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- 1 - A STUDY OF OXYGEN EVOLUTION ON SEMICONDUCTING
OXIDES IN ALKALINE MEDIA.
- 2 - AN ELECTROCHEMICAL - CHEMICAL METHOD FOR THE
EXTRACTION OF OXYGEN FROM AIR.

A thesis submitted for the
degree of
Doctor of Philosophy
by

SAMEER M. JASEM

at
Department of Chemistry
The City University
London

This work was carried out under the supervision
of Dr. A.C.C. Tseung.

TO MY MOTHER AND FATHER

A C K N O W L E D G E M E N T

I would like to express my sincere thanks to my Supervisor, Dr. A.C.C. Tseung, for his continuous interest, constructive suggestions and encouragement during the course of this work.

I would like to thank [REDACTED] [REDACTED] [REDACTED] and the other colleagues in the Electrochemical Research Group for many helpful discussions. Thanks are also due to the Iraqi Government for its financial support.

S.M. JASEM,

Department of Chemistry,
The City University,
St. John Street,
London E.C.1.

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A B S T R A C T

Oxygen Evolution

The oxygen evolution reaction is of particular interest to secondary metal-air batteries, water electrolysis plants and oxygen extractors. Criteria have been suggested for the selection of possible active materials for the oxygen evolution reaction. A survey of various metal oxides based on these criteria suggested that NiCo_2O_4 is of particular interest. Teflon bonded electrodes based on this material gave $3\text{A}/\text{cm}^2$ at 1.72V vs D.H.E., 70°C , 5N KOH. The anodic performance of the other compositions in the $\text{Ni}_y\text{Co}_x\text{O}_4$ series, where $0 \leq x \leq 3$; $0 \leq y \leq 2$, were evaluated at different temperatures.

Two types (Teflon bonded and non Teflon bonded) of NiCo_2O_4 porous electrodes were investigated, the Teflon bonded electrodes displayed higher performance and greater mechanical strength during the evolution of oxygen.

The effect of modifying the hydrophobic nature of Teflon bonded NiCo_2O_4 electrode surfaces by depositing a thin layer of NiCo_2O_4 (by thermal decomposition of Co/Ni nitrates) on the surface was investigated and the modified surface electrode showed a significant improvement in anodic performance.

Steady state measurements for oxygen evolution on porous electrodes are inaccurate for the determination of the kinetic parameters necessary for the kinetic studies due to the concentration polarization and the continuous change of the available surface area with current densities due to the

formation of bubbles. Therefore it is suggested that potentiostatic pulse technique could solve the above problems.

Reliable pulse measurements could be obtained, providing that the electrodes were initially anodized sufficiently to form stable higher oxides and that the potentials of these electrodes were maintained above that for reduction of the higher oxides.

Oxygen Extraction

A novel, integrated electrochemical-chemical method is described in this study. The system consists of a Teflon bonded graphite cathode, which reduces oxygen via a two electron process with the formation of HO_2^- ions in alkaline solution (5N KOH). The HO_2^- ions are chemically decomposed, using a suitable catalyst, to yield oxygen and a Teflon bonded NiCo_2O_4 anode is used to evolve oxygen electrolytically. At 40°C , 5N KOH, the power consumption of this device is only 2.69 Kwhr/1000 litres of oxygen, significantly lower than conventional electrochemical oxygen extractors (4.4 Kwhr/1000 litres oxygen).

Oxygen reduction on high surface area graphite in 5N KOH was investigated and the concentration of the peroxide ions produced was measured at different currents.

For the decomposition of hydrogen peroxide, two catalysts (CoFe_2O_4 and NiCo_2O_4) were evaluated, and the kinetics of H_2O_2 decomposition on these catalysts was investigated.

C O N T E N T S

	<u>Page</u>
<u>CHAPTER ONE</u>	
THE IMPORTANCE OF OXYGEN GAS AND OXYGEN PRODUCTION TECHNOLOGY.	
1.1. INTRODUCTION	1
1.2. OXYGEN PRODUCTION TECHNOLOGY	2
1.2.1. Separation of Air	2
1.2.2. Electrolysis	2
1.2.3. Different Methods for Oxygen Production	6
1.3. PROBLEMS IN OXYGEN UTILIZATION	7
1.4. A POSSIBLE EFFICIENT METHOD FOR OXYGEN PRODUCTION	8
<u>CHAPTER TWO</u>	
EXPERIMENTAL TECHNIQUES	
2.1. PREPARATION METHODS	10
2.1.1. Preparation of High Surface Area Graphite	10
2.1.2. Freeze Drying	11
2.2. CHARACTERIZATION TECHNIQUES	13
2.2.1. The B.E.T. Technique for Surface Area Measurement	13
2.2.2. X-Ray Analysis	17
2.2.3. Electron Microscopy	18
2.2.4. Electrical Conductivity Measurements	19
2.2.5. Atomic Absorption Spectroscopy	20
2.3. ELECTROCHEMICAL TESTING	20
2.3.1. Fabrication of Hydrophobic Electrodes	20
2.3.2. The Floating Electrode Cell System	22
2.3.3. The Reference Electrode System	24
2.3.4. Steady State Polarization	24
2.3.5. Ohmic Correction of Polarization Curves	26

