensitivity increased with the thickness of the film, he found that the fastest responses were produced by the 328 nm film. A hydrogen concentration of 50 ppm is possible by this method.

Another example of a SAW device is the development of a detector for SO₂. In order to achieve this a triethanolamine coating was incorporated with a lithium niobate substrate. This work was expanded to detect H₂S by the utilisation of a sputtered tungsten oxide coating on the same substrate type. Detection limits of 10 ppm H₂S and 70 ppb SO₂ were achieved at room temperature.

The above examples illustrate the high sensitivities of gaseous analyte which can be detected with SAW sensors, however, they are not without their problems, as their characteristic frequency is sensitive to temperature and, to some extent, pressure. Also, the problem of fabricating the catalytic coating to be selectively absorbing to a specific chemical species is a factor which will ultimately dictate the commercial availability of these devices.

1.3.11 Metal Oxide Semiconducting Gas Sensors.

In 1975, Lundstrom et al described the first gas sensor based on a metal oxide semiconductor field effect transistor (MOSFET) for the sensing of hydrogen. Since then, work has concentrated on modifying the materials of the device, for example, changing the transition metal used for the gate electrode. It is now well known that these devices can detect other hydrogen-containing gases, such as
ammonia and unsaturated hydrocarbon vapours, with modifications made to detect CO. The devices can be produced by standard microelectronic fabrication techniques and should therefore be easily mass produced, providing low cost units.

(a) Operating Principles.

A MOSFET is a transistor device which consists of two n-type areas; the source and drain, separated by a p-type region, usually a silicon substrate. This is covered by an insulating layer (gate insulator), on which lies a metallic contact called the gate electrode. Figure 1.19 indicates a schematic diagram of an n-channel MOSFET.

![Schematic Diagram of an n-type MOSFET Device.](image)

When a potential is applied between the gate electrode and substrate, a so called gate voltage, a field is created across the gate insulator and the p-type properties of the silicon substrate directly beneath it can be inverted to an n-type conductor. This inverted area of silicon may create a 'channel' such that a current can flow between the source and drain. The gate potential must be above a threshold value in order to observe the phenomenon, if the potential is below this threshold, the device acts as two back-to-back diodes and a current cannot flow.

If an ion or gas is adsorbed onto the surface of the gate electrode it may induce a change in either the charge or potential on the gate, by either affecting the Fermi level of the gate material or inducing dipoles onto the gate electrode. If the resulting change on the gate is above the threshold voltage then it is capable of producing an electronic response which is dependent upon the concentration of the
gas species present. The sensitivity of the device depends on the temperature, composition and morphology of the gate.

(a) Detection of Hydrogen and Hydrogen-containing Molecules.

Lundstrom’s MOSFET detector for hydrogen incorporated a palladium gate and since then the device has been made sensitive to a range of gases. The key requirement is that the gate electrode must be composed of a material which is capable of catalytically decomposing the gaseous analyte to hydrogen atoms. The ability of palladium to solvate a large amount of hydrogen is well known, making it an ideal electrode material in this application. The adsorbed hydrogen atoms can then diffuse into the bulk of the electrode to the gate-insulator interface, where it creates a dipole. The height of the energy barrier between the metal and the oxide is reduced, thereby altering the channel conductivity. This design can rapidly respond to a concentration of hydrogen in the range 1-5000 ppm at an operating temperature of 150 °C.

Theory predicted that the device should be ammonia-sensitive and early results from Lunstrom et al confirmed this. Ross et al have shown that a MOSFET device, with a platinum gate electrode deposited by thermal evaporation, could successfully detect ammonia. More recently, Filippov et al have published results for the detection of 10 ppm NH3 at 175 °C, with a photolithographically deposited palladium gate.

Other workers have shown the sensitivity of MOSFET devices to unsaturated hydrocarbons, saturated hydrocarbons, hydrogen sulphide and ethanol. The mechanism of detection of these gases is believed to be the catalytic dissociation if the molecules yielding hydrogen atoms, which are then adsorbed as described above. One of the drawbacks with this method is for the detection of chlorinated compounds, as the resulting chloride can poison the gate electrode, reducing the activity. Also, the selectivity is a difficult factor to control, and to date, none of these devices have been found to be completely specific to a particular gas analyte.
(b) Detection of Carbon Monoxide by MOSFET Devices.

CO molecules lack hydrogen atoms, however some success has been established for these sensors to detect this analyte. In order for a MOSFET device to be sensitive to CO, the gate insulator layer must be exposed to the gas through pores in the gate electrode. This is thought to enable the adsorption of CO at the gate electrode-insulator interface. The adsorbed CO molecules then create a dipole affecting the energy barrier.

Maclay et al.\textsuperscript{96} and Dobos and Zimmer\textsuperscript{97} have shown that the gate metal in such a device can be platinum or palladium, with the platinum gates being more reliable. However, they discovered that after two months at elevated concentrations of CO in air, that the adhesion of the metal films became weak, reducing their sensitivity.

1.3.12 Biosensor Methods of Gas Sensing.

A biosensor is defined as an analytical device incorporating a biological or biologically-derived sensing element, either intimately associated with, or integrated within a physico-chemical transducer.\textsuperscript{98} A method which is capable of detecting the consumption of substrates or the formation of products is essential. Microelectronic and micromechanical technologies have been adapted, which are capable of converting the response of biological or chemical sensing to an electrical signal.

The general aim of any biosensor is to produce a signal that is proportional to the concentration of a chemical. Existing sensor technology has been modified in order to produce biosensor devices. For example, MOSFET sensors (section 1.3.11) have been modified. The usual gate metal material, palladium or platinum, is replaced by a membrane containing an immobilised enzyme, these devices are known as ENFETS. In this way, penicillinase has been immobilised and concentrations of penicillin in the range $10^{-4}$-$10^{-2}$ mmole/l have been detected within 30 seconds.\textsuperscript{99} SAW sensors (section 1.3.10) are currently being
investigated for detecting the formation of antibody-antigen complexes in fluids. Enzyme reactions can alter the optical properties of some substances. Hence, the use of chemically-sensitive fibre-optic probes (section 1.3.9) containing, for example, pH-sensitive dyes have been studied.  

(a) Gas Detection With Enzymes.

Several biosensor configurations have been reported that are capable of responding to gases such as neurotoxins, methane, ammonia, nitrogen dioxide and formaldehyde.

In 1985 Turner et al published work describing the purification of carbon monoxide: acceptor oxidoreductase from autotrophically grown pseudomonas thermocarboxydovorans strain C2. This enzyme catalyses the oxidation of CO to CO₂ with various electron acceptors including methylene blue, phenazine and ferrocene derivatives. The CO oxidoreductase was dispersed into a gel and was retained by a disc of polycarbonate membrane, as indicated in figure 1.20.

Figure 1.20 Schematic Diagram of an Enzyme Based CO Probe.

Turner et al discovered that CO could be determined in either solution or gas phase with a good response time. However, they concluded that further work was necessary to improve the stability of the system.

Valentine et al have concentrated on biosensors based on colour changes in metalloproteins. After demonstrating the initial stability and reactivity of the proteins in a biogel, their approach was to monitor changes in the absorption spectra and correlate them with changes in the concentration of a particular ligand.
As myoglobin binds CO, the myoglobin biogel can be used as a sensor for CO by utilising the distinct changes in the absorption spectrum at 436 nm. The device indicated chemical and thermal stability and Valentine et al believe that with the application of thin-film technology, these devices should gain better selectivity and reduced response times.

A possible drawback with these biosensor devices may be the irreversible nature of CO adsorption onto the sensor, which allows very low levels of CO to occupy the active sites without their removal. As the active materials continue to adsorb the low level of CO, it reaches a ‘lethal’ concentration on the sensor, triggering a false alarm.

1.4 Sensor Markets.

Sensor markets range from those characterised by very inexpensive devices that are sold in their millions, through to high cost process transmitters and discharge monitors which tend to sell in far smaller numbers, for example LIDAR. Several sectors of the global sensor markets have been quantified by Frost and Sullivan, and the available data for the electrochemical and semiconductor gas sensor markets in Western Europe and the US is illustrated in table I.15 below.

<table>
<thead>
<tr>
<th>Table I.15 Gas Sensor Market.</th>
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<tr>
<td>Electrochemical - wet electrolytes</td>
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<tr>
<td>Electrochemical - solid electrolyte</td>
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<tr>
<td>◦ Combustion applications</td>
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<td>◦ Catalytic converter applications</td>
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<tr>
<td>Semiconductor - metal oxides</td>
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<td>TOTAL</td>
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Based on the figures of Frost and Sullivan, the global market for all classes of sensors is estimated to be in the region of US$ 15 billion. This market also has the potential to grow, some factors driving this growth are global industrialisation in the East, environmental considerations, requirements of the automotive industry, demands for improved product quality. A conservative estimate suggests that the World sensor market is probably growing at a rate of 7% per annum.
CHAPTER 2

THE SENSOR FABRICATION

2.1 General.

The present work was undertaken with the aim of establishing suitable materials, designs and production methods in order to develop a reliable and inexpensive CO sensor that functions at ambient temperature.

The sensor has a relatively low power consumption and as a result, it is conceivable that the power source of such as a sensor could be a battery, which could power a microcontroller and the comparatively simple diagnostic testing equipment. It is envisaged that the sensor and battery unit will be disposed of once the battery has reached the end of its lifetime, when a new sensor-battery unit can be purchased and placed into the sensor casing.

The basic sensor design was based on research carried out by Yasuda et al.\textsuperscript{111-116} The CO sensor design was planar and it comprised of three electrodes; platinum working and counter electrodes (CE) and a gold reference electrode. Platinum is employed for the working electrode (WE) since it is highly catalytic to CO oxidation and chemically stable.\textsuperscript{117,118} Gold is employed as the reference electrode (RE) since its potential is stable in the presence of CO gas.\textsuperscript{119} Therefore, this project has incorporated the method of screen printing platinum and gold inks onto polished 96% alumina substrates in order to produce electrodes. In addition to the inks, strips of catalyst loaded carbon cloth were utilised to produce electrodes in a second sensor design.

A solid polymer electrolyte, which conducts protons and permits the permeation of gases was utilised. These solid polymer electrolytes are available as a solution of the polymer dissolved in lower alcohols, so that films of the electrolyte can be cast on top of the screen printed platinum and gold electrodes. The solid polymer electrolytes are also available as a ready-prepared commercial membrane, for
example, Nafion® 115 and Nafion® 117 (polymers with an equivalent weight of 1100, and thicknesses of 130 and 180μm respectively).

In the second design mentioned above, a ready-prepared commercial membrane acted as a substrate, rather than incorporating an alumina sheet, and strips of catalyst loaded carbon cloth material were pressed onto the membrane to produce the electrodes. A plastic frame was placed around the resulting membrane and electrodes to provide a flat arrangement.

Figures 2.1a and b indicate the two basic designs. In the case of the design shown in figure 2.1a, the basic rectangular electrodes are indicated, however, further designs, such as larger working electrode area and interdigitated working and counter electrodes have been studied.

![Figure 2.1 Basic Designs of Sensors (Printed and Pressed Designs).](image)

The materials and production processes utilised are described in greater detail in the remainder of this chapter. The characterisation of the planar working electrode and gold reference electrode are discussed in chapter 3 and the testing requirements of the CO sensors are described in chapter 4.

### 2.2 The Solid Polymer Electrolytes.

Many electrochemical gas sensors are based on liquid acid electrolytes such as sulphuric acid, which may be difficult to handle and limit the lifetime of the sensor as the acid electrolyte has a tendency to attack the packaging (section 1.3.6). Sensors based on solid polymer electrolytes offer an alternative to liquid acid
electrolytes. In this project two electrolyte materials have been used; Nafion® (Du Pont) and DAIS (DAIS Corporation). Descriptions of these materials follow.

2.2.1 Nafion® as a Solid Polymer Electrolyte.

Nafion® is a copolymer of tetrafluoroethylene and a vinyl sulphonic acid, which has thermal and chemical stability similar to Teflon®. (Nafion® and Teflon® are registered trade names of E.I. Du Pont de Nemours and Company). Nafion® membranes incorporate poly(tetrafluoroethylene) (PTFE) like backbones with perfluorocarbon sulphonate side chains (figure 2.2), where, \( m \) is nearly unity and \( n \) varies from 5 to 10, thus generating polymers with possible equivalent weights in the range \( 1000 - 1500 \).

Figure 2.2 The Structure of Nafion®.

\[
\left[ \text{(CF}_2 - \text{CF}_2 \right)_n - \text{CF} - \text{CF}_2 \Bigg]_x \\
\text{(OCF}_2 - \text{CF})_m - \text{OCF}_2 - \text{CF}_2 - \text{SO}_3 \text{H}^+ \\
\text{CF}_3
\]

The unique properties of Nafion® covered electrodes have been extensively studied in many applications during the last decade. These include protection of semiconductors against photocorrosion,\(^{120}\) use as a support for photosensitizers,\(^ {121}\) support of catalysts such as platinum,\(^ {122-126}\) use in fuel cells,\(^ {127-130}\) as ion selective electrodes,\(^ {131}\) as sensors\(^ {132,133}\) or biosensors for the detection of neurotransmitters,\(^ {134,135}\) metals\(^ {136}\) or glucose.\(^ {137,138}\)

The perfluorinated cation exchange sites in Nafion® cause the material to be permeable to cations while rejecting anions. The structure of the membrane has been proposed by Gierke et al.\(^ {139-141}\) based on the results obtained by small angle X-ray scattering, mass transfer experiments including hydraulic permeation, water diffusion and electron microscopy.
It has been proposed that Nafion® possesses an inverted micellar structure, with spherical (40-50 Å diameter) clusters lined with sulphonic acid groups. This so-called cluster-network model, describes the polymeric ions and absorbed water existing as approximately spherical domains as ionic clusters. These clusters are separated from the insulating PTFE matrix and they are assumed to be interconnected via 10 Å channels. It was revealed that the cluster size grows with an increasing amount of absorbed water.

(a) Ionic Conductivity of Nafion®.

Experimental data142,143 and theoretical calculations141,144 indicate that Nafion® represents a multiphase system. In such a cluster-network model, appreciable ionic conductivity is observed only when a critical volume fraction of the ionic conductivity cluster is reached. The material then undergoes an insulator to conductor transition as indicated in figure 2.3.

Figure 2.3 Changes in Reactive Resistance for Proton Conducting Nafion® as a Function of Cluster Volume.

As the volume fraction of the ionic conducting clusters increases, there is initially very little change in the resistance of the polymer. At this point the highly conductive clusters are well separated and do not form a continuous path through the polymer. The resistance is controlled by the poorer conducting polymer phase. At the critical volume fraction, the highly conductive phase forms a
continuous path across the polymer and a sudden decrease in resistance is observed. This process is described as the percolation mechanism.\textsuperscript{145,146}

(b) Hydration Effects and Gas Permeation in Nafion\textsuperscript{®}.

Permeability is the product of the diffusion coefficient and the solubility, and it is often used to describe the transport of gases through polymers. Ogumi \textit{et al.}\textsuperscript{147} described how gas permeation through Nafion\textsuperscript{®} takes place in the intermediate region between the rigid hydrophobic backbone and the ionic cluster region. Ogumi reported that the hydrogen solubility in Nafion\textsuperscript{®} was thirty times greater than in water and that this was due to the hydrophobic perfluoro-carbon region of the film. Hence it is possible to conclude that CO gas permeation takes place through a path different from that for proton diffusion.

Sakai \textit{et al.}\textsuperscript{148} studied the diffusion in both dried and hydrated membranes using time lag experiments. They found that hydrated membranes exhibited (i) a smaller gas solubility and (ii) a higher gas diffusivity as compared to the dry membranes. Yasuda \textit{et al.}\textsuperscript{113} have studied the effect of the atmospheric relative humidity (RH) on the water content of Nafion\textsuperscript{®}, (figure 2.4).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.4.png}
\caption{Water Content of a Nafion\textsuperscript{®} Film at 20°C.}
\end{figure}

Experiments\textsuperscript{149} suggest the existence of two hydration regimes in Nafion\textsuperscript{®} at room temperature. The first regime corresponds to the hydration of ionic clusters. The second regime corresponds to the expansion of the clusters, allowing easier conduction of the ionic species through the Nafion\textsuperscript{®}, due to the narrowing of the
hydrophobic region between the clusters. Therefore, the concentration of water plays an important part in the electrical and physical properties of Nafion®, since the proton conductivity and permeability of O₂ and CO in Nafion® depend strongly on the water content of the membrane. ¹⁵⁰ (figure 2.5). It can be seen that the CO permeability coefficient is almost proportional to the relative humidity.

Finally, a schematic diagram of the presently accepted structure of Nafion® is shown below in figure 2.6. It indicates the features described above which provide Nafion® with its conductivity and gas permeation characteristics. ¹³⁹-¹⁴¹

**Figure 2.5 Relative CO Permeability Coefficient of Nafion® at 20°C.**

**Figure 2.6 Schematic Diagram of the Permeation Region Through Nafion®.**
2.2.2 DAIS as a Solid Polymer Electrolyte.

As described above, it has been proposed that Nafion® possesses an inverted micellar structure, with spherical (40-50 Å diameter) clusters lined with sulphonic acid groups which are interconnected via 10 Å channels. Serpico et al.\(^{151,152}\) sought to mimic this arrangement using inexpensive sulfonated, hydrocarbon-based block co-polymers. Currently the DAIS Corporation is marketing a Patented base polymer designed to be an alternative fuel cell membrane. The DAIS 585 polymer was developed to meet the low cost criteria of the fuel cell product line.

DAIS 585 is a sulfonated styrene-ethylene / butylene-styrene triblock copolymer. The material is an elastic, hydrocarbon-based hydrogel with a cation exchange ability, and good optical transparency. The block copolymer contains approximately 29 wt% styrene units. Sulphonation levels (based on styrene units) can range from 15-60%. The structure of the sulfonated styrene-ethylene / butylene-styrene triblock copolymer is shown in figure 2.7.

\[\text{Figure 2.7 The Structure of Sulphonated Styrene-Ethylene / Butylene-Styrene Triblock Polymer (DAIS 585).}\]

Water uptake and extent of swelling of the sulfonated domains depend on the sulphonation level. Transmission electron microscopy suggests that these sulphonated polystyrene domains are cylindrical and ≤ 400 nm in diameter. Therefore, as swelling occurs, the sulfonated domains become interconnected, leading to a high conductivity. When fully hydrated, films in the acid form have
ionic conductivities greater than $7 \times 10^{-2}$ S/cm, which are comparable to those of the fluoropolymer Nafion®. Proton conductivity is thought to occur via the sulphonated domains, in a similar cluster network model as described for Nafion® above, and gas permeation takes place in the intermediate region between the hydrophobic backbone and the sulphonated domain regions.

2.2.3 Deposition of the Electrolyte Layer.

Both solutions of the polymer electrolytes and ready-prepared commercial membranes were utilised in this research project.

(a) Nafion® and DAIS Solutions.

In 1982 Martin et al. published the method for the dissolution of perfluorosulphonate ionomers. They showed that a Nafion® membrane would dissolve in a 50:50 ethanol-water solution when heated to 250 °C at high pressure. Since then solutions of Nafion® have become commercially available and many workers have cast films of Nafion® onto electrodes and other surfaces.

The polymer electrolyte in this project was fabricated by casting a 5 w/v% solution of Nafion® in low alcohols (2-propanol, 1-propanol and methanol) and water, (equivalent weight 1100, prepared from Nafion® 117 perfluorinated membrane, Aldrich Chem Co.). If dilution was required then additions of 2-propanol were used to obtain the desired concentration. DAIS is available at sulphonation levels of 45% and 55-70% as either a pre-cast film or as a solution in alcohols. A 5.5 w/v% solution at 70% sulfonation level was obtained from the DAIS Corporation. If dilution was required, analytical grade 1-propanol was used to obtain the required level of dilution.

Films of Nafion® and DAIS were cast with a thicknesses of 10, 15 and 20 µm. The amount of Nafion® or DAIS solution required in the casting process was calculated by using the area to be covered and assuming a Nafion® density of 2.1 gcm$^{-3}$. 154
The DAJS Corporation suggested that a DAJS film had approximately the same density as Nafion®. This provided the mass of polymer required to produce a certain film thickness, and knowing that 100 cm$^2$ of undiluted solution contains 5 g of Nafion®, or 5.5 g of DAJS, the volume of solution required could be obtained.

Initially, surface tension affected the results by drawing the solution towards the sides of the containment. This was resolved by the use of glass reinforced PTFE blocks and a clamp arrangement which reduced the unfavourable effects of surface tension, (figure 2.8).

**Figure 2.8 The Clamp and Blocks Arrangement**

*for Casting the Electrolyte.*

![Diagram of Clamp and Blocks Arrangement](image)

The cast Nafion® solution was then left to dry at room temperature for 24 hours. The dry re-cast films were pale yellow in colour, this colouration is associated with oligomers and other low molecular weight impurities. The substrate would then be removed from the clamp and block arrangement and it was then positioned in a desiccator to remove any remaining solvent for a further 24 hours. Optical microscope images at x 200 magnification indicated a film with a smooth surface.

Optical microscope images of re-cast DAJS films that were left to dry at room temperature had a cracked appearance (x 200 magnification). Also, a practical problem when casting at room temperature was encountered; the solvent evaporated at a relatively fast rate such that the surface tension effects which pull the solution to the edges of the PTFE mould forced the solution to leak out of the PTFE blocks. When the films were allowed to evaporate to dryness at 10 °C these
adverse effects of surface tension were not observed to the same extent, and as it took longer for the films to dry, a smoother film was produced.

(b) **Thermal Activation Process for Cast Nafion® Films.**

As-received (ready-prepared commercial) films are pliant, coherent, elastic and totally insoluble in all solvents below 200 °C. When re-cast Nafion® films are produced from a solution, the resulting films are hard and brittle. These films are also soluble in a variety of polar solvents at room temperature. Martin and Moore carried out small angle X-ray scattering (SAX) and differential scanning calorimetry (DSC) experiments. The results indicated that (i) both as-received and re-cast Nafion® films contained ionic clusters, (ii) the as-received films showed a degree of crystallinity, whereas no evidence for crystallinity could be detected in the re-cast films. It is the crystalline regions within a polymer film that supply the cross-linking in the structure, therefore, the solubility and poor mechanical properties of the re-cast films could possibly be attributed to this lack of crystallinity. Martin and Moore stated that crystallinity can occur if the main polymer chains are mobile, as a consequence a thermal annealing process above the glass transition temperature would allow the main polymer chains to gain mobility and reorientation would be possible. Such a process was reported by Gebel et al in 1987, in which they claimed that adequate thermal excitation had been provided in order to produce a film with good mechanical strength and which was insoluble at room temperature. So, if there is insufficient thermal energy during the casting of a film from solution, how can ionic clusters of sulphonic acid groups exist? This is thought to be due to the mobility of the side polymer chains which are shorter and therefore more mobile than the main chains, also charged groups are present on the end of these short side chains. It therefore seems possible that reorientation of the side chains can occur allowing cluster formation.
The DSC results showed that, although present, there were fewer ionic clusters in the re-cast films, showing that full mobility of the main polymer chain dictated the maximum ionic cluster formation. Therefore, the thermal activation step will not only provide crystallites in the structure, improving the mechanical integrity of the membrane, but the process would increase the number of ionic clusters present. This would establish further connectivity of the ionic clusters in the cast film, hence increasing the conductivity of the electrolyte film. However, Quah proposed that there may be a possibility of a structural re-inversion after the re-hydration of the film.\textsuperscript{159}

Zook and Leddy have investigated the temperature and time over which a recast 0.2 mm thick Nafion\textsuperscript{®} film has to be thermally activated in order to obtain an insoluble film with characteristics of an as-received film.\textsuperscript{160} The glass transition temperature of protonated Nafion\textsuperscript{®} is 109 °C, they therefore chose an activation temperature of 140 °C and found that the films became progressively more insoluble with heating time. After one hour of thermal activation, the films showed complete insolubility in a 50:50 ethanol-water solution at room temperature.

Therefore, for the re-cast Nafion\textsuperscript{®} films used in this project, an activation temperature of 140 °C was employed for one hour on films which had been dried in a desiccator for 24 hours. The oven could be thermostatically set at the required temperature, (Grundy Equipment Ltd., 08-300 Electronic). Re-cast films of DAIS do not require a thermal activation process.

(c) Treatment of As-received Commercial Films.

Nafion\textsuperscript{®} 115 (equivalent weight 1100) was obtained (Aldrich). This membrane is 0.13 mm thick. Du Pont suggested a cleaning and protonation treatment prior to use. Therefore, Nafion\textsuperscript{®} membranes used in this work were placed in boiling 1 mol dm\textsuperscript{-3} sulphuric acid for one hour, followed by two hours in boiling distilled water. The membranes were then allowed to dry for 24 hours, lightly weighted down so that the membranes remained as flat sheets.
DAIS 585 membrane was obtained from the DAIS Corporation. DAIS is a softer polymer than Nafion® and the membranes can be purchased with Teflon® reinforcement to improve the mechanical strength. The membrane obtained for this work was a circular sample of reinforced membrane, with a 10 inch diameter and 0.007 inches thick (0.18 mm), with a sulphonation level of 57%. DAIS Corporation stated that no further treatment was required prior to use.

2.3 The Deposition of the Electrodes.

An electrode depth in the region of microns was required. Such a depth would be sufficiently conductive without wasting the metal and with an adequate surface area to promote the adsorption of CO on the surface of the platinum electrode. Various methods of metal deposition were considered and tested for feasibility. The surface morphology of the films were then studied using the surface analysis techniques of scanning tunnelling microscopy (STM) and atomic force microscopy (AFM).

In order to obtain a successful adherent electrode, the substrate had to be free from contaminants, such as grease. The alumina substrates (96% Al₂O₃, Coors Ltd.) were cut into 25x10 mm tiles with a diamond tipped cutter. They were cleaned prior to use by rinsing with acetone followed by placing in boiling distilled water for thirty minutes.¹⁶¹

2.3.1 Vacuum Evaporation Deposition.

This method involves the heating of a filament or boat which contains the target metal with a large current at low pressure. The filament is commonly a tungsten wire with the target metal wrapped around it, (figure 2.9). In the case of the boat, the target metal is placed into a molybdenum or tungsten crucible, (figure 2.10).
The method which uses a filament tends to be wasteful of the target metal. The boat method was applied using Edwards evaporation equipment with a maximum power output of 900 watts at $10^{-4}$ Torr pressure. Gold and platinum wire (0.2 mm diameter., 99.9 % purity, Agar Scientific) were used as the target. Initially a molybdenum boat containing 10 cm of the gold wire was used. A multimeter was used to measure the resistance from one corner to the diagonally opposite corner of the metallic film, it was discovered that a film with a resistance of 1 Ω was deposited onto the substrate. Film resistance values in the remainder of this section are referring to the same ‘corner-to-corner’ resistance measurement.

However, a problem was encountered when depositing platinum due to its higher melting point value i.e. 1773 °C compared to 1064 °C for gold. The molybdenum boat snapped as the current was increased to supply the higher temperature. This
is because platinum forms a solid solution with molybdenum, causing it to break at a weak point of the boat. The platinum experiment was repeated using a tungsten boat (0.05 mm thick) from Agar Scientific. Some platinum was deposited before yet again the boat snapped at a weak point.

It was thought that the Agar Scientific boats were too thin. The experiment was repeated with thicker tungsten boats (0.12 mm thick, R.D.Mathis Co.). Some platinum was deposited, giving a film with a resistance of 600 Ω, before yet again the boat snapped. Thicker tungsten boats were obtained, (0.25 mm, R.D.Mathis Co.). With 10 cm of coiled platinum wire in the boat the current was set to maximum, however the platinum did not melt. It was thought that the tungsten was too thick, and the output of the evaporator was not sufficient to produce the high temperature required. Tungsten sheets of an intermediate thickness could not be obtained. Also, a sheet of tungsten, of 0.2 mm thickness for example, is very brittle and is difficult to cut and shape into a boat/crucible.

2.3.2 DC Sputter Coating.

A Fisons Polaron SC500 sputter coater was used to deposit gold and platinum. A deposition current and pressure of 30 mA and 0.05 Torr with a 20 mm target-specimen distance can deposit 30 nm of gold and 16 nm of platinum per minute. Hence, to obtain a 1 μm depth of gold and platinum it would require 34 and 63 minutes respectively. This relatively slow deposition rate was due to the equipment being ideally suited to the preparation of samples for SEM imaging, as opposed to the deposition of a 1μm thick film. However, 1 μm of gold and platinum were deposited using this method. The resistances of the gold and platinum films produced had resistances of 1 Ω and 60 Ω respectively.

2.3.3 Screen Printing.

This method uses a stencil-like image supported on a fabric mesh stretched across a rectangular frame. The ink is forced through the openings in the stencil onto the
substrate by drawing it across the mesh with a rubber bladed squeegee, figure 2.11. Whether the printing machine is simple and hand operated or large and automatically controlled the principles remain the same.

Figure 2.11 The Principle of Screen Printing.

One of the most attractive features about screen printing is its versatility in being able to print on almost all known materials in a variety of shapes. With care it is possible to deposit a film of gold or platinum of 2-5μm. Most inks contain a binder or plasticiser which must be removed by baking the deposited metals at a high temperature. For this work various 325 stainless steel meshes were prepared lithographically and a DEK model 1200 automatic screen printer was used.

