

THE DEVELOPMENT OF ELECTROCHEMICAL SENSORS
FOR BLOOD GAS ANALYSIS

by

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To Nicola

ABSTRACT

Electrochemical devices for the estimation of the respiratory gases, oxygen and carbon dioxide, have been developed and improved. A study of the mechanism of the reduction of CO_2 and O_2 in Dimethylsulphoxide on rotating disc and ring disc electrodes is described and mechanisms for the reduction of CO_2 and O_2 are presented. The results were used to develop new membrane electrodes for CO_2 detection. A theory about CO_2 reduction in a membrane electrode is presented and experimentally verified that supports the CO_2 reduction mechanism presented. An electrode is described that uses a metallised membrane as an electrochemical oxygen filter to allow simultaneous detection of oxygen and CO_2 . Joint CO_2/O_2 electrodes for transcutaneous blood gas analysis and breath analysis are described. Improvements to conventional oxygen membrane electrodes by using the $\text{Ni}(\text{OH})_2$ couple as counter electrode to prolong the electrode life, and 1,8 Dihydroxyanthroquinone in the electrolyte to improve the response time of the electrode are discussed.

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CHAPTER 1

INTRODUCTION

The work described in this thesis has been to develop and improve electrochemical devices for the estimation of the respiratory gases, oxygen and carbon dioxide. Although detection of these gases is important in many environments, this work is primarily concerned with medical devices. This chapter will discuss why and where respiratory gas measurement is necessary. Present techniques for the determination of these gases are described, and previous studies on the electrochemistry of oxygen and carbon dioxide will be discussed.

1.1. Applications of Gas Sensors

Electrochemical sensors have been developed for many gases and environments. Of particular importance are medical applications, where measurement of carbon dioxide and oxygen is often required. Anaesthetic gases (nitrous oxide and halothane) are also important, and it is necessary to measure their partial pressures in anaesthetic gas mixtures in order to prevent often tragic accidents^(1,2) occurring in operations. Electrochemical devices have recently been developed for this purpose.^(3,4)

Oxygen and CO₂ levels are measured in the blood and in inspired and exhaled gases in order to measure the oxygen uptake of a patient. The measurement of blood gas

levels is necessary in preterm (premature) babies in respiratory distress.⁽⁵⁾ In, for example, the Munich area, 10% of all newborn babies need special care in children's hospitals.⁽⁶⁾ Table 1.1 shows the first day diagnoses of a sample of ill newborn infants. The main problem is surfactant deficiency syndrome. A surfactant coats the interior of the lungs and stops the alveoli (where blood gas exchange occurs) from collapsing due to surface tension. Lack of surfactant means the baby is unable to breathe efficiently, so blood oxygen levels fall and CO₂ levels rise (hypoxemia), causing the baby to turn blue in extreme cases.

If the baby is given an excess of oxygen, leading to an abnormally high blood oxygen level (hyperoxemia), then a condition called retrolental fibroplasia can result - fibrous tissue accumulates in the retina, causing retinal detachment and hence blindness.^(7,8)

The baby's blood oxygen and CO₂ levels need therefore to be continually monitored. Continuous measurement is important for two reasons:-

- 1) The baby has a small blood volume (typically 85 cm³) so it is unwise to extract frequent blood samples. Also the trauma involved in inserting a needle into the baby may put its life in jeopardy.
- 2) Single measurements are not particularly useful as blood oxygen and CO₂ levels are subject to considerable variation.⁽⁹⁾

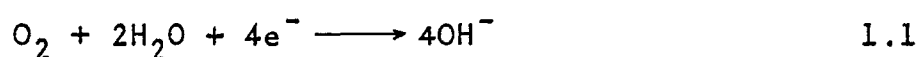
Table 1.1. First day diagnoses at the Newborn Intensive
Care Unit, Munich Children's Hospital -
June 30, 1976

	Premature infants n = 236		
	Full term infants n = 223		
	Total	in cardio- respiratory failure	respiratory supporting treatment necessary
Surfactant deficiency syndrome	84	84	82
Wet lung syndrome	20	20	1
Postapphyxia syndrome	25	20	13
Sepsis	42	22	14
Malformations	35	12	8
Normal premature	52		
Small for dates	38		
Infants of diabetics	12	4	
Hyperbilirubinemia	41	10	8
Maladaptation	110	40	13
	459	217	139

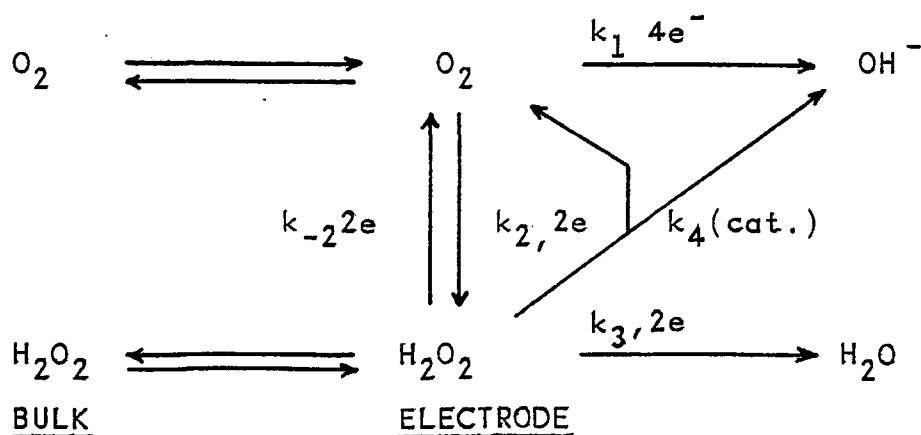
In conclusion, continuous monitoring of blood gas levels is essential, as only continuous monitoring will allow instant diagnosis of hypoxemia or hyperoxemia. Methods of continuous blood gas analysis will be discussed later in this chapter.

1.2. Membrane Electrodes

Gas concentrations are frequently measured by polarography. A potential is applied to an electrode sufficient to cause reduction or oxidation of the gas at a transport limited rate. The resulting current is proportional to the gas concentration. The most common polarographic gas electrode is the oxygen electrode, which measures gaseous and dissolved oxygen levels. Oxygen is reduced in aqueous solutions at the electrode by a very complex process, the simplified overall equation being:-



The actual reaction scheme is far more complex.^(10,11) Merkulova^(12,13) has described the various processes in terms of the following reaction scheme:-



Oxygen at the electrode surface may be reduced by a four electron pathway (rate constant k_1) to give water, or it may be reduced by a two electron process to give peroxide (rate constant k_2). The peroxide may then either escape to the bulk of the solution, be reduced further (r.c. k_3), or undergo disproportionation. Disproportionation may occur via a local cell mechanism involving the processes described by k_{-2} and k_3 (14,15,16), or by a heterogeneous mechanism involving surface oxide formation, characterized by k_4 . (17)

In a practical polarographic oxygen sensor the number of electrons transferred, and therefore the sensitivity, may change if peroxide escapes from the electrode surface. It is therefore necessary to prevent bulk peroxide formation. (18)

In many applications bare metal electrodes are unsuitable for the measurement of gases, due to electrode poisoning. For example blood oxygen cannot be determined by a bare electrode due to protein contamination. Also the current at a stationary electrode is greatly dependent on stirring effects. These problems were overcome by Clark (19) who proposed a device in which a thin gas permeable polymer membrane separated the external environment from the electrode. A typical electrode is shown in Figure (1.1). The membrane prevents contamination of the electrode and serves to establish a more reproducible diffusion layer, thereby reducing stirring effects.

to current measuring circuit

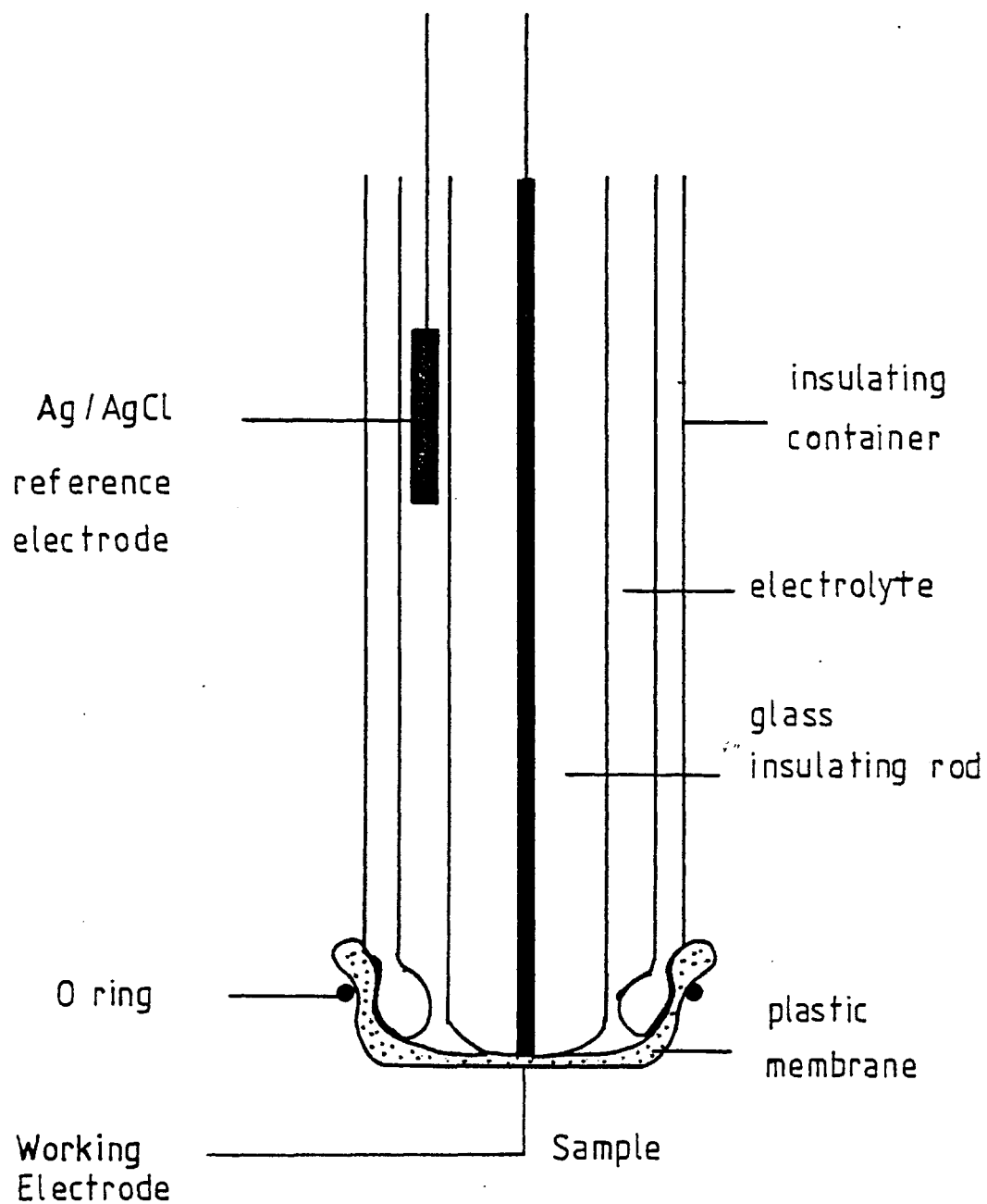
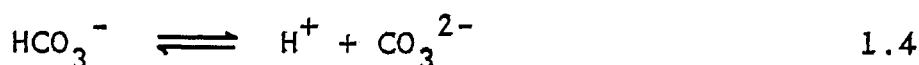
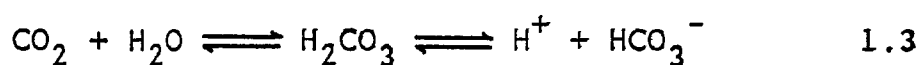
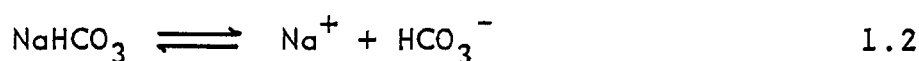


FIGURE 1.1. A Clark Membrane Electrode

The electrode materials and electrolyte are dependent upon the gas to be measured. For oxygen the electrode is typically gold, platinum or silver with a reference electrode of silver chloride and a buffered alkaline electrolyte. Typical membrane materials are polypropylene, polyethylene and PTFE, of thickness from ca 6 μm to 50 μm . Oxygen membrane electrodes have been extensively reviewed by Fatt⁽²⁰⁾ and Hitchman.⁽²¹⁾

Carbon dioxide detection is presently achieved with a different type of membrane electrode^(22,23,24,25) shown in Figure (1.2). A thin film of sodium bicarbonate solution in contact with a p.H. electrode is enclosed by a CO_2 permeable membrane, and is in equilibrium with CO_2 in the external environment. The equilibria existing in the electrode (Figure (1.3)) are:-



$$K_1 = \frac{a_{\text{HCO}_3^-} a_{\text{H}^+}}{a_{\text{H}_2\text{CO}_3}} \quad 1.5$$

$$K_2 = \frac{a_{\text{H}^+} a_{\text{CO}_3^{2-}}}{a_{\text{HCO}_3^-}} \quad 1.6$$

Electroneutrality gives:-

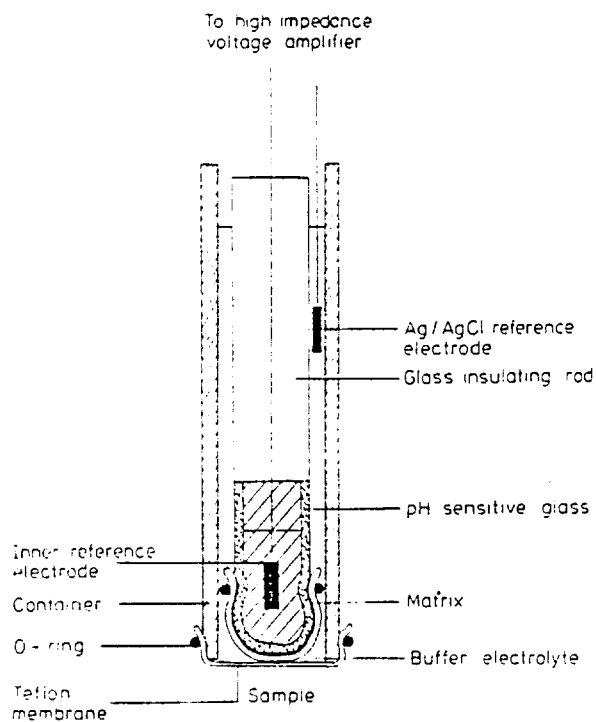


FIGURE 1.2. A CO₂ Membrane Electrode

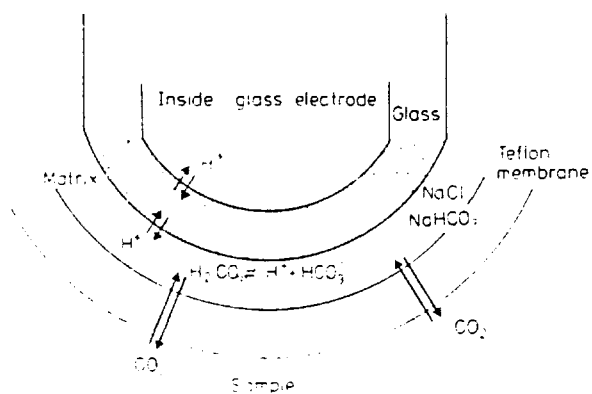


FIGURE 1.3. Equilibria in the CO₂ membrane electrode.

$$a_{H^+} + a_{Na^+} = a_{OH^-} + a_{HCO_3^-} + 2a_{CO_3^{2-}} \quad 1.7$$

$$\text{Also } a_{OH^-} = \frac{K_w}{a_{H^+}} \quad 1.8$$

Where K_w is the ionic product of water

Substituting for a_{OH^-} and $a_{CO_3^{2-}}$ gives

$$a_{H_2CO_3} = \alpha_{pCO_2} = \frac{a_{H^+}^2 + a_{H^+}a_{Na^+} - K_w}{K_1(1 + 2K_2/a_{H^+})} \quad 1.9$$

Where α is the Henry's Law solubility coefficient of CO_2 . In water without sodium bicarbonate eqn. 1.9 approximates to:

$$\alpha_{pCO_2} = a_{H^+}^2/K_1 \quad 1.10$$

Hence, the relation between p_{CO_2} change and pH change is given by:

$$\Delta \log p_{CO_2} = 2\Delta pH \quad 1.11$$

When the solution contains sodium bicarbonate above 1 mM, equation 1.9 approximates to:

$$\alpha_{pCO_2} = \frac{a_{H^+} a_{Na^+}}{K_1} \quad 1.12$$

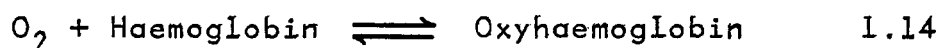
$$\text{Hence } \Delta \log p_{CO_2} = \Delta pH. \quad 1.13$$

The addition of sodium bicarbonate therefore doubles the electrode sensitivity, which is defined as $\Delta \text{pH} / \Delta \log \text{pCO}_2$. Severinghaus⁽²⁵⁾ found the response of a pCO_2 electrode to be linear in the range 1.4% to 11.4%, but the response to a fall in pCO_2 was found to be much slower than to a pCO_2 increase.

A new pCO_2 electrode, which measures conductance changes in the bicarbonate solution layer has recently been described^(26,27), and a conductance CO_2 electrode for breath analysis has been developed.⁽²⁸⁾

1.3. Electrochemical Blood Gas Analysis

The respiratory function of blood is to transport oxygen from the environment to the tissues, where aerobic metabolism takes place, and carbon dioxide back to the lungs. Oxygen is transported as dissolved gas, and as oxyhaemoglobin. The shape of the oxygen binding curve, which indicates the position of the equilibrium:



is sigmoidal and pH dependent (Figure 1.4).⁽²⁹⁾

Haemoglobin, which permits blood to carry about sixty-five times as much oxygen as plasma,⁽³⁰⁾ is saturated with oxygen at the pO_2 in the lung alveoli, and liberates oxygen where the pO_2 and pH are lower.⁽³¹⁾

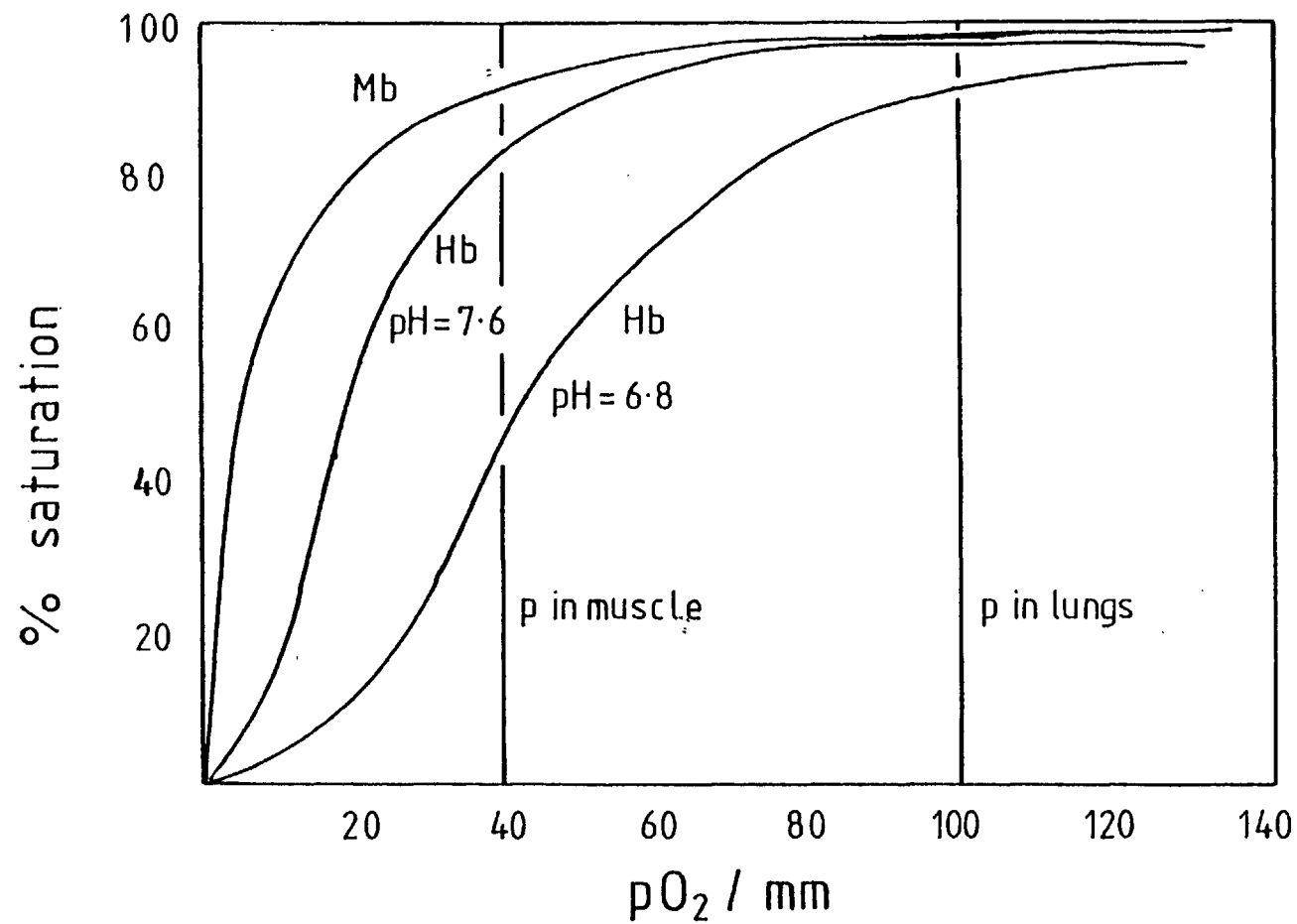


FIGURE 1.4. The oxygen binding curves for myoglobin (Mb) and haemoglobin (Hb). Note the pH dependence of the latter.

Sixty percent of carbon dioxide in the blood is transported as a carbamino complex with terminal aliphatic amino groups on the haemoglobin. Remaining CO_2 is transported as dissolved gas and as bicarbonate.

1.3a. In Vitro Analysis

In vitro blood gas analysis involves the transfer of a blood sample from patient to analyser, therefore gas tight sampling is necessary. Speed is also important, because metabolism of the blood sample will change its pO_2 and pCO_2 .⁽³²⁾ The sample is injected into a cuvette maintained at 37°C , which houses the oxygen and CO_2 electrodes.

1.3b. In Vivo Analysis

Intravascular and transcutaneous electrodes are used for in vivo analysis. Intravascular electrodes are commonly used for preterm infants. The electrode measures arterial gas levels, and is housed in a catheter tip which is surgically inserted into the umbilical artery of the infant so the electrode is situated in the abdominal aorta. The catheter is also used for blood sampling, infusion and blood pressure measurement. Figure (1.5) shows a typical catheter electrode for the measurement of oxygen.

Many intravascular oxygen electrodes have been described (e.g. (33,34,35,36,37)) in the literature, which

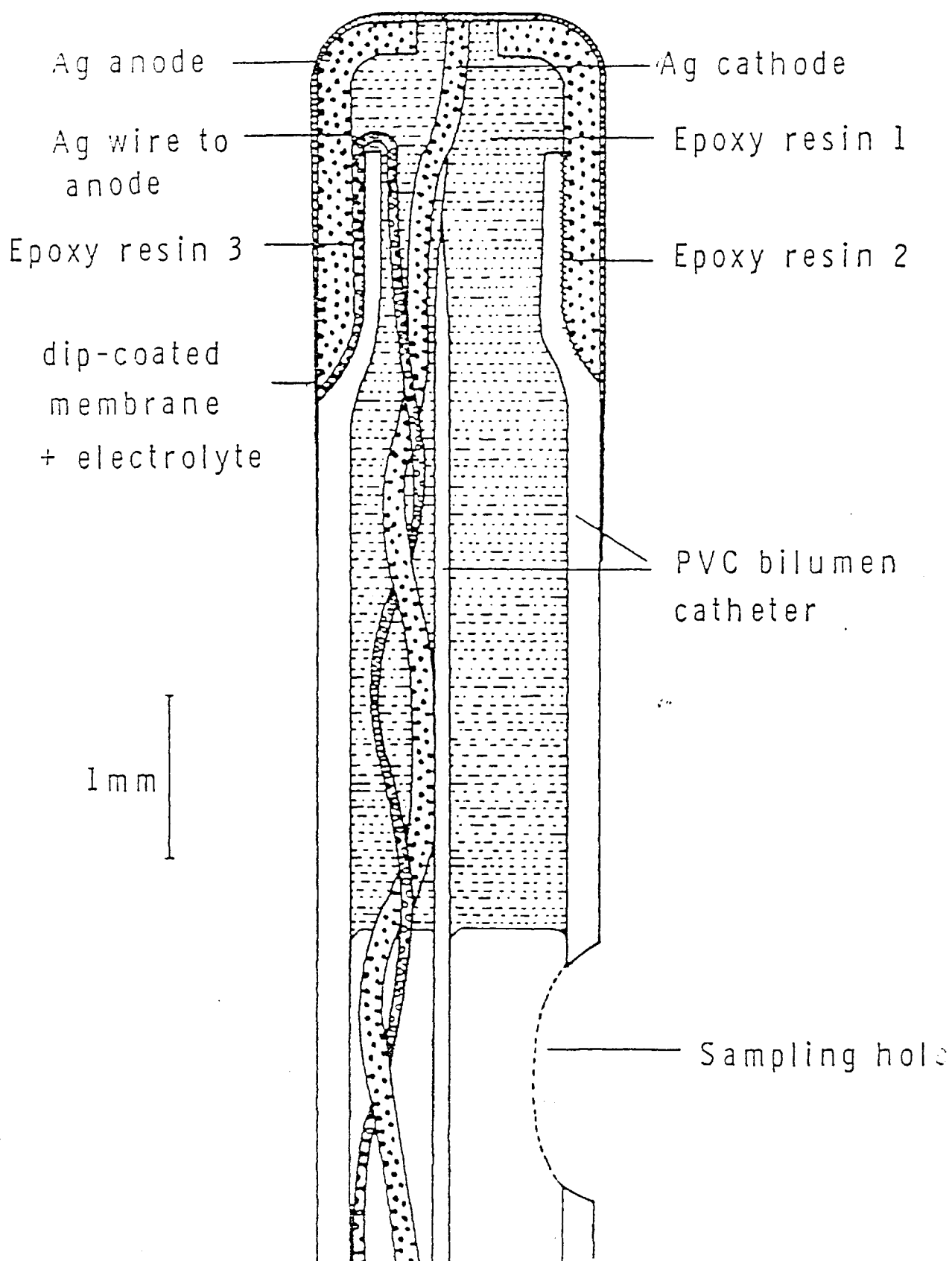


FIGURE 1.5. A typical catheter electrode, manufactured by Searle.

has been reviewed by Fatt.⁽²⁰⁾ The devices are miniature Clark type electrodes which typically fit into a 1-2 mm diameter catheter. The membrane is normally dip-coated onto the electrode.

Intravascular CO₂ electrodes are not as common as oxygen electrodes - as it is not practical to fit two catheters into an infant a joint electrode is necessary to measure both CO₂ and O₂. Such a device has been described by Parker et al.⁽³⁸⁾

The main drawback of intravascular electrodes lies in the risk of thrombosis and infection, as the technique is invasive. A non-invasive technique for blood gas analysis was introduced in the early 1970's by Huch⁽³⁹⁾ and Eberhard,⁽⁴⁰⁾ which measures blood gas levels transcutaneously. A heated (42°C-44°C) membrane electrode sited on the skin surface causes vasodilation of the dermal capillaries, allowing a higher rate of blood gas perfusion to the electrode. The oxygen tension at the skin surface rises from a normal value of ca 1-4 mm Hg⁽⁴¹⁾ to arterial levels. The correlation between skin surface pO₂/CO₂ and arterial pO₂/CO₂ values is particularly good in infants.

A typical transcutaneous electrode is shown in Fig. (1.6). The heater is controlled by an electronic circuit (see Chapter 3), which incorporates the two thermocouples monitoring skin surface temperature. Various transcutaneous pO₂ sensors have been developed⁽⁴²⁻⁴⁵⁾

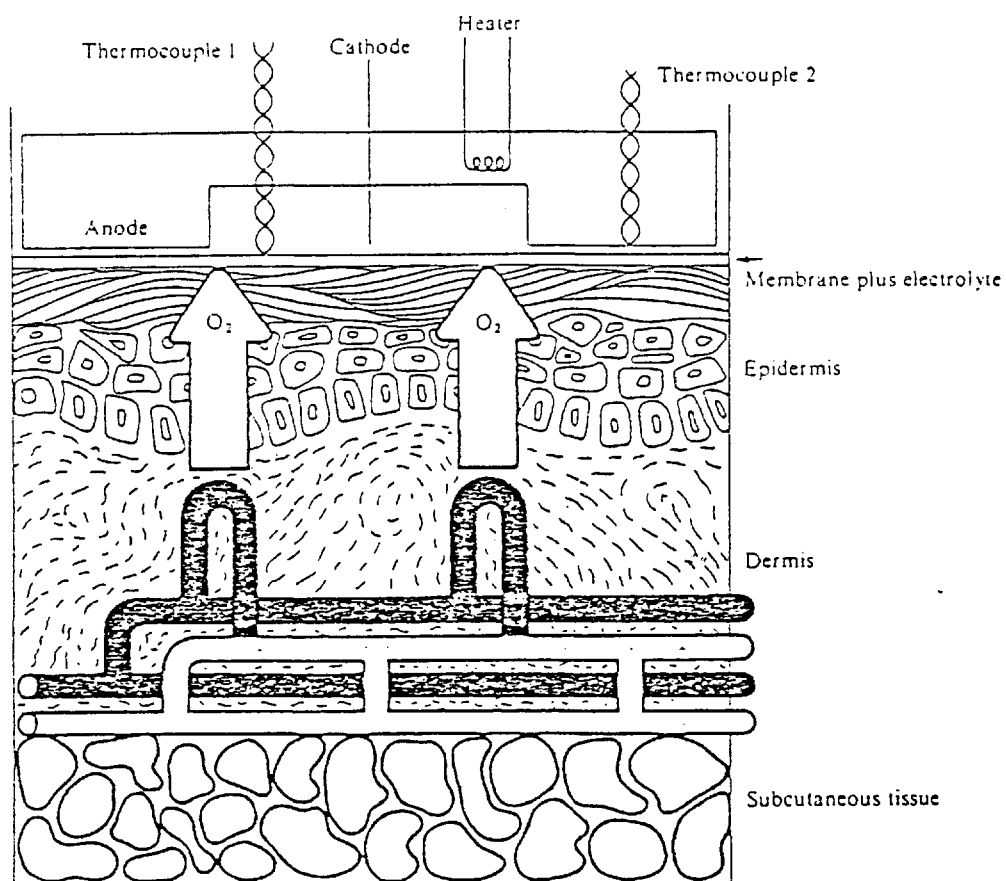


FIGURE 1.6. Transcutaneous blood gas analysis. The heated electrode causes vasodilation of the dermal capillaries, allowing a high rate of blood gas perfusion.

and such electrodes are now commercially available (e.g.⁽⁴⁶⁾), and commonly used in neonatal intensive care units.

Transcutaneous $p\text{CO}_2$ electrodes have also been described in the literature^(47,48), but are not yet in clinical use.

A joint transcutaneous CO_2/O_2 sensor has been developed^(49,50) because of difficulties in using two separate skin sensors.

The main disadvantage of transcutaneous measurements is that even in infants transcutaneous $p\text{O}_2/\text{CO}_2$ tensions do not correlate well with arterial values under certain physiological conditions - for example shock may cause vasoconstriction of surface capillaries and lead to low t.c. $p\text{O}_2/\text{CO}_2$ readings.⁽⁵¹⁾ A summary of the characteristics of transcutaneous and intravascular blood gas measurement⁽⁶⁾ is shown in Table (1.2).

1.3c. Other Methods of Blood Gas Measurement

Blood gas partial pressures can also be measured in vivo by mass spectrometric and gas chromatographic^(52,53) techniques. Both techniques permit simultaneous measurement of carbon dioxide and oxygen, but gas chromatography does not allow continuous monitoring due to the time lag of several minutes between successive measurements.⁽³⁷⁾

Mass spectroscopy systems for both intravascular⁽⁵⁴⁻⁵⁸⁾ and transcutaneous⁽⁵⁹⁻⁶¹⁾ measurement of CO_2 and O_2 have been developed. Both systems contain a gas permeable membrane fixed over a porous support. Gas molecules that

Table 1.2. Characteristics of transcutaneous and intravascular measurements.

	Umbilical Catheter Electrode	Transcutaneous Electrode
Method	Invasive	Non-invasive
Complications	Infrequent but sometimes thrombosis	Rare - main problem is local burns
Utilization	Comprehensive: pO_2/CO_2 , blood pressure, free access to blood sampling, infusion.	Only pO_2/CO_2
Electrode	Ready for use, disposable (∴ expensive?)	Toilsome preparation but reusable (∴ cheap)
Reliability	Very good. <u>In vivo</u> calibration useful.	Good, but <u>in vivo</u> calibration essential, especially when circulation is not normal.
Electrode siting	Limited by age of infant, risk, skill of personnel	Very easy.

pass through the membrane are led by high vacuum into the molecular sorting system of the spectrometer and are then analysed. The height of the peaks corresponding to N_2 , O_2 and CO_2 can be directly converted to partial pressures. The main disadvantages of mass spectroscopy are problems due to gas leaks, slow time response, and the cumbersome and expensive nature of the instrument.

1.4. Review of CO_2 and O_2 Electrochemistry in DMSO

A new technique for CO_2 detection is described in this thesis, where the CO_2 is electrochemically reduced in Dimethylsulphoxide (DMSO). The main advantage of this method is that it is a direct technique, where the current obtained is directly proportional to pCO_2 .

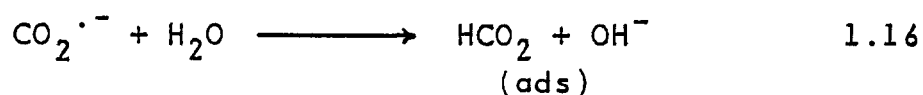
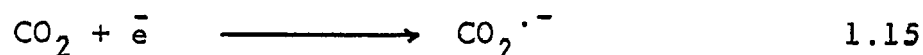
This section will give a review of electrochemical CO_2 reduction. As oxygen is also present in blood, the electrochemistry of oxygen in DMSO will also be considered.

1.4a. CO_2 Reduction

The electroreduction of CO_2 in aqueous solutions has been extensively studied, particularly in connection with the electrosynthesis of various organic materials. CO_2 has been reduced on cathodes of Mercury,⁽⁶²⁻⁶⁵⁾ Lead⁽⁶⁶⁾ and tin.⁽⁶⁷⁾ Reduction of CO_2 on a Platinum cathode due to reaction with chemisorbed Hydrogen has also been reported.⁽⁶⁸⁾ Takahashi et al.⁽⁶⁹⁾ have described the

electrocatalytic behaviour of metal porphyrins in CO_2 reduction.

Formate has been reported as the main reduction product, formed by the reaction⁽⁶⁵⁾:



Due to interference of the solvent, aqueous solutions are of little analytical use.

The reduction of CO_2 in aprotic solvents has been studied in DMF on mercury,^(70,71) mercury and lead,⁽⁷¹⁾ in propylene carbonate on lead,⁽⁷²⁾ and in DMSO and acetonitrile on mercury,⁽⁷³⁾ and mercury and gold.^(74,75) The larger negative range in aprotic solvents meant that analytically useful voltammograms were obtained, particularly in DMSO,⁽⁷⁴⁾ where the residual current was very low. Sawyer and Roberts⁽⁷⁴⁾ found the CO_2 concentration by analysing a cyclic voltammogram obtained at a stationary electrode.

The mechanism of CO_2 reduction in aprotic solvents is dependent on water content.^(71,75) A summary of the reduction processes is shown in Figure (1.7).⁽⁷¹⁾ CO_2 is reduced by one electron to form the radical anion(1).

In the anhydrous environment dimerisation can occur to form oxalate via reactions (2), or (3,4/4'). Saveant et al.⁽⁷¹⁾ have shown the major pathway is reaction (2). Another possible pathway is reaction (3',5/5'), where CO and CO_3^{2-} are formed by dismutation of species A at the electrode (5) or in solution (5').

When the solvent is damp reactions (7,8,9) compete, and formate is also formed.

1.4b. Oxygen Reduction

Several studies have been performed using cyclic voltammetry or chronopotentiometry on the electrochemistry of oxygen reduction in non-aqueous aprotic solvents.⁽⁷⁶⁻⁸⁰⁾ Two reduction waves have been reported. The first reversible wave is at -0.75 V vs. S.C.E. on gold, platinum or mercury cathodes, and corresponds to:

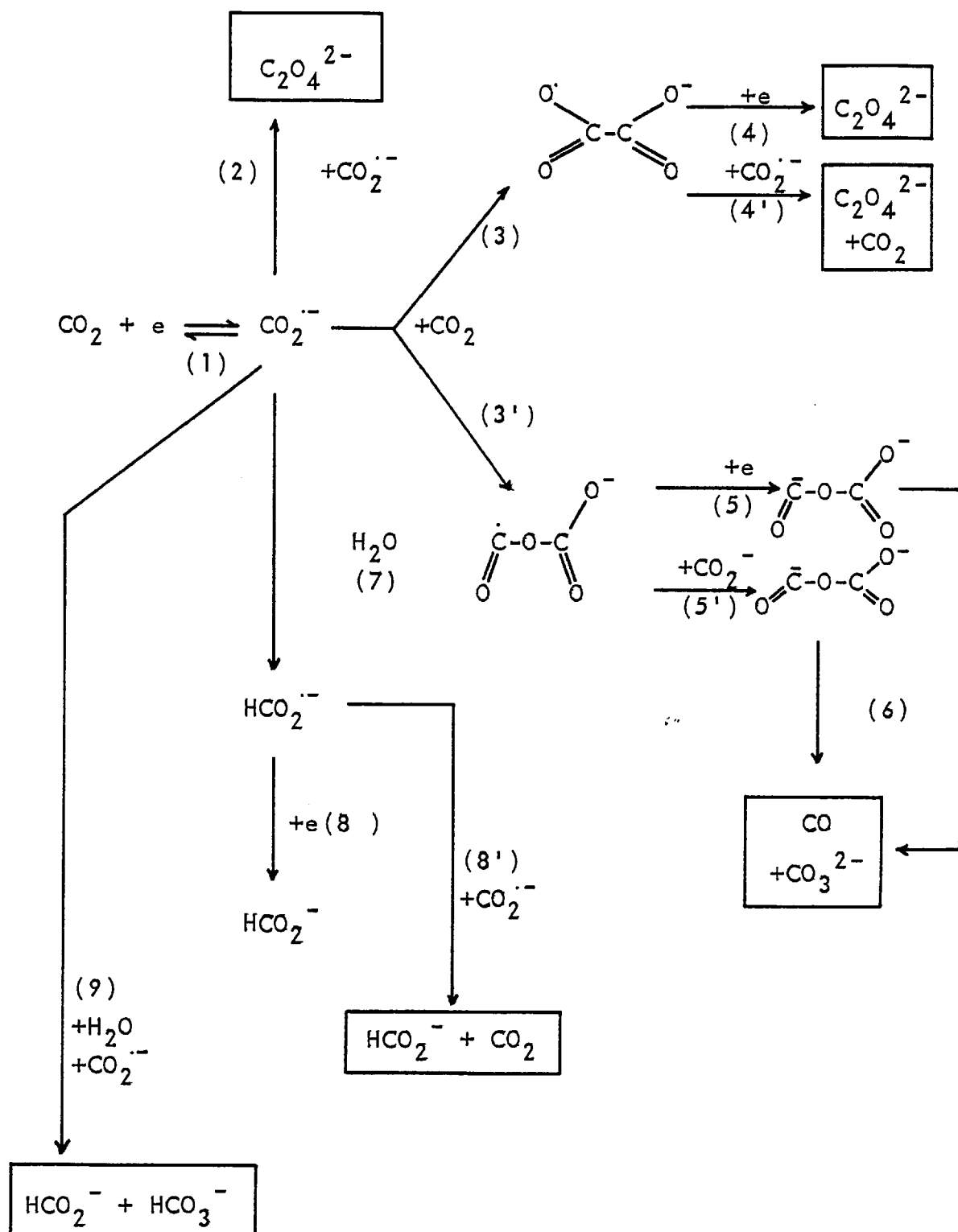


At ca -2.0 V vs, S.C.E. a second irreversible reduction wave is obtained on gold and mercury, corresponding to:

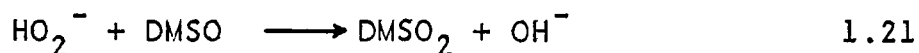
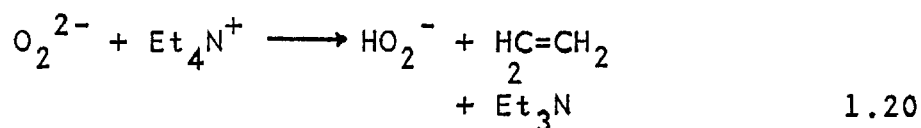
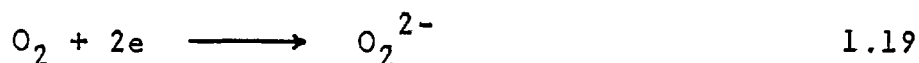


Oxidation waves were obtained at -0.73 V for superoxide oxidation and +0.75 V for oxidation of the two electron reduction product. Initially the two electron

Figure 1.7.



product was thought to be peroxide, but Goolsby and Swayer⁽⁸⁰⁾ have shown it to be hydroxide when Tetraethylammonium perchlorate (TEAP) is used as supporting electrolyte. The reactions are:



1.5. Metallised Membranes

Metallised membrane electrodes for polarographic oxygen detection were first introduced by Bergman,^(81,82) and have also been described by Pletcher.⁽⁸³⁾ In these devices the electrode is a thin metal layer coated onto the membrane. In operation the gas diffuses through the membrane and metal and is reduced at the metal/electrolyte interface. Electrodes have also been developed for CO^(84,85) and other gases.⁽⁸⁶⁾ The chief advantage of metallised membrane electrodes is the response to a change in gas feed is substantially quicker than normal Clark electrodes. The use of metallised membranes as gas filters for separating gas mixtures is discussed in Chapter 5 of this thesis.

1.6. The Nickel Hydroxide Reference/Counter Electrode

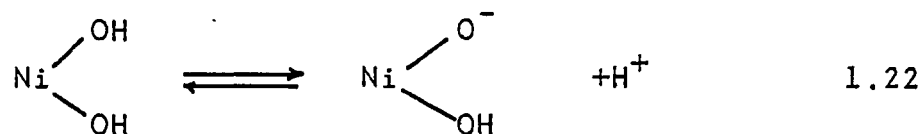
In 1975, a study of the operation of clinical oxygen electrodes was carried out at the John Radcliffe Hospital, Oxford.⁽⁸⁷⁾ The study found that many of the electrodes were failing by suddenly passing a much increased current, several orders of magnitude higher than normal. This effect was found to be due to silver dendrites "shorting" the anode and cathode, which in clinical electrodes are in close proximity.

The dendrites were formed by electrodeposition on the cathode of colloidal silver particles, which have been found⁽⁸⁸⁾ to break off from the silver chloride anode. It was therefore necessary to replace the silver chloride anode with some other electrochemical couple that did not interfere with the cathode. The properties required of the couple are:

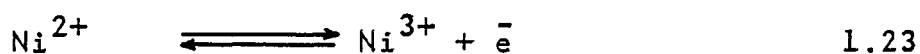
- 1) The couple should be reversible, i.e. its potential should not vary substantially with current density.
- 2) The potential should not vary with time.
- 3) The potential should not vary considerably as active electrode material is consumed.
- 4) The potential of the couple should be suitable.
- 5) The couple should preferably be a solid system for ease of manufacture, and it should be possible to

recycle the electrode material with the electrode in situ. (This means the counter electrode could then be made smaller which would help in miniaturisation of the electrode assembly.)

The nickel hydroxide couple has been used as a battery material⁽⁸⁹⁾ for many years. The process of charging and discharging the electrode has been suggested^(90,91) to be:



Accompanied by the electron transfer:



$\text{Ni}(\text{OH})_2$ is insoluble ($K_{\text{sp}} = 6.10^{-18} \text{ mol}^3 \text{ dm}^{-9}$) and therefore no dendrites would form on a clinical electrode cathode. Previous papers^(90,91,92) indicated the couple may possess the required electrochemical properties for use as a clinical electrode anode. Work on $\text{Ni}(\text{OH})_2$ is described in Chapter 6.

CHAPTER 2

GENERAL THEORY OF ROTATING RING DISC

AND MEMBRANE ELECTRODES

This chapter will begin by discussing the theory of the rotating disc electrode (R.D.E.), and rotating ring disc electrode (R.R.D.E.). The R.R.D.E. is particularly well suited to the investigation of electrochemical processes, and has been extensively used in the work described in this thesis.

The second part of this chapter will discuss the theory of membrane electrodes, and the current obtained at a Clark type and metallised membrane electrode. A model for the gas concentration profiles beneath a transcutaneous electrode will also be discussed.

2.1a. The Rotating Disc Electrode^(93,94)

A rotating disc electrode consists of an electrode disc surrounded by an insulating mantle on the end of a cylinder spinning vertically about its axis in solution. The system is best described in cylindrical polar coordinates ϕ , r and x (Figure 2.1). Von Karman⁽⁹⁵⁾ and more exactly Cochran⁽⁹⁶⁾ solved the pattern of laminar flow set up in the solution by the spinning disc. The flow velocities along the three coordinates are given by:-

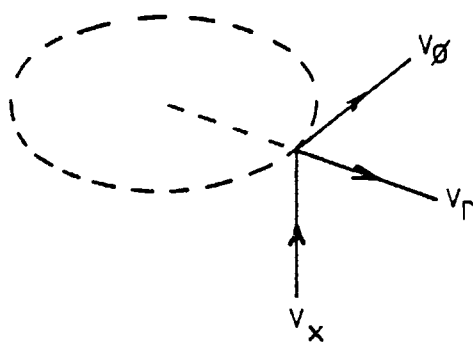
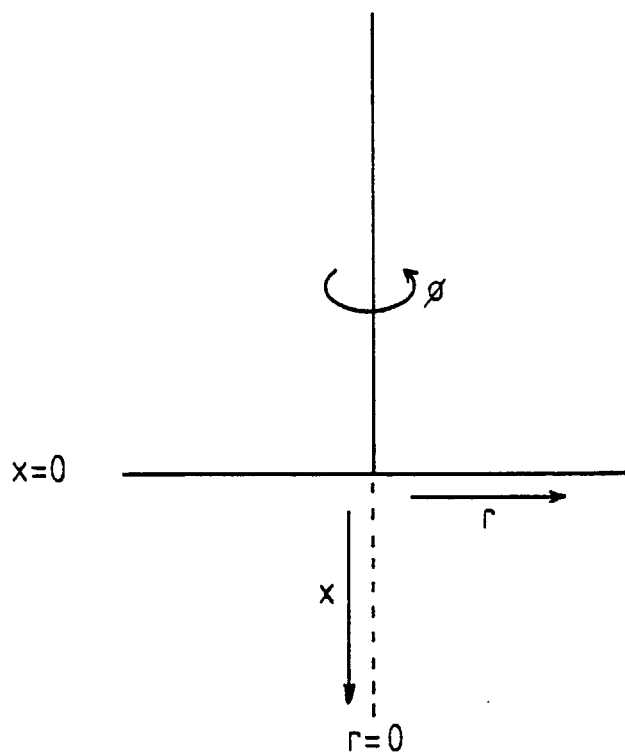


FIGURE 2.1. Coordinates and velocity components for the rotating disc system.

$$v_{\phi} = r\omega G(T) \quad 2.1$$

$$v_r = r\omega F(T) \quad 2.2$$

$$v_x = -(\omega\nu)^{\frac{1}{2}} H(T) \quad 2.3$$

where ν is in $\text{cm}^2 \text{s}^{-1}$

ω is the rotation speed in radians s^{-1}

$\nu = \eta/\rho$ is the kinematic viscosity in $\text{cm}^2 \text{s}^{-1}$.

$$\text{and } T = \left(\frac{\omega}{\nu}\right)^{\frac{1}{2}} x = \frac{x}{X_H} \quad 2.4$$

$X_H = (\nu/\omega)^{\frac{1}{2}}$ is the thickness of the hydrodynamic layer in cm, and is typically 0.1 - 1 mm.

The pattern of flow and the flow functions F, G and H are shown in Figures (2.2) and (2.3). Solution is sucked up to the disc from below. Close to the rotating surface its angular velocity increases and it is flung out sideways. Very close to the disc there is a stagnant layer, the diffusion layer, which rotates with the disc. Laminar flow continues to a Reynolds number ($R_e = r^2\omega/\nu$ for a rotating disc) of ca 10^5 , when turbulence begins.

To obtain an expression for the disc current it is necessary to solve the convective diffusion equation for transport of reactant of bulk concentration c_{∞} to the disc surface, which can be simplified^(93,97) to:-

$$\frac{\partial c}{\partial t} = \underbrace{D \frac{\partial^2 c}{\partial x^2}}_{\text{Diffusion term}} - \underbrace{v_x \frac{\partial c}{\partial x}}_{\text{convective transport term}} \quad 2.5$$

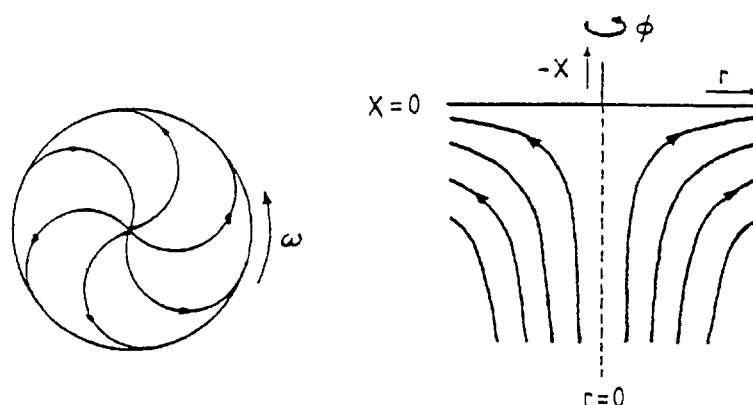


FIGURE 2.2. Schematic streamlines for the rotating disc system.

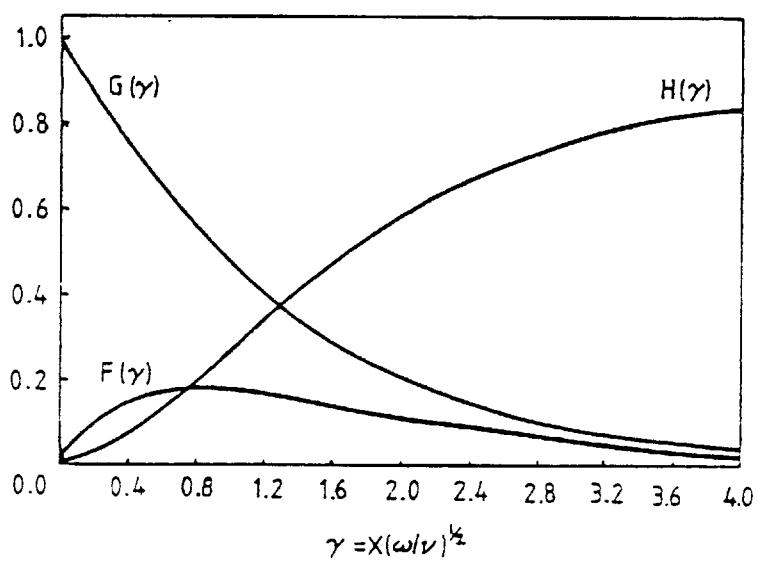


FIGURE 2.3. Variation of the velocity components with γ at an R.D.E.
 $v_\phi = r\omega G(\gamma)$
 $v_r = r\omega F(\gamma)$
 $v_z = -(\omega/\nu)^{1/2} H(\gamma)$

As $x \longrightarrow \infty$, $c \longrightarrow c_\infty$

For forced convection $\frac{\partial c}{\partial t} = 0$. Levich⁽⁹⁷⁾ used the approximations:-

$$v_r = Crx \quad 2.6$$

$$v_x = -Cx^2 \quad 2.7$$

$$\text{where: } C = 0.51 \omega^{3/2} \nu^{-1/2} \quad 2.8$$

and solved eqn. 2.5 to obtain

$$X_D = 0.643 \omega^{-1/2} \nu^{1/6} D^{1/3} \quad 2.9$$

where X_D is the diffusion layer thickness in cm

and ω is the rotation speed in Hz.

X_D is independent of r , which means that all parts of the disc are uniformly accessible for transport of reactant.

The flux j , of reactant to the electrode surface is given by:

$$j/D = \left(\frac{\partial c}{\partial x} \right)_{x=0} = \frac{c_\infty - c_0}{X_D} \quad 2.10$$

where j is in $\text{mol cm}^{-2} \text{ s}^{-1}$

and c_0 is the surface concentration in mol cm^{-3}

Figure 2.4 shows a plot⁽⁹⁸⁾ of c as a function of x obtained by integrating equation 2.5. X_D is the boundary

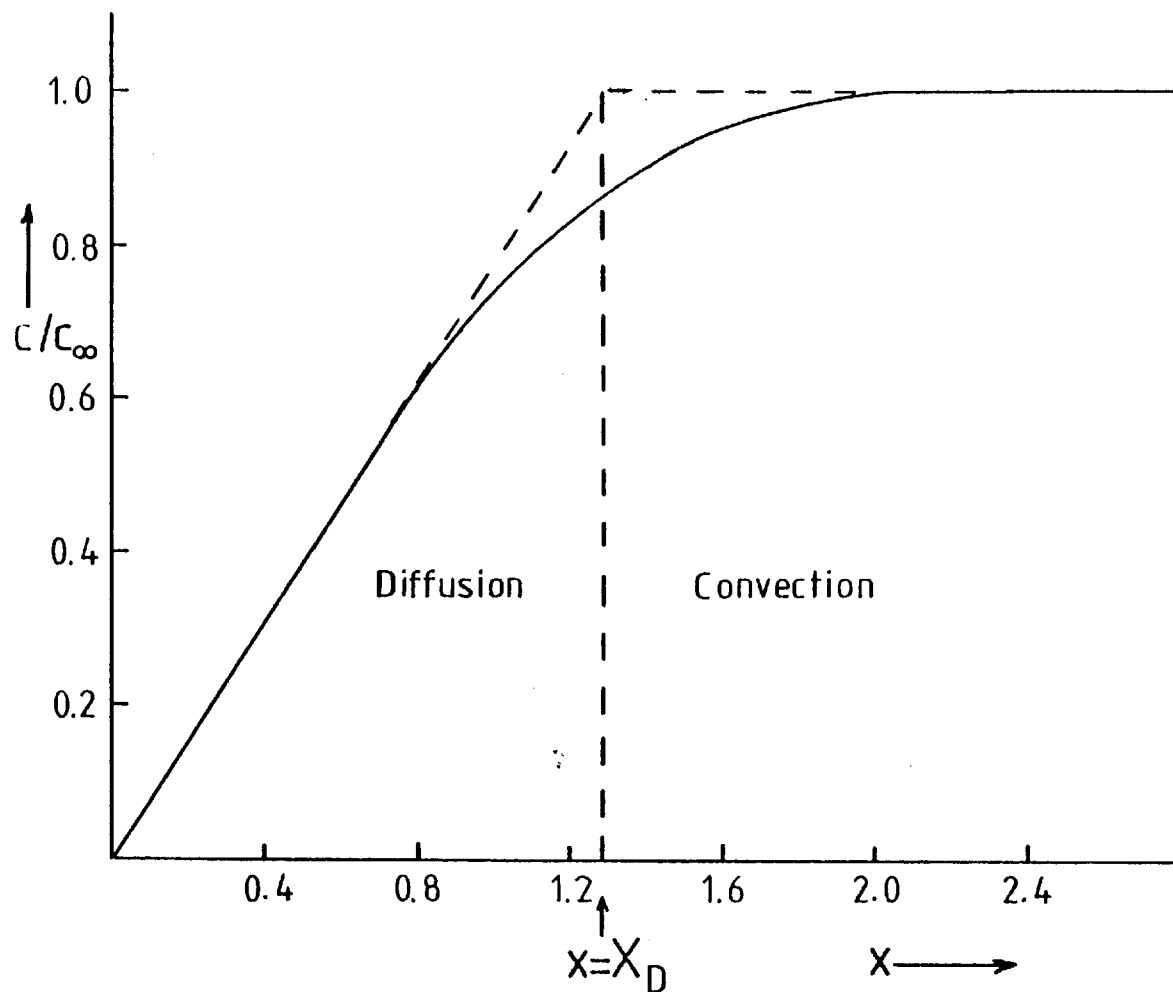


FIGURE 2.4. Concentration profile for transport limited current at an R.D.E.

between the well stirred bulk solution and the stagnant solution layer that rotates with the electrode.

The total flux of reactant to the electrode is controlled by its rate of transport across the diffusion layer and by the rate of its electrochemical removal:

$$1/j = \frac{1}{k'c_{\infty}} + \frac{1}{k_D c_{\infty}} \quad 2.11$$

where k' is the heterogeneous electrochemical rate constant and k_D is the diffusion rate constant. k' is given by:-

$$k' = k'_0 \exp(-E\alpha F/RT) \quad 2.12$$

$$\text{Also } k_D = D/X_D \quad 2.13$$

There are two limiting cases of equation 2.11:-

- (A) $k_D \gg k'$; $j = k'c_{\infty}$ and $c_0 = c_{\infty}$
(The current is controlled by the electrode kinetics)
- (B) $k' \gg k_D$; $j = k_D c_{\infty}$ and $c_0 \ll c_{\infty}$
(The current is controlled by transport of reactant).

The limiting value of the flux in the transport limited case is given by j_L , where:-

$$j_L = k_D c_{\infty} = Dc_{\infty}/X_D \quad 2.14$$

Using the relation:-

$$i_L = nFAj_L \quad 2.15$$

where i_L is the transport limiting current

n is the number of electrons in the reaction

F is Faraday's constant

A is the electrode area in cm^2

From equation 2.10 we obtain:-

$$i_L = 1.554nFAD^{3/4}\omega^{-1/6}c_\infty\omega^{1/2} \quad 2.16$$

Equation 2.16 is the Levich equation, and shows the limiting current at a rotating disc electrode is proportional to the square root of rotation speed and the bulk reactant concentration.

From equation 2.11:-

$$\left(\frac{1}{j} - \frac{1}{j_L}\right) = 1/kc_\infty \quad 2.17$$

Hence, using equation 2.14:

$$-\ln\left(\frac{1}{j} - \frac{1}{j_L}\right) = \frac{-\alpha FE}{RT} + \ln c_\infty + \ln(k')_{E=0} \quad 2.18$$

From equation 2.12 k' is proportional to $e^{-\alpha FE/RT}$ and therefore a plot of $-\ln(1/j - 1/j_L)$ vs. potential is a straight line. From the slope the transfer coefficient α may be obtained. The shape of the current voltage curve therefore contains information about the reversibility of the electrochemical reaction.

Equations 2.16 and 2.18 mean we are able to calculate the current at all points along the current voltage curve at a given rotation speed.

Consider now the limiting current transient when a rotation speed step is applied to the R.D.E. The convective constant C (eqn. 2.8) changes with time:-

$$C' = C F(t) \quad 2.19$$

$F(t)$ describes the change in C with time caused by the rotation step. If the reduced time variable τ is defined as:

$$\tau = t D^{\frac{1}{3}} (C'/F)^{\frac{2}{3}} = 4.02 W_0 Sc^{-\frac{1}{3}} t \quad 2.20$$

$$\text{Where } Sc = \nu/D \quad 2.21$$

and W_0 is the rotation speed before the rotation step. Albery et al. (99) showed:-

$$f_p = (8/\sqrt{\pi}) \tau^{3/2} - 4\tau^3 \quad 2.22$$

f_p is the fraction of the overall limiting current response at time t .

After adjusting τ to allow for hydrodynamic relaxation, the Schmidt number correction, (100) and the ϵ^2 correction, Albery et al. also showed:-

$$\tau_c = (4 W_\infty t - 0.164) Sc^{-\frac{1}{3}} (1 - Sc^{-\frac{1}{3}}) \quad 2.23$$

τ_c is the corrected value of τ , and W_∞ is the final value of the rotation speed after the step. Equation 2.23 is the corrected form of equation 2.20.

Hence a plot of τ_c vs. t is a straight line. From the slope Sc , and therefore D may be obtained. The rotation step method is particularly useful for measuring the diffusion coefficients of volatile substances, where the method of depleting bulk concentrations⁽¹⁰¹⁾ is inapplicable.

2.1b. The Rotating Ring Disc Electrode

The R.R.D.E. was first proposed in 1959 by Frumkin and Nekrasov.⁽¹⁰²⁾ The electrode is similar to an R.D.E., except there is a second annular ring electrode around the disc. The two electrodes are separated by an insulating gap as shown in Figure (2.5.). The electrode dimensions are characterised by the radii r_1 , r_2 and r_3 (Figure 2.5). The potentials of the two electrodes can be controlled independently, and their currents measured separately. The ring electrode is "downstream" from the disc (Figure 2.6) and can be used to monitor products of the disc reaction, thereby providing extra information about processes occurring on the disc electrode.

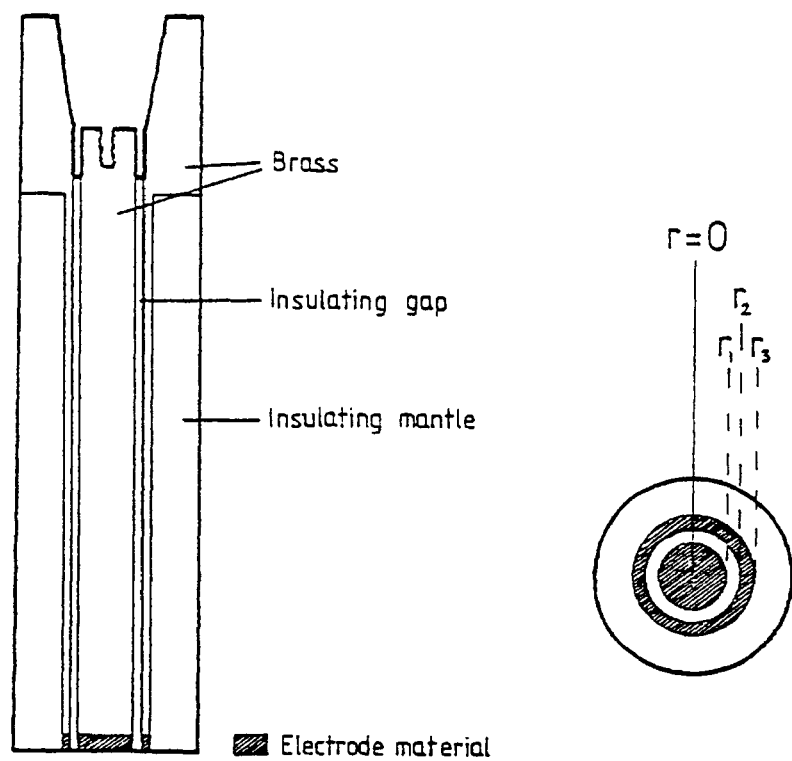


FIGURE 2.5. A ring-disc electrode.

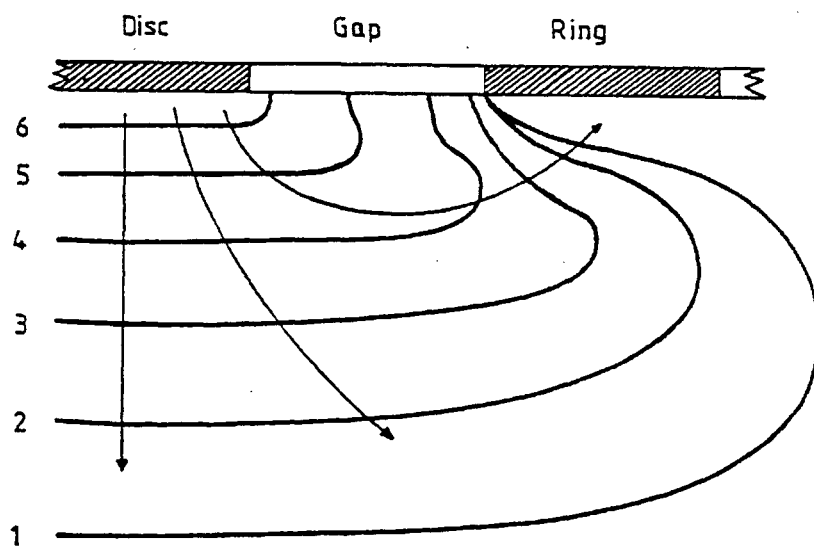
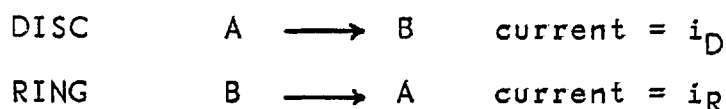


FIGURE 2.6. Schematic concentration profile at a ring-disc electrode.

Consider the processes:-



where the potential of the ring is such that all the product B reaching the ring is destroyed. The collection efficiency, N_o , of the electrode is defined by the expression:-

$$N_o = -i_R/i_D \quad 2.24$$

N_o will always be less than unity, as a proportion of species B will escape into the solution bulk.

A schematic concentration profile is shown in Figure 2.6.

An approximate solution for N_o was found by Ivanov and Levich,⁽¹⁰³⁾ and later more exactly by Albery and Bruckenstein.^(104,105) The result obtained was:-

$$N_o = 1 - F(\alpha/\beta) + \beta^{2/3} (1 - F(\alpha)) - (1 + \alpha + \beta)^{2/3} [1 - F((\alpha/\beta)(1 + \alpha + \beta))] \quad 2.25$$

$$\text{Where } \alpha = (r_2/r_1)^3 - 1 \quad 2.26$$

$$\beta = (r_3/r_1)^3 - (r_2/r_1)^3 \quad 2.27$$

and $F(x)$ is given by:-

$$F(x) = \frac{3^{1/2}}{4\pi} \ln \left(\frac{1+x^{1/3}}{1+x} \right)^3 + \frac{3}{2\pi} \tan^{-1} \left(\frac{2x^{1/3}-1}{3^{1/2}} \right) + \frac{1}{4} \quad 2.28$$

Therefore N_o is calculated solely from the electrode geometry.

$\beta^{2/3}$ is the proportionality constant which relates the limiting current at a ring electrode when no reaction occurs at the disc $i_{R,L}$, to the limiting current at the disc, $i_{D,L}$:-

$$i_{R,L} = \beta^{2/3} i_{D,L} \quad 2.29$$

When the same reaction is occurring at the ring and disc the disc "shields" a proportion of reactant from the ring. The ring current is then given by:-

$$i_{R,L} = (1 - N_o \beta^{-2/3}) i_{D,L} \quad 2.30$$

$N_o \beta^{-2/3}$ is called the shielding factor, and describes the maximum reduction in the ring current that can be achieved by the disc electrode.

If the disc generated intermediate B reacts with a non-electroactive species C in the solution, the amount of B detected at the ring will be reduced. At small disc currents all of B will be destroyed and i_R will be zero. At a critical disc current M, the flux of B from the disc is equal to the convective flow of C to the disc, hence:-

$$M = 1.554nFAD_c \nu^{-1/6} c_\infty^{2/3} \omega^{1/2} \quad 2.31$$

When $i_D \geq M$, a B dominated region of solution occurs, which reaches the ring when⁽¹⁰⁶⁾:-

$$|i_D| = M/(1 - F(\alpha)) \quad 2.32$$

When the B dominated region reaches the outside of the ring i_R becomes a linear function of i_D :-

$$i_R = N_o i_D - M\beta^{2/3} \quad 2.33$$

Flux of B Limiting flux of C
when no C
present

The shape of the $i_R - i_D$ curve (called a titration curve), is illustrated in Figure 2.7. Extrapolation of the linear portion of the titration curve to $i_R = 0$ gives:-

$$i_D = M\beta^{2/3}/N_o \quad 2.33$$

Equations 2.30 and 2.27 allow accurate determinations of C_∞ as low as 10^{-7} M. If the reaction boundary between the B dominated region and C dominated region extends to a radius r_J , and $r_2 < r_J < r_3$, then⁽¹⁰⁷⁾:-

$$N' = |i_R/i_D| = 1 - F(\alpha/\beta_J)$$

$$- \frac{(1 - \alpha)}{(1 + \alpha + \beta_J)^{1/3}} \left[1 - F\left(\frac{(1 + \alpha + \beta_J)^\alpha}{\beta_J}\right) \right] \quad 2.34$$

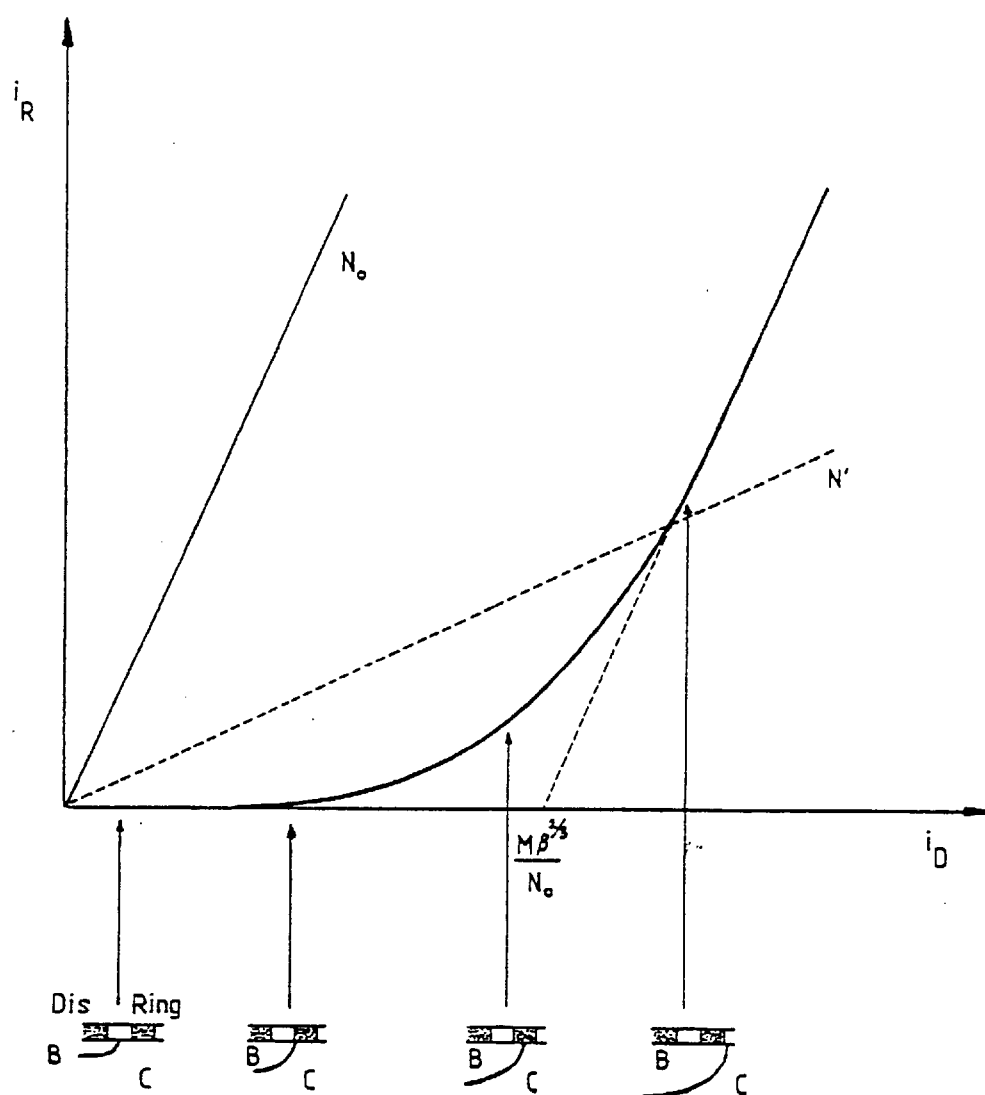


FIGURE 2.7. Ring-disc electrode titration curve.

$$\frac{M}{i_D} = 1 - F(\alpha) - \frac{\beta_J^{\frac{1}{3}}}{(1+\alpha+\beta_J)^{\frac{1}{3}}} \left[1 - F\left(\frac{(1+\alpha+\beta_J)\alpha}{\beta_J}\right) \right] \quad 2.35$$

$$\text{Where } \beta_J = (r_J/r_1)^3 - (r_2/r_1)^3 \quad 2.36$$

and $F(x)$ is defined in equation 2.28.

Equations 2.34 and 2.35 depend solely on electrode geometry. The shape of the titration curve indicates the "diffuseness" of the reaction boundary, and the rate constant of the reaction between B and C can be determined.⁽¹⁰⁸⁾ A curve of the type shown in Figure (2.7) indicates a rate constant faster than 10^9 Ms^{-1} .

2.2. MEMBRANE ELECTRODES

2.2.a. Steady State Models

2.2.a.1. Linear Diffusion

The one dimensional linear diffusion model only considers diffusion perpendicular to the cathode, along the z axis. The model is illustrated in Figure 2.8.

The flux through the membrane must be equal to the flux through electrolyte and the rate of the electrochemical reaction:-

$$j/A = k'c_1 = \frac{D_m}{b} (c_4 - c_3) = \frac{D_e}{a} (c_2 - c_1) \quad 2.37$$

Where:-

A is the electrode area

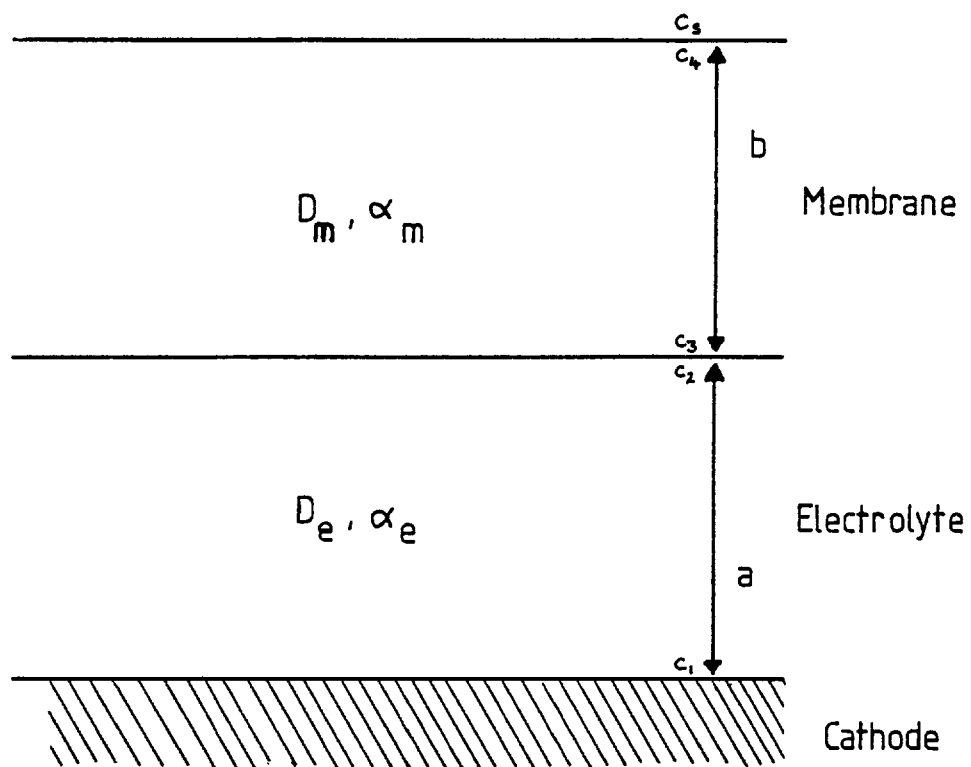


FIGURE 2.8. The one-dimensional linear diffusion model.

D_e, D_m are the diffusion coefficients of the gas in the electrolyte layer and membrane respectively.

a, b are the thicknesses of the electrolyte layer and membrane respectively.

c_n is the gas concentration at the points defined in Figure 2.8.

k' is the electrochemical rate constant, defined in equation 2.12.