	<u>Page</u>
<u>CHAPTER THREE</u>	
OXYGEN REDUCTION	
3.1. REVIEW OF PREVIOUS WORK	31
3.1.1. Electrode Materials for Oxygen Reduction	31
3.1.2. Oxygen Reduction on Carbon and Graphite in Alkaline Solution	34
3.1.3. Oxygen Reduction on Nobel Metals in Alkaline Solution	36
3.2. SELECTION OF MATERIAL FOR OXYGEN REDUCTION	39
3.3. POROUS ELECTRODE	39
3.4. MATERIALS AND METHODS	42
3.4.1. Preparation of High Surface Area Graphite	42
3.4.2. Fabrication of Teflon bonded Graphite Electrode	42
3.4.3. The Electrolyte	42
3.4.4. Polarization Runs	44
3.5. RESULTS AND DISCUSSION	45
3.5.1. Steady State Performance	45
3.5.2. Effect of Graphite Loading and Teflon Ratio on the Performance of Teflon bonded Graphite Electrode for Oxygen Reduction	46
3.5.3. Corrosion Scans	49
3.5.4. Current Stability of Oxygen Reduction on Graphite Electrodes	49
3.6. HYDROGEN PEROXIDE PRODUCTION	51

CHAPTER FOUR

HYDROGEN PEROXIDE DECOMPOSITION	
4.1. SELECTION OF CATALYST FOR HYDROGEN PEROXIDE DECOMPOSITION	54
4.2. EXPERIMENTAL	59
4.2.1. Preparation of CoFe_2O_4 and NiCo_2O_4	59
4.2.2. Determination of Catalytic Activity	60

	<u>Page</u>
4.2.2a. H_2O_2 Decomposition Apparatus	61
4.2.2b. Analysis of Hydrogen Peroxide	61
4.2.2c. Description of a Typical Run	65
4.3. RESULTS AND DISCUSSION	66
4.3.1. X-Ray Analysis	66
4.3.2. The Initial Rate Constant	66
4.3.3. The Reaction Order and Reaction Rate Constant	70
4.3.4. Activation Energy for H_2O_2 Decomposition	71
4.3.5. The Stability of the Catalysts (Storage Effect)	78
 <u>CHAPTER FIVE</u>	
OXYGEN EVOLUTION	
5.1. REVIEW OF ELECTRODE MATERIALS FOR OXYGEN EVOLUTION	79
5.2. CRITERIA FOR SELECTING A MATERIAL FOR OXYGEN EVOLUTION	80
5.2.1. Metal/Metal Oxide and Lower Metal/Oxide/ Higher Metal Oxide Couples	80
5.2.2. Electrical Resistivity	81
5.2.3. Corrosion Resistance	83
5.2.4. Catalytic Properties of Semi-conducting Oxides	83
5.2.5. Electrocatalyst Microstructure	83
5.3. LIST OF CANDIDATE MATERIALS	84
5.4. MATERIALS AND METHODS	86
5.4.1. Preparation of Catalysts	86
5.4.1a. Nickel Cobalt Oxides	86
5.4.1b. Lithiated Nickel Oxide	86
5.4.2. Electrode Fabrication	86
5.4.3. Steady State Potentiostatic Measurements	87
5.5. RESULTS AND DISCUSSION	
5.5.1. Physical Properties of Nickel Cobalt Oxide Samples	87