(a) Commercial inks.

Gold and platinum organometallic resinate pastes (GGPE 7251-12.5% and RP 10001-145B-12.5%) were purchased from Heraeus. The advantage of these organometallic inks is that they can produce very thin (0.1-0.2 μm after firing) and high adherent films on the substrate due to the sintering of non-precious metal oxides. After printing on clean alumina substrates the paste was laid flat for ten minutes, to even out, and the solvent was evaporated at 80 °C. This was followed by firing at 850 °C over a firing cycle of thirty minutes observing the manufacturers recommended firing temperature profiles. After firing, films with the full metallic lustres of gold and platinum and low electrical resistances of 0.1 Ω were produced.
Cost is an important factor when considering the commercialisation of a sensing device. The use of platinum and gold films will dictate a large proportion of the production costs. Therefore, in an attempt to reduce the catalyst loading of the electrodes, platinum-doped carbon inks were made. Other workers in the sensors field have produced carbon inks and doped carbon inks. Wang et al prepared palladium-doped inks by mixing palladium powder with a commercial carbon ink, and Taliene et al hand-mixed graphite powder and Nujol oil thoroughly using a pestle and mortar to produce uniform carbon electrodes after printing. Wilson and Gottesfeld produced platinum-carbon inks by adding platinum-on-carbon powder to water and glycerol in a 1:5:20 ratio. The glycerol was necessary to provide the desired ink viscosity. They painted the ink onto a Teflon® substrate and produced electrodes for fuel cell applications with a platinum loading of 0.4 mg Pt cm⁻².

For this work a platinum ink was made by mixing platinum black powder (as part of a metal-loan with Johnson Matthey/Alfa 183000), carbon powder (Cabot Carbon Ltd.) and glycerol (Sigma Chemicals). The platinum black powder particulates were 0.25 μm in diameter, had a high surface area for catalytic capacity of 5.9 m²g⁻¹ and was 99.9% pure.

The ink was produced by initially mixing platinum black with carbon powder. The mass of platinum black to the mass of carbon powder was in the ratio of 1:4, and after some experimentation it was discovered that a ratio of this Pt/C powder to glycerol of 1:8 gave the ideal viscosity, therefore an overall Pt:C:glycerol ratio of 1:4:40 was used. The mixture was thoroughly mixed using a pestle and mortar in order to produce 4.5 g of homogenous ink.

The resulting ink was printed onto clean alumina substrates, a DEK model 1200 automatic screen printer was used to print the working electrode and counter electrode. After laying the printed ink flat for ten minutes, to even out, a firing process at 150 °C was carried out for thirty minutes to remove the glycerol. A
catalyst loading of 0.053 mg Pt cm$^{-2}$ was deposited. The ‘corner-to-corner’ resistance of a Pt/C electrode was 6 Ω. The reference electrode for this design was gold, deposited from an organometallic ink (Heraeus).

Scanning electron microscopy (SEM, JEOL Superprobe 733) was employed to study the surface of the Pt/C electrodes. Figure 2.12 is an image at x 100 magnification, obtained by SEM. The alumina substrate is visible where the ink has not spread throughout the surface of the substrate immediately after printing, as a result the lines from the warp and weft of the 325 stainless steel printing mesh can be seen. Shrinking during the firing process could also add to this effect. The analysis of the X-rays in the reflected beam clearly indicated the presence of platinum, silicon and aluminium, presumably from the 96% alumina substrate. No other elements were found to be present.

Figure 2.12  SEM Image of Home-made Pt/C Ink at x 100 Magnification.
2.3.4 Pressing of Catalyst Loaded Cloth Electrodes.

Büchi and Scherer\textsuperscript{171} and Broka and Ekdunge\textsuperscript{129} have reported the use of commercial electrodes with a platinum loading of 0.60 and 0.35 mg cm\(^{-2}\) respectively on carbon cloth backing (E-TEK Inc.) for fuel cell applications. Büchi and Scherer have described a method of hot-pressing an as-received commercial Nafion\textsuperscript{®} film to the Pt/C cloth backing. Initially the Pt/C electrode material was painted with Nafion\textsuperscript{®} solution, they then applied 50 atm. pressure, i.e. 0.5 kN cm\(^{-2}\) at 125 °C for a dwell time of one minute, so that the Pt/C electrode became impregnated into a Nafion\textsuperscript{®} 117 membrane. The use of the Nafion\textsuperscript{®} solution improved the intimate contact of the catalyst with the membrane, allowing an extension of the three phase region; catalysed carbon, proton conducting membrane and reactant.

Therefore, a second sensor design in this project utilised strips of catalyst-loaded carbon cloth to produce electrodes. A sample of 0.35 mg Pt cm\(^{-2}\) loaded catalyst cloth was obtained (E-TEK Inc.) and the method of hot-pressing onto Nafion\textsuperscript{®} 115 membrane was modified.

The method adopted required the heating of the membrane and catalyst layer to 80°C and spraying a sufficient amount of 5 wt/v\% Nafion\textsuperscript{®} solution onto three strips of catalyst material to provide a 0.9 mg cm\(^{-2}\) coverage of dry Nafion\textsuperscript{®}. The dimensions of the three strips of catalyst were 50x5 mm for the counter and reference electrodes and 50x10 mm for the working electrode. The membrane was then placed on the base of a press, the three strips were then placed on top in the required configuration and a stainless steel bar with an area of 1.75 cm\(^{2}\) was placed across them. An Instron press, model 4204, was used to supply 0.57 kN cm\(^{-2}\), and as this pressing was carried out at room temperature, a longer dwell time of two minutes was employed. This method provided adequate time and pressure to impregnate the E-TEK catalyst material into the surface of the Nafion\textsuperscript{®} film.
This pressing method was also used to produce a sensor of the same design with the as-received DAIS 585 membrane. Again, the application of 0.57 kN cm\(^2\) for two minutes was successful.

2.4 The Electrode and Electrolyte Configurations.

Various designs of planar sensors have been produced, which have incorporated different materials and fabrication processes. Also, parameters such as deviations in the area of the working electrode and the use of interdigitated electrodes have been examined.

2.4.1 The Printed Design Configurations.

The designs of the planar sensors are shown in figure 2.13 below. The working electrodes have been printed as 50 mm\(^2\), 75 mm\(^2\) and 100 mm\(^2\) areas on the alumina substrates. The electrolyte layer covered half of the electrode area, therefore, the active area, i.e. where the catalyst, electrolyte and reactant can be in intimate contact, were 25 mm\(^2\), 37 mm\(^2\) and 50 mm\(^2\).

Figure 2.13 The Electrode Configuration of the Printed Sensors.
2.4.2 The Pressed Design Configuration.

The sensors produced by pressing catalyst loaded carbon cloth onto Nafion® 115 and DAIS 585 membranes had an active working electrode of 50 mm$^2$. This is due to the cloth strip having a width of 10 mm and the steel bar used for pressing having a width of 5 mm. Figure 2.14 indicates the design for these sensors.

Figure 2.14 The Electrode Configuration of the Pressed Sensors.
CHAPTER 3

ELECTROCHEMICAL CHARACTERISATION OF THE ELECTRODES

3.1 Introduction.

The sensor incorporates a reference electrode as part of the three-electrode arrangement. This electrode should be made from a material which can be easily and reproducibly prepared and stable over time under the experimental conditions. The printed CO sensor design utilises a gold reference electrode. Its potential with respect to the standard hydrogen electrode (SHE) in the situation in which we use the reference electrode cannot be found in the literature. Its mechanism may involve the formation of a hydroxide or oxide. In order to characterise the gold reference electrode its electrochemistry was studied using cyclic voltammetry with well documented standard electrochemical reactions.

Cyclic Voltammetry Theory.

Cyclic voltammetry is a popular technique for the initial study of a new electrochemical system. In this technique, the applied potential is varied with time in a symmetrical saw-tooth waveform, while the resulting current is recorded over the entire cycle of the reverse and forward sweeps.

Cyclic voltammetry can provide information on:

(i) the reversibility of an oxidation/reduction process,
(ii) the determination of mechanisms and the identification of intermediate species.

A number of experimental conditions can be altered in order to obtain the above information:

(i) the potential scan rate (the rate of change of potential with respect to time),
(ii) the potential limits; \( E_{\text{initial}} \), \( E_{\text{limit}} \) and \( E_{\text{final}} \) and the direction of the sweep.

Theoretical diagnostic requirements define the complete reversibility of electron transfer processes within a system, these are outlined in table 3.1 below. Also,
figure 3.1 indicates the reversible cyclic voltammograms (CVs) of the potassium ferricyanide system.

Table 3.1 Diagnostic Tests for a Reversible Electron Transfer
Cyclic Voltammetric Response at 298 K.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E_p = E_p^A - E_p^C$</td>
<td>$= 59/n$ mV</td>
</tr>
<tr>
<td>$E_p - E_{p/2}$</td>
<td>$= 59/n$ mV</td>
</tr>
<tr>
<td>$-I_p^C/I_p^A = 1$</td>
<td>($I_p^C$ &amp; $I_p^A$ are of opposite sign)</td>
</tr>
<tr>
<td>$I_p \propto \nu^{1/2}$</td>
<td></td>
</tr>
<tr>
<td>$E_p$ are independent of $\nu$</td>
<td></td>
</tr>
<tr>
<td>at potentials beyond $E_p$, $I^2 \propto t$</td>
<td></td>
</tr>
</tbody>
</table>

where,

$E_p$ is the peak potential (A=anodic, C=cathodic), $I_p$ is the peak current, $\nu$ is the scan rate, and $t$ is time.

3.1.1 The Study of a Gold Reference Electrode - Experimental.

Cyclic voltammetric studies of the gold reference electrode were performed using an EG&G Princeton Applied Research, Model 173 potentiostat/galvanostat with a model 175 universal programmer. A three compartment electrochemical cell was employed (figure 3.2), with a three electrode system; a reference electrode, a platinum wire working electrode and a platinum-mesh counter electrode.

Figure 3.2 The Three Compartment Electrochemical Cell.
Figure 3.1 CVs at 20, 50 and 100 mV s$^{-1}$ in an aqueous solution containing 10 mM potassium ferricyanide in 1 M potassium nitrate. Potentials are given versus saturated calomel reference electrode.
Both counter and reference electrodes were separated from the working electrode compartment of the electrochemical cell by glass frits. The platinum working electrodes were pre-treated before an investigation was carried out by immersion in concentrated sulphuric acid: anodization, then cathodization, (two minutes each at 100 mA in 1.0 mol dm⁻³ sulphuric acid), followed by washing in distilled water.

Studies were performed in two aqueous electrolyte systems; (i) a solution of 10x10⁻³ mol dm⁻³ potassium ferricyanide (K₃Fe(CN)₆), in 1 mol dm⁻³ potassium nitrate supporting electrolyte, (ii) a solution of 10x10⁻³ mol dm⁻³ ferric chloride (FeCl₃.6H₂O), in 1 mol dm⁻³ potassium chloride. The solutions were purged with nitrogen from below for ten minutes in the glass cell before the experiment and continuously purged above the solution throughout the experiment to remove oxygen.

Initially the electrode potentials were measured with respect to a Radiometer sodium chloride saturated calomel reference electrode (SSCE) at 22±2 °C. The potential was scanned between -0.10 V and +0.45 V and 0.00 V and +0.70 V for ferricyanide and ferric chloride electrolytes respectively. A scan rate of 50 mV s⁻¹ was employed and the resulting cyclic voltammograms were recorded by a Goerz Servogor 790 chart recorder. A gold wire (8 cm long, 0.5 mm diam., 99.9% purity, Johnson Matthey) and planar screen printed gold electrodes on alumina (Heraeus) were both used as reference electrodes in the experiments.

3.1.2 Results.

With the SSCE in place, the oxidation and reduction peaks of the iron species in the ferricyanide electrolyte occur at +0.27 V and +0.18 V respectively. With the ferric-chloride electrolyte the oxidation and reduction peaks occurred at +0.50 V and +0.41 V respectively. These results were reproducible. The SSCE was then replaced by the gold wire and the screen printed gold planar electrode, in both cases a cathodic perturbation in the oxidation and reduction peaks of 0.34 V was observed in the cyclic voltammograms with both electrolyte solutions.
The experiments were carried out in triplicate, with fresh electrolyte, a clean cell and electrochemically cleaned electrodes at the beginning of each set of experiments. As the SSCE is $+0.2360$ V versus the SHE,\textsuperscript{175} the cathodic perturbation obtained with the gold wire electrode can be used to calculate the potential of a gold reference electrode versus the SHE.

In this way, the average potential was found to be $+0.556$ V versus the SHE for a gold reference electrode ($22 \pm 2 ^\circ$C). Table 3.2 below summarises the results obtained from the experiments with the planar gold reference electrode. It was fortuitous that the difference in the activity coefficients for the two supporting electrolytes (KNO$_3$ and KCl) appeared to be negligible.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$E^\text{a}$/ V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferricyanide (1 M KNO$_3$)</td>
<td>0.561</td>
</tr>
<tr>
<td></td>
<td>0.556</td>
</tr>
<tr>
<td></td>
<td>0.557</td>
</tr>
<tr>
<td>Ferric chloride (1 M KCl)</td>
<td>0.555</td>
</tr>
<tr>
<td></td>
<td>0.546</td>
</tr>
<tr>
<td></td>
<td>0.561</td>
</tr>
<tr>
<td>Average</td>
<td>0.556</td>
</tr>
</tbody>
</table>

Yasuda \textit{et al} obtained a value of $+0.53$ V versus SHE by experiment.\textsuperscript{116} This value was acquired by the comparison of the cyclic voltammetry characteristics of a gold reference electrode with respect to a silver / silver chloride reference electrode.

Admittedly, the surface of the gold reference electrode in this sensor application is partly covered by water from the hydrated ionic clusters of the solid polymer electrolyte and partly exposed to the air, also the electrochemical couples of the electroactive species studied will impose their own potential on the gold reference electrode. However, these experiments carried out in solution indicated a stable
reference electrode potential and the value of 0.556 V versus the SHE was employed during the testing of the sensors in the presence of the analyte gas.

3.1.3 The Study of a Silver / Silver Chloride Reference Electrode - Experimental

The gold reference electrode held a stable potential, however, workers in the sensors field have carried out investigations on another type of reference electrode. Fontes et al.\(^{176}\) have attempted to use a planar silver / silver chloride electrode (Ag/AgCl) as a reference in a NO sensor and have obtained promising results with their arrangement.

Initially a method of depositing silver was sought. A silver particulate ink was obtained, (Heraeus C 1075). A 325 stainless steel screen was fabricated and the ink was printed using a DEK 1200 screen printer. After printing, the paste was laid flat for 10 minutes to even out, and the solvent was then evaporated at 80 °C. This was followed by firing at 850 °C over a firing cycle of thirty minutes observing the manufacturers recommended firing temperature profiles. After firing, a 11-13 μm film of silver was produced in a rectangular area of dimensions 5x10 mm.

It was then necessary to undergo a chloridization process. The silver electrodes were cleaned in acetone, followed by distilled water and a crocodile clip connection made. A resistance of 0.1 Ω between the clip and the edge of the silver was typical. A 6.0 mol dm\(^{-3}\) hydrochloric acid solution was prepared. A platinum wire electrode and the planar silver electrode were positioned in the solution.

A Thurlby PL310 power supply was used to supply 4 mA to the circuit for thirty minutes.\(^{176}\) This current was found to be adequate for the chloridization process. During this time a plum/brown layer was observed to form on the surface of the silver electrode. The chloride layer always appeared to form uniformly across the surface. The experimental set-up is shown below in figure 3.3.
After chloridization the electrodes were immersed in distilled water for 1-2 days before testing. Characterisation of the planar Ag/AgCl reference electrodes was carried out in much the same way as for the gold planar reference electrodes. Therefore, studies were performed in two liquid electrolyte systems; (i) a solution of 5x10^-3 mol dm^-3 potassium ferricyanide (K₃Fe(CN)₆), in 1 mol dm^-3 potassium nitrate supporting electrolyte, (ii) a solution of 4x10^-3 mol dm^-3 ferric chloride (FeCl₃.6H₂O), in 1 mol dm^-3 potassium chloride.

It was considered very important to characterise the Ag/AgCl reference electrode in an environment free of chloride ions, such as a ferricyanide electrolyte. This is because the Nernst equation shows that the potential is dependent on the activity of the chloride anions. Therefore, a difference in the electrode responses in environments with and without chloride present would be interesting to study. Once the home-made Ag/AgCl reference electrodes had been studied a commercial Ag/AgCl reference electrode (Russell, PHM-105-050T) was also positioned in the cell and the results compared. The filling solution of the commercial Ag/AgCl reference electrode utilised in this project was saturated KCl.

Initially the electrode potentials were measured with respect to a Radiometer sodium chloride saturated calomel reference electrode (SSCE) at 22±2 °C. The potential was scanned between 0.00 V and +0.50 V and +0.20 V and +0.80 V for ferricyanide and ferric chloride electrolytes respectively. A scan rate of 50 mV s⁻¹
was employed and the resulting cyclic voltammograms were recorded by a Goerz Servogor 790 chart recorder.

3.1.4 Results.

With the SSCE in place, the oxidation and reduction peaks of the iron species in the ferricyanide electrolyte (1M KNO₃) occur at +0.27 V and +0.18 V respectively. With the ferric-chloride electrolyte (1 M KCl) the oxidation and reduction peaks occurred at +0.50 V and +0.41 V respectively. These results were reproducible. The SSCE was then replaced by the home-made Ag/AgCl reference electrodes, in both cases an anodic perturbation in the oxidation and reduction peaks of 0.044 V was observed in the cyclic voltammograms with both electrolyte solutions.

As with the work in the characterisation of the gold planar electrodes, the experiments were carried out in triplicate, with fresh electrolyte, a clean cell and electrochemically cleaned electrodes at the beginning of each set of experiments. Knowing that the SSCE is +0.2360 V versus the SHE, the anodic perturbation obtained with the Ag/AgCl electrode can be used to calculate the potential of a Ag/AgCl reference electrode versus the SHE. In this way, the average potential was found to be +0.192 V versus the SHE for a Ag/AgCl reference electrode (22±2 °C). Table 3.3 below summarises the results obtained from the experiments with the planar Ag/AgCl reference electrode.

Table 3.3 Standard Potentials of a Planar Ag/AgCl Reference Electrode.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Home-made E⁰/V</th>
<th>Commercial E⁰/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferricyanide</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1 mol dm⁻³ KNO₃)</td>
<td>0.189</td>
<td>0.216</td>
</tr>
<tr>
<td></td>
<td>0.199</td>
<td>0.226</td>
</tr>
<tr>
<td></td>
<td>0.189</td>
<td>0.216</td>
</tr>
<tr>
<td>Ferric chloride</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1 mol dm⁻³ KCl)</td>
<td>0.191</td>
<td>0.206</td>
</tr>
<tr>
<td></td>
<td>0.186</td>
<td>0.216</td>
</tr>
<tr>
<td></td>
<td>0.196</td>
<td>0.196</td>
</tr>
<tr>
<td>Average</td>
<td>0.192</td>
<td>0.213</td>
</tr>
</tbody>
</table>
The potential of a Ag/AgCl reference electrode is 0.22233 V versus the SHE.\textsuperscript{175} Although the home-made Ag/AgCl reference electrodes do not agree with this value as closely as we would like, the home-made electrodes do seem stable at the E\textsuperscript{o} value of 0.192 V, and are probably most acceptable to use in this application.

However, the characteristic of solid polymer electrolyte materials to exchange the protons within the structure, with cations is often utilised, for example, in the production of the sodium and potassium forms of Nafion\textsuperscript{®}, indeed these films are often referred to as ‘proton-exchange membranes’.\textsuperscript{177} Hence the presence of silver ions in close proximity to the Nafion\textsuperscript{®} or DAIS electrolytes may create problems. It is possible that protons in the membrane will exchange with Ag\textsuperscript+ ions, causing the electrolyte to lose activity, with a possible increase in the electrolyte the impedance.

3.2 The Electrochemistry at Planar Electrodes.

Electrochemical reactions at a planar working electrode possess characteristics different to those obtained at a wire working electrode.\textsuperscript{178} Experiments were carried out to investigate: (i) the electrochemistry at a planar Pt working electrode (5x10 mm), and (ii) the electrochemistry at a planar Pt working electrode with a 4 µm polyelectrolyte film cast onto the surface.

3.2.1 Experimental.

The Pt planar electrodes were cleaned in acetone, followed by immersion in dilute sulphuric acid, and then thoroughly washed in distilled water and air-dried. Electrical connections with negligible resistance were made to the electrode. An electrochemical cell of the design indicated in figure 3.2, of larger dimensions than the usual cell, was designed and fabricated.

Electrochemical studies were performed using a EG&G Princeton Applied Research, Model 173 potentiostat/galvanostat with a model 175 universal programmer. Studies were performed in two liquid electrolyte systems; (i) a solution of $40 \times 10^{-3}$ mol dm\textsuperscript{-3} potassium ferricyanide (K\textsubscript{3}Fe(CN)\textsubscript{6}), in 1 mol dm\textsuperscript{-3}
potassium nitrate supporting electrolyte, (ii) a solution of $40 \times 10^{-3}$ mol dm$^{-3}$ ferric chloride (FeCl$_3$·6H$_2$O), in 1 mol dm$^{-3}$ potassium chloride. The solutions were purged with nitrogen from below for ten minutes in the glass cell before the experiment and continuously purged above the solution throughout the experiment to remove oxygen which may effect the results.

All of the electrode potentials were measured with respect to a Radiometer sodium chloride saturated calomel reference electrode (SSCE) at $22\pm2$ °C. The potential was scanned between +0.10 V and +0.50 V and +0.10 V and +0.70 V for ferricyanide and ferric chloride electrolytes respectively. A scan rate of 50 mV s$^{-1}$ was employed and the resulting cyclic voltammograms were recorded by a Goerz Servogor 790 chart recorder. Prior to the experiment the platinum working electrode was pre-treated by immersion in concentrated sulfuric acid: anodization, then cathodization, (two minutes each at 100 mA in 1.0 mol dm$^{-3}$ sulphuric acid), followed by washing in distilled water.

Initially experiments were carried out with a Pt mesh counter electrode and a platinum wire working electrode (0.32 cm$^2$ surface area). The Pt wire working electrode was then replaced by a Pt planar working electrode (0.37 cm$^2$ surface area) and cyclic voltammetry carried out again. Nafion© and DAIS films (4 μm) were cast onto Pt working electrodes and these were also positioned in the solution and cyclic voltammetry carried out.

3.2.2 Results.

The electrochemistry at a plain Pt planar working electrode showed diffusion limited characteristics. The $\Delta E_p$ values for the oxidation and reduction peaks for the ferric species were shifted, i.e. compared to the results obtained at a Pt wire working electrode; the oxidation peak occurred at a more anodic potential and the reduction peak occurred at a more cathodic potential. An increase in $\Delta E_p$ generally indicates a slow electron transfer or a resistance effect. The reversible nature of the electroactive species was also decreased on the reverse reduction scan to some
extent, again this can be attributed to the behaviour of mobile species at the surface of a planar electrode and hence, slow electron transfer kinetics. Figure 3.4 compares the cyclic voltammograms obtained with a Pt wire and a Pt planar working electrode.

These results suggested that a broad oxidation peak for CO would be observed when the sensors were tested in an environment containing CO, i.e. the resulting peak would lie over a large potential window. This was indeed found to be the case (chapter 5).

DeWulf and Bard,179 and Fedkiw and Ye180 have studied the diffusion of ferricyanide through Nafion® membranes in order to determine the quality of films cast from a Nafion® solution. One of the characteristics of such proton conducting membranes is their anion rejection ability. Therefore, if the oxidation current of Fe(CN)₆³⁻⁺ or the reduction current of Fe(CN)₆³⁻ is to be measured at an electrode covered by such a membrane then the observed current is attributable to gaps or pinholes in the film. Indeed, Fedkiw and Ye discovered that the electrode/membrane had to be immersed in the electrolyte solution for a period of time before a current was observed in the cyclic voltammogram, to allow the diffusion of anions through the pinholes to the surface of the electrode.

The cyclic voltammograms carried out at a Pt planar working electrode with a 4 µm Nafion® film on the surface showed an even greater shift in $\Delta E_p$, and to overcome the resistance in the system the concentration of electroactive species was increased. The concentration of the solution was increased from $40 \times 10^{-3}$ mol dm$^{-3}$ to $80 \times 10^{-3}$ mol dm$^{-3}$ ferric chloride (FeCl$_3$.6H$_2$O), in 1 mol dm$^{-3}$ potassium chloride solution. Figure 3.5 compares the cyclic voltammograms obtained with a Pt wire and a Pt planar working electrode with a 4 µm Nafion® film.

The required soak time which Fedkiw reported for a membrane covered electrode was observed here. This soak time for the 4 µm thick Nafion® film on a planar Pt electrode was in the region of 2-3 minutes and its effect is indicated in figure 3.6.
The results obtained with the 4 μm DAIS film on a Pt planar working electrode showed very similar results as those with the Nafion® film. However, the requirement of a soak time was not apparent for this DAIS film arrangement. Also, the shift in ΔE_p values was not as considerable as that with the Nafion®. Figure 3.7 compares the cyclic voltammograms obtained with a Pt wire and a Pt planar working electrode with a 4 μm DAIS film.

Table 3.4 shows the peak potentials for the oxidation and reduction of the electro-active species and compares the shifts in E_p for the Nafion® and DAIS experiments. The results are both taken from experiments performed in 80 x 10^-3 mol dm^-3 ferric chloride (FeCl₃·6H₂O), in 1 mol dm^-3 potassium chloride solution at room temperature.

<table>
<thead>
<tr>
<th>Film details</th>
<th>Oxidation peak pot. Pt wire /V</th>
<th>Oxidation peak pot. Pt/film /V</th>
<th>Reduction peak pot. Pt wire /V</th>
<th>Reduction peak pot. Pt/film /V</th>
<th>Diff. in oxidation peaks /V</th>
<th>Diff. in reduction peaks /V</th>
<th>Average of peak diff. /V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion®</td>
<td>0.510</td>
<td>0.580</td>
<td>0.395</td>
<td>0.330</td>
<td>0.070</td>
<td>0.065</td>
<td>0.068</td>
</tr>
<tr>
<td>DAIS</td>
<td>0.515</td>
<td>0.550</td>
<td>0.385</td>
<td>0.355</td>
<td>0.035</td>
<td>0.030</td>
<td>0.033</td>
</tr>
</tbody>
</table>

Therefore, it is possible to conclude that the DAIS electrolyte exhibits a smaller perturbation in E_p values, perhaps indicating that a cast DAIS film contains more gaps or pinholes than a cast Nafion® film of the same thickness.

This finding has implications for a CO sensor. If one of the factors which dictates the response time of the sensor is the diffusion rate of the gas thorough the solid polymer electrolyte, either through the regions for gas diffusion within the structure of the polymer electrolyte (figure 2.6) or through pinholes in the film, then the membrane with more gaps or pinholes may produce a faster response time for the detection of the gaseous analyte.

69
Figure 3.4 Cyclic Voltammograms at 50 mV s⁻¹ of a Pt Wire Electrode and a Pt Planar Electrode in 40 mM FeCl₃·6H₂O + 1 M KCl.
Figure 3.5 Cyclic Voltammograms at 50 mV s\(^{-1}\) of a Pt Wire Electrode and a Nafion\textsuperscript{®} Coated Pt Planar Electrode in 80 mM FeCl\(_3\cdot6\)H\(_2\)O + 1 M KCl.
Figure 3.6 Cyclic Voltammograms at 50 mV s\(^{-1}\) of a Nafton\textsuperscript{®} Coated Pt Planar Electrode in 80 mM FeCl\(_3\).6H\textsubscript{2}O + 1 M KCl.
Figure 3.7 Cyclic Voltammograms at 50 mV s⁻¹ of a Pt Wire Electrode and a DAIS Coated Pt Planar Electrode in 80 mM FeCl₃·6H₂O + 1 M KCl.
CHAPTER 4

REQUIREMENTS FOR SENSOR TESTING

4.1 The CO Sensor Test Rig Design.

Certain criteria for the testing of the sensors were considered, for example the sensing chamber was robust, compact, and could withstand a humid atmosphere. The chamber also had an adequate input and output to introduce and remove the humidified gases. A gas blending system allowed the gas sensor to be exposed to a specific concentration of test gas in a reproducible manner. Also, a reliable method of introducing moisture into the test gas was devised which could supply a constant relative humidity ±5% RH within a range 40% RH to 60% RH for the duration of the tests. This range covered the standard RH% values required in the testing of gas sensors of this nature.5

(a) The Gas Blending System.

A Siemens gas analyser was used to calibrate a Signal Series 850 gas blender for the concentration of carbon monoxide diluted in air. After calibration the required concentration was selected by changing the potential applied to the servo of the blender by adjusting the input voltage on a Thurlby PL310 power supply. The gas inlet was a 8 cm copper pipe with holes drilled through every 1 cm. This pipe lay parallel to one wall of the sensing chamber. In this way, the inlet gas was introduced into the chamber along the length of one wall of the container, rather than from one source, this provided a better flow of analyte gas into the chamber.