From Nernst's distribution law the partial pressure of gas on either of the electrolyte/membrane and membrane/outside environment interfaces must be equal, hence:-

$$\frac{c_3}{\alpha_m} = \frac{c_2}{\alpha_e} ; \quad \frac{c_4}{\alpha_m} = \frac{c_s}{\alpha_s} = p \quad 2.38$$

Where α_m and α_e are the solubilities of the gas in the various phases. The permeability P is defined by:-

$$P = \alpha D \quad 2.39$$

Equation 2.37, using equations 2.38 and 2.39 can be rearranged to:-

$$j = Ap \left(\frac{a}{P_e} + \frac{b}{P_m} + \frac{D_e}{P_e k_1} \right)^{-1} \quad 2.40$$

When the current is transport limited k_1 is large, therefore:-

$$j = \frac{A_p}{\left(\frac{a}{p_e} + \frac{b}{p_m}\right)} \quad 2.41$$

The current is given by:-

$$i_L = nFj = \frac{nFAp}{\left(\frac{a}{p_e} + \frac{b}{p_m}\right)} \quad 2.42$$

Normally $p_e \gg p_m$, therefore $b/p_m \gg a/p_e$

$$\text{and:- } i_L = nFAp \frac{p_m}{b} \quad 2.43$$

Equation 2.43 is accurate for very large electrodes, of radius greater than 150 μm . For smaller cathodic radii there is a radial component of diffusion leading to larger values of i_L . This can be allowed for in the cylindrical diffusion model.

2.2.a.2. Cylindrical Diffusion Model

In this model the Fick equation is:-

$$D\bar{\nabla}^2 c = D \left[\frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial z^2} \right] = 0 \quad 2.44$$

Saito,⁽¹⁰⁹⁾ Siu and Cobbold,⁽¹¹⁰⁾ Hahn⁽¹¹¹⁾ and Jensen⁽¹¹²⁾ have produced cylindrical diffusion models. The boundary conditions (Figure 2.9) are:-

$$\text{Membrane surface: } p(r, z_2) = p_s \quad 2.45$$

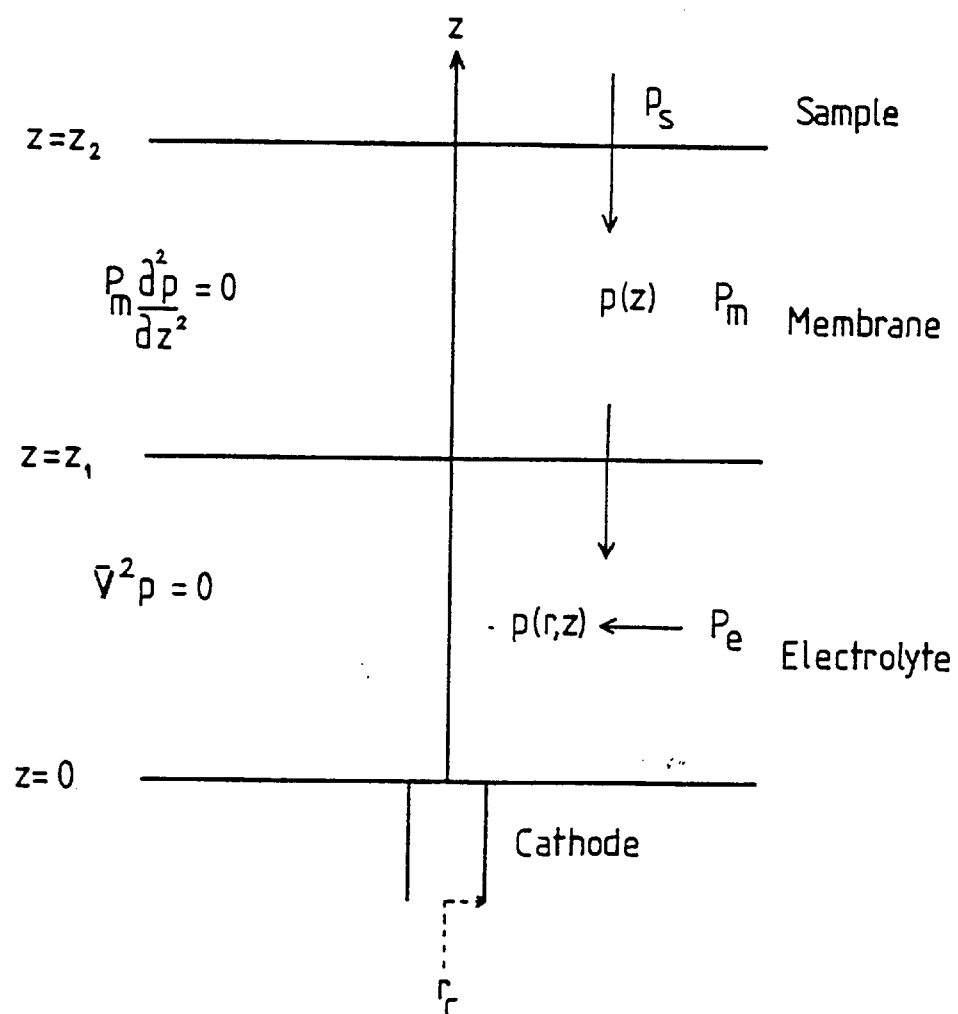


FIGURE 2.9. The cylindrical diffusion model.

Within the membrane ($z_2 > z > z_1$):

$$P_m \frac{\partial^2 p}{\partial z^2} = 0 \quad 2.46$$

Within the electrolyte ($z_1 > z > 0$):

$$\bar{V}^2 p = 0 \quad 2.47$$

$$\frac{\partial p}{\partial r} \rightarrow 0 \text{ as } r \rightarrow \infty \quad 2.48$$

$$p \rightarrow p_s \text{ as } r \rightarrow \infty \quad 2.49$$

$$\text{For } r > r_c, \text{ at } z = 0, \frac{\partial p}{\partial z} = 0 \quad 2.50$$

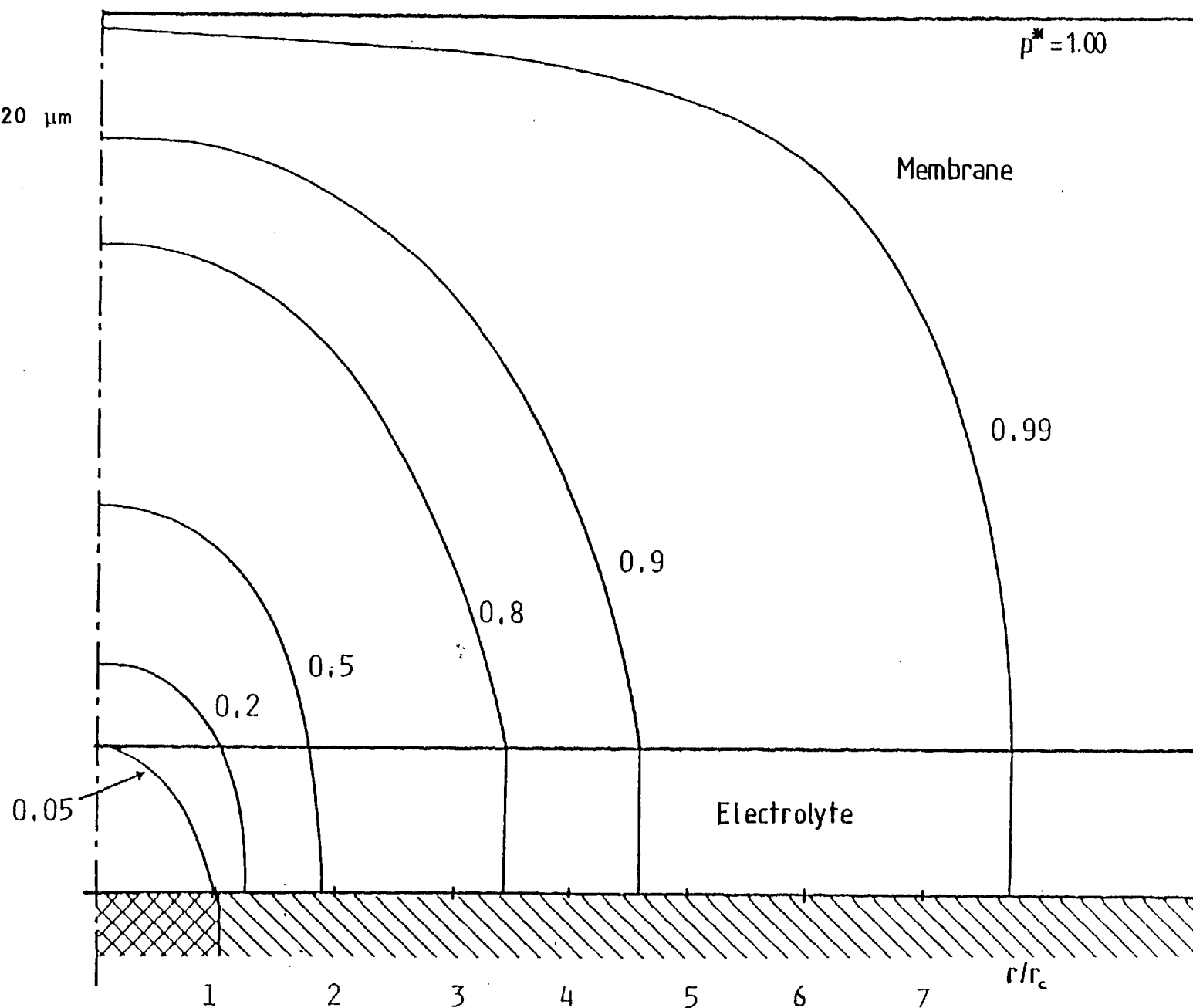
$$\text{For } r \leq r_c, \text{ at } z = 0, P_e \frac{\partial p}{\partial z} \bigg|_{z=0} = k' p(r, 0) \quad 2.51$$

The current is given by:-

$$i = 2\pi n F P_e \int_0^{r_c} \left(\frac{\partial p}{\partial z} \right)_{z=0} \cdot r \cdot dr \quad 2.52$$

Hahn⁽¹¹¹⁾ used a computer to solve equations 2.45 to 2.52 at discrete (r, z) grid points, and obtained oxygen partial pressure isobars. Brooks⁽¹¹³⁾ plotted isobars for a 20 μm cathode, and a 1 mm cathode, which are shown in Figures 2.10 and 2.11. The 1 mm cathode case shows the linear diffusion model to be a good approximation, but in the 20 μm case the isobars are nearly hemispherical.

FIGURE 2.10.
 pO_2 isobars for a 20 μm
 cathode.



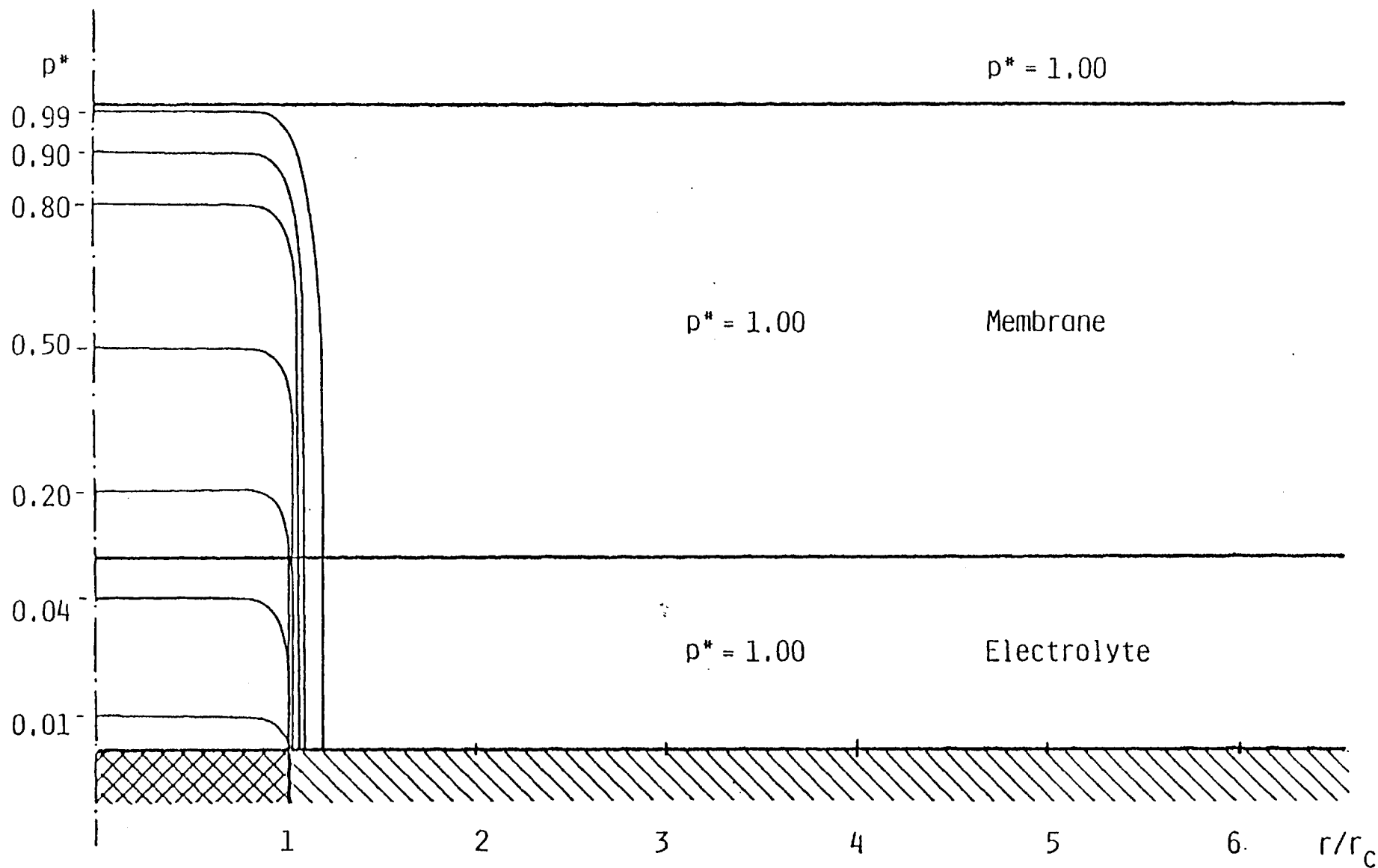


FIGURE 2.11. pO_2 isobars for a 1 mm cathode

Jensen et al. ⁽¹¹²⁾ obtained an analytical solution for the current by making several approximations to the cylindrical diffusion model. They divided the model into two zones, bounded by a cylinder of radius r_c . The model is shown in Figure 2.12.

Jensen et al. made the following assumptions:-

- 1) For $r < r_c$, diffusion is considered to be linear.
- 2) For $r > r_c$, diffusion in the electrolyte is considered to be purely radial.
- 3) For $r > r_c$, diffusion in the membrane is considered to be purely linear.
- 4) All oxygen reaching the cathode is destroyed, i.e. the electrode is polarised in the limiting current region.

The following analytical solution was obtained:-

$$i = nF\pi r_c^2 \frac{P_m}{b} \left(1 + \frac{2}{\chi(r_c)} \frac{K_1(\chi(r_c))}{K_0(\chi(r_c))} \right) \quad 2.53$$

$$\text{Where } \chi_r = r_c \sqrt{\frac{P_m}{P_e ab}} \quad 2.54$$

K_0 and K_1 are modified Bessel functions. ⁽¹¹⁴⁾

The bracketed term shows by how much the current of this model exceeds that of the linear diffusion model. When r_c is of the order of b :-

$$\frac{2K_1(\chi(r_c))}{\chi(r_c)K_0(\chi(r_c))} \approx 10 \quad 2.55$$

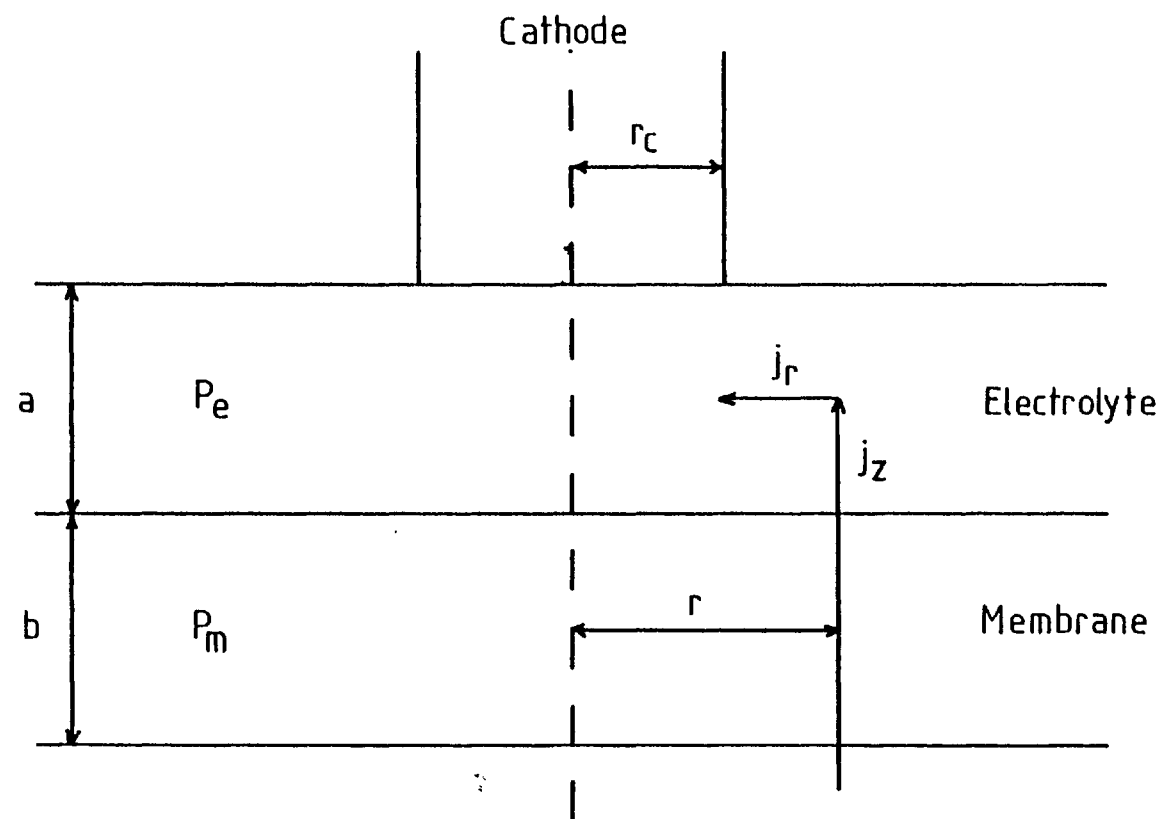


FIGURE 2.12. The model of Jensen, Jacobsen and Thomsen.

The current predicted by this model is an order of magnitude higher than the linear diffusion model predicts, and illustrates the importance of radial diffusion for small cathodes.

2.2.b. Non Steady State Models

This section will consider two types of transient behaviour at a membrane electrode. The first part will consider the transient obtained when the electrode is switched from a non-reacting potential to the limiting current potential. The second part is concerned with the response of a membrane electrode to a gas concentration step in the external environment.

2.2.b.1. Voltage Step Transient

Mancy et al.⁽¹¹⁵⁾ have published a model for the time response of the membrane electrode current after a voltage step was applied to the electrode. The model is illustrated in Figure 2.13. Linear diffusion only is considered in this model, and therefore it is only valid for large electrodes. The concentration c_s of gas in the outside solution is given by equation 2.38:-

$$\frac{c_s}{\alpha_s} = p \quad 2.38$$

Before the electrode is switched on the gas is in equilibrium in the three phases, hence:-

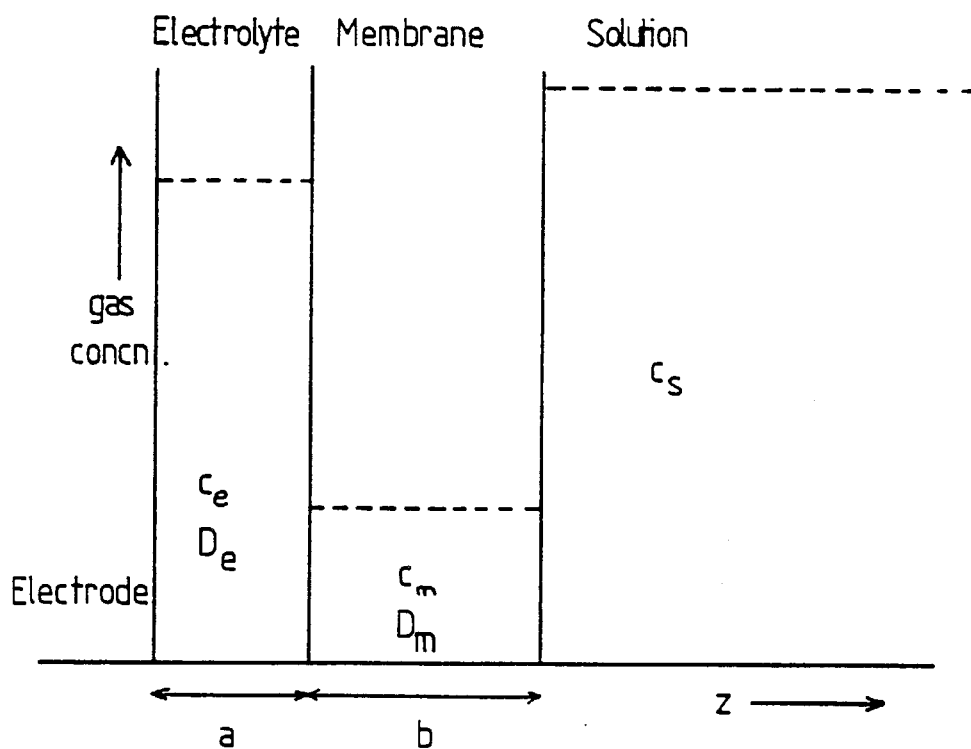


FIGURE 2.13a. The model of Mancy, Okun and Reilley.
Concentration profiles:
a) Before electrode is switched on.

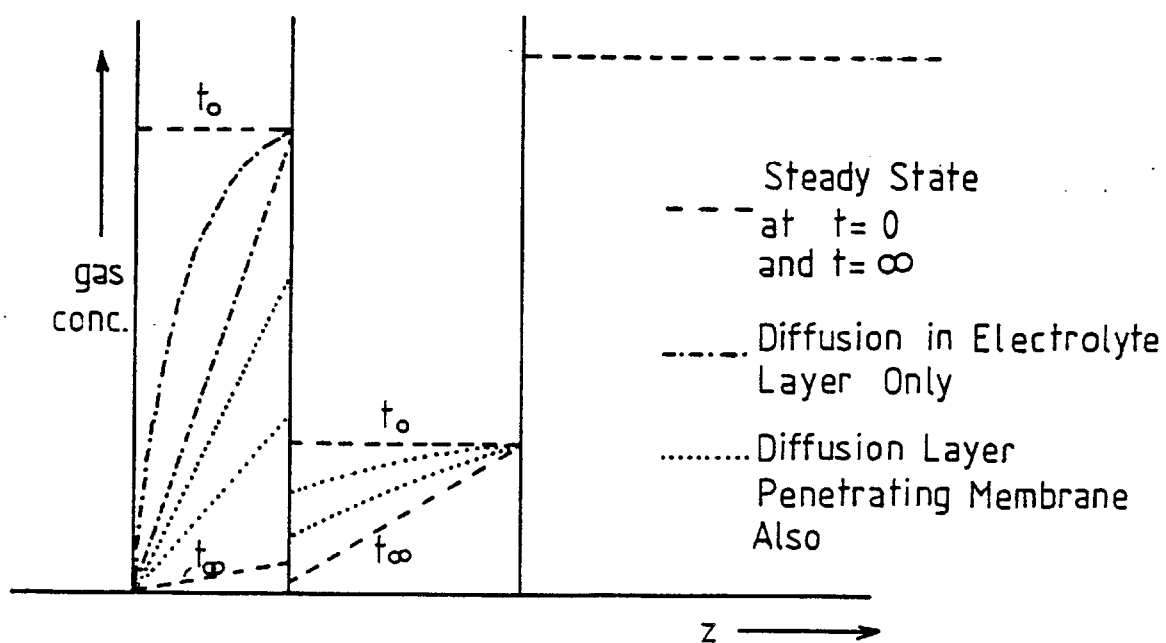


FIGURE 2.13b. During attainment of the steady state.

$$c_m = K_o c_e = K_b c_s \quad 2.56$$

K is the Nernst distribution coefficient. From equation 2.38:-

$$K_o = \frac{\alpha_M}{\alpha_e} = \frac{c_m}{c_e} \quad 2.57$$

$$K_b = \frac{\alpha_M}{\alpha_s} = \frac{c_m}{c_s} \quad 2.58$$

As soon as the electrode potential is stepped all the gas at $z = 0$ reacts, and the current is diffusion controlled. Initially $\left(\frac{\partial c_e}{\partial z}\right)_{z=0}$ is steep, and the current is high. The flux falls off as the electrolyte gas level decreases. As time progresses depletion of the gas also occurs in the membrane, however $c_{s(z=z_2)}$ remains constant (the model assumes the sample solution is stirred). As $t \rightarrow \infty$ a steady state is observed. Concentration profiles during attainment of the steady state are shown in Figure 2.13b.

Mancy et al. gave solutions for three general cases:-

- (a) $\frac{a}{\sqrt{D_e}} \gg \frac{b}{\sqrt{D_m}}$ [Diffusion in the electrolyte is rate limiting, corresponding to very short times after the potential step]
- (b) $\frac{a}{\sqrt{D_e}} \approx \frac{b}{\sqrt{D_m}}$ [Intermediate case]

- (c) $\frac{a}{\sqrt{D_e}} \ll \frac{b}{\sqrt{D_m}}$ [Diffusion in the membrane is rate determining, corresponding to longer times after the step]

The solutions obtained were:-

$$(a) \quad i = \frac{nFAK_b}{K_o} c_s \left(\frac{D_e}{\pi t} \right)^{\frac{1}{2}} \left[1 + 2 \sum_{n=1}^{\infty} \exp \left(-\frac{n^2 a^2}{D_e t} \right) \right] \quad 2.59$$

(very short times)

$$(b) \quad i = nFAC_s \left(\frac{P_m}{\pi t} \right)^{\frac{1}{2}} \left[1 + 2 \sum_{n=1}^{\infty} \exp \left(-\frac{n^2 b^2}{D_m t} \right) \right] \quad 2.60$$

(intermediate times)

$$(c) \quad i = nFAC_s \left(\frac{P_m}{b} \right) \left[1 + 2 \sum_{n=1}^{\infty} \exp \left(-\frac{n^2 \pi^2 D_m t}{b^2} \right) \right] \quad 2.61$$

(longer times)

Case (a) is valid while the diffusion layer is extending into the electrolyte layer which assuming a $\sim 10 \mu\text{m}$ and $D_e \sim 10^{-5} \text{ cm}^2\text{s}^{-1}$, is up to $t \sim 0.1 \text{ s}$. For $t < 0.1 \text{ s}$ the summation in equation 2.59 is negligible, so equation 2.59 can be replaced by:-

$$i = \frac{nFAK_b}{K_o} c_s \left(\frac{D_e}{\pi t} \right)^{\frac{1}{2}} \quad 2.62$$

If $b \sim 20 \mu\text{m}$ and $D_m \sim 10^{-7} \text{ cm}^2\text{s}^{-1}$ then for $t < 10 \text{ s}$ equation 2.60 reduces to:-

$$i = nFAC_s \left(\frac{P_m}{\pi t} \right)^{\frac{1}{2}} \quad 2.63$$

For $t > 20$ s, equation 2.61 gives the steady state linear diffusion current:- $i = nFAC_s \frac{P_m}{b}$ 2.43
which was derived earlier (Section 2.2.a.1.).

The variation of current with time obtained from equations 2.61, 2.62, 2.63 and 2.43 is shown in Figure 2.14.

2.2.b.2. Concentration Step Transient

The equation describing the increase in current corresponding to a step increase in sample concentration at time $t=0$ has been derived by Hitchman.^(21,116) The result is:-

$$\frac{i_L(t) - i_L(t=0)}{i_L(t=\infty) - i_L(t=0)} = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp \frac{-n^2 \pi^2 D_m t}{b^2}$$

$$= F(\tau_A) \quad 2.64$$

Where $i_{t=0}$, i_t , $i_{t=\infty}$ are the limiting currents at times 0, t and ∞ respectively, and:-

$$\tau_A = \frac{D_m t}{b^2} \quad 2.65$$

$F(\tau)$ represents the fraction of the total change achieved at time t . A plot of t vs. τ_A has a slope of D_m/b^2 , so D_m can be found. Polarographic oxygen sensors often respond slower to an oxygen concentration step than equation 2.64 predicts. Hale⁽¹¹⁷⁾ has shown that this is due to hydrogen peroxide formation, and its subsequent slow removal.

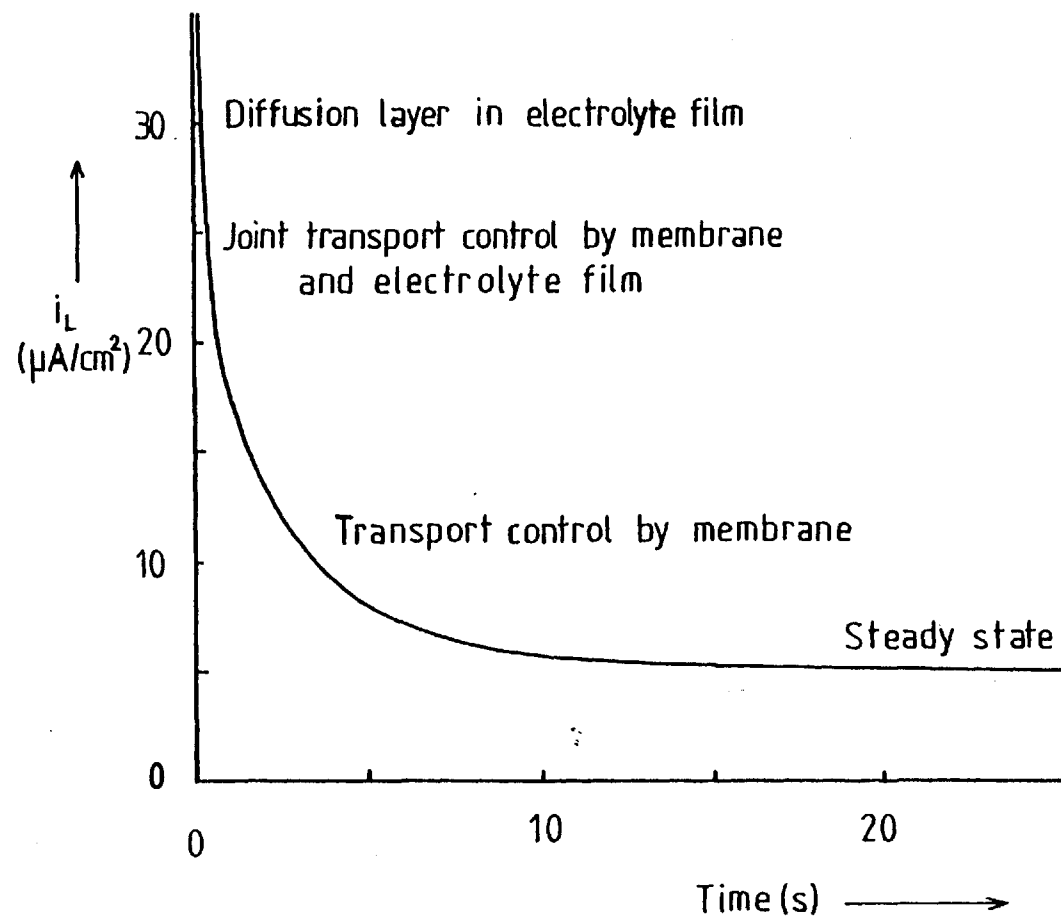


FIGURE 2.14. Variation of current with time after switching on a Clark type membrane electrode.

2.2.c. Transcutaneous Blood Gas Transport

The current at a transcutaneous membrane electrode is due to blood gas diffusing across three barriers - the avascular layer, the stratum corneum and the membrane. The avascular layer consists of living cells which consume oxygen and liberate CO_2 .

Ideally the effect of heating the skin should be to adjust skin surface pO_2 and pCO_2 to their arterial levels. This is illustrated in Figure 2.15.⁽¹¹⁸⁾ It is assumed that no depletion of the skin layers occurs, except that caused by cell metabolism in the avascular layer.

In practise the actual values of skin surface pO_2 and pCO_2 depend on the depletion caused by the gas consuming electrode. Some modelling work on the depletion caused by a hole in a mass spectrometer probe has been done by Rolfe et al.^{(119),(120)} The depletion caused by an electrode is exactly analogous as in each case the partial pressure of gas at the probe side of the membrane is zero.

The relevant equations are (Figure 2.16):-

$z = 0$:-

At hole/electrode surface:-

$$c = 0 \quad 2.66$$

At support surface:-

$$\frac{\partial c}{\partial z} = 0 \quad 2.67$$

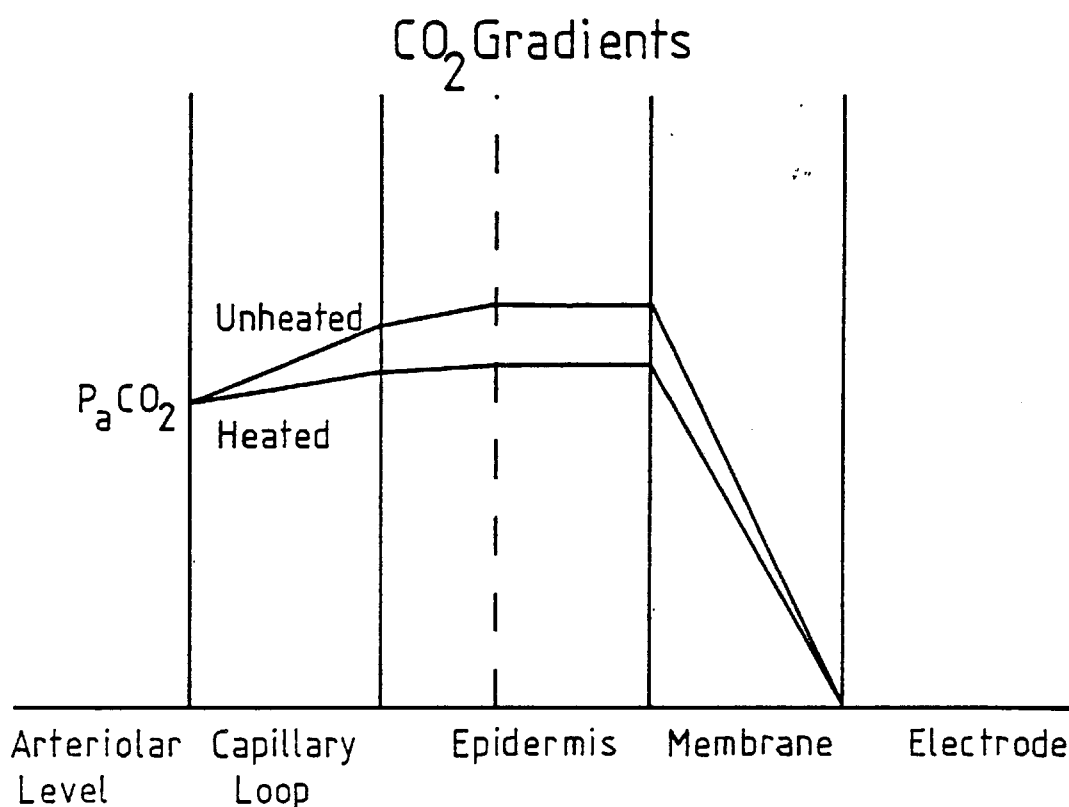
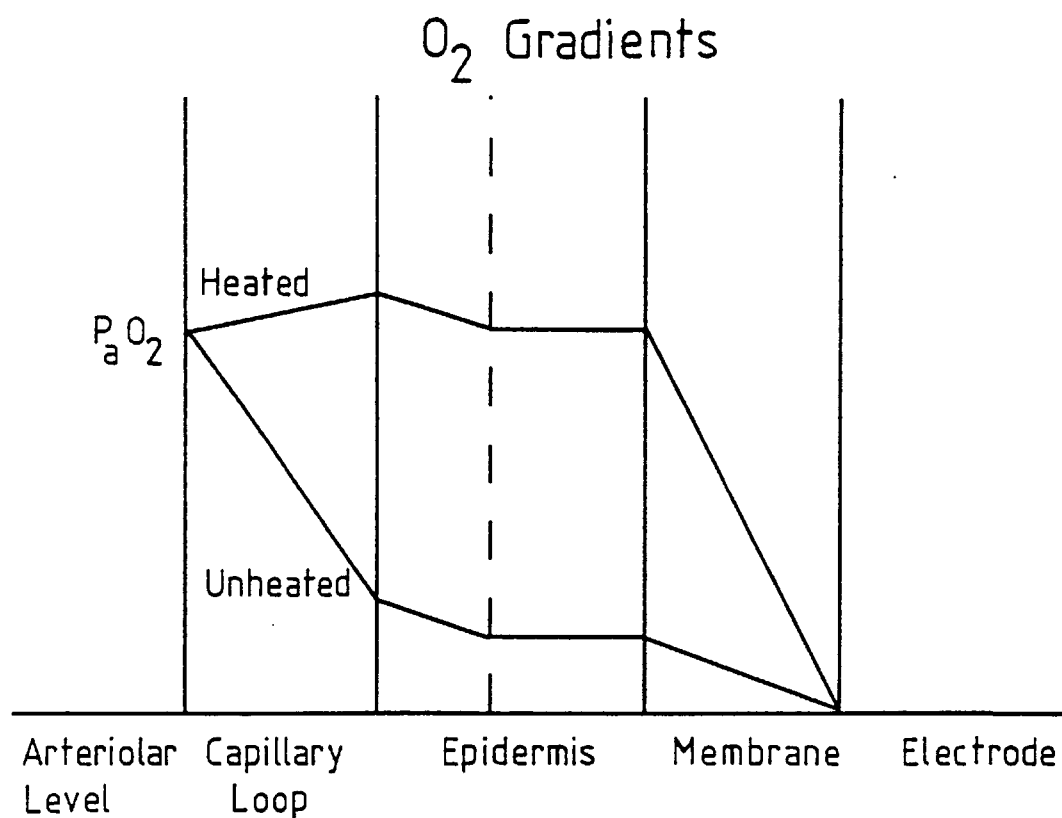


FIGURE 2.15. CO_2 and oxygen gradients through the skin to an electrode or mass spectrometer probe.

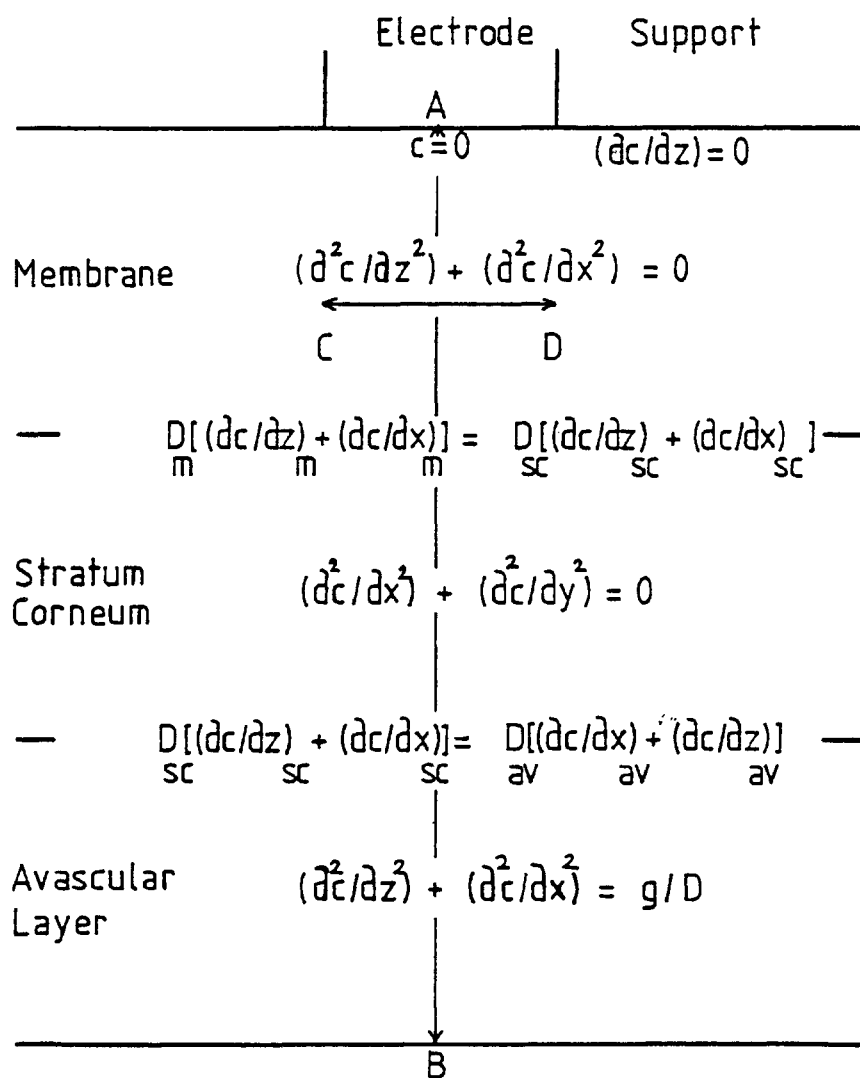


FIGURE 2.16. Diagram of the model of Rolfe et al., showing the relevant equations.

In the Membrane:-

$$\frac{\partial^2 c}{\partial z^2} + \frac{\partial^2 c}{\partial x^2} = 0 \quad 2.68a$$

$z = z_1$:-

$$D_m \left[\left(\frac{\partial c}{\partial z} \right)_m + \left(\frac{\partial c}{\partial x} \right)_m \right] = D_{s.c.} \left[\left(\frac{\partial c}{\partial x} \right)_{s.c.} + \left(\frac{\partial c}{\partial x} \right)_{s.c.} \right] \quad 2.69$$

In the stratum corneum:-

$$\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} = 0 \quad 2.68b$$

$z = z_2$:-

$$D_{s.c.} \left[\left(\frac{\partial c}{\partial z} \right)_{s.c.} + \left(\frac{\partial c}{\partial x} \right)_{s.c.} \right] = D_{a.v.} \left[\left(\frac{\partial c}{\partial x} \right) + \left(\frac{\partial c}{\partial z} \right) \right] \quad 2.70$$

In the avascular layer:-

$$\frac{\partial^2 c}{\partial z^2} + \frac{\partial^2 c}{\partial y^2} = g/D \quad 2.71$$

The g value in equation 2.69 accounts for oxygen consumption in the avascular layer.

The model used numerical approximation methods with finite difference equations, where grid points were related to one another using a digital computer.

Figure 2.17 shows the qualitative results obtained in references (119 and 120) for diffusion of oxygen along

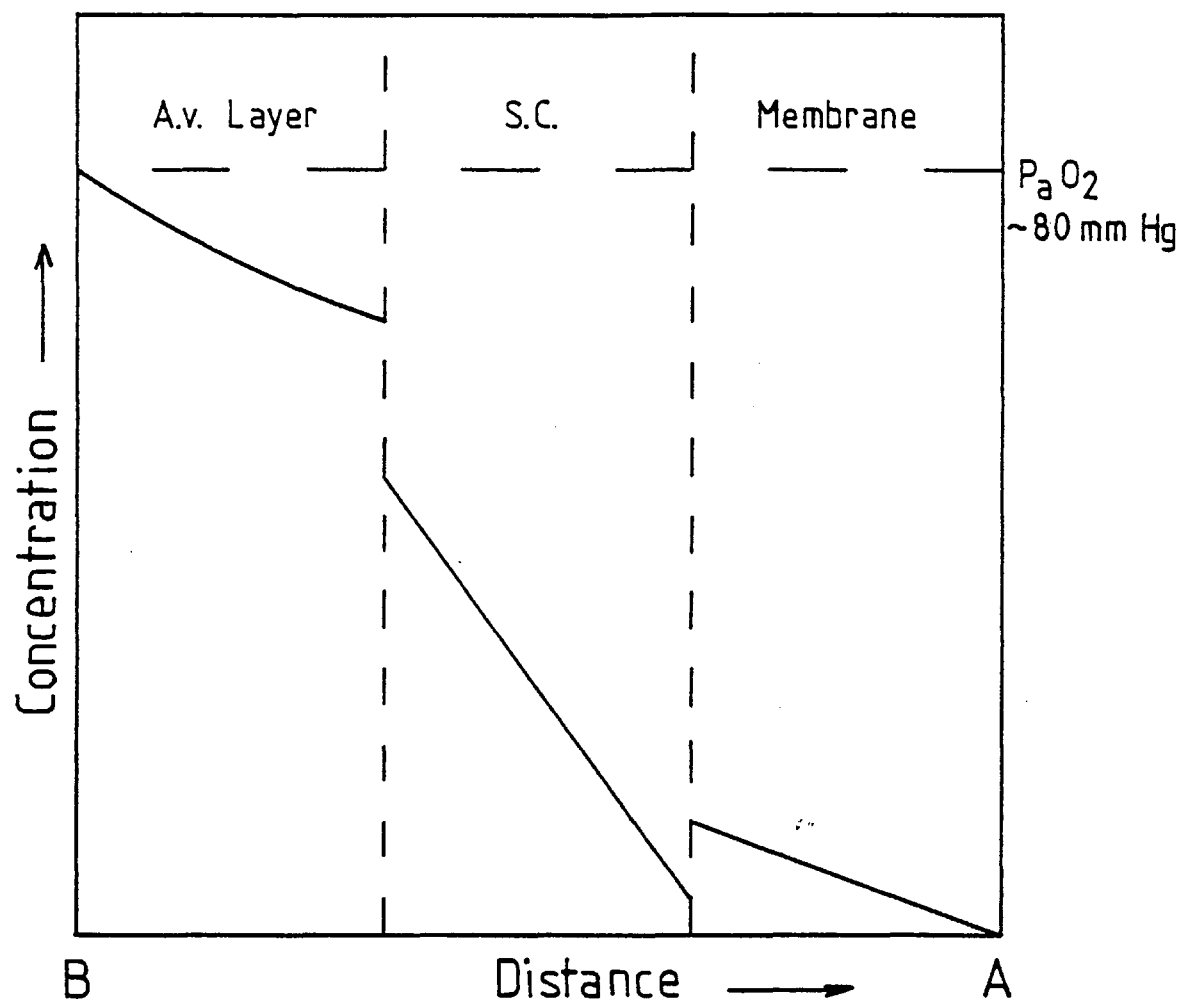


FIGURE 2.17. Schematic concentration profile along the line AB (see Figure 2.16).

the centre line AB of a mass spectrometer hole or an electrode from the dermis/a.v. layer interface to the probe side of the membrane. Diffusion of CO_2 is calculated by changing the sign and value of g in equation 2.71.

Figure 2.18 shows the effect of hole/electrode size on the extent of depletion along the line CD (Figure 2.16). Minimum depletion is achieved when the working electrode is small, as radial diffusion is then more important.

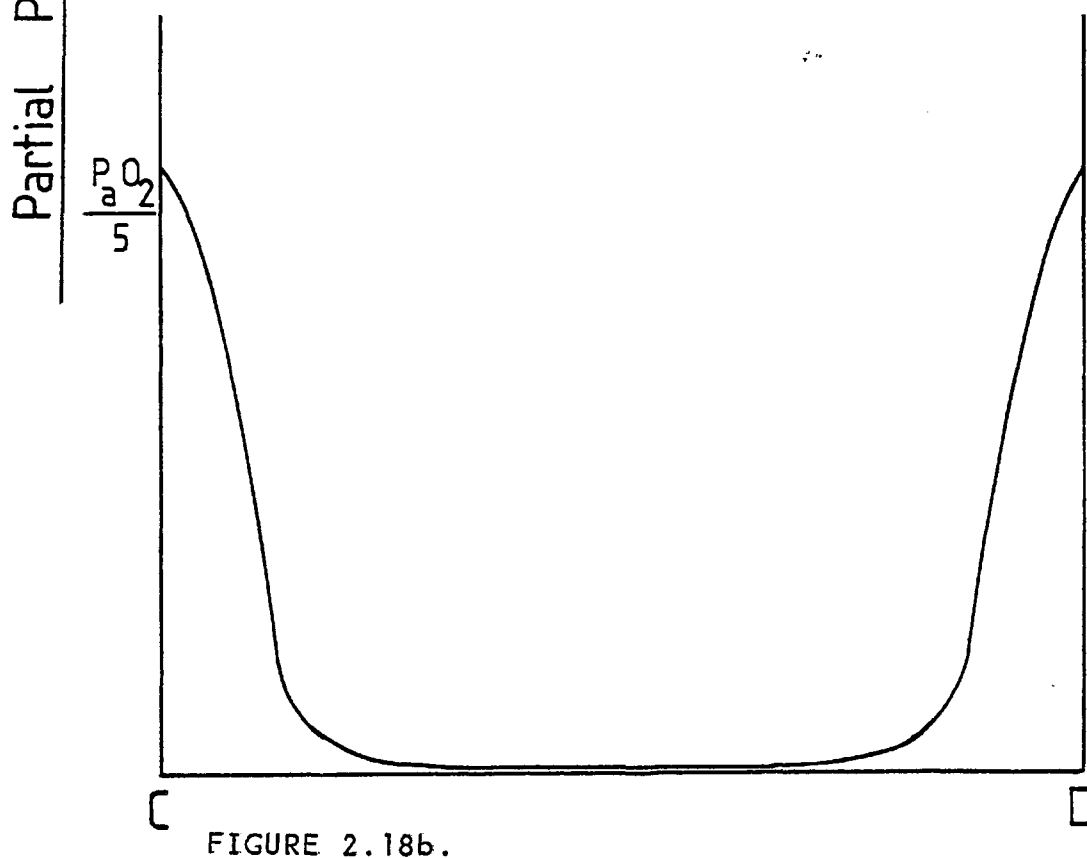
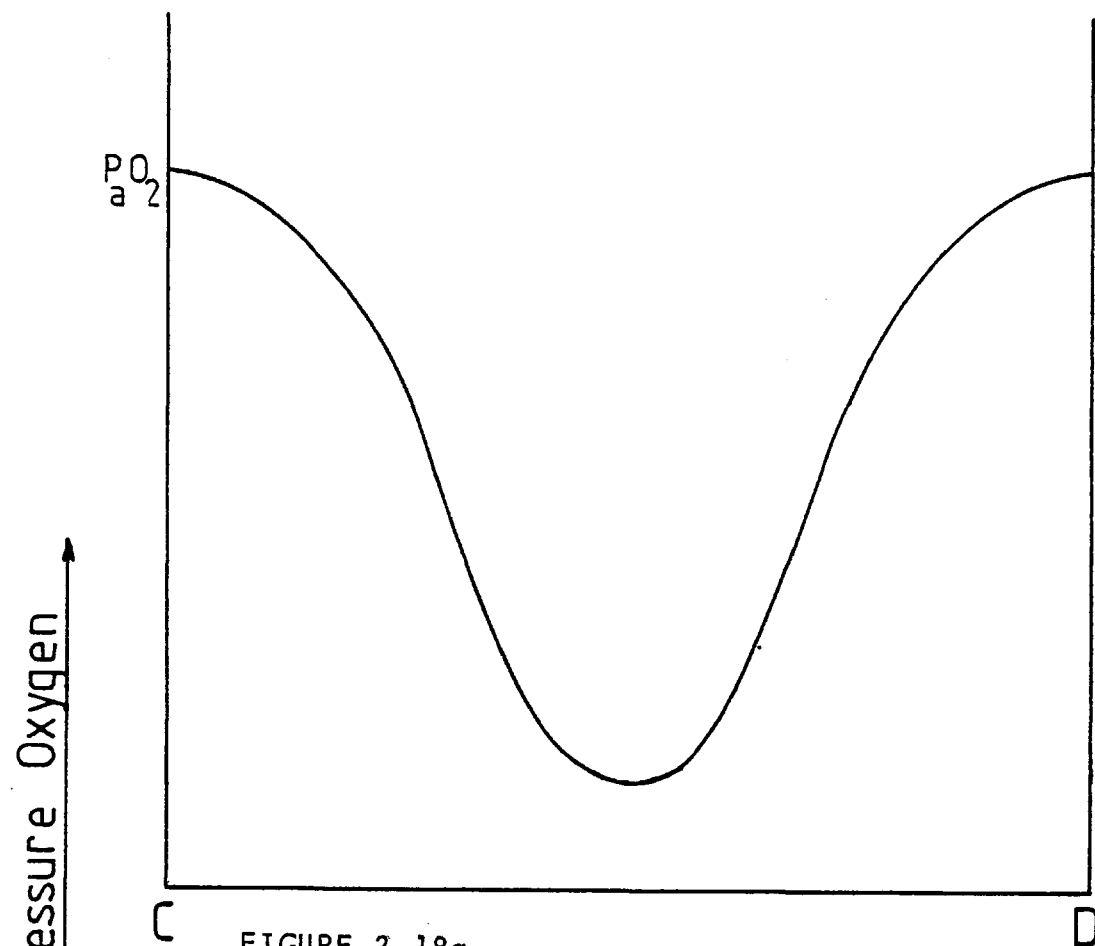


FIGURE 2.18. The effect of electrode size on the extent of depletion along the line CD (see Figure 2.16).
 a) Small cathode ($r \sim 15 \mu\text{m}$)
 b) Large cathode ($r \sim 1 \text{ mm}$)

CHAPTER THREE

EXPERIMENTAL DETAILS

This chapter contains details of apparatus, experimental procedures and reagents. The chapter contains the following sections:-

Section 3.1. contains details of apparatus and experimental procedures used with the rotating disc and ring disc electrodes.

Section 3.2. details apparatus and additional procedures involving membrane electrodes.

Section 3.3. outlines the supporting electronics.

Section 3.4. describes reagents used in this study.

Section 3.5. covers other experimental details.

3.1. ROTATING ELECTRODE APPARATUS AND EXPERIMENTAL PROCEDURES

3.1a. The Rotating Electrode Assembly

The rotating disc and ring disc electrodes used in this work are tabulated in Table 3.1. Prior to use the rotating electrodes were mechanically polished to a mirror finish by the following procedure:-

- 1) The electrodes were lapped flat and machine marks removed with 400 grit silicon carbide paper.
- 2) The electrodes were then polished with 25 μm alumina, then with 6 μm and 3 μm diamond lapping compound with

Table 3.1 Rotating Electrodes Used

Electrode	Electrode and Insulating Mantle Material	Dimensions			Characteristics				
		r_1	r_2	r_3	α (a)	β (b)	$\beta^{\frac{2}{3}}$ (b)	N_o (c)	
A	Au disc Pt ring Delrin body	1.487			0.168				
			1.566			0.758			
				1.850			0.831		0.323
A' (d)	Au disc Pt ring Kel-F body				0.312				
		1.383				0.728			
			1.514				0.809		0.289
				1.754					
B	Ag disc Pt ring Kel-F body				0.346				
		1.344				0.758			
			1.484				0.831		0.278
				1.706					
C	Pt disc Araldite body	3.506							
D	Ni disc Araldite body	3.527							
E	Tin disc	3.512							
F (e)	Pt disc	0.712							

(a) Calculated from equation 2.26

(b) " " " 2.27

(c) " " " 2.27

(d) This electrode was the original electrode A, but was remade due to a "leak" that developed between ring and disc.

(e) This electrode was plated with mercury by gold plating the electrode, then amalgamating the electrode with mercury.

a water soluble lubricant, Hyprez W. An Oxford Electrodes polishing table was used to ensure the electrodes were polished flat in a plane perpendicular to the rotation axis.

3) The electrode was hand polished with a paste of $1\text{ }\mu\text{m}$ alumina in water.

Before each experiment it was polished with $0.3\text{ }\mu\text{m}$ alumina slurry to prevent turbulence due to surface roughness.

The radii of the electrodes were accurately measured with a travelling microscope to 0.001 mm . The value of N_0 for ring disc electrodes was calculated from equation 2.25, using a Texas Instruments SR52 programmable desk top calculator.

The electrode was screwed on to a steel dual shaft mounted in a plastic bearing block. The bearing block was mounted on two steel rods and could be lowered to immerse the electrode in solution. Electrode contact was made with sealed mercury pools inside the bearings, which contacted the ring and disc via the dual shaft.

Rotation of the electrode was achieved with a printed armature D.C. servomotor (Printed Motors Ltd.), mounted on top of the bearing block. The rotation speed was controlled with an Oxford Electrodes motor controller, which employed optical feedback using a slotted i.r. opto switch and slotted disc. A rotation speed step was

achieved by switching on an external voltage source connected to a voltage input B.N.C. socket on the motor controller. The rotating assembly and motor controller is shown in Figure 3.1.

3.1b. The Electrochemical Cell

The electrochemical cell is shown in Figure 3.2. The cell is a double walled glass vessel which allows the electrolyte to be maintained at $25 \pm 0.1^{\circ}\text{C}$ by means of a circulating pump and an external thermostatted water reservoir. One side arm contains the reference electrode, and the other holds a sintered counter electrode compartment. The counter electrode was made of platinum gauze. On top of the cell was a close fitting teflon lid, with a central hole for the electrode. The gas bubbler allows the electrolyte to be deoxygenated with oxygen-free nitrogen, or equilibrated with other gas mixtures. During experiments the gas was passed over the top of the solution to prevent bubbles impinging on the electrode and causing noise. A photograph of the cell is in Figure 3.1.

The reference electrode used in aqueous solutions was a saturated calomel electrode, prepared by the method of Ives and Janz.⁽¹²¹⁾ In DMSO solutions a silver/silver ion reference electrode was used. A silver wire was immersed in DMSO containing 0.01 M silver nitrate and the same concentration of supporting electrolyte as the main solution. The reference electrode was housed in a calomel electrode outer body.

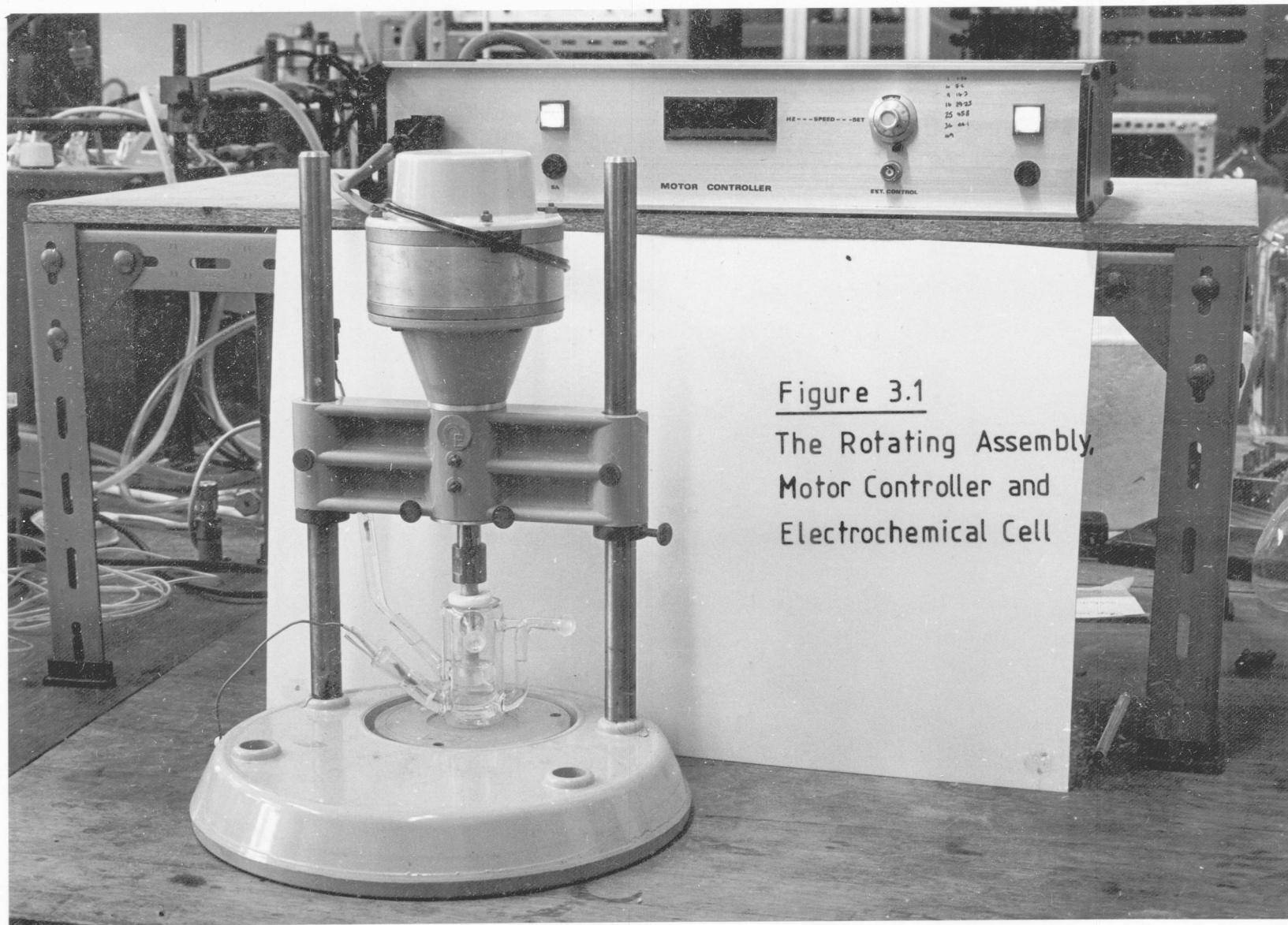


Figure 3.1

The Rotating Assembly,
Motor Controller and
Electrochemical Cell

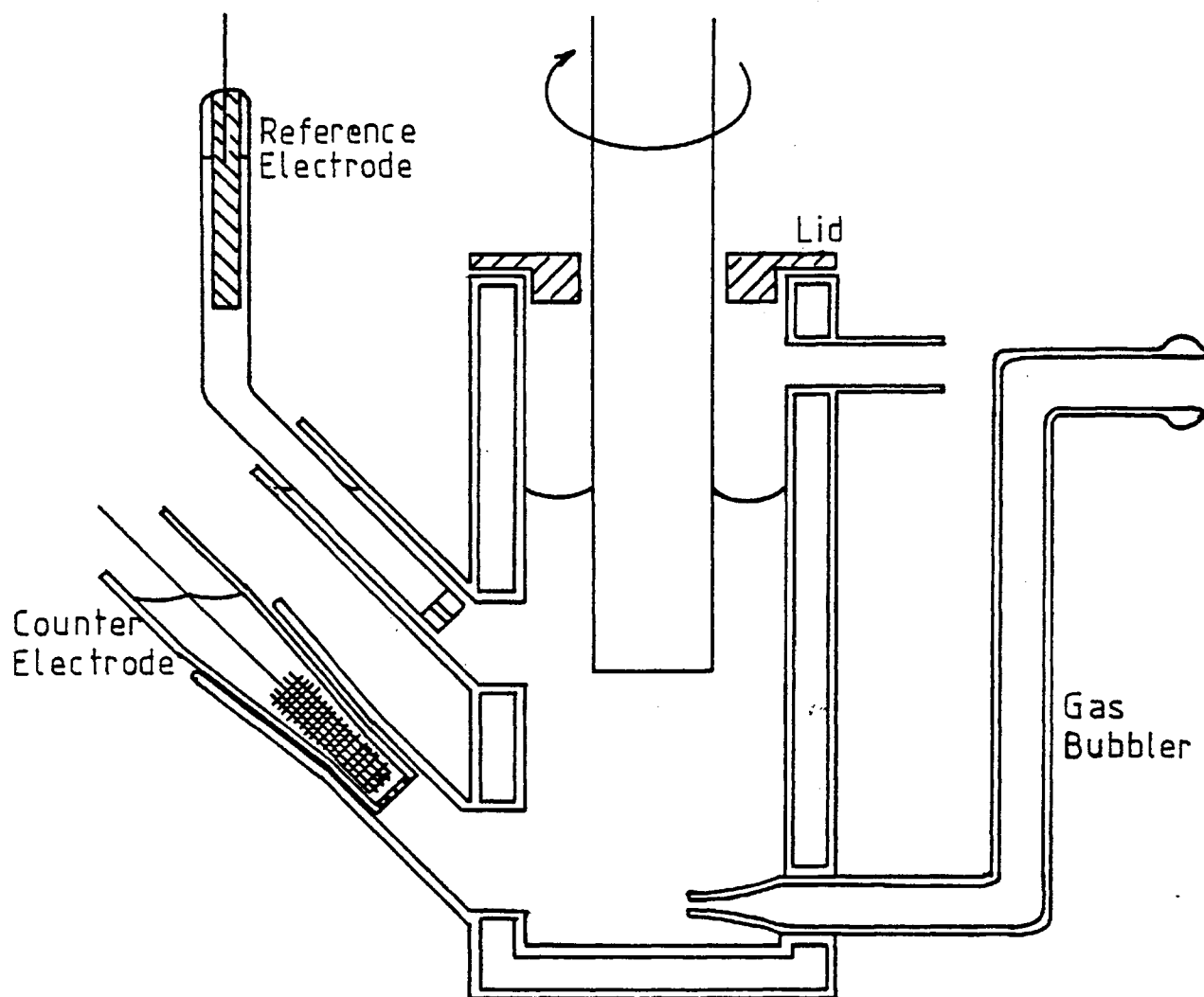


FIGURE 3.2. The electrochemical cell.

3.1c Gas Mixtures

Aqueous solutions were deoxygenated with nitrogen from which trace oxygen had been removed by passing the gas through sodium anthroquinone-2-sulphonate solution. The anthroquinone was maintained in the reduced form by zinc amalgam.

Gas mixtures were prepared using two pairs of G.E.C. Marconi series 1100 flowmeters. One pair allowed flows of 10-300 ml/min to be measured while the other pair allowed flows up to 1400 ml/min. The flow of the separate gases in the gas mixture were measured, then the gases were mixed and passed through or over the solution. When a DMSO solution was in the pot the gas mixture was dried by passing the mixture through a dreschel bottle immersed in a cardice-methanol mixture.

Each flowmeter was separately calibrated with a bubble flowmeter. The time taken for a soap bubble to pass along a known volume of a tube connected in series with the flowmeter was measured. Each flowmeter was calibrated for CO_2 , O_2 and N_2 .

3.2. APPARATUS AND PROCEDURES USED IN EXPERIMENTS WITH MEMBRANE ELECTRODES

3.2a Electrode Designs

Six different types of membrane electrode were used. All were made at Imperial College by Mr. M. Pritchard except the transcutaneous electrode, which was made at

the John Radcliffe Infirmary, Oxford. The electrodes are individually described below.

3.2a.1. Joint Carbon Dioxide/Oxygen Electrodes

Two prototype CO_2/O_2 electrodes were constructed. Both contained an inner DMSO solution which was separated from the outer aqueous solution by a Teflon membrane. The aqueous solution was enclosed by a metallised membrane.

In both electrodes electrical contact to the metallised membrane was achieved with a silver loaded epoxy resin stud mounted on the front of the electrode. The metallised membrane was fixed to the stud with fresh silver loaded epoxy adhesive, which was allowed to set before the aqueous solution was added. On dismantling the electrode the stud was scraped clean. The electrode designs are detailed below:-

Type 1 (Electrode 1)

The first of the two electrodes is shown in Figures 3.3 and 3.4. The body of the assembly was made of Delrin. The Teflon Membrane T was held in place by the tight fitting Teflon ring A, and enclosed a thin DMSO solution layer. The DMSO solution layer was contacted by a cathode E, of radius 0.5 mm, reference electrode R and counter electrode C, all made of silver.

The inner system was assembled by first trapping the membrane T with the ring B - the membrane was placed over

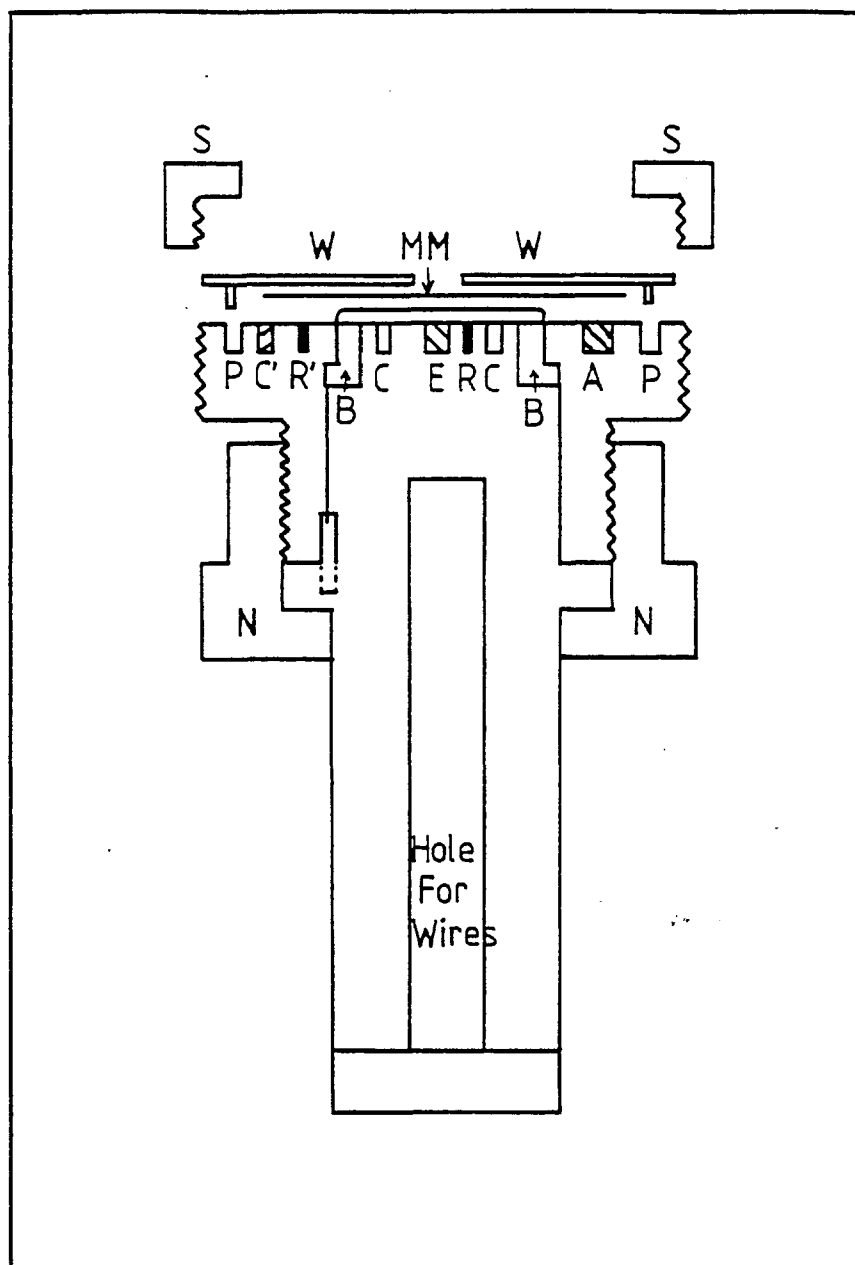


FIGURE 3.3. CO_2/O_2 electrode type 1 (Electrode 1)

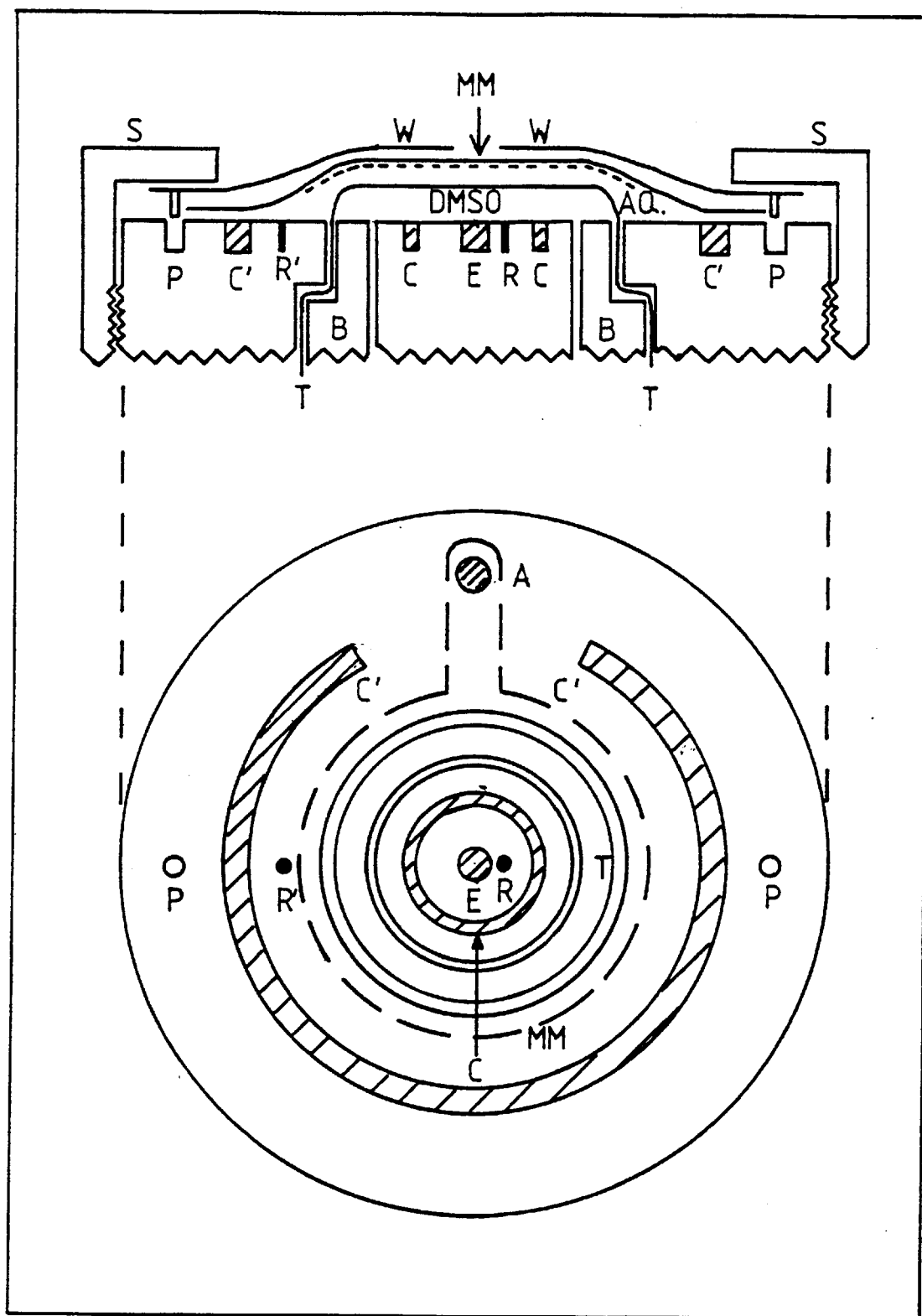


FIGURE 3.4. Detail of Figure 3.3.

the washer, which was then inserted into the housing from behind. A small amount of DMSO was placed on the inside surface of the membrane, and trapped in place by the inner electrode assembly, which was fastened by the nut N.

The metallised membrane MM, enclosing a thin layer of aqueous electrolyte, was held in place by the Delrin washer W, the central aperture of which was 2 mm diameter, and secured by the screw cap S on the silver epoxy stud A. The washer prevented any leakage of electrolyte. The reference electrode R' and counter electrode C' were made of silver. Contact between the metallised membrane and reference was prevented by a 50 μ m diameter nylon spacer (Radiometer).