	<u>Page</u>
5.5.2. The Importance of Aggregate Surface Area	93
5.5.3. EDAX. - Analysis	96
5.5.4. Steady State Oxygen Evolution	102
5.5.5. Effect of Preanodization on Teflon bonded Electrodes	109
5.5.6. Oxygen Evolution on Metal Substrates	112
5.5.7. The Contribution of the Current Collector to the Overall Performance of the Teflon bonded Electrode	119
5.5.8. Effect of the Catalyst/Teflon Ratio on the Anodic Performance of Teflon bonded NiCo_2O_4 Electrode	121
5.5.9. Electrode Structure	121
5.5.10. Modification of the Surface of Teflon bonded NiCo_2O_4 Electrodes	125
5.5.11. Mechanical Strength of Teflon and non-Teflon bonded porous NiCo_2O_4 Electrodes	126
5.5.12. Stability of Teflon bonded NiCo_2O_4 Electrodes	130
5.5.13. Physical Disruption During Oxygen Evolution at High Current Density	133
5.5.14. Storage Effect	133
5.6. ALTERNATIVE OXIDE SYSTEMS	133
5.6.1. Anodic Performance of NiCo_2O_4 and Lithiated Nickel Oxide	134
5.6.2. Relative Activities of the Different Catalysts	134

CHAPTER SIX

A POTENTIOSTATIC PULSE STUDY OF OXYGEN EVOLUTION ON TEFLON BONDED NiCo_2O_4 ELECTRODES

6.1. KINETIC STUDIES OF OXYGEN EVOLUTION ON METALS	137
6.2. THE PROBLEMS OF KINETIC MEASUREMENTS ON POROUS ELECTRODES	141
6.3. EXPERIMENTAL	142
6.4. RESULTS AND DISCUSSION	143
6.4.1. Steady State Measurements for Oxygen Evolution on Teflon bonded NiCo_2O_4 Electrodes	143

	<u>Page</u>
6.4.2. Linear Sweep Voltammetry	146
6.4.3. Potentiostatic Pulse Technique	152
6.4.3a. Possible Errors in the Pulse Measurements	155
6.4.3b. Measurement of Double Layer Charging Time	155
6.4.4. Effectiveness Factor	158
6.4.5. Tafel Slopes and the Potentiostatic Pulse Measurements	160

CHAPTER SEVEN

AN INTEGRATED ELECTROCHEMICAL-CHEMICAL METHOD FOR THE EXTRACTION OF OXYGEN FROM AIR

7.1.	INTRODUCTION	168
7.2.	OXYGEN GENERATION BY ELECTROCHEMICAL METHODS	168
7.3.	AN INTEGRATED ELECTROCHEMICAL-CHEMICAL APPROACH TO THE PROBLEM	169
7.4.	EXPERIMENTAL	170
7.4.1.	Selection of Materials	170
7.4.2.	Preparation of Electrodes and Experimental Methods	171
7.5.	RESULTS AND DISCUSSION	171
7.5.1.	Steady State Performance	171
7.5.2.	Hydrogen Peroxide Production	173
7.5.3.	Hydrogen Peroxide Decomposition	173
7.5.4.	Oxygen Extraction from Air	176
7.6.	A POSSIBLE DESIGN FOR THE PRESENT OXYGEN EXTRACTION CELL	179

CHAPTER EIGHT

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

8.1.	CONCLUSIONS	182
8.1.1.	Oxygen Reduction	182
8.1.2.	The Decomposition of H_2O_2	182

	<u>Page</u>
8.1.3. Oxygen Evolution	183
8.1.4. The Present Electrochemical-Chemical Method for Oxygen Extraction	185
8.2. SUGGESTIONS FOR FURTHER WORK	186
8.2.1. Oxygen Evolution	186
8.2.2. Oxygen Extraction	188
REFERENCES	190
APPENDIX A	198
APPENDIX B	200

INDEX OF TABLES

	<u>Page</u>
1.1. Summary of electrolysis cell performance	5
3.1. Hydrogen peroxide concentration produced from oxygen reduction on graphite at different current densities	53
4.1. Activity of a series of catalysts for H_2O_2 decomposition at $22^\circ C$	55
4.2. Comparison of catalyst activities for H_2O_2 decomposition	57
4.3. X-ray analysis of $CoFe_2O_4$ and A.S.T.M. x-ray powder data for $CoFe_2O_4$ and the possible impurities in $CoFe_2O_4$ prepared by hydroxide co-precipitation	67
5.1. Properties of semiconducting oxides	85
5.2. Weights of cobalt/nickel nitrates used for the preparation of (10g) nickel-cobalt oxides, by freeze drying	89
5.3. X-ray analysis of nickel cobalt oxides prepared by freeze drying	90
5.4. A.S.T.M. X-ray powder data for $NiCo_2O_4$ and the possible impurities in nickel cobalt oxides	91
5.5. Physical properties of the nickel cobalt oxides	94
5.6. EDAX analysis of nickel and cobalt in freeze dried nickel cobalt oxides	97
6.1. Tafel slopes and i_0 (obtained from steady state measurements) for oxygen evolution on preanodized Teflon bonded $NiCo_2O_4$ electrode at different temperatures	146
6.2. Double layer charging time measurements on Teflon bonded $NiCo_2O_4$ electrode at different pulse amplitude	156
6.3. Tafel slopes and i_0 (obtained from potentiostatic pulse measurements) for oxygen evolution on pre-anodized Teflon bonded $NiCo_2O_4$ electrode	164