(b) The Humidity Control.

A characteristic of the solid polymer electrolytes used in this project is that they must contain water in order to conduct protons. The accepted humidity standard of 60% RH was utilised throughout the testing procedure (unless otherwise stated).
The simplest method of introducing a level of humidity into a gas is to use a bubbler system with two rotameters. The balance of the gas flow through the two rotameters supplied the RH value required. It was discovered that a gas flow of 80 cm$^3$/min through both of the rotameters provided a 60% RH level.

(c) The Sensing Chamber.

The sensing chamber was a glass fibre reinforced poly-carbonate box with a clear poly-carbonate lid and had dimensions of 160 x 80 x 85 mm (R.S. Components 138-161). The box was modified and an array of 4 mm insulated sockets were positioned on one side of the box. Sites were also designed to accommodate the gas inlet and outlet pipes and the humidity probe (Rotronic Hygrometer A1 R.S. Components 205-479). The box was earthed and lined with non-adhesive EMI copper shielding (R.S. Components 240-674). The sensors were placed on a block of insulating glass reinforced PTFE in the centre of the box. Figure 4.1 indicates the important features incorporated into the sensing chamber.

Figure 4.1 The Sensing Chamber Arrangement.

(d) Electrical Connections to the Sensor.

Two approaches were taken to make reliable electrical connections to the sensor. Keymec modular edge connectors (Farnell Electronic Components 104-612) were utilised. The ninety pin block was cut into smaller two pin sections, it was found
that such connectors could be easily slipped onto the electrodes making a contact with negligible resistance.

The alternative approach, and perhaps the more reliable method, was to deposit silver epoxy contacts along the edge of the electrode and approximately 3 mm wide (R.S. Components 186-3616). This required a curing period of 24 hours to attain the maximum conductivity. Small crocodile clips could then be attached and a negligible resistance connection was produced.

(e) The Sensors Rig.

The test rig was commissioned at British Gas Research and Technology (CO sensor test rig no. 2057). The completed test rig set-up is shown below in figure 4.2. Prior to the electrochemical measurements the sensor was positioned in the sensing chamber, and compressed air set to deliver 60% RH, was introduced to the sensor. This conditioning would last for 24 hours in order to allow the humidity level in the electrolyte film to equilibrate.

Figure 4.2 The CO Sensor Testing System.

4.2 Details of Sensors Tested.

Table 4.1 describes the sensors that were produced in this project. Sensors 1-28 inclusive were produced by printing inks onto an alumina substrate and casting the polymer electrolyte on top (figure 2.13), sensors 29 and 30 were produced by
pressing catalysed carbon cloth onto as-received commercial membranes (figure 2.14).

Table 4.1 Details of the Sensors Tested.

<table>
<thead>
<tr>
<th>Sensor no.</th>
<th>Electrolyte material</th>
<th>Electrolyte thickness</th>
<th>Active area of Pt WE</th>
<th>DC and/or AC tests?</th>
<th>Special treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nafion®</td>
<td>70 μm</td>
<td>0.25 cm²</td>
<td>DC</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Nafion®</td>
<td>95 μm</td>
<td>0.25 cm²</td>
<td>DC</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Nafion®</td>
<td>10 μm</td>
<td>0.25 cm²</td>
<td>DC</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Nafion®</td>
<td>4 μm</td>
<td>0.25 cm²</td>
<td>DC</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Nafion®</td>
<td>10 μm</td>
<td>0.25 cm²</td>
<td>DC</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Nafion®</td>
<td>10 μm</td>
<td>0.37 cm²</td>
<td>DC</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Nafion®</td>
<td>5 μm</td>
<td>0.25 cm²</td>
<td>DC</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Nafion®</td>
<td>5 μm</td>
<td>0.50 cm²</td>
<td>DC</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Nafion®</td>
<td>20 μm</td>
<td>0.37 cm²</td>
<td>DC &amp; AC</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Nafion®</td>
<td>70 μm</td>
<td>0.37 cm²</td>
<td>DC &amp; AC</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Nafion®</td>
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<td>0.37 cm²</td>
<td>DC &amp; AC</td>
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</tr>
<tr>
<td>12</td>
<td>Nafion®</td>
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<td>0.37 cm²</td>
<td>DC &amp; AC</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Nafion®</td>
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<td>0.50 cm²</td>
<td>DC &amp; AC</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Nafion®</td>
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<td>0.37 cm²</td>
<td>DC &amp; AC</td>
<td></td>
</tr>
<tr>
<td>15</td>
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<td>0.50 cm²</td>
<td>DC &amp; AC</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Nafion®</td>
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<td>0.50 cm²</td>
<td>DC &amp; AC</td>
<td></td>
</tr>
<tr>
<td>17</td>
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<td>0.25 cm²</td>
<td>DC &amp; AC</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>Nafion®</td>
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<td>0.25 cm²</td>
<td>DC &amp; AC</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>DAIS</td>
<td>20 μm</td>
<td>0.50 cm²</td>
<td>DC &amp; AC</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>DAIS</td>
<td>10 μm</td>
<td>0.50 cm²</td>
<td>DC &amp; AC</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>DAIS</td>
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<td>0.50 cm²</td>
<td>DC &amp; AC</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>DAIS</td>
<td>20 μm</td>
<td>0.50 cm²</td>
<td>DC &amp; AC</td>
<td>WE/CE</td>
</tr>
<tr>
<td>23</td>
<td>Nafion®</td>
<td>20 μm</td>
<td>0.50 cm²</td>
<td>DC &amp; AC</td>
<td>ΔH</td>
</tr>
<tr>
<td>24</td>
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<td>0.50 cm²</td>
<td>DC &amp; AC</td>
<td>ΔH</td>
</tr>
<tr>
<td>25</td>
<td>Nafion®</td>
<td>20 μm</td>
<td>0.50 cm²</td>
<td>DC &amp; AC</td>
<td>ΔH</td>
</tr>
<tr>
<td>26</td>
<td>Nafion®</td>
<td>20 μm</td>
<td>0.50 cm²</td>
<td>DC &amp; AC</td>
<td>WE/CE &amp; ΔH</td>
</tr>
<tr>
<td>27</td>
<td>DAIS</td>
<td>20 μm</td>
<td>0.50 cm²</td>
<td>DC &amp; AC</td>
<td>WE/RE</td>
</tr>
<tr>
<td>28</td>
<td>DAIS</td>
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<td>0.50 cm²</td>
<td>DC &amp; AC</td>
<td>Pt/C ink WE</td>
</tr>
<tr>
<td>29</td>
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<td>130 μm</td>
<td>0.50 cm²</td>
<td>DC &amp; AC</td>
<td>Pressed</td>
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<tr>
<td>30</td>
<td>DAIS</td>
<td>180 μm</td>
<td>0.50 cm²</td>
<td>DC &amp; AC</td>
<td>Pressed</td>
</tr>
</tbody>
</table>

WE/RE and WE/CE correspond to these electrodes being interdigitated, and ΔH refers to the thermal activation treatment of the cast polymer film (section 2.2.3b).
4.3 Electrochemical Testing Techniques.

The testing methods have utilised the open cell potential (OCP), (sometimes referred to as the open circuit potential), cyclic voltammetry (CV) and AC impedance techniques. The theory and experimental details of the electrochemical techniques used are described below. The results obtained by these methods are outlined in chapter 5. Unless otherwise stated, the experimental conditions of 60% RH and 22±2 °C were observed throughout all of the experiments described below.

4.3.1 DC Techniques (OCP and CV).

The theory of cyclic voltammetry was outlined in section 3.1. The oxidation current of CO was observed at the platinum working electrode of the CO sensors. The desired electrochemical reactions for the oxidation of CO are as follows:-

Working electrode:  \[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2e^- \] (4.1)

Counter electrode:  \[ 2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2e^- \rightarrow \text{H}_2\text{O} \] (4.2)

The gases diffuse through the polymer electrolyte layer to the electrodes, while protons diffuse in the polymer electrolyte layer from the working to the counter electrode. The oxidation current of CO between the working and counter electrodes has been studied by cyclic voltammetry.

Cyclic voltammetry was performed using a Solartron SI 1286 potentiostat and controlled with Solartron CorrWare and CorrView software. Initially, the OCP of the system would be studied over a five minute period. Only when this OCP value had stabilised would cyclic voltammetry be carried out. The OCP between the working and reference electrodes is due to the species present at the surface. Therefore, in clean air the OCP value measured is due to oxygen evolution and reduction reactions. This was shown to be the case, because after carrying out the CV cycles, where oxygen will have been generated, the OCP value becomes more positive. For example for sensor number 21, the average OCP value in clean air was 84 mV versus the gold reference electrode, however after three ‘conditioning’ CVs had been carried out the OCP became 230 mV, and for sensor no 24, prior to the
CVs the OCP was 123 mV, and the CVs caused the OCP to increase by 196 mV to 319 mV.

Sensor numbers 21 and 24 possessed a gold reference electrode, however, the pressed sensor designs have a reference electrode produced from the same material as the working electrode and the OCP value in clean air would be expected to be very close to 0.00V. This was found to be the case with sensor number 30, which possessed an OCP of 2 mV, which increased to 132 mV after three successive CVs had been carried out.

In every instance the OCP was allowed to decrease until almost at the original OCP value prior to carrying out the three CVs. An hour was allowed for this stabilisation of the perturbed OCP before further tests were performed.

The parameters used when carrying out the CVs on the sensors are as follows. The applied potential on the working electrode was scanned between 0.00 V to +1.00 V versus the built-in gold reference electrode at 50 mV s\(^{-1}\). The resulting CVs of the sensor in an atmosphere of CO and in an atmosphere absent of CO gas were compared for the different sensor designs (chapter 5). The current responses obtained by cyclic voltammetry were automatically converted to the current density values, so that direct comparisons of different sensor designs could be made. As the technique of cyclic voltammetry oxidises the CO which is adsorbed on the surface of the Pt working electrode, it can be used as a method of removing any CO in order to obtain a 'clean' electrode prior to the addition of CO in a new experiment. Therefore, CVs were applied as a 'conditioning' process prior to carrying out AC impedance spectroscopy and the addition of CO.

4.3.2 AC Impedance Spectroscopy Technique.

A method which has been recognised as a valuable tool in the study of electrochemical systems is AC impedance. This method allowed a diagnostic study of the sensor system.\(^{181}\) In this project a Solartron SI 1260 Frequency Response Analyser was used in conjunction with the Solartron SI 1286 potentiostat. The
Solartron software packages ZPlot and ZView were used. The theory of AC impedance is quite involved, an explanation of AC impedance theory follows.

(a) Aim.

The conductivity of a polymer intended for electrochemical application is an important characteristic. It can supply many details on the mechanism of the electrolyte in its working environment, such as the charge transfer effects at the interface, information on the electrolyte boundaries and details of the bulk electrolyte. However, conductivity measurements are not necessarily simple.

The use of DC measurements can induce the movement of mobile species under the influence of the electric field. Thus causing an enrichment of mobile species in the electrolyte adjacent to the electrode - and a corresponding depletion near the other electrode. A further factor which makes DC measurements virtually useless, is it can only measure resistance - whereas, capacitance and inductance have impedance which is only visible in an AC environment. These impedances must be probed before a complete look at the mechanism can be undertaken. It is therefore very difficult to accurately determine conductivities from DC measurements.

Such problems of concentration polarisation can be avoided using an alternating current.

"When a small amplitude sinusoidal voltage is superimposed on an applied or equilibrium potential there is a shift in amplitude and phase from the voltage and the electrode reaction behaves in an equivalent way to an electrical circuit with impedance. "\textsuperscript{181}

This impedance varies with the frequency of the AC current and the electrochemical information is extracted by finding an idealised equivalent circuit which mimics the system with resistance, capacitance etc. (the circuit elements) in series or parallel.
(b) The Circuit Elements.

Consider the test cell in figure 4.3 below:

Figure 4.3 A Test Cell.

The Dispersive Elements

- A geometrical capacitance, $C_g$, will occur as a consequence of the charge on the electrodes themselves.
- A double layer capacitance, $C_{dl}$, is a result of a charge build up when ions cannot pass from electrode $\rightarrow$ electrolyte and vice versa.
- The kinetics of the charge transfer at the interfaces gives rise to a resistance, $R_{ct}$, which in turn, can cause a build up of charge on either side of the interface, $C_{ct}$, which is in parallel with $R_{ct}$.
- There is also an uncompensated resistance, $R_u$, due to resistances between the probe or Luggin capillary of a test cell and the electrode surface.
- Therefore an equivalent circuit for the test cell shown, with a bulk resistance, $R_b$, could be as shown in figure 4.4:-

Figure 4.4 An Equivalent Circuit.
Inductance, \( L \), can also be present in many systems, however, it is not a very important factor for polymer systems.

The Diffusion Elements.

The constant phase element, \( Q \), is a hybrid, somewhere between a resistor and a capacitor. These are present in polymer electrolyte systems due to the presence of roughness at the electrode-electrolyte interface.

When one boundary blocks the diffusion of a diffusing species, a tangent hyperbolic function, \( T \), is present, and a cotangent hyperbolic function, \( O \), is involved when one boundary imposes a fixed concentration of a diffusing species. This can often occur in corrosion related diffusion processes.

Finally, the Warburg impedance, \( W \), is a special type of constant phase element. It occurs when \( R_{ct} = 0 \), and when the real and complex part of the constant phase element are equal. Hence, the relative size of \( R_{ct} \) and \( Z_w \) at a given frequency is a measure of the balance between the kinetics and diffusion control.

(c) Impedance - A Complex Quantity.

Impedance is a complex quantity, i.e. it is made up of two parts, one is a real (\( Z' \)) and the other is called imaginary (\( Z'' \)). The imaginary part is as a result of a phase difference. \( Z' \) and \( Z'' \) are connected to \( Z \) by:

\[
Z = Z' - jZ''
\]

The circuit elements are connected together and contribute to the real and imaginary parts.

(d) Displaying the Results.

The frequency dependence can be displayed in several ways. The complex plane or Nyquist plot is favoured in the polymer electrolyte field and plots \(-Z'' \) versus \( Z' \).
Typical Nyquist plots are shown below in figure 4.5, showing the corresponding circuit elements. A constant phase element in parallel with a resistor flattens or depresses a semicircle and a constant phase element or Warburg element in series with a resistor cause the vertical line to become tilted, as shown below in figure 4.6.

Figure 4.5 The Nyquist Plot.

![Figure 4.5 The Nyquist Plot.](image)

Figure 4.6 The Effect of a Constant Phase Element.

![Figure 4.6 The Effect of a Constant Phase Element.](image)

Data can also be displayed as a Bode representation. This plots log $Z$ versus log frequency, as well as displaying the variation of the phase angle vs. log frequency. An example of this plot and its uses is shown below in figure 4.7.

Figure 4.7 The Bode Representation.

![Figure 4.7 The Bode Representation.](image)
The gradient of the line and phase angle provides details on the circuit elements present, (table 4.2).

Table 4.2 The Characteristics of the Circuit Elements.

<table>
<thead>
<tr>
<th>Line details</th>
<th>Element</th>
<th>Phase angle / degrees</th>
</tr>
</thead>
<tbody>
<tr>
<td>horizontal line</td>
<td>$R$</td>
<td>0</td>
</tr>
<tr>
<td>gradient = -1</td>
<td>$C$</td>
<td>-90</td>
</tr>
<tr>
<td>gradient = -$\frac{1}{2}$</td>
<td>$W$</td>
<td>-45</td>
</tr>
</tbody>
</table>

The Bode plot becomes very useful in a situation where a large difference in the size of two resistors is apparent, as it may be easy to miss one of the semicircles on the Nyquist plot as indicated in figure 4.8.

Figure 4.8 Bode Versus Nyquist Plot.

(e) AC Impedance Software.

Software is available, such as the ZPlot and ZView program available with the Solartron SI 1260 Frequency Response Analyser. It uses a combination of finding semicircles and lines, followed by the subtraction of each determined element. The use of a non-linear least square fit can determine a best fit with relatively small errors and can produce error plots to determine the closeness of the fit to the experimental data.
(f) Why was AC Impedance Useful For This Application?

Consider the sensor system with a polymer electrolyte. In the simplest case, the polymer acts as a resistor, $R_b$, in series with a double layer capacitance at the interface, and in parallel with a geometric capacitance. This as indicated below in figure 4.9.

![Figure 4.9 The Sensor System and Predicted Equivalent Circuit.](image)

To use this technique in a diagnostic way, the range of frequencies applied to the system should be as wide as possible. Ideally, a range of 6 to 7 decades of frequency, e.g. $10^{-2}$ to $10^5$ Hz should be used.

To summarise, AC impedance has been shown to be a method which can provide a study of the mechanisms involved in an electrochemical system which is sensitive to any change in the output of the sensor as a function of time, such as CO concentration or the relative humidity of the test gas.

4.4 Electrochemical Testing Procedure.

Only when the OCP value had stabilised were cyclic voltammetry and AC impedance scans carried out. Cyclic voltammetry was then used as a conditioning process to ensure a ‘clean’ surface on the Pt working electrode, i.e. a surface free from adsorbed CO molecules. Three CV cycles were utilised, with the applied potential on the working electrode scanned between 0.00 V and +1.00 V versus the built-in gold reference electrode at 50 mV s$^{-1}$. Any CO present was removed on the first cycle, however, in order to have a reproducible testing procedure, three cycles were applied every time. At the more positive applied potential range, the oxygen evolution reaction occurred (equation 4.2). A perturbation in the OCP in a more
positive direction was observed, which would decrease with time to an OCP value which corresponded to a clean air environment. The explanation for this perturbation in OCP is outlined in section 4.3.1.

It was also possible to remove the CO by a potentiostatic method. Experiments were carried out when the applied potential, versus the gold reference electrode, was held at +0.625 V for 30 seconds and at +0.800 V for 30 seconds. A current was observed due to the oxidation of CO present on the working electrode. Therefore in a commercial sensor system, it is conceivable that it will only be necessary to pulse an applied constant potential over a defined time period in order to condition the system prior to applying the AC impedance scan to detect CO in the atmosphere.

When the OCP value had stabilised, an AC impedance scan would be carried out at the OCP potential with an AC amplitude of 10 mV, over a frequency range 60 kHz to 0.1 Hz, except for the sensors which incorporated a thermally activated Nafion® electrolyte (sensors 23,24,25 and 26), which were tested over a frequency range of 10 kHz- 0.003 Hz. The results were adjusted for the surface area of the working electrode before they were displayed and analysed.

A known concentration of CO would then be introduced to the sensing chamber. Initially the chamber would be ‘isolated’ by closing the inlet pipe, the potential on the blender servo was adjusted to supply a defined concentration of CO mixed with air determined from a calibration graph. The blender was allowed to equilibrate for ten minutes before the inlet pipe was opened and the CO/air mixture at the required RH% level (usually 60%) was introduced into the sensing chamber.

Before the inlet pipe was opened, the chamber contained an atmosphere of clean air, the majority of which had to be replaced by a CO/air mixture prior to the start of an AC impedance scan. The volume of the sensing chamber was calculated to be 1088 cm³ and with a gas flow of 160 cm³ min⁻¹ (section 4.1b) it would take almost seven minutes to replace the air, (assuming no void volumes in the chamber where the movement of air was limited). If the diffusion processes of the analyte gas
through the polymer electrolyte were to be studied, then it was necessary to start the AC impedance scan as soon as possible, therefore only five minutes were allowed to elapse from the start of CO/air introduction, before the impedance scan was started.

This first scan in the presence of CO was referred to as the ‘time = 0’ scan, although it must be remembered that the CO concentration in the testing chamber may have reached approximately 70% of the required concentration at that time. AC impedance scans in the frequency range 60 kHz to 0.1 Hz were repeated every ten minutes, with a scan taking five minutes. For the impedance scans in the 10 kHz to 0.003 Hz range, the scans took three times as long, therefore, these plots were repeated at fifteen minute intervals. OCP values and CV scans were carried out at ‘time = 60 min’ with the same experimental details as outlined above.

After the CVs had been carried out in an atmosphere containing CO, the analyte gas was removed from the inlet gas by reducing the servo potential on the blender to zero. Up to two hours was allowed for the box to be purged with clean air, before another conditioning process and an experiment with a CO/air mixture was carried out.
CHAPTER 5

RESULTS FROM SENSOR TESTING IN CLEAN AIR AND IN ENVIRONMENTS CONTAINING CARBON MONOXIDE

5.1 An Introduction to the Observed Responses of the Sensors to CO.

The same basic responses were observed, to a greater or lesser extent, with the different sensor designs when tested by the DC and AC techniques described in the previous chapters. The generalised responses obtained by the sensors are provided before the discussion of each sensor design, and the interpretation described below is then applied to the individual results.

5.1.1 General Changes Observed in the Open Cell Potential Values.

The application of three CVs as the ‘conditioning’ process caused the evolution of oxygen from water at the working electrode. The oxidation current relating to this reaction was clearly observed on the forward scan of the CVs. The resulting oxygen could then chemisorb onto the surface of the platinum catalyst. This perturbation caused the OCP value to shift in a positive direction. Lukacs et al. have also investigated the affect of CO at platinum electrodes with a stabilised zirconia solid electrolyte. They discovered that the OCP was affected by the partial pressures of O₂ and CO in the analyte gas, but suggested that OCP measurements alone would not provide all of the mechanistic information required.

Their results showed a shift in the OCP value in the cathodic direction of approximately -150 mV on the addition of CO to the clean air environment. It was mentioned in section 4.3.1 that the OCP is defined as the electrode potential relative to the reference electrode, consequently in clean air the value is dependent on the relative quantities of oxygen activity occurring at the working and reference electrodes. Hence, when CO is present there exists a competition for the active surface sites of adsorption on the surface of the supported platinum catalyst between the O₂ and CO molecules, and a mixed cell potential is formed at a more
negative potential. In this project, a typical sensor indicated a shift in the OCP value between -30 mV and -140 mV, depending on the CO concentration in the analyte gas and sensor design. Examples which demonstrate the formation of this mixed cell potential with the sensor designs studied, will be given later in this chapter.

5.1.2 General Response Observed by the Cyclic Voltammetry Testing Technique.

For the designs of CO sensors produced for this project, cyclic voltammetry was shown not to be a sensitive enough technique for the detection of a certain concentration of CO. The response of the sensor to an applied potential was seen as either a change in the gradient of the current-applied potential plot, and with some sensor designs, the appearance of a broad oxidation peak for CO.

When this oxidation current of CO was obtained, it was superimposed onto the current response obtained in clean air and the peak oxidation potential of CO on the platinum working electrode was established to be over a potential range of +0.50 - +0.80 V versus the gold reference electrode. Examples of the CVs obtained for the different designs of sensors in the presence of varying concentrations of CO in air are presented and discussed later in this chapter. Where possible, the first CV cycle obtained is indicated in the figures, however, on some occasions the second or third cycle is presented. Figure 5.1 indicates the responses observed by the sensors in a clean air environment and when CO was present in the analyte gas. The response in clean air exhibited an anodic current on the forward scan due to the oxidation of water at the working electrode evolving oxygen, and the reverse scan indicated a cathodic current which corresponded to the reduction of the oxide layer which was present on the surface of the platinum electrode.

Figure 5.1 General Responses Obtained by the Sensors in the CV Plots.
5.1.3 General Response to the AC Impedance Spectroscopy Testing Technique.

All of the AC impedance plots follow the same approximate shape, i.e. initially a flattened semicircle at high frequency, followed by the start of a large semicircle over a lower frequency range. Differences in response for the various sensor designs, lie in where the data is positioned on the Nyquist plots with respect to \( Z' \) and \( Z'' \) values (the real and imaginary impedance respectively).

It is suggested that the equivalent circuit elements for an electrode, when a polymer film is present, is dominated by the magnitude of the bulk resistance \( (R_b) \), the capacitance due to the geometry of the electrodes \( (C_g) \), the kinetics of the charge transfer at the interface \( (R_{ct}) \), the double layer capacitance \( (C_{dl}) \) and the impedance which exists between the probe (the reference electrode) and the surface of the electrode \( (R_s) \). As a consequence the positioning of the two semicircles observed within the frequency range studied will be defined by the relative values of these elements. A flattened semicircle is generally due to a constant phase element (CPE) in parallel with the bulk resistance. The CPE most often found in the case of a solid electrolyte is denoted as \( \Phi_i \). Figure 5.2 indicates one of the sensor designs, the equivalent circuit and a generalised AC impedance response from such a sensor, in both clean air and in the presence of CO.

Figure 5.2 The AC Impedance Response and the Equivalent Circuit.
When CO is present the second semicircle in the Nyquist plot is pulled down towards the x-axis indicating that the interfacial impedance is affected ($R_{ct}$ and $C_{dl}$). Also the Bode plot indicates a reduction in the capacitance over the lower frequency range ($C_{dl}$) with an overall reduction in the total impedance ($|Z|$). The results obtained for each sensor design are now discussed and examples demonstrating the features such as broad CO oxidation peaks on the CV plots, and variations on the appearances of the Nyquist and Bode plots from the AC impedance spectroscopy tests are described below. The full interpretation and explanations for the observed responses are discussed in detail in chapter 7. A calibration curve which describes one of the sensor’s response to CO is also included.

5.2 Results Obtained with the Planar Sensor with a Cast DAIS Electrolyte.

AC impedance and CV responses from sensors with screen printed rectangular platinum and gold electrodes, on an alumina substrate with a cast DAIS electrolyte film will be discussed here. Refer to figure 2.13 for the five electrode arrangements studied. Sensor number 17 had a rectangular working electrode area of 0.25 cm² and a DAIS film thickness of 20 μm, whereas, sensor numbers 19, 20 and 21 had rectangular working electrode areas of 0.5 cm² and electrolyte film thicknesses of 20, 10 and 15 μm respectively. Sensor number 22 also had a working electrode area of 0.5 cm² and a film thickness of 20 μm, however the platinum working and counter electrodes were interdigitated.

5.2.1 Effect of Working Electrode Area.

(a) AC Impedance Spectroscopy Response.

Figure 5.3 compares the AC impedance responses of sensor numbers 17 and 19 in clean air conditions at 60% RH and 22±2 °C. It was discovered that sensor number 17 had an uncompensated cell resistance (at 60 kHz) of 4 kΩ and the sensor with
an electrode area twice as large had an uncompensated resistance \( (R_e) \) of 1.3 k\( \Omega \).
As this resistance parameter is due to the resistances between the probe and the electrode surface, then not surprisingly, these results indicate that as the active electrode area is increased, the resistance in the system is reduced.

Further study of the clean air responses for the two sensors shown in figure 5.3 indicate that the electrolyte impedance equivalent circuits are extremely similar. If the first semicircles are compared, the bulk resistance and the geometrical capacitance parameters are of a similar magnitude. On comparison of the second semicircles, it can be said that the double layer capacitance and the charge transfer resistance are also in the same range of values. In fact all that has happened is that the AC impedance plot for sensor number 17 is translated across the \( Z' \) axis to higher impedance values due to \( R_e \) (the electrode resistance) being three times greater compared to sensor number 19.

Figure 5.4 shows the Nyquist plots for sensor no 17 in both clean air and in the presence of 5% (50000 ppm) CO. It can be seen that the presence of CO does not affect the electrode resistance \( (R_e) \), or the electrolyte resistance \( (R_h \) and \( C_h) \) to any great extent, if at all. However, the interfacial impedance \( (R_{el} \) and \( C_{el}) \) is affected, as the second semicircle is pulled down towards the x-axis, indicating an overall reduction in the impedance of the system.

Figure 5.5 indicates the Nyquist plots for sensor no 19 in the same experimental conditions. A similar effect is observed on the addition of CO, i.e. the reduction in size of the second semicircle corresponding to an overall reduction in the interfacial impedance. Figure 5.6 shows the Bode plots relating to the information shown in the Nyquist plot in figure 5.5.

These plots reveal a close agreement to the conclusions stated above, i.e. over the high frequency scan, the capacitance and resistance hardly vary \( (C_e \) and \( R_e) \), however, over the lower frequency range the theta versus frequency plot points towards a decrease in capacitance \( (C_{el}) \) whilst the \( |Z| \) versus frequency plot clearly indicates a decrease in the overall impedance \( (C_{el} \) and \( R_{el}) \).
Figure 5.3 Nyquist Plots Indicating the Responses of Sensor Numbers 17 and 19 in Clean Air (60% RH and 22±2 °C).
Figure 5.4 Nyquist Plots Indicating the Responses of Sensor Number 17 in Clean Air and on the Addition of 5% CO with Time (60% RH and 22±2 °C).

'Clean Air' and 't=0' Plots were Measured Between 60 kHz and 0.1 Hz.

the Remaining Plots were Measured Between 1.0 and 0.1 Hz.
Figure 5.5 Nyquist Plots Indicating the Responses of Sensor Number 19 in Clean Air and on the Addition of 5% CO with Time (60% RH and 22±2 °C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
Figure 5.6 Bode Plots Indicating the Responses of Sensor Number 19 in Clean Air and on the Addition of 5% CO with Time (60% RH and 22±2 °C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
It was also noticed that the second semicircle on the Nyquist plot dropped towards the x-axis to a greater extent after a greater period of time had passed in the presence of CO. This could be due to two factors; the diffusion rate of the CO gas through the solid polymer electrolyte film allowing more CO through to the electrode/electrolyte interface with respect to time, causing a larger decrease in the interfacial impedance. Another possibility for the variation of impedance with time may be due to the concentration of CO increasing in the sensing chamber until it reached the desired level. This is because the AC impedance scan at ‘t=0’ was initiated when the CO concentration was only at 70% of the desired value, the reason for this is outlined in section 4.4.