Type 2 (Electrode 2)

The second CO₂ electrode was made because of problems detailed in Chapter 5 that occurred with type 1. The electrode was made of Kel-F and is illustrated in Figures 3.5 and 3.6. The main features different from type 1 are the much larger solution reservoirs (0.4 ml DMSO and 3.0 ml aqueous), and the remote placing of the counter electrodes. The Teflon membrane (23) was held in place by a Teflon ring (24), which was a tight fit, into the recess (24A). The washer (25) the central aperture of 5 mm diameter, was made of Teflon, and its inner face was ridged to provide a tight electrolyte seal around the edge of the membrane and provide a good metallised layer

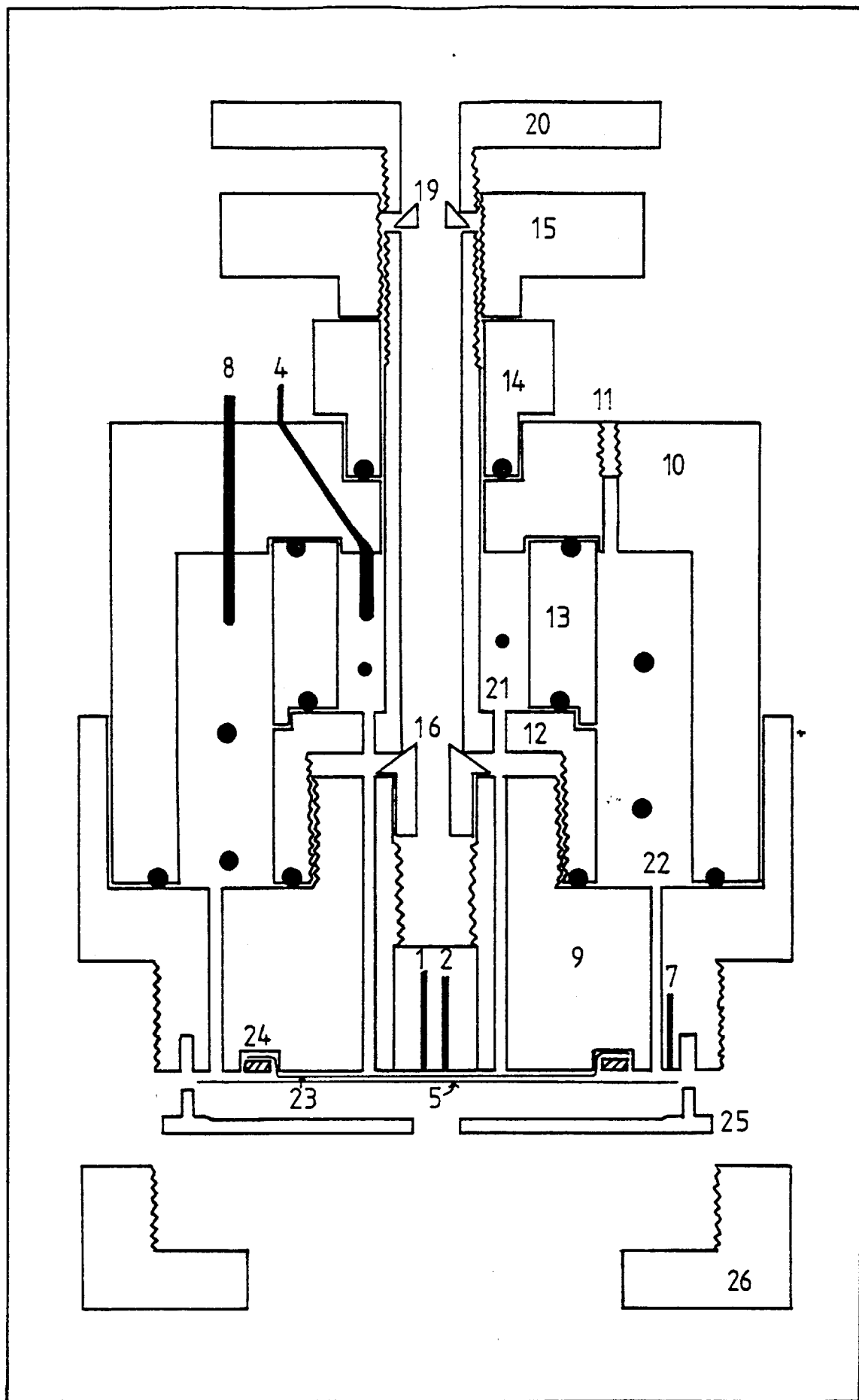


FIGURE 3.5. CO₂/O₂ electrode type 2 (Electrode 2)

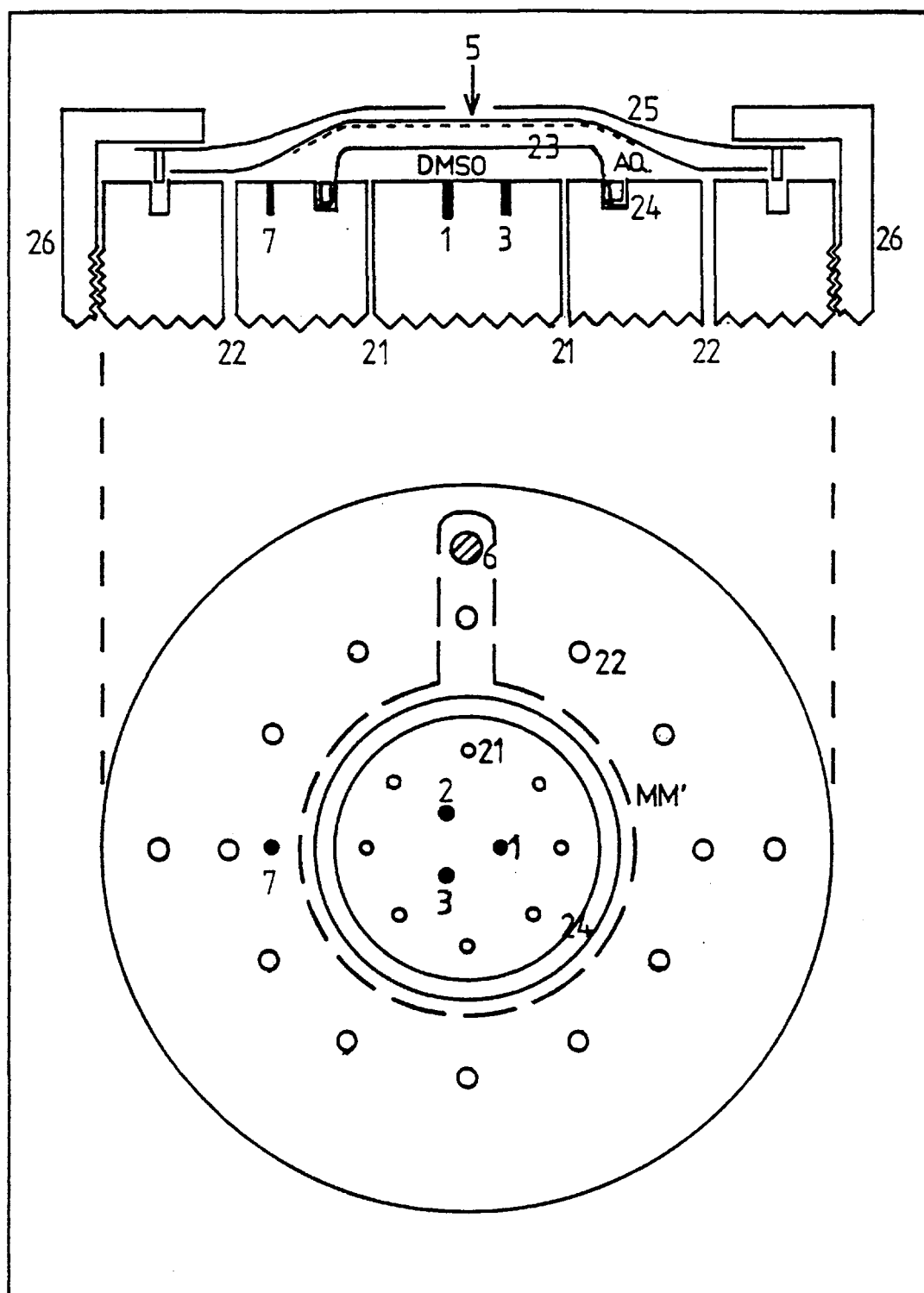


FIGURE 3.6. Detail of Figure 3.5.

1. Silver wire ($\emptyset$ 0.5 mm) working electrodes for CO₂ detection
 2. Gold wire ($\emptyset$ 0.5 mm)
 3. Reference electrode (silver wire)
 4. Counter electrode (ca. 5 cm long silver wire, laid in spiral around 12)
 5. Metallized membrane
 6. Silver epoxy stud (where met. mem. is glued on)
 7. Reference electrode (silver wire)
 8. Counter electrode (ca. 20 cm long silver wire, laid in a spiral around 13)
 9. Main body of the electrode
 10. Part enclosing the outer electrolyte reservoir
 11. Hole for changing electrolyte
 12. Central core providing access for the leads to the electrode wires 1 - 3
 13. Annulus sealing the inner from the outer compartment
 14. Teflon annulus sealing the outer compartment
 15. Screw pressing parts 9, 10, 12, 13 and 14 together
 16. Teflon piece sealing wires and contacts from inner electrolyte compartment
 17. Screw to clamp down wires
 18. Flexible rubber piece pressing wires together as screw 17 is screwed down
 19. Teflon ring pressing on lead as screw 20 is screwed down
 20. Screw to hold lead in fix position
 21. Holes connecting inner electrolyte reservoir with solution under membrane 23
 22. Holes connecting outer electrolyte reservoir with solution under met. memb. 5
 23. Membrane separating the two electrolyte systems
 24. Ring to clamp down membrane 23
 25. Washer with locator pins
 26. Screw cap
- o Rubber "o-rings" (seals)
- Optimal shape of metallized membrane

Key for figures 3.5 and 3.6

contact. The middle of the washer face was also ridged to provide a gas tight seal against the metallised membrane, thereby preventing excessive metallised membrane currents.

Solution contact between the inner reservoirs and the outer electrode face was achieved by a series of drilled holes (21 and 22). The electrode was assembled by screwing nuts 15 and 20 tight, then filling the inner reservoir with DMSO through the drilled holes (21) with a syringe. An excess of DMSO was left on the electrode face. A piece of Teflon membrane was stretched over the electrode and the Teflon ring (24) was inserted. Care was taken not to trap air bubbles under the membrane. The outer reservoir was also filled using a syringe and the rest of the electrode assembly procedure was the same as type 1.

Photographs of the two types of electrodes are shown in Figure 3.7.

3.2a.2. Medical Electrodes

Transcutaneous Electrode (Electrode 3)

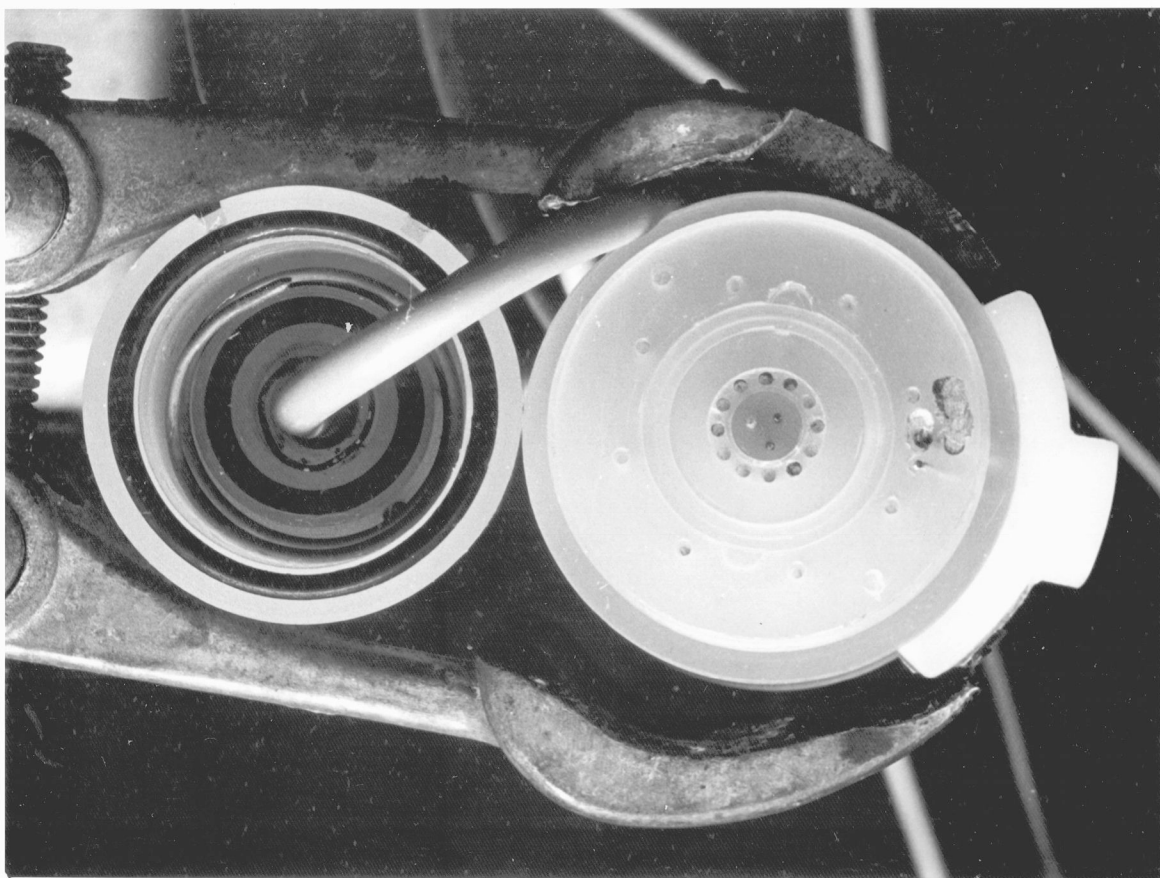
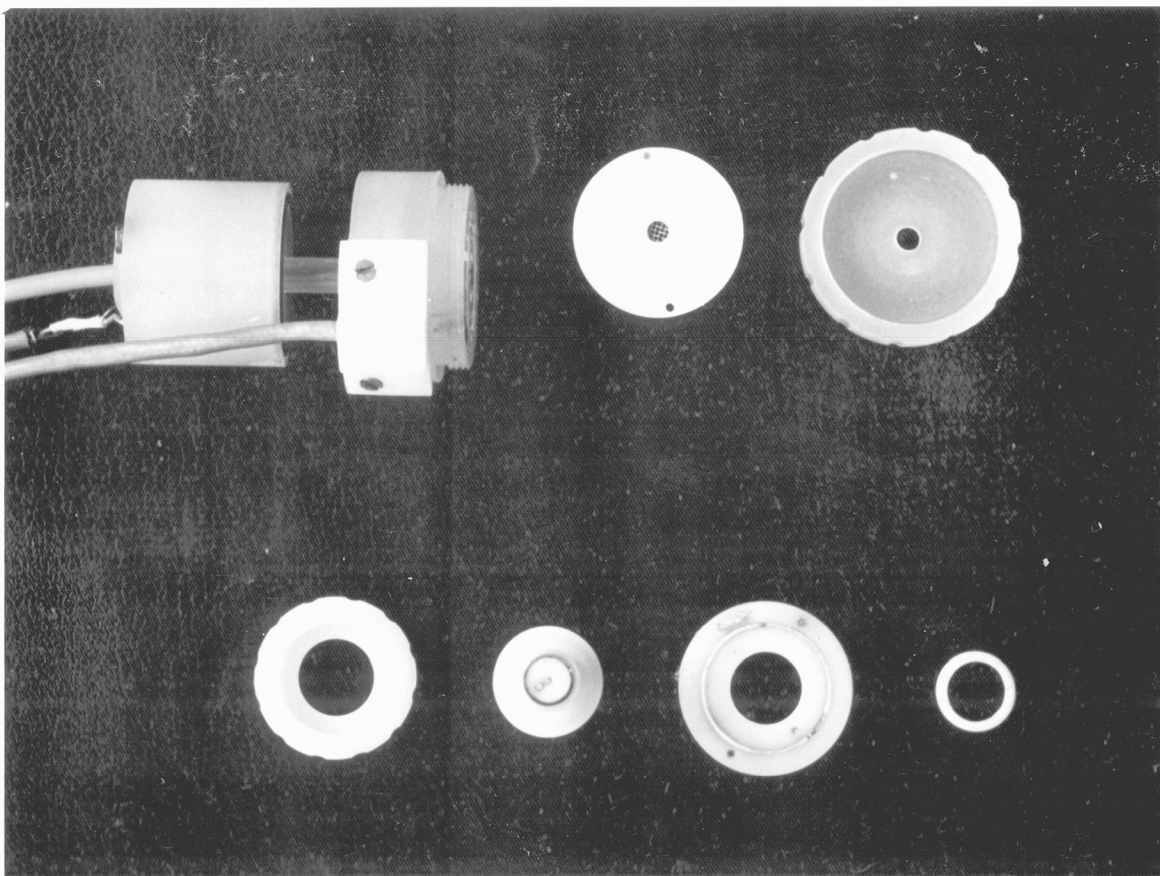
The transcutaneous electrode is shown in Figure 3.8. The silver cathode (1), gold cathode (2), silver reference electrode (3) (all of radius 0.25 mm), and silver counter electrode (4) were all mounted on the face of the electrode. The electrolyte was enclosed by a membrane (10) which was

Electrode 2

Electrode 1

Figure 3.7 Carbon Dioxide / Oxygen Electrodes

Detail of Electrode 2



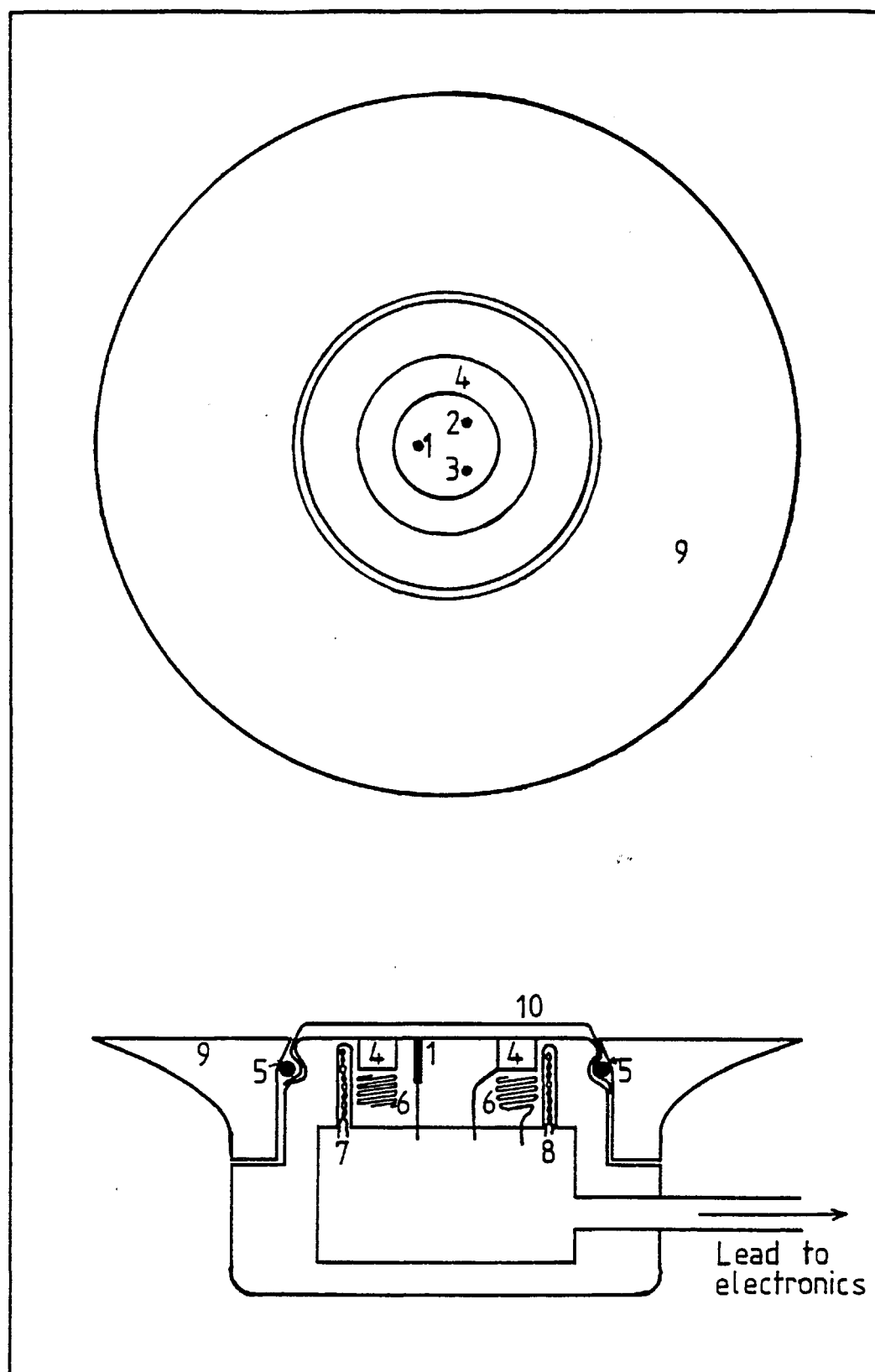


FIGURE 3.8. The transcutaneous electrode (Electrode 3).

held in place by a rubber "O" ring (5). The body of the electrode was made of TPX (4 methyl pentane, Mitsui Petroleum Chemical Industry). The electrode also consisted of a heating coil (6) mounted beneath the counter electrode, and two thermistors (7,8). The thermistors measured the skin surface temperature beneath the electrode, and were situated in drilled "blind" holes which terminated just below the electrode face.

The electrode was mounted on the skin by inserting the electrode into a collar (9) (see Figure 3.8) which was stuck to the skin with a ring of double sided sticky tape (Hellige). Good thermal contact between electrode and skin was achieved by placing a drop of contact gel (Radiometer type 543716) on the skin enclosed by the collar before inserting the electrode. A photograph of the transcutaneous electrode is shown in Fig. 3.9.

Single Membrane CO₂ Electrode (Electrode 4)

This electrode was a forerunner of the transcutaneous electrode and was used for breath analysis in Chapter 5, and to test the feasibility of joint CO₂/O₂ determination with a single membrane electrode. Basically the electrode consisted of the same electrodes as in the transcutaneous electrode, mounted in a Delrin body. The membrane was again held in place by a rubber "O" ring. The electrode is shown in Figures 3.9 and 3.10.

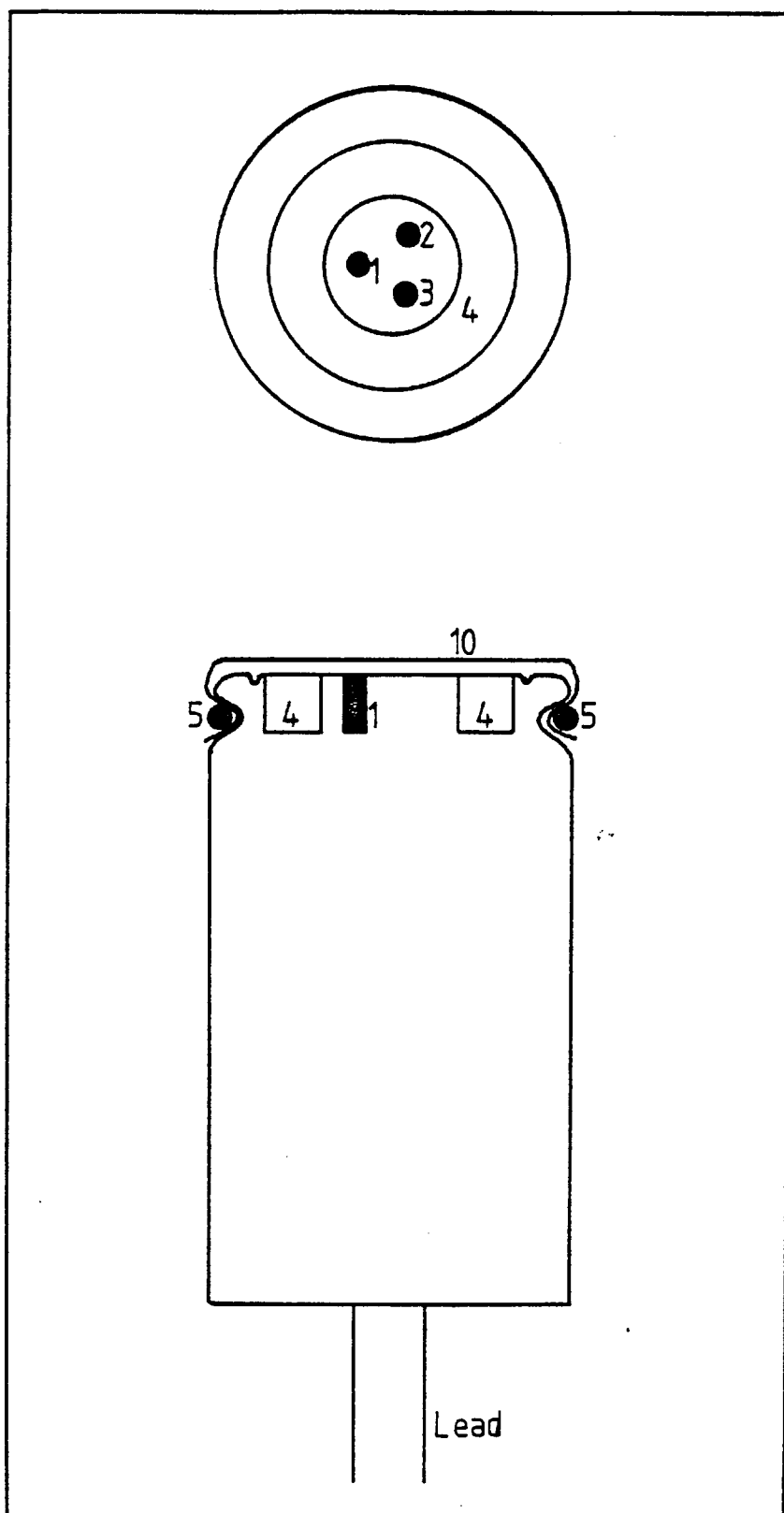
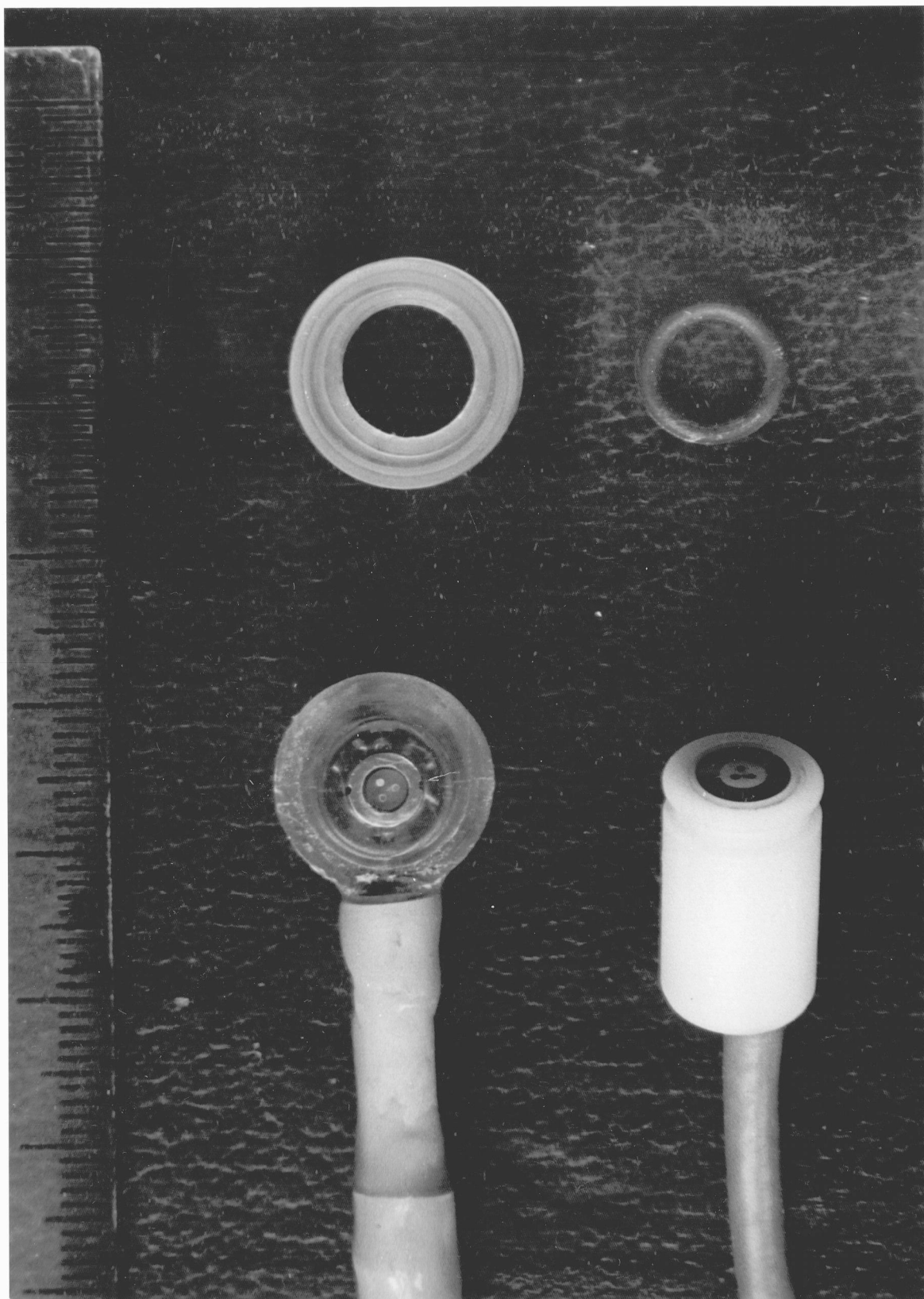


FIGURE 3.9. Single membrane CO₂ electrode (Electrode 4)

Transcutaneous Electrode

Figure 3.9 Medical Electrodes

Electrode 4



3.2a.3. Test Electrodes

Both these electrodes were used to test the performance of systems developed with rotating ring disc electrodes.

Test Electrode A (Electrode 5)

The design of this electrode is shown in Figure 3.11. It consisted of a platinum cathode of radius 0.5 mm (1), silver reference electrode (2) and silver counter electrode (3). The membrane was stretched across a grooved Teflon collar (4), which was a tight fit on the shoulder of the electrode body, and fixed by an "O" ring (5).

The electrode was assembled by placing the collar on a flat surface, membrane face downwards, and then placing a few drops of solution on to the membrane. The electrode body was then inserted into the electrode from above. This technique avoided trapping air bubbles under the membrane.

This electrode was useful as a test electrode because it only used a small volume of solution. Secondly the membrane was not damaged when the electrode was dismantled, and therefore it was reusable.

Ring Disc Test Electrode (Electrode 6)

The use of this electrode is described in Chapter 6. The electrode design was loosely based on the Radiometer E5046 electrode, and consisted of an inner body which held the electrodes and an outer plastic (Delrin) container, which held the membrane.

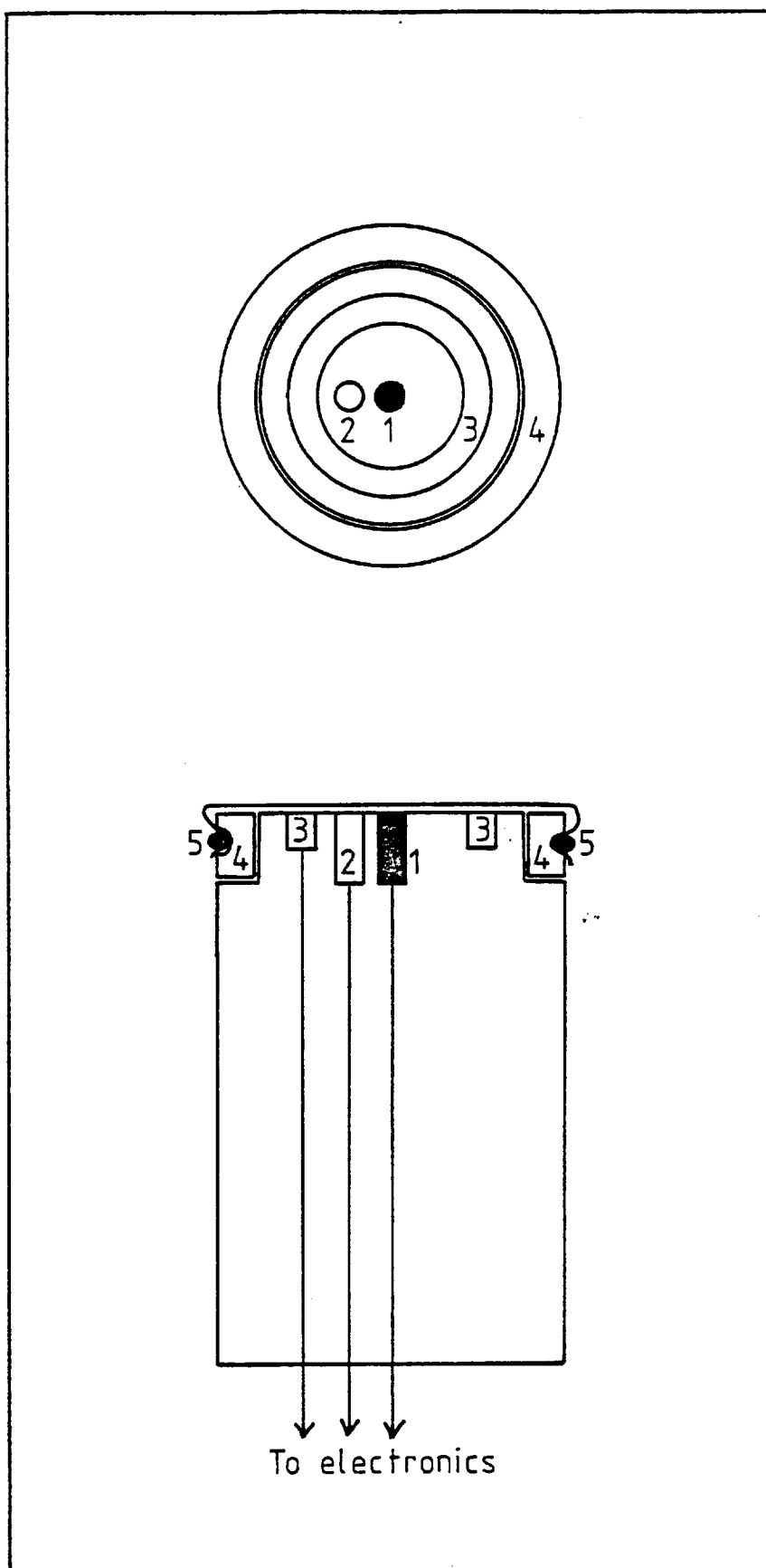


FIGURE 3.11. Test electrode 1 (Electrode 5)

The electrode is shown in Figure 3.12. The gold disc (1) and gold ring (2) both served as cathodes, the silver ring (3) was used as a reference electrode, and the silver coil (4) wrapped around the araldite electrode body was used as counter electrode. The Teflon ring (5) covered a small hole in the outer container. A tongued washer (6) made of Delrin fitted into the grooved outer electrode body, and prevented the inner body twisting when the electrode was being assembled.

The electrode was assembled by fastening the membrane over the outer body with an "O" ring (7). The Teflon ring was moved to uncover the hole in the outer body. Electrolyte was placed inside the outer body, then the inner body was fastened into position by tightening the nut (8). The hole in the outer container, which allowed excess electrolyte to be removed, was then covered with the Teflon ring.

Photographs of the two test electrodes are shown in Figure 3.13.

3.2b. Metallised Membranes

Two types of metallised membranes were used. The first type was made by Dr. M. Lee, at the Department of Electrical Engineering, Imperial College. It was made by electrostatically sputtering a thin film of gold on to a 25 μm Teflon membrane.

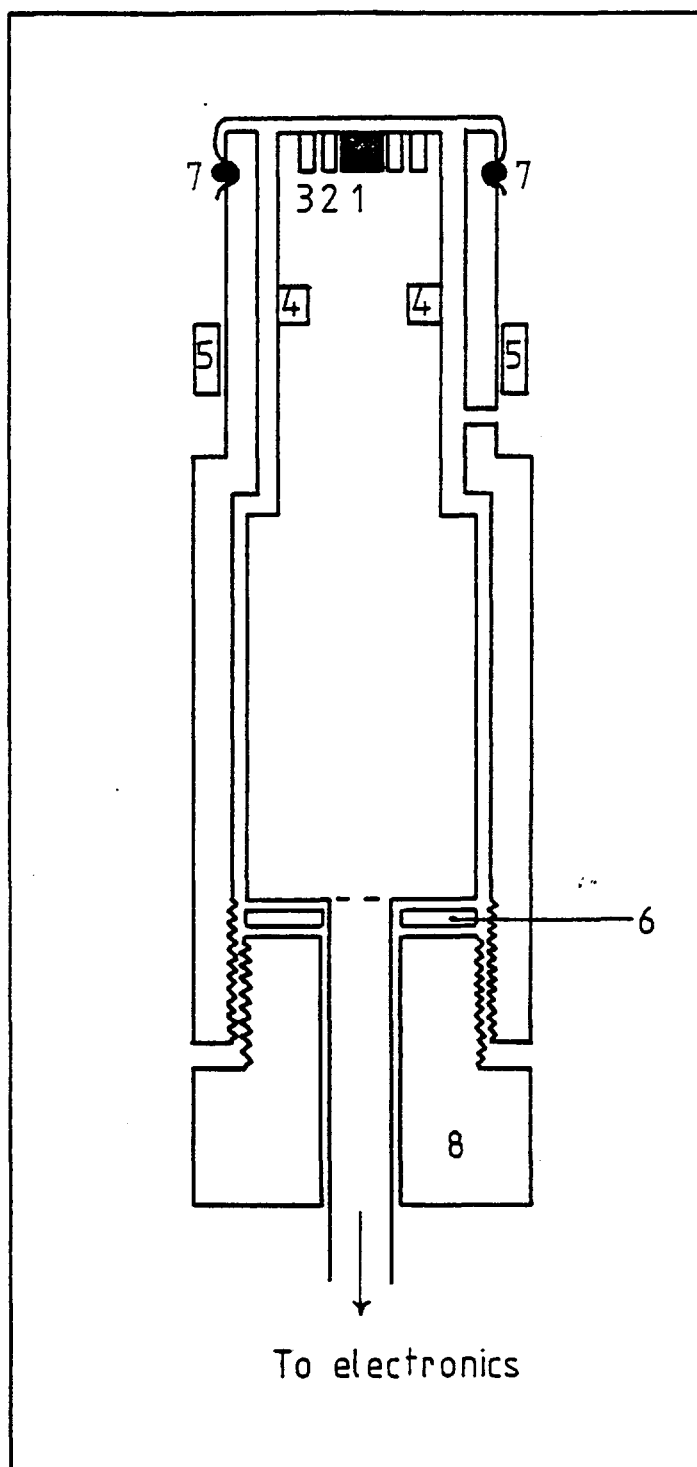


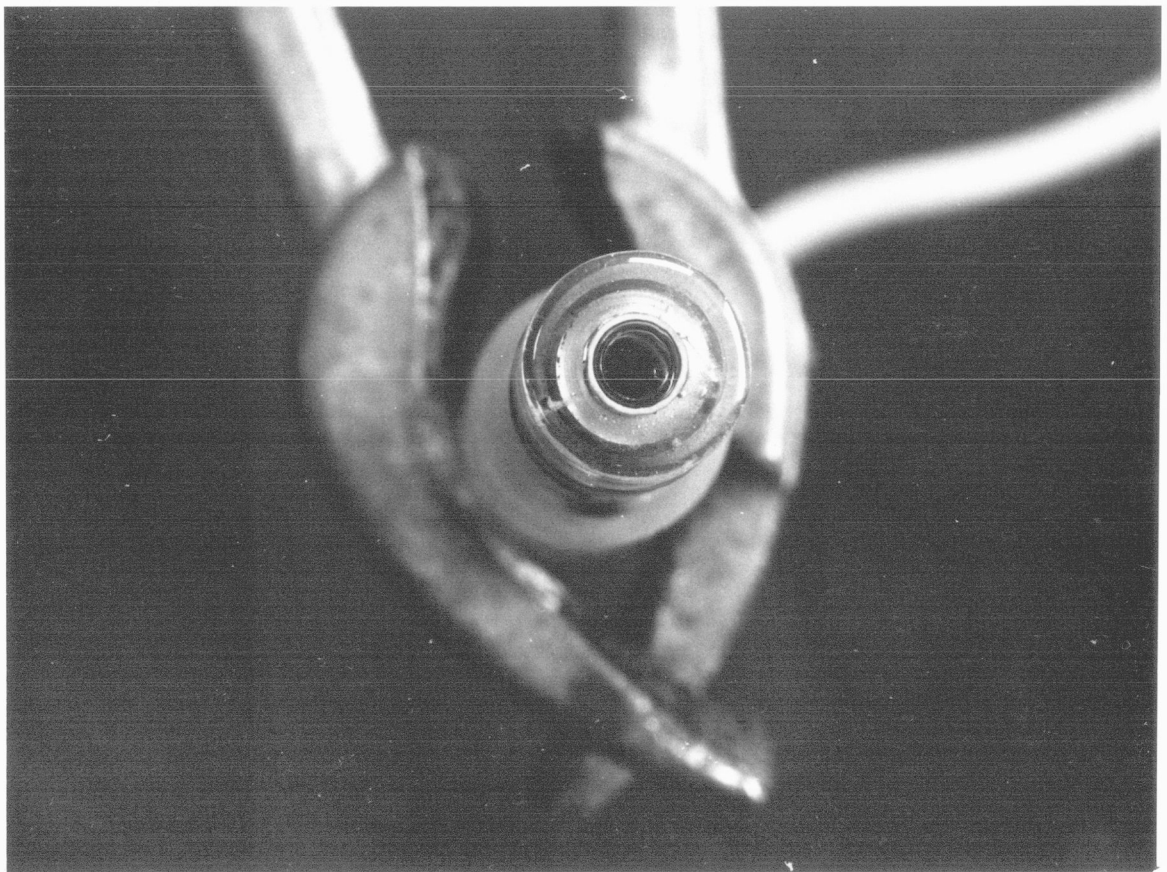
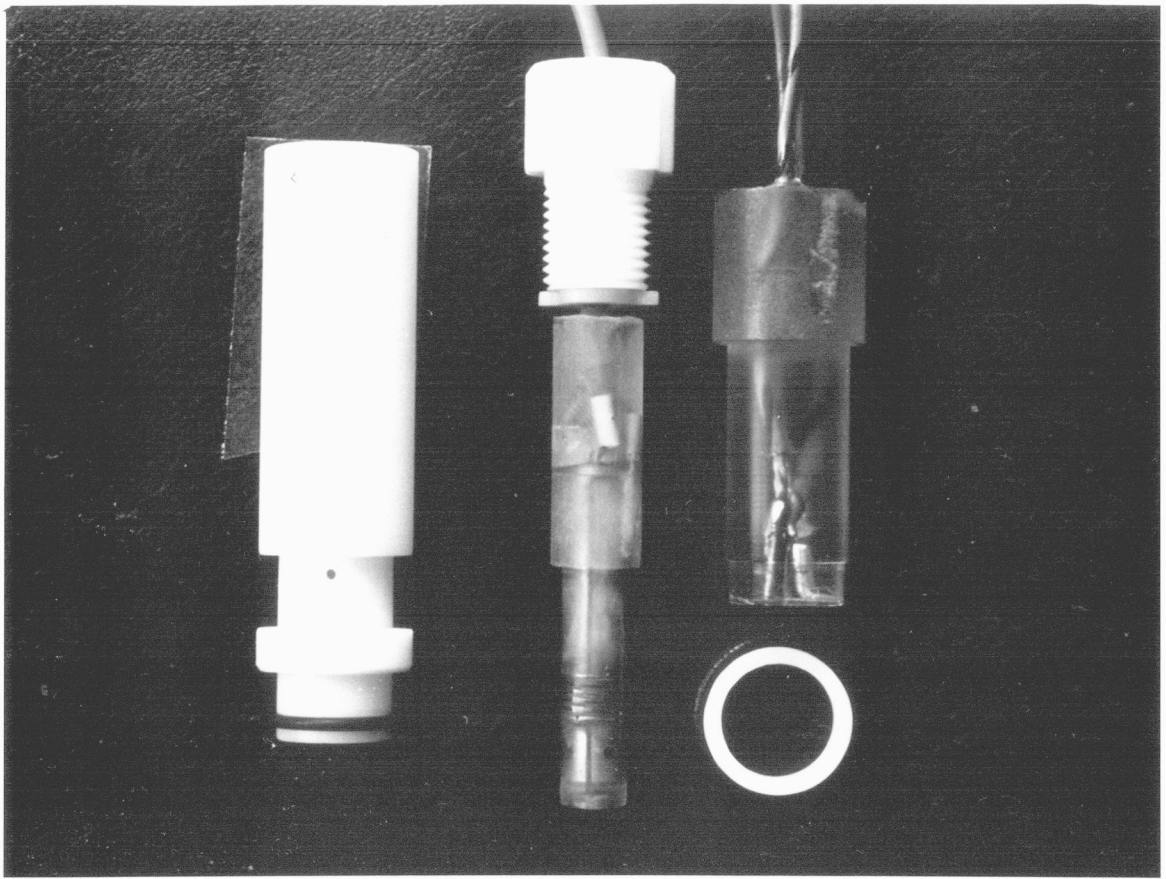
FIGURE 3.12. Ring-Disc test electrode (Electrode 6).

Electrode 6

Electrode 5

Figure 3.13 Test Electrodes

Detail of Electrode 6



A second type of metallised membrane was made in the laboratory according to a technique developed by Bruckenstein.⁽¹²²⁾ A gold resinate solution (Englehardt Ind. no. 8300) was painted with a small brush onto a porous Teflon membrane (Goretex - W.L. Gore and Associates Inc.), and allowed to dry. The membrane was then carefully heated with a hot air gun (Raychem Thermogun C.V.1980) set at 600°C, which meant the organic material was "driven off", leaving a brown gold coating. The metallised membrane was then potential cycled in the membrane electrode solution, between the solvent limits, at a frequency of $5 \cdot 10^{-3}$ Hz.

3.2c. Miscellaneous Details

The reference electrode used in all membrane electrodes except the ring disc membrane electrode was a silver chloride electrode, prepared by the method of Ives and Janz.⁽¹²¹⁾ The ring disc electrode used a silver oxide electrode.

Gas mixtures were again regulated with the flow meters described in Section 3.1c. The electrode was fitted into a water jacketed glass vessel, with a Teflon lid. A gas inlet was also fitted to the vessel. Experiments were carried out with the electrode either in an atmosphere of test gas, or with the electrode immersed in doubly distilled water saturated with the gas mixture.

When the response of an electrode to a step change in gas composition was examined, a smaller glass vessel

was used, with a dead space of only 5 cm^3 . Gas flow rates of $>15 \text{ cm}^3/\text{s}$ were used, and the electrode face was situated as close as possible to the gas inlet.

The membrane mainly used in this work was $12 \text{ }\mu\text{m}$ Teflon (Radiometer D602). Also used was $6 \text{ }\mu\text{m}$ Teflon (Pallflex Products Corpn., U.S.A.) and $25 \text{ }\mu\text{m}$ polypropylene (Radiometer D604).

3.3. SUPPORTING ELECTRONICS

3.3a. Operational Amplifiers

The basis of the control electronics used in this work is the operational amplifier.⁽¹²³⁾ A schematic operational amplifier is shown in Figure 3.14. It is a high gain amplifier with an inverting input V_{in}^- , a non-inverting input V_{in}^+ and an output V_o . An ideal (theoretical) operational amplifier has the following characteristics:-

- 1) When $V_{in}^+ = V_{in}^-$, $V_o = 0V$.
- 2) When $V_{in}^+ - V_{in}^- \neq 0$, $V_o \rightarrow \pm \infty$ (i.e. the open loop gain A_o is infinite, where $A_o = V_o / (V_{in}^+ - V_{in}^-)$).
- 3) The inputs have infinite impedances, hence the input bias current $i_b = 0$.
- 4) The output impedance is zero.

The characteristics of the two operational amplifiers mainly used in this work are shown in Table 3.2. In practise the open loop gain is ca 10^5 (gain (dB) = $20 \log A_o$).

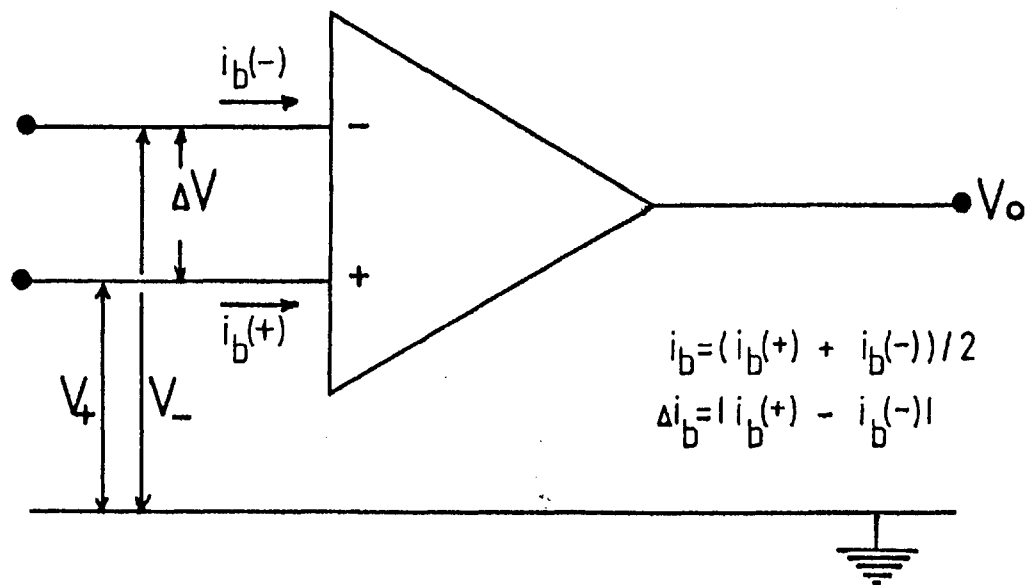


Figure 3.14. Schematic Operational Amplifier.

TABLE 3.2. Operational Amplifier Specifications

Op-Amp	LH0042CD	μ AF355TC	Ideal
Radiospares No.	305-945	307-058	
Output voltage	± 15 V	± 15 V	large
Output current	5 mA	5 mA	large
Open-loop gain, A_o	100 dB	106 dB	infinite
Input impedance	$10^{12} \Omega$	$10^{12} \Omega$	infinite
Input offset voltage	Adj. to zero	Adj. to zero	zero
-temp. coefficient	5 μ V/ $^{\circ}$ C	5 μ V/ $^{\circ}$ C	zero
Input bias current, i_b	10 pA	30 pA	zero
Input offset current, Δi_b	1 pA	10 pA	zero

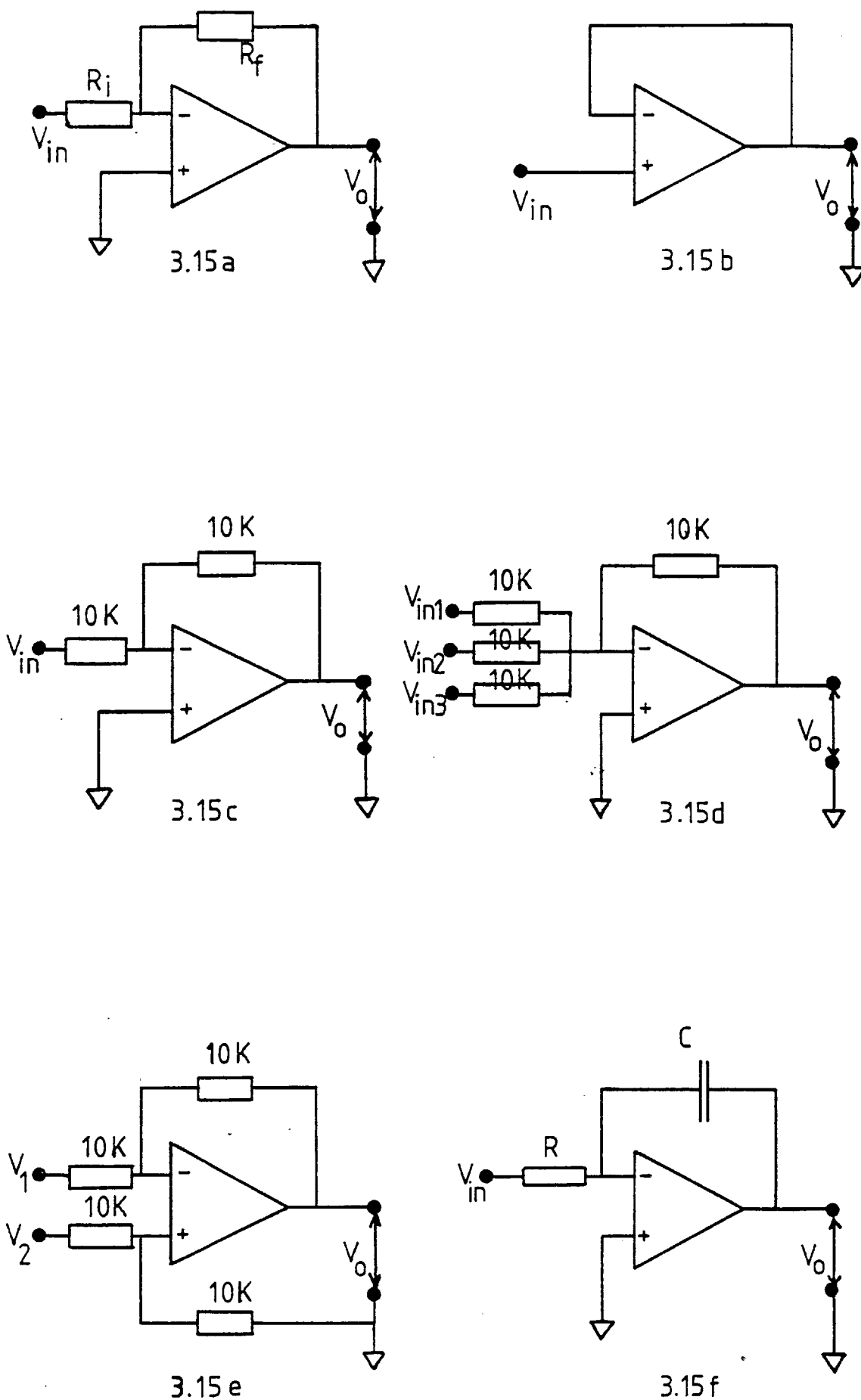


FIGURE 3.15. Some commonly used electronic circuits, which were constructed as modular units.

plug leads that interconnected the modules did not need shielding. External connections to the electrodes, chart recorder etc. were made using BNC plugs, sockets and shielded leads. The modules were powered by an R.S. components $\pm 15V$ supply (no. 591124).

Modules were constructed of the following circuits:-

- a) Voltage follower - A uni gain amplifier that ensures no current is drawn from a source (e.g. a reference electrode) (Figure 3.15b).

$$V_o = V_{in}$$

- b) Inverting amplifier (Figure 3.15c)

$$V_o = -V_{in}$$

- c) Summing inverting amplifier (Figure 3.15d)

$$-V_o = V_{in\ 1} + V_{in\ 2} + V_{in\ 3}$$

- d) Subtractor (Figure 3.15e)

$$V_o = V_1 - V_2$$

- e) Potential Source (Figure 3.16)

This module produces voltages from 0V to $\pm 5 V$ with respect to either earth or an input voltage.

- f) Triangular Wave Generator

The triangular wave generator is illustrated in

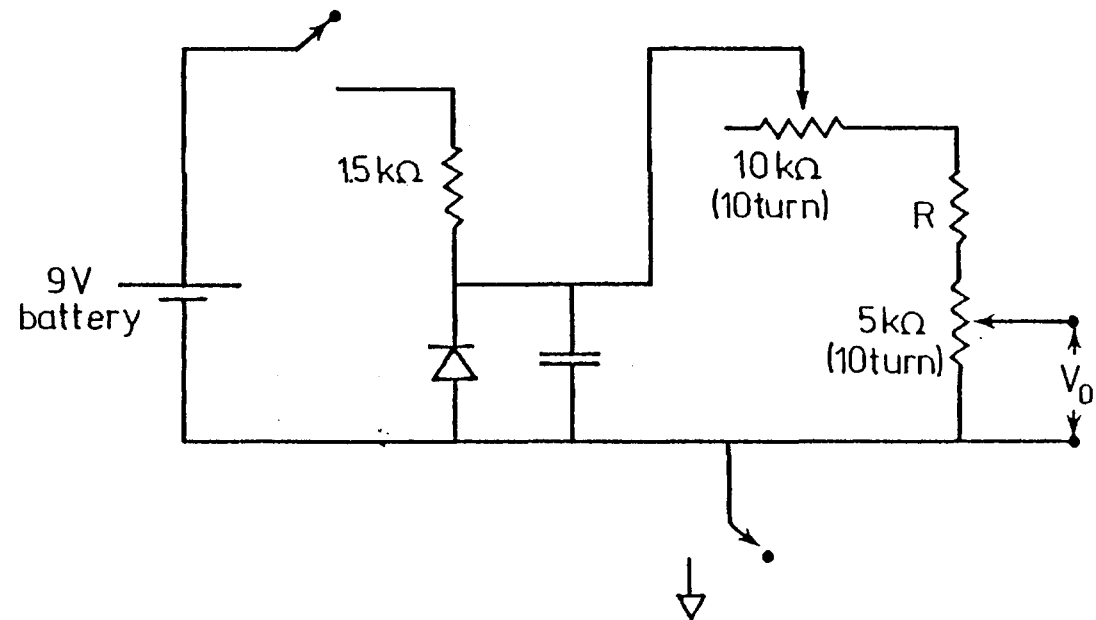


FIGURE 3.16. Potential source.

Figure 3.17. It consisted of a power supply which converted ± 15 V to ± 9 V and ± 5 V, and a wave generator. The basis of the wave generator is the integrator, shown in Figure 3.15f.

The additional elements in Figure 3.17 control the potential limits of the sweep and allow the sweep direction to be reversed, held or manually changed to any starting potential. The sweep limits were ± 5 V, and the sweep direction was indicated with Light Emitting Diodes. Variation of the sweep rate was achieved by varying the input resistor - sweep rates from 1 mV s^{-1} to 2 V s^{-1} were attainable.

g) Potentiostat (Figure 3.18)

The potentiostat is a device which maintains a constant potential between the working and reference electrodes, irrespective of cell resistance and the current passing through the cell. The reference electrode potential is the same as V_1 because there is feedback between the reference and counter electrodes through the solution.

The disc and ring potentials are independently governed by the voltages V_2 and V_3 . The amplifiers 2 and 3 are current to voltage convertors, and the output voltages of these two amplifiers are:-

$$V_o = iR_f + V_{in}$$

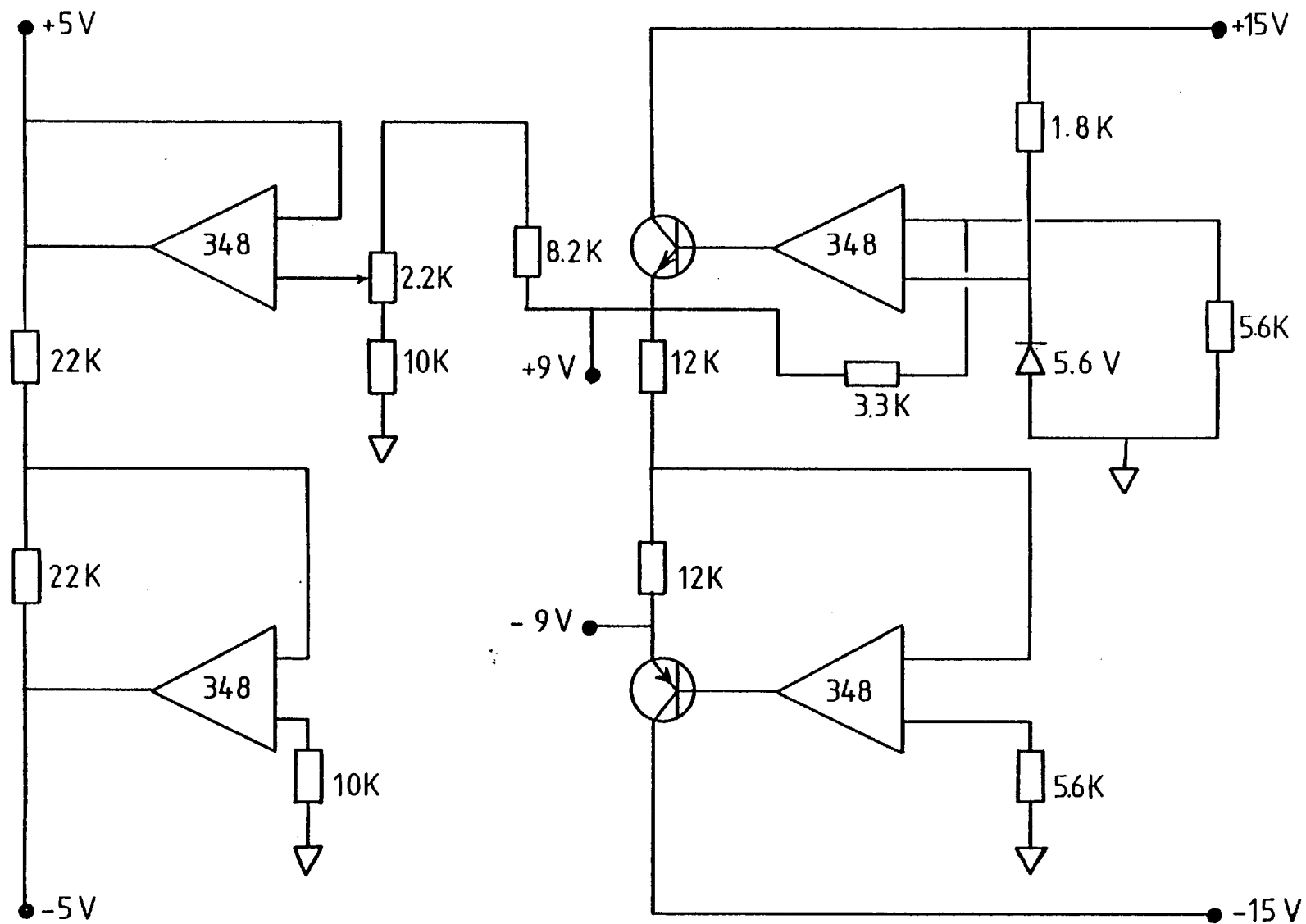


FIGURE 3.17a. Power supply for the triangular wave generator.

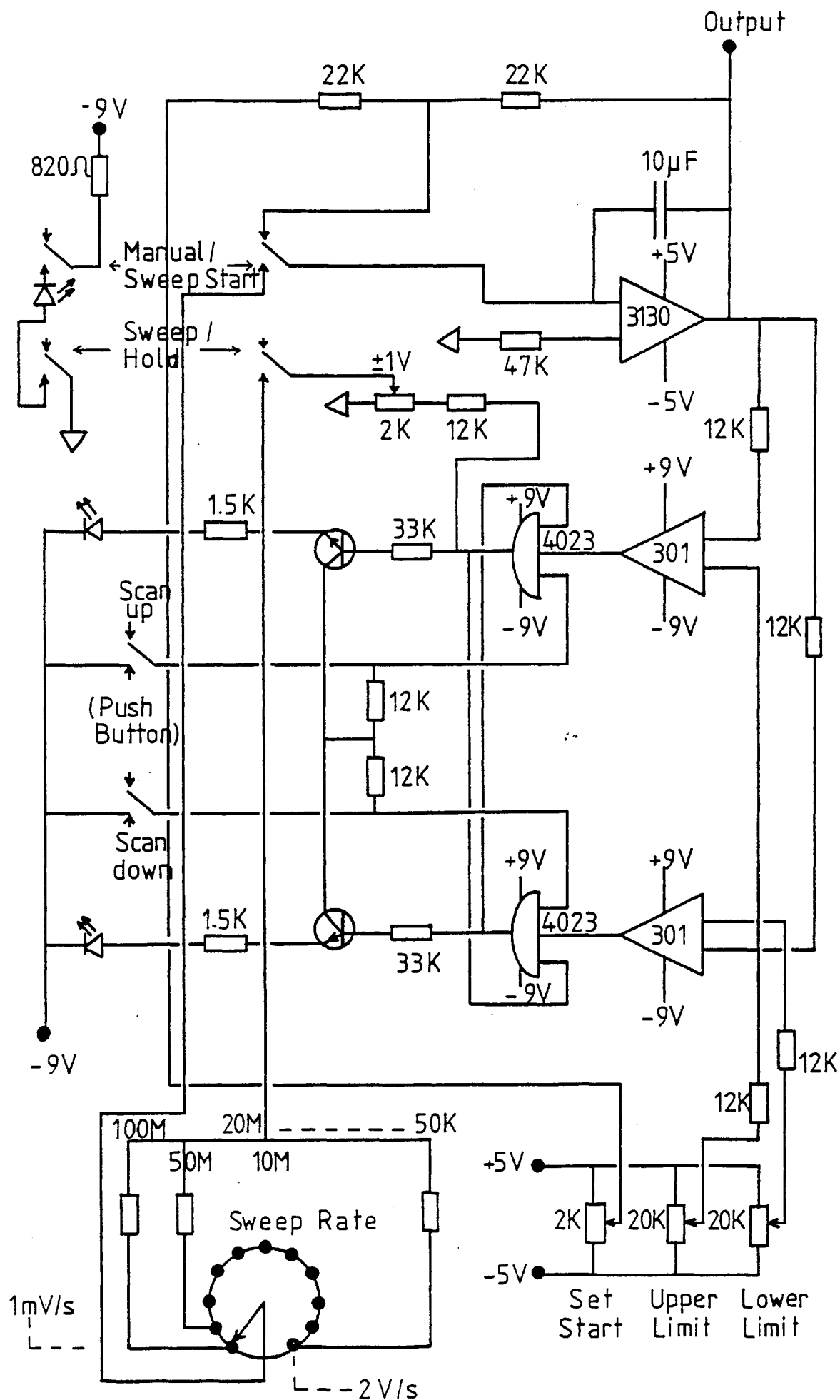


FIGURE 3.17b. Triangular wave generator.

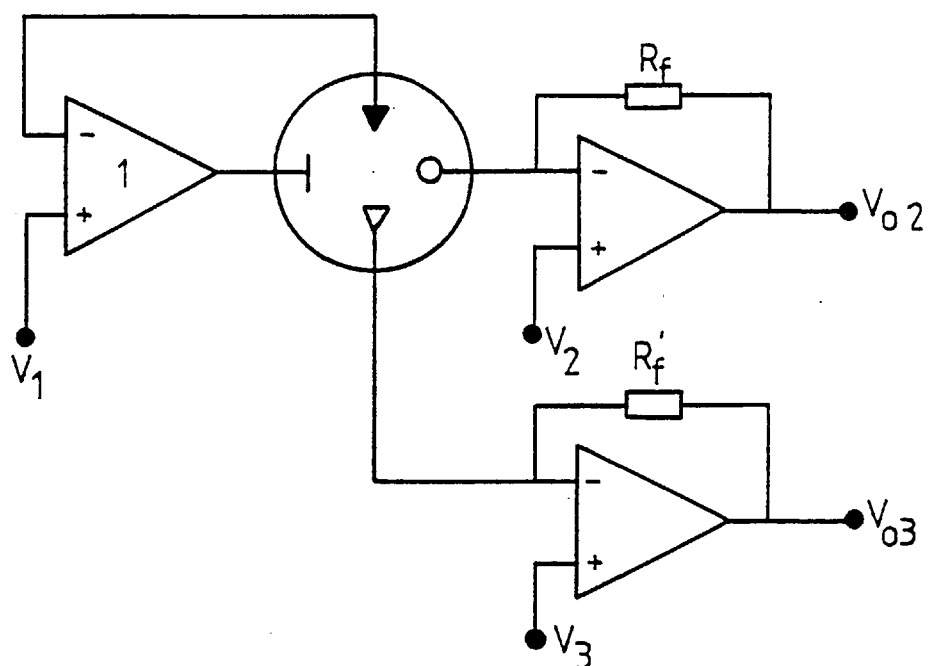


FIGURE 3.18. Potentiostat

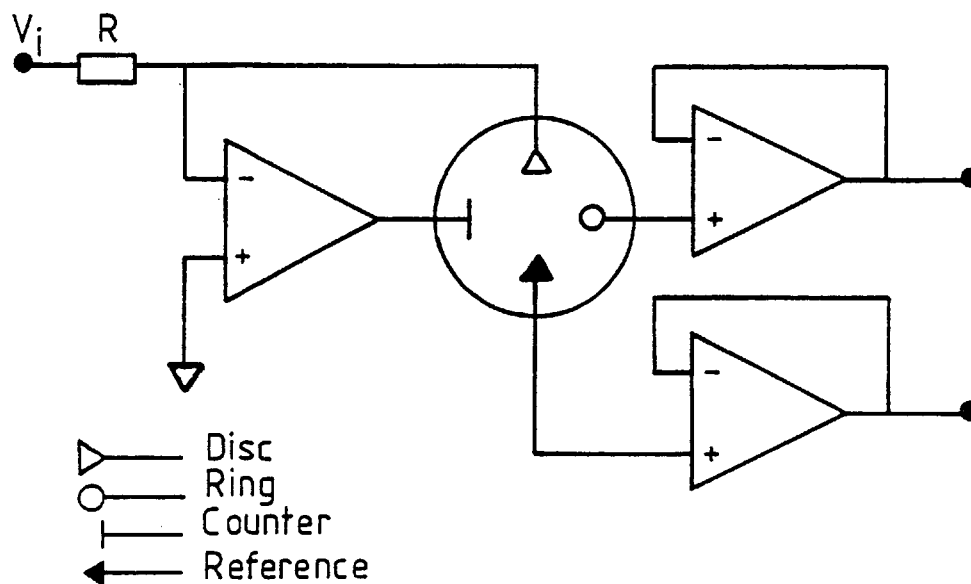


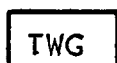
FIGURE 3.19. Galvanostat

h) Galvanostat

The galvanostat module allows a constant current to be passed between the reference and counter electrodes. Feedback is through the solution between working electrode and counter electrode, and the current is given by $i = V_i/R$. The reference and ring electrodes are connected to voltage followers. The galvanostat is shown in Figure 3.19. It was used in collection efficiency experiments and to control electro-plating currents.

3.3c. Practical Electronic Circuits

The modules were connected together to give the circuits used in experiments described in this thesis. The circuits most commonly used were the polarogram circuit and the collection efficiency circuit. To avoid unnecessary complication to Figures 3.20 and 3.21 the triangular wave generator is represented by:-

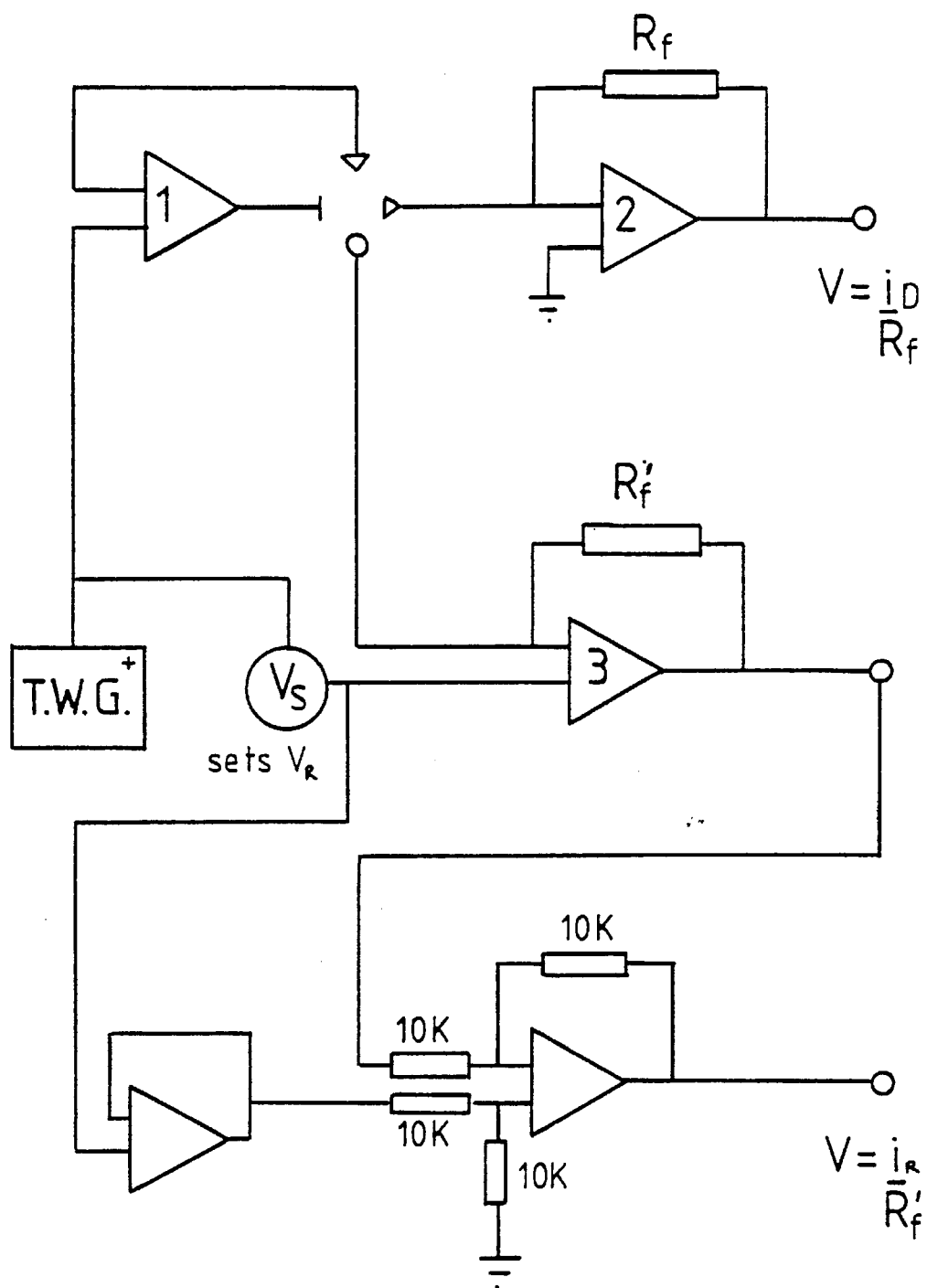


and the voltage source by:-



Polarogram Circuit

This circuit is illustrated in Figure 3.20. The output from the triangular wave generator was fed into



+ voltage source in
some circuits

FIGURE 3.20. Polarogram circuit.

the input of amplifier 1 of the potentiostat (Figure 3.18), and so controlled the reference electrode potential. The disc was held at earth, so the reference potential was ramped in the opposite direction to the intended sweep direction of the disc. The advantage of this configuration is the voltage output of amplifier 2 (Figure 3.18) is directly proportional to the disc current.

When the ring electrode was used to monitor the products from the disc electrode during a polarogram, its potential was adjusted with respect to the reference electrode with the floating voltage source V_s .

Collection Efficiency Circuit

The same circuit was used for determination of experimental collection efficiencies and recording of titration curves. This circuit is illustrated in Figure 3.21. The disc current was varied:-

$$i_D = V_{TWG}/R$$

The ring potential was adjusted with respect to the reference potential with the floating voltage source, and its current was measured with the ring electrode current to voltage convertor of the potentiostat.

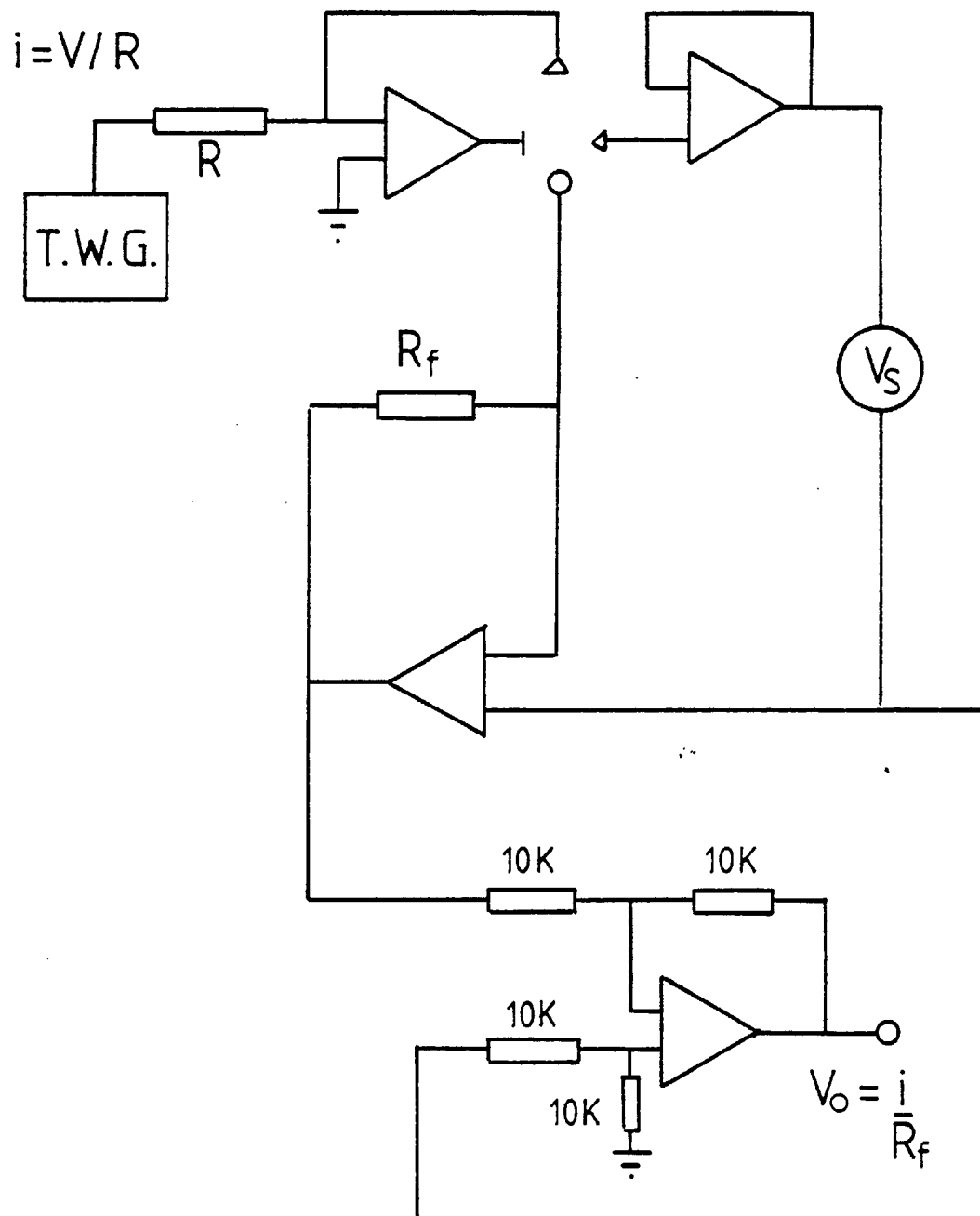


FIGURE 3.21. Collection efficiency circuit

3.3d. Frequency to Voltage Convertor

A frequency to voltage convertor was used to measure the response of the rotating electrode motor in a rotation step. It is illustrated in Figure 3.22. The output of the slotted i.r. opto switch described in Section 3.1 is fed into a 555 timer. This converts the pulses from the switch (of frequency proportional to the rotation speed of the motor) into sharp pulses of length 0.11 ms (1.1 RC). The operational amplifier (741) integrated the pulses, while the 500 K Ω resistor provided a voltage "drain". Therefore V_{out} is proportional to the rotation speed.