	<u>Page</u>
7.1. The first order rate constant ($K_{f,m}$) and the initial rate constant ($K_{I,m}$) for the H_2O_2 decomposition reaction on $NiCo_2O_4$ powder, $CoFe_2O_4$ powder, Teflon bonded $NiCo_2O_4$ electrode and porous $NiCo_2O_4$ electrode	175
7.2. Summary of the results obtained for the extraction of oxygen from air.	178

INDEX OF FIGURES

	<u>Page</u>
1.1. Principal components of an oxygen production (air separation) plant	3
2.1. The nickel mill	12
2.2. Freeze drying apparatus	12
2.3. B.E.T. Apparatus	16
2.4. The floating electrode cell	23
2.5. Dynamic hydrogen electrode (D.H.E.)	25
2.6. Schematic circuit for potentiostatic polarization studies	29
2.7. Schematic circuit for galvanostatic polarization studies	29
2.8. Circuit diagram for interrupter measurements	30
2.9. Traces of electrode potential and currents obtained using the interrupter circuit	30
2.10. Porous electrode equivalent ohmic circuit	30
3.1. (a-d) Stages in the peroxide mechanism	40
3.2. Rate of change of surface area with grinding time for graphite	43
3.3. Steady state measurements of oxygen reduction on Teflon bonded graphite and Pt black electrodes	47
4.1. The hydrogen peroxide decomposition apparatus	62
4.2. The injection device used in the H_2O_2 decomposition experiments	63
4.3. The new method of delivering the catalyst in the H_2O_2 decomposition experiments	63
4.4. Volume of oxygen evolved versus time for H_2O_2 decomposition, at $25^\circ C$, by $CoFe_2O_4$ (prepared by hydroxide co-precipitation)	68

	<u>Page</u>
4.5. Volume of oxygen evolved versus time, for H_2O_2 decomposition, at 25°C , by NiCo_2O_4 (prepared by freeze drying)	69
4.6. $\log(1 - \frac{c}{a})$ versus time plot for H_2O_2 decomposition at 25°C , by CoFe_2O_4 (hydroxide co-precipitation)	72
4.7. $\log(1 - \frac{c}{a})$ versus time plot, for H_2O_2 decomposition, at 25°C , by NiCo_2O_4 (freeze drying)	73
4.8. Activation energy plot for H_2O_2 decomposition, using $K_{f,m}$ on NiCo_2O_4 (freeze drying)	76
4.9. Activation energy plot for H_2O_2 decomposition, using $K_{I,m}$ on NiCo_2O_4 (freeze drying)	77
5.1. The cell used in oxygen evolution study	88
5.2. (a - E) Electron micrographs of nickel cobalt oxides, prepared by freeze drying	98-100
5.3a. A typical EDAX analytical concentration count for cobalt and nickel in NiCo_2O_4	101
5.3b. An EDAX analytical concentration count for cobalt and nickel in cobalt oxide and nickel oxide respectively	101
5.4. Steady state measurements for oxygen evolution on Teflon bonded Co_3O_4 electrode, at different temperatures	103
5.5. Steady state measurements for oxygen evolution on Teflon bonded NiCo_2O_4 electrode, at different temperatures	104
5.6. Steady state measurements for oxygen evolution on Teflon bonded $\text{Ni}_{1.5}\text{Co}_{1.5}\text{O}_4$ electrode, at different temperatures	105
5.7. Steady state measurements for oxygen evolution on Teflon bonded Ni_2CoO_4 electrode, at different temperatures	106