When the Nyquist plots showing the responses of sensor numbers 17 and 19 to 5% CO are compared (figures 5.4 and 5.5) then it can be seen that within the same period of time, sensor number 19 produced a greater response to the analyte. This indicates that the larger working electrode area available for CO adsorption led to a greater decrease in the interfacial impedance than that observed for sensor number 17.

Therefore, it can be concluded that a larger active working electrode area can produce an enhanced response to CO, therefore optimisation of the screen printed CO sensor design would incorporate a working electrode area of dimensions \( \geq 0.5 \text{ cm}^2 \) rather than 0.25 cm\(^2\).

(b) Response Obtained by Cyclic Voltammetry.

Figure 5.7 compares the typical CV scans obtained with sensor numbers 17 and 19 in clean air conditions. As the current output was normalised to A cm\(^{-2}\), it may be expected that the two CV responses would be identical. However, the results obtained by sensor number 19 indicated a slightly greater current on the forward scan for the same value of applied potential. This difference is possibly explained by the difference in the positioning of the larger working electrode with respect to the reference and counter electrodes, i.e. a geometrical factor. Figure 5.8 indicates the response of sensor number 17 in clean air and in the presence of 5% CO.
Figure 5.7 Cyclic Voltammograms at 50 mV s\(^{-1}\) Comparing the Results Obtained with Sensor Numbers 17 and 19 in a Clean Air Environment.

Applied Potential Values are Stated Versus the Gold Reference Electrode.
Figure 5.8 Cyclic Voltammograms at 50 mV s\(^{-1}\) Comparing the Results Obtained with Sensor Number 17 in a Clean Air Environment and 5% CO.

Applied Potential Values are Stated Versus the Gold Reference Electrode.
A peak corresponding to the oxidation current of CO was not observed, however, an increase in the gradient of the current-applied potential plot was detected. If Ohm’s Law is applied to this result, it can be concluded that the resistance of the electrochemical sensor system decreased when CO was present. Both the Nyquist and Bode plots for the same experimental conditions agree with this finding as they indicated a decrease in the overall impedance (|Z|) and more specifically the interfacial impedance when CO was in the vicinity.

Again, an oxidation peak was not observed when sensor number 19 was tested in the presence of CO and a very similar change in gradient on the current-applied potential plot was obtained on the introduction of CO to the sensing chamber.

5.2.2 Effect of the Electrolyte Film Thickness.

(a) AC Impedance Spectroscopy Response.

The AC impedance spectroscopy responses of sensor numbers 20, 21 and 19 with cast DAIS films of 10 μm, 15 μm and 20 μm respectively are compared in figure 5.9. All of the sensors have an active working electrode area of 0.5 cm² and all scans were carried out over a frequency range between 60 kHz and 0.1 Hz, with the exception of sensor number 20, which were carried out between 60 kHz and 0.05 Hz. This was because sensor number 20 possessed a large bulk resistance which dominated the scan at frequencies greater than 0.1 Hz.

It can be seen that the system with the greatest impedance is the sensor with the thinnest electrolyte film, and the sensor with the lowest impedance value has a DAIS electrolyte thickness of 20 μm. The response of the sensor with a 15 μm film (sensor number 21) lies closer to the response of the sensor with the 20 μm film. These results indicate that an electrolyte thickness of only 10 μm is not ideal as the film does not possess adequate conductivity characteristics to display a large response to the presence of CO.
Figure 5.9 Nyquist Plots Comparing the Responses of Sensor Numbers 20, 21 and 19 with Cast DAIS Films of 10 μm, 15 μm and 20 μm Respectively in Clean Air (60% RH and 22±2 °C).
Figure 5.10 compares the Nyquist plots showing the responses of sensor numbers 19 and 21 in clean air and in the presence of 1000 ppm CO. The plots which indicate the effect of CO were the first plots recorded as the CO was added, i.e. the ‘t=0’ plot (refer to chapter 4). Sensor number 19 which had a 20 μm DAIS film, had a much greater response to the analyte gas than sensor number 21. Therefore the sensor which possessed the greatest conductivity produced a more enhanced response.

A trend in the response of the sensors with respect to the concentration of CO was also visible. The second semicircle moved down towards the x-axis to a greater extent with a larger concentration of CO. Figure 5.11 indicates the response of sensor number 20 in a clean air environment and in the presence of 500 ppm, 1000 ppm, 0.5%, 1%, 2%, 3% and 5% CO. Clean air was re-introduced in between each experiment and the reproducibility of the AC impedance response in clean air was sought prior to the addition of the next concentration of CO. Figure 5.12 reveals how a similar trend was observed for sensor number 21, in this case the sensor was tested in environments containing 500 ppm, 1000 ppm, 1460 ppm, 2500 ppm and 5000 ppm CO. The results for sensor number 19 when 130 ppm, 1000 ppm, and 5% CO were present in the test gas are shown in figure 5.13.

(b) Response Obtained by Cyclic Voltammetry.

A change in the gradient on the current-applied potential plots for sensor numbers 19, 20 and 21 were observed, however a resolved peak at the potential window for CO oxidation was not detected. A typical example of this is shown in figure 5.14 for sensor number 20 in clean air conditions and when 5% CO was present.

(c) Open Cell Potential Variations.

The three ‘conditioning’ CVs displaced the OCP values to a more positive potential for sensor numbers 19, 20 and 21. Table 5.1 outlines the sensor details and OCP values before and after the CV cycles, all in clean air conditions. The presence of CO shifted the OCP to a more negative value due to the formation of a mixed cell potential. Indeed a trend with this shift in OCP was observed with respect to the CO concentration. Table 5.2 presents the trend observed for sensor number 20.
Figure 5.10 Nyquist Plots Indicating the Responses of Sensor Numbers 19 and 21 in Clean Air and in the Presence of 1000 ppm CO (60% RH and 22±2 °C). All Plots were Measured Between 60 kHz and 0.1 Hz.
Figure 5.11 Nyquist Plots Indicating the Response of Sensor Number 20 (10 μm DAIS Electrolyte) in Clean Air and in the Presence of Various CO Concentrations (60% RH and 22±2 °C).

Clean Air Environment
- On the Addition of 500 ppm CO
- On the Addition of 1000 ppm CO
- On the Addition of 0.5% (5000 ppm) CO
- On the Addition of 1% CO
- On the Addition of 2% CO
- On the Addition of 5% CO
Figure 5.12 Nyquist Plots Indicating the Response of Sensor Number 21 (15 μm DAIS Electrolyte) in Clean Air and in the Presence of Various CO Concentrations (60% RH and 22±2 °C).

The Nyquist plots show the response of Sensor Number 21 in clean air and in the presence of various CO concentrations ranging from 500 ppm to 5000 ppm. The plots are labeled as follows:

- Clean Air Environment
- On the addition of 500 ppm CO
- On the addition of 1000 ppm
- On the addition of 1460 ppm
- On the addition of 2500 ppm
- On the addition of 5000 ppm

The plots are measured at frequencies of 0.1 Hz and 60 kHz. The x-axis represents the real part of the impedance (Z'), and the y-axis represents the imaginary part of the impedance (Z'').
Figure 5.13 Nyquist Plots Indicating the Response of Sensor Number 19 (20 μm DAIS Electrolyte) in Clean Air and in the Presence of Various CO Concentrations (60% RH and 22±2 °C).

Clean Air Environment
On the addition of 130ppm CO
On the addition of 1000ppm CO
On the addition of 5% CO

0.1 Hz
60 kHz
Figure 5.14  Cyclic Voltammograms at 50 mV s\(^{-1}\) Comparing the Results Obtained with Sensor Number 20 in Clean Air and 5% CO.

Applied Potential Values are Stated Versus the Gold Reference Electrode.
Table 5.1 OCP Values Before and After the ‘Conditioning’ CVs for Sensor Numbers 19, 20 and 21.

<table>
<thead>
<tr>
<th>Sensor number</th>
<th>DAIS film thickness</th>
<th>OCP prior to ‘conditioning’</th>
<th>OCP after ‘conditioning’</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>10 μm</td>
<td>+8.5 mV</td>
<td>+293 mV</td>
</tr>
<tr>
<td>21</td>
<td>15 μm</td>
<td>+84 mV</td>
<td>+230 mV</td>
</tr>
<tr>
<td>19</td>
<td>20 μm</td>
<td>+153 mV</td>
<td>+232 mV</td>
</tr>
</tbody>
</table>

Table 5.2 OCP Values for Sensor Number 20 in Various CO Concentrations. The Value was Recorded after CO had been in the Sensing Chamber for One Hour.

<table>
<thead>
<tr>
<th>CO concentration</th>
<th>OCP value</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 ppm</td>
<td>-9 mV</td>
</tr>
<tr>
<td>1 %</td>
<td>-14 mV</td>
</tr>
<tr>
<td>2 %</td>
<td>-29 mV</td>
</tr>
<tr>
<td>3 %</td>
<td>-41 mV</td>
</tr>
<tr>
<td>5 %</td>
<td>-62 mV</td>
</tr>
</tbody>
</table>

5.2.3 Effect of the Electrode Design

- Interdigitated Working and Counter Electrodes.

Sensor number 22 was produced with a cast DAIS electrolyte film thickness of 20 μm. The platinum working and counter electrodes were screen printed in an interdigitated design with three inter-spaced ‘fingers’. This arrangement of electrodes is becoming popular with sensor producers and has been used in the design of SAW sensors for some time. The working electrode area was 0.5 cm² and the results obtained from this design were compared to those gained from sensor number 19, which shared the same design parameters, however, it possessed the normal rectangular working electrode arrangement.
(a) AC Impedance Spectroscopy Response.

Figure 5.15 compares the AC impedance plots in clean air conditions for sensor numbers 19 and 22 over the frequency range 60 kHz to 0.1 Hz. It can be seen that a lower uncompensated cell resistance (corresponding to the resistance between the probe (the reference electrode), and the electrode surface) was obtained when the working and counter electrodes are brought closer together in the arrangement of sensor number 22. Also, the first semicircle relating to the electrode impedance ($C_g$ and $R_b$) was still observable but greatly reduced in magnitude when the platinum electrodes were interdigitated. It is probable that a decrease in the size of $C_g$ is the dominant factor here.

The start of the second semicircle relating to the interfacial impedance was observed lying at approximately the same gradient as the response to sensor number 19. Therefore, in clean air the values for $R_{ct}$ and $C_{dl}$ values for the two sensors numbers 19 and 22 are of the same order of magnitude. Figure 5.16 is the Bode plot corresponding to the data indicated in the Nyquist plot in figure 5.15.

A variation in the shape of the second semicircle is again observed on the Nyquist Plots obtained with sensor number 22 on the addition of CO to the analyte gas. Figure 5.17 indicates the responses of the sensor to 760 ppm CO, just as the CO was added and every plot recorded at ten minute intervals for one hour. The plots tended towards the x-axis, following the trend obtained for sensors 17, 19, 20 and 21 in the presence of CO.

In addition to this response, the trend of a greater decrease in the interfacial impedance as the CO concentration is increased was detected with sensor number 22. Figures 5.18 and 5.19 are the Nyquist and Bode plots for this sensor design in a clean air environment and in the presence of 500 ppm, 760 ppm, 1000 ppm, 1460 ppm, 2500 ppm and 5000 ppm CO. The response of this sensor indicated a particularly clear trend with respect to the analyte concentration and also produced reproducible AC impedance plots in a clean air environment prior to the introduction of the next CO concentration.
Figure 5.15 Nyquist Plots Indicating the Responses of Sensor Numbers 19 and 22 in Clean Air (60% RH and 22±2 °C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
Figure 5.16  Bode Plots Indicating the Responses of Sensor Numbers 19 and 22 in Clean Air (60% RH and 22±2 °C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
Figure 5.17 Nyquist Plots Indicating the Response of Sensor Number 22 in Clean Air and on the Addition of 760 ppm CO with Time (60% RH and 22±2 °C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
Figure 5.18 Nyquist Plots Indicating the Response of Sensor Number 22 in Clean Air and in the Presence of Various CO Concentrations (60% RH and 22±2 °C).

All Plots were Measured Between 60 kHz and 0.1 Hz.

-10000
-7500
-5000
-2500
0
2500
5000
7500
10000

Z'

Z''

Clean Air Environment
On the Addition of 500 ppm CO
On the Addition of 780 ppm CO
On the Addition of 1000 ppm CO
On the Addition of 1460 ppm CO
On the Addition of 2500 ppm CO
On the Addition of 5000 ppm CO

0.1 Hz
60 kHz
Figure 5.19  Bode Plots Indicating the Response of Sensor Number 22 in Clean Air and in the Presence of Various CO Concentrations, (60% RH and 22±2 °C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
(b) Response Obtained by Cyclic Voltammetry.

The sensor with the interdigitated working and counter electrodes (sensor number 22) gave a different response in a clean air environment when compared with the sensor possessing a rectangular working electrode arrangement (sensor number 19). Figure 5.20 illustrates the difference observed in the CV scans for sensor numbers 19 and 22. This difference indicated that the sensor which had electrodes closer together in an interdigitated arrangement exhibited greater capacitive and oxidation currents at a specific applied potential value, hence maintaining a lower impedance in the electrochemical system. The AC impedance spectroscopy results described above substantiate this finding.

Figure 5.21 indicates the CV scans for sensor number 22 in a clean air environment and when concentration values of 500 ppm, 1000 ppm, 2500 ppm and 5000 ppm CO were present. It can be seen that the oxidation peaks were superimposed onto the background resistance of the system. This is in contrast to the variation in the gradient observed with the sensors which possessed a cast DAIS electrolyte and a rectangular working electrode arrangement.

(c) Open Cell Potential Variations.

The OCP value of the sensor with interdigitated working and counter electrodes also increased when the ‘conditioning’ process involving CV cycles was carried out. Prior to this process, the OCP was found at an average value of +208 mV, the value after the three CVs was at a more positive potential of +236 mV. This apparent increase is thought to be due to the evolution of oxygen as a result of the applied potential at the working electrode during the ‘conditioning’ process.

The addition of various CO concentrations shifted the OCP value to a more negative potential, whereby the greater the concentration, the more negative the shift. This trend has already been described for sensor numbers 19, 20 and 21 in section 5.2.2(c). Table 5.3 presents the OCP values observed for sensor number 22.
Figure 5.20 Cyclic Voltammograms at 50 mV s$^{-1}$ Comparing the Results Obtained with Sensor Numbers 19 and 22 in a Clean Air Environment, (60% RH and 22±2 °C). Applied Potential Values are Stated Versus the Gold Reference Electrode.
Figure 5.21 Cyclic Voltammograms at 50 mV s⁻¹ Comparing the Results Obtained with Sensor Number 22 in a Clean Air and in the Presence of Various CO Concentrations, (60% RH and 22±2 °C). Applied Potential Values are Stated Versus the Gold Reference Electrode.
Table 5.3 OCP Values for Sensor Number 22 in Various CO Concentrations

The Value was Recorded after CO had been in the Sensing Chamber for One Hour.

<table>
<thead>
<tr>
<th>CO concentration</th>
<th>OCP value</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 ppm</td>
<td>+223 mV</td>
</tr>
<tr>
<td>760 ppm</td>
<td>+190 mV</td>
</tr>
<tr>
<td>1000 ppm</td>
<td>+157 mV</td>
</tr>
<tr>
<td>1460 ppm</td>
<td>+131 mV</td>
</tr>
<tr>
<td>2500 ppm</td>
<td>+106 mV</td>
</tr>
<tr>
<td>5000 ppm</td>
<td>+82 mV</td>
</tr>
</tbody>
</table>

5.2.4 Effect of Electrode Design
- Interdigitated Working and Reference Electrodes.

Sensor number 27 was prepared with a cast film of DAIS with a thickness of 20 \( \mu \)m and working electrode area of 0.50 cm\(^2\). The mesh and stencil arrangement used to produce sensor number 22 was utilised for number 27, however the platinum interdigitated electrode was inter-spaced with the gold interdigitated reference electrode. The counter electrode design was a rectangular 5 x 10 mm platinum area, positioned at one end of the alumina substrate. Comparison of the response of this sensor will be made to the results obtained from sensor number 22.

(a) AC Impedance Spectroscopy Response

The AC impedance spectroscopy response of sensor number 27 closely resembles the response obtained by sensor number 22 in clean air conditions. Figure 5.22 compares these responses. The reduced size of the semicircle observed at the high frequency range is seen again. This is due to the interdigitated design of the working electrode, since when the working electrode is of the rectangular design, this semicircle appears enlarged due to a higher value of \( C_{p} \) (refer to figure 5.15).
Figure 5.22 Nyquist Plots Indicating the Responses of Sensor Numbers 22 and 27 in Clean Air (60% RH and 22±2°C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
In the presence of CO, the usual trend of a variation in the shape of the second semicircle observed over the lower frequency range was detected. A greater change in the response of sensor number 27 was obtained as the CO concentration was increased in the analyte gas. Figures 5.23 and 5.24 demonstrate the variation observed on the Nyquist and Bode plots respectively on the introduction of 250 ppm, 500 ppm and 1000 ppm CO to the sensing chamber.

(b) Response Obtained by Cyclic Voltammetry.

When CO was present, a broad current peak was observed in the potential window corresponding to the oxidation of CO. As the CO concentration was increased, the height of the current peak also increased. Figure 5.25 indicates this result in the presence of 250 ppm, 500 ppm and 1000 ppm CO to the sensing chamber.

(c) Open Cell Potential Variations.

Prior to the ‘conditioning’ process, the OCP was stable at a value of +73 mV, which increased to +250 mV after the three CVs were carried out. The presence of CO shifted this potential value in a negative direction, and once again, the magnitude of this shift was dependant on the CO concentration in the test gas. Table 5.4 outlines the relative shifts in the OCP value with respect to gas concentration.

<table>
<thead>
<tr>
<th>CO concentration</th>
<th>OCP value</th>
</tr>
</thead>
<tbody>
<tr>
<td>250 ppm</td>
<td>+113 mV</td>
</tr>
<tr>
<td>500 ppm</td>
<td>+96 mV</td>
</tr>
<tr>
<td>1000 ppm</td>
<td>+86 mV</td>
</tr>
</tbody>
</table>
Figure 5.23 Nyquist Plots Indicating the Responses of Sensor Number 27 in Clean Air and in Various CO Concentrations (60% RH and 22±2°C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
Figure 5.24  Bode Plots Indicating the Responses of Sensor Number 27 in Clean Air and in Various CO Concentrations (60% RH and 22±2°C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
Figure 5.25 Cyclic Voltammograms at 50 mV s\(^{-1}\) Comparing the Results Obtained with Sensor Number 27 in Clean Air and in the Presence of Various CO Concentrations, (60\% RH and 22±2°C). Applied Potentials are Stated Versus the Gold Reference Electrode.
Effect of Electrode Material

- Pt/C Working and Counter Electrodes

Sensor number 28 was based on the same electrode configuration and electrolyte film thickness as sensor number 19, i.e. rectangular working electrode design with an area of 0.50 cm² and a 20 μm thick cast DAIS electrolyte. However, the working and counter electrodes were produced by screen printing the home-made platinum loaded carbon ink with a platinum catalyst loading of 0.053 mg Pt cm⁻². Refer to section 2.3.3(b) for the preparation details of the Pt/C ink. The reference electrode was gold, deposited from an organometallic ink (Heraeus).

(a) AC Impedance Spectroscopy Response

Over the frequency range of 60 kHz to 0.1 Hz, a semicircle was observed, however in order to obtain the start of the second semicircle (relating to the charge transfer and double layer characteristics) the frequency range was extended to the lower frequency value of 0.01 Hz. This was due to the values of $C_g$ and $R_h$ dominating the characteristics of the response over the original frequency range applied to the system.

Comparison of the responses obtained from sensor number 28 (over the extended frequency range) and sensor number 19 indicated that the same general characteristics were observed, but the overall impedance was approximately four times lower indicating an improved conductivity in the electrochemical system, and as a result the Pt/C ink had produced a highly conductive electrode material. A further point to mention is that the values of $R_s$ (probe-electrode surface resistance) are relatively similar, however, this is expected as both sensors possess the same electrode configuration.

Figure 5.26 compares the response of sensor number 28 over the frequency range 60 kHz to 0.01 Hz with the response obtained by sensor number 19 over the usual frequency range, 60 kHz to 0.1 Hz, on the Nyquist plot. Figure 5.27 shows the same data in a Bode plot representation.
Figure 5.26 Nyquist Plots Indicating the Responses of Sensor Numbers 19 and 28 in a Clean Air Environment (60% RH and 22±2°C).

The Plots for Sensor Number 19 were measured between 60 kHz and 0.1 Hz, and the Plots for Sensor Number 28 were measured between 60 kHz and 0.01 Hz.
Figure 5.27 Bode Plots Indicating the Responses of Sensor Numbers 19 and 28 in a Clean Air Environment (60% RH and 22±2°C).

The plots for Sensor Number 19 were measured between 60 kHz and 0.1 Hz, and the plots for Sensor Number 28 were measured between 60 kHz and 0.01 Hz.
On the addition of 1000 ppm CO, the usual trend whereby the second semicircle would reduce in size indicating a smaller impedance was not observed. The experiment was repeated with a much greater concentration of CO. However, on the addition of 5% (50 000 ppm) CO a change in the appearance of the response on the Nyquist plot was still not observed. Figure 5.28 presents the Nyquist plots for sensor number 28 in clean air and in the two CO environments.

When platinum electrodes were produced from the printing of an organometallic ink, a metal loading of approximately 0.4 mg cm^{-2} was deposited. Sensor number 28 possessed only 12.5% of this Pt coverage, and the results in the presence of CO described above, indicate that an inadequate amount of catalyst was present to allow the adsorption of CO on the surface of the electrode to any great extent.

(b) Response Obtained by Cyclic Voltammetry.

Figure 5.29 compares the CV cycles obtained by sensor numbers 19 and 28 in a clean air environment. The response from sensor number 28 does not indicate the usual increase in current at applied potential values above 0.70 V with respect to the gold reference electrode. The response is linear, but appears at a greater gradient, indicating a lower resistance (when Ohm's Law is applied), a finding which is supported by the AC impedance spectroscopy results.

(c) Open Cell Potential Variations.

Prior to the three CV scans the OCP value was +28 mV, which increased to +260 mV after the 'conditioning' process, therefore the oxygen evolution reaction had occurred at the working electrode during the applied potential scans. A noticeable change in the OCP was not observed on the addition of CO, indicating little or no adsorption of CO onto the surface of the platinum loaded carbon electrode.
Figure 5.28 Nyquist Plots Indicating the Responses of Sensor Number 28 in a Clean Air Environment and in the Presence of Various CO Concentrations (60% RH and 22±2°C).

The Clean Air Plot was Measured Between 60 kHz and 0.01 Hz, and all other Plots were Measured Between 0.1 Hz and 0.01 Hz.
Figure 5.29 Cyclic Voltammograms at 50 mV s\(^{-1}\) Comparing the Results Obtained with Sensor Numbers 19 and 28 in a Clean Air Environment. (60\% RH and 22\pm2\degree C). Applied Potentials are Stated Versus the Gold Reference Electrode.
5.3 Results Obtained with the Planar Sensor

with a Cast Nafion® Electrolyte.

Sensor numbers 1 to 16 and 18 were prepared with electrodes deposited from organometallic inks and had electrolyte films produced by casting a volume of Nafion® solution. After drying at room temperature, no further pre-treatment was carried out prior to placing the sensor in the sensing chamber. Experiments were carried out at 60% RH and 22±2°C.

5.3.1 Effect of Working Electrode Area.

Sensor numbers 15, 12 and 13 were prepared with cast Nafion® films of thickness 20 μm and with 0.25 cm², 0.37 cm² and 0.50 cm² respectively. The results obtained from these sensors will be compared.

(a) AC Impedance Spectroscopy Response.

Figure 5.30 compares the response of sensor numbers 15, 12 and 13 in a clean air environment on a Nyquist plot representation. The results clearly indicated that this sensor design gave rise to a high impedance in the region of 10⁷-10⁸ Ω, and as the area of the working electrode is increased, the impedance of the electrochemical system decreased. Only one enlarged semicircle was observed within the frequency range 60 kHz to 0.1 Hz relating to an equivalent circuit with a capacitance ($C_\text{eq}$) in parallel with a resistance ($R_\text{eq}$).

On the addition of CO to the sensing chamber, only relatively small variations on the appearance of the semicircle were observed for the three sensors. Figure 5.31 indicates the Nyquist plots obtained by sensor number 15 on the addition of 30% CO. The semicircle appeared slightly enlarged, hence falling across the x-axis at a higher $Z'$ value. A corresponding change in the Bode plot was not obtained and figure 5.32 shows the Bode plot obtained for the same experimental results.
Figure 5.30 Nyquist Plots Indicating the Responses of Sensor Numbers 15, 12 and 13 in a Clean Air Environment (60% RH and 22±2°C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
Figure 5.31 Nyquist Plots Indicating the Responses of Sensor Number 15 in a Clean Air Environment and in the Presence of 30% CO (60% RH and 22±2°C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
Figure 5.32 Bode Plots Indicating the Responses of Sensor Number 15 in a Clean Air Environment and in the Presence of 30% CO (60% RH and 22±2°C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
Again, the observed semicircle for sensor number 13 became slightly enlarged on the addition of 30% CO. Figure 5.33 indicates the Nyquist plots obtained in these experimental conditions. A variation on the Bode plot was not observed.

(b) Response Obtained by Cyclic Voltammetry.

When the CV scan response for sensors 15 and 12 are compared (0.25 cm$^2$ and 0.37 cm$^2$ respectively, with an electrolyte film thickness of 20 μm), there appears a difference in the gradient on the current-applied potential plot in clean air. Figure 5.34 indicates the response of these sensors. It can be seen that extremely small currents in the nA range were obtained due to the high impedance of the electrochemical system. If Ohm’s Law is applied to this response, it can be seen that as the electrode area is increased the gradient of the plot decreases, indicating a decrease in the resistance of the system, a result which was supported by the AC impedance spectroscopy response for these sensor designs.

When 30% CO was introduced to the analyte gas, the appearance of the scan was not affected indicating no response to CO. Figure 5.35 shows the plots obtained by sensor number 15 in both clean air and in an environment of 30% CO, thirty minutes after CO was introduced. Results were also obtained from sensor numbers 3 and 6, (0.25 cm$^2$ and 0.37 cm$^2$ respectively, with a 10 μm Nafion$^\circledR$ film), which provided further evidence for the conclusion that as the electrode area increased the resistance of the system decreased. Figure 5.36 compares the results of these sensors in clean air conditions.

5.3.2 Effect of the Electrolyte Film Thickness.

(a) AC Impedance Spectroscopy Response.

Sensor numbers 10, 11 and 12 were produced with a platinum working electrode of 0.37 cm$^2$, but had cast Nafion$^\circledR$ film thicknesses of 70 μm, 50 μm and 20 μm respectively.
Figure 5.33 Nyquist Plots Indicating the Responses of Sensor Number 13 in a Clean Air Environment and in the Presence of 30% CO (60% RH and 22±2°C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
Figure 5.34 Cyclic Voltammograms at 50 mV s\(^{-1}\) Comparing the Results Obtained with Sensor Numbers 15 and 12 in a Clean Air Environment, (60% RH and 22±2°C). Applied Potentials are Stated Versus the Gold Reference Electrode.
Figure 5.35 Cyclic Voltammograms at 50 mV s$^{-1}$ Comparing the Results Obtained with Sensor Number 15 in a Clean Air Environment and in the Presence of 30% CO (60% RH and 22±2°C). Applied Potentials are Stated Versus the Gold Reference Electrode.
Figure 5.36  Cyclic Voltammograms at 50 mV s\(^{-1}\) Comparing the Results Obtained with Sensor Numbers 3 and 6 in a Clean Air Environment.

(60\% RH and 22±2\(^{\circ}\)C). Applied Potentials are Stated Versus the Gold Reference Electrode.
If the plots obtained by AC impedance spectroscopy from sensor numbers 10, 11 and 12 in clean air are compared a trend is visible (figure 5.37). As the thickness of the electrolyte layer is increased the semicircle became enlarged, indicating an increased impedance value ($Z'$). As already mentioned in section 5.3.1(a), this semicircle corresponds to the electrolyte impedance of the system. $C_g$ will not vary to any great extent as the electrode arrangement is consistent for all three sensor designs, however, it is highly plausible that the bulk resistance will vary.

The same trend was observed in the semicircle obtained over a high frequency range for sensor numbers 19, 20 and 21 which were prepared with cast DAIS electrolytes. Refer to figure 5.9 to examine these results.

(b) Response Obtained by Cyclic Voltammetry.

When the CV responses of the sensors with film thicknesses of 70 μm, 50 μm and 20 μm are compared, it can be seen that the resistance of the system increased as the electrolyte film thickness increased, this was observed as a decrease in gradient on the current-applied potential plot (figure 5.38).