3.3e. Transcutaneous Heater Control

The temperature of the transcutaneous electrode was controlled with the circuit shown in Figure 3.23. It is an adaption of the control circuit designed for use with transcutaneous oxygen probes used in the Paediatric Intensive Care Unit at the John Radcliffe Infirmary, Oxford. The circuit worked by applying a known accurate voltage (10 V) across a fixed resistance and the thermistor (bridge section). One side of the thermistor is connected to earth. The voltage across the thermistor is referenced to a preset voltage (set point amplifier) and the transistor, driven by the temperature control amplifier, drives current through the heating coil.

Safety trips in the circuit prevented burns if the thermistor went open circuit, or if the electrode became too hot for any other reason.

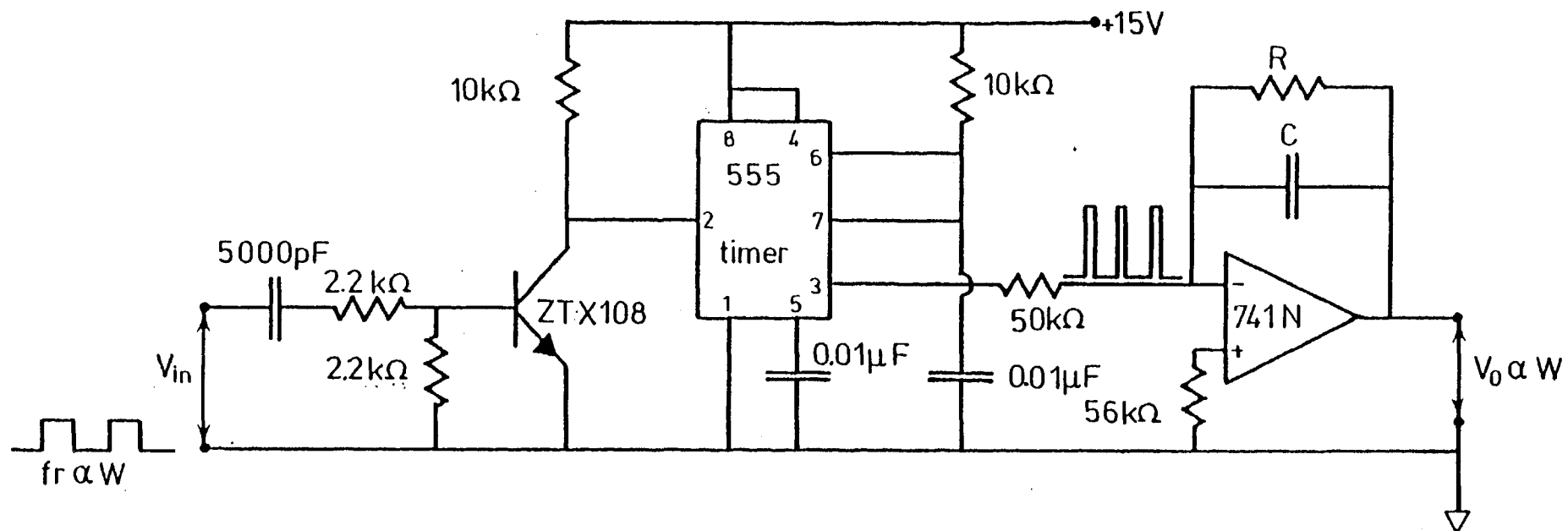


FIGURE 3.22. Frequency to voltage convertor.

3.3f. Commercial Instrumentation

Currents and potentials were measured on a Fluke 8000A digital multimeter. Polarograms and cyclic voltammograms were recorded on a Bryans Southern Instruments 29000 X-Yt A4 chart recorder. Transients were recorded on a Gould Advance double channel digital storage oscilloscope OS4000. Signals stored on the screen were transferred to the X-Yt recorder with the Gould OS4001 output unit.

3.4. CHEMICALS USED

All chemicals used were of AnalaR grade and, except for DMSO and tetraethylammonium perchlorate, were used without further purification.

The DMSO was prepared by the following procedure: (124)

- 1) The DMSO was slowly frozen in ice until about 80% was frozen. The remaining liquid was discarded.
- 2) Benzene was added (50 ml/litre), and the mixture was distilled to remove residual water. The fraction boiling between 140°C and 170°C was discarded.
- 3) The DMSO was vacuum distilled over type 5A molecular sieves. The boiling point of the liquid was noted (ca 55°C at 1 mm Hg), and the distillation was stopped when the boiling point had risen by 3°C. The DMSO was stored over type 5A molecular sieves.

The TEAP was purified by recrystallisation from water, and then dried under vacuum at 60°C. (125)

Gases used were supplied by BOC. The nitrogen was oxygen-free (white spot), and the oxygen and carbon dioxide were industrial grade.

3.5. OTHER EXPERIMENTAL DETAILS

Scanning electron micrographs were taken with a Temscan Jeol 120CX electron microscope. This system can combine standard transmission E.M. optics with scanning and energy dispersion X-ray analysis.

CHAPTER 4

THE REDUCTION OF CARBON DIOXIDE AND OXYGEN IN DMSO

A study of carbon dioxide reduction was undertaken in order to develop a new, direct technique for CO₂ detection.

This chapter presents results obtained with rotating disc and ring disc electrodes on the electroreduction of CO₂ and oxygen in DMSO. The first section concerns a study of the reduction of CO₂ on gold, mercury, tin and silver electrodes.

In virtually all of the situations where estimation of CO₂ is necessary, (especially in medical applications) oxygen is also present. The second section presents work on the reduction of oxygen in DMSO. It will be shown that a difficulty exists in isolating the carbon dioxide and oxygen components of a gas mixture. Section 4.2. also discusses a study of the reaction between a quinone intermediate and oxygen, which was undertaken in an attempt to separate the CO₂ and oxygen reduction waves.

4.1a. A Rotating Disc Study of the Reduction of CO₂ in DMSO

The reduction of CO₂ has previously only been studied on stationary electrodes. A rotating disc electrode has better defined diffusion characteristics which are time independent at constant rotation speed, and an easily calculable current at all points along the current voltage curve (Chapter 2).

Levich Plots

Polarograms of CO_2 reduction at various rotation speeds on R.D.E.'s of gold, mercury, tin and silver are shown in Figures 4.1. to 4.4 respectively. In all cases the limiting current was proportional to the square root of rotation speed, as equation 2.16 predicts. The carbon dioxide is therefore being reduced quantitatively.

The diffusion limiting current region is well defined on all the electrodes, particularly silver, where the region is about 0.7 V at 1 Hz. The half-wave potential is also dependent on rotation speed. For an irreversible reduction the half wave potential is related to the diffusion rate constant by:-(99)

$$E_{1/2} = E^\ominus + \frac{\alpha RT}{F} \ln \frac{k_D'}{k_o'} \quad 4.1$$

$$\text{Where } k_D' = \frac{D}{X_D} = 1.554 D^{2/3} \nu^{-1/6} W^{1/2} \quad 2.13$$

and k_o' is defined in equation 2.12

Figure 4.5 shows the linear relationship between $E_{1/2}$ and $\ln W$ obtained with the silver electrode, which means the reduction of CO_2 is irreversible.

The Diffusion Coefficient of CO_2 in DMSO

The response of the motor in a rotation step was measured with the frequency-voltage convertor described in Chapter 3, and is shown in Figure 4.6. The $t_{1/2}$ response was 13 ms, and this was used as a correction to t in equation 2.23. Figure 4.7 shows a typical current transient.

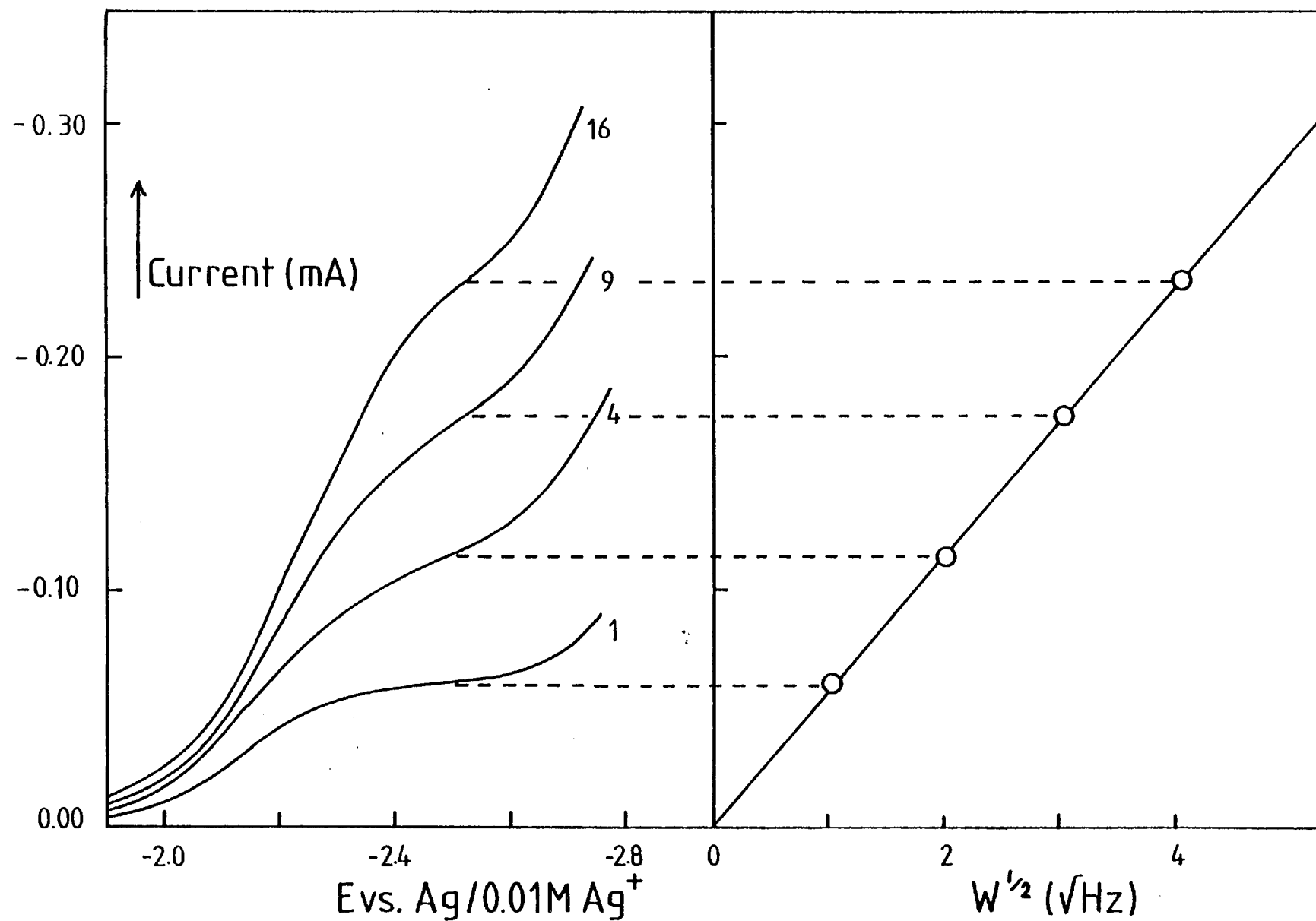


FIGURE 4.1. CO₂ reduction on a rotating gold disc electrode.

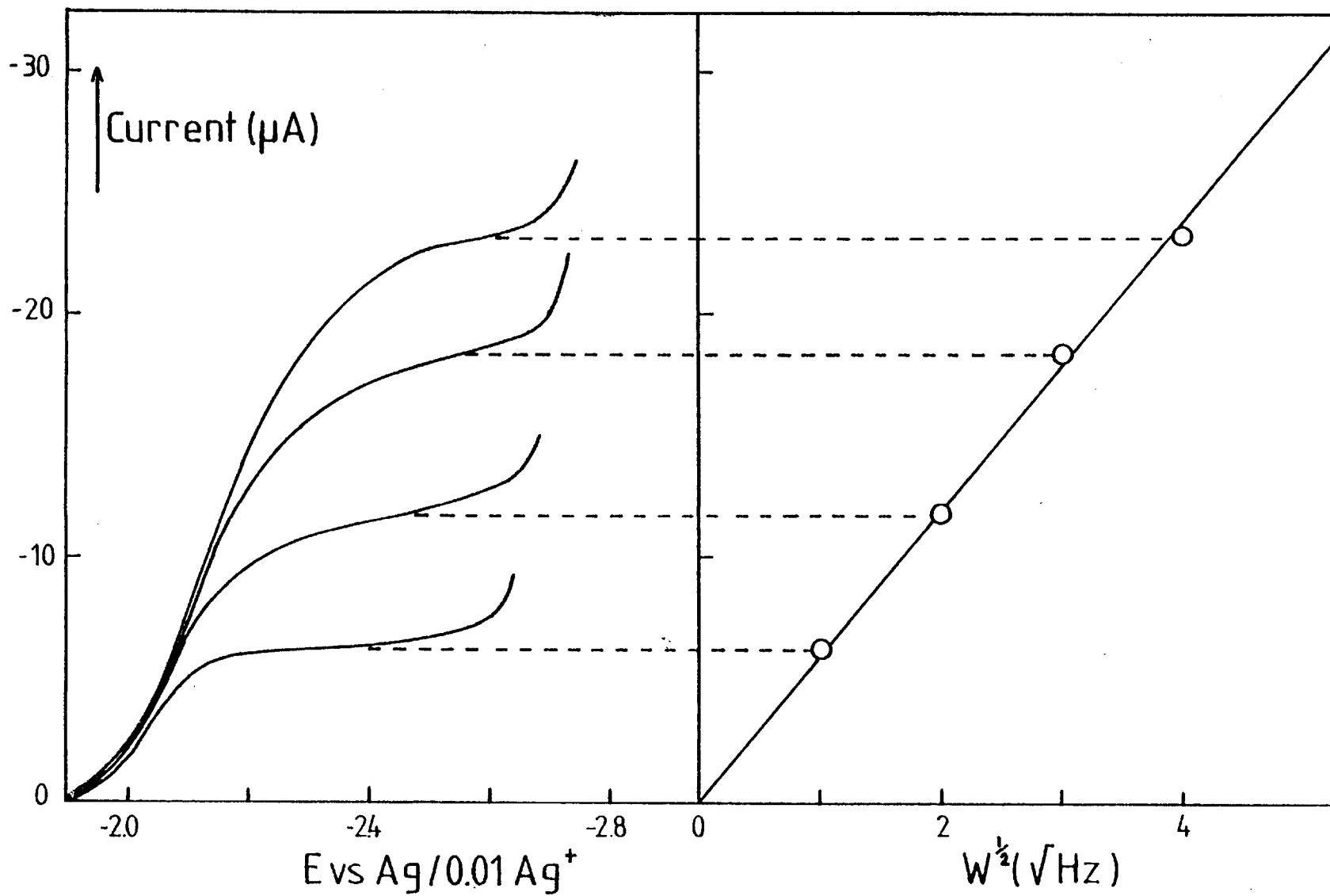


FIGURE 4.2. CO_2 reduction on a rotating mercury disc electrode.

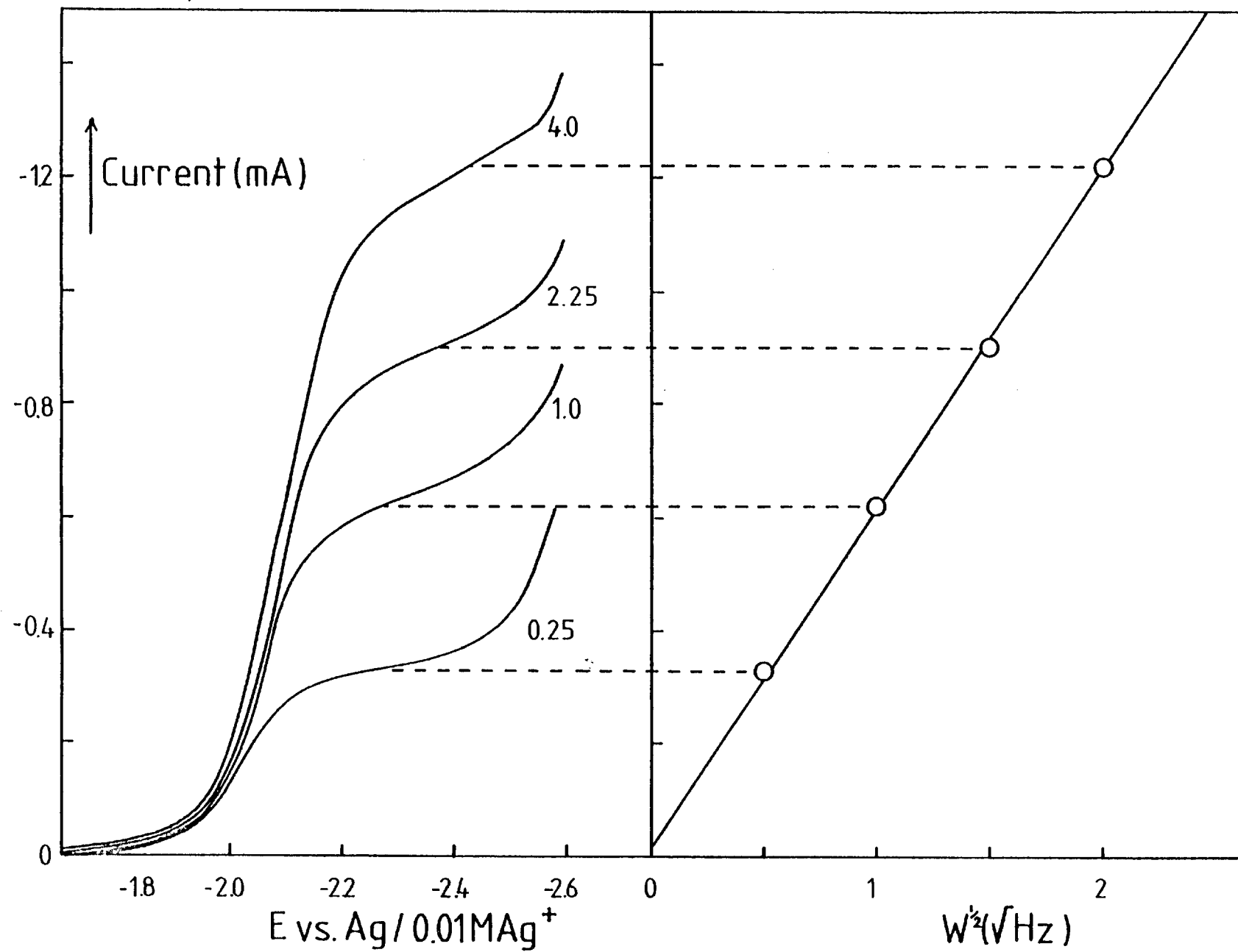


FIGURE 4.3. CO_2 reduction on a rotating tin disc electrode.

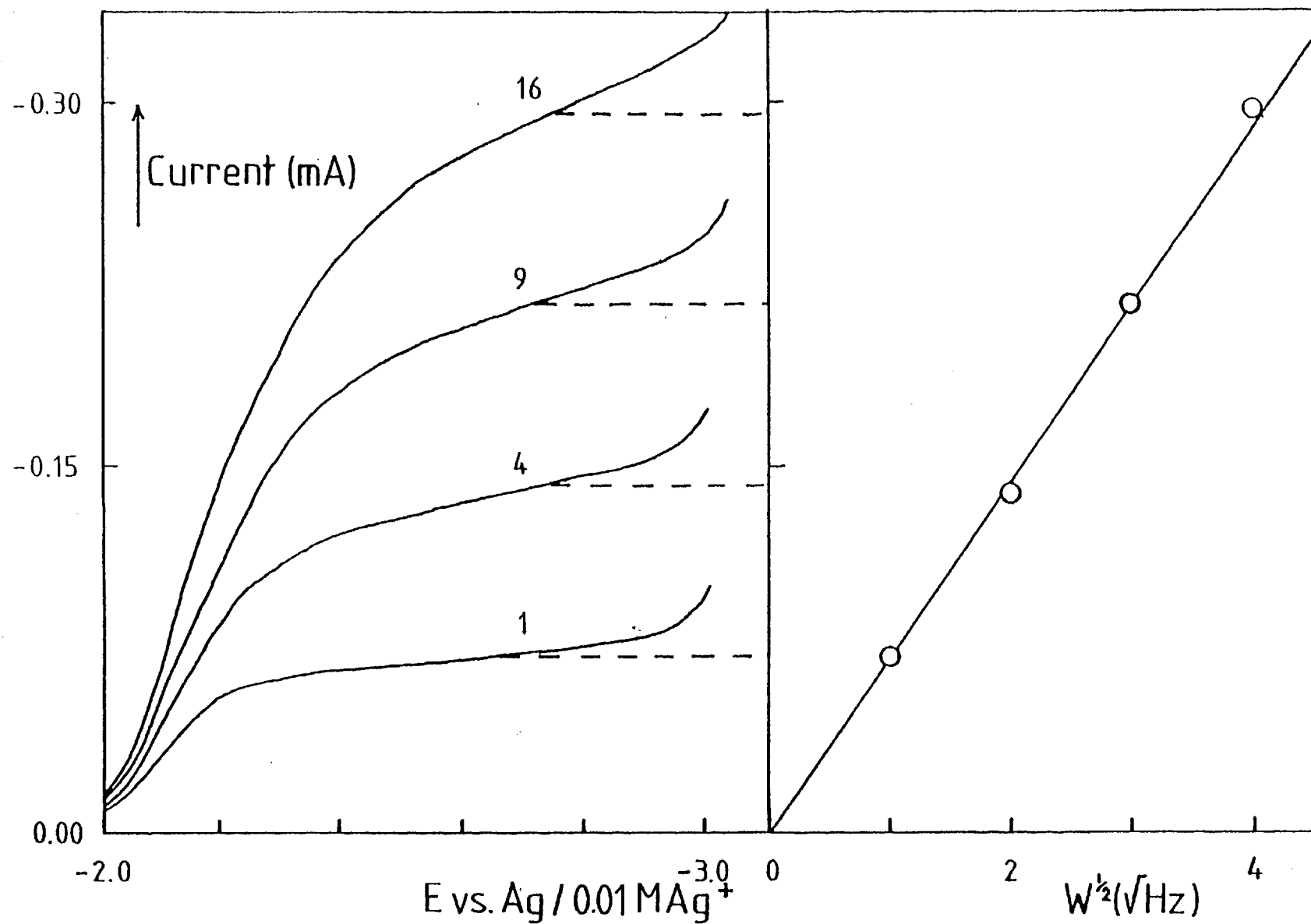


FIGURE 4.4. CO_2 reduction on a rotating silver disc electrode.

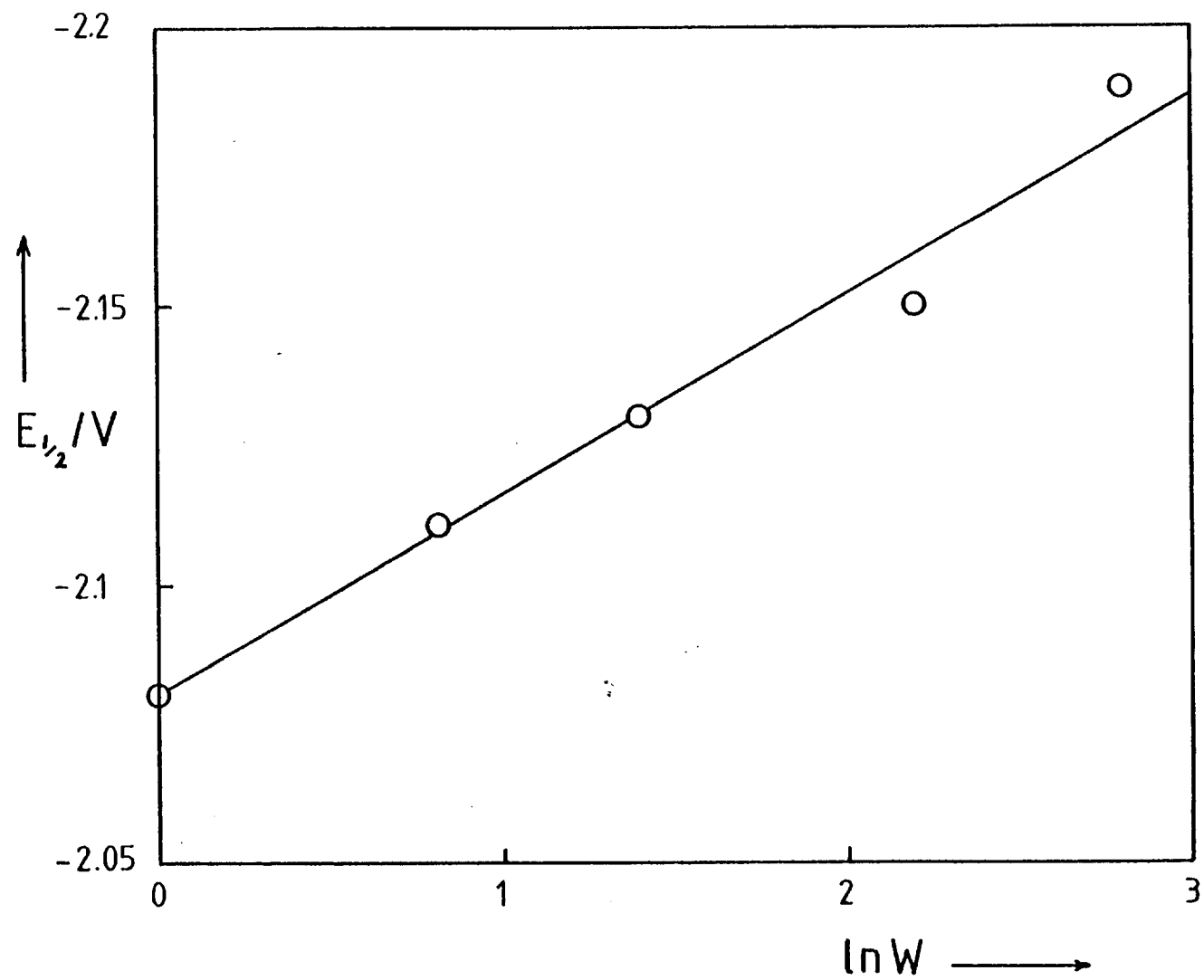


FIGURE 4.5. A graph of $E_{1/2}$ vs. $\ln W$ obtained with the silver rotating disc electrode.

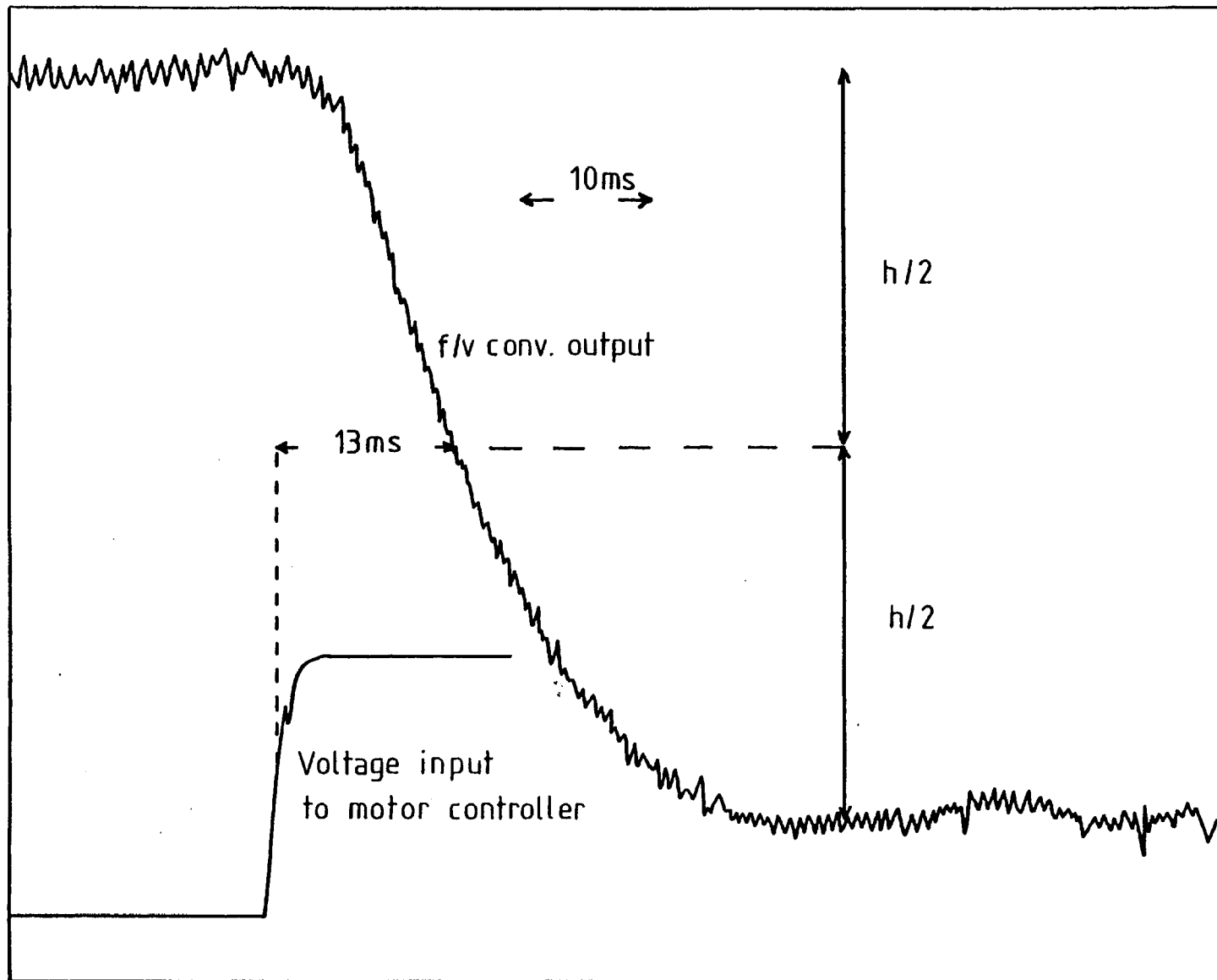


FIGURE 4.6. The response of the motor in a rotation step measured with the frequency to voltage convertor shown in Figure 3.22.

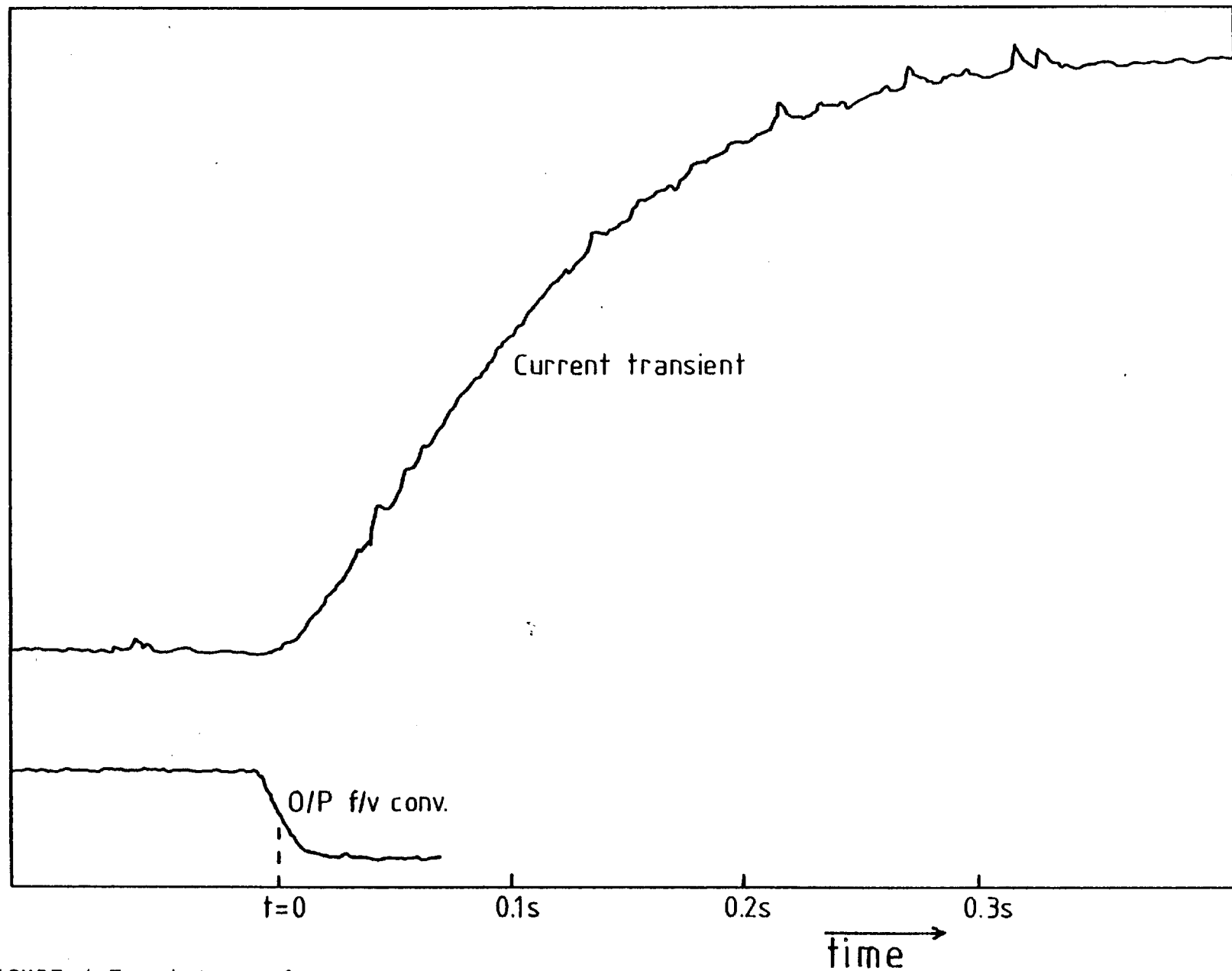


FIGURE 4.7. A typical current transient obtained in response to a rotation step.

Rotation steps of 5-10, 6-10, 7-11, 7-12 and 8-12 Hz were applied, and four current transients were recorded for each step. Various $f_p - t$ measurements were made on each of the twenty transients, and the mean values obtained are shown in Table 4.1.

Table 4.1. Rotation Speed Transient Responses

f_p	$\tau^{(a)}$	t/s
0.2	0.14	0.038 ± 0.004
0.3	0.2	0.056 ± 0.006
0.4	0.25	0.072 ± 0.007
0.6	0.4	0.111 ± 0.010
0.8	0.6	0.171 ± 0.012
0.9	0.8	0.225 ± 0.013

(a) Calculated from equation 2.22

Figure 4.8 shows a plot of $(W_\infty t - 0.04)$ vs. τ . The slope of the line was found to be 3.09 ± 0.04 by linear regression analysis, with a correlation of 0.9997. From equation 2.23:-

$$Sc^{-\frac{1}{3}} = 1 - \frac{\sqrt{1 - 1/3.09}}{2}$$

$$\therefore Sc^{-\frac{1}{3}} = 0.088 \pm 0.001$$

4.2

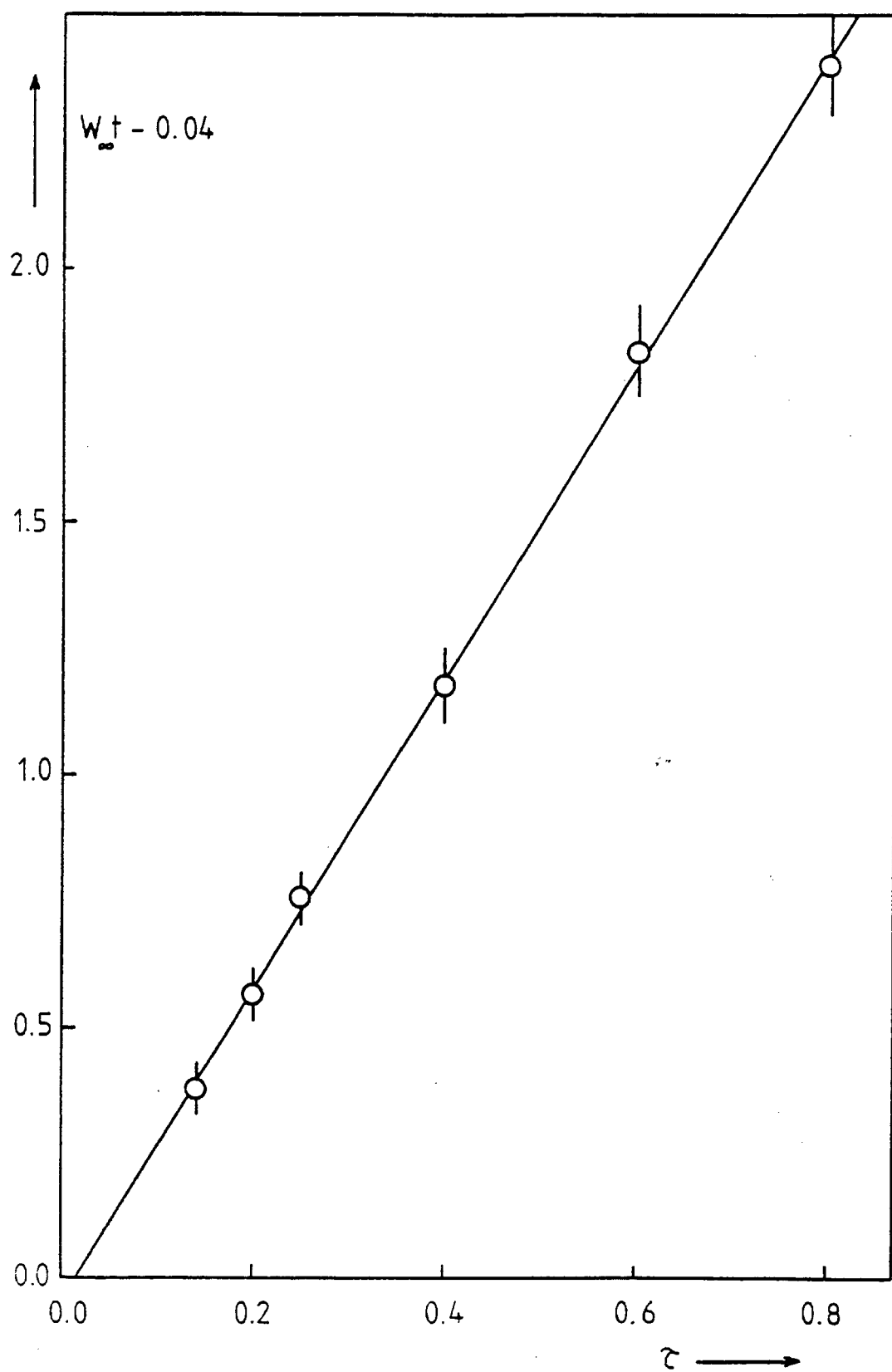


FIGURE 4.8. A graph of $(W_\infty t - 0.04)$ vs. τ .

In order to find D the kinematic viscosity of the DMSO solution was measured with an Ostwald viscometer.

The ratio of the kinematic viscosities of water and DMSO was measured, and found to be:-

$$\nu_{\text{DMSO}}/\nu_{\text{H}_2\text{O}} = 2.47 \quad 4.3$$

$$\text{Since } \nu_{\text{H}_2\text{O}} = 0.862 \times 10^{-2} \text{ cm}^2\text{s}^{-1} \quad 4.4$$

$$\nu_{\text{DMSO}} = 2.13 \times 10^{-2} \text{ cm}^2\text{s}^{-1} \quad 4.5$$

From equation 2.21:-

$$D_{\text{CO}_2} = (1.45 \pm 0.05) \times 10^{-5} \text{ cm}^2\text{s}^{-1} \quad 4.6$$

The Solubility of CO_2 in DMSO

The solubility of CO_2 in DMSO was determined by adding aliquots of DMSO solution equilibrated with different CO_2 - N_2 gas mixtures to a 0.1 M sodium hydroxide solution and back titrating with 0.1 M hydrochloric acid.⁽⁷⁴⁾ Figure 4.9 shows the effect on the titration curve of addition of 2 ml of a CO_2 saturated DMSO solution. A linear relation was found between CO_2 concentration and its partial pressure p_{CO_2} :-

$$C/\text{mM} = 84 p_{\text{CO}_2}/\text{atmospheres} \quad 4.7$$

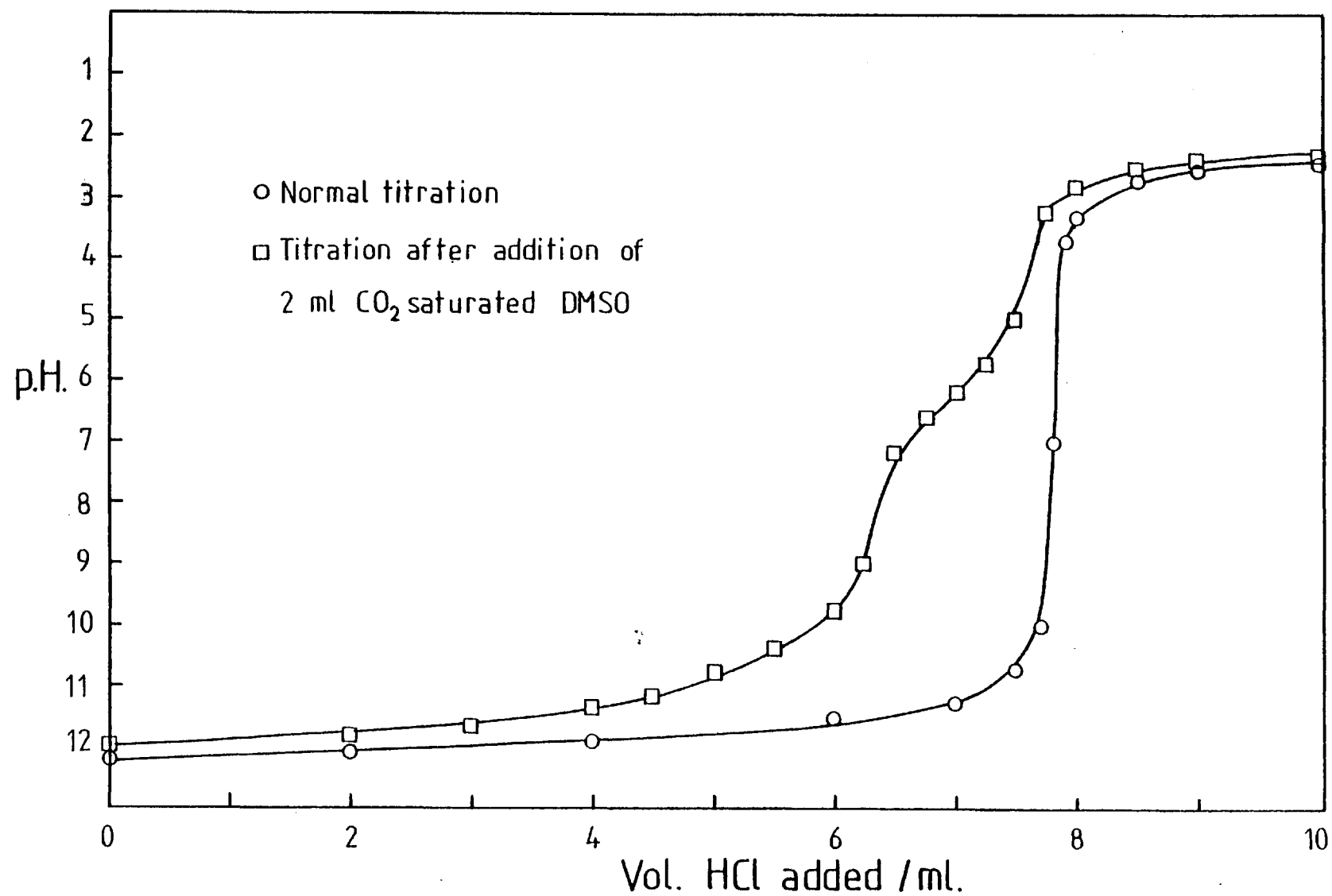


FIGURE 4.9. Determination of the CO₂ concentration in DMSO by titration of NaOH solution.

This result is in good agreement with the result of Haynes and Sawyer,⁽⁷⁵⁾ but not with the earlier result of Sawyer and Roberts.⁽⁷⁴⁾

The Number of Electrons Involved in the Reduction of CO₂

Since D , c and v were now known, the number of electrons involved in the reduction was calculated from the Levich plots in Figures 4.1 to 4.4. In all cases the number of electrons involved in the reduction was found to be one. This finding is discussed later in this chapter.

The Transfer Coefficient for CO₂ Reduction

Equation 2.18 predicts a linear relation between $\ln(1/i - 1/i_L)$ and E . Tafel plots are shown in Figures 4.10 to 4.13 for CO₂ reduction on gold, mercury, tin and silver respectively. The reduction is most reversible on mercury and tin, and least reversible on gold. The α values indicate a rate determining step consisting of the addition of an electron to a CO₂ molecule.

Summary of Rotating Disc Results

Table 4.2 presents the results obtained on the electroreduction of CO₂ on rotating disc electrodes.

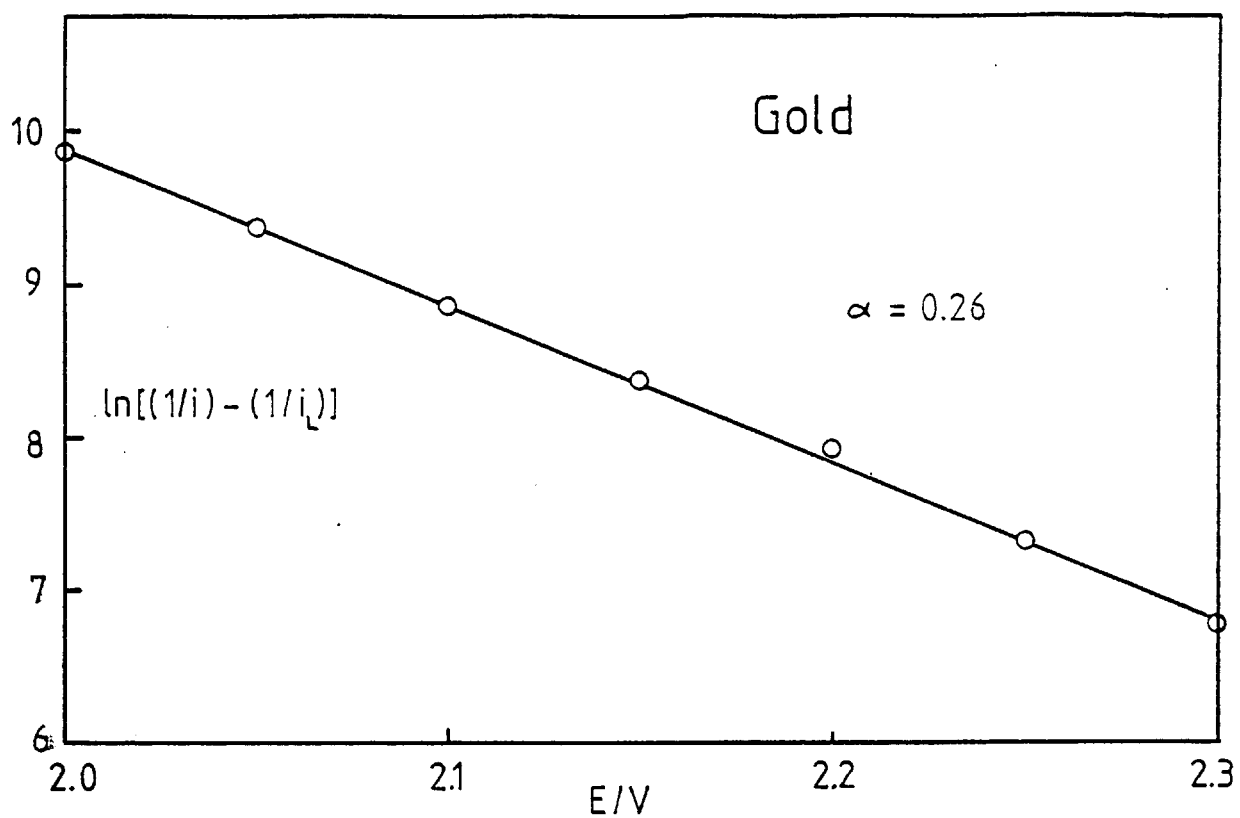


FIGURE 4.10. Tafel plot for CO₂ reduction on gold.

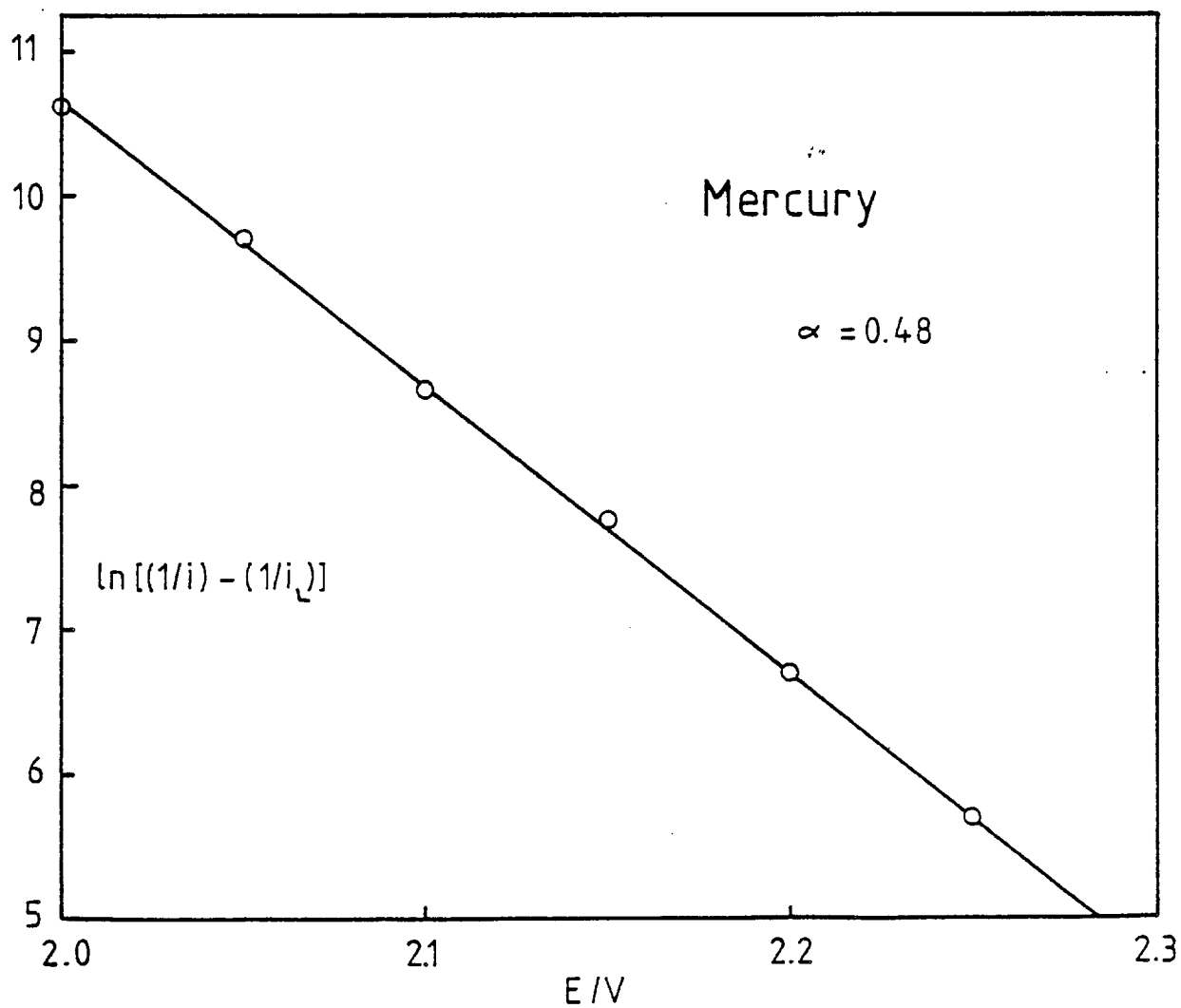


FIGURE 4.11. Tafel plot for CO₂ reduction on mercury.

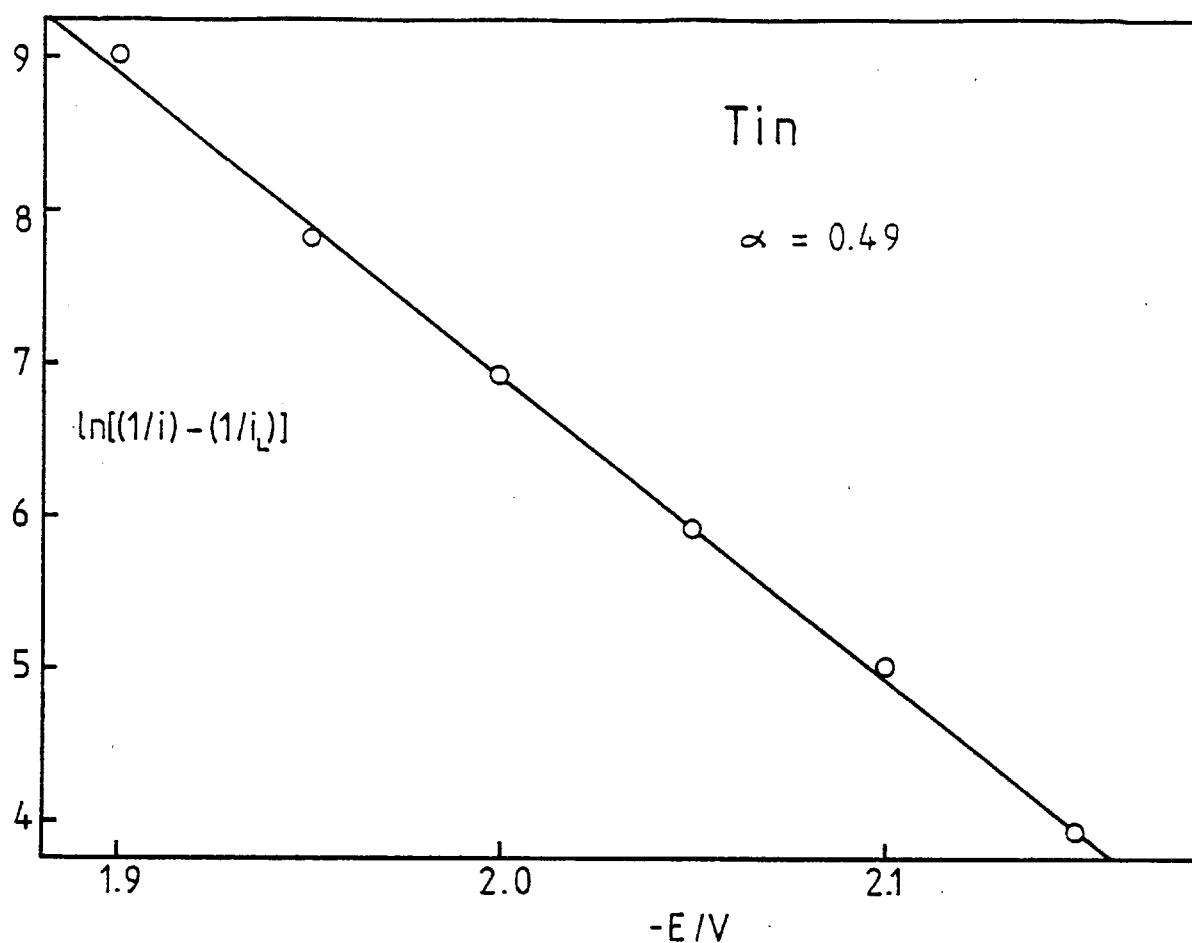


FIGURE 4.12. Tafel plot for CO_2 reduction on tin.

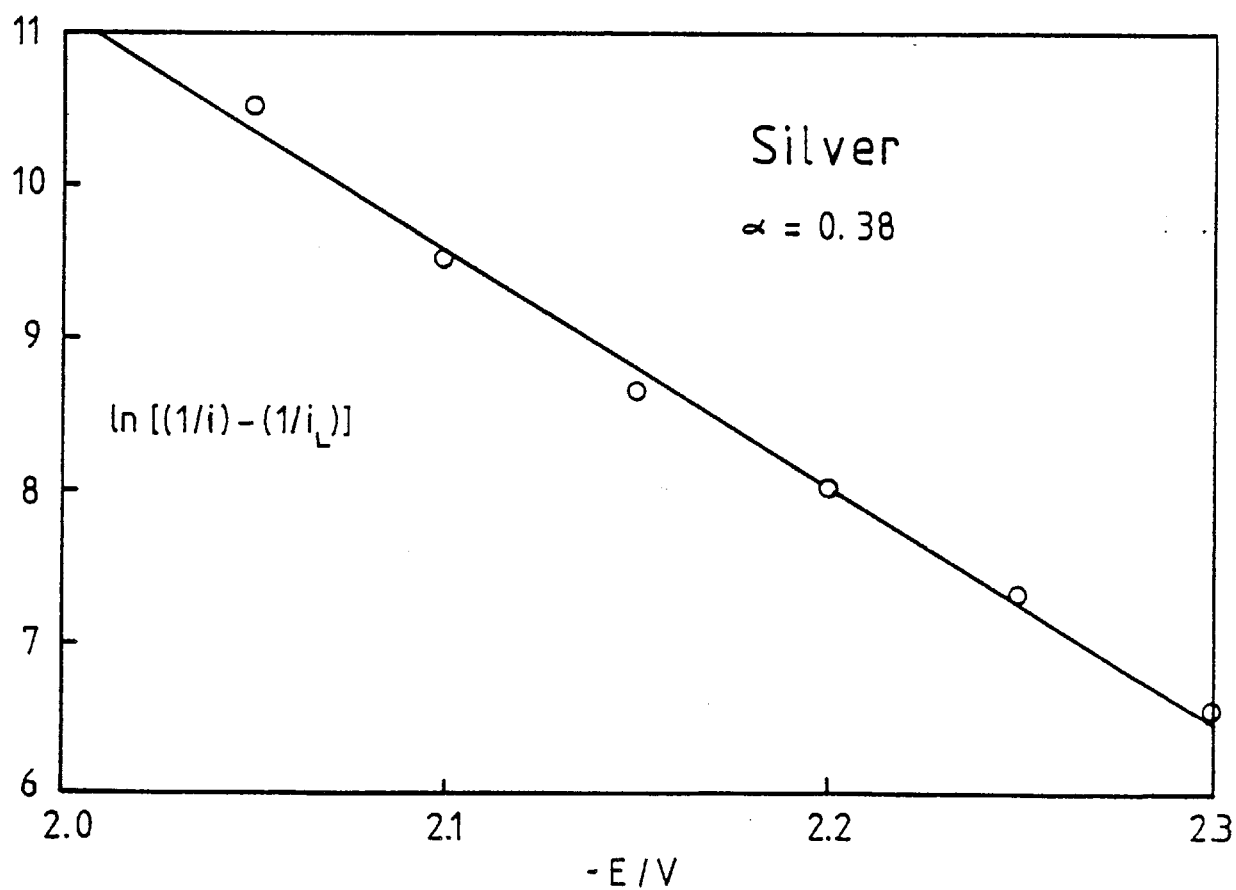


FIGURE 4.13. Tafel plot for CO_2 reduction on silver.

Table 4.2 Electrochemical Parameters for the Reduction of CO₂

Electrode	n	$E_{1/2}/V^*$	α^*	$E_{\text{solvent wave}}/V^*$
Gold (Electrode B)	0.98	-2.18	0.26	-2.65
Mercury (Plated electrode E)	1.05	-2.08	0.48	-2.65
Tin (Electrode F)	1.07	-2.08	0.49	-2.55
Silver (Electrode C)	0.99	-2.13	0.38	-2.95

*Measured at a rotation speed of 4 Hz.

Although the reduction is less reversible on silver than on mercury or tin, the solvent wave occurs at more negative potentials. Silver is therefore the best material for use in a membrane electrode.

4.1b. A Rotating Ring Disc Study of CO₂ Reduction in DMSO

A rotating ring disc study of CO₂ reduction in DMSO was undertaken in order to identify the reaction products. This was necessary in order to ensure that their long-term accumulation in a membrane electrode would not affect the CO₂ electrode reaction in any way.

Electrode A was used in all experiments described in this section. Its theoretical collection efficiency was 0.32, and this was verified experimentally with an aqueous solution of 1,8-dihydroxyanthroquinone using the circuit shown in Figure 3.21. A value of 0.30 was obtained.

Disc Product Oxidation on the Platinum Ring

Haynes and Sawyer^(75.) found an electroactive CO_2 reduction product using chronoamperometry, where a constant current passed through the disc generates the CO_2 reduction product, which is then oxidised by reversing the current.

A polarogram of the platinum ring with the gold disc on the CO_2 reduction plateau is shown in Figure 4.14, where it is compared with a blank run in which the disc was disconnected. Figure 4.15 is the polarogram due to product oxidation only, and is the difference between the two polarograms in Figure 4.14.

The peak height in Figure 4.15 is about 15 μA . Since the disc current was 0.123 mA the maximum collection efficiency was 0.12. The peak in the subtraction polarogram, and the large amount of hysteresis indicates the ring electrode is being poisoned. When the ring potential was held at +0.6 V, the ring current decayed to about half its original value in a minute. The ring surface was regenerated for the oxidation when

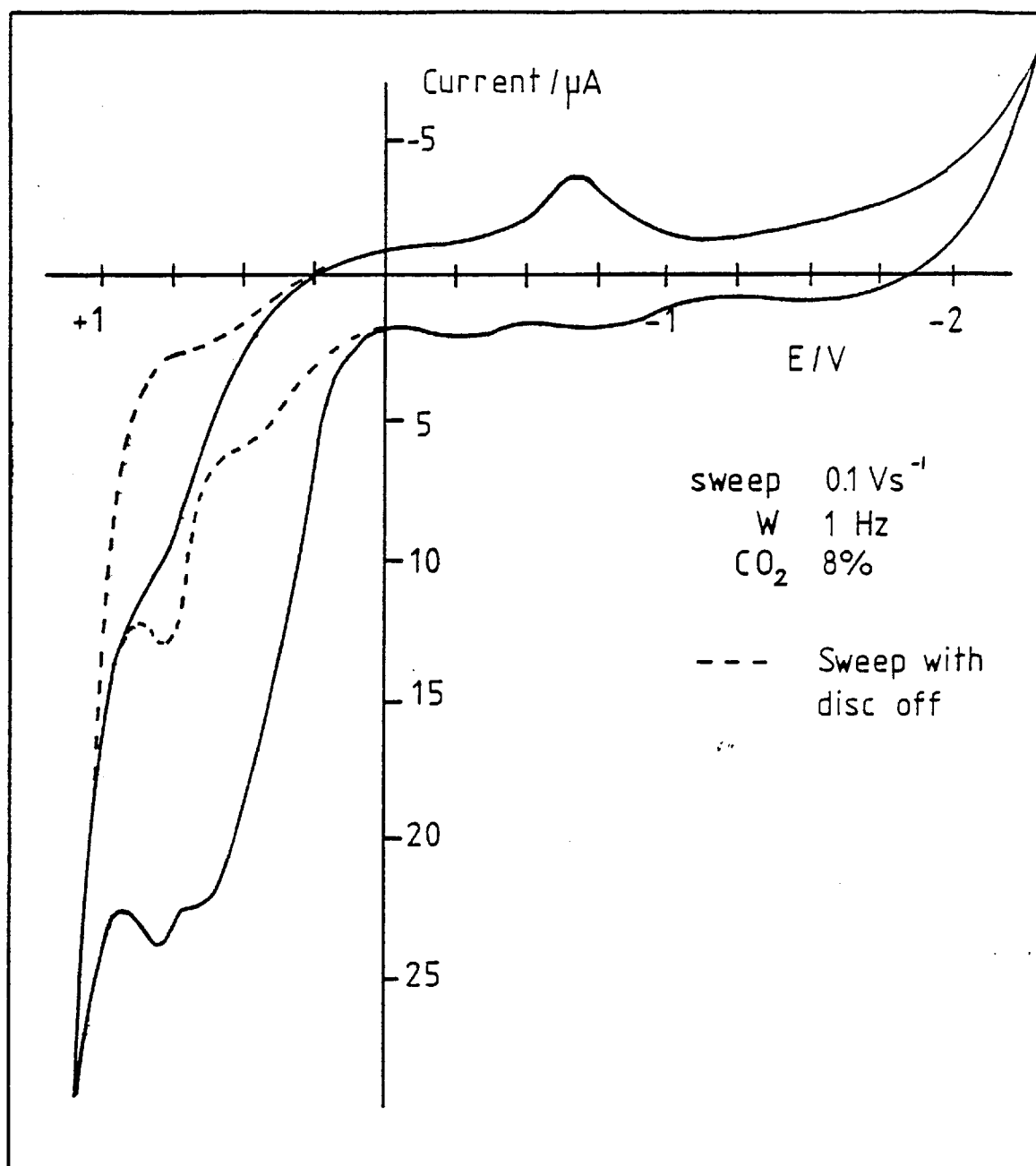


FIGURE 4.14. Polarogram of the platinum ring with the gold disc on and off

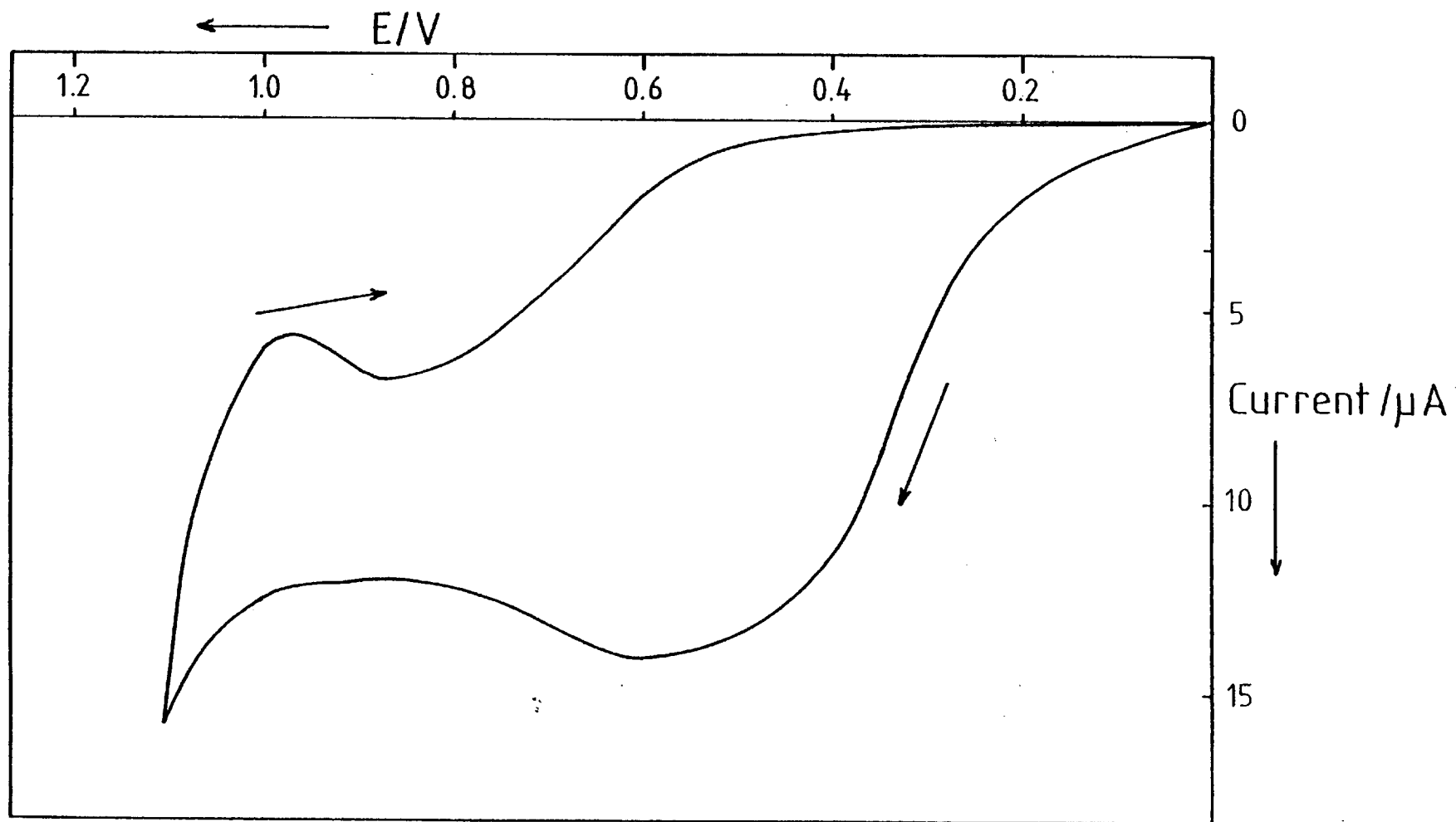


FIGURE 4.15. Polarogram due to product oxidation only.

the ring potential was swept more negative than -0.8 V, and very reproducible cyclic voltammograms were then obtained. The peak at -0.8 V in Figure 4.14 is therefore removal of the ring surface poisoning.

Figure 4.16 presents results obtained when the ring was held at a potential of $+0.6$ V and the disc was switched to the CO_2 reduction plateau. Also shown is the expected shape of the current transient when no ring poisoning occurs and the collection efficiency rises to N_0 . The actual transient decays rapidly.

To investigate the poisoning processes further the ring potential was switched from -0.7 V to $+V$, where $+0.5 \text{ V} \leq V \leq +0.7\text{V}$. The rotation speed was kept constant, and after a delay of t seconds the disc potential was switched on to the CO_2 reduction plateau. The variation of the peak height of the ring transient with t was noted. The peak current initially decayed at a rate which was proportional to t . The rate of decay was dependent on V , and varied as shown in Table 4.3.

Table 4.3.

V/volts	0.5	0.6	0.7
$\frac{di_{\max}}{dt} / \mu\text{As}^{-1}$	0.8	1.4	3

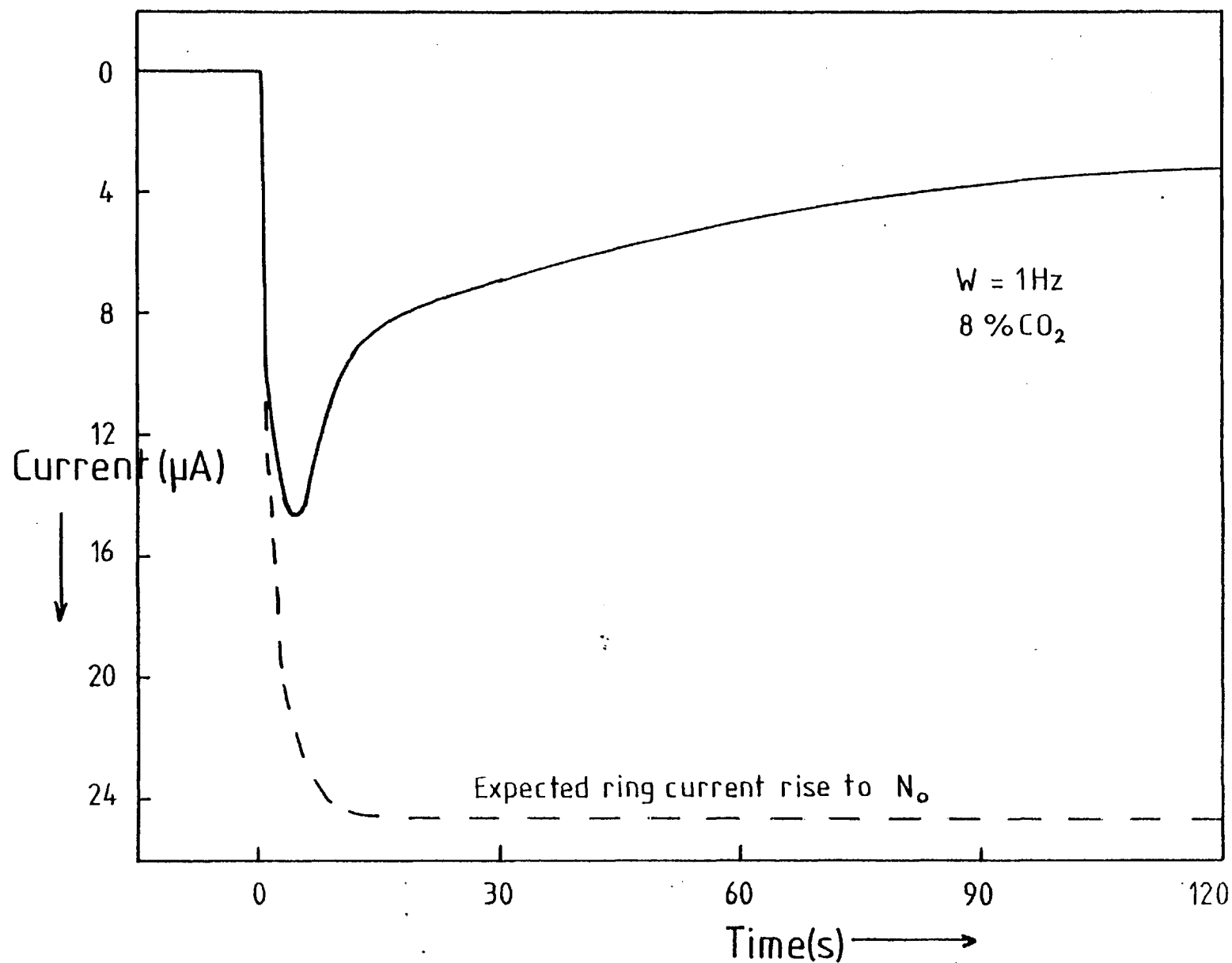


FIGURE 4.16. Ring current transient obtained when the ring was held at +0.6 V and the disc was switched on to the CO₂ reduction plateau. Note the rapid decay.

As the peak current was dependent on t PtO formation is almost certainly the poisoning process, PtO being less active in oxidising the disc product. The cathodic peak in Figure 4.14 corresponds to a two electron reduction of a monolayer of the ring surface, which is consistent with PtO ring poisoning.

Disc Product Oxidation on a Gold Ring

In order to alleviate the problem of PtO formation on the ring, the ring was gold plated. A plating solution of 0.185 g NaAuCl_4 and 1.75 g NaCN in 100 ml of doubly distilled water was used. A high current density of 16 mA/cm^2 was used. After plating the electrode was polished with $0.3 \mu\text{m}$ alumina, and a shiny gold ring surface resulted.