A further three film thicknesses can be compared if the responses of 7, 5 and 15 are studied. These sensors were prepared with working electrode areas of 0.25 cm$^2$, but with electrolyte film thicknesses of 5 μm, 10 μm and 20 μm respectively. Figure 5.39 compares the clean air responses of these sensors, and it can be seen that as the Nafion$^®$ film thickness is increased, the gradient of the plot decreases again, thus corresponding to a greater resistance, which the AC impedance results showed to be the due to the bulk resistance ($R_b$) of the electrolyte.
Figure 5.37 Nyquist Plots Indicating the Responses of Sensor Numbers 10, 11 and 12 in a Clean Air Environment (60% RH and 22±2°C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
Figure 5.38  Cyclic Voltammograms at 50 mV s\(^{-1}\) Comparing the Results Obtained with Sensor Numbers 10, 11 and 12 in a Clean Air Environment, (60% RH and 22±2°C). Applied Potentials are Stated Versus the Gold Reference Electrode.
Figure 5.39 Cyclic Voltammograms at 50 mV s\(^{-1}\) Comparing the Results Obtained with Sensor Numbers 7, 5 and 15 in a Clean Air Environment, (60% RH and 22\(\pm\)2°C). Applied Potentials are Stated Versus the Gold Reference Electrode.
5.4 Results Obtained with the Planar Sensor with a
Cast Thermally Activated Nafion® Electrolyte.

Sensor numbers 23, 24, 25 and 26 were produced by screen printing platinum
working electrodes with an active surface area of 0.50 cm². In order to be
consistent with the other planar sensor designs, the platinum counter electrode and
gold reference electrode possessed the usual active area of 0.25 cm². All four
sensor designs were prepared with an electrolyte layer of Nafion® of thickness 20
µm. Both working electrode area and film thickness parameters were chosen
because these values were suggested as being the favourable choice from the results
produced by sensor numbers 1 to 22.

After the cast Nafion® films had dried they went through a further pre-treatment
stage, referred to as thermal activation. The experimental method for this process
is described in section 2.2.3(b). This process is thought to allow re-structuring of
the side-chains of the polymer, permitting cluster formation to occur, hence
increasing the conductivity and improving the mechanical strength of the Nafion®
film.

On electrochemical testing it was discovered that sensor number 23 produced
anomalous results, which was due to a problem in the production process. The
results for this sensor will not be discussed here. Therefore, the production method
was modified by soaking the sensor in 5 mol dm⁻³ nitric acid for 24 hours after the
thermal activation step, prior to placing in the sensing chamber. This soaking
allowed adequate re-hydration of the polymer film after the heating process at
140 °C had de-hydrated the film.¹⁶⁰

Sensor numbers 24 and 25 were produced 35 days apart with the same design
configuration under the same experimental conditions, so that the reliability of this
production method could be studied. Sensor number 26 was produced with
interdigitated platinum working and counter electrodes. Again, having a working electrode area of 0.50 cm$^2$ and a thermally activated Nafion$^\circledR$ electrolyte of 20 μm.

5.4.1 The Observed Effects Due to the Thermal Activation Production Method.

(a) AC Impedance Spectroscopy Response.

It was discovered that for this sensor design, a probe frequency greater than 60 kHz induced noise from the potentiostat which effected the results. This affect is a common occurrence with the AC impedance spectroscopy technique when high frequencies are utilised. Therefore, the initial scan range was modified to cover the range 10 kHz to 0.1 Hz. When the AC impedance response of sensor number 24 was studied, it was found that the impedance was approximately one hundred times less compared with sensor number 13, which also possessed a working electrode of 0.5 cm$^2$ and a Nafion$^\circledR$ (not thermally activated) film of 20 μm. This indicated that the thermal activation process had been a beneficial step in the sensor production.

However, if the AC impedance response is compared to a sensor which has a working electrode area of 0.50 cm$^2$ and a DAIS film thickness of 20 μm (sensor number 19) then it can be seen that the impedance of the Nafion$^\circledR$ based sensor is still relatively high. Figure 5.40 compares the response obtained by sensor numbers 19 and 24 in clean air.

It appeared that the response obtained from sensor number 24 within the 10 kHz to 0.1 Hz range was the start of the first semicircle observed for sensor number 19, i.e. the electrolyte impedance ($C_\infty$ and $R_\infty$). Therefore, the frequency range was extended to a much lower frequency value of 0.003 Hz, (figure 5.41). A scan of 10 kHz to 0.003 Hz took the exceptionally long time of fifty minutes, however, the remainder of the first semicircle and the start of the second semicircle (corresponding to the interfacial impedance) became apparent.
Figure 5.40  Nyquist Plots Indicating the Responses of Sensor Numbers 19 and 24 in a Clean Air Environment (60% RH and 22±2°C).

The Plots were Measured Between 60 kHz and 0.1 Hz and 10 kHz and 0.1 Hz Respectively.
Figure 5.41 Nyquist Plot Indicating the Response of Sensor Number 24 in a Clean Air Environment (60% RH and 22±2°C).

The Plot was Measured Between 10 kHz and 0.003 Hz.
A scan time of 50 minutes was unacceptable as a testing technique when the analyte gas was present, therefore, a method of measuring over a short frequency range when CO was present was developed. Figure 5.42 indicates the effect that 1000 ppm CO had on the sensor over a 0.006 Hz to 0.0035 Hz frequency range. Each scan took 20 minutes, therefore over a testing period of 60 minutes three sets of data were recorded. Figure 5.43 presents these results in a Bode plot representation. A trend was observed. The interfacial impedance semicircle was reduced in size when CO was present. The variation increased as a greater period of time had elapsed.

(b) **Response Obtained by Cyclic Voltammetry.**

Figure 5.44 compares the CVs obtained by sensor numbers 24 and 19 in clean air conditions. It can be seen that sensor number 24 could only attain 10% of the current value at a certain value of applied potential compared with sensor number 19. This indicates a greater resistance in the system of number 24, a finding which was supported by the AC impedance results described above. On the addition of CO a change was not observed in the response of sensor number 24.

(c) **Open Cell Potential Variations.**

Prior to a 'conditioning' process the OCP value was stable at +123 mV, the three CVs gave rise to an increase to the OCP value to +319 mV. On the addition of 1000 ppm CO, the OCP value stabilised at +98 mV (value taken after CO present in the sensing chamber for 60 minutes).

5.4.2 **Reliability of the Production Method.**

(a) **AC Impedance Spectroscopy Response.**

Figure 5.45 presents the AC impedance response of sensor numbers 24 and 25 in clean air over the frequency range 10 kHz to 0.1 Hz. The results obtained were extremely similar in appearance.
Figure 5.42 Nyquist Plots Indicating the Responses of Sensor Number 24 in a Clean Air Environment and in the Presence of 1000 ppm CO (60% RH and 22±2°C).

The Clean Air Response was Measured Between 10 kHz and 0.0035 Hz, all other Measurements were Taken Between 0.006 Hz and 0.0035 Hz.
Figure 5.43  Bode Plots Indicating the Responses of Sensor Number 24
in a Clean Air Environment and in the Presence of 1000 ppm CO
(60% RH and 22±2°C).
The Clean Air Response was Measured Between 10 kHz and 0.0035 Hz, all other
Measurements were Taken Between 0.006 Hz and 0.0035 Hz.
Figure 5.44  Cyclic Voltammograms at 50 mV s$^{-1}$ Comparing the Results Obtained with Sensor Numbers 19 and 24 in a Clean Air Environment, (60% RH and 22±2°C). Applied Potentials are Stated Versus the Gold Reference Electrode.
Figure 5.45 Nyquist Plots Indicating the Responses of Sensor Numbers 24 and 25 in a Clean Air Environment (60% RH and 22±2°C).

Both Plots were Measured Between 10 kHz and 0.1 Hz.
Sensor number 25 also indicated a response to 1000 ppm CO in the frequency range 0.006 Hz to 0.0035 Hz (figure 5.46). Therefore, it could be said that these results indicated good reliability in the production method used.

(b) **Response Obtained by Cyclic Voltammetry.**

Figure 5.47 indicates the CV scan results in clean air for sensor numbers 24 and 25, again a very similar response was obtained.

(c) **Open Cell Potential Variation.**

Prior to the conditioning process, sensor number 25 exhibited a stable OCP value of +129 mV (6 mV greater than for number 24). After the three CVs, the OCP shifted in a positive direction to +343 mV (14 mV higher), which decreased to +97 mV on the addition of 1000 ppm CO.

5.4.3 **Effect of Electrode Design**

- Interdigitated Working and Counter Electrodes.

(a) **AC Impedance Spectroscopy Response.**

The response between 10 kHz and 0.1 Hz obtained for sensor number 26 was compared with the responses gained from sensor numbers 24 and 25. A difference in the gradient of the first semicircle was observed (figure 5.48). Further experiments were carried out on sensor number 26 where the frequency range was extended to 0.0035 Hz. A very different response with respect to sensor numbers 24 and 25 was observed (figure 5.49). The typical appearance of the first semicircle was diminished so that the semicircle which corresponds to the interfacial impedance dominated the scan.
Figure 5.46 Nyquist Plots Indicating the Responses of Sensor Number 25 in a Clean Air Environment and in the Presence of 1000 ppm CO (60% RH and 22±2°C).

The Clean Air Response was Measured Between 10 kHz and 0.0035 Hz, all other Measurements were Taken Between 0.006 Hz and 0.0035 Hz.
Figure 5.47  Cyclic Voltammograms at 50 mV s\(^{-1}\) Comparing the Results Obtained with Sensor Numbers 24 and 25 in a Clean Air Environment, (60\% RH and 22±2°C). Applied Potentials are Stated Versus the Gold Reference Electrode.
Figure 5.48  Nyquist Plots Indicating the Responses of Sensor Numbers 24, 25 and 26 in a Clean Air Environment (60% RH and 22±2°C).

All Plots were Measured Between 10 kHz and 0.1 Hz.
Figure 5.49 Nyquist Plots Indicating the Responses of Sensor Numbers 25 and 26 in a Clean Air Environment (60% RH and 22±2°C).

All Plots were Measured Between 10 kHz and 0.0035 Hz.
When these results are compared to those obtained with sensor number 22, which also possessed an interdigitated working and counter electrode arrangement and had a 20 μm electrolyte film (DAIS), then it is possible to draw the conclusion that sensors with this electrode arrangement can typically produce such a response, whereby the electrolyte resistance is almost negligible with an enhanced interfacial impedance response on the Nyquist plot representation.

Figure 5.50 and 5.51 indicate the Bode and Nyquist plot results for sensor numbers 26 and 22 respectively in a clean air environment.

On the addition of 1000 ppm CO to sensor number 26, a variation in the interfacial impedance response was observed (figure 5.52), the decrease in impedance increases with time. 500 ppm CO was also introduced to the test gas and a response was obtained. Figure 5.53 compares the responses of sensor number 26 on the addition of 500 ppm and 1000 ppm CO.

(b) Response Obtained by Cyclic Voltammetry.

Figure 5.54 compares the CVs in clean air for sensor numbers 24, 25 and 26 on the addition of 1000 ppm CO, a change in response on the current-applied potential plot was not observed.

(c) Open Cell Potential Variation.

Prior to the ‘conditioning’ stage, the OCP value was found to be +70 mV, which increased to +265 mV after the three CV cycles had been applied. The addition of 500 ppm and 1000 ppm CO reduced this value to +9 mV and +4 mV respectively.
Figure 5.50  Bode and Nyquist Plots Indicating the Response of Sensor Number 26 in a Clean Air Environment (60% RH and 22±2°C).

The Plot was Measured Between 10 kHz and 0.0035 Hz.
Figure 5.51 Bode and Nyquist Plots Indicating the response of Sensor Number 22 in a Clean Air Environment (60% RH and 22±2°C).

The Plot was Measured Between 60 kHz and 0.1 Hz.
Figure 5.52 Nyquist Plots Indicating the Response of Sensor Number 26 in a Clean Air Environment and in the Presence of 1000 ppm CO (60% RH and 22±2°C).

The Plot was Measured Between 10 kHz and 0.1 Hz.
Figure 5.53 Nyquist and Bode Plots Indicating the Response of Sensor Number 26 in a Clean Air Environment and in the Presence of 500 ppm and 1000 ppm CO (60% RH and 22±2°C).

The Plots were Measured Between 10 kHz and 0.1 Hz.
Figure 5.54 Cyclic Voltammograms at 50 mV s$^{-1}$ Comparing the Results Obtained with Sensor Numbers 24, 25 and 26 in a Clean Air Environment, (60% RH and 22±2°C). Applied Potentials are Stated Versus the Gold Reference Electrode.
Sensor number 29 was prepared by the pressing of platinum impregnated carbon electrode material (ETEK) onto a commercially available Nafion® 115 electrolyte membrane. For the preparation details refer to section 2.3.4. All three electrodes were produced from the Pt/C cloth and the working electrode area was 0.5 cm².

(a) AC Impedance Spectroscopy Response.

Lower values of $Z'$ and $Z''$ were attained on the AC impedance plots for this design of sensor compared with the responses obtained by sensor numbers 1-28, indicating a system with a reduced impedance. Figure 5.55 indicates the response obtained by sensor number 29 in clean air and in the presence of 1000 ppm CO. It was noted that $R_s$ (the probe-electrode surface resistance) was the relatively low value of 340 Ω, indicating that the conductivity of the commercial membrane is superior to the cast electrolyte from a solution of the polymer.

The response to CO was apparent in the second semicircle corresponding to a decrease in the interfacial impedance ($C_{dl}$ and $R_{ct}$). Very little change was observed in the appearance of the semicircle found at the high frequency range (the electrolyte impedance) on the addition of CO to the test gas. Lower concentrations of CO were introduced to the sensing chamber and a response to 100 ppm CO was observed. Figure 5.56 presents the data obtained when the sensor was in a clean air environment and when 100 ppm, 200 ppm, 500 ppm and 1000 ppm CO were present.

(b) Response Obtained by Cyclic Voltammetry.

A larger current was obtained at a certain applied potential value in comparison with sensor numbers 1 to 28. When CO was present an extremely broad peak was observed over the potential window +0.25 to +0.80 V with respect to the Pt/C
Figure 5.55 Nyquist Plots Indicating the Response of Sensor Number 29 in a Clean Air Environment and in the Presence of 1000 ppm CO,
(60% RH and 22±2°C).
All Plots were Measured Between 60 kHz and 0.1 Hz.
Figure 5.56 Nyquist Plots Indicating the Response of Sensor Number 29 in a Clean Air Environment and in the Presence of 100 ppm, 200 ppm, 500 ppm and 1000 ppm CO (60% RH and 22±2°C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
reference electrode and the relative magnitude of the current obtained was dependant on the concentration of CO (figure 5.57).

(c) Open Cell Potential Variation.

As the working and reference electrodes were produced from the same material an OCP value close to 0.000 V would be expected. Therefore, the value of +9 mV was satisfactory. Oxygen evolution occurred at the working electrode due to the three conditioning CVs, as an OCP of +124 mV resulted. The addition of CO did shift this value in a negative direction (table 5.5), however the usual trend of the greater the CO concentration producing a greater potential shift was not observed.

Table 5.5 OCP Values for Sensor Number 29 in Various CO Concentrations. The Value was Recorded after CO had been in the Sensing Chamber for One Hour.

<table>
<thead>
<tr>
<th>CO concentration</th>
<th>OCP value</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 ppm</td>
<td>+22 mV</td>
</tr>
<tr>
<td>200 ppm</td>
<td>-31 mV</td>
</tr>
<tr>
<td>500 ppm</td>
<td>-17 mV</td>
</tr>
<tr>
<td>1000 ppm</td>
<td>+4 mV</td>
</tr>
</tbody>
</table>

5.6 The Sensor with Catalyst Loaded Cloth Pressed onto DAIS Electrolyte.

Sensor number 30 was produced using an identical method as sensor number 29, however, a commercially available DAIS 585 membrane was utilised as the electrolyte. The Pt/C cloth working electrode area was kept as 0.50 cm².
Figure 5.57 Cyclic Voltammograms at 50 mV s⁻¹ Comparing the Results Obtained with Sensor Number 29 in a Clean Air Environment and in the Presence of 200 ppm, 500 ppm and 1000 ppm, (60% RH and 22±2°C).

Applied Potentials are Stated Versus the Pt/C Reference Electrode.

![Cyclic Voltammograms](image)

- Clean Air Environment
- 200 ppm CO Present
- 500 ppm CO Present
- 1000 ppm CO Present
(a) **AC Impedance Spectroscopy Response.**

Over the frequency range 60 kHz to 0.1 Hz a relatively small response was observed. It was discovered that 100 ppm CO could affect the response, again indicating a decrease in the impedance. Figure 5.58 shows the Nyquist and Bode plot responses obtained by sensor number 30 in a clean air environment and when 100 ppm, 250 ppm, 500 ppm and 1000 ppm CO were present.

The $R_a$ value of 1750 $\Omega$ is five times greater than that found for sensor number 29 with a commercially available Nafion® 115 membrane. However the value of 1750 $\Omega$ is comparable to the $R_a$ value obtained with the planar sensor which possessed a cast DAIS film $\geq 15$ $\mu$m in thickness (sensor numbers 17, 19, 21 and 22). This suggests that the cast DAIS 585 membrane from solution has a proton conductivity comparable to that of the commercially available DAIS membrane. It is also interesting to note that the results obtained by sensor numbers 24, 25, 26 and 29 indicated that the conductivity of the cast Nafion® film (even when thermally activated) is much greater than the value obtained by the commercial Nafion® 115 membrane.

(b) **Response Obtained by Cyclic Voltammetry.**

The CV response in clean air of sensor number 30 indicated a higher resistance than that of sensor number 29 (figure 5.59). The AC impedance results agree with this finding. A change in the characteristics of the current-applied potential plot was not observed on the addition of CO.

(c) **Open Cell Potential Variation.**

An OCP of $+2$ mV prior to the ‘conditioning’ process was anticipated as the working and reference electrodes were produced from the same type of Pt/C material. The forward scan of the CVs clearly indicated a current relating to the evolution of oxygen and the OCP value was seen to increase to $+132$ mV.
Figure 5.58 Nyquist and Bode Plots Indicating the Response of Sensor Number 29 in a Clean Air Environment and in the Presence of 100 ppm, 250 ppm, 500 ppm and 1000 ppm CO, (60% RH and 22±2°C).

The Plot was Measured Between 60 kHz and 0.1 Hz.
Figure 5.59  Cyclic Voltammograms at $50 \text{ mV s}^{-1}$ Comparing the Results Obtained with Sensor Numbers 29 and 30 in a Clean Air Environment, (60% RH and $22\pm2^\circ\text{C}$). Applied Potentials are Stated Versus the Pt/C Reference Electrode.
The usual shift in value to a negative potential value was observed again on the addition of CO (table 5.6), but a trend with respect to the CO concentration was not obtained.

Table 5.6 OCP Values for Sensor Number 30 in Various CO Concentrations. The Value was Recorded after CO had been in the Sensing Chamber for One Hour.

<table>
<thead>
<tr>
<th>CO concentration</th>
<th>OCP value</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 ppm</td>
<td>-5 mV</td>
</tr>
<tr>
<td>500 ppm</td>
<td>-1 mV</td>
</tr>
<tr>
<td>1000 ppm</td>
<td>-25 mV</td>
</tr>
</tbody>
</table>

5.7 Summary.

This chapter has presented the AC impedance spectroscopy and DC (CVs and OCP) responses of sensor numbers 1 to 30 in environments of clean air, and when concentrations of CO were present. Trends have been observed, such as the presence of two semicircles on the Nyquist plot representations, and an overall decrease in impedance on the Bode plot representations when CO was present, as well as the appearance of a broad CO oxidation peak on the CV scans for some of the sensor designs. The responses of the different sensor designs have been compared and suggestions for the optimum dimensions for the working electrode area and electrolyte film thickness have been discussed.

Other parameters, such as the relative humidity of the test gas and the effect of other analytes, in particular hydrogen and methane, have been studied with one of the sensor designs. Also, long term tests have been carried out in order to study the ageing effects. The results from these tests will be presented in chapter 6.

Conclusions from all of the sensor testing and a full interpretation of the findings will be discussed in chapter 7.
CHAPTER 6

RESULTS FROM SENSOR TESTING IN SIMULATED DOMESTIC ENVIROMENTS

- The Effects Of Time, Humidity And Other Likely Gases.

6.1 Effect of Test Gas Relative Humidity Level on the Sensor Response.

The relative humidity (RH) levels found in domestic premises can vary over a range of values depending on the position in the dwelling. Therefore, further experiments were carried out on sensor number 22 where the RH of the test gas was varied. Sensor number 22 was prepared by the screen printing of platinum working and counter electrodes in an interdigitated arrangement and a gold rectangular reference electrode on an alumina substrate. The proton conducting electrolyte utilised was a 20μm membrane of DAIS, cast from a solution of DAIS 585 polymer, providing a working electrode with an area of 0.50 cm² in contact with the electrolyte.

This sensor was well characterised by AC impedance spectroscopy and DC electrochemical techniques in clean air conditions and in environments containing various concentrations of CO (section 5.2.3). All of these tests were carried out when the humidity content of the test gas was regulated at a RH value of 60%. For these experiments the RH was adjusted by changing the flow rates of the input gas through the two rotameters of the humidifying section of the test rig (refer to figure 4.2). To ensure a test gas with a consistent RH level, 24 hours were allowed to elapse before electrochemical testing was carried out. The following section describes the results obtained when the RH was reduced to 52% and 35% in a clean air environment and when 1000 ppm CO was introduced to the test gas. As before, all experiments were carried out at 22±2 °C.

6.1.1 Effect of RH Level on the Sensor's Response in Clean Air.

(a) AC Impedance Spectroscopy Response.

AC impedance plots were carried out with a 10 mV AC amplitude over the frequency range 60 kHz to 0.1 Hz. Figure 6.1 compares the responses of sensor
Figure 6.1 Nyquist Plots Indicating the Responses of Sensor Number 22 in a Clean Air Environment in RH Conditions of 60%, 52%, and 35%, (22±2 °C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
number 22 in the three RH conditions in clean air. The ‘conditioning’ procedure of three CVs prior to the addition of the analyte was maintained. The general variation in the responses of the sensor in the different RH conditions implied that as the humidity decreased, the impedance of the system increased. This is probably due to the removal of water in the cluster arrangements in the electrolyte film, therefore causing a decrease in the proton conducting characteristics.

Points to mention are;
(1) The impedance between the probe and the electrode surface \((R_u)\) increased as the relative humidity was decreased. This value is measured off the x-axis on the Nyquist plot for the data point which corresponded to 60 kHz. Table 6.1 presents the values of \(R_u\) with respect to the RH value. This variation is shown graphically in figure 6.2 below.

<table>
<thead>
<tr>
<th>RH %</th>
<th>(R_u) value</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>52.3 Ω</td>
</tr>
<tr>
<td>52</td>
<td>77.7 Ω</td>
</tr>
<tr>
<td>35</td>
<td>218.6 Ω</td>
</tr>
</tbody>
</table>

Figure 6.2 Graph Illustrating the Variation in \(R_u\) Versus the RH of the Test Gas.
When the RH value was decreased the semicircle which corresponds to the electrolyte impedance \((R_h \text{ and } C'_q)\) at the high frequency range became enlarged in size, hence causing a translation of the response across the x-axis to a higher real impedance \((Z')\) value.

The gradient at the start of the second semicircle (over a lower frequency range), which corresponds to the interfacial impedance \((R_{ct} \text{ and } C_{dl})\) was approximately the same.

(b) **Response Obtained by Cyclic Voltammetry.**

Figure 6.3 indicates the responses of the sensor in the three relative humidity environments, by the CV testing technique in a clean air atmosphere. The potential was cycled between 0.00 V and 1.00 V versus the gold reference electrode, at a scan rate of 50 mV s\(^{-1}\). A trend is apparent in the current value obtained at a certain value of potential with respect to the RH; as the RH level was reduced, the current obtained decreased. If Ohm’s Law is applied to this response, then a smaller current indicates a system with a larger value of resistance, a result which is consolidated by the AC impedance spectroscopy responses.

Another point worth mentioning here, is the appearance of the first CV cycle recorded for this design of sensor. The CVs shown in figure 6.3 which correspond to the 60% RH conditions, indicate the first three CVs recorded for sensor number 22. The evolution of oxygen from the electrochemical oxidation of water at the working electrode was observed at an applied potential \(\geq 500\) mV on the first cycle. Subsequent cycles only indicated the evolution of oxygen at potentials \(\geq 800\) mV with respect to the gold reference electrode.

(c) **Open Cell Potential Variations.**

Table 6.2 presents the OCP values observed from sensor number 22 measured in all three RH environments before and after the three CVs in the ‘conditioning’ step.
Figure 6.3  Cyclic Voltammograms at 50 mV s\(^{-1}\) Comparing the Results Obtained with Sensor Number 22 in Clean Air in Various RH Conditions. Applied Potentials are Stated Versus the Gold Reference Electrode.
Table 6.2 OCP Values Before and After the 'Conditioning' CVs for Sensor Number 22 in Clean Air in Various RH Conditions.

<table>
<thead>
<tr>
<th>RH %</th>
<th>OCP prior to 'conditioning'</th>
<th>OCP after 'conditioning'</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>+208 mV</td>
<td>+236 mV</td>
</tr>
<tr>
<td>52</td>
<td>+209 mV</td>
<td>+250 mV</td>
</tr>
<tr>
<td>35</td>
<td>+195 mV</td>
<td>+248 mV</td>
</tr>
</tbody>
</table>

The CV cycles have permitted the oxygen evolution reaction to occur and have therefore shifted the OCP to a more positive value. The values in each column are relatively similar and no obvious trend with respect to the RH value can be observed.

6.1.2 Effect of RH Level on the Sensor's Response to CO.

(a) AC Impedance Spectroscopy Response.

Figures 6.4 and 6.5 indicate the response observed on the Nyquist plots when 1000 ppm CO in air was introduced into the sensing chamber when the RH conditions were 52% and 35% respectively. A response to CO was observed in both cases. The change observed in the response was the variation in the characteristics of the second semicircle (lower frequency range) which suggested a decrease in the interfacial impedance value when CO was present. The response of the sensor in 60% RH conditions was outlined in section 5.2.4.

Figure 6.6 compares the responses of the sensor in clean air and on the addition of CO. The sensor responded with the same characteristics for each RH condition, i.e. a change in the response observed in the data corresponding to the interfacial impedance.
Figure 6.4 Nyquist Plots Indicating the Responses of Sensor Number 22 in a Clean Air Environment and in the Presence of 1000 ppm CO.

(52% RH and 22±2 °C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
Figure 6.5 Nyquist Plots Indicating the Responses of Sensor Number 22 in a Clean Air Environment and in the Presence of 1000 ppm CO.

(35% RH and 22±2 °C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
Figure 6.6 Nyquist Plots Indicating the Responses of Sensor Number 22 in a Clean Air Environment and in the Presence of 1000 ppm CO

(60%, 52% and 35% RH and 22±2°C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
(b) **Response Obtained by Cyclic Voltammetry.**

Figure 6.7 indicates the CVs in clean air and when 1000 ppm CO was present in a 52% RH environment. Refer to figure 5.21 for the response of this sensor to 1000 ppm CO in 60% RH conditions. As the current obtained in clean air at 52% RH is less than that found in the 60% RH environment, then it was expected that the peak current for CO oxidation would be lower than that found at the higher humidity level. Indeed this lower peak current response was found to be the case.

(c) **Open Cell Potential Variation.**

The addition of CO was found to affect the OCP in the much the same way as that observed before with these sensor designs. The OCP values were shifted to a more negative value due to the formation of a mixed cell potential. Table 6.3 presents the OCP values in each RH condition on the addition of 1000 ppm CO in air. No particular trend was observed in the variation of the OCP values.

<table>
<thead>
<tr>
<th>RH %</th>
<th>OCP value</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>+157 mV</td>
</tr>
<tr>
<td>52</td>
<td>+159 mV</td>
</tr>
<tr>
<td>35</td>
<td>+153 mV</td>
</tr>
</tbody>
</table>
Figure 6.7 Cyclic Voltammograms at 50 mV s\(^{-1}\) Comparing the Results Obtained with Sensor Number 22 in Clean Air and in the Presence of 1000 ppm CO (52% RH and 22±2 °C). Applied Potentials are Stated Versus the Gold Reference Electrode.
6.2 Effect on the Sensor’s Responses to Alternative Analyte Gases.

Section 1.2 outlined the British Standard Institution (BSI) requirements for electrically operated CO detectors. The cross-sensitivity of such sensors to other gases which may be present on domestic premises is an important factor. It states that the response to hydrogen should be less than that for CO with the further requirement that the sensor should not respond to 500 ppm methane.

Therefore further experiments were carried out on sensor number 22 in environments containing these analytes in the test gas and the results in each case are compared to the sensor’s response in an environment containing CO. All of the tests in this set of experiments were carried out with a RH of 60% and at 22±2 °C.

6.2.1 Effect of Methane.

Commercial methane detectors respond in the 5%-20% lower explosive limit (LEL) range. The LEL for CH₄ is 5.3% by volume in air, and to measure the affect of the 5% LEL level on the sensor, a concentration of 0.265% by volume \( \frac{5.3 \times 5}{100} \) or 2650 ppm CH₄ would have to be introduced to the sensing chamber. The maximum CH₄ concentration possible with the blend of CH₄ in air utilised, was 5000 ppm, i.e. the 9.5% LEL value.