Polarograms of the gold plated ring are shown in Figures 4.17 and 4.18. During the anodic sweep of the ring the ring current rises to a collection efficiency of 0.25, and then decays. The half wave potential of the oxidation was +0.35 V. The cathodic sweep shows the electrode was poisoned by the solvent oxidation wave. The decay of the anodic sweep was sweep rate dependent, as Figure 4.18 shows, and could have been due to either gold oxide formation or poisoning due to the disc product.

Polarising the ring electrode at +0.5 V, then switching the disc on gives a ring current transient of

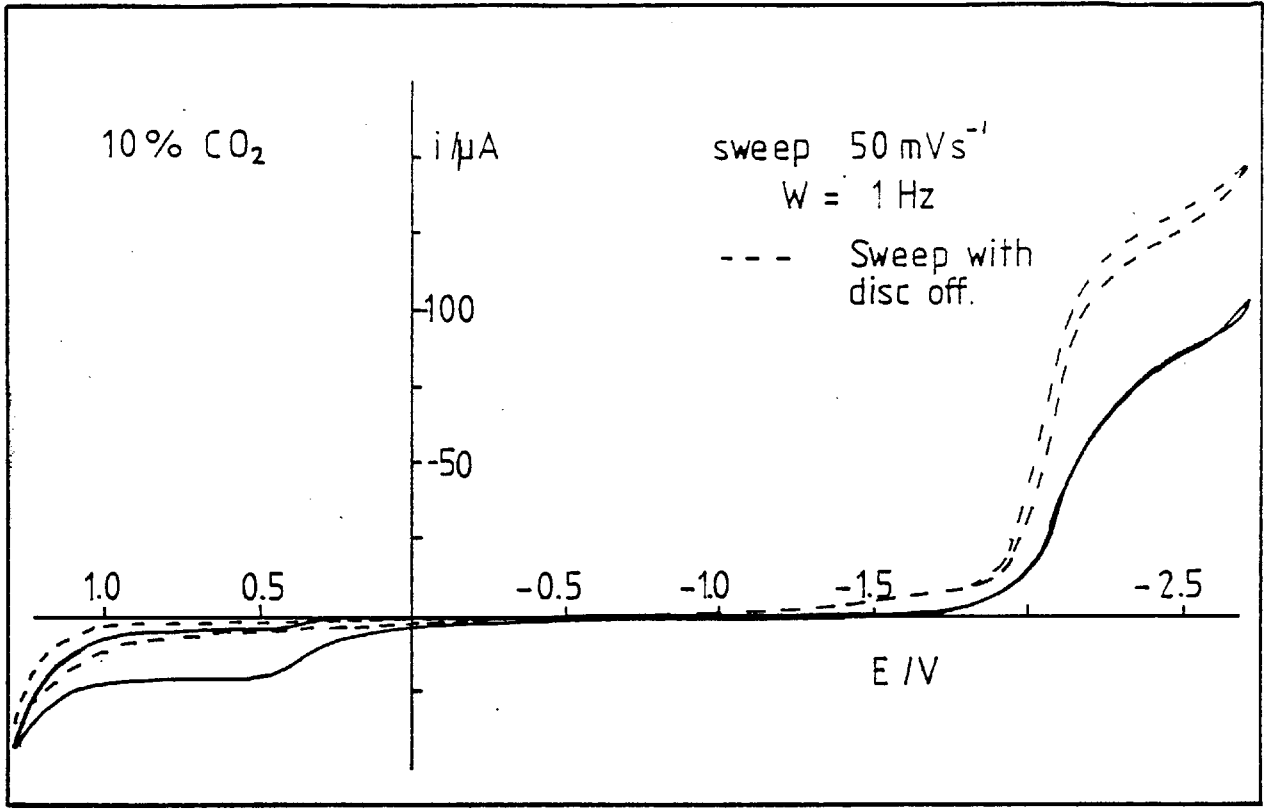


FIGURE 4.17. Polarogram of the gold plated ring.

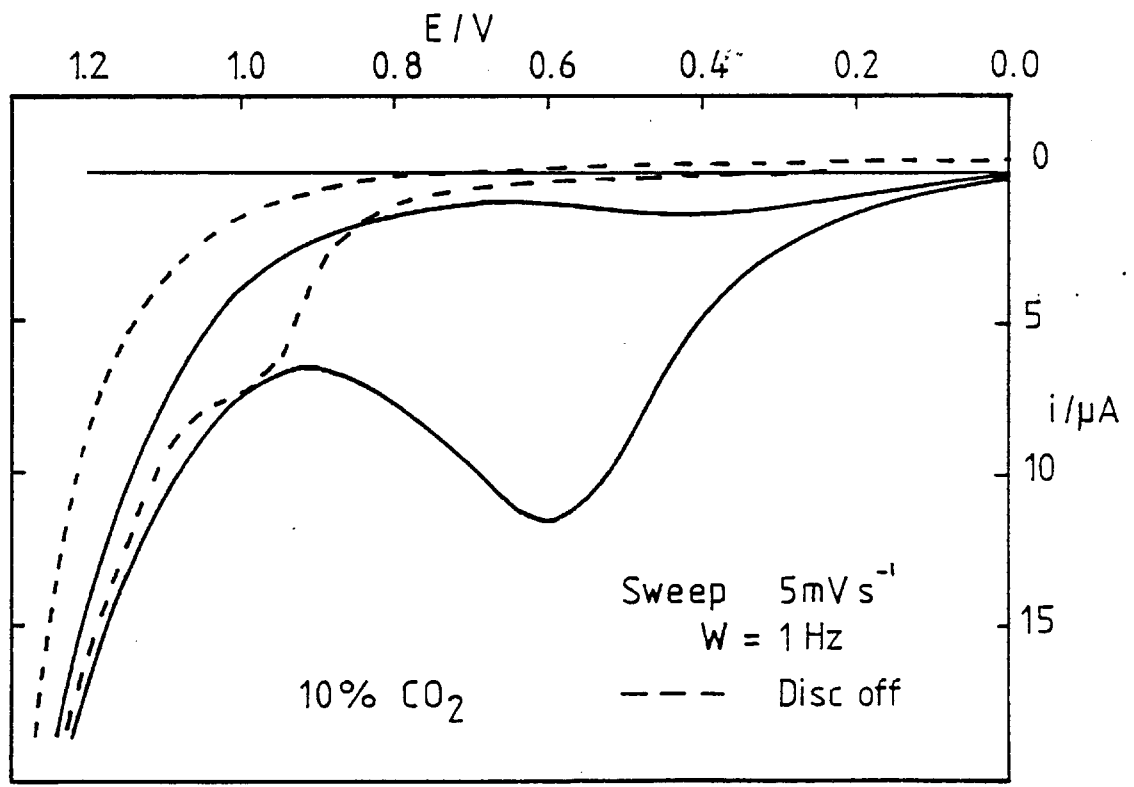


FIGURE 4.18. Positive sweep of the gold plated ring.

the type shown in Figure 4.19. The decay in ring current was slow, and could easily be extrapolated back to when the disc was switched on to give the collection efficiency. Table 4.4 shows the collection efficiencies at $t = 0$ when the rotation speed and ring potential were varied. The maximum collection efficiencies were obtained at a ring potential of +0.5 V with a low rotation speed.

The poisoning process is very sensitive to ring potential changes from +0.5 V to +0.7 V, irrespective of the collection efficiency at +0.5 V. This indicates the main poisoning process is gold oxide formation.

The decrease in collection efficiency with increased rotation speed is due to the oxidation being irreversible. The half-wave potential of the oxidation becomes more positive, and AuO formation means the diffusion limited current plateau is not reached.

In conclusion, collection efficiencies of the order of N_0 were obtained, and the half-wave potential of the disc product oxidation was about +0.35 V.

Table 4.4. Collection efficiency variation with rotation speed and ring potential

Ring Potential	Collection efficiency at a rotation speed of:-		
	1 Hz	4 Hz	9 Hz
+0.3 V	0.102	0.078	0.056
+0.5 V	0.270	0.210	0.170
+0.7 V	0.131	0.053	0.029

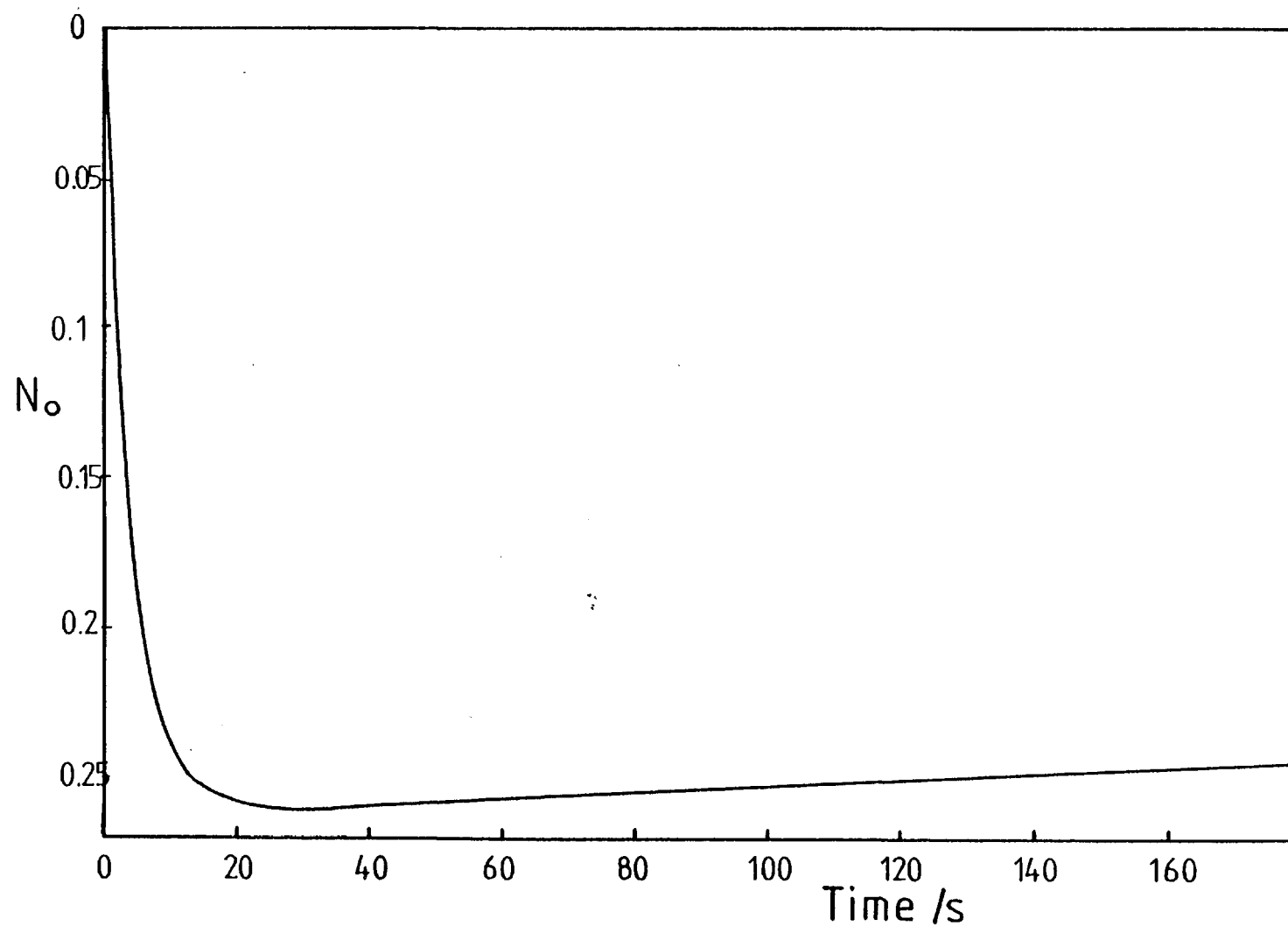


FIGURE 4.19. Ring current transient obtained when the ring was held at +0.5 V and the disc switched on to the CO₂ reduction plateau. Note the much slower decay compared to Fig. 4.16.

The Disc Reduction Product

The initial disc reduction product is $\text{CO}_2^{\cdot-}$ but this rapidly reacts and could form a variety of other products, as Figure 1.8 shows. In the very dry case only carbon monoxide and carbonate, or oxalate could be formed, but DMSO always contains a residual amount of water, so formate and bicarbonate are possible products also.

In order to identify the disc product ring polarograms were run on solutions of tetraethylammonium bicarbonate, tetraethylammonium carbonate, sodium formate and sodium oxalate. The tetraethylammonium carbonate and bicarbonate were prepared by bubbling CO_2 through an aqueous solution of tetraethylammonium hydroxide and monitoring the pH. Two breaks in the pH were obtained, corresponding to Et_4NHCO_3 and $(\text{Et}_4\text{N})_2\text{CO}_3$ formation respectively. The resulting solutions were evaporated, then the product was dried in a vacuum dessicator. An accumulation experiment was also carried out where the disc reduction was carried out for several hours, then solution polarograms were run.

Polarograms of the carbonate and bicarbonate solutions gave no oxidation waves. Polarograms of the oxalate, formate, accumulated product and disc product collected on the ring are shown in Figures 4.20 to 4.23, where the effect of added water is also shown. The half-wave potential data is summarised in Table 4.5

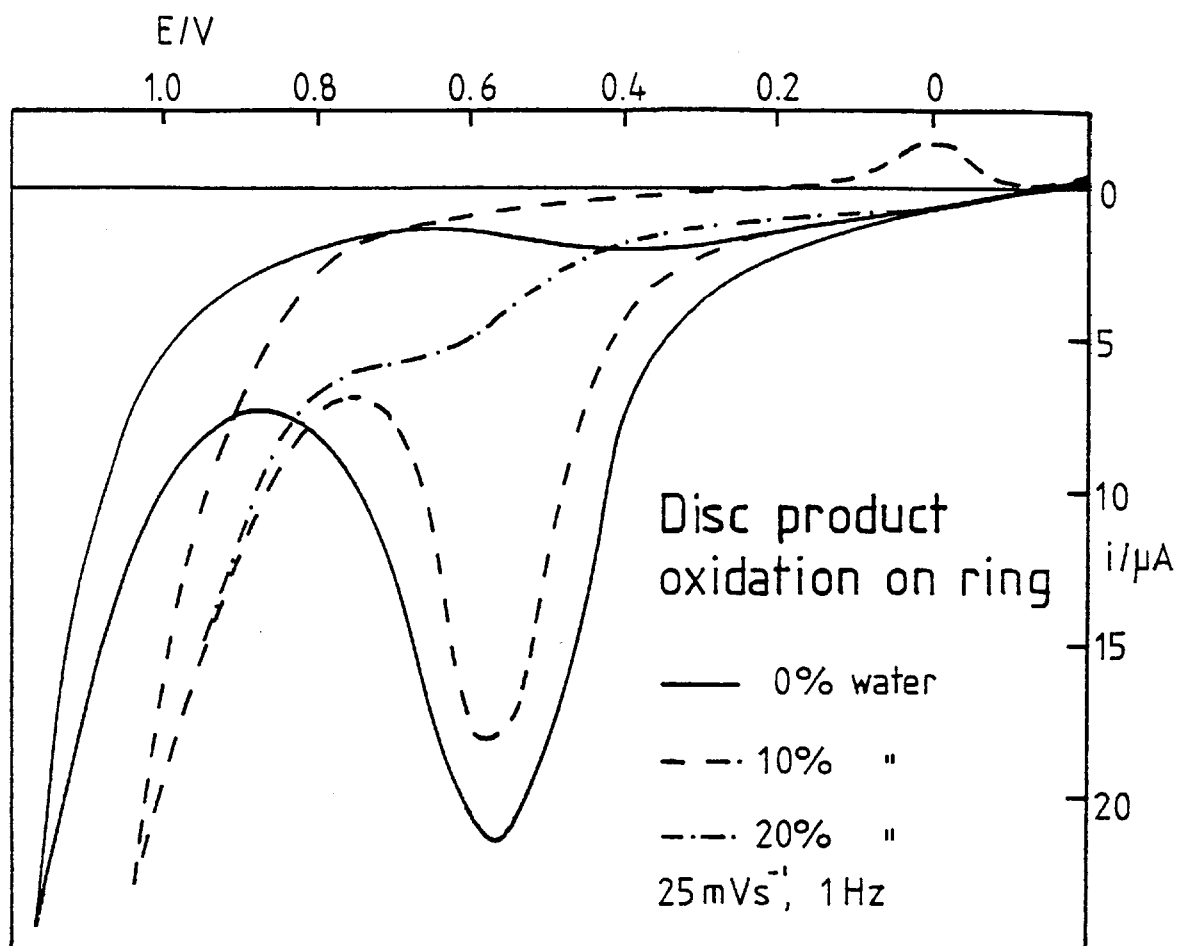


FIGURE 4.20

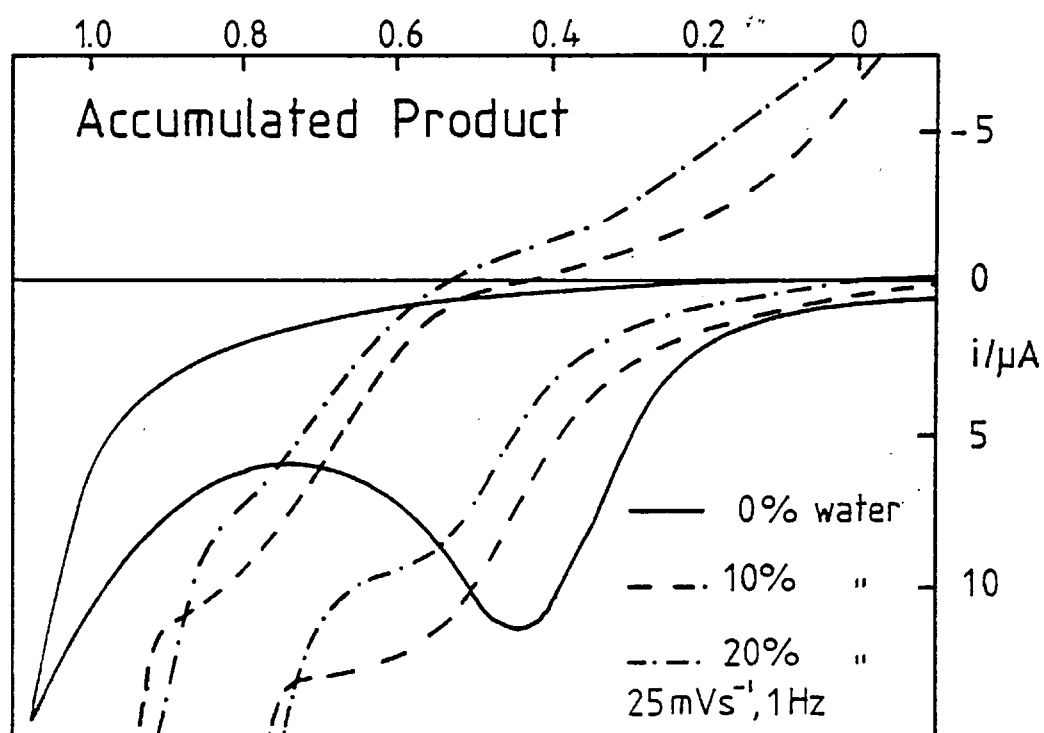


FIGURE 4.21.

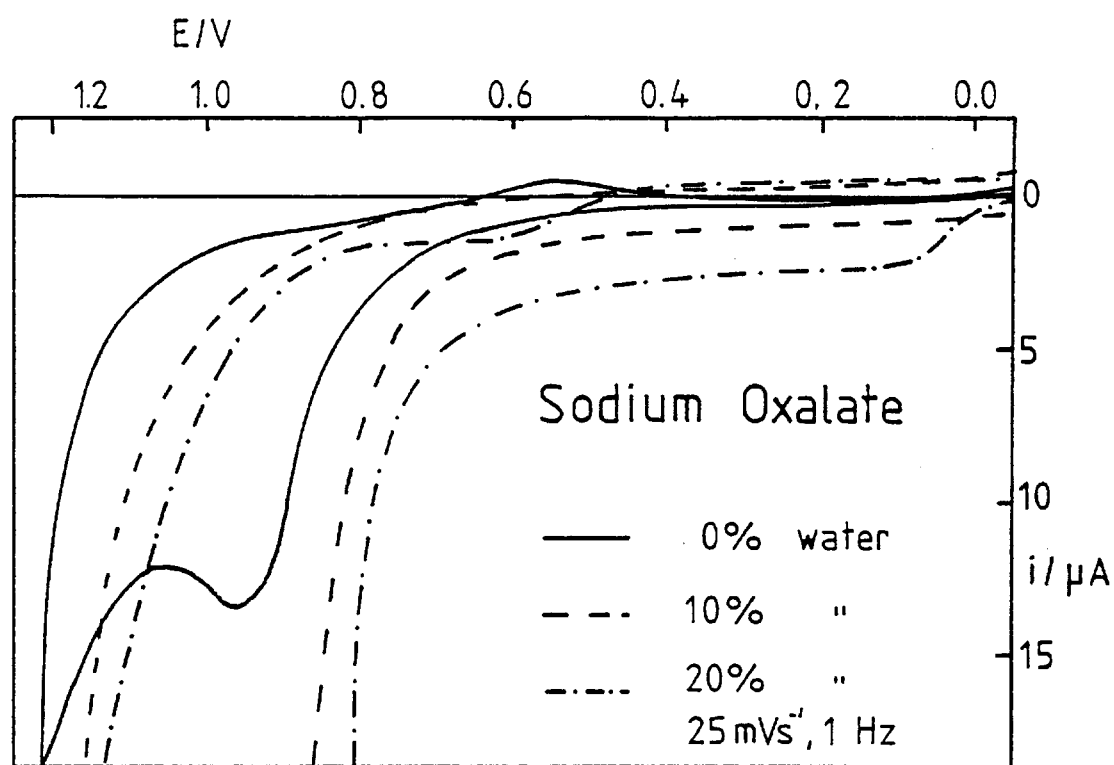


FIGURE 4.22.

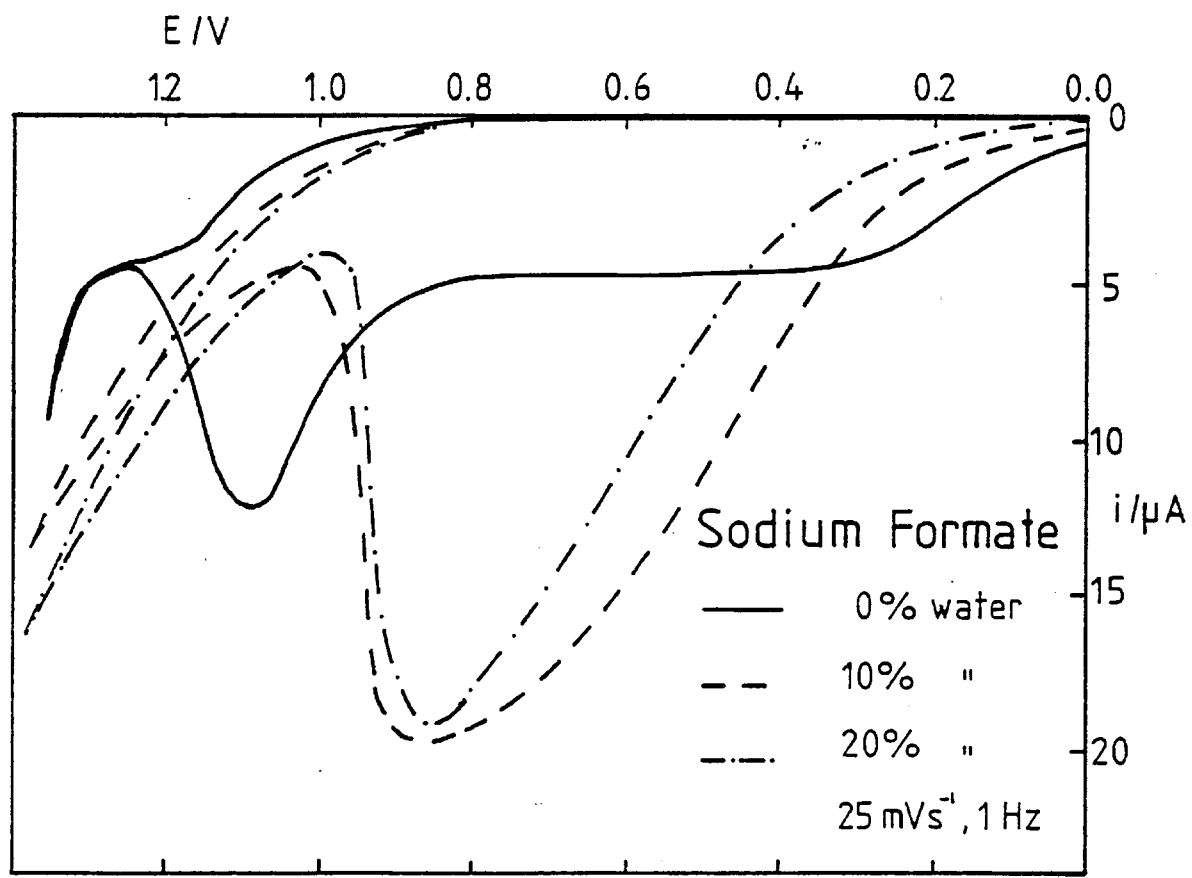


FIGURE 4.23.

Table 4.5. Half-wave potentials from Figures 4.21 to 4.24

	WATER LEVEL		
SAMPLE	0%	10%	20%
Ring collection of Disc Product	+0.40	+0.46	+0.51
Accumulated Disc Product	+0.32	+0.38	+0.44
Sodium Oxalate	No wave seen	-0.03	+0.05
Sodium Formate	+0.18	+0.46	+0.57

The data indicates that formate is the main reduction product, and this is proved by Figure 4.24. This conclusion is surprising in view of the earlier rotating disc data, which showed the number of electrons in the reduction was one - normally CO_2 reduction to formate would mean a two electron reduction per CO_2 molecule, as processes (7) and (8), or (7) and (8') in Figure 1.7 shows.

The Mechanism of CO_2 Reduction

The one electron reduction per CO_2 molecule, and formate product are explained by the following mechanism:-

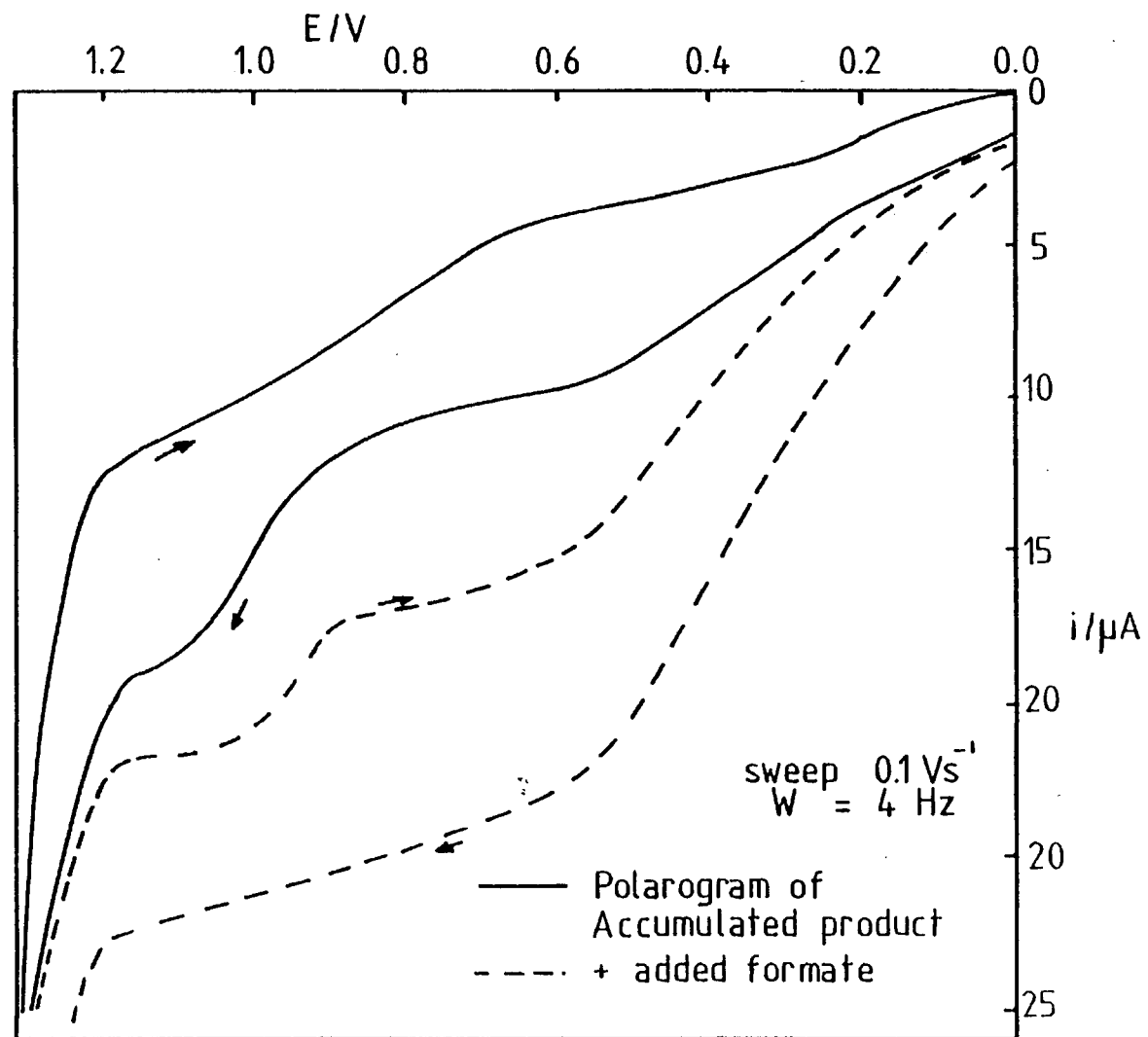
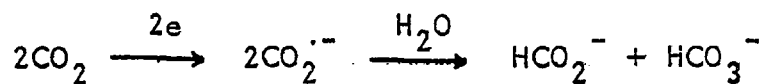
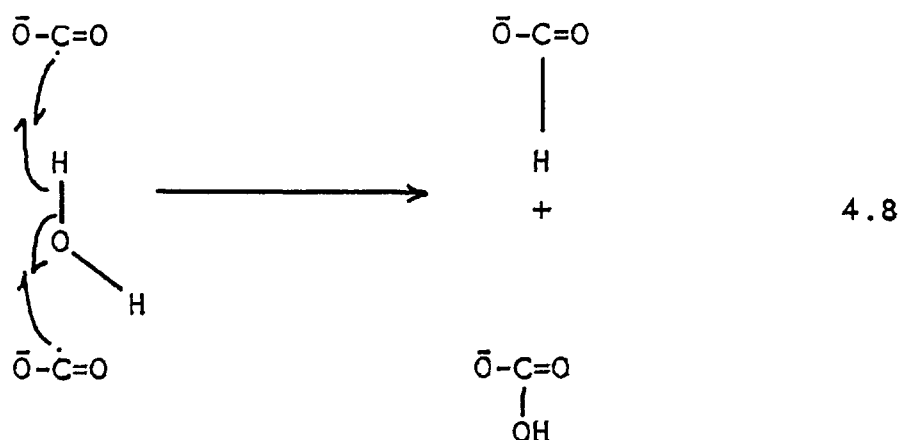


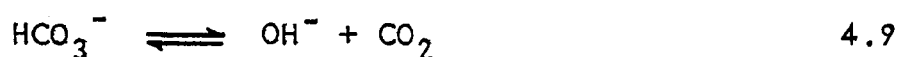
FIGURE 4.24. Comparison of the electrochemistry of accumulated product and formate.



The second step of this mechanism must be fast for formate to be detected at the ring, and is probably a concerted process, as shown by process (9) of Figure 1.7.



Bicarbonate is in equilibrium with CO_2 by the process:-



In a non-aqueous environment this equilibrium will be slow compared to the diffusion time across the diffusion layer of an R.D.E., so it is reasonable to assume no extra CO_2 will become available for reduction at the disc electrode. Further evidence of this mechanism is presented in the next chapter.

4.2a. The Reduction of Oxygen in DMSO on a Rotating Disc Electrode

The reduction of oxygen in DMSO was studied on rotating disc electrodes of mercury, gold and silver. Very similar electrochemistry was found on all three metals, so the following section will concentrate on results obtained with the gold disc of electrode A.

Oxygen Polarograms

Figure 4.25 shows polarograms of a 0.7mM solution of oxygen in DMSO at various rotation speeds. Two reduction waves of equal height were obtained, with $E_{1/2}$ values of -0.805 V and -2.14 V at a rotation speed of 9 Hz. Table 4.6 shows the variation of half-wave potential with rotation speed.

Table 4.6 Variation of $E_{1/2}$ with W .

W/Hz	$E_{1/2}$ (1st reduction)/V	$E_{1/2}$ (2nd reduction)/V
1	-0.804	-2.06
4	-0.805	-2.11
9	-0.805	-2.14
16	-0.806	-2.17
25	-0.807	-2.19

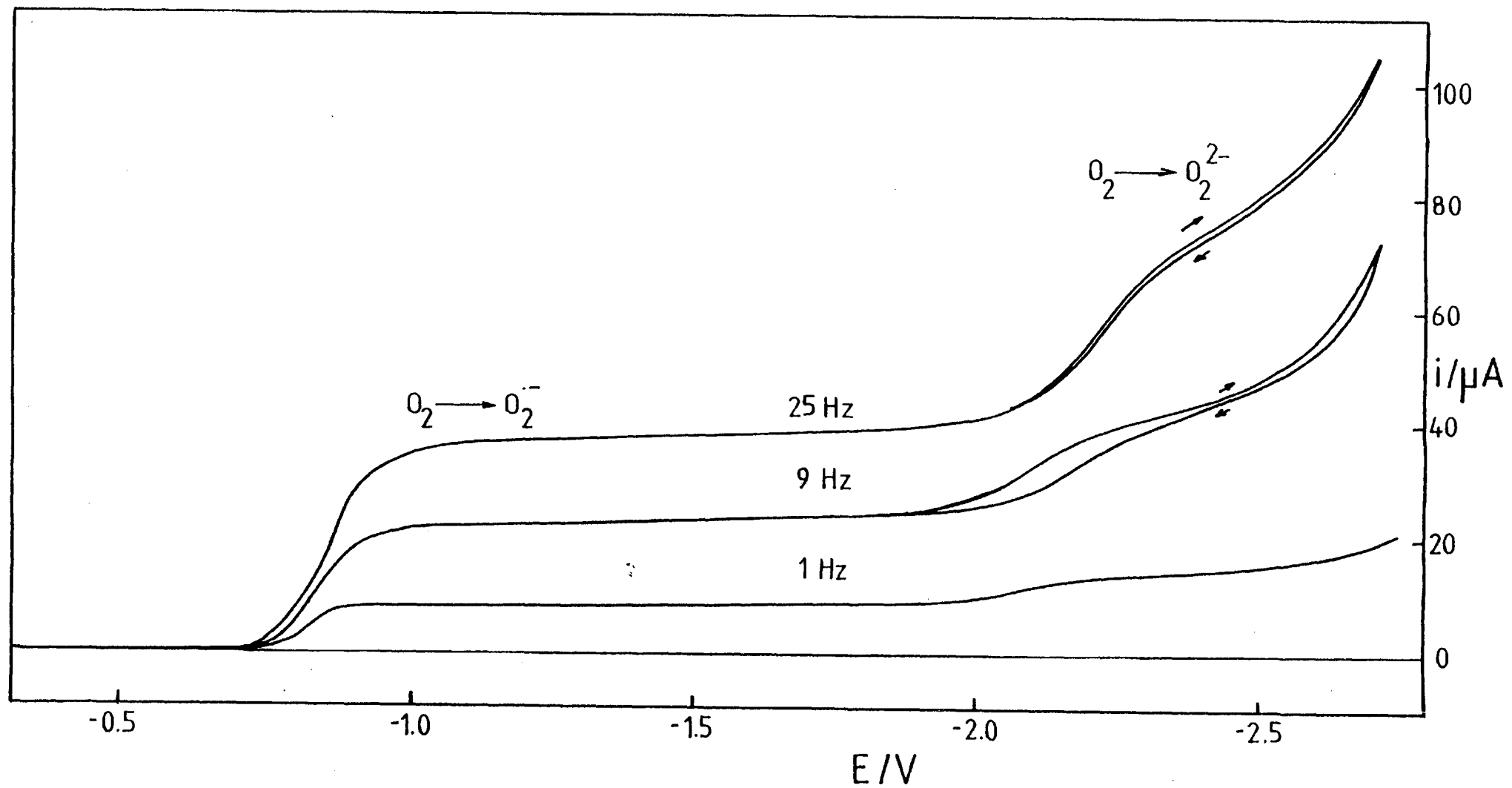


FIGURE 4.25. The reduction of oxygen in DMSO.

The half-wave potential of the first wave varies only slightly with rotation speed, showing the reduction is nearly reversible. Figure 4.26 is a plot of $E_{1/2}$ of the second wave vs. $\ln W$. The graph is linear, showing the second reduction is irreversible.

Levich Plots

Plots of the limiting current vs. root of rotation speed for both reduction waves are shown in Figure 4.27. Both Levich plots are linear.

The Diffusion Coefficient of Oxygen in DMSO

Rotation steps of 5-10, 6-10, 6-11, 7-11 and 8-12 Hz were applied with the gold disc polarised at -1.5 V, and four current transients were recorded for each step. Figure 4.28 is a graph of $(W_{\infty}t - 0.04)$ vs. τ . The slope of the straight line was found to be 2.18 ± 0.04 by linear regression analysis, with a correlation coefficient of 0.9995. The diffusion coefficient of oxygen in DMSO was therefore found to be $2.05 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

The Number of Electrons in the Reduction

The Levich plots in Figure 4.27 have gradients of $9.2 \mu\text{A}/\sqrt{\text{Hz}}$ and $1.84 \mu\text{A}/\sqrt{\text{Hz}}$. The concentration of a saturated solution of oxygen in DMSO has been accurately found⁽¹²⁶⁾ to be 2.1 mM. Assuming a linear relation between C_{O_2} and the oxygen partial pressure, a 33% saturated oxygen solution has an oxygen concentration of 0.69 mM. From Figure 4.27:-

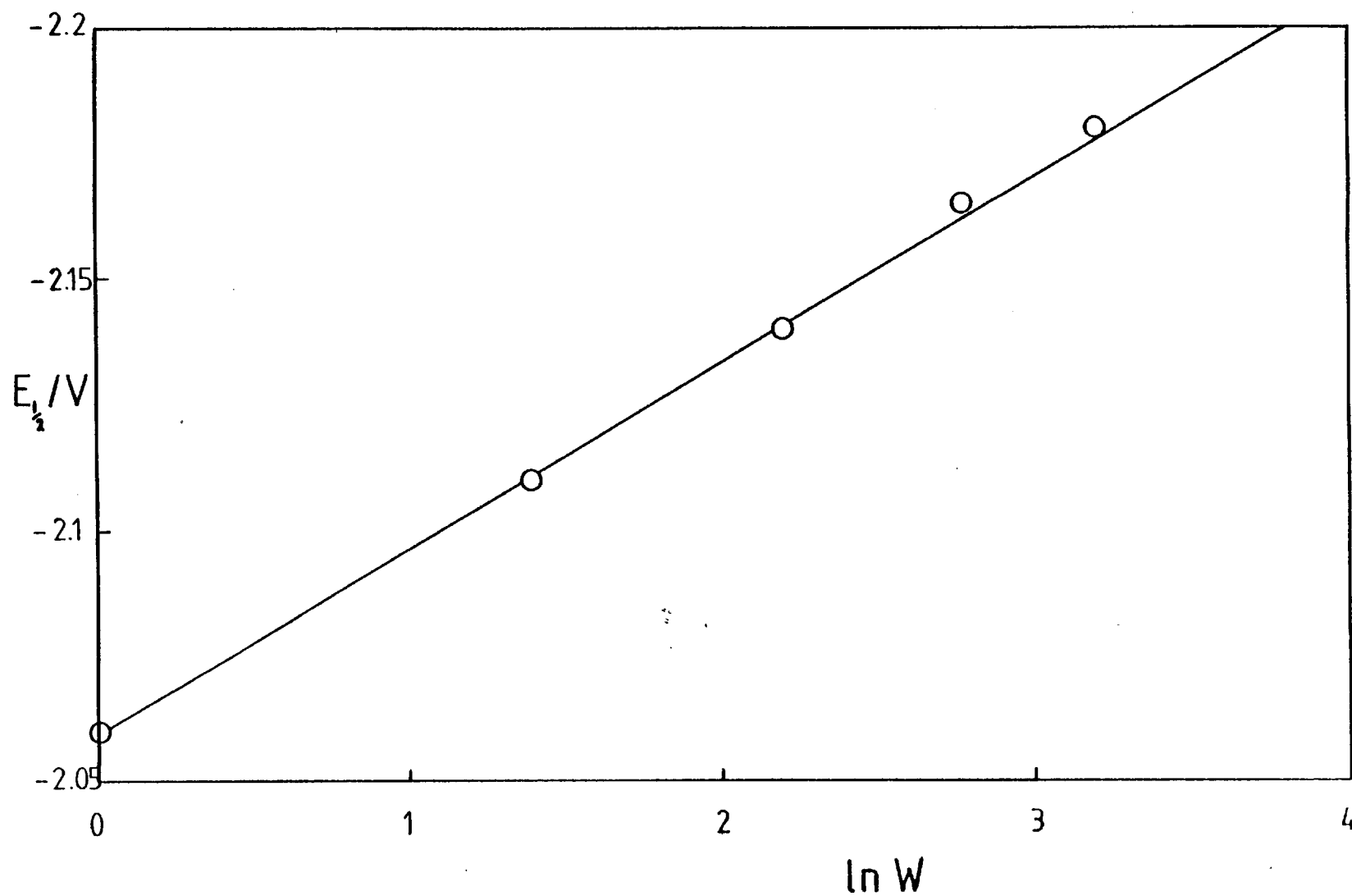


FIGURE 4.26. Plot of $E_{1/2}$ vs. $\ln W$ for the second oxygen reduction wave, showing the reduction is irreversible.

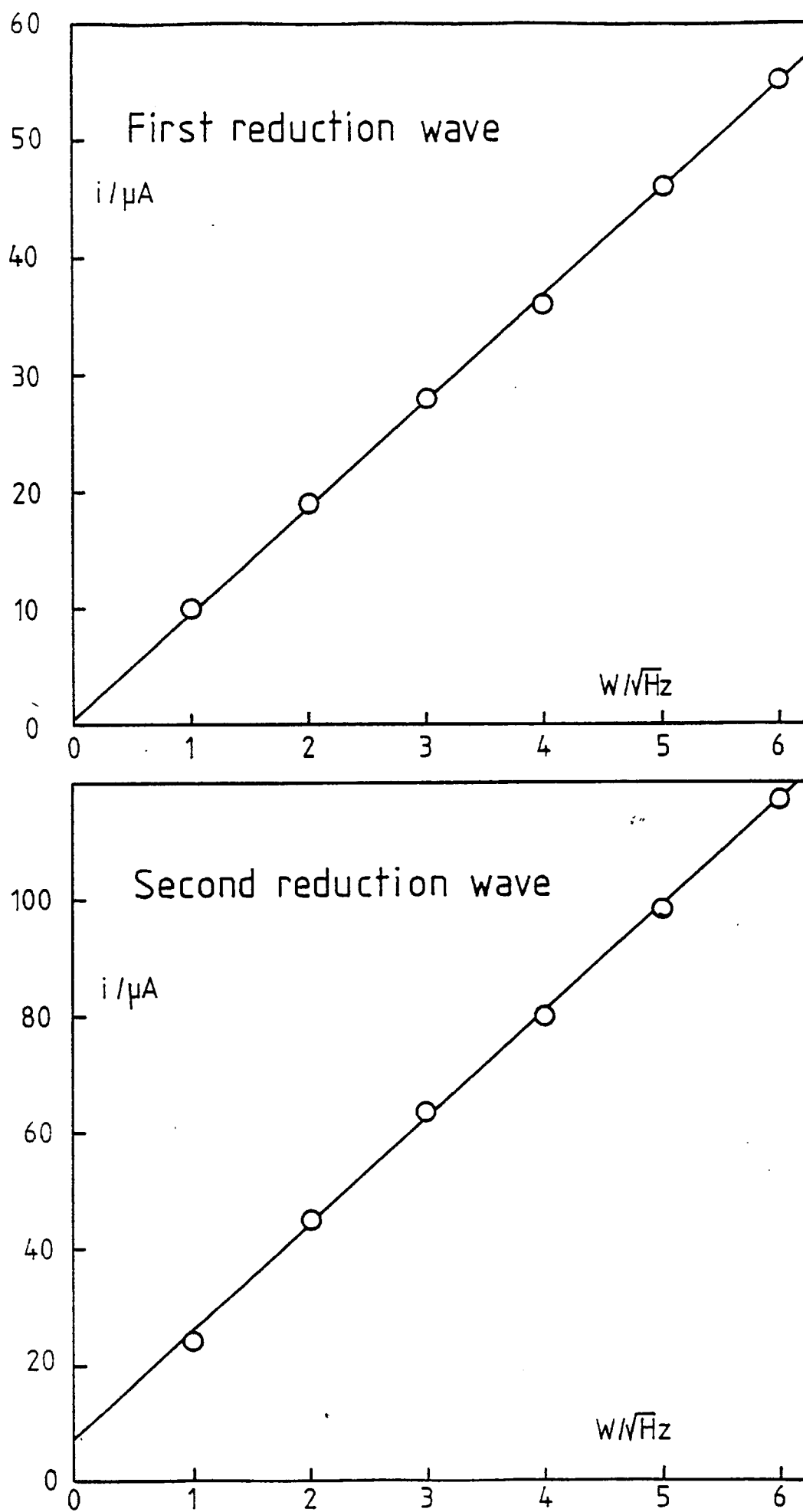


FIGURE 4.27. Levich plots for oxygen reduction in DMSO.

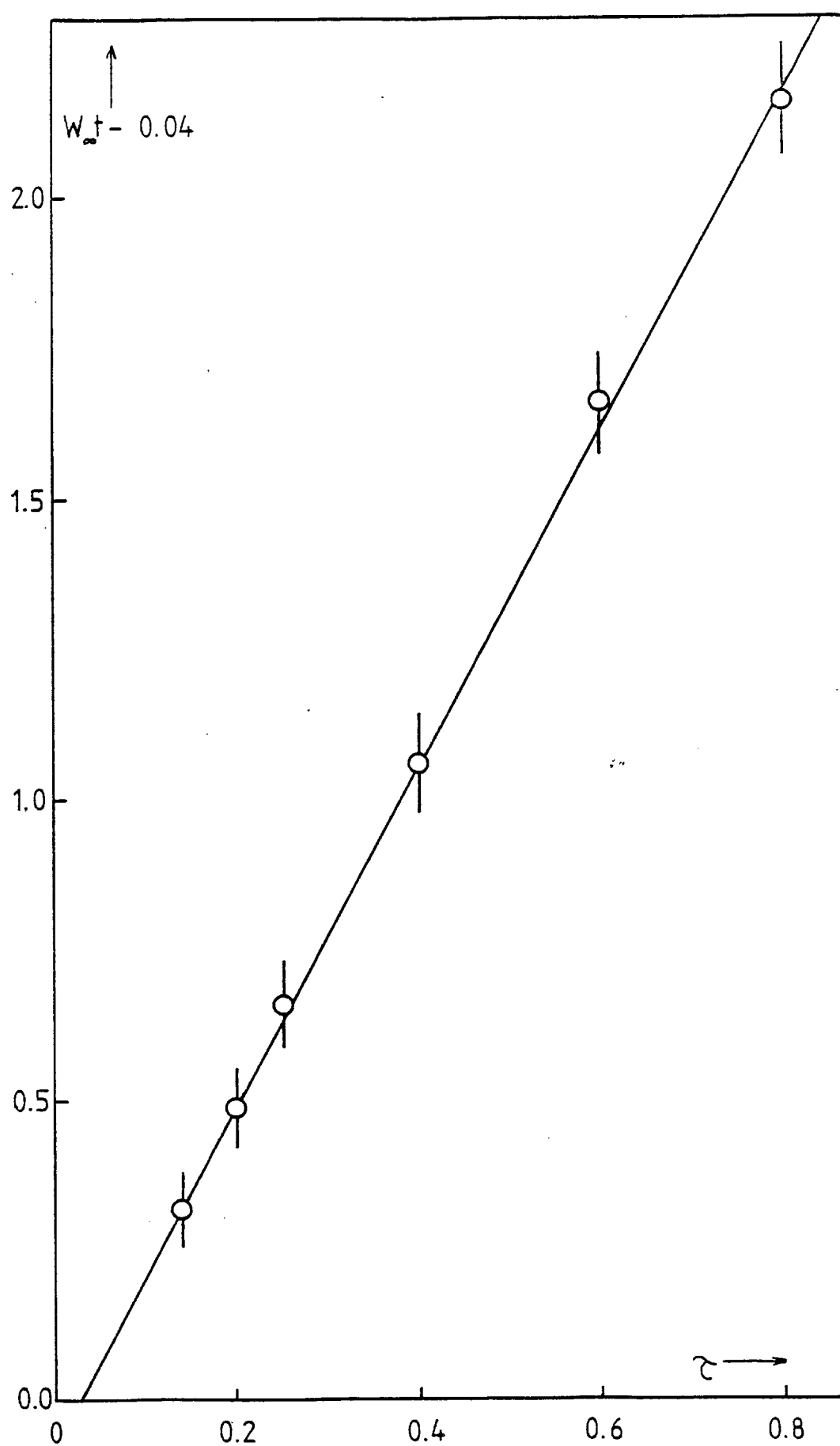


FIGURE 4.28. Graph of $W_\infty t - 0.04$ vs. τ obtained from rotation step data on oxygen reduction in DMSO.

$n(\text{1st reduction wave}) = 1.01$ 4.10

$n(\text{2nd reduction wave}) = 2.02$ 4.11

Tafel Plots

Tafel plots of the two reduction waves are shown in Figures 4.29 and 4.30. Both are good straight lines. The transfer coefficients of the two reductions are 0.48 for the first reduction, and 0.30 for the second.

4.2b. A Ring Disc Study of Oxygen Reduction

Electrode A' was used in this study. Its theoretical collection efficiency was 0.29. A value of 0.32 was found experimentally. Polarograms of the ring with the disc at -1.5 V, -2.4 V and disconnected are shown in Figure 4.31. The limiting disc current for the first wave was 50 μA , so the shielding equation (equation 2.30) is obeyed.

The polarograms in Figure 4.31 show two intermediates, with oxidation half wave potentials of ca -0.8 V and ca 0 V. This again indicates the near reversibility of the first reduction wave and the irreversibility of the second wave.

Collection Efficiency

The collection efficiency variation with disc and ring potential is shown in Table 4.7. The collection efficiency of the first reduction product does not change

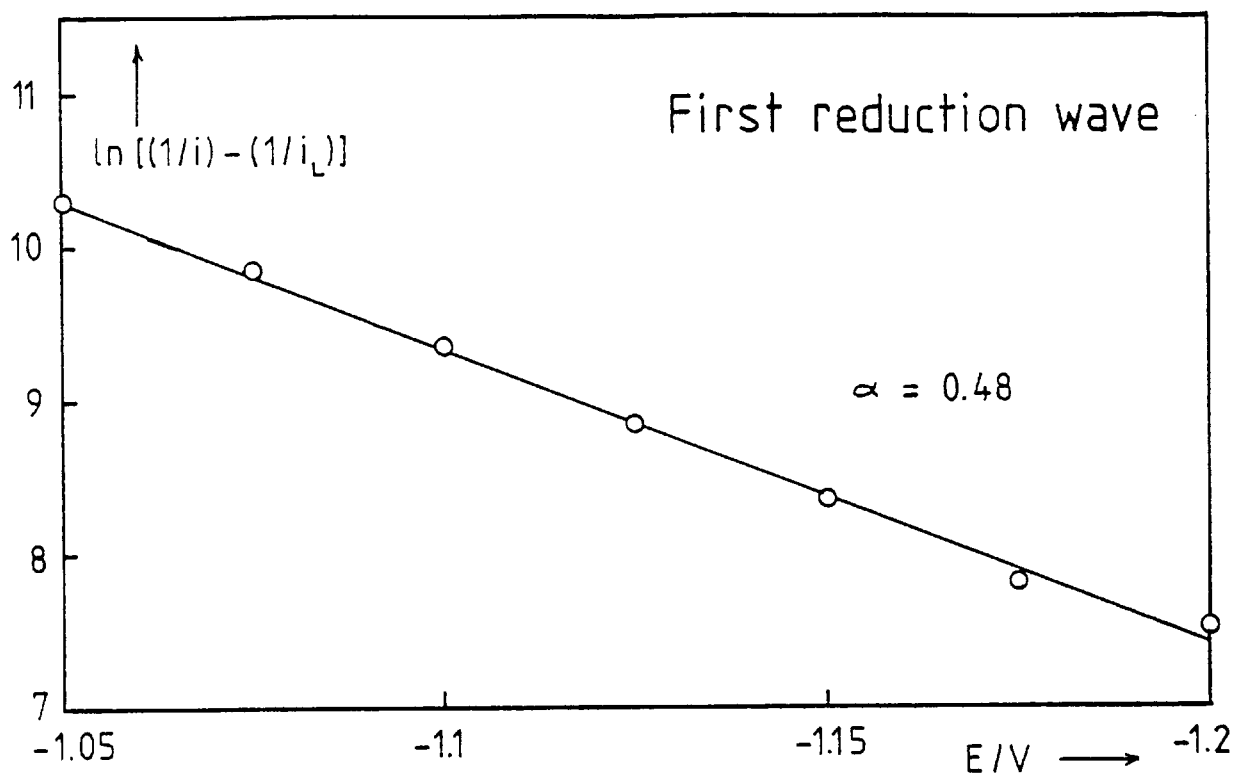


FIGURE 4.29. Tafel plot for the first oxygen reduction wave.

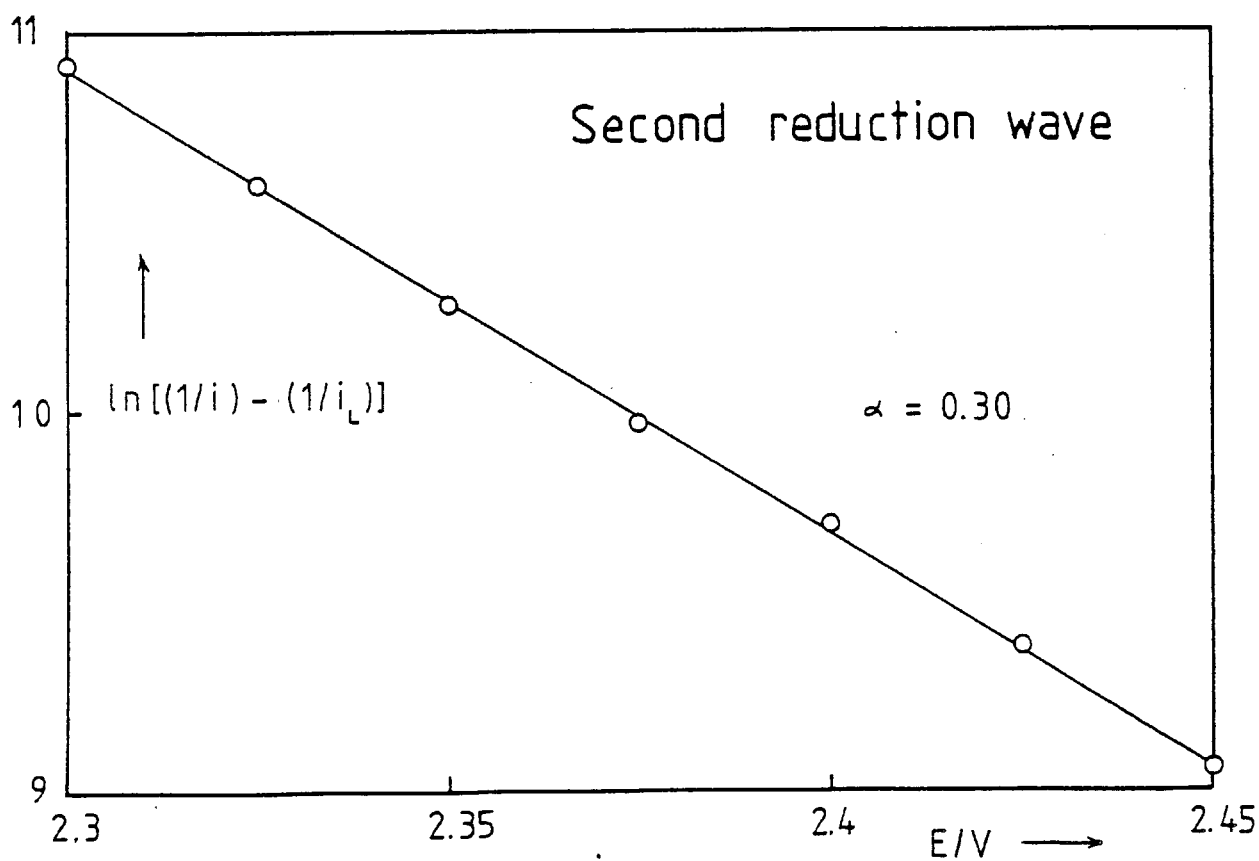


FIGURE 4.30. Tafel plot for the second oxygen reduction wave.

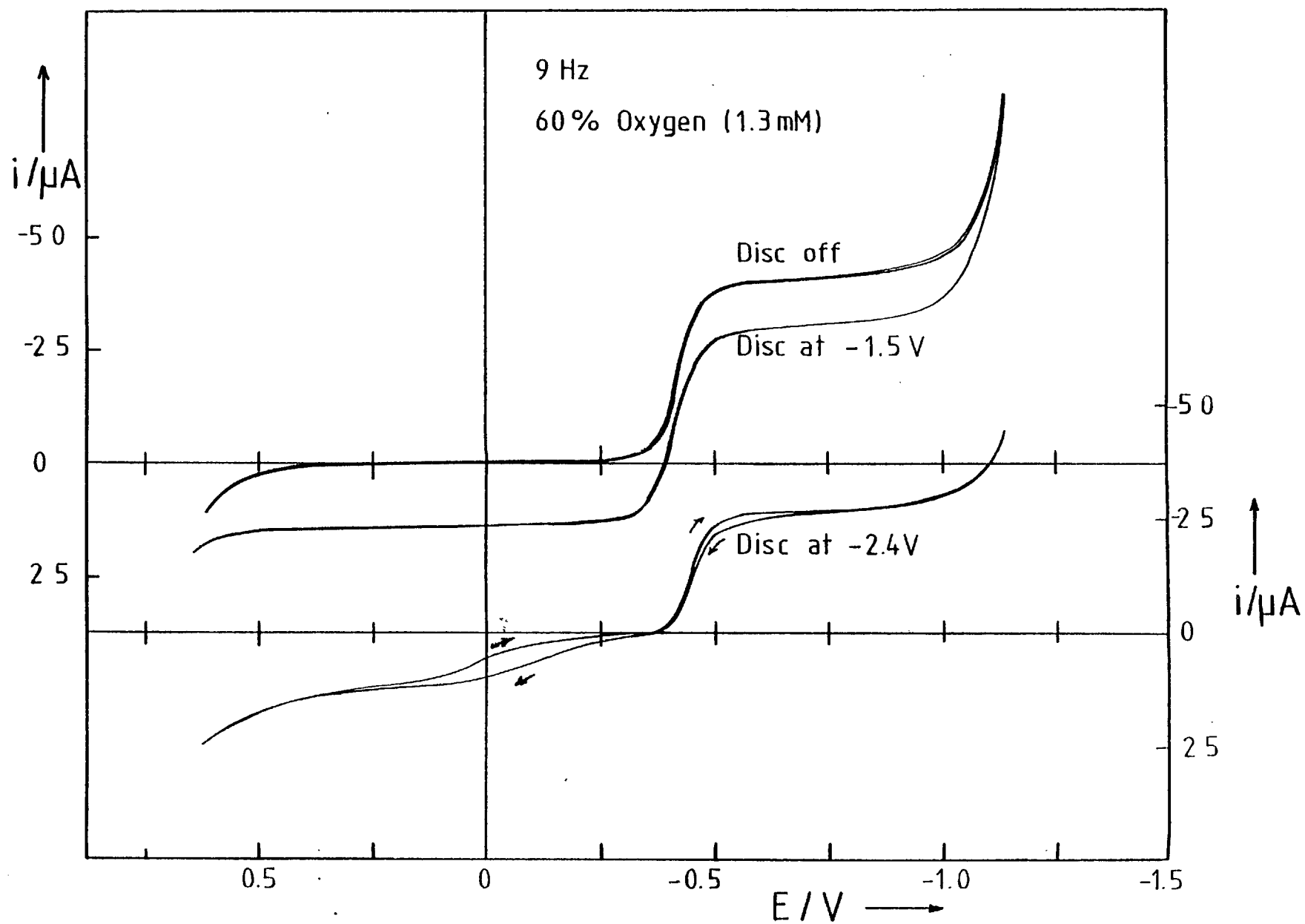
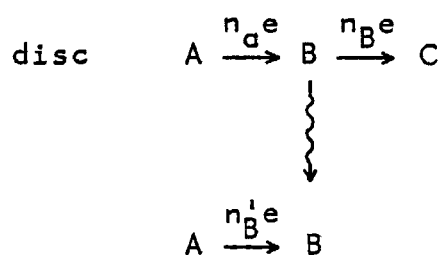


FIGURE 4.31. Ring polarograms showing the presence of two oxygen reduction intermediates.

Table 4.7 Collection efficiency variation with disc and ring potential

W/Hz	N with Disc at -1.5 V and Ring at 0.0 V	N with Disc at -2.4 V and Ring at +0.25
1	0.32	0.127
4	0.32	0.150
9	0.32	0.160
16	0.32	0.167
25	0.32	0.170

with rotation speed, but collection of the irreversible product is dependent on W . Figure 4.32 is a plot of i_D/i_R vs. $W^{-1/2}$. The graph is a straight line, which has been shown⁽¹⁰³⁾ to indicate a reaction scheme of the type:-



where C is not electroactive at the ring electrode.

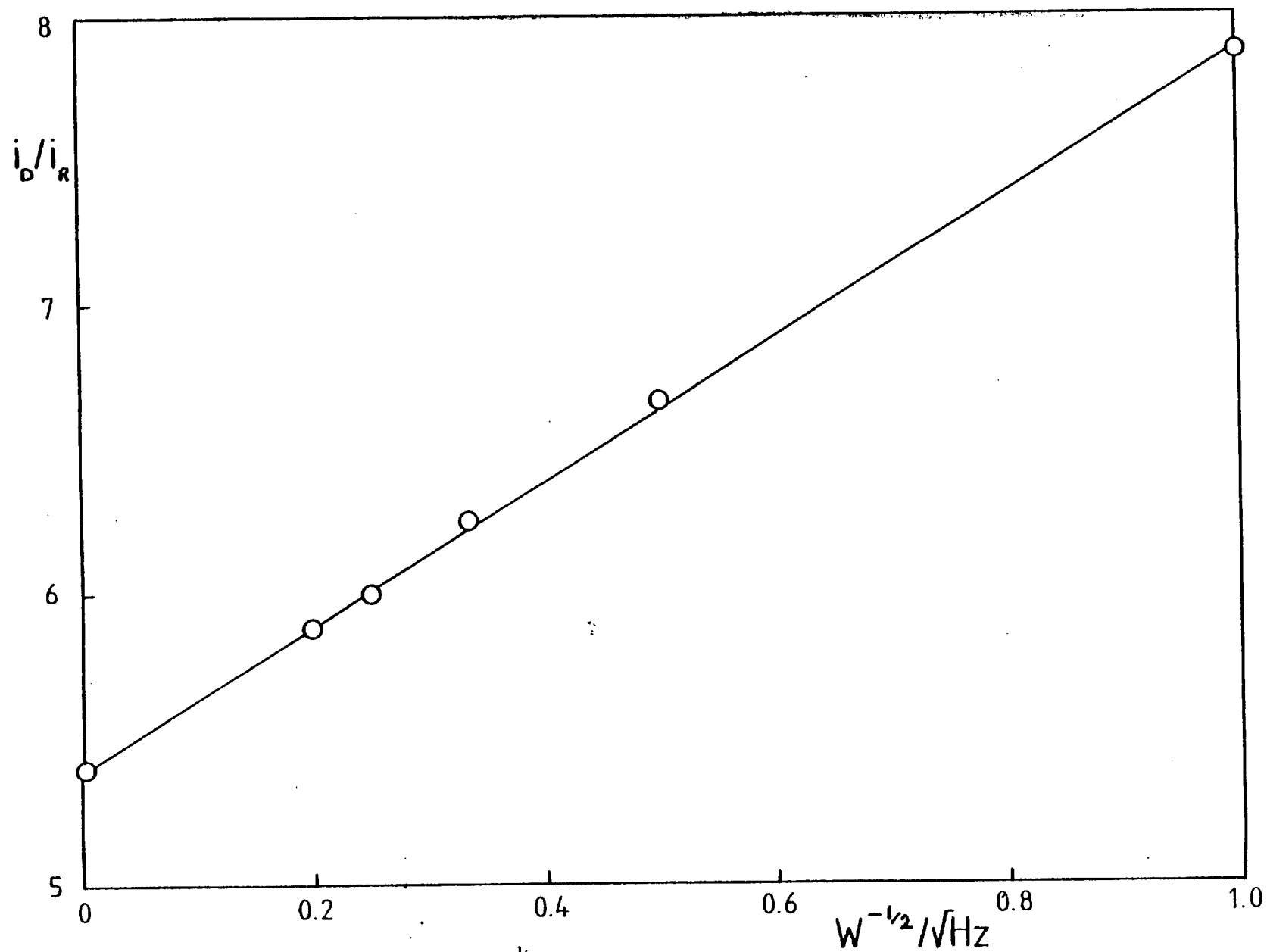


FIGURE 4.32. Graph of i_D/i_R vs. $W^{-1/2}$. Note the increase in collection efficiency as the rotation speed increases.

The Mechanism of the Reduction

The first reduction wave is nearly reversible, and clearly corresponds to the reduction of oxygen to superoxide:-



The second reduction wave is a two electron irreversible reaction. The mechanism of Goolsby and Sawyer⁽⁸⁰⁾ (Chapter 1) postulates hydroxide ion as product. Since the collection efficiency for oxidation of the two electron product is rotation speed dependent, clearly the intermediate oxidised at $E_{1/2} = 0\text{V}$ is not the final product. In order to identify the intermediate detected on the ring, ring polarograms were run of hydroxide ion, peroxide ion and hydrogen peroxide. The polarograms are shown in Figure 4.33. The data is summarised in Table 4.8.

Table 4.8. Oxidation Half Wave Potentials of possible Oxygen reduction products

	Substance		
	NEt ₄ OH	Na ₂ O ₂	H ₂ O ₂
	+0.83 V	0 V +0.82	Shoulder seen on solvent wave
$E_{1/2}$ values			

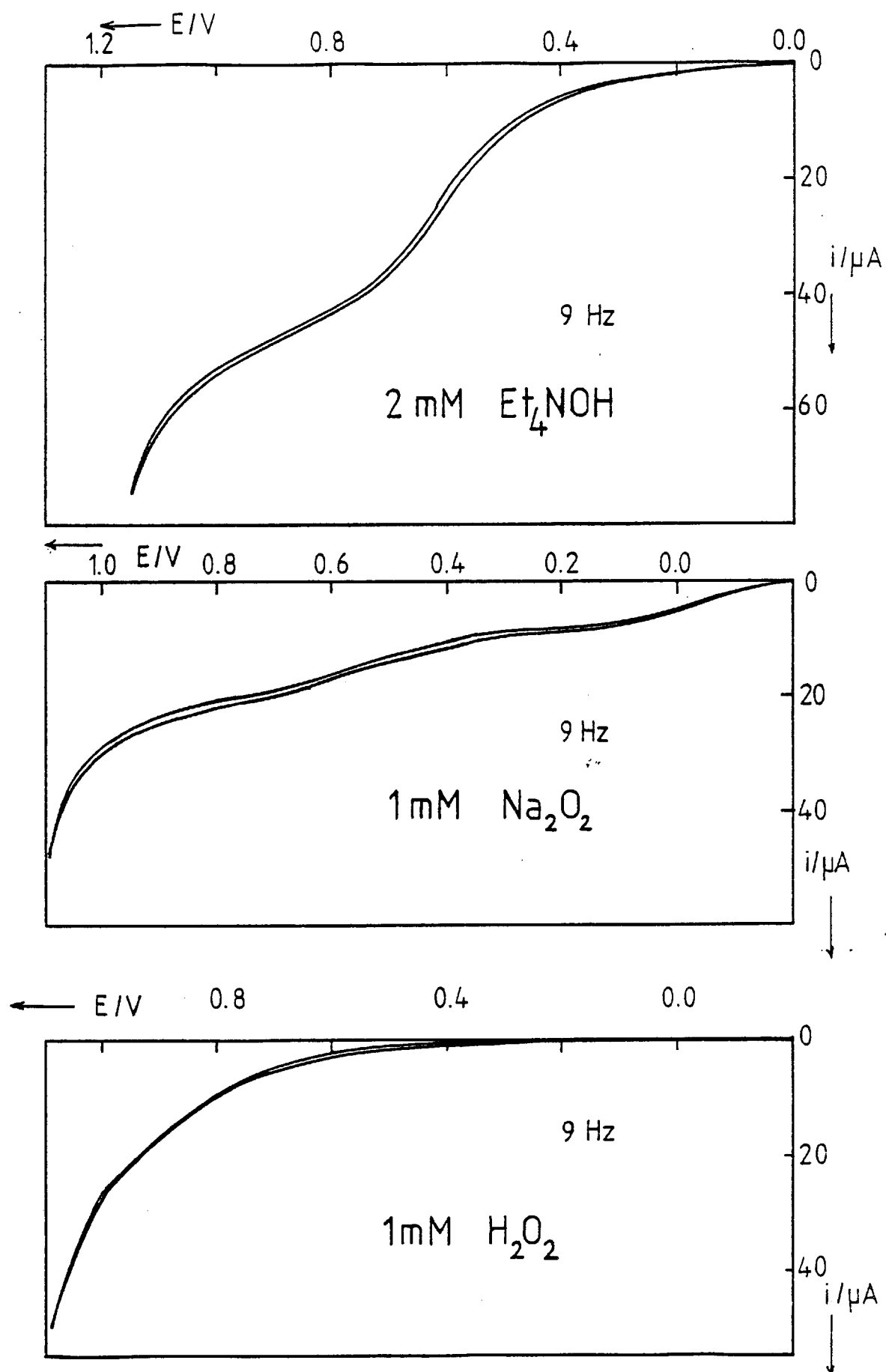
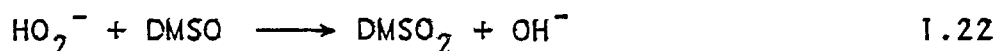
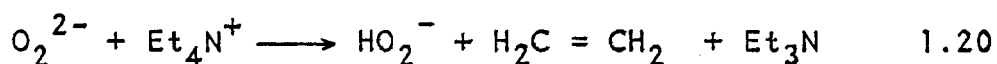


FIGURE 4.33. Ring polarograms of the possible disc reduction products.

The polarogram of sodium peroxide shows two oxidation waves. The main oxidation wave is at $E_{1/2} = +0.82$ V, which corresponds very closely to the hydroxide oxidation wave. There is also an oxidation at $E_{1/2} = 0$ V, which corresponds to the disc product oxidised on the ring. The polarogram indicates the peroxide has undergone the processes described by equations 1.20 and 1.21.



An accumulation experiment was also carried out. The oxidation polarogram of the accumulated product was identical to the hydroxide oxidation polarogram (Figure 4.33a.). It is likely that the mechanism of Goolsby and Sawyer is correct, and O_2^{2-} is the intermediate oxidised on the ring.

The Effect of Added Protons on Superoxide

The collection efficiency of the oxygen reduction products often showed a titration effect - there was no ring current at small but finite disc currents. This was found to be due to the DMSO being damp, so the effect of added protons on the collection efficiency was studied.

A typical titration curve is shown in Figure 4.34, and lines of gradient N' are drawn through the curve.

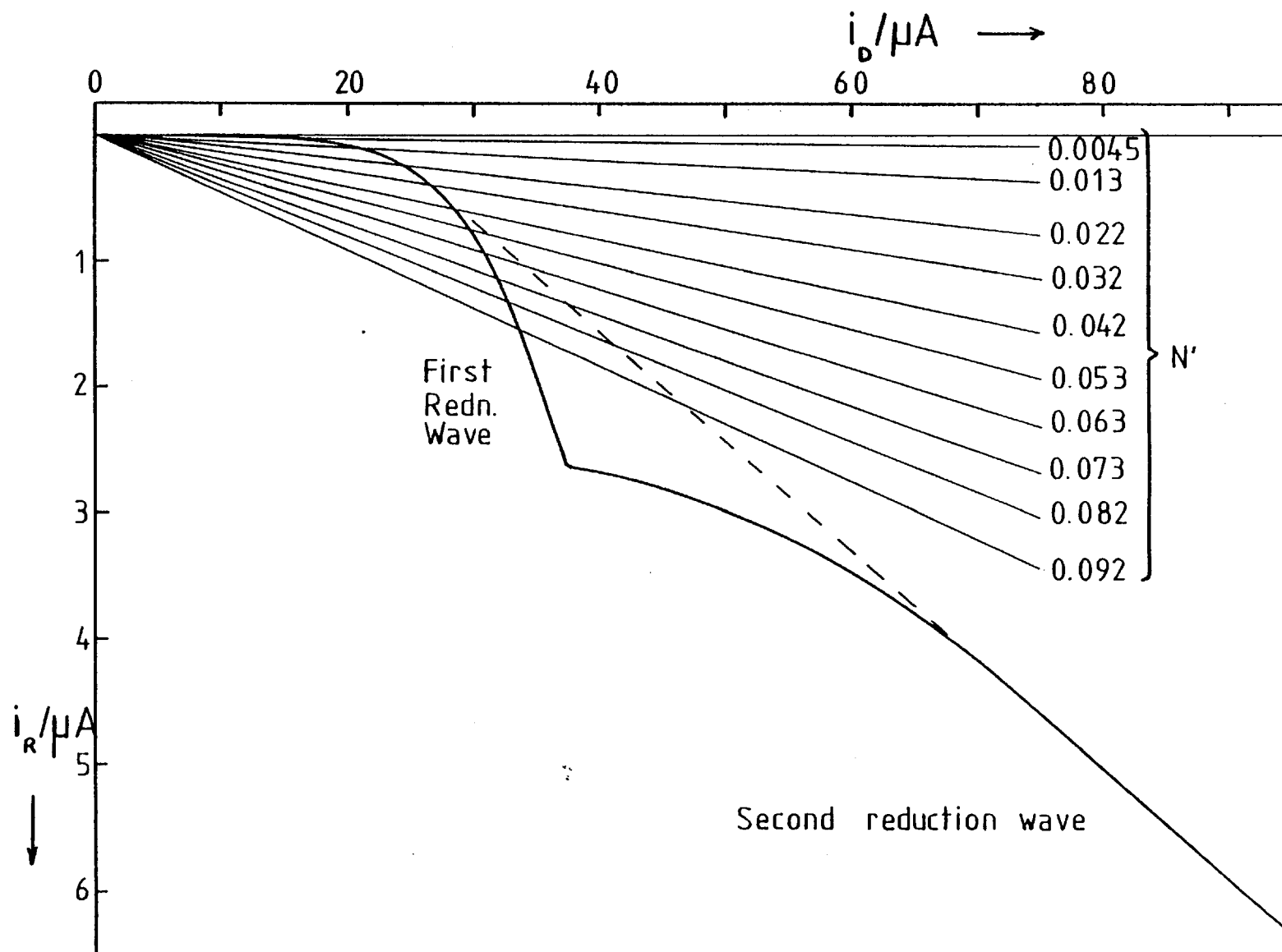


FIGURE 4.34. A typical titration curve obtained when oxygen (concentration ~ 2.1 mM) is reduced in the presence of ~ 2 mM H^+ in DMSO.

Figure 4.35 shows plots of i_D vs. $|i_D|/M$ at several rotation speeds. M was found to be proportional to $W^{1/2}$ and C_∞ , as equation 2.31 predicts.