(a) AC Impedance Spectroscopy Response.

Figure 6.8 indicates the Nyquist and Bode representations for the response of sensor number 22 to 2650 ppm CH₄. It can be seen that no change was observed on the plots on the addition of this concentration of CH₄. If this response is compared to that obtained by the same sensor to 2500 ppm CO (figure 6.9), it can be seen that the sensor responded very well to this CO concentration.

The concentration of CH₄ was almost doubled to 5000 ppm CH₄ (9.5% LEL), however, again, it was discovered that a change in the sensor’s response was not observed in this environment of methane.
Figure 6.8 Nyquist and Bode Plots Indicating the Responses of Sensor Number 22 in a Clean Air Environment and in the Presence of 2650 ppm CH₄.

(60% RH and 22±2 °C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
Figure 6.9 Nyquist and Bode Plots Indicating the Responses of Sensor Number 22 in a Clean Air Environment and in the Presence of 2500 ppm CO. (60% RH and 22±2 °C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
(b) Response Obtained by Cyclic Voltammetry.

Figure 6.10 indicates the CV responses of sensor number 22 in clean air conditions and when 5000 ppm CO and 5000 ppm CH₄ were present in the test gas. Again, the cycle in clean air shows the evolution of oxygen from the oxidation of H₂O at the surface of the working electrode. An oxidation peak corresponding to CO oxidation was observed when CO was present at this concentration, however, a peak corresponding to any CH₄ electrochemistry was not observed in this applied potential range. The reasons for these observations are outlined in chapter 7.

(c) Open Cell Potential Variation.

As mentioned previously, after the ‘conditioning’ step in clean air conditions, the OCP obtained for sensor number 22 was +236 mV. On the addition of 5000 ppm CH₄, the variation in OCP was almost negligible, as it stabilised at a value of +232 mV. The addition of 5000 ppm CO produced the more dramatic effect of shifting the OCP in a negative direction to +82 mV. Again, indicating little or no response by the sensor to methane.

6.2.2 Effect of Hydrogen.

Hydrogen is produced alongside CO during combustion processes, usually at half the CO concentration. It can also be produced during the cooking of food. Therefore, if a CO sensor can detect H₂, it must produce a smaller response than with the same concentration of CO. The sensor was tested in the presence of H₂ in the concentration range 150 ppm to 1000 ppm and the response compared to the results obtained when CO was present.

(a) AC Impedance Spectroscopy Response.

Figure 6.11 indicates the Nyquist and Bode plot representations for the response of sensor number 22 in an environment containing 1000 ppm H₂ in air.
Figure 6.10 Cyclic Voltammograms at 50 mV s\(^{-1}\) Comparing the Results Obtained with Sensor Number 22 in Clean Air and in the Presence of 5000 ppm CO and 5000 ppm CH\(_4\) (60% RH and 22±2 °C). Applied Potentials are Stated Versus the Gold Reference Electrode.
Figure 6.11 Nyquist and Bode Plots Indicating the Responses of Sensor Number 22 in a Clean Air Environment and in the Presence of 1000 ppm H₂.

(60% RH and 22±2 °C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
The response was measured over one hour after the introduction of the gas to the sensing chamber. A response was obtained.

Figure 6.12 shows the same AC plot arrangements for the sensor in the presence of 1000 ppm CO in air. If the relative variations in the characteristics of the second semicircle on the Nyquist plots (low frequency range) are compared, then it is possible to say that response to H₂ is found to be less rapid than the response to CO. In order to draw this conclusion the first plots recorded as the analyte was introduced (the ‘t=0’ plots) were compared.

The sensor was also tested in the presence of 500 ppm H₂. A response was obtained, and if the response is compared to the corresponding concentration of CO then it is possible to conclude that the response to H₂ is less than the response to CO, agreeing with the results obtained with 1000 ppm of the gases. A response to the lower concentration of 150 ppm H₂ was not observed.

(b) Response Obtained by Cyclic Voltammetry.

The cyclic voltammograms carried out in the presence of H₂ did not indicate any differences compared with the CVs carried out in a clean air environment. Therefore, it is possible to confirm that the presence of CH₄ or H₂ is not detectable in the potential window of 0.00 V to 1.00 V versus the gold reference electrode utilised in this CV testing technique.

(c) Open Cell Potential Variation.

Hydrogen gas has a similar effect on the OCP as CO, i.e. a shift in value to a more negative value due to the formation of a mixed cell potential. Table 6.4 indicates the variation in OCP value from the clean air value of +236 mV when CO and H₂ were present. Thus indicating that a mixed cell potential was formed in the presence of these gases. The trend of the higher the analyte concentration the greater the shift in OCP value was observed for both gases.
Figure 6.12 Nyquist and Bode Plots Indicating the Responses of Sensor Number 22 in a Clean Air Environment and in the Presence of 1000 ppm CO (60% RH and 22±2 °C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
Table 6.4 OCP Values for Sensor Number 22 when 500 ppm and 1000 ppm H₂ and CO were Present in Air. Values were Recorded after the Analyte had been in the Sensing Chamber for One Hour.

<table>
<thead>
<tr>
<th>Analyte gas concentration</th>
<th>H₂</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>+236 mV</td>
<td>+236 mV</td>
</tr>
<tr>
<td>500 ppm</td>
<td>+214 mV</td>
<td>+223 mV</td>
</tr>
<tr>
<td>1000 ppm</td>
<td>+168 mV</td>
<td>+157 mV</td>
</tr>
</tbody>
</table>

6.3 Results from Experiments Studying the Ageing Effect.

If the sensors are to be viable detectors for long term use on domestic premises, the responses of the sensor in both clean air and in an atmosphere containing the analyte should be consistent. Therefore, during the testing strategy of this research programme, experiments were carried out over a period of time on sensors which covered each of the design types; sensors with a cast Nafion® electrolyte (thermally activated), sensors which possessed a cast DAIS electrolyte film and one example of the sensors produced by pressing platinum impregnated carbon cloth onto a commercial electrolyte membrane.

The results obtained from sensor numbers 1 to 16, which possessed a cast Nafion® film (without thermal activation) were not particularly encouraging, as they indicated a very high impedance and did not show a significant change on the addition of CO (refer to section 5.3). As a result, ageing effect experiments were not carried out on these sensors.

The AC impedance response was found to be the most indicative approach to observe any change in the sensor’s response with time. CVs continued to be utilised as a ‘conditioning’ step prior to the application of AC impedance spectroscopy.
6.3.1 Ageing Effect Experiments with the Planar Sensors with a Cast DAIS Electrolyte.

Reproducibility of the results in the short term was carried out on sensor number 19, which possessed a Pt working electrode with an area of 0.5 cm² and a cast DAIS electrolyte film 20 μm thick. Figures 6.13 and 6.14 indicate the responses on the Nyquist plot representations of the sensor to 5% CO on two consecutive days. When the results are compared it can be seen that they show good reproducibility.

Tests under the same experimental conditions were carried out on sensor number 21 (electrode area 0.5 cm² and 15 μm electrolyte film), one month apart. 0.25% CO (2500 ppm) was introduced to the sensing chamber. Figures 6.15 and 6.16 present the Nyquist plots corresponding to the two sets of results. Again, good correlation between the two sets of results was observed.

Finally, tests were carried out on sensor number 22 when 4½ months (133 days) had elapsed. The results in clean air and when 0.5% CO in air was present were compared. The plots when the analyte was just added (the ‘t=0’ plot) are shown in figure 6.17. The results are remarkably similar, however, small discrepancies were observed. These may be due to an ageing effect of the sensor, i.e. the cast DAIS membrane may have degraded with time, or the platinum working electrode may have become poisoned in such a way that the ‘conditioning’ step was not sufficient to clean the active surface area. Alternatively, the discrepancy may be due to experimental error. These possible errors and their predicted effect on the electrochemistry of the system will be discussed in chapter 7.

6.3.2 Ageing Effect Experiments with the Planar Sensors with a Cast Thermally Activated Nafion® Electrolyte.

The initial results with sensor number 24 (electrode area of 0.5 cm² and electrolyte film thickness of 20 μm) in an atmosphere containing CO appeared to be promising,
Figure 6.13 Nyquist Plot Indicating the Response of Sensor Number 19 in a Clean Air Environment and in the Presence of 5% CO - Day 1.

(60% RH and 22±2 °C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
Figure 6.14 Nyquist Plot Indicating the Response of Sensor Number 19 in a Clean Air Environment and in the Presence of 5% CO - Day 2, (60% RH and 22±2 °C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
Figure 6.15 Nyquist Plot Indicating the Response of Sensor Number 21 in a Clean Air Environment and in the Presence of 0.25% CO - Day 1.

(60% RH and 22±2 °C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
Figure 6.16  Nyquist Plot Indicating the Response of Sensor Number 21 in a Clean Air Environment and in the Presence of 0.25% CO - 1 Month Later, (60% RH and 22±2 °C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
Figure 6.17 Nyquist Plot Indicating the Response of Sensor Number 22 in a Clean Air Environment and in the Presence of 0.5% CO - Days 1 and 133 (60% RH and 22±2 °C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
the major disadvantage being that the low end of the frequency range had to be extended to 0.003 Hz, making a test scan many minutes long and therefore not particularly practical for a commercial sensor device. However, on subsequent days it was noticed that the positioning of the data on the Nyquist plots was varying. The first semicircle became enlarged and thereby translated the whole plot across the x-axis, indicating a higher $Z'$ value. Figure 6.18 indicates this effect after only three days with sensor number 24 in clean air conditions. Even though the impedance had increased the sensor still produced a significant response on the introduction of 1000 ppm CO to the sensing chamber. Tests were terminated on this sensor after the third day of testing.

Sensor number 25 was produced following exactly the same method as sensor number 24, and the initial studies in clean air indicated a close similarity between the two responses (refer to figure 5.45). Tests carried out on the following days indicated the same variation in response with time as was observed with sensor number 24. Figure 6.19 indicates the responses of this sensor in clean air conditions over three consecutive days. After a further 24 days had elapsed, another experiment in clean air conditions was carried out. This time an even greater change in the appearance of the plot had occurred, following the trend already observed during the first few days of testing. The studies of sensor number 25 were terminated after obtaining these results. Figure 6.20 indicates the Nyquist and Bode plot representations for the results obtained on the third and last day of testing.

The results obtained with the sensors which possessed a cast thermally activated electrolyte film indicated a large ageing effect. As outlined in section 2.2.3(b), the activation process is expected to allow re-orientation of the polymer side chains, thereby increasing the number of ionic clusters available in the electrolyte. This establishes an increase in the proton conductivity in the re-hydrated film.\textsuperscript{160} However, Quah proposed the possibility of a structural re-inversion after the re-hydration step.\textsuperscript{159} This proposal may explain the phenomenon discovered in this work.
Figure 6.18 Nyquist Plot Indicating the Response of Sensor Number 24 in a Clean Air Environment - Days 1, 3 and 4,
(60% RH and 22±2 °C).
All Plots were Measured Between 10 kHz and 0.003 Hz.
Figure 6.19 Nyquist Plot Indicating the Response of Sensor Number 25 in a Clean Air Environment - Days 1, 2 and 3.
(60% RH and 22±2 °C).
All Plots were Measured Between 10 kHz and 0.0035 Hz.
Figure 6.20 Nyquist and Bode Plots Indicating the Response of Sensor
Number 25 in a Clean Air Environment - Days 3 and 27,
(60% RH and 22±2 °C).
All Plots were Measured Between 10 kHz and 0.006 Hz.
6.3.3 **Ageing Effect Experiments with the Sensors which Possessed Catalyst Loaded Carbon Cloth Electrodes Pressed onto a Commercial Electrolyte Membrane.**

Time limitations did not allow many tests to be carried out on the sensors which were produced by pressing catalysed ETEK electrodes onto a Nafion® 115 membrane (sensor number 29) or onto commercial DAIS 585 membrane (sensor number 30). However, tests were carried out on sensor number 30 over three consecutive days and the results are compared as the Nyquist plot representations in figure 6.21.

A shift to a higher impedance was observed over the frequency range 60 kHz to 0.1 Hz as time passed, indicating that the conductivity of the system had decreased. This could possibly be due to a de-lamination of the pressed cloth peeling away from the DAIS membrane, thereby reducing the active area of the electrode in contact with the electrolyte.

### 6.4 Summary.

This chapter has presented the results from the experiments carried out on some of the sensor designs where certain parameters have been varied, such as the relative humidity, the presence of an alternative gaseous analyte and the effect of long term testing in order to study any ageing effects. Throughout the chapter, the results have been compared to those described in chapter 5. This previous chapter contained results from short-term tests carried out at 60% RH, in clean air and when CO was present.

The possible reasons for the observations made have been touched upon, however the extended explanations and the reasoning behind them have not yet been discussed. These topics will be covered in more depth in chapter 7.
Figure 6.21 Nyquist Plot Indicating the Response of Sensor Number 30 in a Clean Air Environment - Days 1, 2 and 3.

(60% RH and 22±2 °C).

All Plots were Measured Between 60 kHz and 0.1 Hz.
INTERPRETATION OF THE RESULTS FROM SENSOR TESTING

7.1 Introduction.

Chapters 5 and 6 presented the results obtained from the testing of the thirty sensors produced in this project. Comparisons of the observations were then made. This chapter covers the interpretation of the results and puts forth the evidence to back-up the explanations given.

Initially the theory of CO chemisorption onto a supported platinum catalyst will be discussed, followed by the interpretation of the results obtained from the DC and AC testing techniques in clean air and in an atmosphere containing CO. A discussion of the results when certain experimental parameters were varied will then be given.

The data were then fitted with the Solartron ZView software in order to obtain approximate values of $R_u$, $R_b$, $C_{gs}$, $R_{ct}$ and $C_{dl}$ and to study the relationship of these elements when the analyte is present. Some examples of the use of this technique are given. Also, formulae which can be used to gain the dimensions of resistance and capacitance at a specific frequency are presented. The values of $Z'$ and $Z''$, stated on the Nyquist plots obtained from the testing of the sensors, have been substituted into the equations. Graphs which indicate how the resistance and capacitance vary with respect to time and the CO concentration have been produced. Finally, a summary of the findings from the testing of the sensors is presented.

7.2 Chemisorption of CO on a Supported Platinum Catalyst.

The decrease in the interfacial impedance obtained by the sensors on the addition of CO can be explained by the adsorption of the gas molecules onto the surface of the platinum electrode. CO molecularly chemisorbs onto the surface of the supported
The $\sigma 2p_x$ electrons of the CO molecule can couple with the electron density of the platinum. The binding in CO may be represented as three electron pairs shared between two atoms.$^{187}$

Figure 7.1 indicates the atomic and molecular orbitals and a diagrammatic representation of the configuration of these orbitals around the CO molecule. The C→Pt bond produced by the donation of the $\sigma 2p_x$ electrons of the CO molecule is weak. A stronger second bond is formed by back bonding or dative $\pi$ bonding. This arises from sideways overlap of a full $d_{xy}$ orbital on the metal with an empty antibonding $\pi^*2p_y$ orbital of the carbon, thus forming a $\pi$ Pt→C bond. The overall bonding is therefore Pt=C=O.

This mechanism forms a linear species, however, Bilmes and co-workers have discovered that a bridged or multi-bonded chemisorbed CO species exists on the surface of platinum$^{188,189}$ i.e. $\text{Pt}_{\text{br}}$ C=O.

This model assumes that there are two types of adsorbed species of different adsorption energy, and the possibility that one species changes into the other by jumping between different adsorption sites, which may involve a single, or two adjacent metal surface atoms. They found that the electro-oxidation of the linear
CO species occurred at a slightly more positive applied potential than that of the bridged form.

7.3 **Explanation of the Variation in OCP Value.**

The initial OCP value attained by the sensor prior to testing, was predominantly determined by the amount of adsorbed oxygen on the surface of the Pt working electrode. This value could also be affected by any remaining CO adsorbed onto the surface which was left from the previous test. Therefore, when the CVs were applied for the ‘conditioning’ step, the adsorbed layers were removed by forcing oxygen evolution and CO oxidation reactions:

\[
\begin{align*}
\text{H}_2\text{O} &\quad \longleftrightarrow \quad \frac{1}{2}\text{O}_2(\text{g}) + 2\text{H}^+ + 2e^- \\
\text{CO}_{\text{ad}} + \text{H}_2\text{O} &\quad \longleftrightarrow \quad \text{CO}_2(\text{g}) + 2\text{H}^+ + 2e^- 
\end{align*}
\]

(7.1) \hspace{1cm} (7.2)

A corresponding current was visible on the CV scans. An example showing this is figure 5.20 which indicates the results obtained for sensor number 22, in clean air conditions. The oxidation current corresponding to oxygen evolution was observed in the applied potential range ≥500 mV on the first CV. The current for this reaction was then observed at ≥800 mV on subsequent cycles. It is this perturbation in current that created the increased OCP value - an effect seen repeatedly in the results (refer to table 5.1 and section (c) in 5.2.3, 5.2.4, 5.2.5 etc.).

This perturbed OCP was allowed to stabilise, so that the AC impedance scan was carried out at the most stable OCP value, without excessive wandering. Of course, the OCP is affected when CO is present. It has been shown to have the effect of shifting the OCP in a negative direction. To explain this phenomenon, it is possible to utilise the findings made by Lukacs *et al.* They discovered that the OCP value they obtained during their studies of a stabilised zirconia solid electrolyte with a Pt working electrode was affected by the partial pressures of O$_2$ and CO in the analyte gas. Therefore, the initial value in clean air, which was dependent on the relative quantities of oxygen activity occurring at the working and reference
electrodes, is now perturbed due to the competing adsorption of CO for the active sites on the surface of the Pt catalyst.

The competition between the two gases gives rise to a new mixed cell potential which causes the OCP to stabilise at a more negative value. The data in tables 5.2, 5.3, 5.4, 5.5 and 5.6 indicate this shift to a more negative potential when a concentration of CO had been introduced into the sensing chamber. Furthermore, for some of the sensor designs, a trend was observed in the magnitude of the shift when the mixed cell potential was produced. The data in tables 5.2, 5.3 and 5.4 (sensor numbers 20, 22 and 27 respectively) indicated a good correlation between the CO concentration present and the resulting OCP value. In these cases the competing adsorption of CO and O₂ had reached an equilibrium, and the partial pressures of CO and O₂ dictated the relative change in OCP value.

For some of the sensor designs, the formation of a mixed cell potential in the presence of CO was observed, however, the trend whereby the greater the concentration, the greater the variation in the OCP value did not apply. This was the case for sensor numbers 29 and 30 (tables 5.5 and 5.6). These sensors were produced by the pressing of Pt loaded carbon cloth onto commercially available electrolyte membranes of Nafion® 115 and DAIS 585. The reference electrode was also manufactured from the same electrode fabric and would not be inert to CO. It is therefore thought that a competition between O₂ and CO for the active sites on the Pt catalyst would occur at the surfaces of both the working and reference electrodes. Therefore the lack of a trend is because the observed shift in OCP value did not exclusively represent the change in surface chemistry at the sensing (working) electrode.

Sensor number 28, which had the working and counter electrodes produced from the screen printing of platinum black powder dispersed into a carbon ink did not indicate a variation in the OCP value on the addition of CO. The reference electrode was produced from gold organometallic ink. This is explained by there not being enough Pt catalyst to make it possible to see a significant change in the
OCP value (section 5.2.5(c)). Also, the AC impedance spectroscopy data did not indicate a response to CO (refer to figure 5.28).

7.4 Explanation of The Response Obtained by Cyclic Voltammetry.

The response obtained by the sensors when CVs were carried out in clean air conditions has already been touched upon in the section above, i.e. forcing the electro-oxidation of water, evolving oxygen, and CO (if present). During the testing of the sensors when a known concentration of CO was present, three types of response were obtained; no variation from the clean air response (sensor numbers 12, 15, 24, 25, 26, 28 and 30), a change in the gradient of the slopes on the CVs compared to the clean air response (sensor numbers 17, 19, 20 and 21) and the appearance of a broad current peak corresponding to the electro-oxidation of CO\textsubscript{(ad)} (sensor numbers 22, 27 and 29).

The reverse scan indicated a current at an applied potential of $\leq 400$ mV, due to the electro-reduction of platinum oxide, which was partly formed by the evolution of oxygen at the working electrode during the forward scan. The standard reversible potential of the reaction shown in equation 7.3 is stated as $1.00$ V at $25^\circ$C.\textsuperscript{190} As the gold reference electrode is considered to be 0.556 V versus the SHE, then the cathodic current corresponding to this reaction would be observed at 440 mV, therefore the observed potential window lies within the correct range of values.

\[
\text{PtO}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{Pt} + 2\text{H}_2\text{O} \tag{7.3}
\]

A change in the gradient of the CV scan indicated a decrease in the overall resistance ($R$) of the electrochemical sensor system when CO was present in the test gas. This was determined by the application of Ohms' Law; as $R=V/i$, the larger the current ($i$) (when CO was present), the smaller the resistance at the same value of applied potential ($V$). The AC impedance results corroborated this finding.

When a broad oxidation peak which corresponded to the oxidation of adsorbed CO on the Pt working electrode was obtained, it was found to be superimposed onto
the response in clean air and contributed a current to the total anodic current. The peak oxidation potential of CO was established to be over a potential range of +0.50-0.80 V versus the gold reference electrode. Hence, with respect to the gold reference electrode, the oxidation potential of CO on the platinum working electrode was found to be +1.06-1.36 V versus the SHE. The standard potential of the reaction shown in equation 7.4 is stated as 1.33 V at 25 °C.\(^{190}\)

\[
\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2
\]  
\[\text{(7.4)}\]

Bilmes et al obtained a CO oxidation peak on a polycrystalline platinum electrode, in 1 mol dm\(^{-3}\) HClO\(_4\) electrolyte, over the applied potential range of 0.82-1.04 V versus the SHE.\(^{188}\) Therefore, the oxidation peaks observed by the CO sensors in this project were observed in the correct potential window on the CV scans.

The CVs carried out on the planar Pt electrodes in solution, indicated a broad oxidation peak (chapter 3). This characteristic was also discovered on the CVs with the gas sensors when CO was present. This is because planar electrodes exhibit a range of potentials over the area of the electrode with respect to the reference electrode.\(^{178}\) In fact the required applied potential is probably only present along the edge of the planar electrode closest to the reference electrode. The example in figure 7.2 below is shown for the instant in time at which the applied potential is at 0.77 V during a CV scan.

Figure 7.2 Possible Potentials at a Planar Working Electrode When the Reference Electrode Establishes a Potential of 0.77 V During a CV Scan.

The incorporation of an interdigitated Pt working electrode and gold reference electrode (sensor number 27), was an attempt to bring the working electrode into a closer proximity to the reference electrode, so that the working electrode would be
held closer to the required applied potential rather than over a potential range. The results obtained by sensor numbers 27 and 22 are compared in figures 5.25 and 5.21 respectively. Table 7.1 indicates the electrode configurations of the sensors and details of the results obtained by cyclic voltammetry in the presence of CO.

It can be seen that the inter-spacing of the working and reference electrodes (sensor number 27) had the effect of narrowing the potential window for CO oxidation, indicating that the potential at the working electrode was held closer to the required applied potential during the CV cycle.

Table 7.1 Comparison of the Oxidation Potentials of CO Obtained by Sensor Numbers 27 and 22. Both Sensors Possessed a 20 μm Cast DAIS Electrolyte and a Working Electrode Area of 0.5 cm². Potentials are Stated Versus the Gold Reference Electrode.

<table>
<thead>
<tr>
<th>Sensor number</th>
<th>Configuration</th>
<th>Potential range for CO oxidation peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td></td>
<td>+0.50 - +0.70 V</td>
</tr>
<tr>
<td>22</td>
<td></td>
<td>+0.50 - +0.80 V</td>
</tr>
</tbody>
</table>

The electrochemical reduction of CO₂ was not observed on the reverse scan of the cyclic voltammograms because of the relatively weak adsorption of CO₂ on the Pt surface, therefore, making the electro-reduction reaction mass transfer limited.

Not only was a broad oxidation peak obtained by some of the sensor designs in an atmosphere containing CO but a further discovery was made. The magnitude of the oxidation current increased as the concentration of CO was increased. Yasuda et al quoted an equation relating the CO oxidation current (i) obtained to the concentration of CO present on the surface of the working electrode ([CO]).¹¹⁵ This equation was based on the two electron reaction of CO oxidation shown in equation 7.5 and the theoretical equation outlined by Yasuda et al is indicated in equation 7.6 below.

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \quad (7.5) \]
The oxidation rate constant, \( k \), relates to the reaction indicated in equation 7.4, and \([H_2O]\) corresponds to the water content of the electrolyte film. It is possible that the working electrode configuration utilised for the sensors in this project produced more adverse effects due to their planarity than those studied by Yasuda et al because although the magnitude of the CO oxidation current obtained followed the general trend, it was not directly governed by the equation suggested by Yasuda et al.

7.5 **Explanation of Response Obtained by AC Impedance Spectroscopy.**

The general response obtained by the sensors in clean air conditions, i.e. two semicircles present on the Nyquist plot representation, was obtained by Chen et al.\(^{191}\) They studied the conductivity of a commercially available Nafton\(^{®} \) 117 membrane over the frequency range 100 MHz to 10 Hz. Figure 7.3 indicates a schematic diagram of Chen et al’s results.

![Figure 7.3 Schematic Diagram of the AC Impedance Spectroscopy Response of Nafton\(^{®} \) 117 Obtained by Chen et al. (50 % RH and 25 °C).](image)

Chen et al assigned the high frequency impedance to the bulk resistance and a capacitance (\( C_g \)) in the usual Randle’s arrangement and attributed the low frequency response to the electrode/interfacial impedance.
The same response was obtained by the sensors in this project and the high and low frequency responses have been interpreted in the same way, i.e. the electrolyte impedance and the interfacial impedance.

For the majority of sensor designs a change in the response was observed when CO was present. A plausible explanation for this occurrence follows. During an AC impedance scan the FRA imposes a small AC interrogative wave (usually 10 mV) and the DC potential is held at the OCP, therefore the sample is not polarised and theoretically this technique does not greatly disturb the electrochemical system during an experiment. However, workers have discovered that the AC input wave can have an effect, albeit small, on the test sample.

Okamoto et al. have studied the EMF of a solid electrolyte concentration cell (stabilised zirconia) at 363 °C, during CO oxidation on platinum by local current measurements. The EMF deviation from the Nernst Equation is brought about by imperfect catalytic activity of the Pt electrode. They stated that the local current \(i_0\) was obtained potentiostatically using the equation:

\[
i_0 = \left(\frac{RT}{2F}\right)\left(\frac{di}{dE}\right)
\]

Therefore, \(di\) is the current observed when the electrode is changed from the OCP by a small amount \(dE\), e.g. ±5 mV. Okamoto et al. discovered that when the partial pressure of oxygen was varied (in the absence of CO) with a potentiostatically applied potential of ±5 mV the OCP of the system increased in the order of 60 mV, hence observing a local current variation of 3 µA. When CO was introduced, with a constant partial pressure of oxygen, \(i_0\) was two or three times greater than in the absence of CO. They concluded that a limited amount of CO oxidation had occurred under these conditions.

Therefore, for the application studied in this project, it can be envisaged that a small amount of local polarisation due to the 10 mV AC amplitude may be adequate to
allow a small amount of the chemisorbed CO to oxidise on the platinum working electrode, therefore not only affecting the double layer capacitance but affecting the kinetics of the charge transfer at the interface \(R_{ct}\) due to a perturbation in the local current.

It was mentioned in section 7.3 that other workers such as Lukacs et al have investigated the affect of CO at platinum electrodes with a stabilised zirconia solid electrolyte.\(^{20,184}\) They discovered that the OCP was affected by the partial pressures of \(O_2\) and CO, and applied the technique of AC impedance spectroscopy at the OCP value with an AC amplitude of 10 mV in the frequency range 10 kHz to 0.01 Hz.

The Nyquist plots that they obtained showed that the second semicircle was pulled down towards the x-axis on the addition of CO. This was interpreted as a significant decrease in the charge transfer resistance \(R_{ct}\) with increasing CO concentration, although \(R_w, R_h, C_R\) and \(C_{di}\) did not vary significantly. Lukacs et al explained this change in \(R_{ct}\) as a decrease in the polarisation resistance of the electrochemical steps 7.1 and 7.2, under the influence of a local current \((di)\) due to a small perturbation in potential \((dE)\) of 10 mV.

The results obtained in this project with the CO sensors also indicated a decrease in the \(R_{ct}\) element of the interfacial impedance, as indicated in the schematic diagram of the Nyquist plot at the start of chapter 5 (figure 5.2). The competition between CO and \(O_2\) for the active sites on the surface of the supported Pt catalyst will undoubtedly affect the double layer characteristics \((C_{di})\). Examples which indicate these observations are indicated in figures 5.4, 5.17, 5.42 and 5.55 for sensor numbers 17, 22, 24 and 29.