The reaction boundary is on the inner edge of the ring when:-

$$|i_D| = M/(1-F(\alpha)) \quad 2.32$$

The titration curve theory described in Chapter 2 predicts $i_R = 0$ when equation 2.32 applies, since the reaction between B and C is assumed to be infinitely fast. When the reaction is not infinitely fast there is a finite ring current, which is related to the second order rate constant k_2 describing the homogeneous reaction between B and C by the equation⁽¹⁰⁸⁾:-

$$i_{R,K} = 0.21\pi r_1^2 n F D \omega^{3/2} \nu^{-1/2} k_2^{-1} \quad 4.13$$

The kinetic collection efficiency, defined by $i_{R,K}/i_{D,K}$ is related to k_2^{-1} by:-

$$N'_k = \frac{0.339 r_2^2 D^{1/3} 1-F(\alpha)}{r_1^2 \nu^{1/3} k_2} \cdot \frac{2\pi W}{C_\infty} \quad 4.14$$

Figure 4.36 is a graph of N'_k vs. W , when $C_{H^+} = 2$ mM. $i_{R,K}$ was found by using equation 2.32 to find $i_{D,K}$, then finding $i_{R,K}$ from the titration curve.

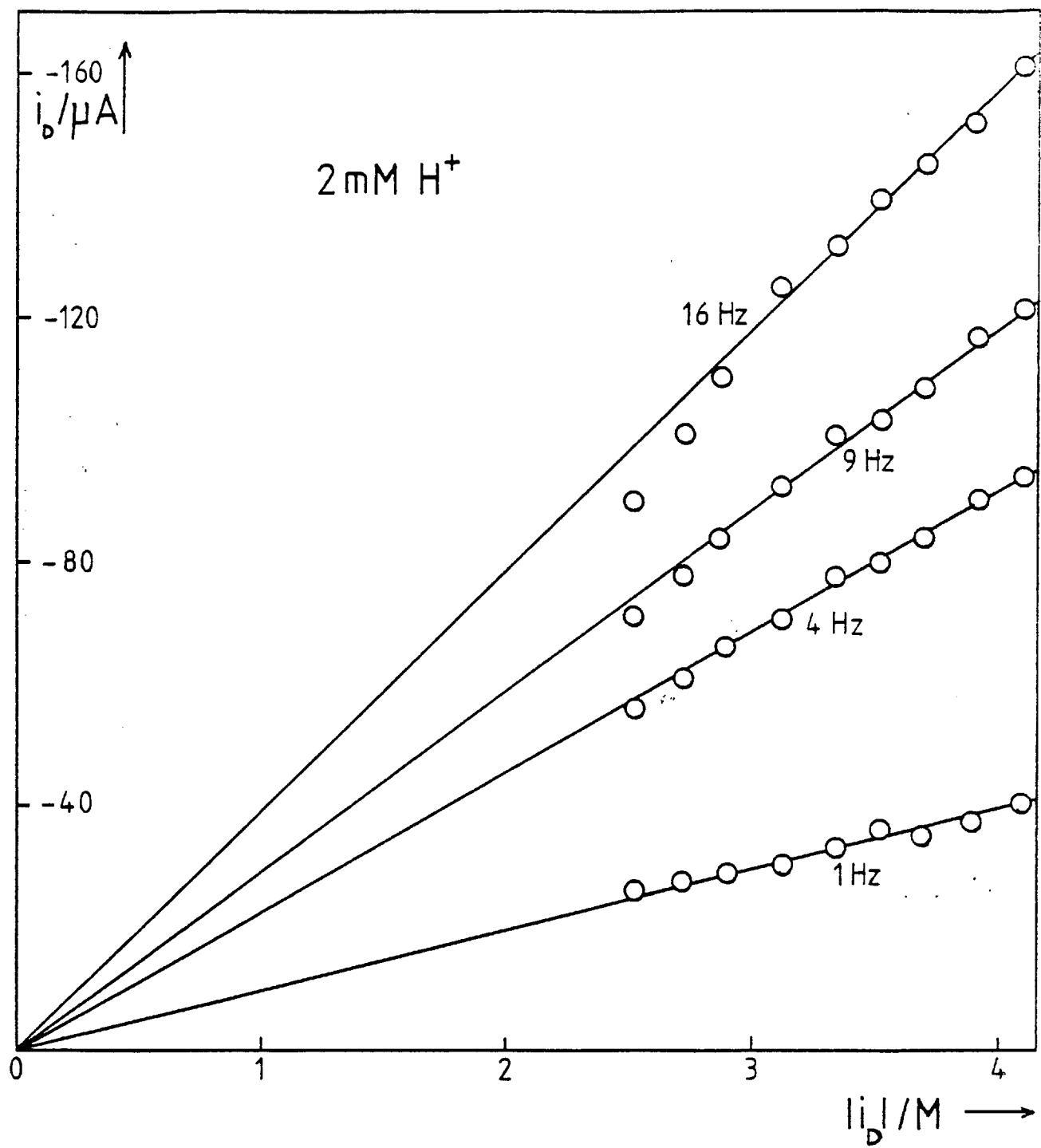


FIGURE 4.35. Graph of i_D vs $|i_D|/M$.

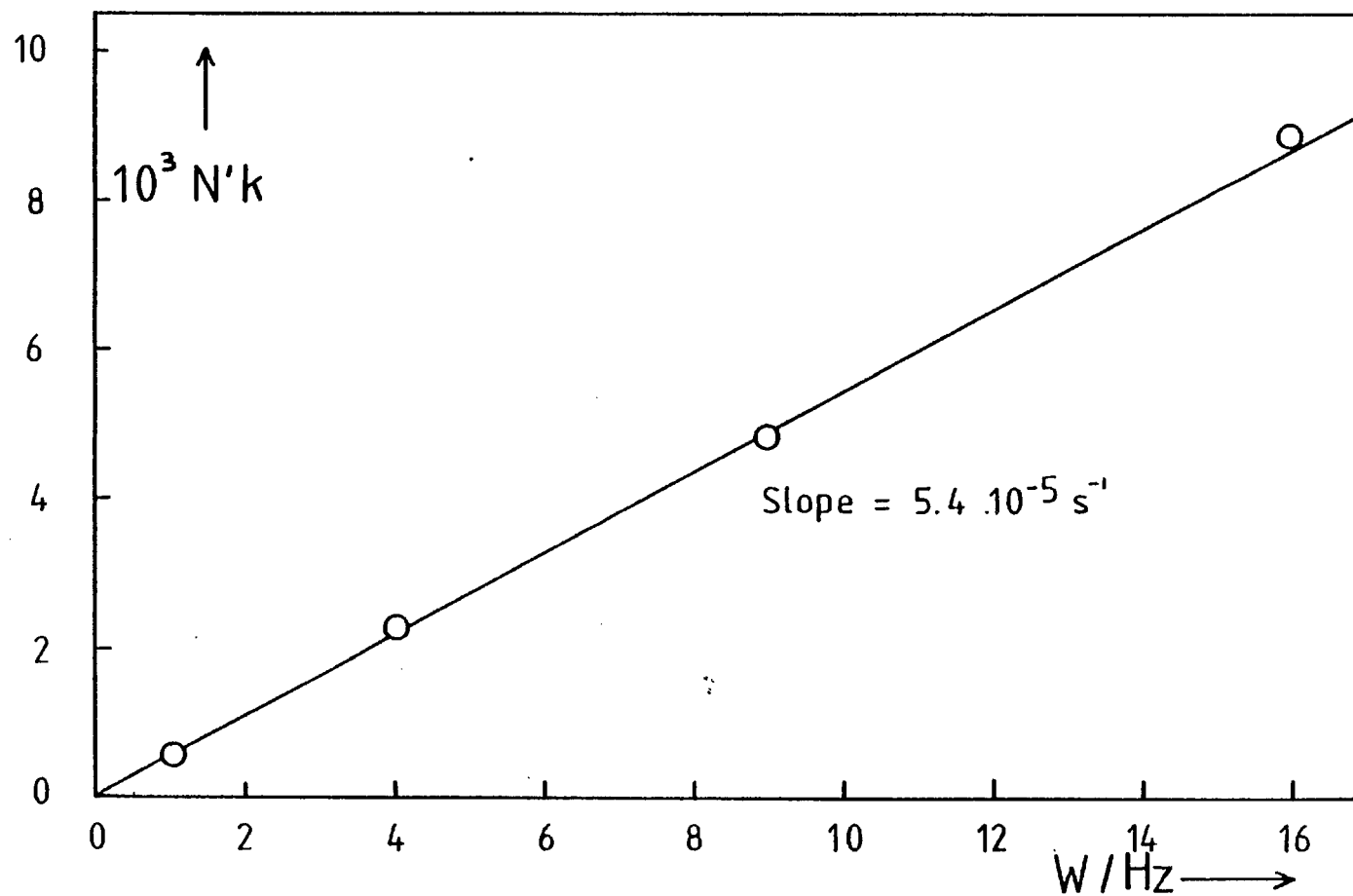


FIGURE 4.36. Graph of N'_k vs W .

The graph is a good straight line of slope $5.4 \cdot 10^{-4} \text{ s}^{-1}$.
Therefore the second order rate constant is:-

$$k_2 = 4.3 \cdot 10^5 \text{ M}^{-1} \text{ s}^{-1}. \quad 4.15$$

The Reaction Between 1,8-Dihydroxyanthroquinone and Oxygen in DMSO

The reduction polarograms of CO_2 and oxygen (Figures 4.1 to 4.4 and 4.25) show it would not be possible to distinguish between oxygen and CO_2 by choice of electrode potential alone. Although the first oxygen reduction wave, which is well separated from the CO_2 wave, could be used to give an idea of the height of the second oxygen wave, this would only be useful where the carbon dioxide and oxygen partial pressures were of the same magnitude, so that slight errors in the measurement of the oxygen level would not give grossly inaccurate CO_2 measurements.

Brooks⁽¹¹³⁾ encountered a similar problem with oxygen and halothane mixtures, and used the reaction between the reduced form of 1,8-dihydroxyanthroquinone and oxygen in a bid to separate the two waves. Brooks used the titration curve technique to show the reaction was fast in M KOH, and that the quinone reduced oxygen to hydroxide ions, as shown in Figure 4.37.

A polarogram of the anthroquinone in DMSO is shown in Figure 4.38. The first of the two waves corresponds

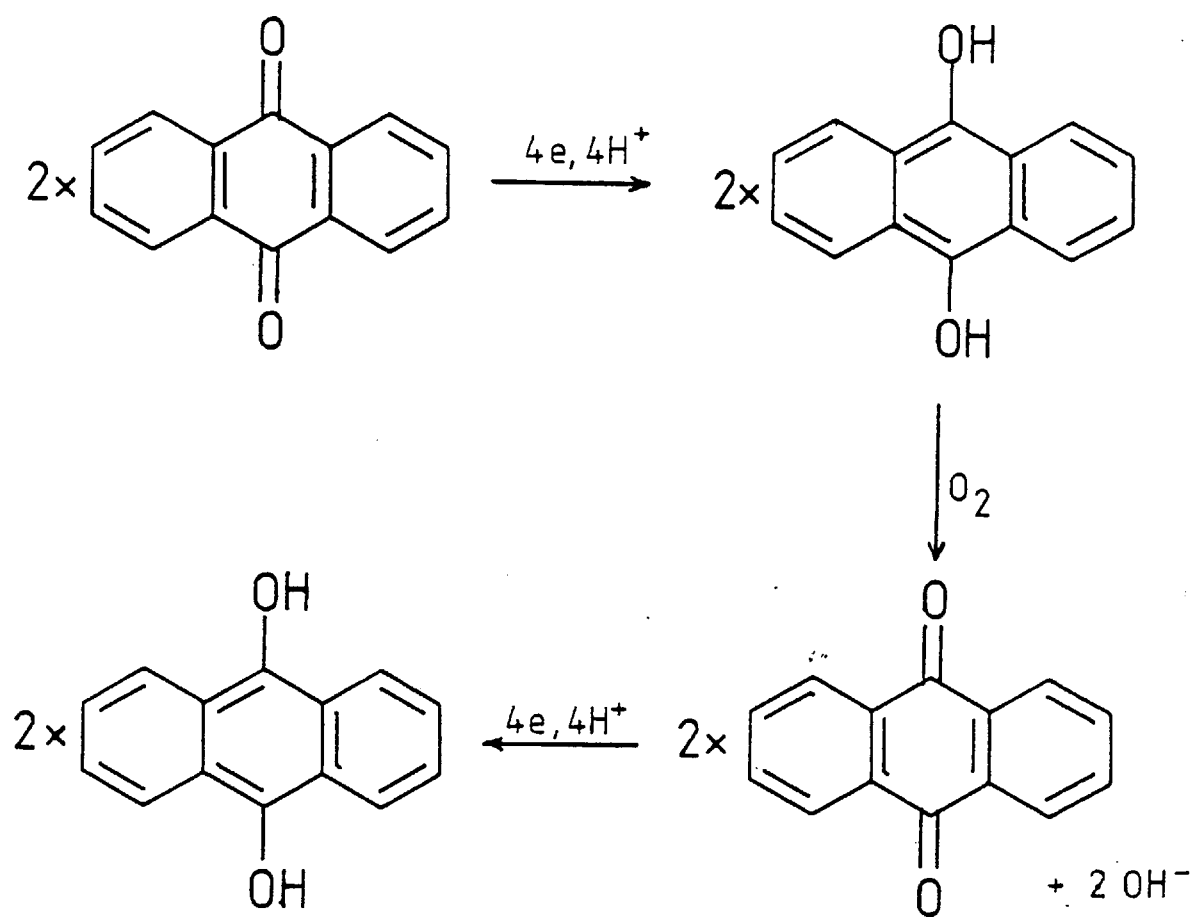


FIGURE 4.37. Reaction in aqueous solution between the reduced form of 1,8 DHAQ and oxygen.

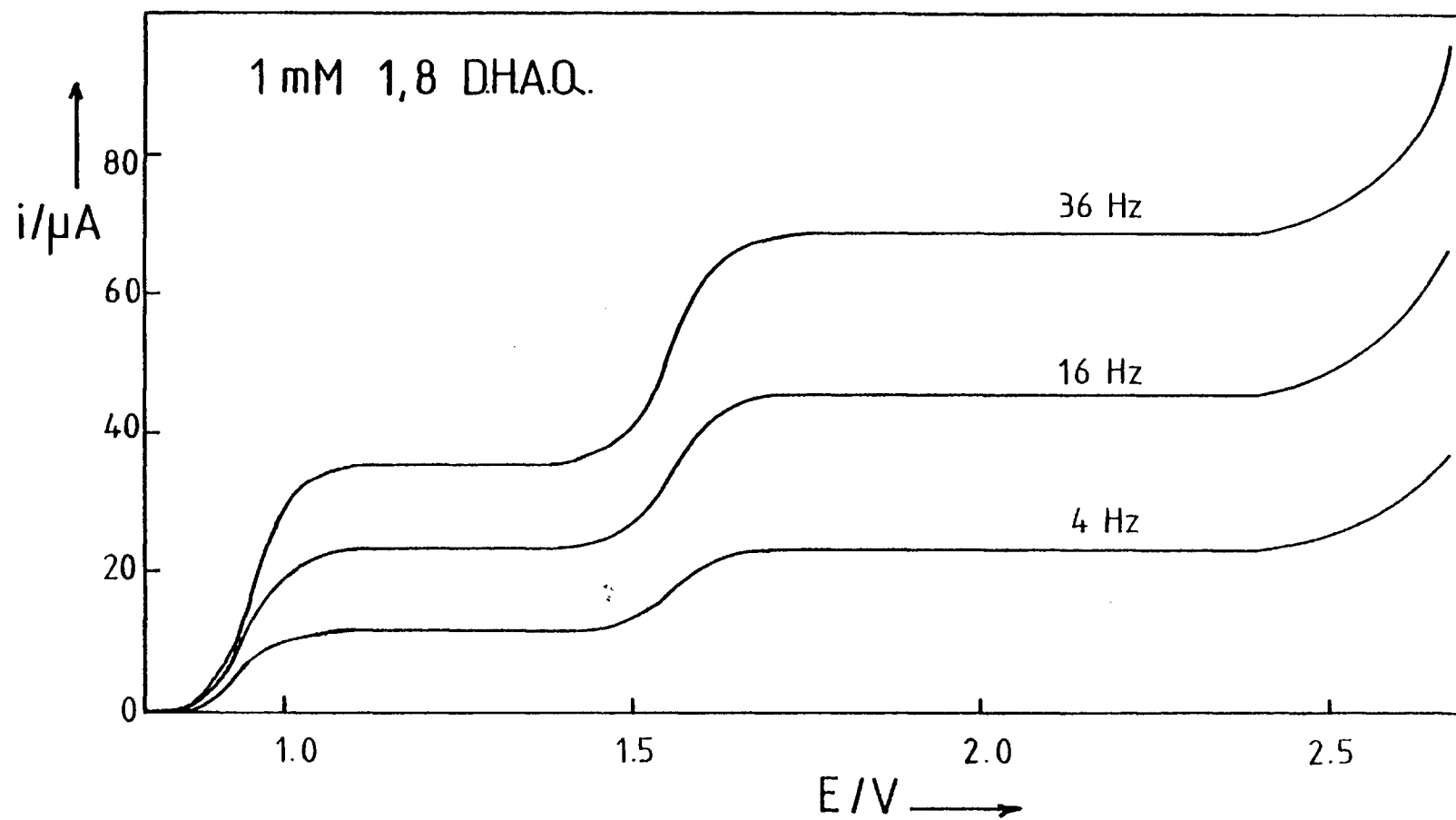


FIGURE 4.38. Polarograms of 1,8 DHAQ in DMSO.

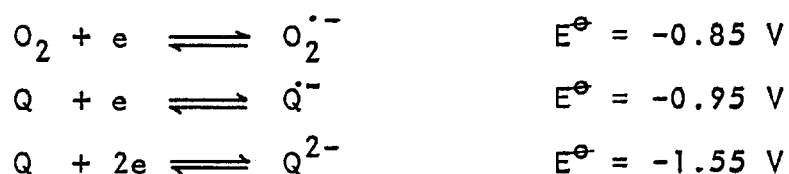
to semiquinone formation, a species not normally stable in aqueous solutions.⁽¹²⁷⁾ The Levich plots (Figure 4.39), assuming $n = 1$ and 2 respectively for the two waves, gave a value for the diffusion coefficient of the quinone of:-

$$D_Q = 4.8 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1} \quad 4.16$$

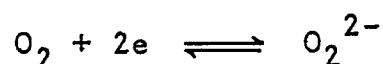
The half-wave potentials of the two waves are independent of rotation speed, showing the reduction is reversible. Ring polarograms, and cyclic voltammetry at a stationary disc electrode, confirmed this.

Electrode Potentials

Clearly the reaction between the reduced quinone and oxygen must be thermodynamically favoured. The standard electrode potentials for reversible reductions are given by⁽⁹⁸⁾ $E^\ominus = E_{1/2}$, so the standard electrode potentials for the reversible reactions (measured against the Ag/Ag^+ reference) are:-



The standard electrode potential for the reaction:-



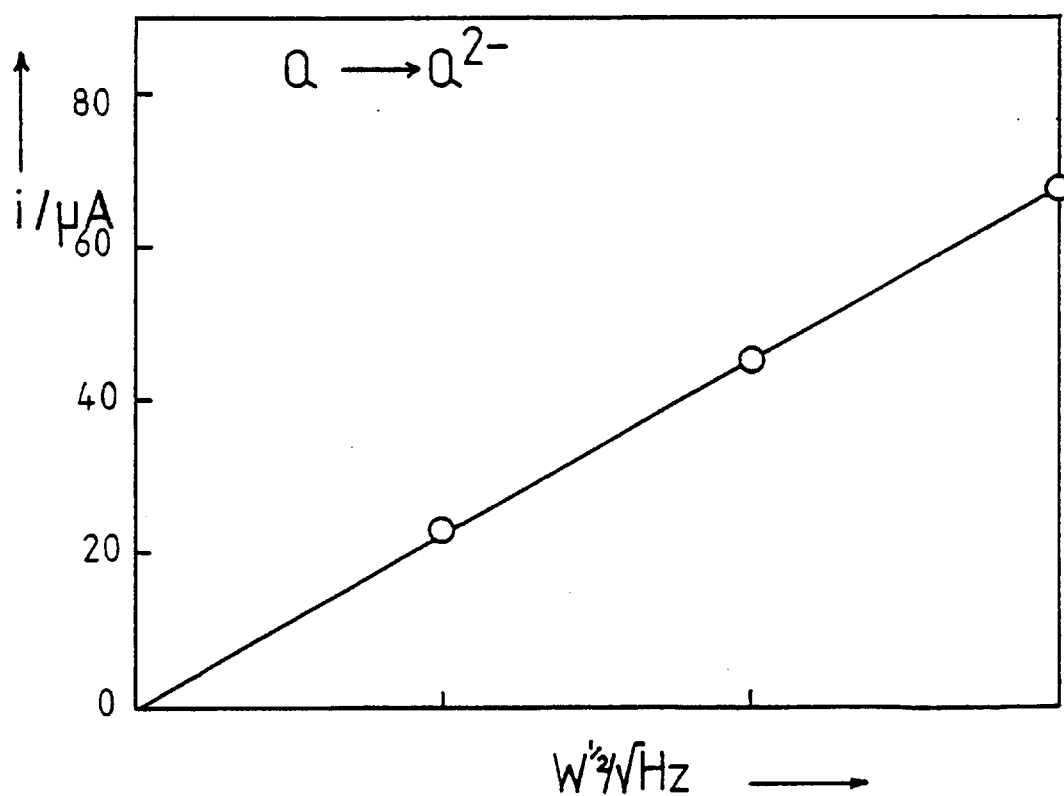
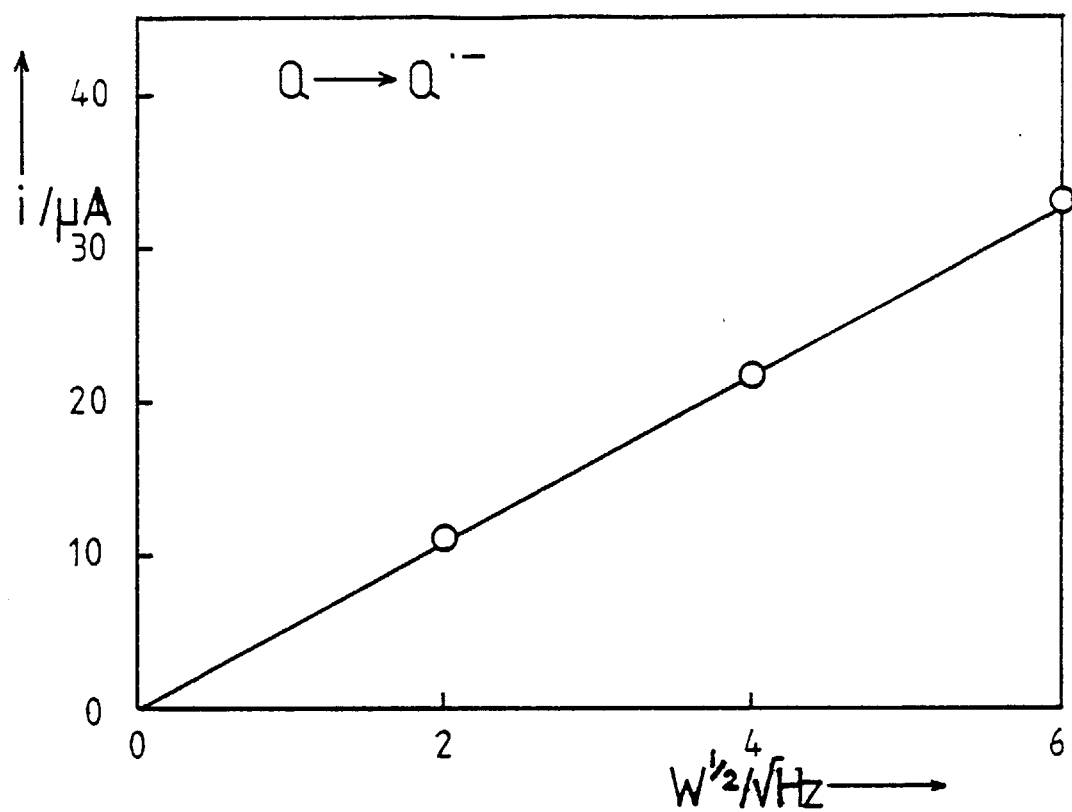


FIGURE 4.39. Levich plots obtained from Figure 4.38.

is more difficult to determine, but it can be approximately placed midway between the two electron oxygen reduction wave and the peroxide oxidation wave, and therefore $E^0 \sim -1.1$ V. Therefore reduction of oxygen by the reduced quinone to the two electron product is thermodynamically favoured.

Titration Curves

The titration curve for the reaction between oxygen and reduced quinone is shown in Figure 4.40. Both reduced forms of quinone titrated the oxygen. Plots of i_D vs. i_D/M were linear, and M was proportional to $W^{1/2}$. A plot of N_k' vs. W is shown in Figure 4.41. The slope becomes linear as $W \rightarrow 0$, and from this limiting slope a value of $k_2 = 8.75 \cdot 10^4 \text{ M}^{-1} \text{ s}^{-1}$ was obtained. This value is only just measurable using the titration curve technique, and explains why the plot of N_k' vs. W only became linear at low rotation speeds.

Oxygen-Quinone Polarograms

Polarograms of various oxygen-quinone solutions were run in order to test whether the quinone reduced oxygen to superoxide only, or to peroxide. The results are shown in Figure 4.42. The first quinone wave is higher than the second by an amount corresponding to a one electron reduction of oxygen. Unfortunately, although the reduction of oxygen to peroxide is favoured thermodynamically, the rate of this reaction is clearly slow on the rotating disc timescale since the second oxygen

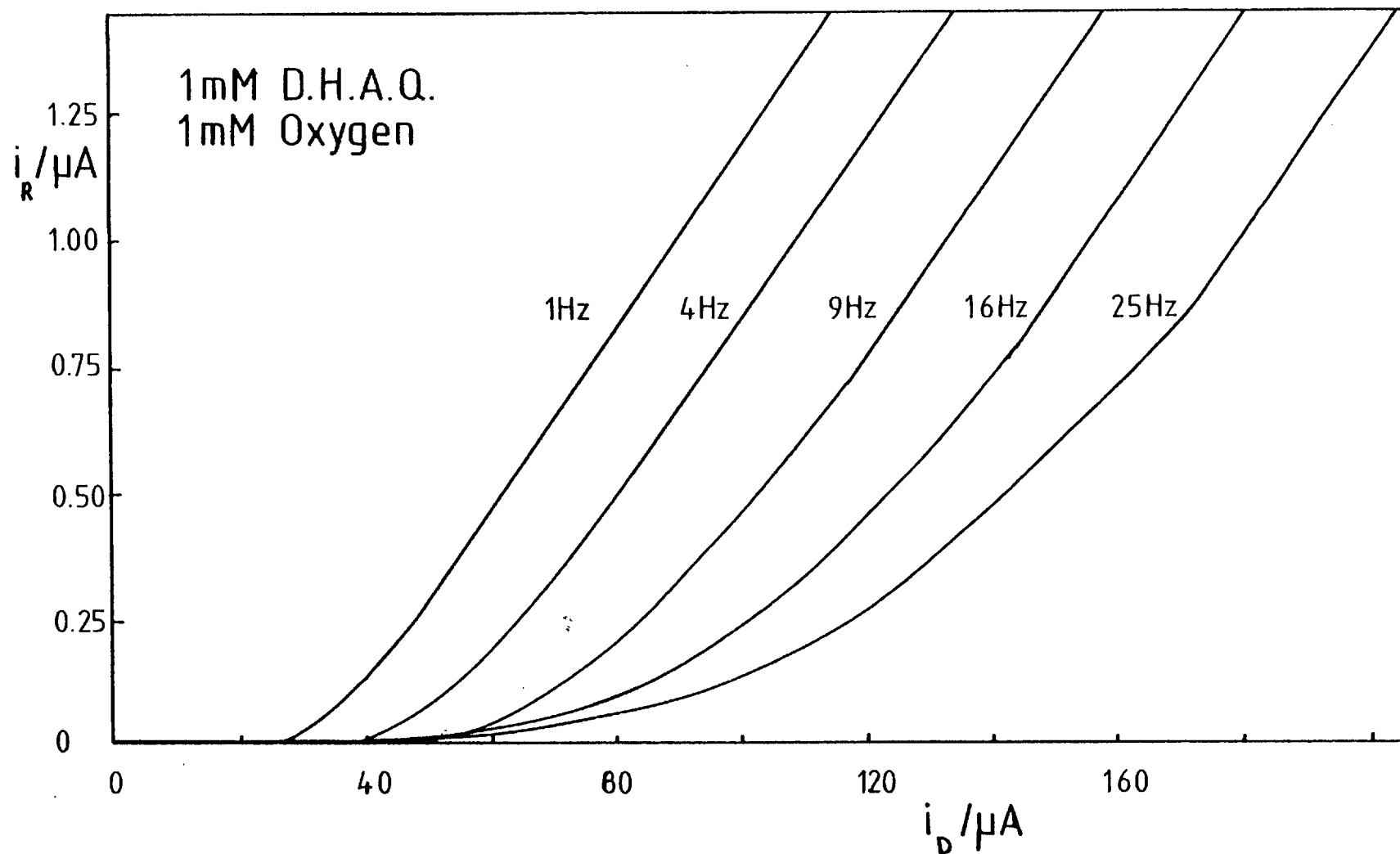


FIGURE 4.40. Titration curves for the reaction between the reduced form of 1,8 DHAQ and oxygen in DMSO.

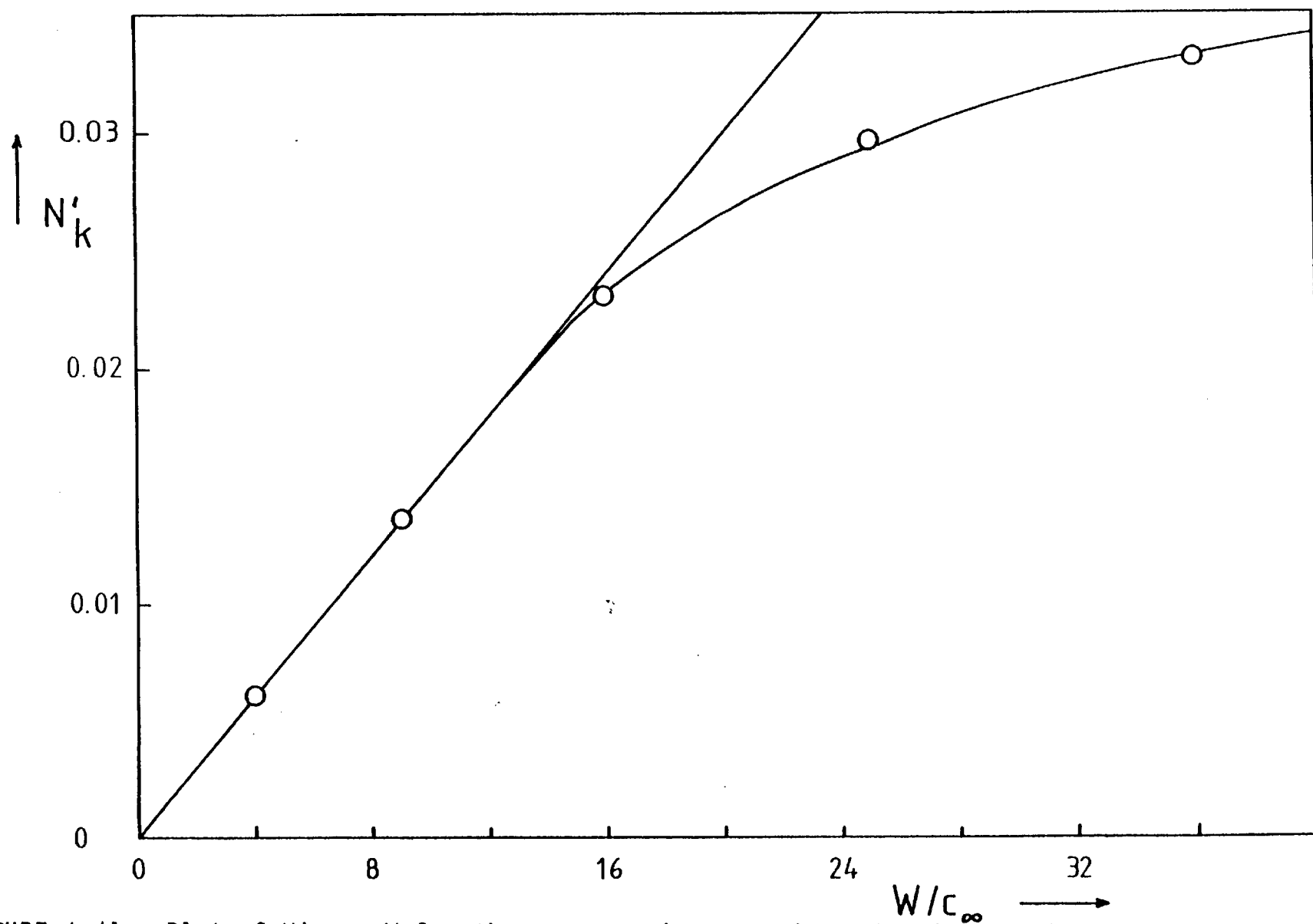


FIGURE 4.41. Plot of N'_k vs. W for the reaction between the reduced form of 1,8 DHAQ and oxygen in DMSO. Note the deviation from linearity at high rotation speeds.

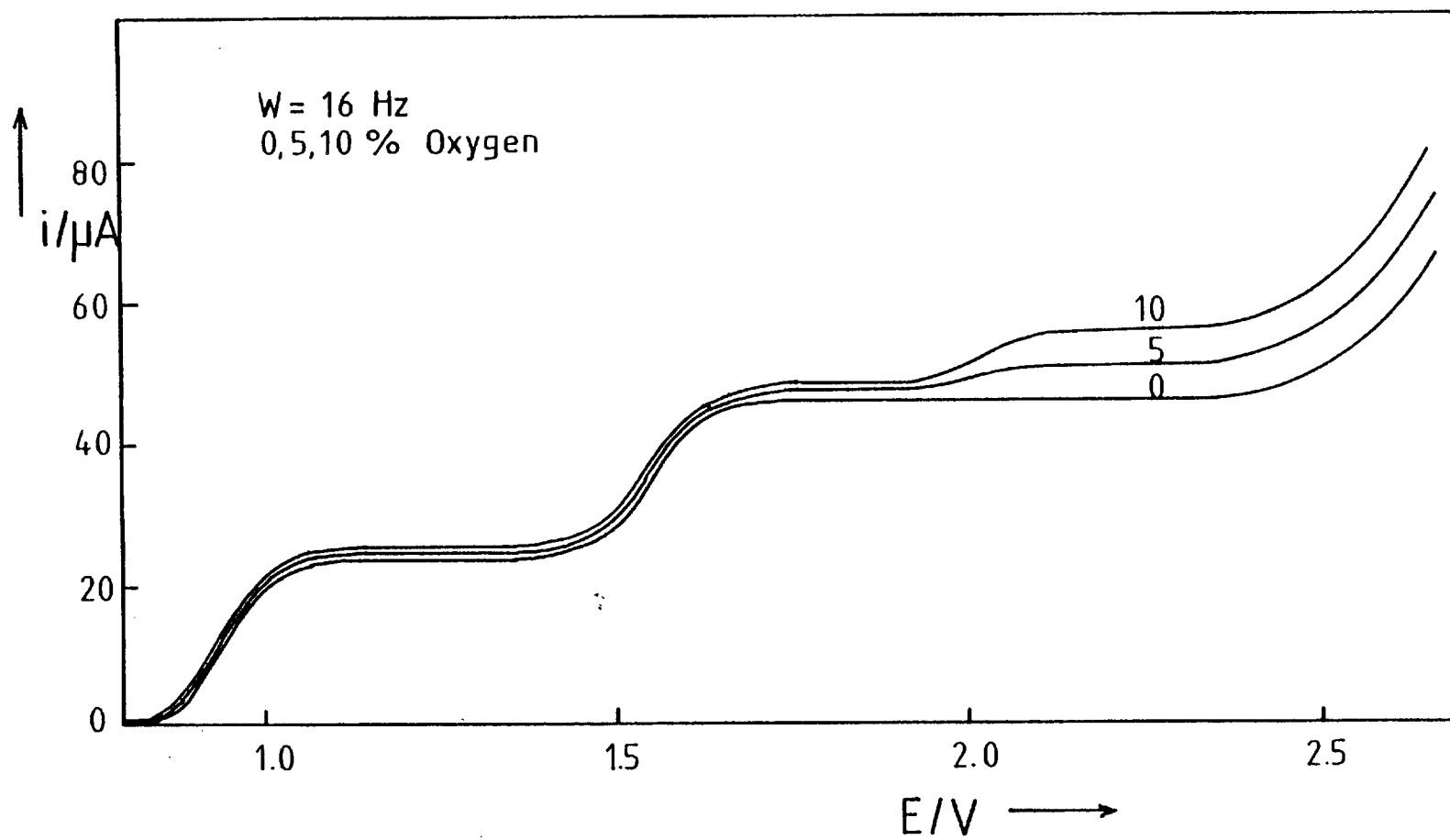


FIGURE 4.42. The reduction of 1,8 DHAQ in the presence of various oxygen concentrations.

reduction wave is seen at more negative potentials than the quinone reduction. The height of the second oxygen reduction wave was constant down to very low rotation speeds of less than 1 Hz. This indicated the reaction would not be sufficiently fast to give the required selectivity between CO_2 and oxygen.

CHAPTER 5
THE DEVELOPMENT OF MEMBRANE ELECTRODES FOR
CARBON DIOXIDE AND OXYGEN DETERMINATION

This chapter presents results obtained with membrane electrodes developed for the amperometric detection of CO_2 and oxygen. The electrodes were developed as a consequence of the work described in the previous chapter, and are detailed in Section 3.2a.

In the first section of this chapter experiments using simple Clark type membrane electrodes with an internal solution of DMSO are described. A theory which proves the mechanism of CO_2 reduction discussed in the previous chapter is presented and experimentally verified.

The second section discusses a new type of electrode which permits joint determination of CO_2 and O_2 even when there is a large difference in their partial pressures. The electrode uses a metallised membrane as an "electrochemical gas filter", which separates the oxygen and CO_2 components of a gas mixture.

In medical applications the CO_2 and oxygen partial pressures are often of comparable magnitude, and the use of single membrane electrodes for breath analysis and transcutaneous blood gas analysis is described in Section 3.

5.1. REDUCTION OF CO₂ IN A CLARK TYPE MEMBRANE ELECTRODE

The rotating disc work of Chapter Four indicates that membrane electrodes with a working electrode of gold, mercury or silver, a suitable membrane, and an internal solution of DMSO are suitable for carbon dioxide determination.

Membrane Material

The permeability of various membranes to oxygen and carbon dioxide is shown in Figure 5.1.⁽¹²⁸⁾ Silicone rubber is by far the most permeable material, however it dissolves in DMSO. Natural rubber is also attacked by DMSO. In general $P_{\text{CO}_2}/P_{\text{O}_2} \sim 4$ or 5 for most membranes. The membrane used in the work described in this chapter was Teflon. Teflon has a reasonably high CO₂ permeability, and also has a low water permeability, which means the electrodes described in Section Two are able to function efficiently.

CO₂ Reduction Polarograms

Membrane electrode polarograms of CO₂ reduction on cathodes of gold, mercury and silver are shown in Figures 5.1 to 5.3. The gold polarogram was obtained after the platinum working electrode of electrode 5 was gold-plated. The mercury electrode was made by amalgamating the gold-plated electrode with mercury. The polarogram on silver (Figure 5.3) used the inner section of electrode 1, without the metallised membrane and screw cap assembly. 12 μm Teflon was used as the membrane.

Table 5.1. Polymer Permeabilities to Carbon Dioxide and Oxygen

Polymer	$P_{CO_2}^a$ (Barrers)	$P_{O_2}^a$ (Barrers)
Silicone Rubber	2700	500
Natural Rubber	131	24
Polyethylene $\rho = 0.914$	12.6	2.9
Polyethylene $\rho = 0.964$	1.7	0.39
FEP copolymer	<u>ca</u> 24	5.9
Teflon 75% crystalline	2.6	-
Chlorosulphonated Polyethylene	15.8	2.1
Nylon 66	0.17	0.034

(a) A Barrer is the c.g.s. unit of permeability which expresses the volume of gas at S.T.P. that permeates a 1 cm thickness of membrane per square centimetre per second with a pressure drop of 1 cm Hg across the membrane.

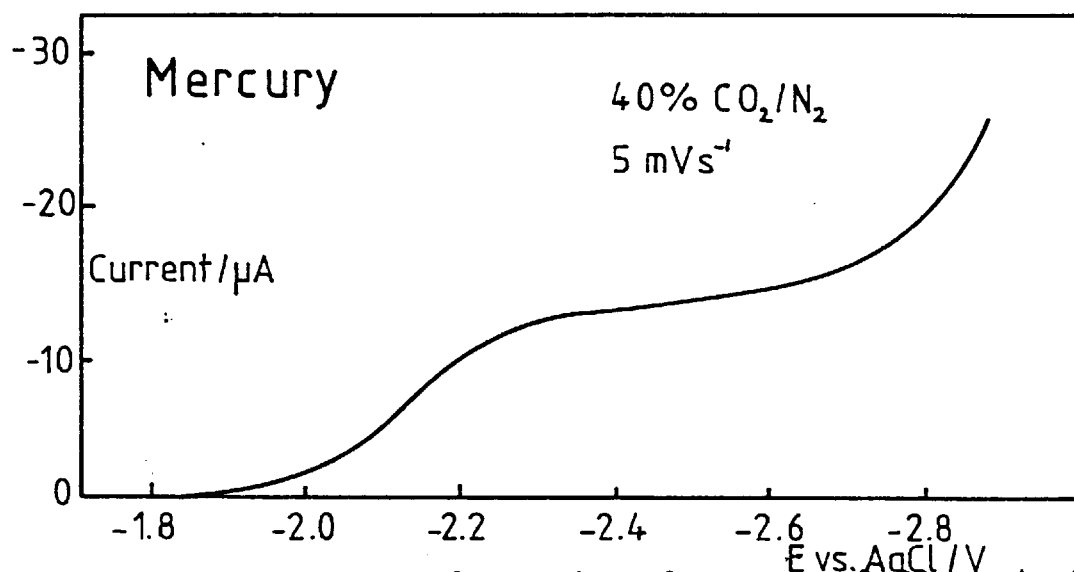
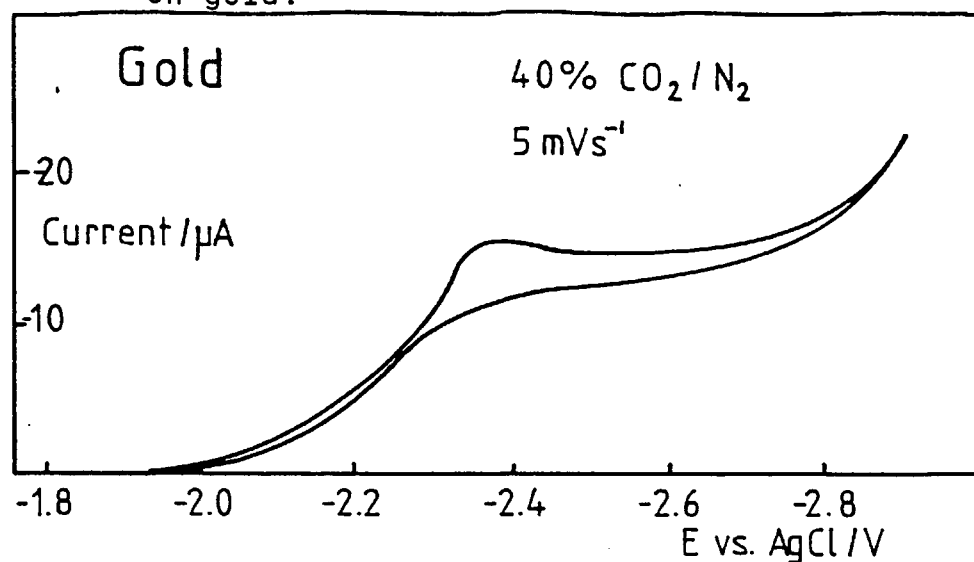


FIGURE 5.2. Membrane electrode polarogram of CO_2 reduction on mercury.

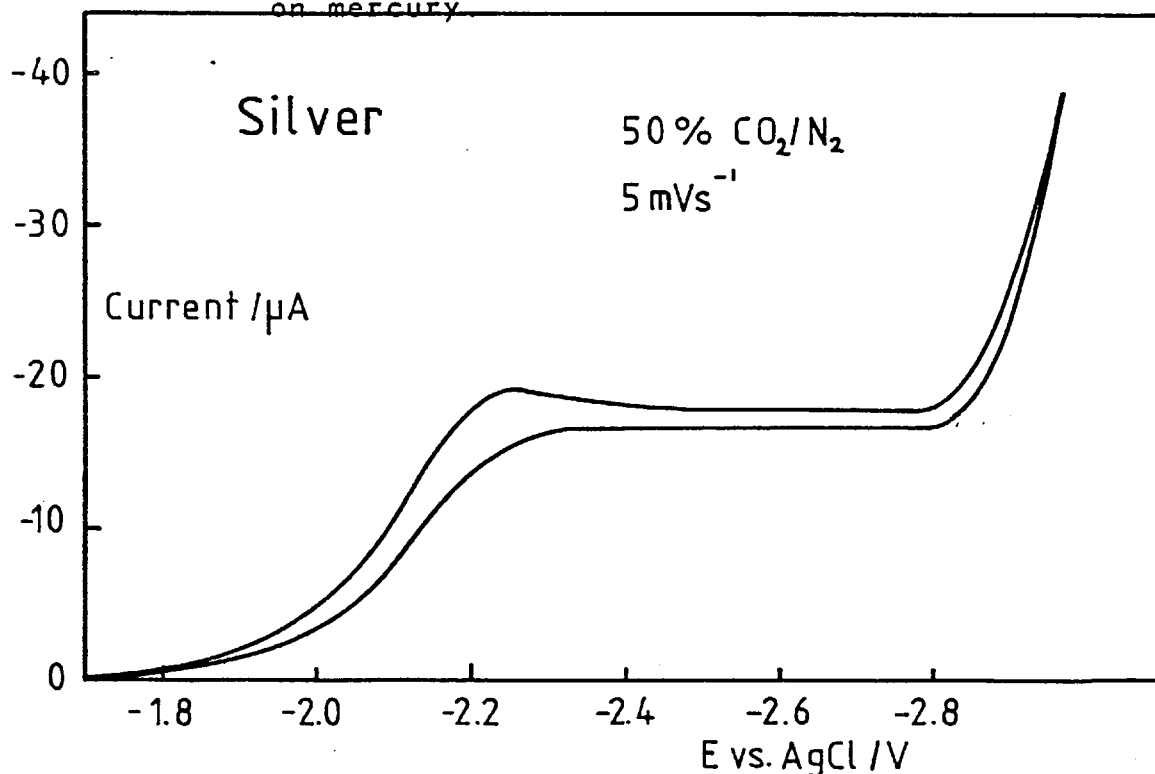


FIGURE 5.3. Membrane electrode polarogram of CO_2 reduction on silver.

In all cases the diffusion limited current allowed quantitative determination of CO_2 partial pressures, but the residual current at a nitrogen partial pressure of one atmosphere was much lower on a silver working electrode than on gold or mercury. The residual current on all the electrodes varied with solvent purity. Figures 5.4 and 5.5 are plots of limiting current vs. the partial pressure of CO_2 in nitrogen, on silver and mercury electrodes obtained after the DMSO and supporting electrolyte had been purified. On a silver electrode partial pressures of CO_2 as low as 10^{-3} atmospheres should be able to be determined.

The current stability of the electrode was high when the electrode was detecting partial pressures of CO_2 below 0.5 atmospheres, and an electrode output consistent to ca 15% was obtained for several days, even when the membrane surface was immersed in DDW[†] throughout. This shows that Teflon is impermeable to water.

The electrode was less stable at CO_2 levels above 0.5 atmospheres, when the output signal often became noisy. As the signal became noisy gas bubbles formed on the working electrode surface. The bubbles were probably carbon monoxide, which is formed as a by-product of CO_2 reduction (see Figure 1.7). At high CO_2 levels the solubility of CO is exceeded before it can diffuse back across the membrane, and so bubbles form.

† Doubly distilled water

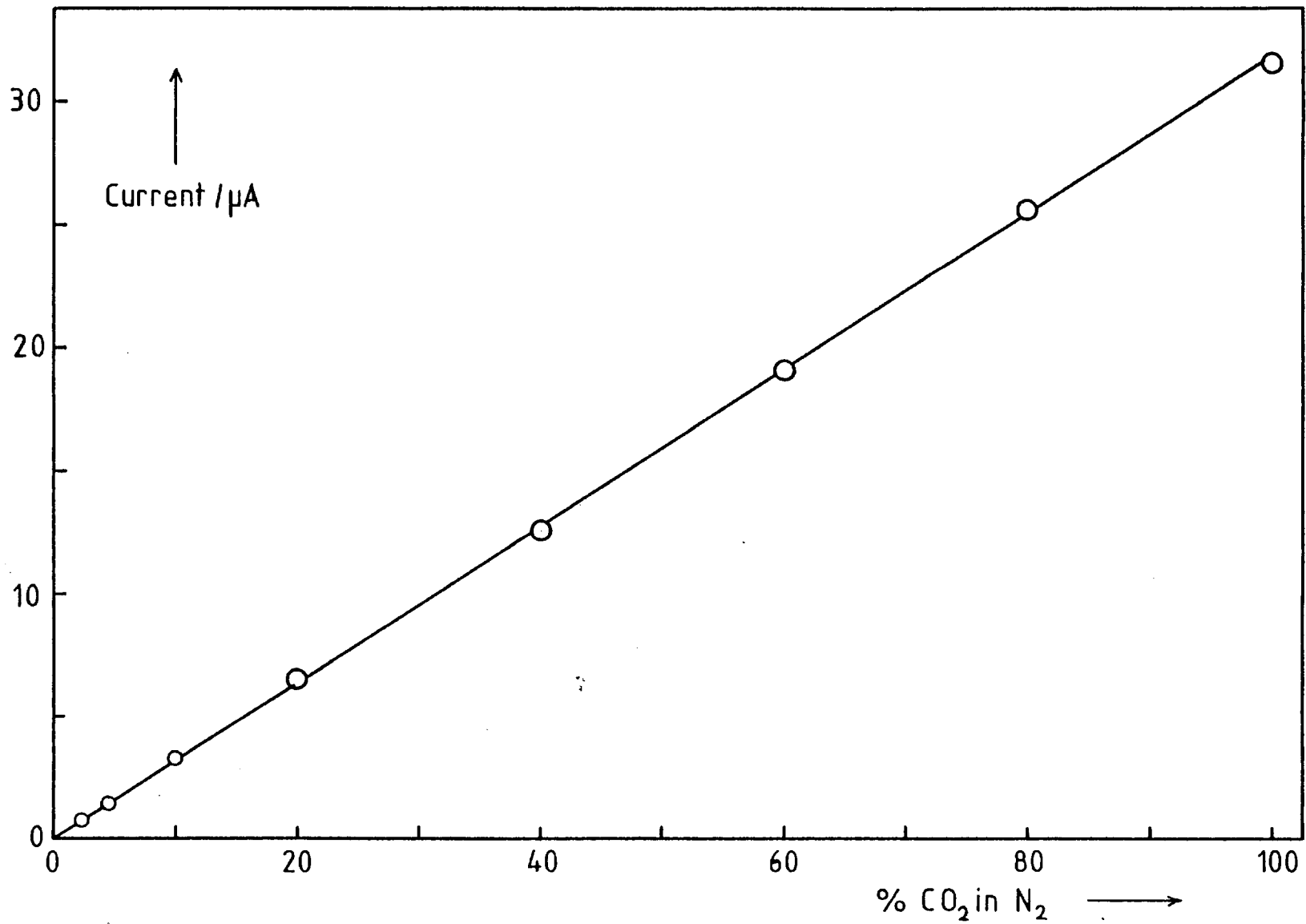


FIGURE 5.4a. Graph of limiting current vs. $p\text{CO}_2$ obtained with the silver cathode of electrode 1.

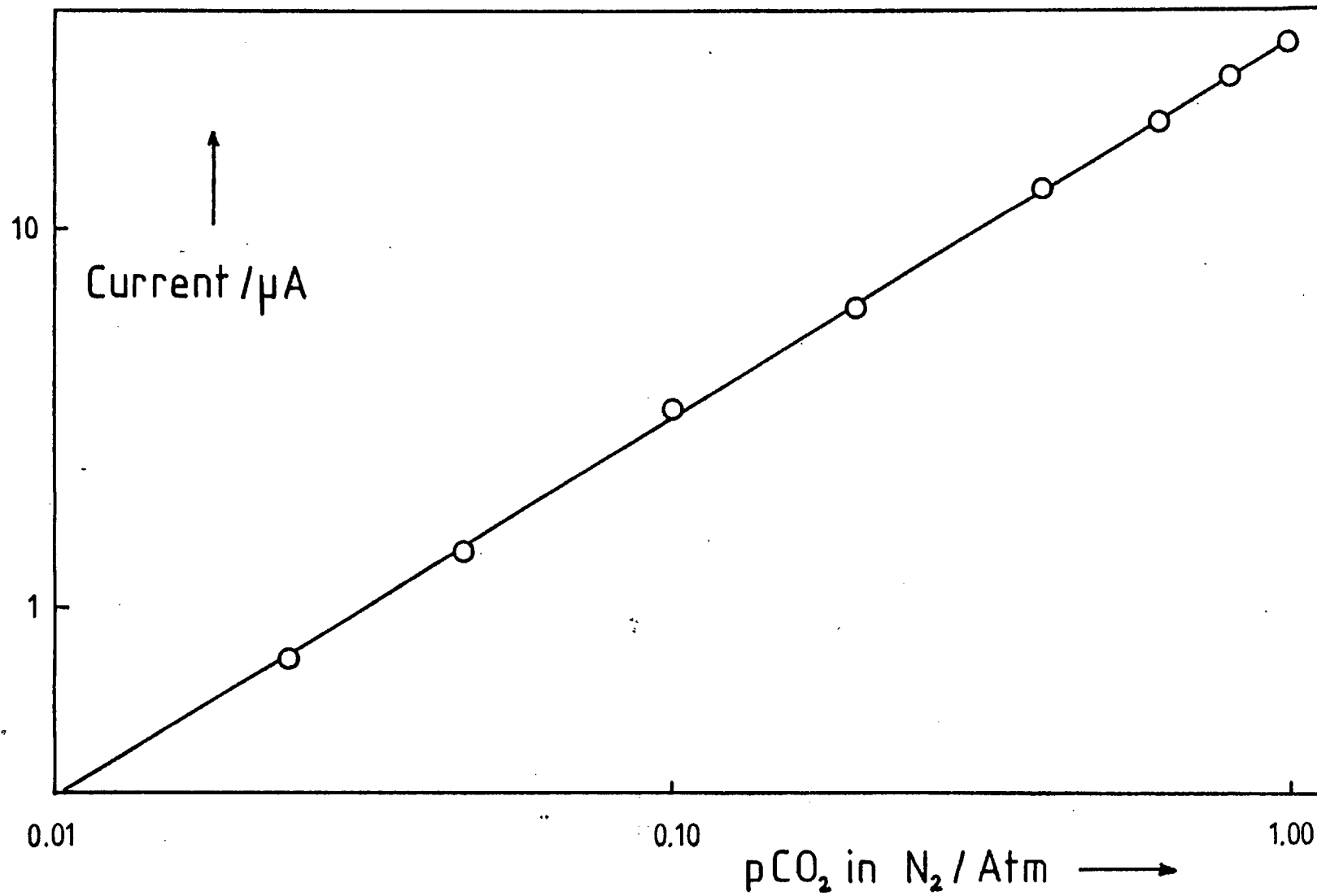


FIGURE 5.4b. Log-log plot of Figure 5.4a.

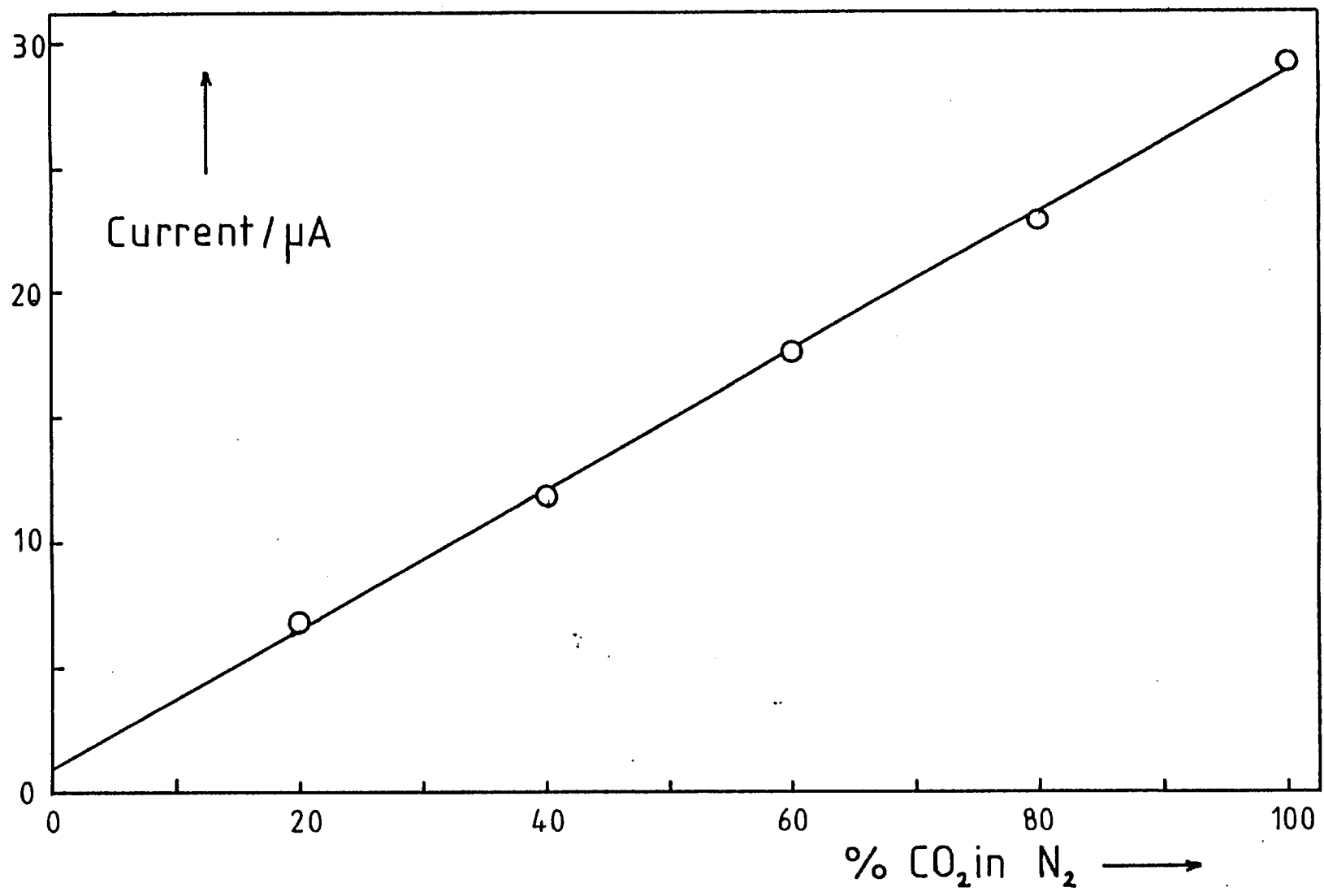


FIGURE 5.5. Graph of limiting current vs. pCO₂ obtained with the mercury coated cathode of electrode 5.

The Permeability of Teflon to CO₂

The current on the silver electrode with the membrane in 1 atmosphere of CO₂ was:-

$$i_{Ag} = 32 \mu A = 4.07 \text{ mA cm}^{-2}$$

Therefore the flux of CO₂ per cm thickness of membrane is:- $j_{CO_2} = 3.75 \cdot 10^{-11} \text{ mol.cm}^{-2} \text{ s}^{-1}$

Where j is the CO₂ flux (assuming the number of electrons in the reduction is ~ 1.4). Therefore, assuming the gas is ideal:-

$$P_m = 11 \text{ Barrers.}$$

Where a Barrer is defined in Table 5.1. Also, from equation 2.43:-

$$i = nFAc_s P_m/b \quad 2.43$$

$$c_{s_{100\%CO_2}} \approx 40 \text{ mM}$$

$$\text{Therefore } P_m = 8.7 \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1}.$$

Diffusion Coefficient of CO₂ in Teflon

The response of the electrode to a CO₂ concentration step is shown in Figure 5.6. The initial current rise is fast, but at longer times the transient has a long

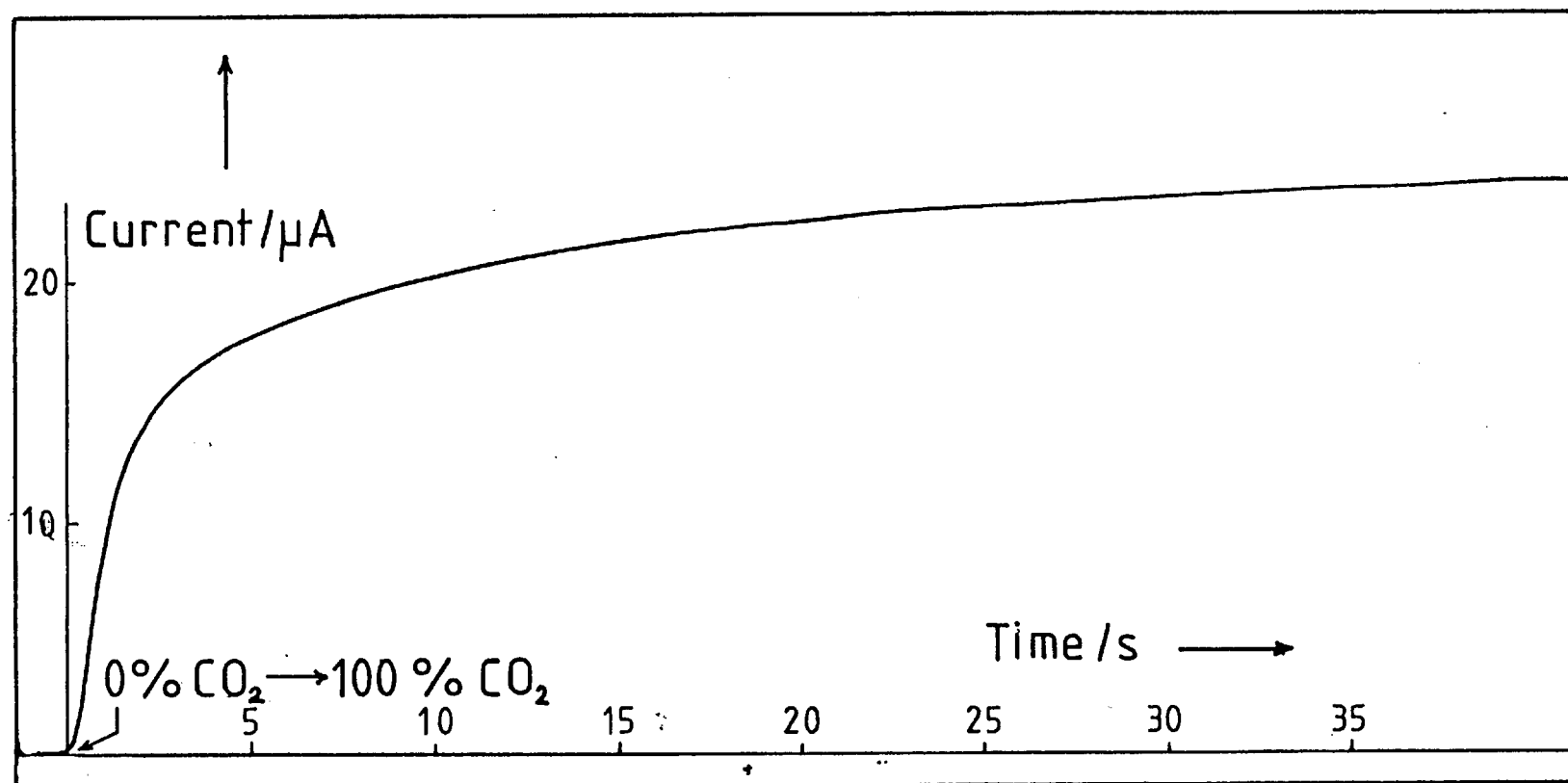


FIGURE 5.6. Response of electrode 1 to a CO₂ concentration step.

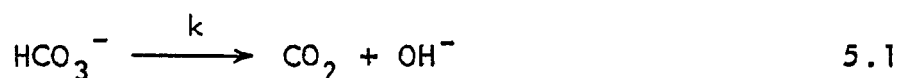
tail. Equation 2.64 predicts a plot of τ_A vs. t has a slope of D_m/b^2 , and this is shown in Figure 5.7. The slope of the straight line observed at values of t less than one second is 0.086.

Therefore:- $D_m = 1.24 \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1}$.

The graph shows a marked deviation from linearity at values of t greater than one second. This is explained by the theory later in this section.

Effect of the $\text{CO}_2/\text{HCO}_3^-$ Equilibrium on the Membrane Electrode Current Theory

The mechanism of carbon dioxide reduction presented in Chapter 4 postulated the formation of half a mole of bicarbonate and half a mole of formate per mole of reduced CO_2 . Bicarbonate can reform CO_2 by the reaction:-



where k is the first order rate constant

Consequently the steady state CO_2 reduction current will be higher than when no CO_2 is regenerated. The following model predicts the time dependence of the current when the electrode is switched on to the transport limited current potential. The model is illustrated in Figure 5.8.

The electrolyte and membrane phases are characterised by thicknesses ℓ and ℓ' , and diffusion coefficients D and D' respectively. The Nernst diffusion coefficient,

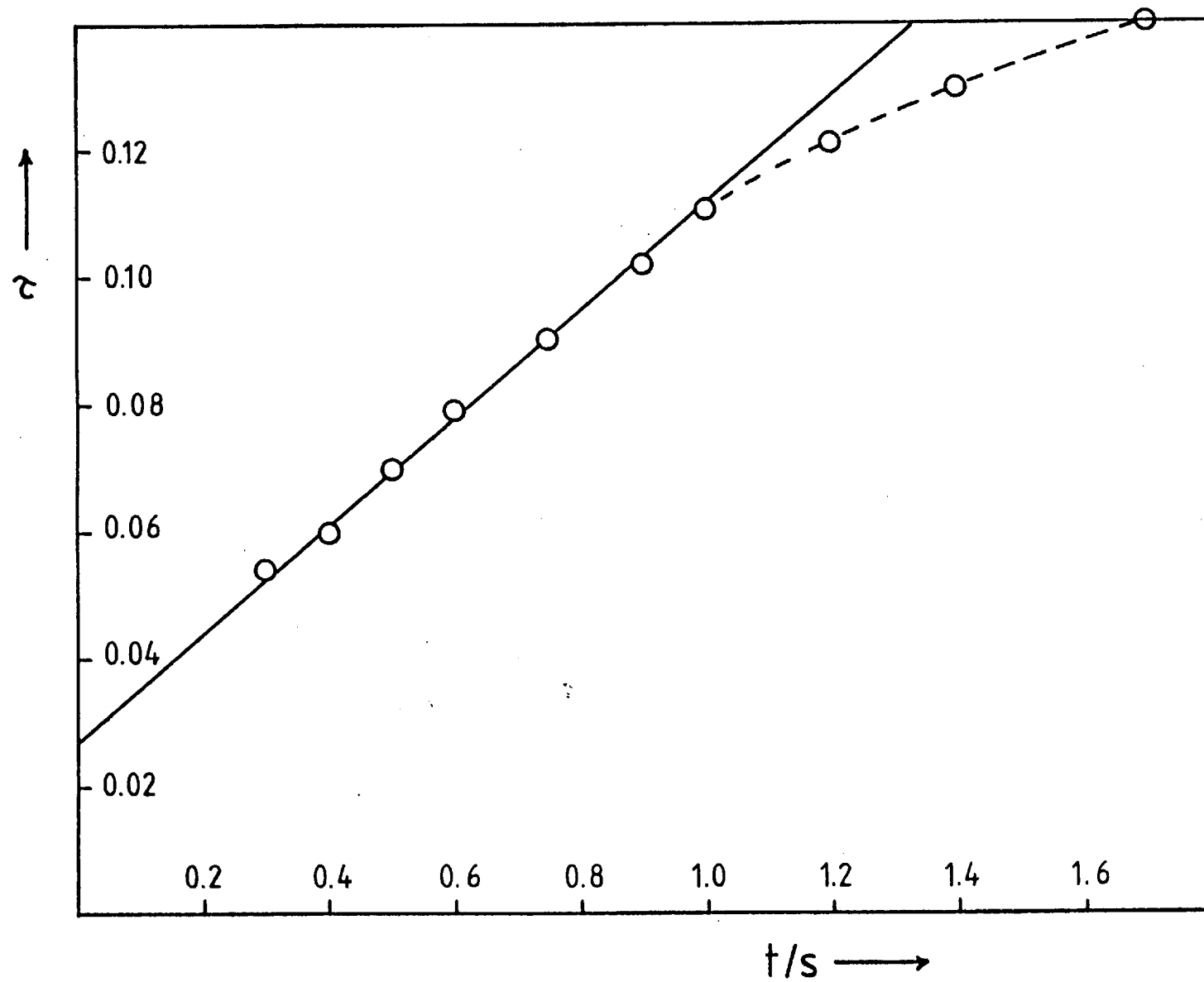


FIGURE 5. 7. Graph of τ vs. t .

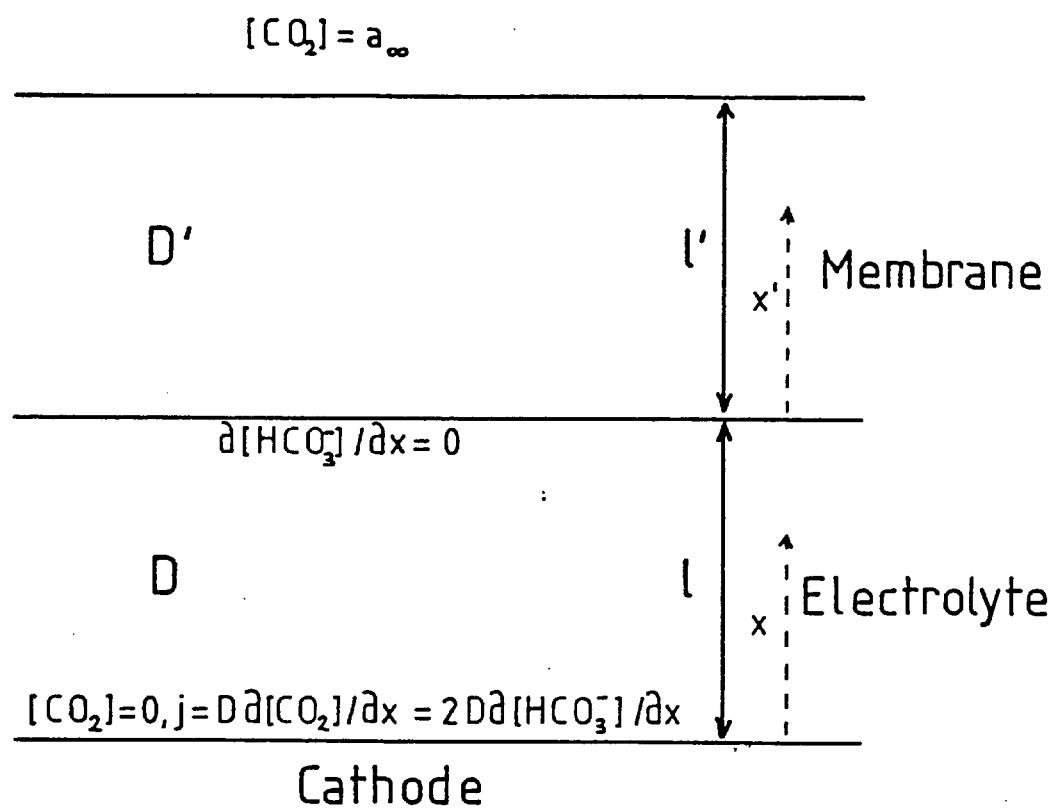


FIGURE 5.8. CO₂ regeneration model.

defined in equations 2.57 and 2.58 is assumed to be equal at the membrane/electrolyte and membrane/sample interfaces. The outside solution is assumed to be well stirred, so c_s is constant. Writing a as the concentration of CO_2 , and b as the concentration of bicarbonate, the following equations apply:-

Within the Electrolyte

$$\frac{\partial a}{\partial t} = D \left(\frac{\partial^2 a}{\partial x^2} \right) + kb \quad 5.2$$

$$\frac{\partial b}{\partial t} = D \left(\frac{\partial^2 b}{\partial x^2} \right) - kb \quad 5.3$$

The following boundary conditions apply:-

At time $t = 0$ (before electrode switch on):-

$$a = a_\infty$$

$$b = 0$$

After switch on:-

$$\text{At } x = 0, \quad a = 0, \quad j_o = D \left(\frac{\partial a}{\partial x} \right)_o = -2D \left(\frac{\partial b}{\partial x} \right)_o$$

Where j_x is the CO_2 flux at x .

$$\text{At } x = \ell, \quad a = a_\ell, \quad j_\ell = D \left(\frac{\partial a}{\partial x} \right)_\ell$$

Also $\left(\frac{\partial b}{\partial x}\right)_l = 0$ (The bicarbonate does not penetrate the membrane)

Within the Membrane

$$\frac{\partial a}{\partial t} = D \left(\frac{\partial^2 a}{\partial x'^2} \right) \quad 5.4$$

With boundary conditions:-

$$\text{At } x' = 0, a = Ka_l, j_o = D' \left(\frac{\partial a}{\partial x'} \right)_o$$

$$\text{At } x' = l', a = Ka_\infty$$

To simplify the diffusion equations the following normalised variables are defined:-

$$\chi = x/l \quad 5.5$$

$$u = \frac{a_\infty - a}{a_\infty} \quad 5.6$$

$$\chi' = x'/l' \quad 5.7$$

$$u' = \frac{Ka_\infty - a}{Ka_\infty} \quad 5.8$$

$$\kappa = kl^2/D \quad 5.9$$

$$v = b/a_\infty \quad 5.10$$

$$\gamma = jl/Da_\infty \quad 5.11$$

$$\tau = tD/\ell^2 \quad 5.12$$

$$\alpha = D/D', \left(\frac{\ell'}{\ell}\right)^2 \quad 5.13$$

α describes the relative transient response of the solution and electrolyte layers.

Equations 5.2 and 5.3 (electrolyte equations) become:-

$$(\partial u / \partial \tau) = (\partial^2 u / \partial \chi^2) - \kappa v \quad 5.14$$

$$(\partial v / \partial \tau) = (\partial^2 v / \partial \chi^2) - \kappa v \quad 5.15$$

With the boundary conditions:-

$$\text{At } \tau = 0, u = 0, v = 0$$

$$\text{At } \chi = 0, \gamma_0 = - \left(\frac{\partial u}{\partial \chi} \right)_0 = -2 \left(\frac{\partial v}{\partial \chi} \right)_0$$

$$\text{and } u = 1$$

$$\text{At } \chi = 1, u = u_1, \gamma_1 = - \left(\frac{\partial u}{\partial \chi} \right)_1$$

$$\text{and } \left(\frac{\partial v}{\partial \chi} \right)_1 = 0$$

Equation 5.4 becomes:-

$$\alpha (\partial u' / \partial \tau) = (\partial^2 u' / \partial \chi'^2) \quad 5.16$$

With boundary conditions:-

$$\text{At } \chi' = 1, u' = 0$$

$$\text{At } \chi' = 0, u' = u_o', j_1 = \frac{\gamma Da_\infty}{\ell} = \frac{-D'Ka_\infty}{\ell'} \left(\frac{\partial u'}{\partial \chi'} \right)_o$$

(This equation equates the fluxes through the membrane and electrolyte).

$$\text{Therefore } \left(\frac{\partial u'}{\partial \chi'} \right)_o = \frac{-D\ell'}{D'K\ell} \gamma_1 = -\beta \gamma_1$$

$$\text{Where } \beta = \frac{D\ell'}{D'K\ell} \quad 5.17$$

β compares the diffusion barriers of the membrane and electrolyte layers in the steady state. $\beta < 1$ if the main barrier is electrolyte, and $\beta > 1$ if the main barrier is membrane. Also, $a = Ka_\ell = Ka_\infty(1-u_1) = Ka_\infty(1-u_o')$

$$\text{Hence } u_1 = u_o'$$

$$\text{And at } \tau = 0, u' = 0$$

Applying the Laplace transform to equations 5.14 and 5.15 gives:-

$$s\bar{u} = (\partial^2 \bar{u} / \partial \chi'^2) - \kappa \bar{v} \quad 5.18$$

$$s\bar{v} = (\partial^2 \bar{v} / \partial \chi'^2) - \kappa \bar{v} \quad 5.19$$

Subtraction gives:-

$$s(\bar{u} - \bar{v}) = (\partial^2(\bar{u} - \bar{v})/\partial \chi^2) \quad 5.20$$

With boundary conditions:-

$$\text{At } \chi = 0, \quad (\partial \bar{v}/\partial \chi)_0 = -1/2 \gamma_0 \quad 5.21$$

$$(\partial(\bar{u} - \bar{v})/\partial \chi)_0 = 1/2 \gamma_0 \quad 5.22$$

$$\bar{u} = 1/s \quad 5.23$$

$$\text{At } \chi = 1, \quad \bar{u} = \bar{u}_1 \quad 5.24$$

$$\gamma_1 = -(\partial \bar{u}/\partial \chi)_1 \quad 5.25$$

$$(\partial \bar{v}/\partial \chi)_1 = 0 \quad 5.26$$

The Laplace transform of equation 5.16 is:-

$$\alpha s \bar{u}' = (\partial^2 \bar{u}'/\partial \chi'^2) \quad 5.27$$

With boundary conditions:-

$$\text{At } \chi' = 1; \quad \bar{u}' = 0 \quad 5.28$$

$$\text{At } \chi' = 0; \quad \bar{u}_1 = \bar{u}_0' \quad 5.29$$

$$\text{and } \left(\frac{\partial \bar{u}'}{\partial \chi'} \right)_0 = -\beta \bar{\gamma}_1 \quad 5.30$$

The general solutions of equations 5.19, 5.20 and 5.27 are:-

$$\bar{v} = \bar{v}_0 \cosh(\sqrt{s+k} \chi) - \frac{1/2 \bar{\gamma}_0}{\sqrt{s+k}} \sinh(\sqrt{s+k} \chi) \quad 5.31$$

$$\begin{aligned} \bar{u} - \bar{v} = & (1/s - \bar{v}_0) \cosh(\sqrt{s} \chi) \\ & - 1/2 \frac{\bar{\gamma}_0}{\sqrt{s}} \sinh(\sqrt{s} \chi) \end{aligned} \quad 5.32$$

$$\bar{u}' = \bar{u}_1 \cosh(\sqrt{\alpha s} \chi') - \frac{\beta \bar{\gamma}_1}{\sqrt{\alpha s}} \sinh(\sqrt{\alpha s} \chi') \quad 5.33$$

Differentiation of equation 5.31, then applying boundary condition 5.26 gives:-

$$\bar{v}_0 = \frac{1/2 \bar{\gamma}_0}{\sqrt{s+k}} \coth(\sqrt{s+k}) \quad 5.34$$

So equation 5.31 becomes:-

$$\bar{v} = \frac{1/2 \bar{\gamma}_0}{\sqrt{s+k}} \left[\frac{\cosh(\sqrt{s+k} \chi)}{\tanh(\sqrt{s+k})} - \sinh(\sqrt{s+k} \chi) \right] \quad 5.35$$

At $\chi = 1$, 5.35 becomes:-

$$\bar{v}_1 = \frac{1/2 \bar{\gamma}_0}{\sqrt{s+k} \sinh(\sqrt{s+k})} \quad 5.36$$

From equations 5.32, 5.34 and 5.36:-

$$\begin{aligned} \text{At } \chi = 1, \bar{u}_1 = & \frac{1/2 \bar{\gamma}_0}{\sqrt{s+\kappa} \sinh(\sqrt{s+\kappa})} [1 - \cosh(\sqrt{s+\kappa}) \cosh \sqrt{s}] \\ & + \frac{\cosh \sqrt{s}}{s} - 1/2 \bar{\gamma}_0 \frac{\sinh \sqrt{s}}{\sqrt{s}} \end{aligned} \quad 5.37$$

Differentiation of equation 5.32, with equation 5.34 and boundary conditions 5.25 and 5.26 gives:-

$$\begin{aligned} (\partial u / \partial \chi)_{\chi=1} = -\bar{\gamma}_1 = & \frac{\sinh \sqrt{s}}{\sqrt{s}} - 1/2 \bar{\gamma}_0 \cosh \sqrt{s} \\ & - \frac{1/2 \bar{\gamma}_0 \sqrt{s} \sinh \sqrt{s}}{\sqrt{s+\kappa} \tanh(\sqrt{s+\kappa})} \end{aligned} \quad 5.38$$

The membrane equation 5.33, and boundary condition 5.28 gives:-

$$\chi' = 1, \bar{u}_1 = \beta \bar{\gamma}_1 \frac{\tanh \sqrt{\alpha s}}{\sqrt{\alpha s}} \quad 5.39$$

At this point there are three equations (5.37, 5.38 and 5.39) and three unknowns (β , $\bar{\gamma}_1$ and $\bar{\gamma}_0$). To solve for $\bar{\gamma}_0$ (the normalised flux at the electrode surface), we write:-

$$\begin{aligned} & \frac{\cosh \sqrt{s}}{s} - 1/2 \bar{\gamma}_0 \frac{\sinh \sqrt{s}}{\sqrt{s}} - \frac{1/2 \bar{\gamma}_0}{\sqrt{s+\kappa} \sinh(\sqrt{s+\kappa})} [\cosh(\sqrt{s+\kappa}) \cosh \sqrt{s} - 1] \\ = \bar{u}_1 = & \frac{\beta \tanh \sqrt{\alpha s}}{\sqrt{\alpha s}} \left[1/2 \bar{\gamma}_0 \cosh \sqrt{s} + \frac{1/2 \bar{\gamma}_0 \sqrt{s} \sinh \sqrt{s}}{\sqrt{s+\kappa} \tanh(\sqrt{s+\kappa})} \right. \\ & \left. - \frac{\sinh \sqrt{s}}{\sqrt{s}} \right] \end{aligned} \quad 5.40$$

Therefore:-

$$\begin{aligned}
 I_{1/2} \bar{Y}_0 &= \frac{\cosh \sqrt{s}}{s} + \frac{\sinh \sqrt{s}}{\sqrt{s}} \frac{\beta \tanh \sqrt{\alpha s}}{\sqrt{\alpha s}} \\
 &= \frac{\frac{\sinh \sqrt{s}}{\sqrt{s}} + \frac{\cosh(\sqrt{s+\kappa}) \cosh \sqrt{s} - 1}{\sqrt{s+\kappa} \sinh(\sqrt{s+\kappa})} + \frac{\beta \tanh \sqrt{\alpha s}}{\sqrt{\alpha s}} [\cosh \sqrt{s} \\
 &\quad + \frac{\sqrt{s} \sinh \sqrt{s}}{\sqrt{s+\kappa} \tanh(\sqrt{s+\kappa})}]
 \end{aligned}$$

5.41

Assuming $\kappa \approx 0$, equation 5.41 becomes:-

$$\begin{aligned}
 I_{1/2} \bar{Y}_0 &\approx \frac{\cosh \sqrt{s}}{s} + \frac{\sinh \sqrt{s}}{\sqrt{s}} \frac{\beta \tanh \sqrt{\alpha s}}{\sqrt{\alpha s}} \\
 &= 2 \left[\frac{\sinh \sqrt{s}}{\sqrt{s}} + \frac{\beta \tanh \sqrt{\alpha s}}{\sqrt{\alpha s}} \cosh \sqrt{s} \right]
 \end{aligned}$$

5.42

Dividing equation 5.42 by $\cosh \sqrt{s}$ gives:-

$$\begin{aligned}
 I_{1/2} \bar{Y}_0 &\approx \frac{1/s [1 + \beta/\sqrt{\alpha} \tanh \sqrt{s} \tanh \sqrt{\alpha s}]}{2 \left[\frac{\tanh \sqrt{s}}{\sqrt{s}} + \frac{\beta \tanh \sqrt{\alpha s}}{\sqrt{\alpha s}} \right]}
 \end{aligned}$$

5.43

When κ is large, $I_{1/2} \bar{Y}_0$ is approximately twice equations 5.42 and 5.43. This is a reasonable result because it shows the recycling process gives double the current.

The approximate solutions to equation 5.43 depend upon the values of s and α . They are shown in Figure 5.9, and are the current equations for the case where no regeneration occurs.

Dividing equation 5.41 by $\cosh s$ gives:-

$$\begin{aligned} \frac{1}{2} \bar{Y}_0 = \frac{1}{s} [1 + \beta / \sqrt{\alpha} \tanh \sqrt{s} \tanh \sqrt{\alpha s}] \\ \frac{\tanh \sqrt{s}}{\sqrt{s}} + \frac{1 - \operatorname{sech} \sqrt{s} \operatorname{sech}(\sqrt{s+\kappa})}{\sqrt{s+\kappa} \tanh(\sqrt{s+\kappa})} + \frac{\beta}{\sqrt{\alpha}} \frac{\tanh \sqrt{\alpha s}}{\sqrt{s}} [1 + \frac{\sqrt{s} \tanh \sqrt{s}}{\sqrt{s+\kappa} \tanh(\sqrt{s+\kappa})}] \end{aligned} \quad 5.44$$

If $\beta / \sqrt{\alpha}$ is made small by using a thin membrane and a thick electrolyte layer then:-

I) When $\kappa > 1$

At short times, i.e. when $s > \kappa > 1$ ($\tau < \kappa^{-1} < 1$)

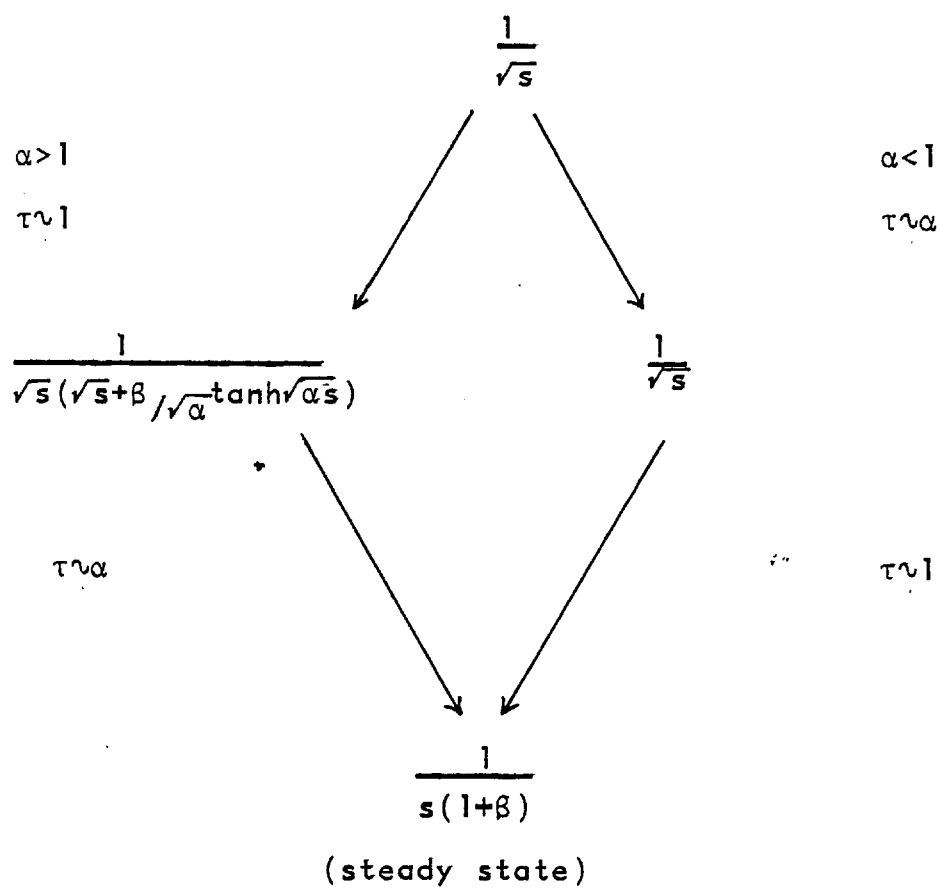
$$\bar{Y}_0 = 1/\sqrt{s} \quad 5.45$$

At longer times, when $\tau \sim \kappa^{-1}$

$$\begin{aligned} \frac{1}{2} \bar{Y}_0 &= \frac{1}{\sqrt{s} + \frac{s}{\sqrt{s+\kappa}}} \\ &= \frac{\sqrt{s+\kappa}}{\sqrt{s^2 + \kappa s} + s} \end{aligned}$$

FIGURE 5.9. The approximate solutions to equation 5.43
for the flux at the electrode surface, $\bar{Y}_0$

Early τ (large s)



$$\begin{aligned}
&= \frac{1}{\sqrt{s}} \left[\frac{\sqrt{s+k}}{\sqrt{s+k} + \sqrt{s}} \right] \\
&= \frac{1}{\sqrt{s}} - \frac{1}{\sqrt{s+k} + \sqrt{s}} \\
&= \frac{1}{\sqrt{s}} - \frac{1}{k} (\sqrt{s+k} - \sqrt{s})
\end{aligned}$$

This transform can be inverted⁽¹²⁹⁾ to give:-

$$\gamma_o = \frac{2}{\sqrt{\pi\tau}} - \frac{1}{k^{1/2}} \cdot \frac{1}{\tau} \exp\left(-\frac{k\tau}{2}\right) I_{1/2}\left(\frac{k\tau}{2}\right) \quad 5.46$$

$I_{1/2}(z)$ is a modified Bessel function of the first kind. Its solution is given in reference⁽¹¹⁴⁾:-

$$I_{1/2}(z) = \frac{\sinh(z)}{z} \times \frac{\sqrt{2 \cdot 2}}{\sqrt{\pi}} \quad 5.47$$

Substitution of equation 5.47 into 5.46, and further manipulation gives:-

$$\begin{aligned}
\gamma_o &= \frac{2}{\sqrt{\pi\tau}} - \frac{1}{\sqrt{\pi\tau}} \left[\frac{1 - \exp(-k\tau)}{k\tau} \right] \\
\therefore \gamma_o &= \frac{1}{\sqrt{\pi\tau}} \left[2 - \left(\frac{1 - \exp(-k\tau)}{k\tau} \right) \right]
\end{aligned}$$

When $k\tau < 1$ equation 5.48 becomes:-

$$\gamma_o = \frac{1}{\sqrt{\pi\tau}} \quad 5.49$$

This is the same solution as that obtained from equation 5.45, and is the case where regeneration is still negligible. When $\kappa\tau > 1$ the solution is:-

$$\gamma_o = 2/\sqrt{\pi\tau} \quad 5.50$$

Equations 5.49 and 5.50 correspond to semi-linear infinite diffusion before and after regeneration of CO_2 from bicarbonate occurs. When $\tau \sim 1$ the steady state applies:-

$$\gamma_o = \frac{2}{(1+\beta)} \quad 5.51$$

Equations 5.45 to 5.51 all apply in the case when $\kappa > 1$. Case II considers the effect of $\kappa \leq 1$.

II) When $\kappa < 1$

We obtain semi-linear infinite diffusion for the initial case of $s > 1 > \kappa$, then when:-

$$\begin{aligned} \tau \gg 1, \quad 1/2 \bar{\gamma}_o &= \frac{1}{s \left[1 + \frac{1 - (1 - \frac{1}{2}s)(1 - \frac{1}{2}s + \kappa)}{s + \kappa} \right]} \\ &= \frac{1}{s \left[1 + \frac{s + \frac{1}{2}\kappa}{s + \kappa} \right]} \end{aligned}$$

$$\begin{aligned}
&= \frac{s+\kappa}{2s [s + 3/4\kappa]} \\
&= \frac{1}{2}s + \frac{1/4\kappa}{2s(s+3/4\kappa)} \\
&= \frac{1}{2}s + \frac{1}{6} \left[\frac{1}{s} - \frac{1}{s+3/4\kappa} \right] \quad 5.52
\end{aligned}$$

Inversion of 5.52 gives:-

$$\gamma_o = 1 + 1/3 - 1/3 \exp(-3/4\kappa\tau) \quad 5.53$$

Equation 5.53 gives the somewhat surprising result that the current increases by $1/3$ when τ is large.

Appendix 1 shows a simpler way of deriving the steady state equations 5.51 and 5.53, while Appendix 2 derives the steady state concentration profiles.

Verification of Theory

The theory predicts that if $\beta/\sqrt{\alpha}$ is made small by using a thin membrane and thick electrolyte layer, then:-

1) For $\kappa > 1$:-

a) The steady state current should correspond to a two electron reduction per molecule of CO_2 .

b) The slope of a plot of current vs. $1/\sqrt{t}$ for larger values of t should be double that for smaller values of t .

β is defined in equation 5.17, and α is defined in equation 5.13. The size of membrane used was $6 \mu\text{m}$, hence if a $50 \mu\text{m}$ spacer is used under the membrane to ensure a thick electrolyte layer under the membrane:-

$$\beta/\sqrt{\alpha} \approx 0.1$$

When no spacer is used $\beta/\sqrt{\alpha} \approx 0.3$.

Figure 5.10a. shows the current transient obtained when electrode 4, with a $50 \mu\text{m}$ thick electrolyte layer, is switched to the CO_2 limiting current potential. The current falls, and then rises to a steady value. A plot of current vs. $1/\sqrt{t}$ for $t < 100$ seconds is shown in Figure 5.10b. Below $t \sim 25$ seconds the slope of the graph is halved. The transition point is predicted by the theory to occur when $\kappa\tau \sim 1$,

$$\text{therefore } k \sim 0.04 \text{ s}^{-1}$$

The rate constant for reaction 5.1 is much slower in DMSO than in aqueous solutions. Addition of water to DMSO should increase k , so that it should be possible by a combination of electrolyte thickness and water content, to vary κ , a function of l and k , between the two regions described by the theory. To test this, the response of the electrode to gas concentration steps was measured. Transients were recorded with and without

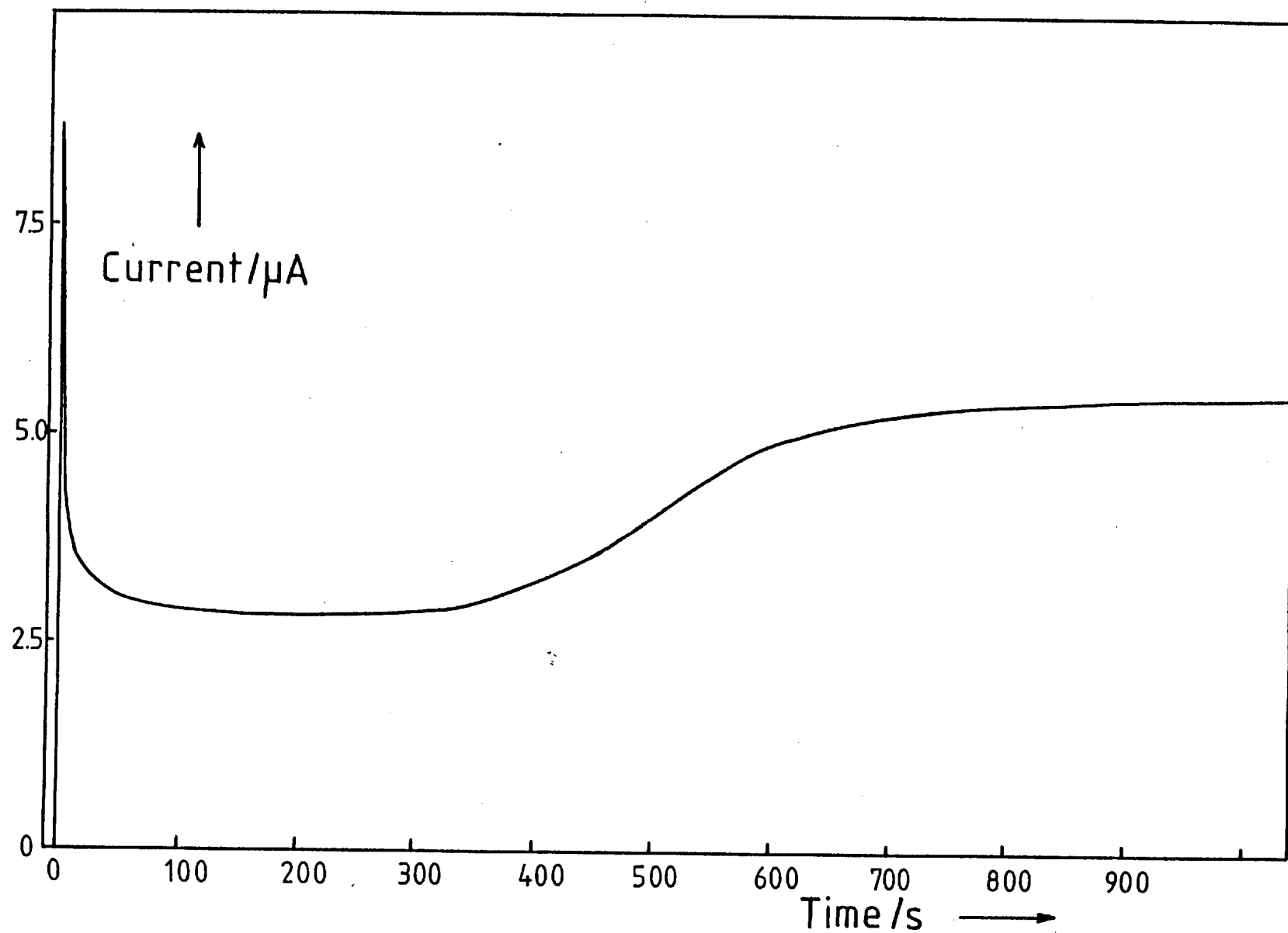


FIGURE 5.10a. The switch on transient obtained when electrode 4 was switched on to the CO_2 reduction plateau.

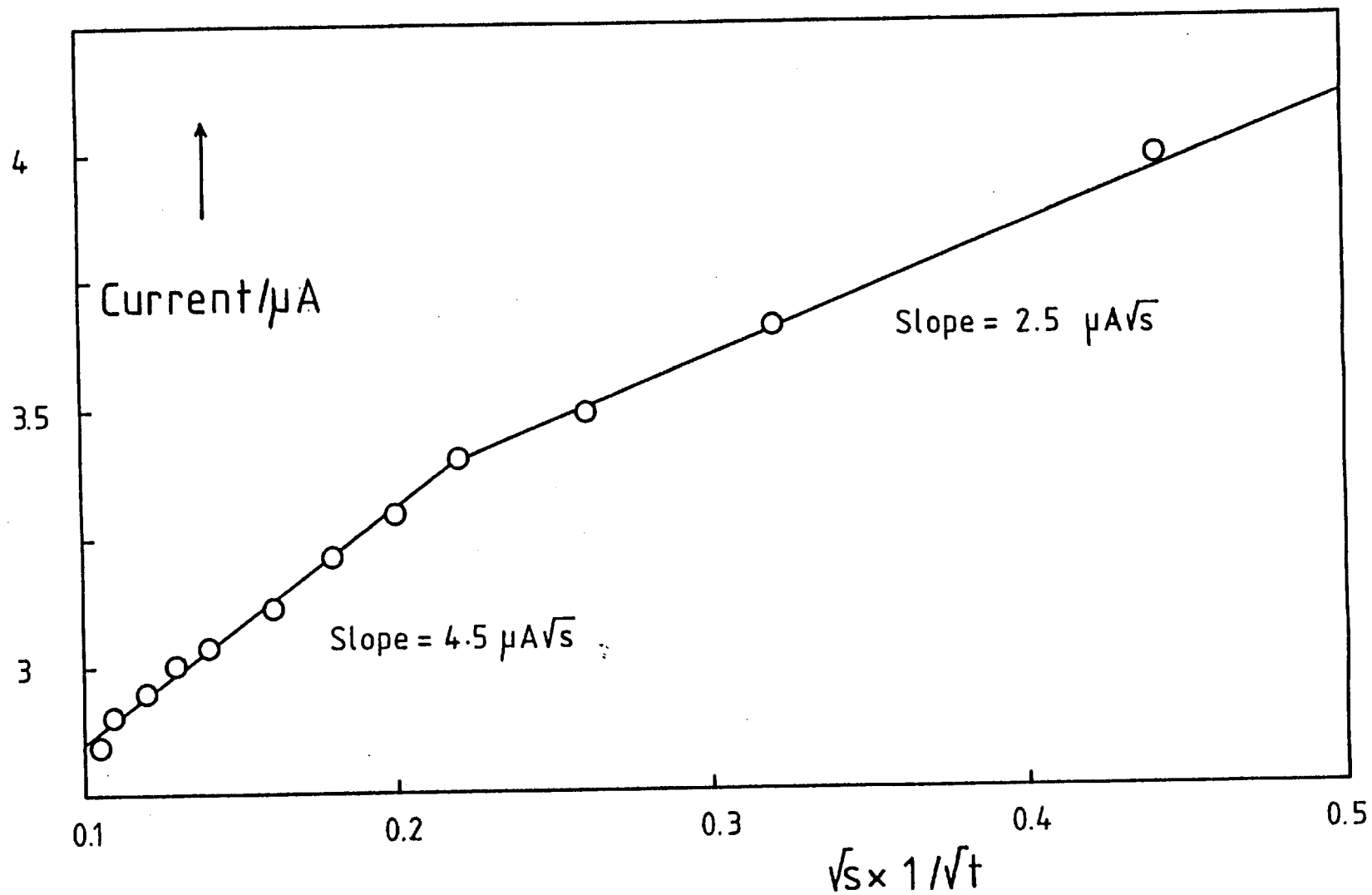


FIGURE 5.10b. Graph of i vs. $1/\sqrt{t}$

spacer, using DMSO solutions of varying water content under the membrane. The transients are shown in Figures 5.11 and 5.12, and the data is summarised in Table 5.2.

The results show the theory is reasonably correct, since they encompass the situations where $\kappa \ll 1$ (zero current rise) to $\kappa > 1$ (current doubles).

Final proof of the mechanism is in Figure 5.13. The bicarbonate was allowed to build up by reducing CO_2 under the membrane until the steady state current was observed. The current was the same each time until the membrane face was wiped over with a cloth to squeeze away the bicarbonate solution from the working electrode face. The current then fell to the pre-bicarbonate level.

In conclusion, the results show the theory to be essentially correct, and show bicarbonate is the reaction product. From the point of view of electrode design maximum electrode sensitivity and minimum response times can be achieved by using a thin membrane and a DMSO solution containing ca 15% water. A paper about this work is being prepared. (130)

5.2. DOUBLE MEMBRANE CO_2/O_2 ELECTRODES

The work described in Chapter 4 and Section 5.1. show it is possible to determine quantitatively CO_2 in nitrogen. When oxygen is also present we see the one

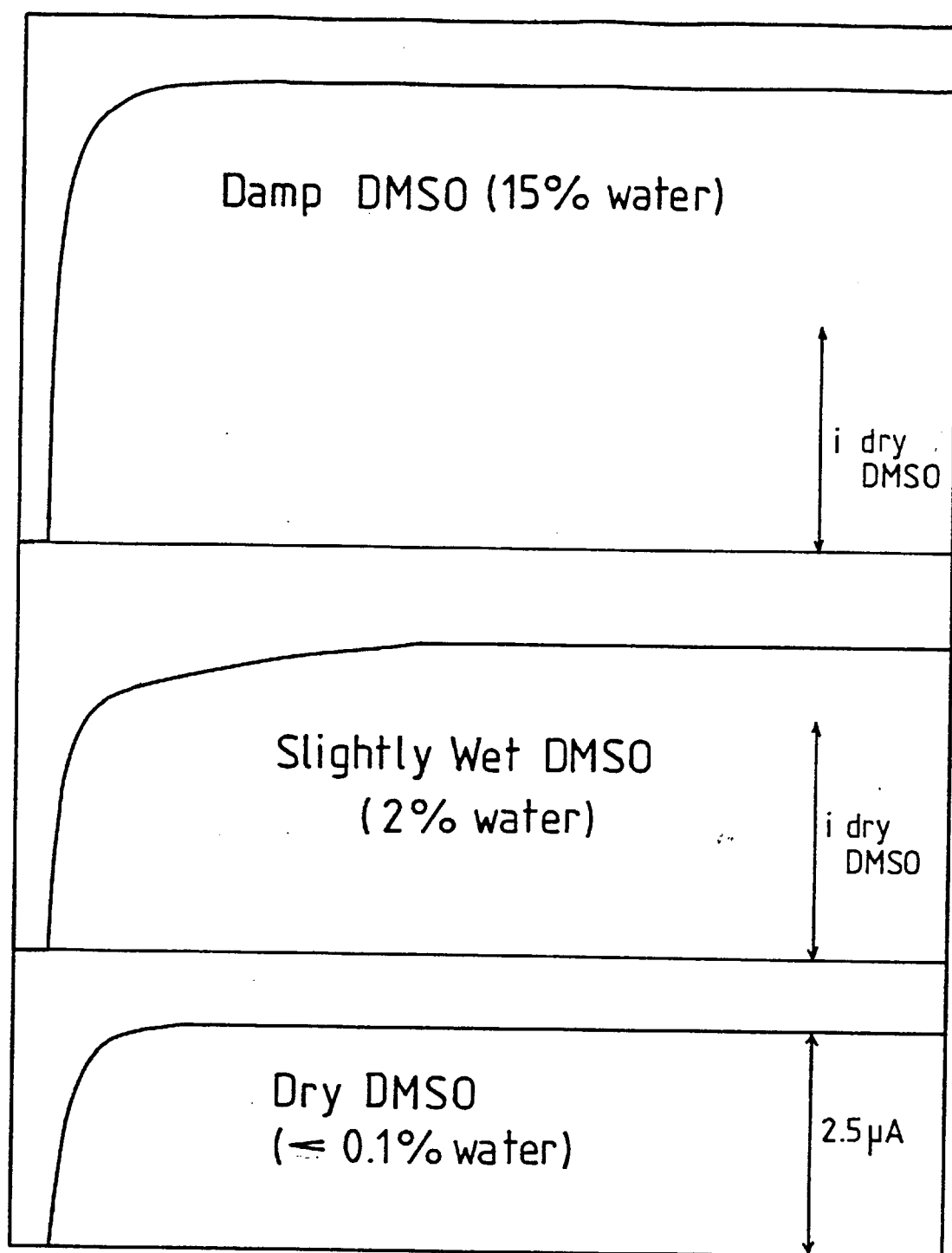


FIGURE 5.11. Concentration step transients with no spacer in the electrolyte layer.

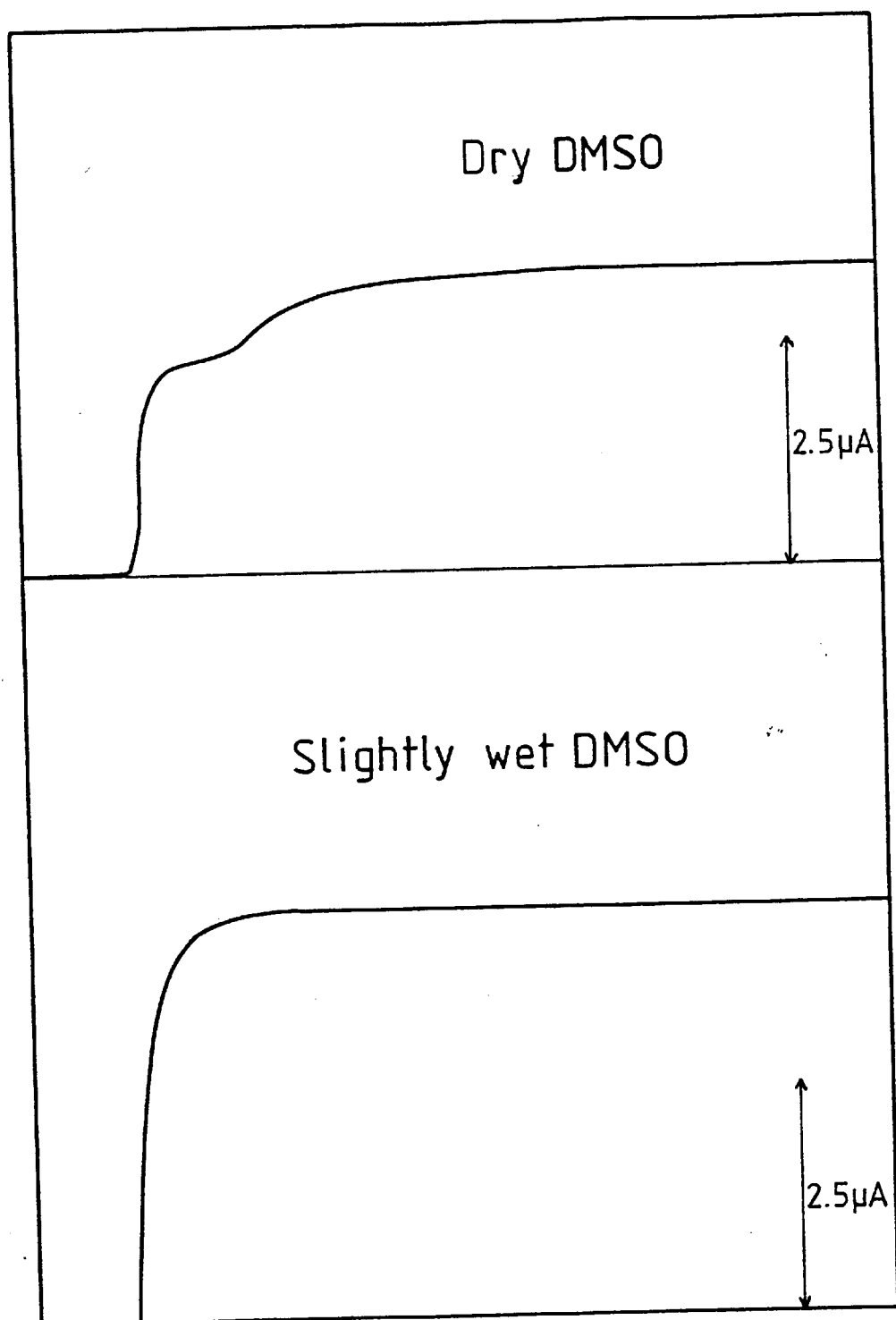


FIGURE 5.12. Concentration step transients obtained with a spacer in the electrolyte layer.

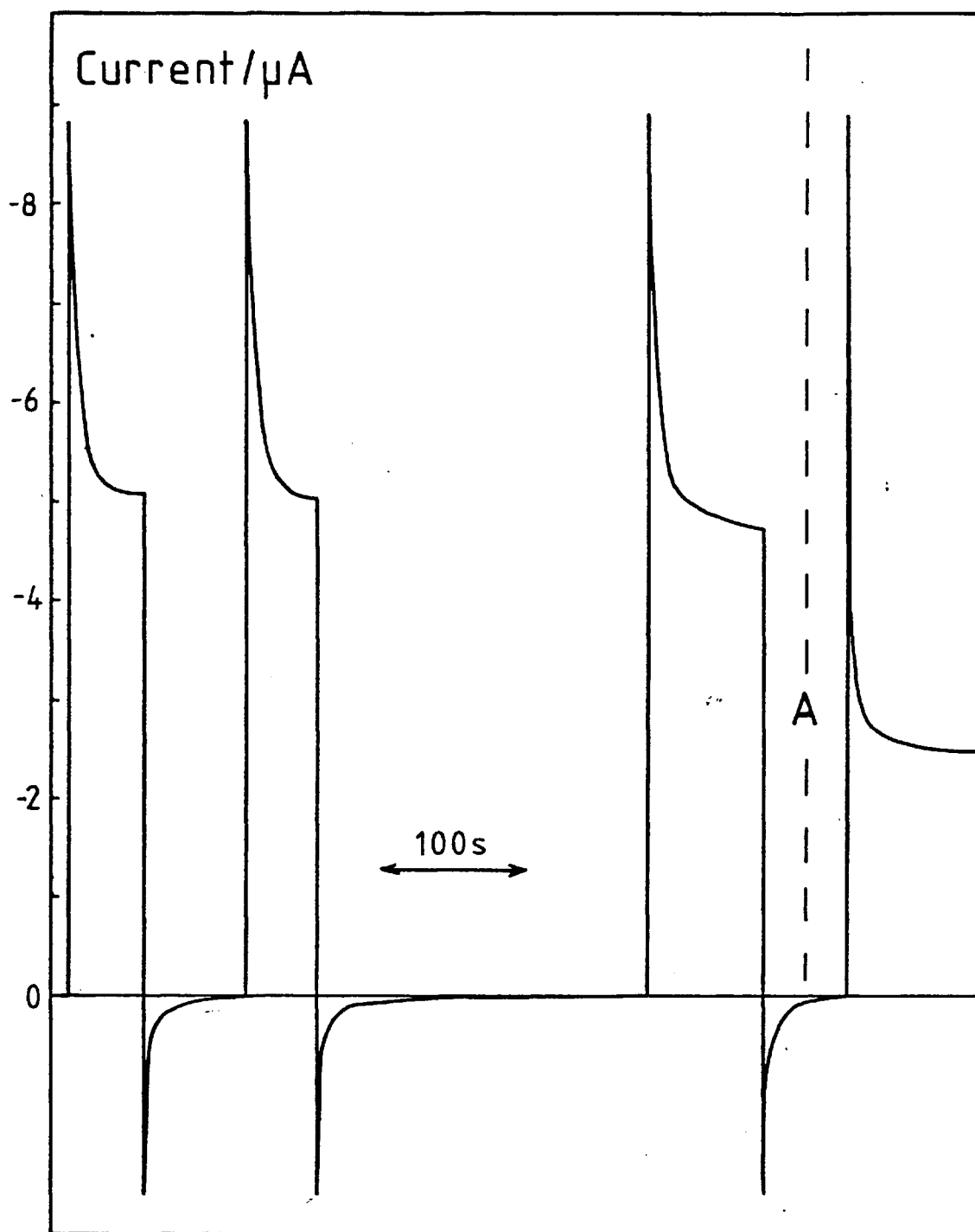


FIGURE 5.13. Switch on current transients. At point A the DMSO containing bicarbonate was squeezed away from the electrode face.

TABLE 5.2. Results from the transients in Figures 5.11 and 5.12. The figures in brackets are the percentage current increases above the initial dry DMSO current

	Initial ^(a) dry current (μ A)	Final dry current (μ A)	Final ^(b) slightly wet current (μ A)	Final ^(c) damp current (μ A)
Without 50 μ m spacer	2.51	2.51 (0%)	3.43 (35%)	5.05 (99%)
With 50 μ m spacer	2.29	3.14 (38%)	4.57 (100%)	-

(a) Dry DMSO contains <0.1% water.

(b) Slightly wet DMSO contains ~2% water.

(c) Damp DMSO contains ~15% water.

electron oxygen reduction wave, then at more negative potentials we have coincident CO_2 and oxygen reduction waves. Although the CO_2 and oxygen levels could be determined by the formula:-

$$\text{CO}_2 \propto i_{\text{CO}_2} = i_{\text{CO}_2 + \text{O}_2} - 2i_{\text{O}_2} \quad 5.54$$

(2nd wave) (1st wave)

$$\text{and } \text{O}_2 \propto i_{\text{O}_2} \quad 5.55$$

(1st wave)

For very different oxygen and CO_2 levels this technique will not be accurate, therefore it is necessary to remove the oxygen before it penetrates to the CO_2 reducing cathode. A metallised membrane could be used to remove the oxygen if the CO_2 and oxygen were reduced at different potentials. As all the gas entering the electrode passes through the metallised layer the layer potential could be set so that it removed oxygen but not CO_2 , but clearly in DMSO the technique is not practical. The use of 1,8-Dihydroxy-anthroquinone is also impractical, since although the reaction:-



is thermodynamically favoured, it is too slow to be of use.

Oxygen is reduced in aqueous solutions at a potential where CO_2 is not reduced, so a double membrane electrode,

the principle of which is shown in Figure 5.14, can be used for jointly determining CO_2 and O_2 .

Electrodes 1 and 2 were used in the work described in this section, with the metallised membranes described in Chapter 3 and an inner membrane of 12 μm Teflon.

5.2a. Metallised Membranes

Testing of the metallised membranes was carried out with electrode 1. A polarogram of the sputtered membrane is shown in Figure 5.15a. The membrane did not produce a well defined polarogram and limiting current, but the current was proportional to the oxygen concentration. Figure 5.15b. is a polarogram of the painted type of membrane, the preparation of which is described in Chapter 3. The limiting current region is well defined. Note the current is higher than on the sputtered membrane - this shows the microporous membrane is more permeable than the non-porous membrane. The metallised layers were both found to be more active than a rotating gold disc for oxygen reduction, as Table 5.3 shows. This is probably because the metal is finely divided.

The filtering efficiency E of the metallised membrane is defined as the percentage of the total oxygen flux that is reduced by the metallised layer. If the potential of a probe electrode behind the metallised membrane is

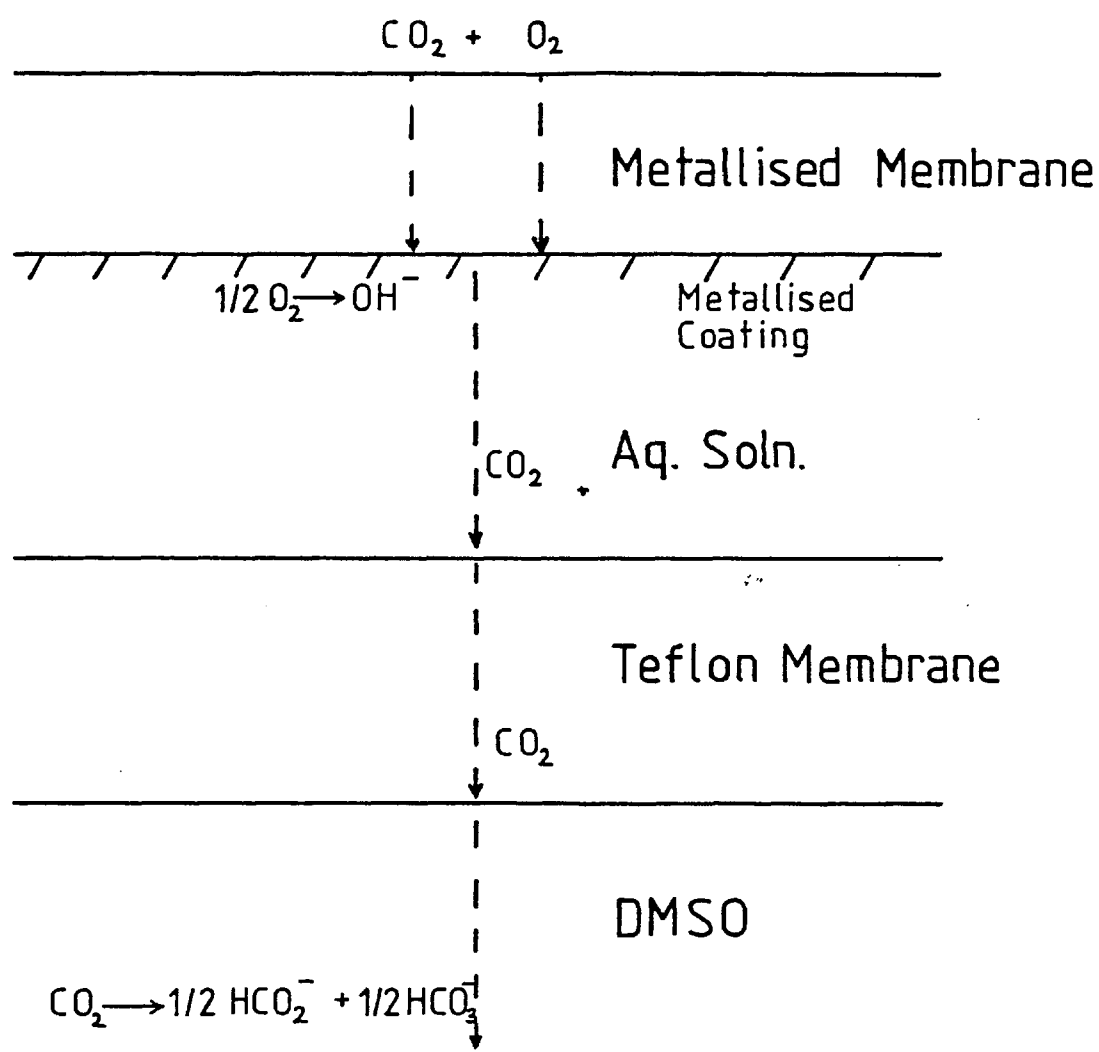


FIGURE 5.14. Principle of the double membrane electrode.

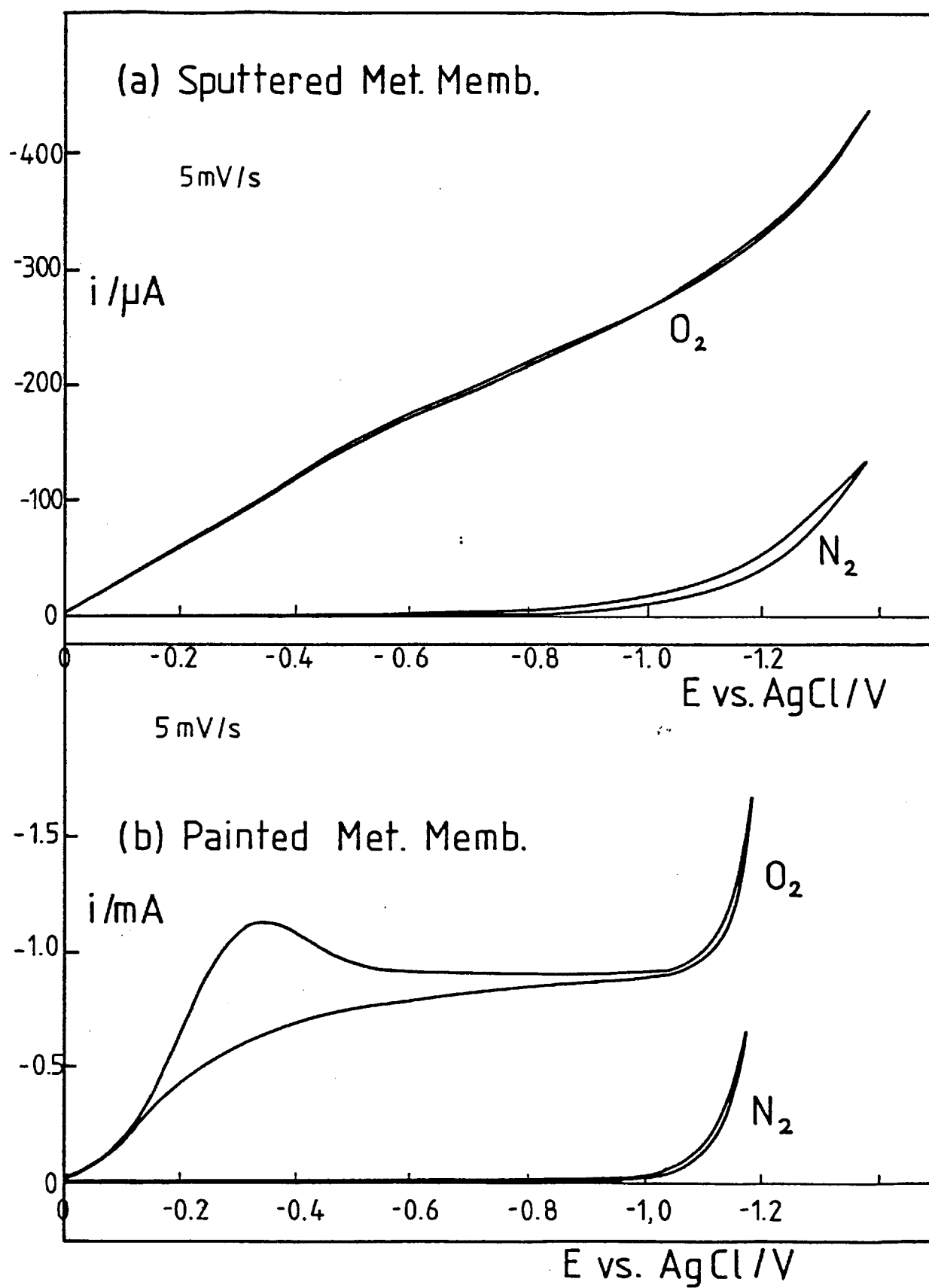


FIGURE 5.15. Metallised membrane polarograms.

TABLE 5.3. Half-wave potentials for oxygen reduction
in pH5 buffer measured against an
Ag/AgCl/MKCl reference

Sputtered Membrane	Painted Membrane	Gold Rotating Disc
-0.35 V	-0.2 V	-0.45 V

held on the oxygen reduction plateau, and the metallised membrane is switched on, then:-

$$E = \frac{i_o - i_{t \rightarrow \infty}}{i_o} \times 100 \quad 5.56$$

Where i_o is the probe electrode current before the membrane was switched on.

$i_{t \rightarrow \infty}$ is the current at long times after the membrane was switched on.

Figure 5.16 shows the effect of the painted membrane on the current obtained at the silver working electrode of electrode 1 (the probe electrode) when there was no DMSO solution layer. With the electrode in air the probe current is reduced to well below 1% of its original value, and so the filtering efficiency E is greater than 99%.

The filtering efficiency of the sputtered membrane was found to vary from sample to sample, but was typically in the range 75% to 95%. The variation was probably due to the coating of gold being insufficient and variable. The resistance of the membranes also indicated this was the case. A typical resistance between two points 1 cm apart on the sputtered membrane was variable and ca 20 Ω , whereas that on the painted membrane was always below 0.5 Ω .

Scanning electron micrographs of the painted type of metallised membrane are shown in Figure 5.17, and

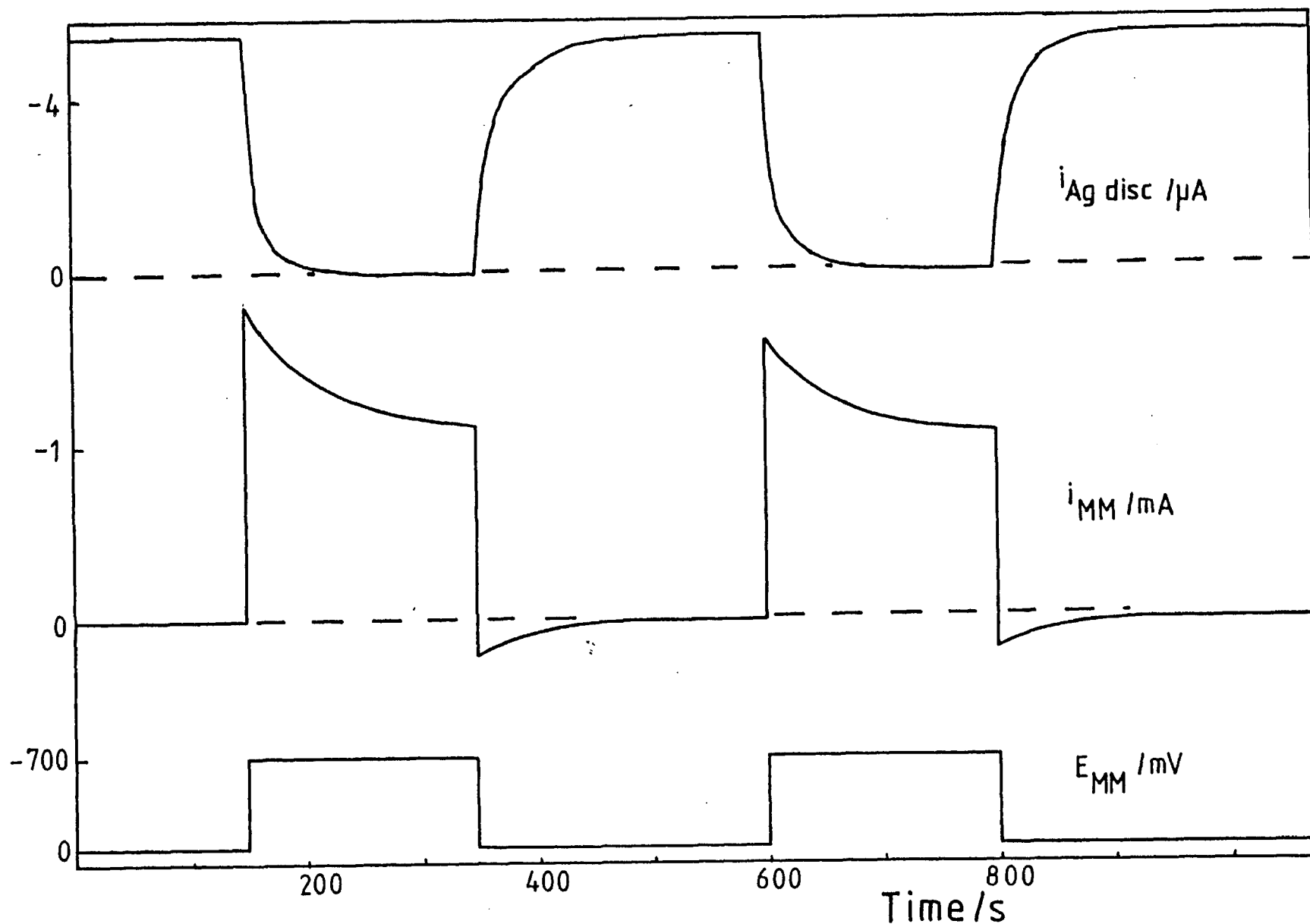
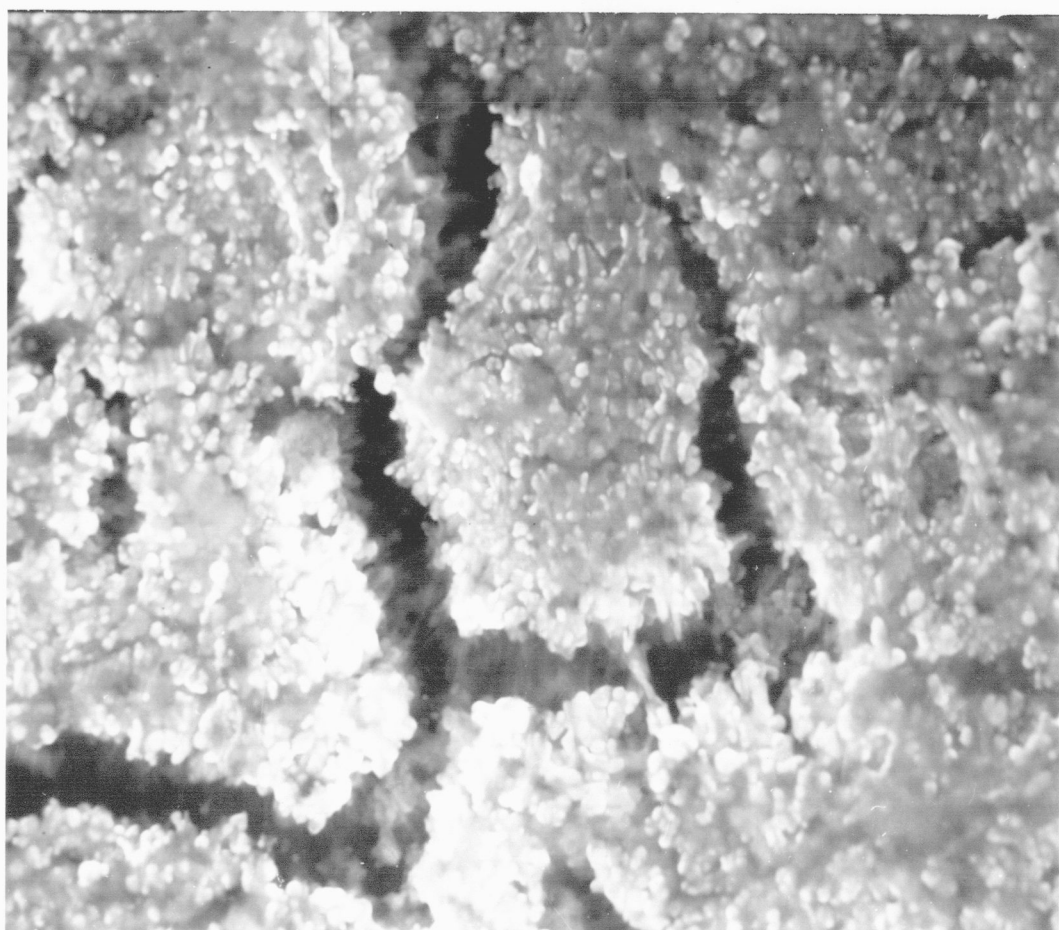
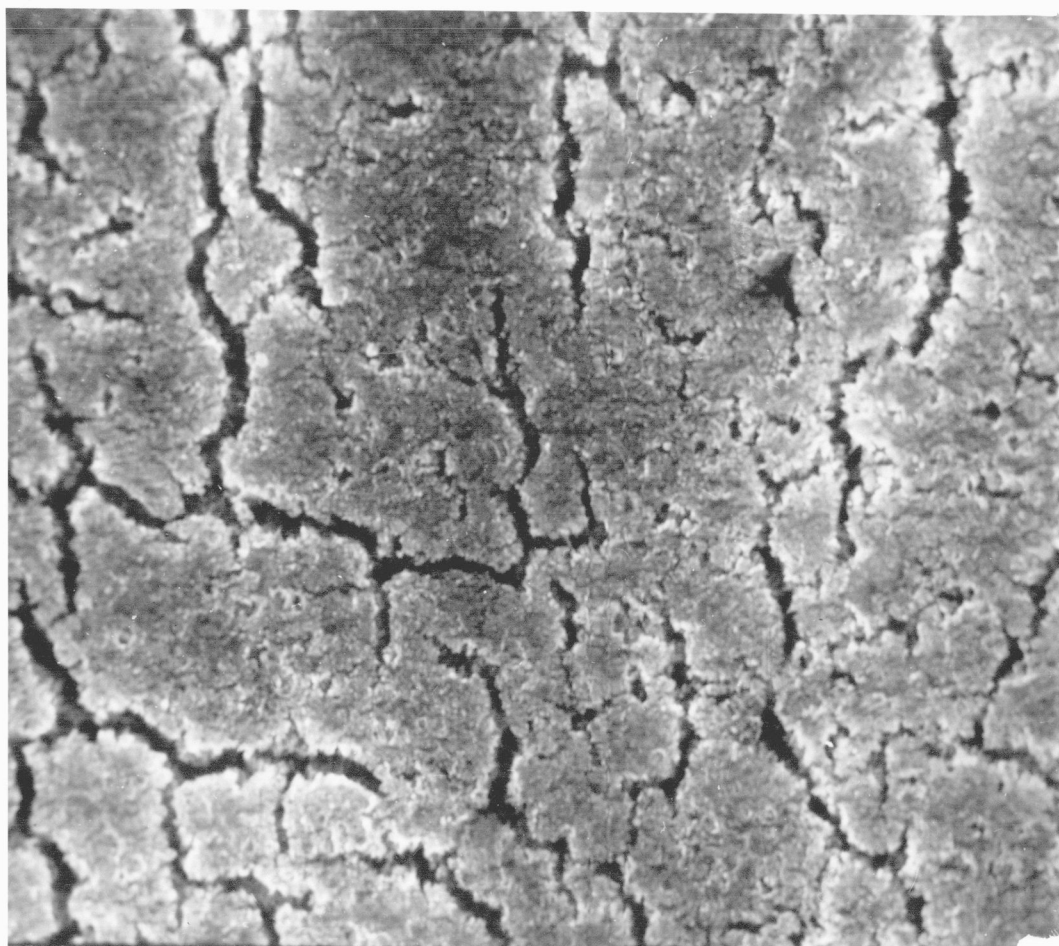
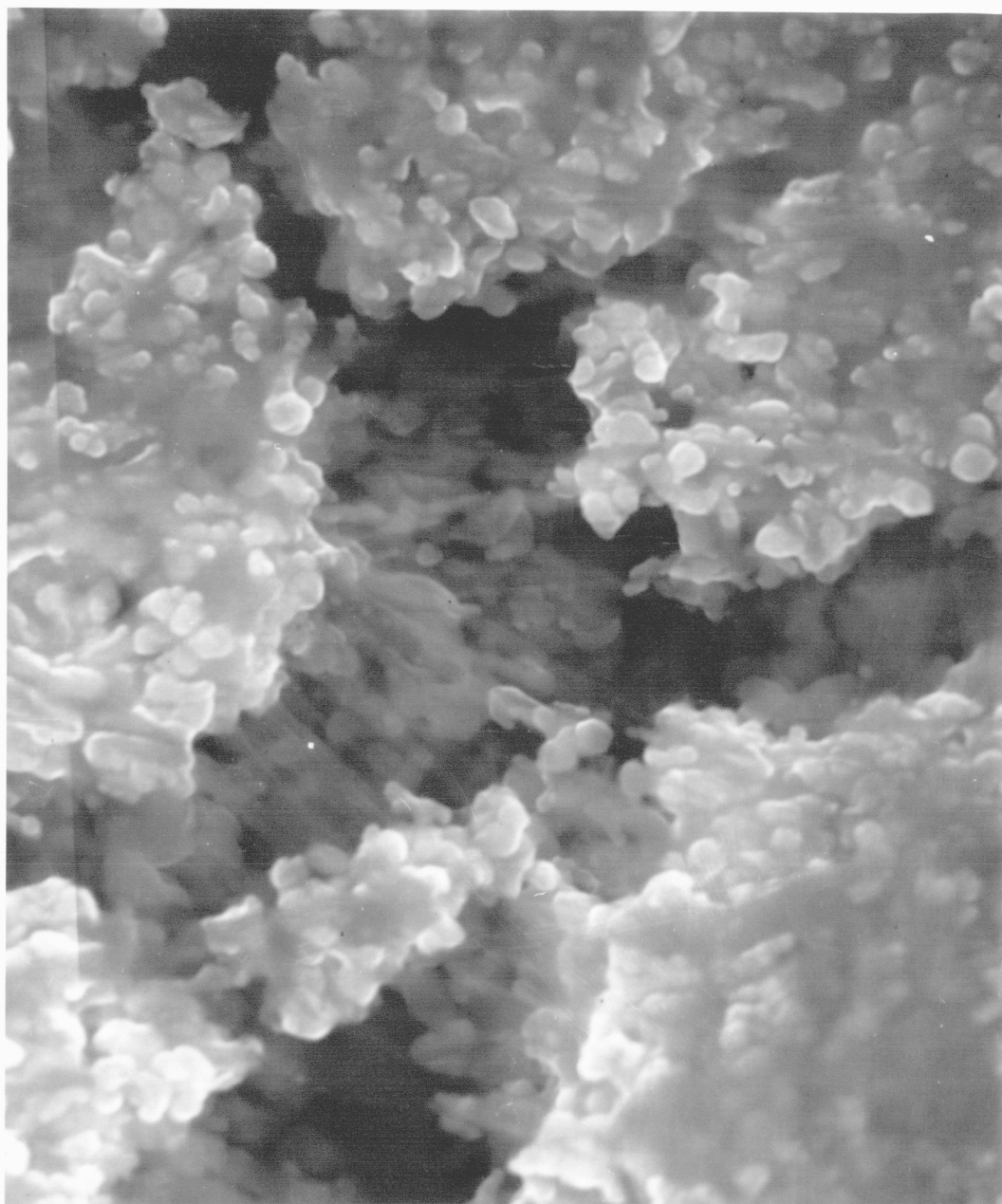


FIGURE 5.16. The filtering effect of the metallised membrane. As the membrane potential (E_{MM}) is changed to -700 mV the metallised membrane causes the current at the silver working electrode ($i_{\text{Ag disc}}$) to fall to zero.

Figure 5.17 S.E.M. Photographs of the painted M.M.'s
5.17a (top) 800x
5.17b (bottom) 4,000x
5.17c (overleaf) 10,000x



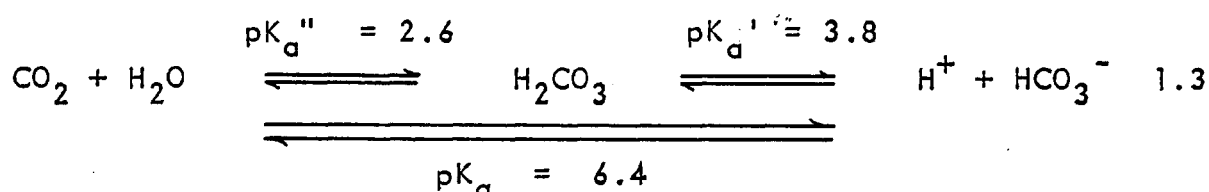


explain why this type of membrane is so efficient as an electrochemical gas filter - the gold crystals penetrate well into the fibres of the membrane (Figure 5.17c), therefore oxygen molecules passing through the membrane have a greater chance of contacting the metallised surface than if there is just a thin coating on the inside surface of the membrane.

It was not possible to take S.E.M.'s of the sputtered type of membrane because the electron beam caused the gold to evaporate from the target area.

The Aqueous Solution

The pH of the aqueous solution is important because of the equilibria described by equation 1.3:-



In order to ensure that CO_2 passes smoothly through the aqueous solution a low pH is required, but in order to obtain good metallised membrane polarograms and therefore high filtering efficiencies a reasonably high pH is required. The electrolyte is therefore pH5 phthalate buffer.⁽¹³¹⁾ At pH5 only 4% of the CO_2 exists as bicarbonate.

Experiments on the Double Membrane Electrodes

Electrode 1

Figure 5.18 shows polarograms of a CO_2/O_2 mixture before and after the metallised membrane was switched on. The first reduction wave is greatly reduced, while the second wave is reduced by the height of the first wave, and is due to CO_2 reduction only. Figure 5.19 shows the effect of varying the CO_2 and O_2 concentrations using a membrane that is 75% efficient as an oxygen filter. The current at the silver electrode with the electrode in 100% oxygen and the filter off was $3.5 \mu\text{A}$, and so the 100% oxygen current was due entirely to oxygen leakage past the filter.

The 63% response time of the electrode was ca 20 s for CO_2 , and 10 s for oxygen. These times could be reduced with thinner membranes.

When the painted metallised membrane was used as a filter the current was found to be very high at high oxygen partial pressures, and it was not possible to remove the oxygen completely due to ohmic drop between the counter electrode and metallised membrane.

Electrode 2

Electrode 1 showed that the oxygen filter worked, but no long-term experiments were possible because the solution volumes were very small - the electrode dried out due to evaporation around the washer and also any

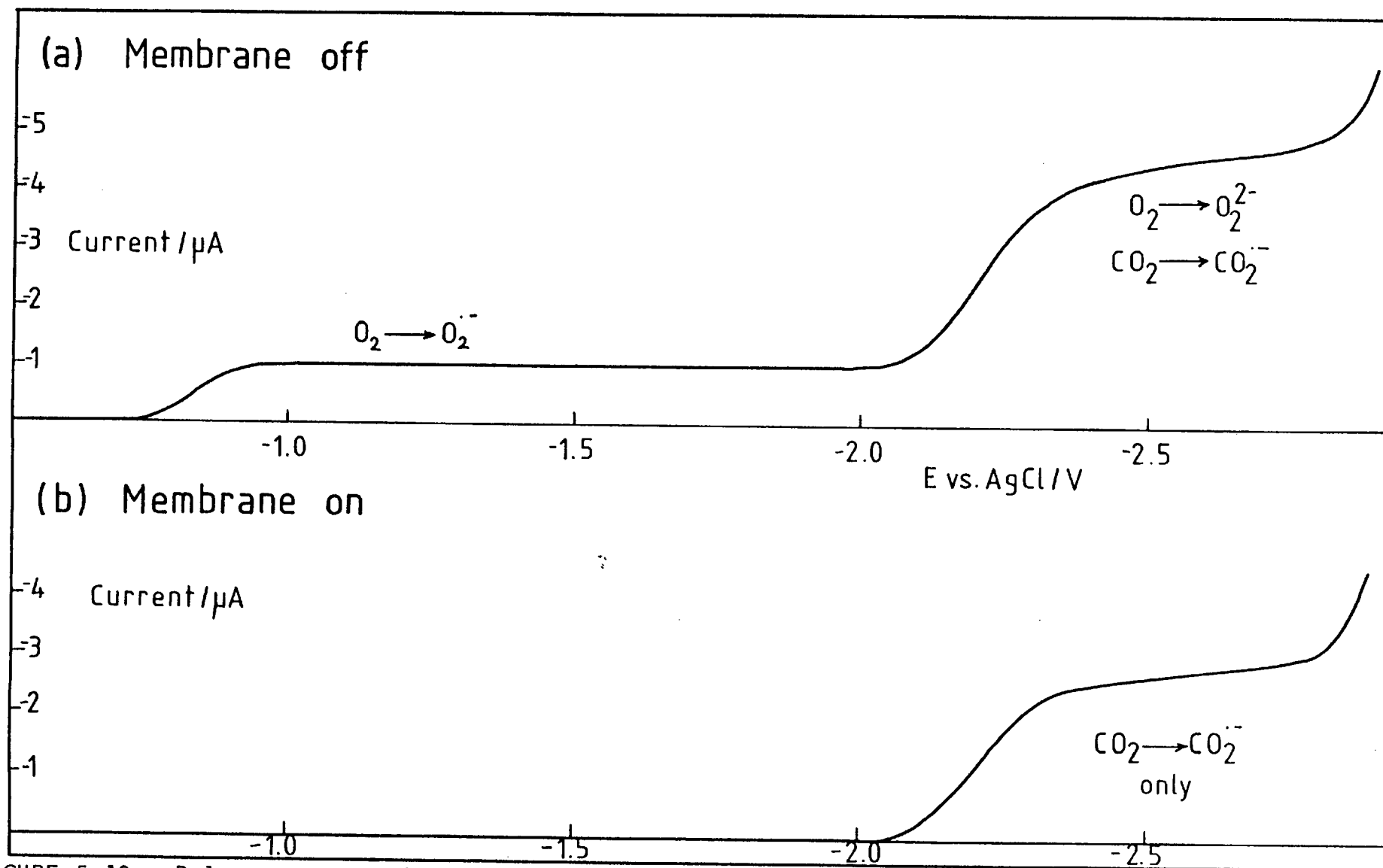


FIGURE 5.18. Polarograms at the silver working electrode of electrode 1 showing the effect of the metallised membrane.

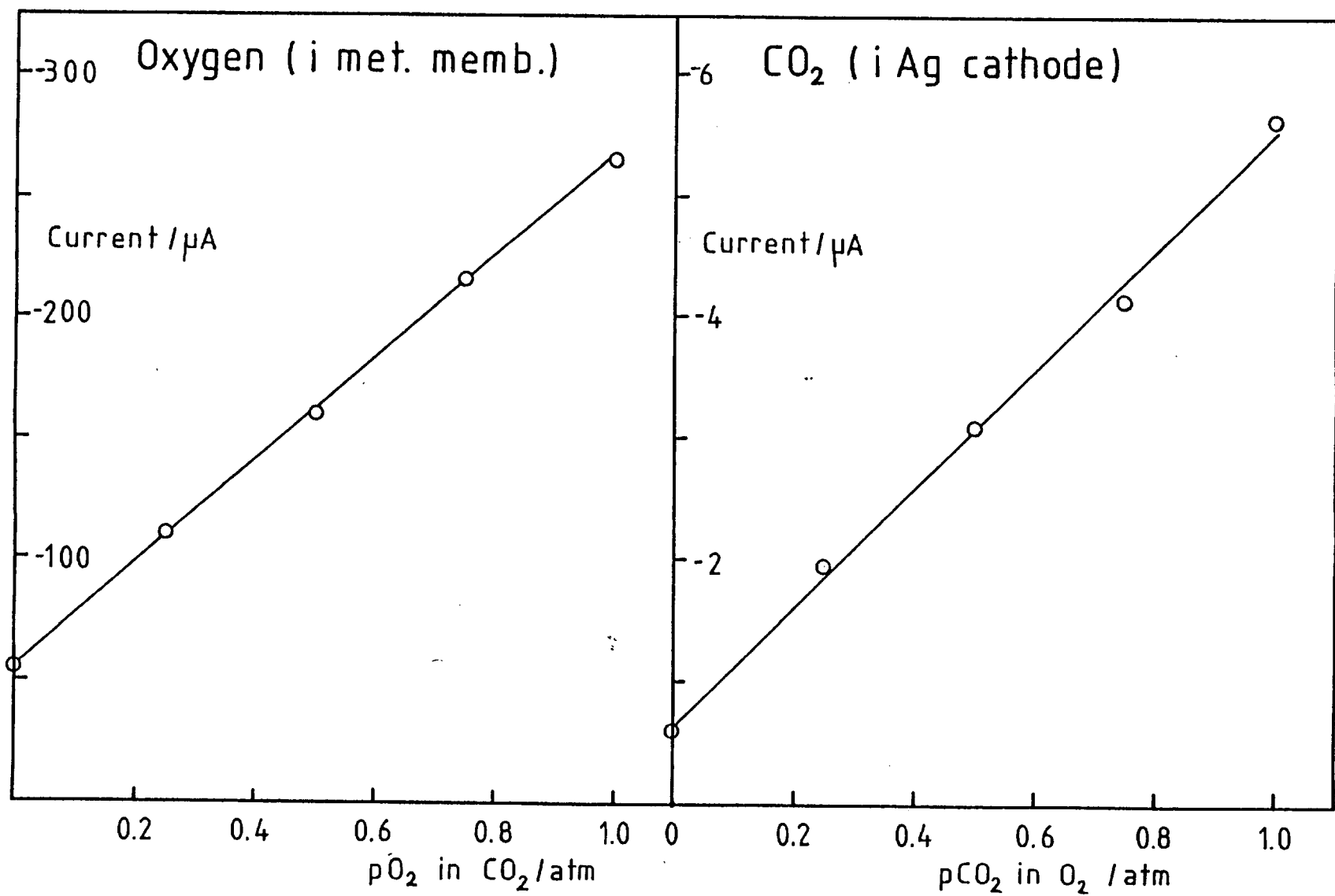


FIGURE 5.19. Current - % gas mixture plots for electrode 1.

slight leaks between the two solution layers meant the electrode rapidly became unusable.

The higher currents obtained with the painted type of membrane meant the filtering efficiency was impaired at higher oxygen levels.

Electrode 2 was designed to alleviate these problems. The solution reservoirs are large, which means drying out and small leaks are unimportant. Also the metallised membrane counter electrode is much larger, which reduces problems caused by ohmic drop. The third modification is the Teflon washer. Teflon is much softer than Delrin, and seals better onto the membrane face thereby preventing excessive filter currents.

The results obtained with this electrode were similar to those with electrode 1, except the polarograms of the sputtered membrane were better, with a well defined limiting current (Figure 5.20). This meant the membranes were more efficient as oxygen filters, and filtering efficiencies up to ~98% were obtained.

The currents on the painted membranes were still high, but the change in electrode design meant good filtering efficiencies were obtained at all values of $p\text{CO}_2$ and $p\text{O}_2$, as Figure 5.21 shows. Although no long-term experiments have yet been done the electrode worked well over a period of several days. Leakage between the two solutions did not occur.

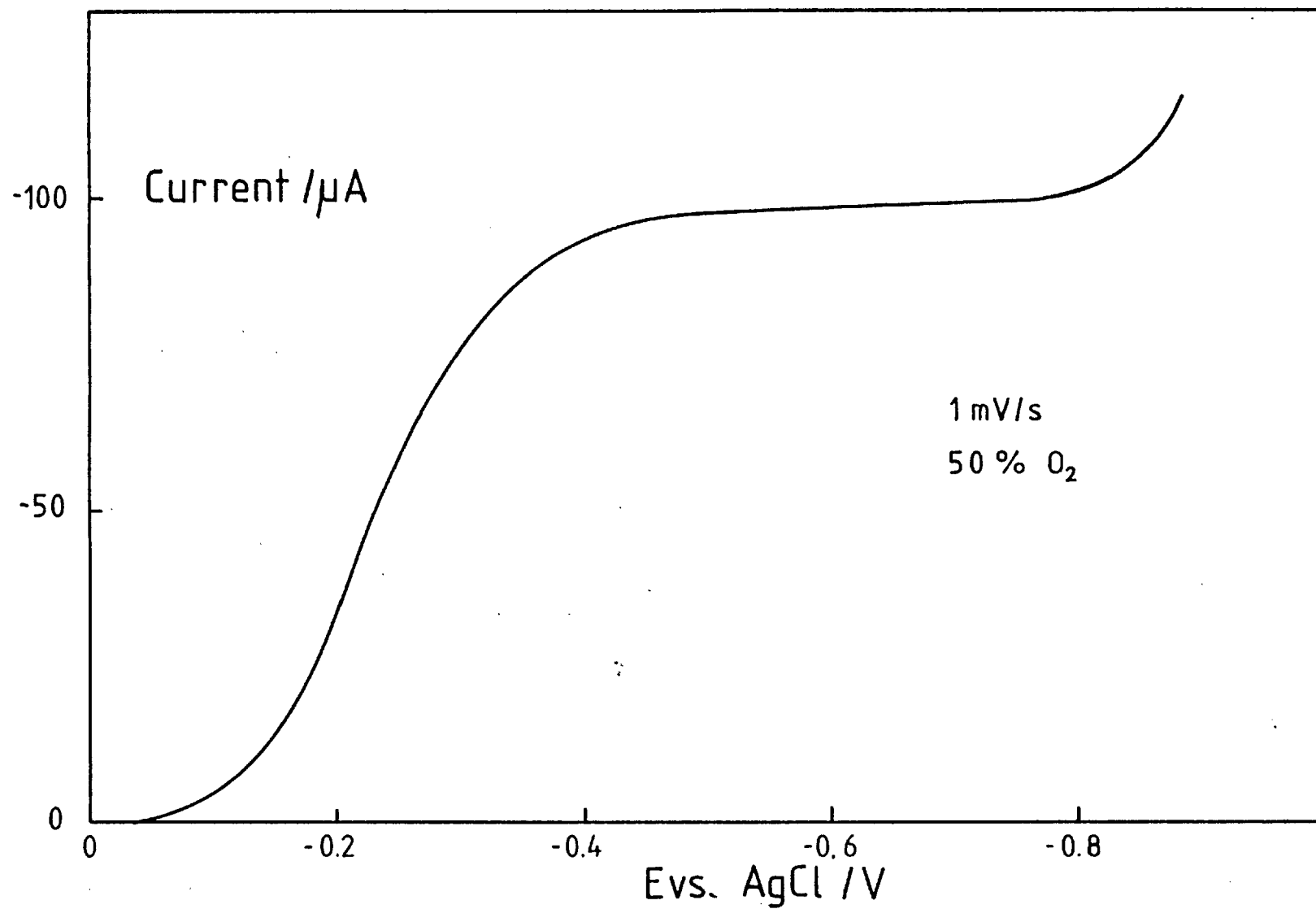


FIGURE 5.20. Sputtered membrane polarogram obtained with electrode 2.