An additional point to mention here, is that as Okamoto et al and Lukacs et al were testing their sensor designs at a working temperature between 363 and 600 °C. This was necessary to provide an adequate conductivity of the stabilised zirconia solid electrolyte which they employed (section 1.3.3). Therefore, the high temperature conditions they used may have encouraged the oxidation reaction
stated in equation 7.2, leading to a greater decrease in the polarisation resistance $(R_{dc})$. However, as mentioned above, the sensors tested at ambient temperature in this project exhibited similar reductions in the overall impedance $(|Z|)$, the double layer capacitance and the charge transfer resistance elements.

Chapter 6 discussed the results obtained from the testing of the sensors when certain parameters were varied, such as the relative humidity, the presence of an alternative gaseous analyte and the effect of long term testing. The interpretation of the responses discussed in this chapter above, will now be extended to explain the responses when these parameters were varied.

### 7.6 Explanation of the Response Obtained when the RH was Varied.

The appearance of the semicircles on the Nyquist plot suggested that as the RH decreased, the impedance of the electrochemical sensor system increased. To explain this variation the chemistry of the electrolytes must be considered. The mechanism of proton conductivity in both Nafion® and DAIS is based on the presence of micellar structures (spherical and cylindrical respectively), which form clusters lined with sulphonated domains. The size of these clusters is dictated by the level of absorbed water and when the clusters are large enough a continuous path of clusters exists throughout the polymer allowing the conduction of protons, (refer to sections 2.2.1 and 2.2.2).

Therefore, the removal of water in the cluster arrangements in the electrolyte film would lead to a decrease in the proton conducting characteristics. This reduction in conductivity as the RH decreased was revealed in the results obtained by AC impedance spectroscopy, (refer to section 6.1.1). The resistance between the probe and the electrode surface $(R_u)$ increased in an almost linear fashion, as the RH decreased, at an approximate rate of $6 \ \Omega / ^\circ C$, the graph indicated in figure 6.2 clearly indicates this rate of change.
Also, the semicircle obtained over the high range of frequencies became enlarged, indicating that the electrolyte impedance ($R_e$ and $C'_g$) elements had increased, hence providing evidence for the explanation that the decrease in RH caused a decrease in the size of the ionic clusters.

This enlarged semicircle would lead to the second semicircle (lower frequency) falling on the x-axis at a higher $Z'$ value indicating an overall increase in impedance. Figure 7.4 indicates a schematic representation of the results in the three RH conditions between the experimental frequency limits of 60 kHz and 0.1 Hz and the predicted response at frequencies less than 0.1 Hz showing how the second semicircle would eventually fall across the x-axis.

Figure 7.4 Schematic Representation of the Obtained and Predicted Response of Sensor Number 22 in the Three RH Conditions.

The decrease in proton conductivity of the electrolyte film was shown yet again in the results obtained by cyclic voltammetry, which was discernible by the gradient of the slope decreasing in lower RH conditions.

Even when the RH was 35%, the sensor responded adequately to 1000 ppm CO without an obvious drop in performance, indicating that the dimensions of the ionic clusters at this RH level still allowed sufficient proton conductivity to take place.
7.7 **Explanation of the Response Obtained when an Alternative Analyte Gas was Present.**

The presence of methane did not produce a change in the response from that found in clean air when all three testing techniques were applied (OCP, CVs and AC impedance spectroscopy). The standard electrode potential for the oxidation reaction of methane (equation 7.8) is stated as 0.19 V versus the standard hydrogen electrode (SHE) and therefore -0.366 V versus the gold reference electrode. An oxidation current relating to equation 7.8 was not observed in the applied potential window utilised during the testing procedure. The overall cell EMF (equation 7.10) is stated as 1.04 V. Also, the relatively weak adsorption of CH₄ on the platinum surface, makes the electro-oxidation reaction mass transfer limited and a high overpotential would be required in order to observe an oxidation current.

\[
\begin{align*}
\text{CH}_4 + 2\text{H}_2\text{O} & \rightarrow \text{CO}_2 + 8\text{H}^+_{\text{(ad)}} + 8\text{e}^- \\
8\text{H}^+ + 2\text{O}_2 + 8\text{e}^- & \rightarrow 4\text{H}_2\text{O}
\end{align*}
\]

(7.8)  

(7.9)

Overall: \[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad \text{(7.10)}
\]

On the other hand, hydrogen is readily adsorbed onto the surface of a platinum catalyst. If the 10 mV AC amplitude was sufficient to induce a limited amount of CO oxidation when the CO(ad) species was present, then it may be viable to suggest that the oxidation of absorbed hydrogen would occur (equations 7.11, 7.12 and 7.13). This limited oxidation would explain the variation observed on the Nyquist plots when H₂ was introduced to the test gas. The standard electrode potential of the oxidation reaction indicated in equation 7.11 is stated as 1.23 V versus the standard hydrogen electrode, i.e. 0.67 V versus the sensor’s gold reference electrode. However, a corresponding oxidation peak was not observed on the CV plots with the sensor design tested. Perhaps, the presence of a hydrogen concentration greater than 1000 ppm would be required before a peak could be observed.

\[
\begin{align*}
\text{H}_2 & \rightarrow 2\text{H}^+_{\text{(ad)}} + 2\text{e}^- \\
2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2\text{e}^- & \rightarrow \text{H}_2\text{O}
\end{align*}
\]

(7.11)  

(7.12)

Overall: \[
\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} \quad \text{(7.13)}
\]
7.8 Explanation of the Response Obtained as a Result of Long Term Testing, (The Ageing Effect).

Different responses were obtained for the different sensor designs. For the sensors produced by screen printing of platinum and gold ink and then casting of an electrolyte film from DAIS 585 solution, the responses indicated good reproducibility over a period of 4½ months (refer to section 6.3.1). The small discrepancy observed with time may be due to an experimental error rather than an actual ageing effect of the sensor.

One such experimental error could be the re-positioning of the crocodile clip contacts onto the silver-epoxy contacts deposited along the edge of each electrode (section 4.1(d)). This would have the possible effect of changing the resistance between the probe and the electrode surface, \(R_s\), and possibly the geometrical capacitance \(C_g\).

The RH of the test gas may be slightly different on two separate testing days, perhaps due to the variations in the ambient temperature or due to a pressure deviation on the input gases. It has already been shown that the RH dictates the electrolyte impedance characteristics of a sensor. There is also the possibility of a relatively thick oxide layer becoming deposited on a Pt working electrode over a period of time, which the ‘conditioning’ step of three CVs would be unable to return the surface to the same state as that found at the start of the testing programme. This additional oxide layer may affect the double layer characteristics.

The sensor which possessed a cast thermally activated Nafion® electrolyte indicated a large ageing effect within a short period of time. The overall impedance was found to increase (figures 6.18 and 6.19). The possible explanation for this apparent increase in impedance may be due to the degradation of the advantageous effect of the thermal activation step. The possibility of a structural re-inversion after the re-hydration of the film has been suggested,\(^{159}\) therefore allowing the re-orientation of the polymer side chains, leading to a decrease in the number of ionic clusters available in the electrolyte. This occurrence is predicted to affect all of the
resistive and capacitive elements, and in particular the bulk resistance \(R_b\) and the probe/electrode surface resistance \(R_u\).

The sensors produced by the pressing of Pt/C electrode material (ETEK) onto commercially available membranes (sensor numbers 29 and 30) indicated an increase in the impedance of the system with time (figure 6.21). It is highly probable that the electrode material peeled away from the electrolyte material with time, i.e. a de-lamination process.\(^{126, 129, 171}\) The active electrode area which is in contact with the electrolyte would now be reduced and has led to an increase in \(R_u\), an adjustment in the geometrical capacitance and a variation in the charge transfer and double layer characteristics of the electrochemical system.

It has already been mentioned above in section 7.3, that this design possessed a Pt/C reference electrode which would not be inert to CO. Hence, a further point to mention with this design of sensor is that although the ‘conditioning’ step is expected to remove any CO from the surface of the working electrode, this process would not clean the adsorbed CO layer on the reference electrode. The ageing effect may be due to this poisoning of the reference electrode.

The Solartron software utilised for the data acquisition could also be used to fit the data to a variety of equivalent circuits, so that the best fit could eventually be obtained. In this way values for the resistive and capacitive elements were estimated. An alternative method which involved relatively simple equations was also used to obtain approximate values of resistance and capacitance.

### 7.9 Fitting of the AC Impedance Spectroscopy Data.

The ZView fitting software was used to study the characteristics of the electrochemical sensor system in clean air and when CO was present. A number of equivalent circuits were experimented with, however the equivalent circuit indicated in figure 7.5 below was found to provide the closest fit.
The constant phase element (CPE), $\Phi_i$, in parallel with the bulk resistance is necessary, as it is this element that introduces the flattened characteristic of the circular arc observed over the high frequency range. This CPE is often found for solid electrolytes when the measured impedance is plotted as the Nyquist representation. The geometrical resistance is indicated as $C_g^*$ in figure 7.5, as the magnitude of $\Phi_i$ affects the capacitive nature of the $C_g^*$ element. If $\Phi_i = 1$, then $C_g^*$ is a pure capacitive element, however, as $\Phi_i$ tends towards zero, $C_g^*$ attains a more resistive nature. Also, if $\Phi_i$ tends towards -1, then an inductive nature is induced, however, in general, inductance is not a significant factor when discussing polymer systems.

The fitting process was repeated on many examples of the experimental data, but only a small selection of diagrams indicating the fitted data super-imposed on the experimental data are presented here, however, tables containing the values of the resistive and capacitive elements obtained by this method are presented. The parameter of the working electrode area was also studied, by comparing the fitting values for sensor numbers 17 and 19 (0.25 and 0.50 cm² respectively). Figure numbers 7.6 and 7.7 indicate the experimental and fitted data obtained for the clean air responses of these two sensors. The values of the resistive and capacitive elements are indicated in table 7.2 below.

The difference in the value of $R_u$ is due to the reduced area of the working electrode for sensor number 17, hence the resistance between the probe and the electrode’s surface will be greater; in this case three times greater. Both $R_b$ and $C_g^*$ are
Figure 7.6 Experimental and Fitted Data for the Response of Sensor Number 17 in Clean Air Conditions.
Figure 7.7 Experimental and Fitted Data for the Response of Sensor Number 19 in Clean Air Conditions.
increased by approximately 20\% when the working electrode was halved. These elements represent the electrolyte impedance and it is possible that this variation is due to the different electrode configuration on the alumina substrate. A \( \Phi \) value of 0.5 created a sufficient amount of flattening of the semicircle, indicating that \( C_g^* \) possessed some resistive nature.

This fitting technique was also carried out on the results obtained by sensor number 19 when various concentrations of CO were present in the test gas. Figure 7.8 indicates the fit for the set of data collected when 5\% CO was present. Table 7.3 presents the values obtained from these fittings.

<table>
<thead>
<tr>
<th>Element</th>
<th>Sensor number 17</th>
<th>Sensor number 19</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_u )</td>
<td>4122 ( \Omega )</td>
<td>1223 ( \Omega )</td>
</tr>
<tr>
<td>( R_b )</td>
<td>15 k( \Omega )</td>
<td>19 k( \Omega )</td>
</tr>
<tr>
<td>( C_g^* )</td>
<td>2.5 ( \mu F )</td>
<td>2.0 ( \mu F )</td>
</tr>
<tr>
<td>( \Phi )</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>( R_{ct} )</td>
<td>136 k( \Omega )</td>
<td>136 k( \Omega )</td>
</tr>
<tr>
<td>( C_{dl} )</td>
<td>1.0 ( \mu F )</td>
<td>1 ( \mu F )</td>
</tr>
</tbody>
</table>
Figure 7.8 Experimental and Fitted Data for the Response of Sensor Number 19 when 5% CO was present.
A clear trend is apparent; $R_n$ was unaffected by the presence of CO. $R_{ct}$ indicated the most dramatic effect, in fact when 5% CO was present the value became only 5% of the original value obtained in clean air conditions. The value of the double layer capacitance also decreased, therefore indicating an overall reduction in the interfacial impedance. This is most probably due to the presence of adsorbed CO on the surface of the Pt catalyst, which introduced charge carriers to the dielectric, therefore increasing the conductivity at that interface. If charge carriers are present then this would explain the relatively small decrease observed in the electrolyte impedance.

The fitting of the data by ZView proved to be a successful method of quantifying the values of the equivalent circuit elements. It made it possible to see that the resistance value obtained at low frequency, $R_{ct}$, varied dramatically when the sensors were tested in an atmosphere containing CO. The results in table 7.3 indicated a trend in the variation with respect to the CO concentration. Therefore, a simple method of calculating a value of resistance from the $Z'$ and $Z''$ values on the Nyquist plots was sought.

7.10 Calculation of the Resistance and Capacitance Values.

Formulae were obtained which predicted the values of resistance and capacitance using the values of $Z'$ and $Z''$ obtained at a specific frequency value. Equations 7.14 and 7.15 indicate the two equations, where $\omega = 2\pi \cdot \text{frequency}$.

Refer to Appendix I for the derivation of these equations.

$$R = \frac{Z'^2 + Z''^2}{Z'^2} \quad (7.14)$$

$$C = \frac{Z''}{\omega (Z'^2 + Z''^2)} \quad (7.15)$$

The equation for the resistance provides relatively accurate values for data obtained when the input frequency is a low value making it ideal for the calculation of $R_{ct}$. However, the accuracy for the value of capacitance calculated by equation 7.15 is improved if the data points used were obtained when the frequency was $\geq 1500$ Hz, consequently making the estimation of $C_d$ inaccurate by this method.
Calculations were carried out to obtain values for the resistance on many of the AC impedance spectroscopy results, and a small number of examples are provided below. The $Z'$ and $Z''$ values were obtained from the Nyquist plots which corresponded to the data point at 0.1 Hz, i.e. the last data point acquired for each set of data (for sensor numbers 17, 19, 20, 21, 22, 27, 29 and 30). The values were substituted into equation 7.14 and an evaluation of the resistance obtained.

Figure 7.9 indicates the variations of the calculated value of resistance at 0.1 Hz versus the CO concentration for sensor number 19. The value of resistance obtained in clean air was 35 kΩ and a decrease in this value was observed when CO was introduced to the test gas; the magnitude of this decrease was dependent on the concentration of the gas.

For a particular CO concentration, the value of resistance at 0.1 Hz gradually decreased over the sixty minutes of sensor testing. This effect was observed on the Nyquist plots, demonstrated by the second semicircle reducing in size with time (refer to figure 5.4). This decrease in resistance was discussed in section 5.2.1(a) and it is thought to be due to either the diffusion properties of CO through the electrolyte film, or the fact that at the start of the experiment, the CO concentration had not reached the desired concentration in the sensing chamber.

The value in clean air obtained by equation 7.14 was four times smaller than the value of $R_{cr}$ obtained by the application of the equivalent circuit (table 7.3). This is because the position of the data point at 0.1 Hz is on the rise of the circular arc on the Nyquist plots and not at the point where the plot crosses the x-axis. Figure 7.10 illustrates this difference. Therefore, the value of the resistance obtained by calculation is not equal to $R_{cr}$, but it does provide a value which makes it possible to compare the relative differences in resistance caused by the various concentrations of CO. A further example of this is shown in figure 7.12 for sensor number 20 in the presence of 500 ppm, 1000 ppm, 5000 ppm, 1%, 2%, 3% and 5% CO.
Figure 7.9  The Variation in the Resistance on the Addition of CO (60% RH, 22±2°C, Sensor Number 19 Data @ 0.1 Hz).
Figure 7.11 The Variation in the Resistance on the Addition of CO (60% RH, 22±2°C, Sensor Number 20 Data @ 0.1 Hz).
If the resistance value calculated from the data point obtained for the ‘t=0’ scan, is plotted versus the CO concentration, a calibration curve is obtained. Figure 7.12 indicates such a curve for the data collected for sensor number 22. The response in this case appears to follow the equation \( y = 0.0004x^2 - 4.92x + 25150 \) where \( y \) refers to the resistance at 0.1 Hz and \( x \) corresponds to the concentration of CO gas.

The application of equation 7.14 also proved useful when considering the effect of RH on the resistance of the sensor system. Figure 7.13 compares the resistance values in clean air in the three RH environments and on the addition of 1000 ppm CO. A similar trend in the variation of the resistance was observed on the addition of the analyte.

For sensors which required an extended frequency range, such as sensor number 24, the data at 0.003 Hz was substituted into equation 7.14 and the trends seen here for sensor numbers 19, 20 and 22 were observed again. Therefore it is possible to say that the use of an equation to calculate the resistance from a data point at a single frequency value, is a beneficial method of comparing the response of the sensors both qualitatively and quantitatively.
Figure 7.12 The Variation in the Resistance on the Addition of CO (60% RH, 22±2°C, Sensor Number 22 Data @ 0.1 Hz).

Trendline: \( y = 0.0004x^2 - 4.92x + 25150 \)

where \( y \) refers to the resistance and
\( x \) refers to the CO concentration.
Figure 7.13  The Variation in the Resistance on the Addition of CO (60%, 52% and 35% RH, 22±2°C, Sensor Number 22 Data @ 0.1 Hz).
7.11 Summary.

This chapter has attempted to interpret the responses of the sensors in an atmosphere containing CO. The formation of a mixed cell potential, due to the competition between \( \text{O}_2 \) and \( \text{CO} \) on the supported platinum catalyst, was used to explain the variation in the OCP value. The planar configuration of the platinum working electrode and gold reference electrode provided the reason for the existence of a broad oxidation peak in the cyclic voltammograms. Also, the results for sensor numbers 22 and 27 were compared, supplying further evidence to this interpretation.

The results published by Lukacs\textsuperscript{20,184} and Okamoto\textsuperscript{24,192} have been discussed. This work described how the small interrogative AC potential during an AC impedance spectroscopy scan allowed a limited amount of electron transfer to occur at the working electrode, causing the charge transfer resistance to decrease when \( \text{CO} \) was introduced to their sensor system. This theory was adopted to explain the reduction in the value of \( R_{ct} \) observed in this work.

The electrochemical testing of the sensor indicated that a working electrode area of 0.5 cm\(^2\), rather than 0.25 cm\(^2\) or 0.37 cm\(^2\), was advantageous for the designs which were produced by the screen printing of platinum and gold inks. Also, a cast electrolyte thickness of 20 \( \mu \text{m} \) was shown to provide an adequate conductivity, whilst allowing the diffusion of the analyte to the working electrode.

The work carried out on sensor number 28, which possessed a Pt/C working electrode, produced by the screen printing of home-made ink, indicated that a platinum loading of 0.053 mg Pt cm\(^{-2}\) was not sufficient to allow adequate adsorption of \( \text{CO} \) on the surface of the working electrode. However, the work carried out with the ETEK catalyst (sensor numbers 29 and 30) indicated that a platinum loading of 0.35 mg Pt cm\(^{-2}\) was sufficient to be able to observe a response on the addition of \( \text{CO} \). Therefore, a home-made Pt/C ink containing between 0.053 and 0.35 mg Pt cm\(^{-2}\) is expected to indicate a response to \( \text{CO} \).
If the response of a sensor produced with a thermally activated Nafion® film (sensor number 24) is compared with a sensor possessing the same thickness of cast DAIS electrolyte (sensor number 19), then only a fraction of the response within the 60 kHz to 0.1 Hz frequency range was observed. This is due to the greater magnitude of the Nafion® electrolyte resistance, and the first semicircle dominated the scan. However, when the frequency range was extended to 0.003 Hz, the start of the circular arc corresponding to the interfacial impedance was again observed. (Refer to figures 5.40 and 5.41).

Sensor number 19 possessed a rectangular working electrode, whereas sensor number 22 possessed an interdigitated working electrode. When the AC impedance responses of these sensor designs were compared (both with an electrode area of 0.5 cm²), then distinct changes in the clean air response were observed within the frequency range 60 kHz to 0.1 Hz. The semicircle observed over the high frequency range was dramatically reduced in size, indicating a significant decrease in the electrolyte impedance. This is most probably due to a reduction in the geometrical capacitance. \( R_c \) and \( C_{dl} \) appear to be approximately the same. Refer to section 5.2.3 for the details of the results.

The results obtained from sensor number 27, which also possessed an interdigitated working electrode, closely resembled those obtained from sensor number 22, therefore indicating that the characteristics of the small semicircle over the high frequency range was due to the incorporation of an interdigitated working electrode in the design, rather than any other factor.

The reduction in the volume of the ionic clusters, reducing the proton conductivity of the polymer electrolytes, has been given to explain the trend observed when the relative humidity of the test gas was reduced to 52% and 35%. It was shown that sensor number 22 still responded adequately to 1000 ppm CO. This sensor design was also shown to be totally inert to the presence of methane. This is thought to be due to mass transfer limitations. However, the sensor did respond to hydrogen, again explained by limited electron transfer occurring with the adsorbed hydrogen at the surface of the catalyst during the AC impedance spectroscopy scan. It was
also noted that the sensor produced a more rapid response to CO than for the same concentration of H₂.

The different designs of sensors indicated different behaviour as time elapsed. The results obtained with sensors which possessed a cast DAIS electrolyte indicated good reproducibility, even after a period of 4½ months. However, those with a cast thermally activated Nafion® electrolyte film aged within 24 hours. This ageing in a very short period of time was explained by a re-inversion of ionic clusters present in the film, therefore reducing the conductivity. The possibility of experimental error during the testing of a sensor over a long period of time was also discussed.

An equivalent circuit was successfully applied to the AC impedance spectroscopy results and values for $R_{eq}$, $R_h$, $C_x$, $R_{ct}$ and $C_{dl}$ were obtained. The trend observed in the value of $R_{eq}$ when CO was introduced to the test gas was thought to be a reliable method of following the response of the sensor. Therefore a relatively simple formula was obtained which made it possible to provide an estimate for the resistance using the $Z'$ and $Z''$ values at a single frequency value. In this way calibration curves were produced which indicated how the resistance at that single frequency value varied with a certain CO concentration, making it a favourable technique of measuring the response of the sensor, both qualitatively and quantitatively.

The thermal activation of a cast Nafion® film dramatically altered the response of the sensor. It was thought that a difference could be observed in the surface morphology of the polymer. Also, different techniques were utilised in order to deposit the platinum working and counter electrodes, and the resulting surface of the catalyst would be another important factor which would dictate the response of the sensor. Therefore, the techniques of scanning tunneling microscopy (STM) and atomic force microscopy (AFM) were utilised in order to study these parameters. The results from this surface analysis study are discussed in chapter 8.
CHAPTER 8

ELECTRODE AND ELECTROLYTE SURFACE ANALYSIS STUDIES

8.1 Scanning Tunnelling Microscopy (STM) Theory and Experimental Details.

The first scanning probe microscope was the scanning profilometer. A stylus probe was brought into contact with a surface and mechanically scanned across it. The image of the surface was constructed from the deflections of the stylus probe. However, the resolution of the scanning profilometer was limited by the sharpness of the probe and the deflection sensitivity.

The key breakthrough in achieving atomic resolution was through work carried out by Binnig et al in 1982. They realised that if an atomically sharp metallic tip could be maintained 10 Å from a conductive surface, tunnelling currents in the nA range could be easily detected. The tunnelling current could then be kept constant using a position feedback loop, which adjusted the tip position over the sample. The tip height as a function of its position over the surface provided atomic resolution images.

For a current to be detected quantum mechanical tunnelling must occur. In classical mechanics, an electron with energy $E$ moving in a potential $U$ is described by:

$$\frac{p^2}{2m} + U = E$$  \hspace{1cm} (8.1)

where $m$ is the mass of an electron and $p$ corresponds to its momentum.

When $E > U$, the electron momentum $p$ is greater than zero, conversely if $E < U$ the electron cannot penetrate into that region and this can be termed as a potential barrier. However, quantum mechanics describes the state of the same electron by a wave function satisfying the Schrödinger equation. This wave nature of the electron can be thought of as a 'cloud', the size of which is related to the
wavelength of the electron (a few angstroms). If the cloud collides with a barrier (≤10 Å thick) part of the cloud may penetrate the barrier and appear on the other side. This process is called tunnelling because the electron does not have enough kinetic energy to travel over the barrier, but is able to exist on the other side. A bias voltage must be applied in order to observe this tunnelling effect. Incidentally, this tunnelling effect explains some of the most basic phenomena observed in nature, for example, radioactive decay of plutonium by the ejection of an alpha particle from the nucleus occurs due to tunnelling.

STM can only be applied to the study of conducting and semiconducting materials. However, experiments can be performed in a variety of conditions, for example, in air, in inert gas, in ultrahigh vacuum, or in liquids and even electrolytes. The operating temperature ranges from absolute zero to a few hundred degrees centigrade. The metallic tip is usually a Pt/Ir, Au, W or Ta wire which is drawn into fine whiskers at the end. One of these whiskers, which is only one atom thick at the end will be predominant and will undergo the tunnelling process in the right conditions.

8.2 Atomic Force Microscopy (AFM) Theory and Experimental Details.

It was realised that the STM method exerts a force between the tip and the surface of the sample. This force is of the same magnitude as that of interatomic forces. This new effect gave rise to the first AFM, published by Binnig et al in 1986.197 Instead of using an STM tip whose direction is normal to the sample, they positioned it in an almost parallel direction so that its sharp edge was just above the surface. The tip, acting as a cantilever, exerts a force on the sample and minute deflections, as small as 10^-4 Å could be resolved.

The cantilever deflections are detected by optical means. A laser beam is bounced off a mirror and focused onto the end of the cantilever, opposite the tip. The back surface of the cantilever reflects the beam onto a split photo diode detector. The signal from this photo diode detector is plotted versus the sample position to form a topographical map of the surface.
A further advantage of this optical measuring system, is that photons impose only a tiny force upon the tip for transmission to the sample. This has allowed AFM to be used non-destructively to image adsorbed organics, for which the force exerted on the sample must be \( \leq 10^{-11} \text{ N} \).

The output of the detector is connected to a feedback controller which regulates the force between the sample and the tip by moving the sample up and down. The tips are either made of silicon or silicon nitride. Images of crystals and polymers have been obtained and AFM cantilevers can be made sufficiently soft to avoid damaging biomaterials, indeed, the entire process of a living cell infected with a virus was investigated \textit{in situ} using AFM. Atomic resolution is possible, for example, AFM images of a Au (111) surface has easily shown a Au-Au spacing of 2.9 Å.\(^{198}\) AFM has been used to image surfaces in ultrahigh vacuum, in air and in liquid.\(^{199}\)

To image a surface with atomic resolution the surface must be moved with the precision of less than that of an atom's length. This motion is accomplished using piezoelectric ceramics. When an electric field is applied across this material, it will expand in one direction and contract in another. The system used nowadays for both STM and AFM has a piezoelectric tube scanner which allows fine control in three directions, but consists of only a single unit.

8.3 STM Imaging of Sputter Coated and Screen Printed Platinum and Gold Electrodes.

An ARIS 3300 personal SPM (Burleigh Instruments) was used to study the surface of platinum and gold. A platinum/iridium tip was used to study areas of the following dimensions:- 2.5x2.5 μm, 1x1 μm, 500x500 nm, 250x250 nm, 100x100 nm, 50x50 nm and 25x25 nm.
The surface of the sputtered platinum was composed of peaks approximately 10 nm across, whereas, the sputtered gold electrode was composed of peaks approximately 30 nm across. This difference in peak size is probably due to a characteristic of the nucleation of gold and platinum atoms. As the rate of nucleation is dependent on the crystal face exhibited it can be proposed that the face exhibited during the deposition of gold in this manner promotes the addition of atoms, thus creating large peaks. Another possibility is that as gold has a lower melting point than platinum, then the gold will have a greater chance to undergo grain growth before fully solidifying. Figures 8.1 and 8.2 indicate the typical STM images of sputter coated platinum and gold films.

In the case of the screen printed platinum, long uniform grooves, 85 nm across, are present across the surface, these grooves appear to be due to the pattern of the screen during the printing process. However, the gold was printed using exactly the same screen type, but there was no evidence of uniform grooves on the surface of the gold. Figures 8.3 and 8.4 show the STM images obtained for screen printed platinum and gold.

Cross section analysis was also carried out on the images to determine groove and cluster sizes. Figure 8.5 indicates the cross section analysis for the image of the platinum. Further study of the screen printed platinum layer at a higher resolution, revealed peaks over the surface of the grooves approximately 15 μm in diameter.

The higher sintering temperature, or melting point, of platinum did not allow an adequate time to elapse during the curing process (at 850°C) for extensive grain growth to occur. Therefore, the pattern on the screen will, on the whole, remain. However, at 850 °C the gold is almost at its melting point, therefore grain growth occurred and a non-uniform surface composed of clusters 20 nm across resulted.
Figure 8.1  STM Image of a Platinum Sample Deposited by Sputter Coating.

Figure 8.2  STM Image of a Gold Sample Deposited by Sputter Coating.
Figure 8.3  STM Image of a Platinum Sample Deposited by Screen Printing.

Figure 8.4  STM Image of a Gold Sample Deposited by Screen Printing.
Figure 8.5 Cross-section of a STM Image of a Platinum Sample

Deposited by Screen Printing.
8.4 AFM Imaging of Cast Films of DAIS and Nafion®.

AFM images of the alumina substrate, freshly cast DAIS and Nafion® films and a Nafion® film which has undergone thermal activation were obtained using a silicon nitride tip and cantilever arrangement. The following areas were studied:-
70x70 μm, 35x35 μm, 7x7 μm, 2.5x2.5 μm, 1x1 μm, 500x500 nm and 25x25 nm.