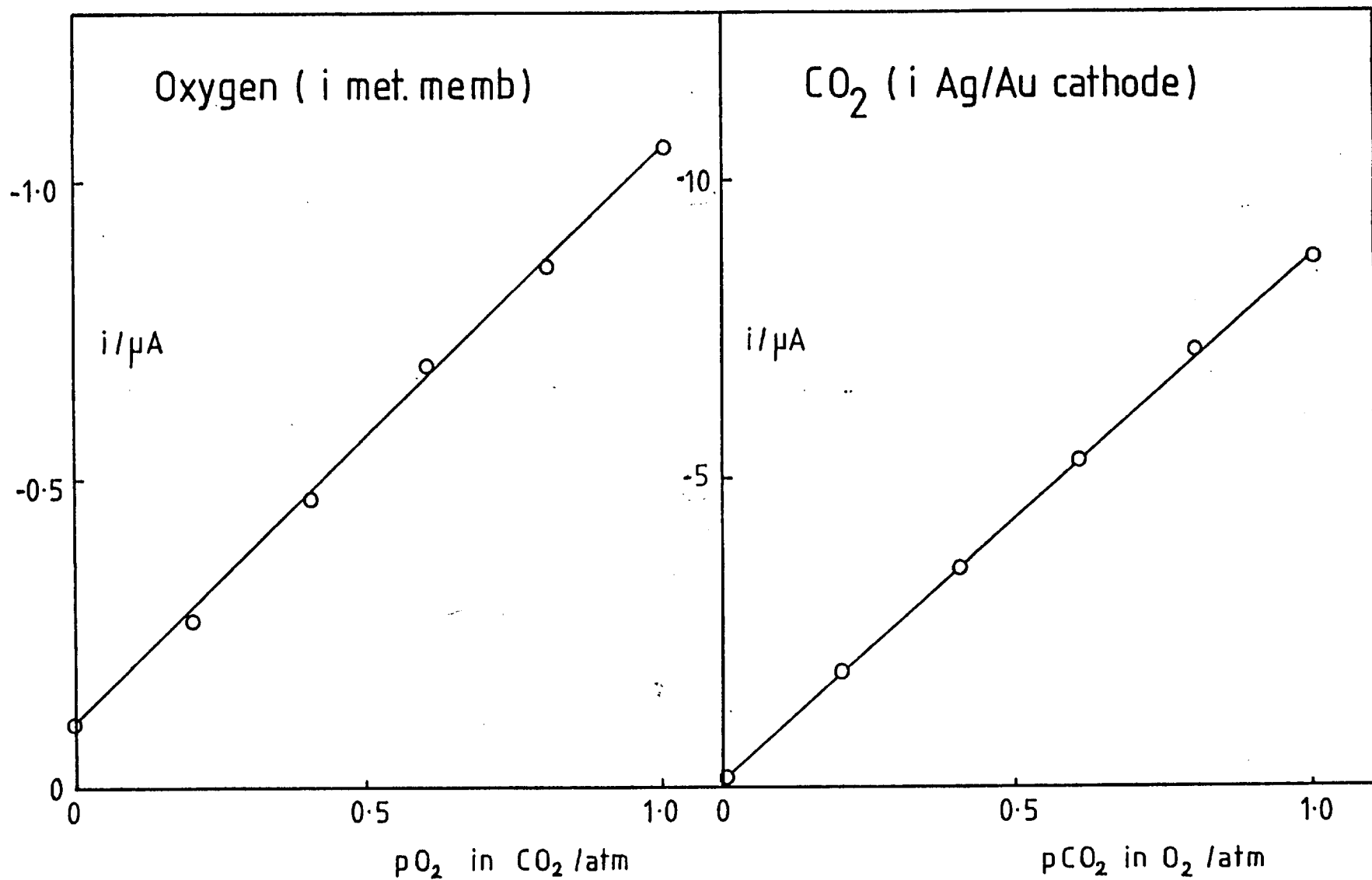


FIGURE 5.21. Current - % gas mixture plots for electrode 2.

Applications of the Electrode

The electrode has a long response time, but this can be improved by the use of thinner membranes, so breath analysis is feasible. The large solution reservoirs of electrode 2 mean the electrode could be used as an on-line sensor, for industrial processes such as fermentation or distillation, since maintenance would be minimal. The double membrane electrode has been patented,⁽¹³²⁾ and a paper will be published shortly.⁽¹³³⁾

5.3. MEDICAL APPLICATIONS

Typical values of oxygen and CO₂ levels in venous blood, arterial blood and lungs of a healthy male aged 20-40 are shown in Table 5.4.⁽³²⁾ In all cases, the oxygen and CO₂ levels are of comparable magnitude, so a single membrane electrode could be used to measure both gases. This section describes the use of a single membrane electrode for breath analysis and transcutaneous arterial blood gas analysis.

TABLE 5.4. Typical oxygen and CO₂ levels in the blood and lungs. 100% is one atmosphere.

Gas	Arterial Level	Venous Level	Alveolar Level	Expired Gas
Oxygen	14%	6%	14%	15%
CO ₂	5½%	7%	5½%	4.5%

Breath Analysis

To test the suitability of using a single membrane electrode for breath analysis electrode 4 was used with a 6 μm Teflon membrane. The potentials of the gold and silver working electrodes were set so that the gold electrode was on the oxygen-superoxide reduction plateau, and the silver electrode on the CO_2 + oxygen reduction plateau. The electronic circuit used was that shown in Figure 3.20, but the gold electrode was connected to a current-voltage convertor with a variable feedback resistor - this meant the gain of the amplifier could be adjusted.

The electrode was initially calibrated in nitrogen and air. The electrode was placed in nitrogen so that any residual currents were "backed off" with floating voltage sources. Then the electrode was placed into air, and the gain of the gold electrode current to voltage convertor was adjusted so that the subtracted current:-

$$i_{\text{Ag}} - i_{\text{Au}} \propto p\text{CO}_2$$

was zero. The response of the electrode to various $\text{O}_2/\text{CO}_2/\text{N}_2$ mixtures is shown in Figure 5.22.

The electrode was then tested for breath analysis by placing the electrode in a small water jacketed glass vessel (which was in fact the electrochemical cell shown in Figure 3.2). The vessel was loosely sealed with parafilm, so there were just two inlet/outlet ports.

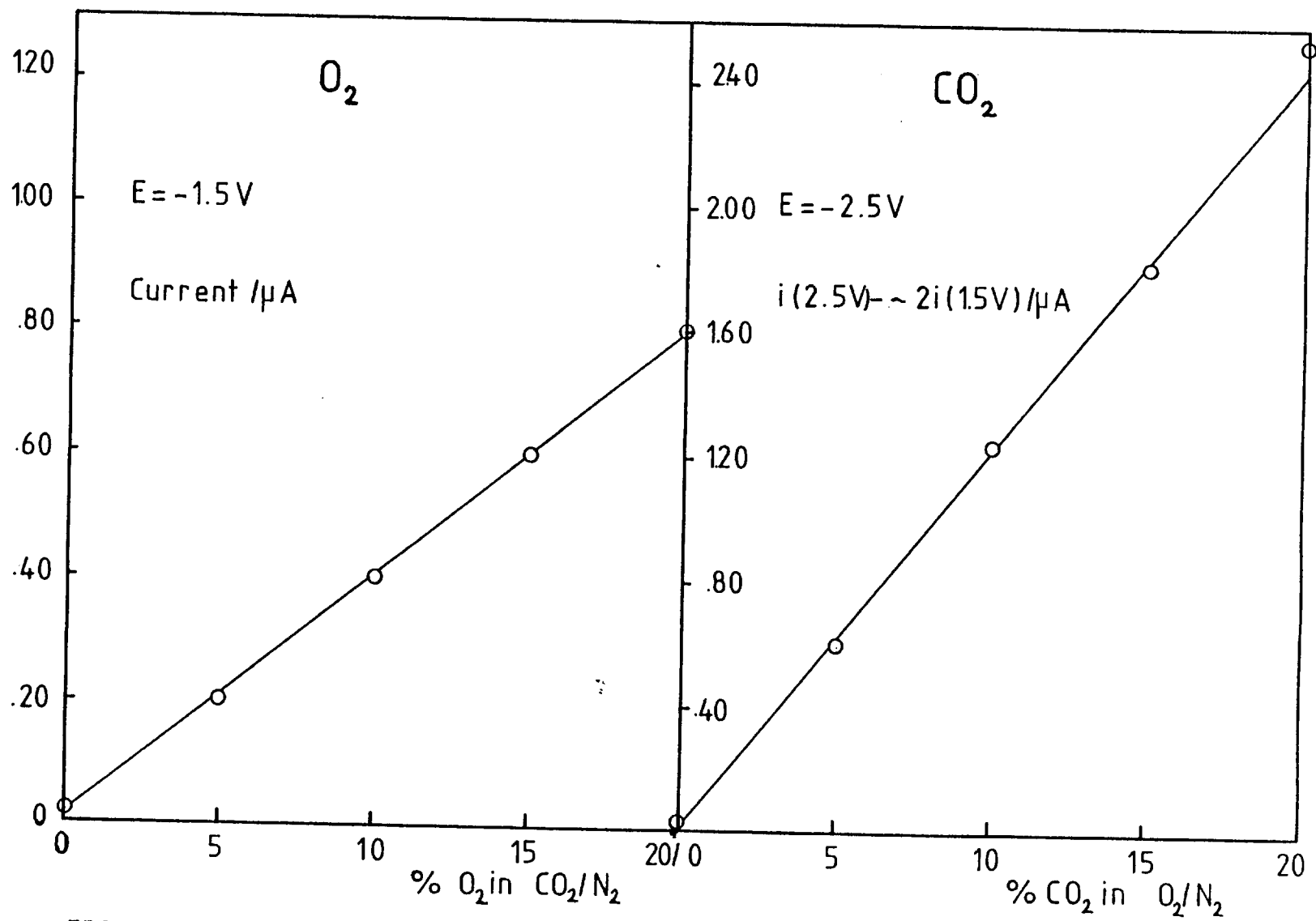


FIGURE 5.22. Response of electrode 4 to various $O_2/CO_2/N_2$ gas mixtures.

The response of the electrode when inspired and expired gases were sucked and blown through the cell is shown in Figure 5.23. The response to oxygen is rapid and shows expired gas still contains ca 15% O_2 . The CO_2 response is less rapid, but still sufficiently fast to show the CO_2 level in expired gas is about 4%, which is close to the value of 4-5% quoted in Table 5.4.

Transcutaneous Blood Gas Analysis

The principle of transcutaneous blood gas analysis was discussed in Chapter 1, and the effect of electrode size and membrane permeability is discussed in Chapter 2. An electrode of the type described in Section 4.2 would not be suitable for transcutaneous blood gas analysis because the large area of the metallised membrane would cause considerable depletion effects, so it is necessary to use a single membrane electrode.

Electrode 3 was used in this work. Its temperature was set to $46^{\circ}C$ and controlled by the circuit shown in Figure 3.23. 25 μm polypropylene was used as membrane. The electrode was sited on an adult forearm using the method described in Chapter 3. The effect of holding exhaled breath, and brachial artery occlusion, both of which cause arterial pO_2 to decrease and pCO_2 to increase, were examined. The electrode was tested after manufacture by using an aqueous electrolyte under the membrane, which was buffered at pH 9.2. The electrode response was compared with that of a commercial (Hellige) transcutaneous oxygen

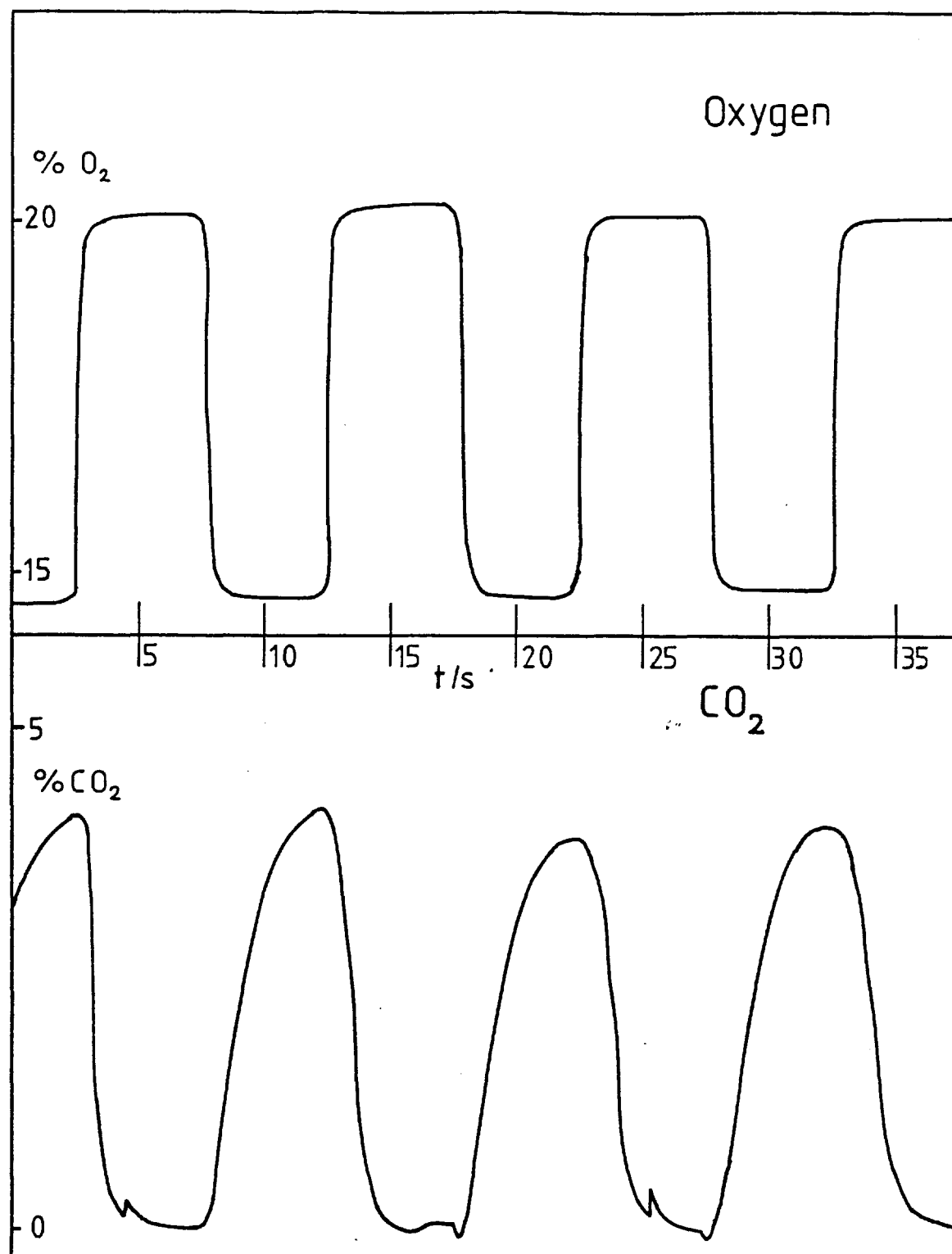


FIGURE 5.23. Breath analysis with electrode 4.

probe. The results are in Figure 5.24. Note that the response is qualitatively similar, however the steady state pO_2 reading on electrode 3 is lower. This is because the working electrodes on electrode 3 are much larger (ca 500 μm dia.) than the Hellige electrode (ca 10 μm), so skin depletion effects occur. However, Figure 5.24b. shows the electrode is suitable for qualitative determination of CO_2 and oxygen.

The electrode potentials were set in the same way as in the breath analysis work, and the electrode was zeroed using air and nitrogen. The response of the electrode when the electrode was sited on the forearm is shown in Figure 5.25. The response to oxygen is very similar to that shown in Figure 5.24b. The CO_2 level initially rises very sharply; this is explained by Figure 2.15b, which shows the unheated skin surface PCO_2 is high. The current then falls due to depletion, and then rises as the skin becomes heated. Brachial artery occlusion or holding exhaled breath caused the pCO_2 to rise in the expected manner.

Conclusions

The results of this section have shown that CO_2 and oxygen can be jointly determined with a single membrane electrode, which is useful in breath analysis and for transcutaneous blood gas analysis. The technique could be extended by pulsing the potential of the working electrode. The work in Chapter 4 showed it was possible

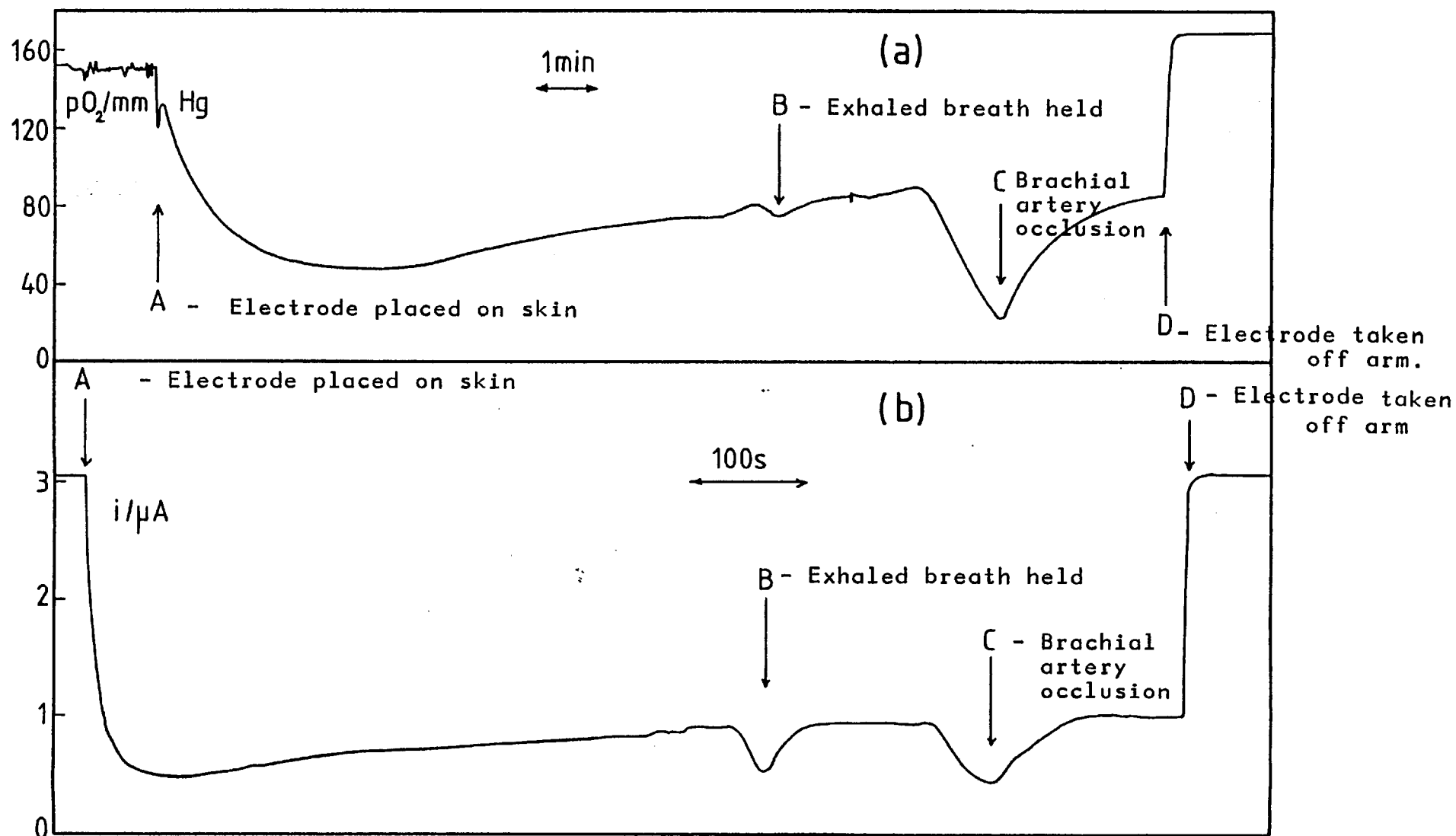


FIGURE 5.24. Comparison of the response of electrode 3 with that of a commercial Hellige electrode.

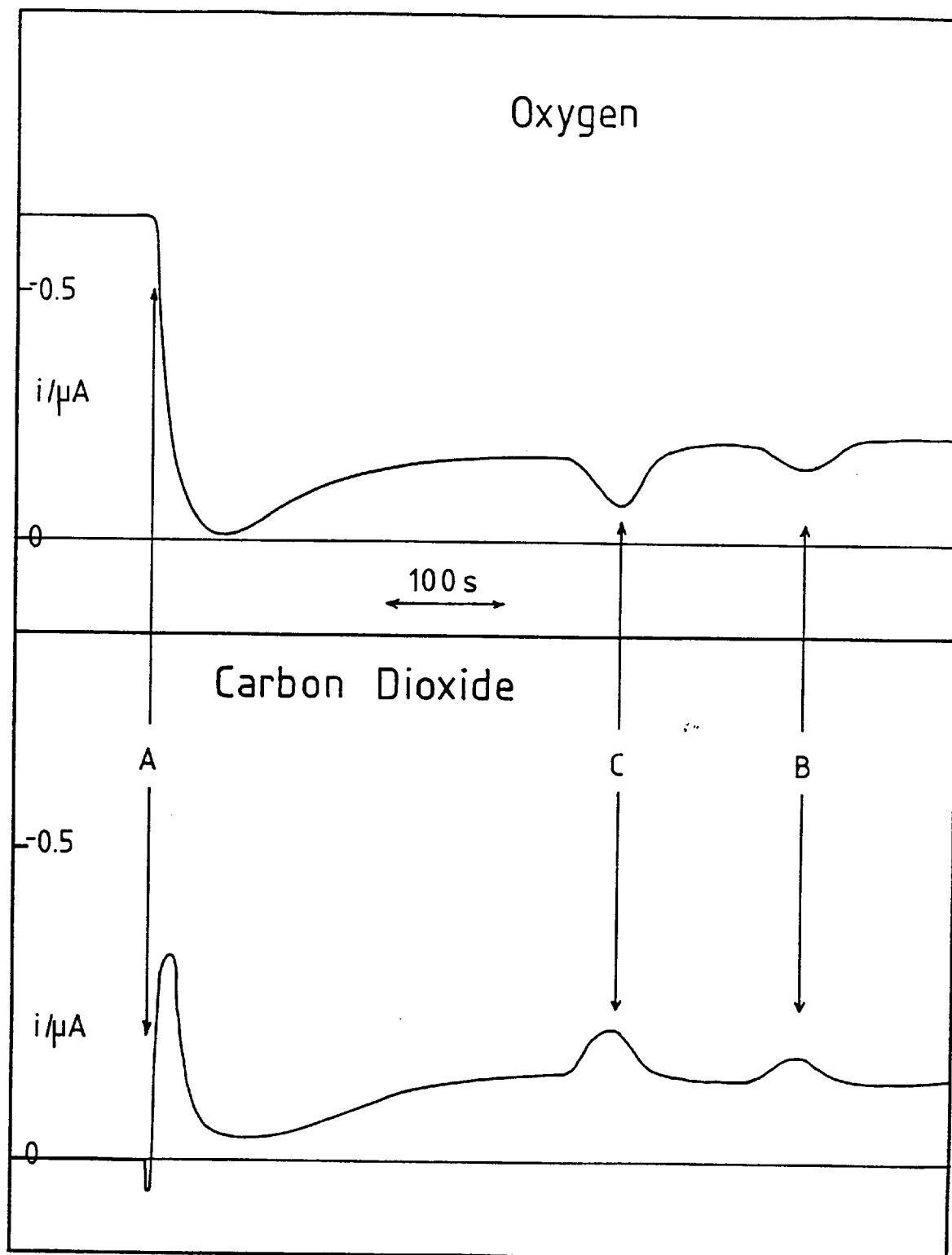


FIGURE 5.25. Response of electrode 3 when used for CO_2 and O_2 blood gas analysis. Points A, B and C are as described in Figure 5.24.

to oxidise the products formed by CO_2 and oxygen reduction. A pulse waveform of the type shown in Figure 5.26 would mean that no skin gas depletion would occur, so very rapid response transcutaneous electrodes with very thin membranes could be designed.

A complex device has recently reported⁽¹³⁴⁾ that causes no net sample depletion of oxygen, and essentially consists of a large number of interdigitated anodes and cathodes. The cathodes reduce oxygen while the anodes regenerate oxygen by oxidising the aqueous solvent. A steady state is set up, where the oxygen is returned to the sample as fast as it is removed by the cathodes. Clearly this technique would be unsuitable for use in transcutaneous blood gas determination. The advantage of the reoxidation technique is the electrode is more easily made, and therefore cheaper.

To conclude this chapter, the technique of detecting CO_2 by electrochemical reduction shows several advantages over conventional CO_2 electrodes:-

Firstly, the detection technique is direct in that the current directly measures the amount of CO_2 reduced.

Secondly, both gases can be determined simultaneously by various techniques, and simultaneous detection poses

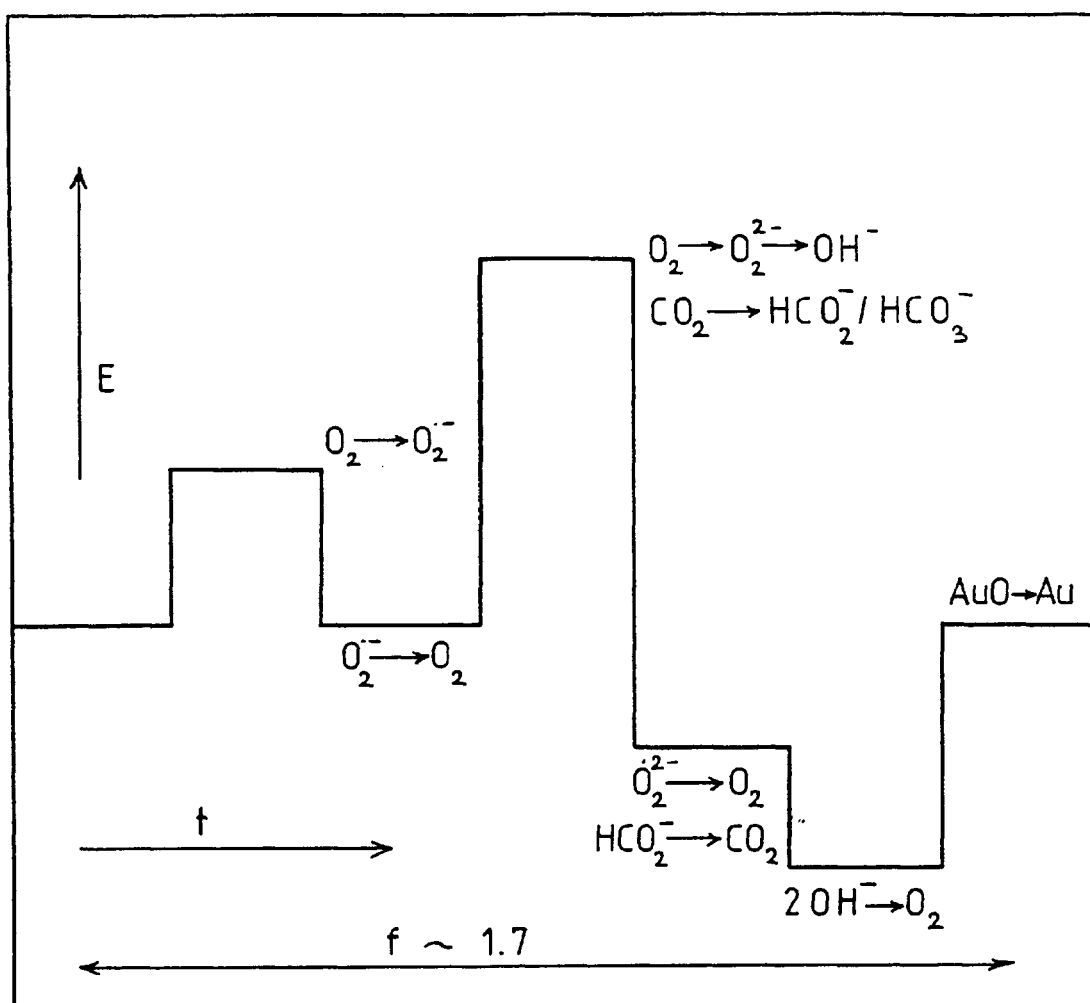


FIGURE 5.26. Pulse waveform which could be used to regenerate CO_2 and O_2 reduction products, thereby causing no skin depletion.

no problems (with conventional joint O_2/CO_2 sensors the oxygen reduction interferes with CO_2 detection because hydroxide ions are produced.)

Lastly, reoxidation of the oxygen and CO_2 reduction products mean electrodes can be easily made that cause no sample depletion.

CHAPTER 6
IMPROVEMENTS IN THE DESIGN OF CONVENTIONAL
OXYGEN ELECTRODES

In this chapter work aimed at improving the performance of conventional oxygen membrane electrodes is described. The first section discusses the use of nickel hydroxide as a counter electrode in place of the conventional Ag/AgCl electrode. The reasons for replacing AgCl in clinical membrane electrodes has been discussed in Section 1.6.

The second section describes the use of an electrolyte containing 1,8-dihydroxyanthroquinone to improve the response time of an oxygen membrane electrode to a sample gas concentration step.

6.1. THE NICKEL HYDROXIDE REFERENCE/COUNTER ELECTRODE

The nickel hydroxide electrodes were prepared by d.c. cathodic deposition on electrode E (Ni disc) from 0.1 M $\text{Ni}(\text{NO}_3)_2$ at 1 mA/cm^2 .⁽⁹⁰⁾ A green layer of $\text{Ni}(\text{OH})_2$ was formed on the electrode surface. Experiments were carried out in 1 M KOH solution.

Potential of the Couple

A cyclic voltammogram of a small amount of $\text{Ni}(\text{OH})_2$ is shown in Figure 6.1. Black NiOOH is formed as the layer is oxidised. The current passed by the layer is proportional to the amount of $\text{Ni}(\text{OH})_2$ deposited.

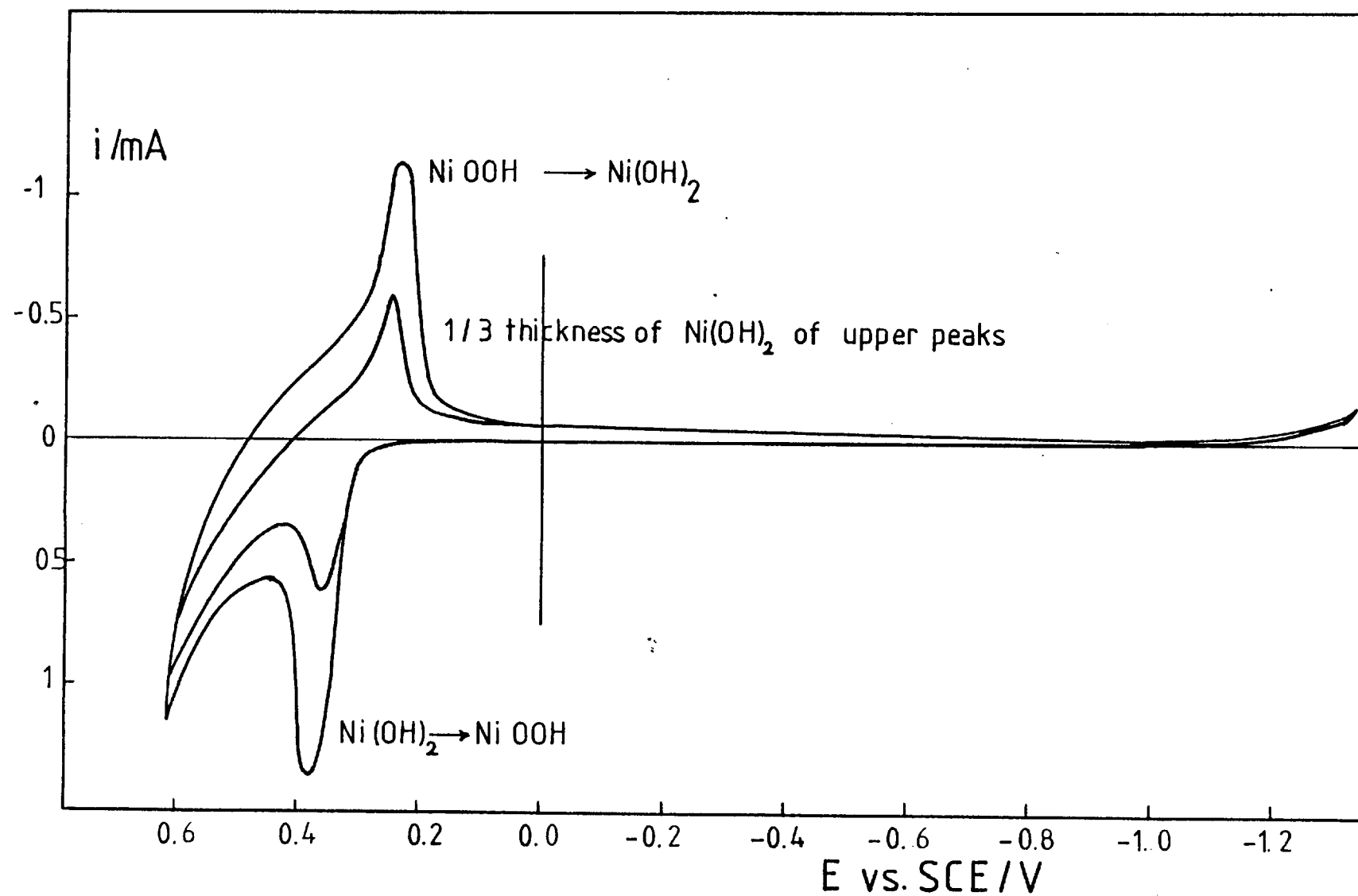


FIGURE 6.1. Cyclic voltammogram of a nickel hydroxide plated nickel electrode.

Since the two peaks are separated by only 150 mV the potential of the couple varies within acceptable limits as the electrode is oxidised. The working electrode will therefore remain polarised on the oxygen reduction limiting current plateau.

The potential variation of the couple as the electrode is oxidised was tested further by passing a constant current of 0.1 mA/cm^2 through the electrode. The potential was measured with respect to a saturated calomel reference electrode. The layer was deposited at 1 mA/cm^2 for two minutes, then the layer was cycled several times before the experiment shown in Figure 6.2 was carried out. The potential of the layer varied by only 100 mV over a 92% oxidation of the layer. About 70% of the current passed in plating was found to form electrochemically active nickel hydroxide. After a further ten complete cycles no appreciable loss of electrode material occurred.

The variation of electrode potential with current density was also tested. Figure 6.3 is a plot of potential vs. $\log$ (current density). A potential variation of only 100 mV occurred as the current density changed over five orders of magnitude.

Use of the Couple as a Reference/Counter Electrode

The use of the couple as an anode is illustrated in Figure 6.4, where a polarogram of a platinum disc (electrode F) in oxygen saturated molar potassium hydroxide

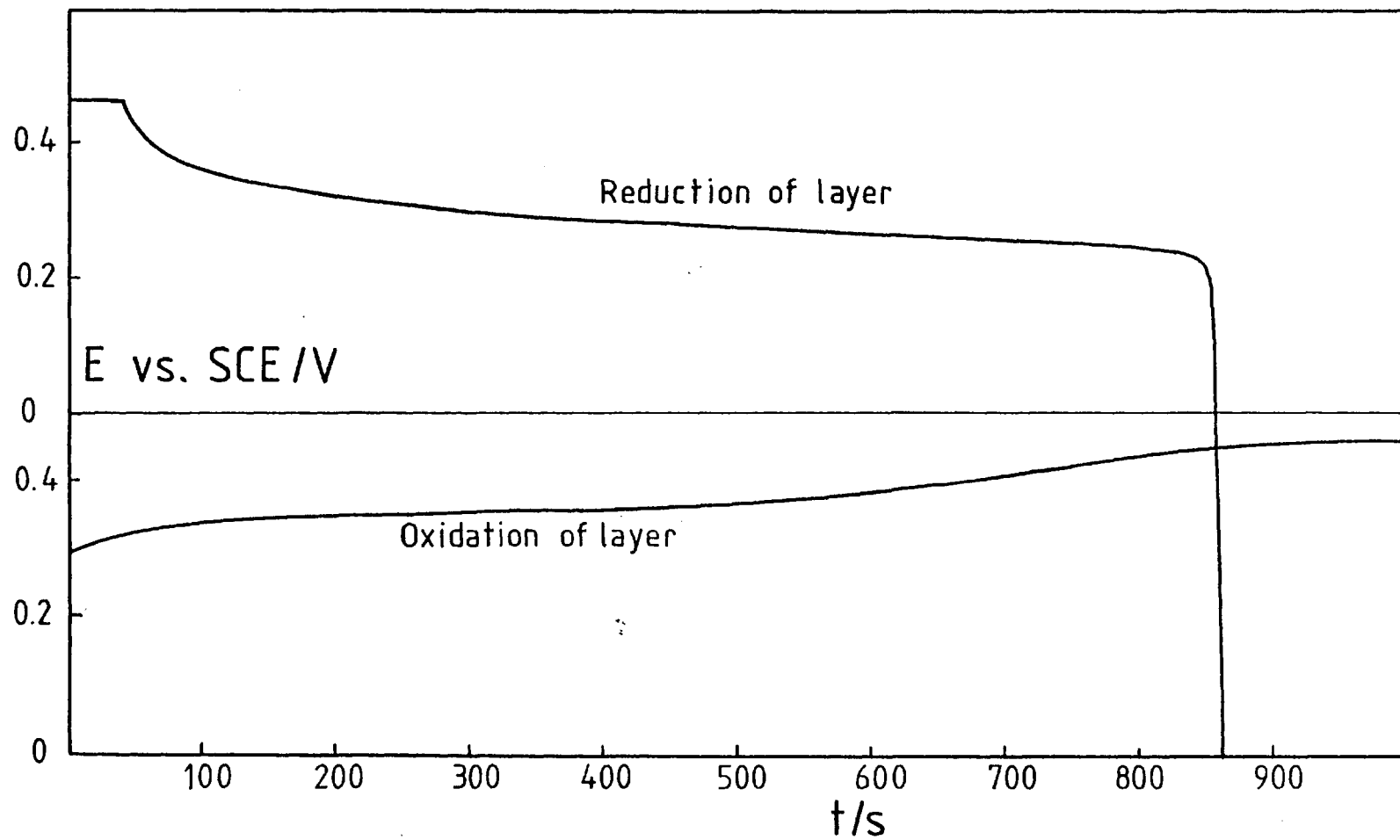


FIGURE 6.2. Potential variation of a nickel hydroxide electrode as a constant current is passed through the electrode.

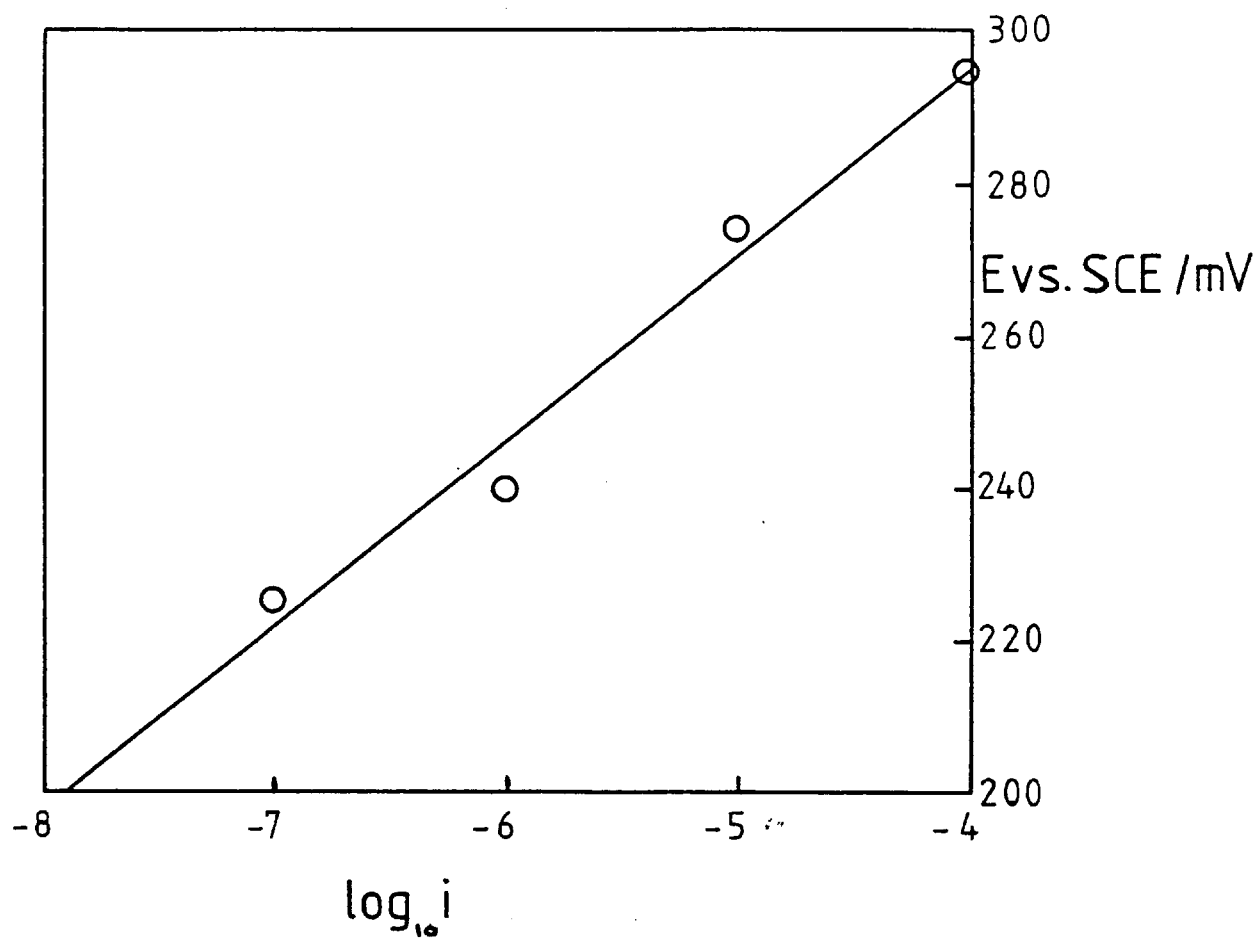


FIGURE 6.3. Variation of the potential of a nickel hydroxide electrode with current density.

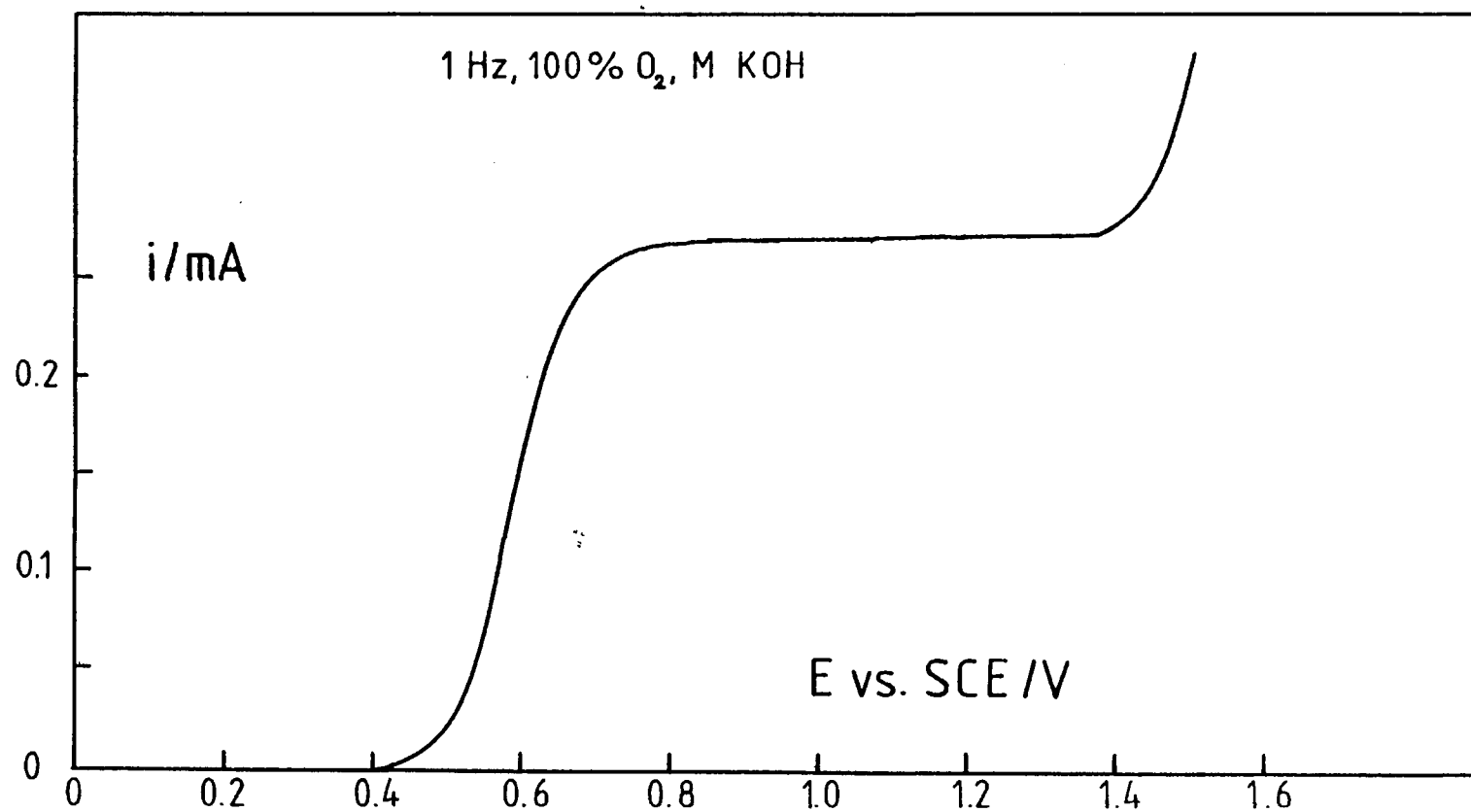


FIGURE 6.4. A polarogram of oxygen reduction on a rotating platinum disc electrode with a nickel hydroxide electrode as reference/counter.

solution is shown. The polarogram was run against a $\text{Ni}(\text{OH})_2$ reference/counter electrode of area 15 cm^2 , with a nickel hydroxide surface coverage of about $50 \mu\text{M}/\text{cm}^2$, giving a stored capacity of 75C. The platinum disc was held on the oxygen reduction plateau for three days, and in this time the oxygen reduction current decreased by only 5%, while about 65C were passed.

The Levich plot of oxygen reduction on the Pt disc was linear when the $\text{Ni}(\text{OH})_2$ surface area was large, with a slope of $0.28 \text{ mA}/\sqrt{\text{Hz}}$. Decreasing the anode area to 0.2 cm^2 caused the Levich plot to become curved, as shown in Figure 6.5a. A plot of $1/i$ vs. $1/W$ (Koutecky Levich) is shown in Figure 6.5b, and gives the limiting value of i as $W \rightarrow \infty$ as:-

$$i_{\text{Lim}} = 15 \text{ mA}/\text{cm}^2 \quad 6.1$$

This value is in good agreement with that found by Briggs et al. ⁽⁹¹⁾

Dendrite Formation

In order to ensure that nickel dendrites would not form on oxygen electrode cathodes, polarograms were run of $\text{Ni}(\text{NO}_3)_2$ solutions on Pt, Au and Ag cathodes. No Ni^{2+} reduction waves were observed.

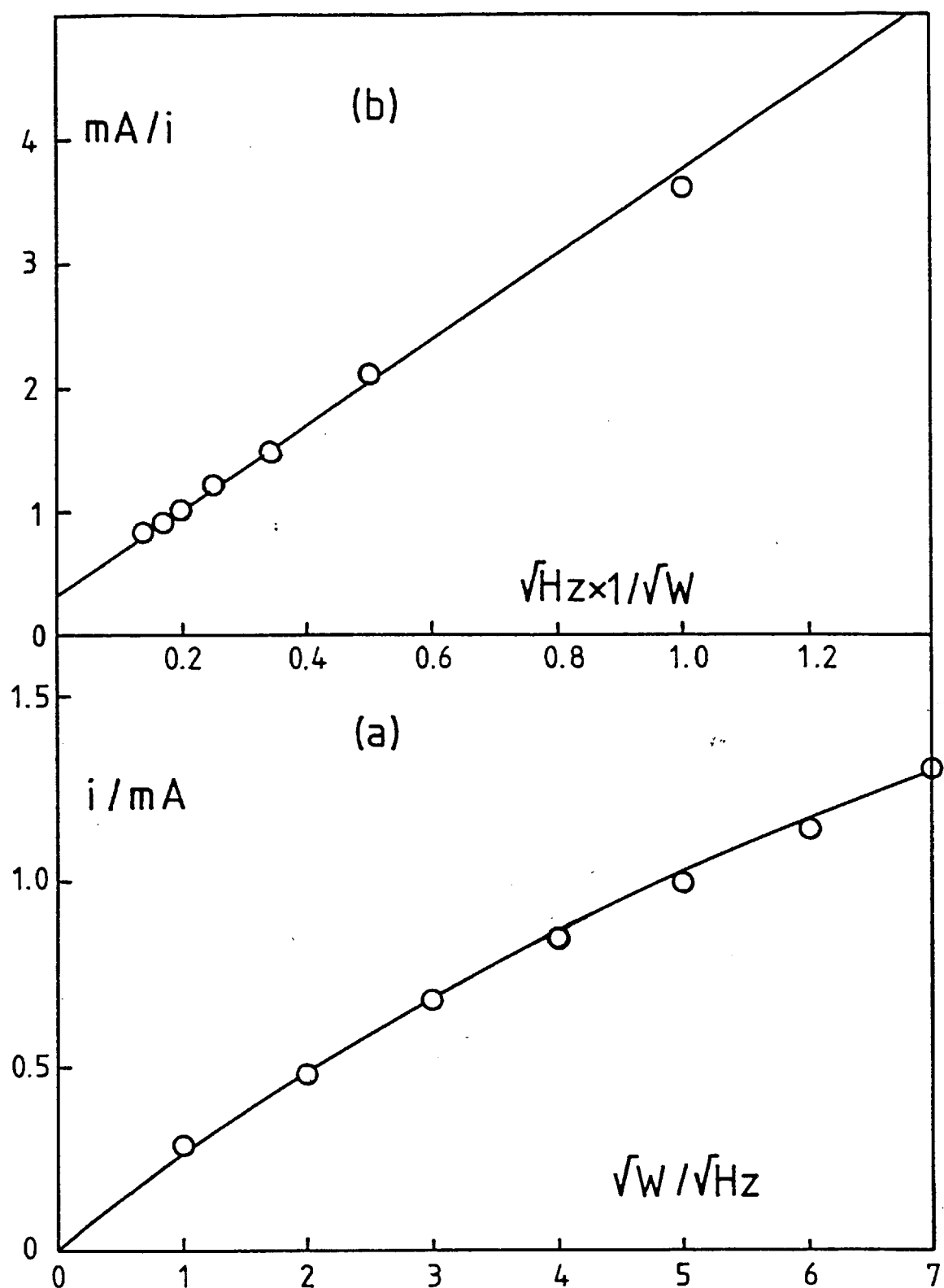


FIGURE 6.5. Levich plot and Koutecky-Levich plot for oxygen reduction when a nickel hydroxide electrode of area $\sim 0.2 \text{ cm}^2$ was used as reference/counter.

Clinical Electrode Work

At this point in the development of the electrode, membrane electrodes were made with nickel hydroxide anodes at the John Radcliffe Infirmary, Oxford, where they were tested by S. Putnam. The electrodes were designed with the anode and cathode in close proximity, so that the clinical electrode situation was closely mimicked.

Initial results have been very encouraging.⁽¹³⁵⁾ To minimize the effects of CO_2 , buffered pH 10 carbonate electrolyte was used as the internal solution. The potential of the $\text{Ni}(\text{OH})_2$ couple was shifted, but the electrode still functioned well. The electrodes were used for up to four weeks, and in that time the electrode output remained stable. No electrode failures due to dendrite formation were observed. A paper has recently been presented on the $\text{Ni}(\text{OH})_2$ anode.⁽¹³⁶⁾

6.2. RESPONSE TIMES OF AN OXYGEN MEMBRANE ELECTRODE

The theoretical response of an oxygen membrane electrode to a step increase in sample concentration is described by equation 2.64. If $i_{(L, t=\infty)} = 0$, we obtain:-

$$i_L(t) = 2i_{L(t=0)} \sum_{n=0}^{\infty} (-1)^n \exp \frac{-n^2 \pi^2 D_m t}{b^2} \quad 6.2$$

Hale⁽¹¹⁷⁾ has shown the response of an oxygen electrode to a large perturbation in sample concentration, such as an air-nitrogen step, is not well described, and the rate of change of current following such a perturbation is much more sluggish than is predicted theoretically. He presented and experimentally verified a model which showed that hydrogen peroxide formation, and its subsequent slow removal by heterogeneous disproportionation, is the cause of this sluggish response.

In order to improve the response time of an electrode it is necessary to ensure that hydrogen peroxide does not accumulate in the electrolyte bulk. Brooks⁽¹¹³⁾ showed that 1,8-DHAQ reacted quickly (r.c. $\sim 10^6 \text{ M}^{-1} \text{ s}^{-1}$) with both oxygen and hydrogen peroxide, thereby reducing the oxygen to hydroxide ions. The response time of an oxygen membrane electrode should be able to be reduced and equation 6.1 followed more accurately by using the quinone in the electrolyte. The quinone should also prevent drift in the electrode output, since bulk peroxide formation is eliminated.

The test electrode used in this work was electrode 6. The gold ring prevented edge effects at the working electrode, ensuring that no lateral diffusion of quinone could occur, which would have caused a sluggish time response. The electrode was used with 12 μm Teflon membrane, and the electrolyte was molar KOH, saturated with 1,8DHAQ.

Stability of the Electrode

A polarogram of the gold working electrode is shown in Figure 6.6a. Note the anodic wave in air is smaller than in nitrogen, because of the hydroquinone-oxygen reaction. When the disc was polarised at -0.9 V the current was proportional to the oxygen partial pressure (Figure 6.6b). The electrode stability in air saturated water was tested. The output was found to be stable for up to two weeks.

Response Times

The response of the electrode to an air to nitrogen step change is shown in Figure 6.7a. The response was found to be very reproducible when the electrolyte contained the anthhoquinone, and was independent of electrode age and pretreatment of the electrode surface.

Figure 6.7b is a typical transient obtained when the electrolyte was 1 M KOH without the quinone. The response was very dependent on electrode pretreatment and age, which shows the hydrogen peroxide is removed by heterogeneous disproportionation, as Hale found.

In Figure 6.8 plots of $\log(i_L/i_{L,0})$ vs. t are shown. Equation 6.2 predicts the plots should be linear. The linearity is extended by about two orders of magnitude by using the quinone. The lack of linearity at values of $(i_{L,t}/i_{L,0})$ less than 10^{-3} may be due to residual oxidised quinone in the gap between the electrodes.

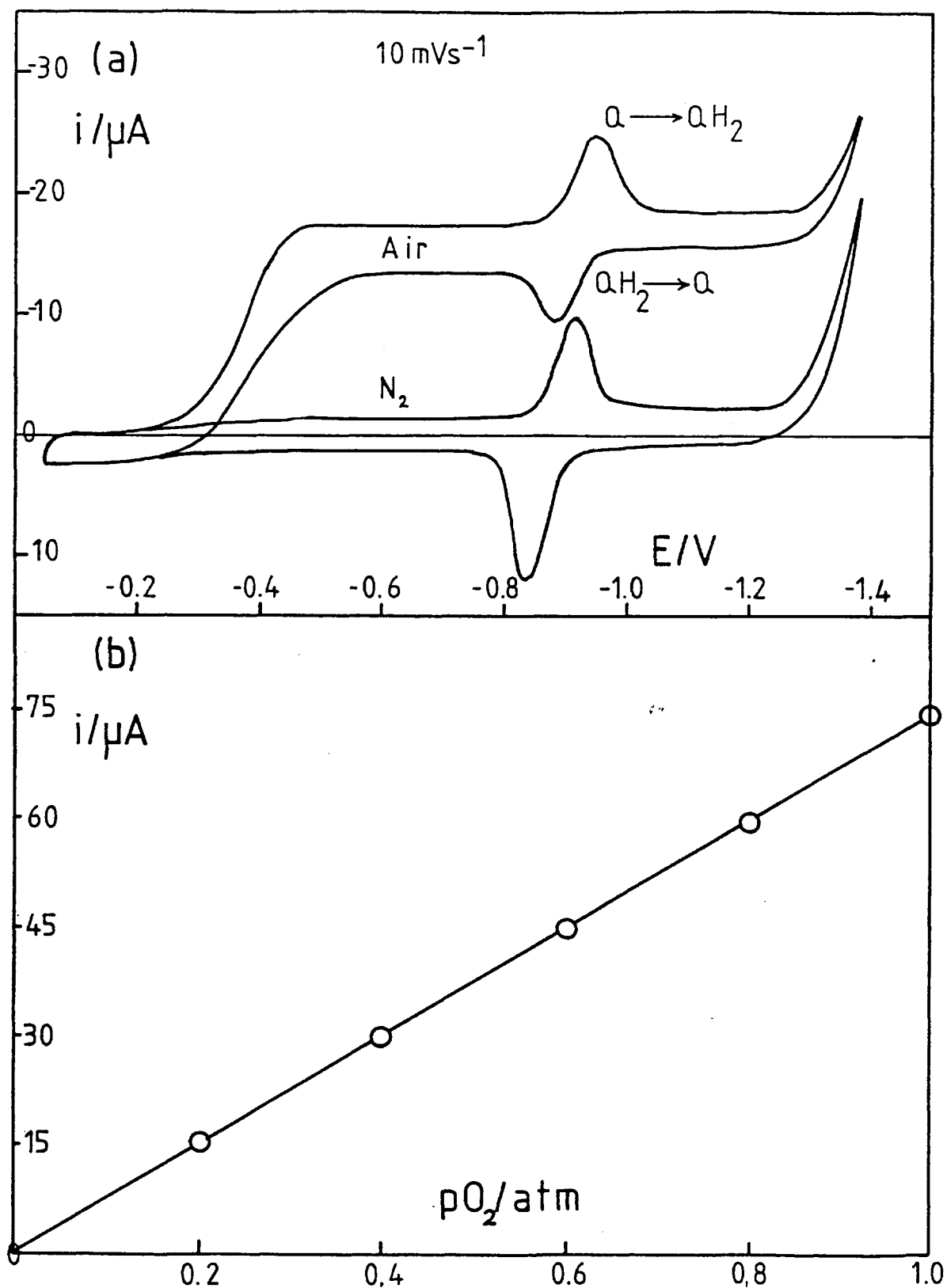


FIGURE 6.6. Polarogram of the gold disc of electrode 6 when the electrolyte contained 1,8 DHAQ and a plot of current vs. pO_2 .

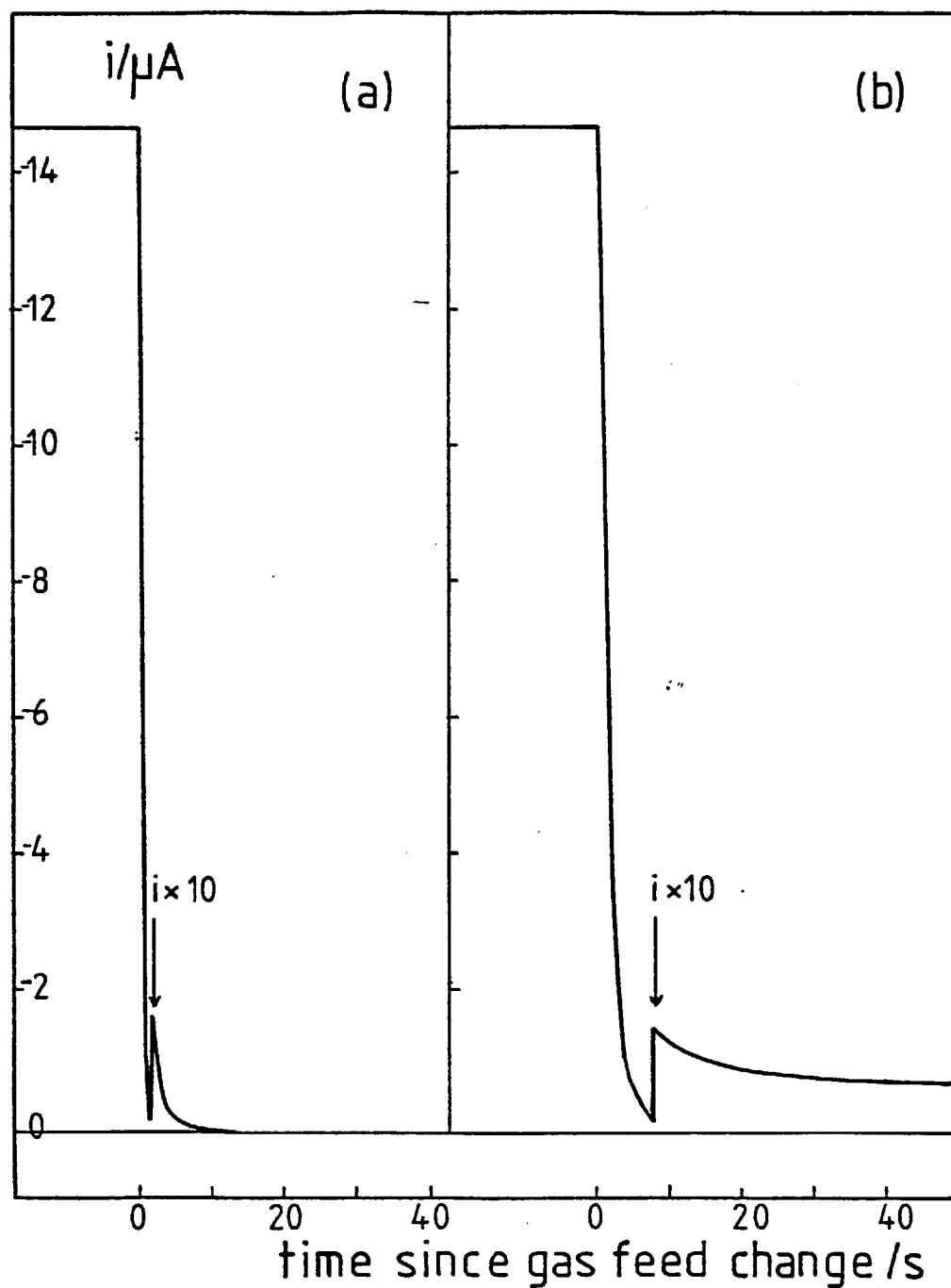


FIGURE 6.7. Response of electrode 6 to an air-nitrogen step change when the electrolyte was 1 M KOH with and without 1,8 DHAQ.

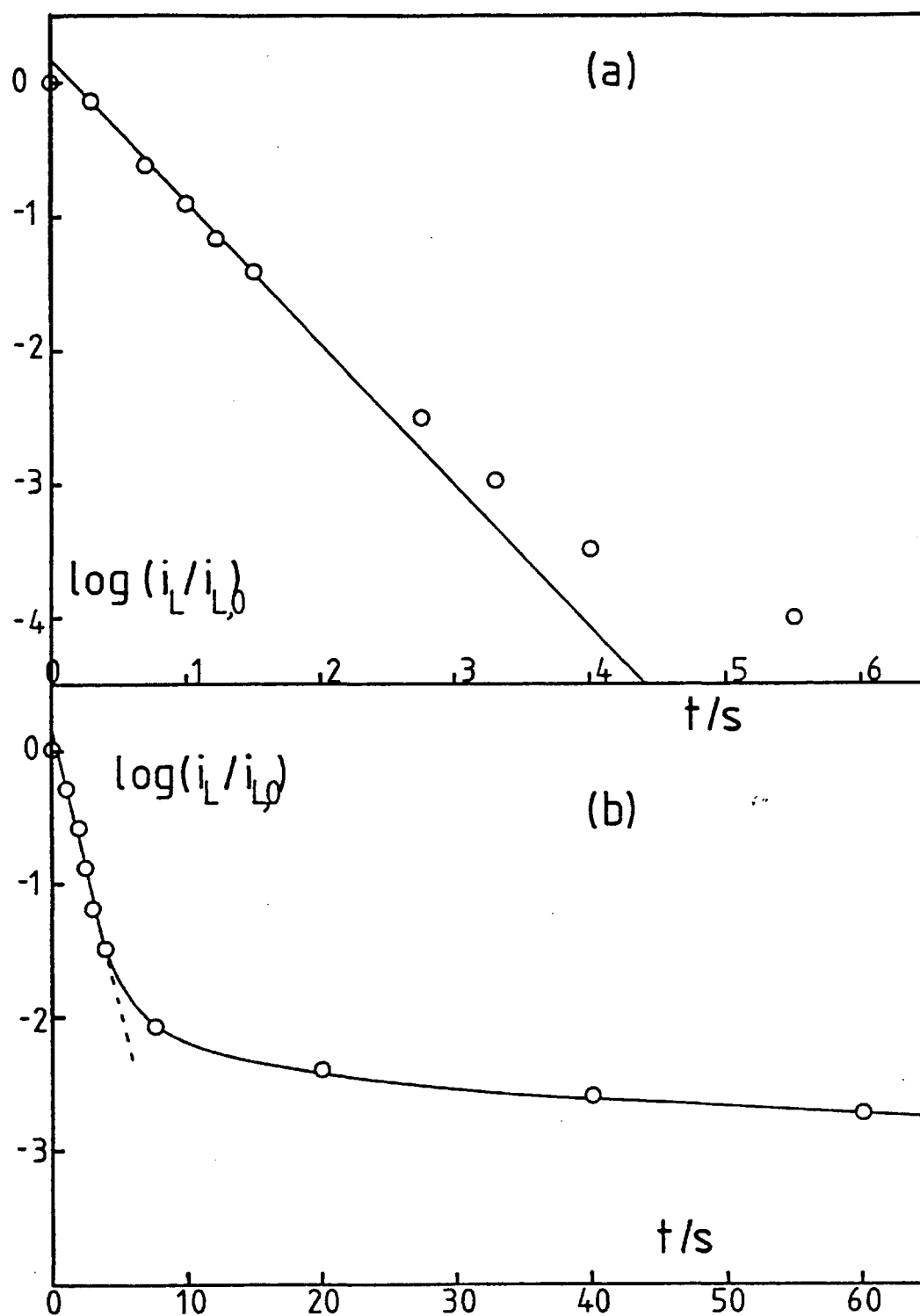


FIGURE 6.8. Plots of $(i_L/i_{L,0})$ vs. t from the transients shown in Figure 6.7.

6.8a. Electrolyte contains 1,8 DHAQ.

6.8b. Electrolyte is 1 M KOH.

APPENDIX 1. The Steady State Current at a CO₂ Membrane Electrode

In the steady state, equations 5.14 and 5.15 become:-

$$\frac{\partial^2 u}{\partial \chi^2} - \kappa v = 0 \quad 5.14$$

$$\frac{\partial^2 v}{\partial \chi^2} - \kappa v = 0 \quad 5.15$$

With boundary conditions:-

$$\chi = 0 \quad \gamma_0 = - \frac{\partial u}{\partial \chi}_0 = -2 \frac{\partial v}{\partial \chi}_0$$

$$u = 1$$

$$\chi = 1 \quad u = 0$$

$$\frac{\partial v}{\partial \chi}_1 = 0$$

The general solution to equation 5.15 is:-

$$v = v_0 \cosh(\sqrt{\kappa} \chi) - \frac{\gamma_0/2}{\sqrt{\kappa}} \sinh(\sqrt{\kappa} \chi) \quad A1.1$$

Differentiation of equation A1.1 and substitution of the $\chi = 1$ boundary conditions gives

$$v_o = \frac{1/2 \gamma_o}{\sqrt{\kappa} \tanh \sqrt{\kappa}} \quad A1.2$$

$$\therefore v = \frac{1/2 \gamma_o}{\sqrt{\kappa}} \frac{\cosh \sqrt{\kappa} \chi - \sinh \sqrt{\kappa} \chi}{\tanh \sqrt{\kappa} \chi} \quad A1.3.$$

Subtraction of equations 5.14 and 5.15 and integration gives:-

$$\begin{aligned} u - v &= (1 - v_o) - 1/2 \gamma_o \chi \\ &= 1 - \frac{1/2 \gamma_o}{\sqrt{\kappa} \tanh \sqrt{\kappa}} - 1/2 \gamma_o \chi \end{aligned} \quad A1.4.$$

At $\chi = 1$, $u = 0$, therefore

$$v_1 = 1/2 \gamma_o \left(1 + \frac{1}{\sqrt{\kappa} \tanh \sqrt{\kappa}} \right) - 1 \quad A1.5.$$

Also, from equation A1.3.

$$v_1 = \frac{1/2 \gamma_o}{\sqrt{\kappa} \sinh \sqrt{\kappa}} \quad A1.6.$$

Equations A1.5. and A1.6 give:-

$$\gamma_o = \frac{2}{1 + \frac{\cosh \sqrt{\kappa} - 1}{\sqrt{\kappa} \sinh \sqrt{\kappa}}} \quad A1.7.$$

$\therefore \gamma_o = 2$ when κ is large

$\gamma_o = 4/3$ when κ is small

APPENDIX 2. Derivation of the Steady State Concentration Profiles at a CO₂ Membrane Electrode

From equations A1.3, A1.4 and A1.5 we get:-

$$v = \frac{1}{\sqrt{\kappa} + \frac{\cosh\sqrt{\kappa}-1}{\sinh\sqrt{\kappa}}} \cdot \frac{\cosh\sqrt{\kappa}\chi}{\tanh\sqrt{\kappa}} - \sinh\sqrt{\kappa}\chi \quad \text{A2.1.}$$

And:-

$$u = v + 1 - \left(\chi + \frac{1}{\sqrt{\kappa}\tanh\sqrt{\kappa}} \cdot \frac{1}{1 + \frac{\cosh\sqrt{\kappa}-1}{\sqrt{\kappa}\sinh\sqrt{\kappa}}} \right) \quad \text{A2.2.}$$

For κ small, we obtain from equation A2.1:-

$$v = \frac{1}{\sqrt{\kappa}(1+\frac{1}{2})} - \frac{1}{\sqrt{\kappa}} - \sqrt{\kappa}\chi + \frac{1}{2\sqrt{\kappa}}\chi^2 \quad \text{A2.3.}$$

$$\therefore v = \frac{2}{3} - \frac{1}{\kappa} - \chi + \frac{1}{2}\chi^2 \quad \text{A2.4.}$$

Therefore from equation A2.2. and A2.4.:-

$$u = \frac{2}{3} - \frac{1}{\kappa} - \frac{2\chi}{3} + 1 + \frac{1}{3}\chi^2 - \left(\chi + \frac{1}{\kappa} \right) \frac{1}{1+\frac{1}{2}} \quad \text{A2.5.}$$

$$\therefore u = 1 - \frac{4}{3}\chi + \frac{1}{3}\chi^2 \quad \text{A2.6.}$$

At the electrode surface, $u = 0$. Therefore from equation 5.6

$$\frac{a}{a_{\infty}} = \frac{4x}{3} - 1/3x^2 \quad \text{A2.7.}$$

Differentiation of equations A2.4 and A2.6 show that throughout the electrolyte:-

$$\frac{\partial u}{\partial x} - \frac{\partial v}{\partial x} = -2/3 \quad \text{A2.8.}$$

Figure A2.1. shows the resulting concentration profiles.

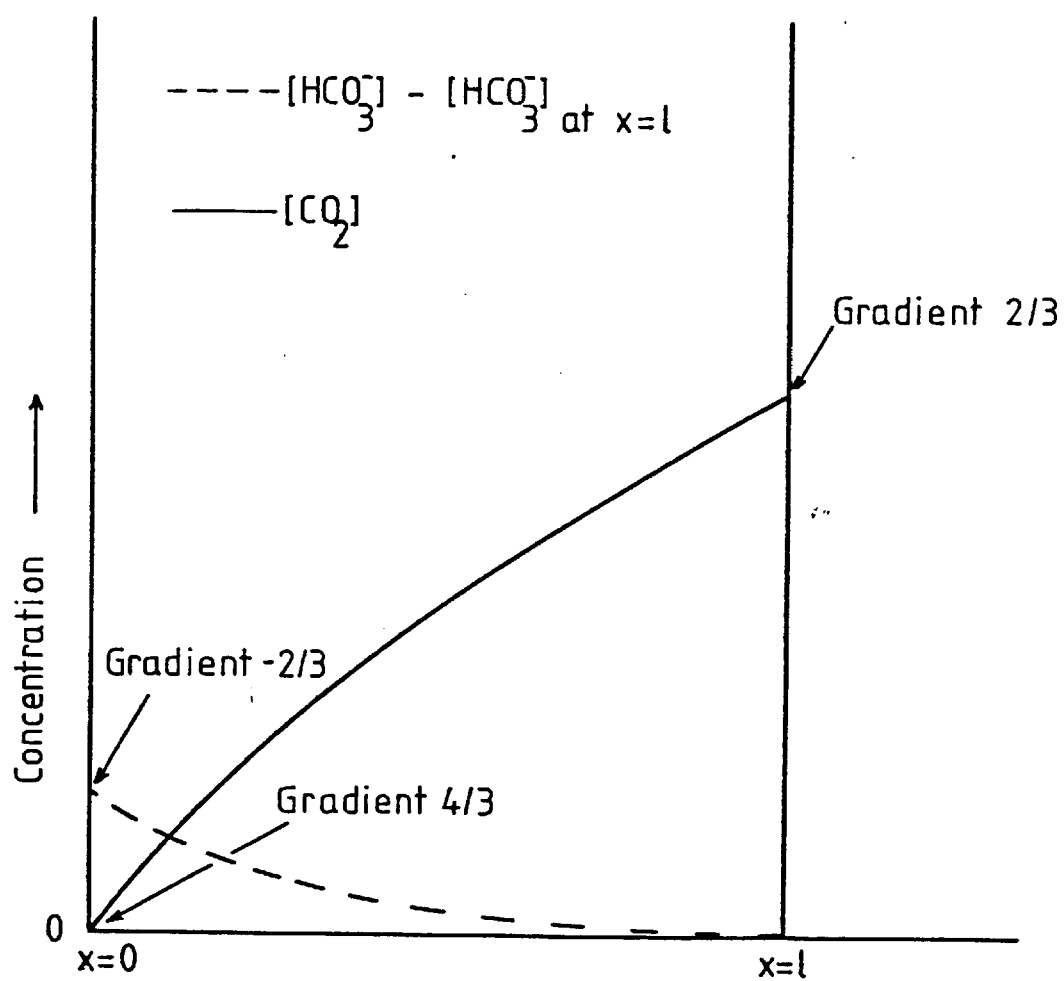


Figure A2.1. Concentration Profiles in the Electrolyte Layer.

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