Figures 8.6 and 8.7 are images of a cast Nafion® film, before and after thermal activation. After cross section analysis it was concluded that both films are constructed from clusters and cavities of various sizes. These cavities were considered to be remnants left from the casting process, i.e. during the evaporation of the solvent, areas which are either rich in polymer or rich in solvent exist. When all of the solvent has evaporated, a cavity will be left in the position where the solvent was in abundance.

There is no uniformity in the dimensions of these cavities. However, there is a trend in the diameter of the clusters. Prior to the heating process, the clusters were in the region of 1.6 μm across, after the thermal activation process, the clusters had amalgamated and the average cluster size became 3.1 μm. This apparent change in the structure is probably due to the thermal annealing above the glass transition temperature of the polymer, giving rise to a re-orientation of the side chains, improving the connectivity within the cast film.160

Figure 8.8 is an image obtained for the cast DAIS film. This polymer is extremely smooth and softer than the Nafion® film. These properties made it difficult to obtain a good resolution. A large cavity was observed which was found to have a diameter of 6.2 μm. To prove that the polymer films and not the substrate were being studied, AFM images of the alumina substrate were obtained. Figure 8.9 indicates the image obtained for this and verified that the polymer films were indeed being studied. The alumina substrate at this resolution shows markings produced by mechanical means, probably produced during the cleaning and polishing processes.
Figure 8.6 AFM Image of a Sample of Cast Nafion® Electrolyte, Prior to the Thermal Activation Process.

Figure 8.7 AFM Image of a Sample of Cast Nafion® Electrolyte, After the Thermal Activation Process.
Figure 8.8 AFM Image of a Sample of Cast DAIS Electrolyte.

Figure 8.9 AFM Image of a Sample of 96% Alumina Substrate.
8.5 Summary.

The STM images of sputtered platinum and gold indicated different grain growth mechanisms. The surface of the gold exhibited peaks three times the diameter of the peak observed on the surface of the sputtered platinum. The screen printed platinum indicated grooves running along the surface due to the warp and weft of the stainless steel mesh used during the printing process. These findings are most probably due to the higher melting point of platinum compared with gold, so that only suppressed nucleation and a reduced re-arrangement of the atoms could occur before the platinum layer fully solidified.

When an average value of the diameter of the platinum clusters produced by screen printing was obtained, it was found to be almost 15 \( \mu \text{m} \). This is approximately the same as the average diameter of the peaks produced by sputtering platinum. Therefore, the surface area and consequently the catalytic abilities of the platinum is expected to be reasonably similar for both methods of platinum metal deposition.

The thermally activated Nafion® film indicated a visible variation in the morphology of the polymer surface. Enlargement of the clusters had occurred, presumably due to the re-orientation of the polymer side chains, allowing greater linking of the ionic clusters throughout the film. The AFM imaging of a cast DAIS 585 film indicated an extremely smooth and pliant material. A relatively large cavity due to the evaporation of the solvent during the casting process was easily visible on the 35x35 \( \mu \text{m} \) image.
CHAPTER 9

GENERAL DISCUSSION AND CONCLUSIONS

9.1 Reiteration of the Original Objectives.

The present work was undertaken with the aim of establishing suitable materials, designs and production methods in order to develop a reliable and inexpensive CO sensor that functions at ambient temperature. All of the sensor designs possessed a planar substrate; either a 25x10 mm strip of 96% alumina (sensor numbers 1 - 28), or a commercially available polymer electrolyte film (sensor numbers 29 and 30), onto which electrodes were applied. This was carried out by either by the application of pressure to impregnate strips of catalysed cloth, or platinum and gold inks have been screen printed onto the alumina substrate, followed by the casting of an electrolyte film from a solution of the polymer.

A reliable test rig was designed and fabricated which could vary the level of humidity present in the test gas and could blend the analyte gas with air, in order to obtain a range of CO concentrations from one gas cylinder mixture.

Suitable electrochemical testing methods were then sought. A Solartron 1286 potentiostat and a 1260 frequency response analyser testing equipment, were incorporated into the test rig. Open cell potential measurements, cyclic voltammetry and AC impedance spectroscopy were utilised. The CVs were not only applied in order to possibly observe a current peak corresponding to the electro-oxidation of CO, but three CVs were applied at the start of each testing session as a ‘conditioning’ process to remove any remaining CO from a previous experiment. A range of CO concentrations were introduced to the test gas and the responses of the different sensor designs were obtained.

The ultimate aim of this project would be to produce a sensor which can be used in domestic premises. The British Standard Institution has produced a specification for electrically operated CO detectors. Consequently, experiments were carried out
to satisfy the requirements laid out in the most recent BSI standard. As a result, the relative humidity of the test gas was varied (in a clean air environment and in the presence of CO), and hydrogen and methane were introduced to the test gas. Also, long term testing of some of the sensor designs was carried out in order to study any ageing effects.

Modelling of the AC impedance responses obtained in clean air and in the presence of the analyte was considered to be a priority. The decrease in the charge transfer resistance due to the adsorption and limited electrochemistry of CO occurring at the surface of the platinum working electrode, was used to quantify the response of the sensor.

Assessment of the surface morphology of the electrodes and the electrolyte films was also considered to be important, especially, the appearance of the cast Nafion® film, before and after the thermal activation process.


9.2.1 Screen printing was found to be the best method of depositing pure platinum and gold electrodes compared with the techniques of sputter coating and vacuum evaporation. A home-made ink was successfully produced by mixing platinum black powder into a paste with carbon powder and glycerol. On printing, electrodes with a loading of 0.053 mg Pt cm⁻² were produced. Analysis of the X-rays produced whilst an SEM image was obtained, clearly verified the presence of platinum over the entire surface of such an electrode.

9.2.2 Application of 0.57 kN cm⁻² and a dwell time of two minutes was adequate in order to impregnate strips of commercial electrodes with a platinum loading of 0.35 mg Pt cm⁻² on a carbon cloth backing (ETEK) onto commercially available membranes of Nafion® 115 and Teflon® reinforced DAIS 585. A small amount of dissolved polymer (purchased in this form) was soaked into the ETEK material prior to pressing. This improved the intimate contact of the catalyst with the membrane.
9.2.3 The designs for sensor numbers 1 - 28, incorporated a gold reference electrode. Cyclic voltammetry was carried out in liquid electrolytes containing potassium ferricyanide and ferric chloride. Initially the presence of the oxidation and reduction peaks of the electroactive species at a platinum wire working electrode was studied when a sodium chloride saturated calomel reference electrode was present. The calomel reference electrode was then replaced by a gold wire reference electrode and a planar gold reference electrode. Both gold reference electrodes indicated a stable reference electrode potential at a value of +0.556 V versus the standard hydrogen electrode.

9.2.4 Electrochemical characterisation of the planar screen printed platinum electrodes in liquid electrolyte containing ferric chloride and potassium ferricyanide electrolytes indicated perturbed oxidation and reduction peaks for the electroactive species, i.e. compared to the results obtained at a platinum wire reference electrode, the oxidation peak occurred at a more anodic potential and the reduction peak occurred at a more cathodic potential. This observation was possibly due to two effects. Firstly, the behaviour of mobile species at the surface of a planar electrode can exhibit slow electron transfer kinetics. Secondly, the geometry of the planar working electrode and the calomel reference electrode in the electrochemical cell can influence the electrochemistry. In this case, the potential at the planar working electrode may be held at a range of potentials less than or equal to the applied potential at any instant in time during a cyclic voltammogram (refer to section 7.4).

9.2.5 The testing procedure of the application of three cyclic voltammograms as a 'conditioning' process was found to be a good technique of ensuring a common standard from which different experiments can be carried out on the sensors and the results could then be directly compared, i.e. the conditioning process is analogous to a calibration step. The subsequent change in the OCP in a positive direction, is attributed to the electro-oxidation of water and CO species on the surface of the platinum working electrode during the CV scans. The conditioning process involved the cycling of an applied potential between 0.00 V and +1.00 V versus the gold reference electrode. However, it is envisaged that it is only necessary to apply a DC potential at a single value which is sufficiently positive, in order to obtain the
same conditioning effect. The reverse scan indicated the electro-reduction reaction of platinum oxide at the working electrode.

9.2.6 The presence of a range of potentials at a platinum planar working electrode influenced the results obtained when the sensors were tested in an atmosphere containing CO. In this case, the gold reference electrode was also planar. The effect of this characteristic was that the current corresponding to the oxidation of CO appeared as a broad peak on the forwards scan of the CV. The electrochemical reduction of CO$_2$ was not observed on the reverse scan of the CVs because of the relatively weak adsorption of CO$_2$ on the Pt surface, therefore, making the electro-reduction reaction mass transfer limited.

9.2.7 AC impedance spectroscopy was utilised as the major testing technique of the sensors in this project. It was found to be a highly sensitive technique which led to a quantitative method of studying the responses of the sensors. The results obtained over an applied frequency range of 60 kHz - 0.1 Hz with a 10 mV AC amplitude produced a displacement on the Nyquist plot representation, indicating an uncompensated resistance, $R_{in}$, i.e. the resistance between the probe and the surface of the electrode. A semicircle relating to the electrolyte impedance was also observed, which is composed of the geometrical capacitance ($C_g$) and the bulk resistance ($R_b$). Many of the sensor designs indicated a second circular arc over the frequency range, which corresponded to the interfacial impedance, which is comprised of the double layer capacitance ($C_{dl}$) and the charge transfer resistance ($R_{ct}$).

9.2.8 On the addition of CO, the appearance of the second circular arc observed over the lower frequency range varied. The arc appeared to reduce in size, therefore suggesting that the overall impedance of the electrochemical system had decreased and that the magnitudes of $C_{dl}$ and $R_{ct}$ had been affected by the presence of the adsorbed analyte on the surface of the platinum working electrode. This apparent change in the interfacial impedance was due to a limited amount of CO oxidation occurring at the platinum working electrode due to the polarising effect of the 10 mV AC amplitude utilised during the AC impedance spectroscopy scan.
The presence of CO affected the double layer characteristics and the electro-oxidation of CO, due to the perturbing AC potential, reducing the polarisation resistance i.e. $R_{cr}$. The OCP value also registered a dramatic shift in a negative direction when CO was present. This was due to the formation of a mixed cell potential on the addition of the analyte, produced by the competition between O$_2$ and CO to adsorb onto the surface of the platinum catalyst.

9.2.9 An increase in the size of the working electrode area led to a reduction in the resistance between the probe and the electrode surface. This was denoted as a decrease in the $R_u$ value at 60 kHz on the Nyquist plot representation when sensor numbers 17 and 19 (working electrode areas of 0.25 cm$^2$ and 0.50 cm$^2$ respectively) were compared. A greater variation in the values of $R_{cr}$ and $C_{di}$ was also observed in the presence of CO when the working electrode area was doubled. Therefore, a working electrode area of 0.50 cm$^2$ for sensors based on the design of sensor numbers 1 - 28 was regarded as an advantage.

9.2.10 As the thickness of the cast electrolyte film was reduced, the overall impedance of the electrochemical system increased. Indeed, sensor number 20, which possessed a 10 μm cast DAIS film, mainly indicated the electrolyte impedance (the semicircle observed over a high frequency range) and only the start of the circular arc due to the interfacial impedance within the frequency range 60 kHz - 0.1 Hz, (refer to figure 5.9). This work also showed that sensor numbers 19 and 21 (20 μm and 15 μm respectively) indicated very similar results in clean air. However, on comparison of their responses to 1000 ppm CO, it was seen that the sensor with a 20 μm DAIS electrolyte underwent the greatest variation in the interfacial impedance (refer to figure 5.10). Therefore, it was concluded that a cast electrolyte film of thickness 20 μm was a beneficial characteristic and the subsequent sensors fabricated in this style incorporated an electrolyte film of this thickness.

9.2.11 Sensor number 19 possessed a rectangular working electrode, whereas sensor number 22 possessed an interdigitated working electrode. When the AC
impedance responses of these sensor designs were compared (both with an electrode area of 0.5 cm²), then distinct changes in the clean air response were observed within the frequency range 60 kHz to 0.1 Hz. The semicircle observed over the high frequency range was dramatically reduced in size, implying a significant decrease in the electrolyte impedance. This is most probably due to a reduction in the geometrical capacitance. \( R_{ce} \) and \( C_{dl} \) appeared to be approximately the same.

9.2.12 The results obtained from sensor number 27, which also possessed an interdigitated working electrode, closely resembled those obtained from sensor number 22. This suggested that the characteristics of the small semicircle over the high frequency range was due to the incorporation of an interdigitated working electrode in the design, rather than any other factor.

9.2.13 The work carried out on sensor number 28, which possessed a Pt/C electrode, produced an AC impedance response which indicated a low overall impedance, even though the lower frequency limit had to be extended to 0.01 Hz in order to observe the interfacial impedance characteristics. Therefore, the screen printing of an ink produced by the mixing of platinum black powder, carbon powder and glycerol produced a highly conductive electrode material. Unfortunately, the results obtained by AC impedance spectroscopy did not register a variation when CO was present in the test gas. It was concluded that the platinum loading of 0.053 mg Pt cm⁻² was not sufficient to allow an adequate adsorption of CO on the surface of the working electrode. However, if this loading was increased, it may be predicted that a response to CO will be observed.

9.2.14 A sensor which possessed a cast Nafion® electrolyte film, with no further pre-treatment, indicated a very large overall impedance in the region of \( 10^7 \) - \( 10^8 \) Ω. Trends in the impedance value with respect to the area of the working electrode and the thickness of the electrolytes were obtained, however, a response to CO was not observed. The thermal activation of a cast Nafion® film, caused the overall impedance of a sensor system to decrease by approximately one hundred times. This implied that the thermal activation process had been a beneficial step in the
production of the sensors. The AFM images of two cast Nafion® films, before and after the thermal activation process, suggested that heating to above the glass transition temperature of the polymer had enlarged the clusters which existed on the surface of the polymer, perhaps signifying that a better connectivity was now present throughout the entire polymer film.

9.2.15 The AC impedance response of sensor number 29, produced by the pressing of catalyst loaded cloth (ETEK) onto a commercially available Nafion® 115 membrane, denoted a system with a low overall impedance of 1000 Ω. A response to a concentration of CO as low as 100 ppm was observed, and a trend in the reduction of the interfacial impedance with respect to this CO concentration was also obtained. The AC impedance response of sensor number 30, produced by the same method as sensor number 29, with a commercially available DAIS 585 electrolyte membrane, showed a system with a higher overall impedance of approximately 3000 Ω, and the value obtained for $R_e$ indicated a similar value to that obtained with a cast film of DAIS electrolyte. Both systems registered a slight increase in impedance with time. It was concluded that this was due to the delamination of the electrode strip, which reduced the active area of the electrode in contact with the electrolyte. If the results of sensor numbers 29 and 30 are compared, it can be concluded that for this design the Nafion® 115 membrane produced the superior results.

9.2.16 If the results of sensor numbers 1-28 are compared, it is possible to conclude that the cast DAIS electrolyte films produced the more beneficial characteristics for a sensing system, such as a low impedance and a good response to CO. Sensor number 22, which possessed a 20 µm DAIS film did not indicate any adverse effects of ageing within a 4½ month time scale. The AFM images of a cast DAIS film implied an extremely smooth and pliant material.

9.2.17 The appearance of the semicircles on the Nyquist plots suggested that as the relative humidity of the test gas decreased, the impedance of the electrochemical sensor system increased. This is due to the removal of water in the
cluster arrangements in the electrolyte film as the RH level decreased. This would lead to a decrease in the proton conductivity characteristics. The reduction in RH caused a change in the impedance in an almost linear fashion, however, tests were not carried out to study the reproducibility or hysteresis of the response as the RH level was continually increased and decreased.

9.2.18 The sensors did not respond to an atmosphere containing methane. This is because of the relatively weak adsorption of CH₄ on the surface of the platinum. Therefore, the electro-oxidation reaction would be mass transfer limited. Hydrogen, which readily adsorbs onto the surface of a platinum catalyst, did perturb the AC impedance from the plot obtained in clean air conditions. It was concluded that a limited amount of oxidation of the analyte had occurred due to the application of a 10 mV AC amplitude during an AC impedance spectroscopy scan. The change in the response of the sensor to H₂ was less rapid compared with the variation obtained by the sensor when the same concentration of CO was present.

9.2.19 An equivalent circuit was successfully applied to the AC impedance spectroscopy results and values for $R_{an}$, $R_b$, $C_s$, $R_{ct}$ and $C_{dl}$ were obtained. The trend observed in the value of $R_{ct}$ when CO was introduced to the test gas was thought to be a reliable method of following the response of the sensor. The circuit was found to contain a resistor ($R_a$) in series with two Randles-type arrangements, i.e. a resistor in parallel with a capacitor. The Randles circuit corresponding to the electrolyte impedance contained a constant phase element (Φ) which was necessary to produce the flattened appearance of the circular arc.

9.2.20 As a trend in the value of $R_{ct}$ was considered to be a reliable parameter to follow the variation of the sensor's output, a relatively simple formula was obtained which made it possible to provide an estimate for the resistance using the $Z'$ and $Z''$ values at a single frequency value. In this way calibration curves were produced which indicated how the resistance at that single frequency value varied with a certain CO concentration, making it a favourable technique of measuring the response of the sensor, both qualitatively and quantitatively.
9.3 Recommendations for Further Work.

Further work in the area of reducing the platinum loading, thereby reducing the production costs of the working electrode, is recommended and the effect of a thicker electrolyte film and a larger surface area of the working electrode would be a beneficial study. Some suggestions for further work are outlined below.

9.3.1 Catalytic Additions to the Working Electrode Material.

The work carried out on a Pt/C ink, produced by mixing platinum black powder with carbon powder and glycerol, suggested that 0.053 mg Pt cm\(^{-2}\) was insufficient to allow an adequate amount of CO adsorption to occur at the surface of the working electrode. However, the work carried out with the commercial Pt/C cloth (ETEK) for sensor numbers 29 and 30 clearly indicated that a platinum loading of 0.35 mg Pt cm\(^{-2}\) was sufficient. Therefore, further work could be carried out to produce more inks with a level of 0.053 < Pt loading < 0.35 mg cm\(^{-2}\) in order to find the minimum loading at which a sensor will respond. This work provides an ideal method of reducing the catalytic loading and therefore, the production costs of these sensor systems.

Laiyuan et al recently compared the effect of CO adsorption on three systems; platinum/alumina, rhenium/alumina and platinum-rhenium/alumina.\(^{203}\) They concluded that the amount of chemisorbed CO on the Pt-Re catalyst was greater than the sum of CO adsorption on the unimetallic catalysts at 25 °C. Catalytic additions of rhodium to platinum on alumina have been carried out by Ward et al.\(^{204}\) They studied the adhesive and catalytic properties of rhodium on alumina and ascertained that such electrodes have enhanced CO adsorption.

Gasteiger recently discovered that CO adsorbs readily on surface sites of ruthenium.\(^{205}\) Shen et al followed this work by making additions of ruthenium and tungsten oxide, WO\(_3\), catalysts to platinum.\(^{206}\) Cyclic voltammetry results with and without the catalysts present indicated a decrease in the applied potential required
for the oxidation of CO by approximately 50 mV. Therefore, when the ideal ratio of Pt:C:glycerol has been determined, the inks could be adapted by replacing some of the platinum with ruthenium or rhodium powder, in the hope of providing an improved performance of the sensing system when CO was present.

9.3.2 Further Long-term Testing.

The sensor design which indicated the most reproducible response over time was the planar design with a cast DAIS membrane. Sensor number 22 was tested over a period of 4½ months and exhibited hardly any adverse effects due to ageing. However, in a real-life situation, the sensor may be expected to function from between one to two years, therefore, testing should be carried out over this time range. The response of the sensors which possess a thermally activated Nafton® electrolyte should also be tested over a longer period of time, in order to see if the increase in impedance stabilised and the response became reproducible.

9.3.3 Further Variation of the Electrode and Electrolyte Parameters.

When the area of the working electrode was increased, an improved response to CO was obtained. The maximum working electrode area possible was 10×10 mm, i.e. an active working electrode area of 0.5 cm². This limitation was due to the dimensions of the alumina strips and the design of the stainless steel screens used during printing. However, these limitations could be overcome and working electrode areas of 0.75 cm² and 1.00 cm² would have been produced to see if another increase in the response to CO was obtainable.

An electrolyte thickness less than 20 μm indicated a high impedance, with the 60 kHz to 0.1 Hz frequency scan dominated by a circular arc corresponding to a large electrolyte impedance. Therefore an electrolyte thickness of 20 μm was used in many of the sensor designs. However, further sensor designs with a working electrode area of 0.5 cm² and cast DAIS electrolytes of 30, 40 and 50 μm could be produced and the AC impedance spectroscopy results would be compared to those
obtained by sensor numbers 20, 21 and 19 (10, 15 and 20 µm DAIS membranes respectively). It is envisaged that the bulk resistance would be observed to decrease again. However, it is possible that the diffusion of gases through the membrane would be impeded if the membrane became too thick. Therefore, a balance between the requirement of a low impedance, but a film thickness that would still allow the diffusion of the gas to the surface of the electrode, would be sought.

9.3.4 Single DC and AC Measurements.

It has been proposed in section 9.2 that a ‘conditioning’ process of three cyclic voltammograms could be replaced by the pulsing of a DC potential at a single value which is sufficiently positive, in order to obtain the same ‘conditioning’ effect. Equation 7.14, which made it possible to obtain an estimate for the resistance using the $Z'$ and $Z''$ values obtained at a single frequency value, has been shown to be an extremely useful and simple method of measuring the response of the sensor.

It is envisaged that it is not necessary to run an AC impedance scan over a frequency range, but to apply a single frequency with an interrogative AC amplitude of 10 mV and to record the values of $Z'$ and $Z''$ at this one value of frequency. For example, if the response of sensor number 22 was to be tested in this way, then the application of an interrogative wave at 0.1 Hz would be adequate. Hence, the requirement of a pulse of a DC potential as a ‘conditioning’ process and the application of an AC impedance measurement at a single frequency value would simplify the testing regime of the detection system.

9.3.5 A Suitable Microcontroller for the Detection System.

Before the sensor can be thought to be a commercial item, it must have adequate electronics incorporated so that the working electrode is active, the atmospheric gases are sampled and so that a signal can be generated when the CO level reaches a certain concentration. After some investigations in this area, it was discovered that a sensor system such as this is an ideal application for electronic controllers
that already exist. Some thought has been put into the requirements of a so-called microcontroller and how the a reasonable system may be accomplished.

The requirements of the sensing system which a microcontroller could provide are:

- Application of a pulsed DC potential across the working electrode and reference electrode as the ‘conditioning’ step at a fixed time interval.
- Application of a single frequency wave with a 10 mV AC amplitude at a fixed time interval.
- Measure the real and imaginary impedance values and calculate the resistance.
- Save two minutes of data (resistance values stored in the RAM).
- Compare the most recent resistance output to previous values held in the memory.
- Sound an alarm in accordance with the BSI standard for CO concentrations.
- Compensate for a possible decrease in output over time, due to:
  - ageing, possibly due to the poisoning of the electrodes,
  - battery output decreasing.

The Philips 87C550 microcontroller is an ideal example of a chip which could control the testing regime of the sensing system. It possesses a sufficient amount of ROM (4 k) to produce an audible alarm and perhaps even an LED display. 128 bytes of RAM represents the amount of memory available to hold the collected data, therefore, if the resistance output of the sensor is measured every ten seconds, there will be twelve lots of values at eight bits each, hence a requirement of 96 bytes.

An important requirement is an analog/digital converter for the measurement of sensor resistance and the output to the alarm. The microcontroller can produce the AC waveform at the desired frequency and amplitude, by the modification of one of the pulse width modulated outputs. It also possesses two timers, which will be utilised for the pulsing of the DC and AC voltages. The other important necessity is a watchdog timer. Its purpose is to reset the microcontroller within a reasonable
amount of time if it enters an erroneous state, possibly due to a programming error, or electrical noise.

The power down option (CMOS) is an added attraction of this particular application. CMOS is the microcontroller’s ability to either have idle mode or total power-down in between sampling to reduce the power consumption and hence, make the battery last a lot longer. An example to show how useful this option could be, is if you consider that a typical microcontroller may consume 10 mA in normal continuous running mode, in a certain application the battery may discharge in 10 hours. If in the same application the idle mode or power down options are used, the battery may remain charged for 66 hours or 800 days respectively.

9.3.6 Evading the Adverse Effect of Relative Humidity.

The value of resistance, calculated by equation 7.14 at 0.1 Hz, indicated a relationship between the resistance and the relative humidity, i.e. as the RH decreased, the resistance increased. The responses of the sensor system in clean air conditions and in an atmosphere containing the gaseous analyte were affected. Research into the variation of the resistance output of the sensor system to a range of CO concentrations (and interfering gases) could be studied in a range of humidity conditions, so that the resistance values corresponding to the dangerous concentrations of CO could be obtained for any possible RH conditions.

It could then be envisaged that the sensing system could also contain a RH monitor, the output of which could be measured by a microcontroller similar to the one described in section 9.3.5. Tables of the variation in the measured resistance value with respect to the gas concentration and the RH level could be stored in the memory (ROM) of the microcontroller, so that false alarms would be avoided if the RH in the domestic premises altered. Hence, a simple and reliable battery powered sensing system would be produced.
REFERENCES


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BIBLIOGRAPHY


## APPENDIX I

**Details of the Sensors Tested.**

<table>
<thead>
<tr>
<th>Sensor no.</th>
<th>Electrolyte material</th>
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<th>Active area of Pt WE</th>
<th>DC and/or AC tests?</th>
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</tbody>
</table>

WE/RE and WE/CE correspond to these electrodes being interdigitated, and ΔH refers to the thermal activation treatment of the cast polymer film.
APPENDIX II

Derivation of Resistance and Capacitance Equations.

A.C. impedance terms:

- $Z'$ = real impedance
- $Z''$ = imaginary impedance
- $C$ = coating capacitance
- $R$ = coating resistance
- $f$ = frequency
- $\omega = 2\pi f$

$$Z' = \frac{R}{1 + \omega^2 R^2 C^2} \quad \text{eq. 1}$$

and

$$Z'' = \frac{\omega CR^2}{1 + \omega^2 R^2 C^2} \quad \text{eq. 2}$$

Obtain $C$ in terms of $Z'$ and $Z''$

$$1 + \omega^2 R^2 C^2 = \frac{R^2}{Z'} \quad \text{eq. 3}$$

and

$$1 + \omega^2 R^2 C^2 = \frac{\omega CR^2}{Z''} \quad \text{eq. 4}$$

$$\Rightarrow \quad R = \frac{Z''}{\omega CZ'} \quad \text{eq. 5}$$

To find an equation for $C$, divide through by $R^2$ and substitute eq. 5 into eq. 2.

$$\therefore \quad Z'' = \frac{\omega C}{\sqrt{\frac{1}{Z'}^2 + \omega^2 C^2}} \quad \Rightarrow \quad Z'' = \frac{\omega C}{\omega^2 C^2 (\frac{Z''^2}{Z''^2} + 1)} \quad \Rightarrow \quad Z'' = \frac{1}{\omega C\left(\frac{Z''^2}{Z''^2} + 1\right)}$$

$$\Rightarrow \quad Z'' = \frac{1}{\omega C\left(\frac{Z''^2}{Z''^2} + \frac{Z''^2}{Z''^2}\right)} \quad \Rightarrow \quad Z'' = \frac{\frac{Z''^2}{\omega Z''^2 (Z''^2 + Z''^2)}}{\omega Z''^2} \quad \Rightarrow \quad C = \frac{Z''^2}{\omega Z''^2 (Z''^2 + Z''^2)}$$

To find an equation for $R$, substitute eq. 5 into eq. 1.

If

$$R = \frac{Z''}{\omega CZ'}$$

then

$$C = \frac{Z''}{Z'\omega R}$$

and

$$Z' = \frac{\frac{R}{1 + \omega^2 R^2 C^2}}{\omega^2 R^2 Z''^2}$$

$$\therefore \quad R = \frac{Z''^2 + Z''^2}{Z''^2} \quad \text{(eq. 1)}$$

Hence,

$$R = \frac{Z''^2 + Z''^2}{Z''^2} \quad \text{(7.14)}$$

and

$$C = \frac{Z''/\omega}{(Z''^2 + Z''^2)} \quad \text{(7.15)}$$
APPENDIX III

Conferences Attended.

- East Midlands Electrochemistry Group Meeting, University of Leicester, 30th March 1995.
- National Instruments Data Acquisition Seminar, Leicester, 14th June 1995.
- Poster Presentation at the Royal Society Analytical Chemistry Conference, R&D Topics and SAC Meeting, University of Hull, 10-14th July 1995.
- Poster Presentation at the 188th Electrochemical Society Meeting, Chicago, IL, 8-13th October 1995.
- East Midlands Electrochemistry Group Meeting, Coventry University, 3rd April 1996.
- Physics World Exhibition, Telford Exhibition Centre, 24th April 1996.
- Participant in the RSC’s Initiative for Emerging Professionals in Analytical Science 1996, Buxton, 26th-29th April 1996.
- Poster Presentation at the Royal Society Analytical Chemistry Conference, R&D Topics, Nottingham Trent University, 22-23rd July 1996.