	<u>Page</u>
5.8. Steady state measurements for oxygen evolution on Teflon bonded NiO electrode, at different temperatures	107
5.9. Variation in current density and activation energy with composition for oxygen evolution on nickel cobalt oxides	108
5.10. Steady state measurements for oxygen evolution on Teflon bonded NiCo_2O_4 electrode before and after anodization	111
5.11. Steady state measurements for oxygen evolution on porous nickel, nickel screen and platinum screen	113
5.12. Oxygen evolution on nickel screen and porous nickel as a function of time	114
5.13. Oxygen evolution on Pt screen as a function of time	118
5.14. Steady state measurements for oxygen evolution on Teflon bonded NiCo_2O_4 electrode (supported on pure Pt screen) at different temperatures	120
5.15. Effect of Teflon content on the performance of Teflon bonded NiCo_2O_4 electrode for oxygen evolution	122
5.16. Effect of catalyst loading on the performance of Teflon bonded NiCo_2O_4 electrodes for the evolution of oxygen	127
5.17. Effect of catalyst loading on the performance of porous (non-Teflon bonded) NiCo_2O_4 electrode for the evolution of oxygen	128
5.18. Steady state measurements for oxygen evolution on Teflon bonded and surface modified Teflon bonded NiCo_2O_4 electrodes	129
5.19. Oxygen evolution on Teflon bonded NiCo_2O_4 electrodes at 25°C , as a function of time	131
5.20. Oxygen evolution on Teflon bonded NiCo_2O_4 electrodes, at 80°C , as a function of time	132
5.21. Steady state measurements for oxygen evolution on Teflon bonded NiCo_2O_4 and lithiated nickel oxide electrodes (at 60°C)	135

	<u>Page</u>
5.22. Steady state measurements for oxygen evolution on Teflon bonded platinum black electrode, at different temperatures	136
6.1. V-log i plot of steady state measurements for oxygen evolution on preanodized Teflon bonded NiCo_2O_4 electrode	144
6.2. V-log i plot of steady state measurements for oxygen evolution on Teflon bonded NiCo_2O_4 electrode	145
6.3. Circuit for linear sweep voltammetry	148
6.4. Cyclic voltammogram for anodic polarization region on Teflon bonded NiCo_2O_4 electrode	150
6.5. Cyclic voltammograms for anodic polarization region on nickel screen at different temperatures	151
6.6. Schematic circuit diagram for potentiostatic pulsing	154
6.7. Schematic circuit diagram for galvanostatic pulsing	154
6.8. Double layer charging trace of Teflon bonded NiCo_2O_4 electrode	157
6.9. Steady state and potentiostatic pulse measurements for oxygen evolution on preanodized Teflon bonded NiCo_2O_4 electrode	161
6.10. V-log i plot of potentiostatic pulse measurements for oxygen evolution on preanodized Teflon bonded NiCo_2O_4 electrode	162
6.11. V-log i plot of potentiostatic pulse measurements (pulsing from 1.5V) for oxygen evolution on preanodized Teflon bonded NiCo_2O_4 electrode	163
6.12. Potentiostatic pulse traces for oxygen evolution on preanodized Teflon bonded NiCo_2O_4 electrode	166
6.13. Potentiostatic pulse traces for oxygen evolution on preanodized Teflon bonded NiCo_2O_4 electrode (pulsing from 1.5V)	167
7.1. Schematic diagram of the oxygen extraction cell	172
7.2. Steady state measurements for oxygen evolution on Teflon bonded Pt black and NiCo_2O_4 electrodes	174
7.3. Design for the present oxygen extractor	181

CHAPTER ONE

THE IMPORTANCE OF OXYGEN GAS AND OXYGEN
PRODUCTION TECHNOLOGY

1.1. INTRODUCTION

Oxygen has many long-established uses in many industrial, medical and scientific areas.

Industrial examples include steel making and metal fabrication (70% of oxygen produced is used in this application)¹. Oxygen is invaluable as a chemical feed stock, along with methane for acetylene production, and in oxidation of hydrocarbons such as ethylene to make ethylene oxide.

In the manufacturing industries oxygen is essential for cutting, welding and brazing where it is used as the oxidant for acetylene, hydrogen or metal powder to attain the extremely high temperatures required.

It is mixed with 5% carbon dioxide as a respiratory gas for use in the treatment of patients. It has similar applications as a life support gas in many hostile environments such as deep mines, space or high altitudes.

Future and limited present applications include sewage treatment and coal gasification. Liquid oxygen is used along with liquid hydrogen in rockets. At present about 1.2 million bottles of oxygen (i.e. 8.16×10^9 liter) are used each month in the U.K. alone.

A recent survey¹ in the United States showed that oxygen is the largest volume industrial gas both in monetary value and physical quantity. Since 1969 oxygen production has grown at a rate of 7% annually and stood at 2.66×10^{12} liter in 1973¹.

1.2. OXYGEN PRODUCTION TECHNOLOGY

The main methods of producing oxygen commercially are the separation of air (cryogenic processes) and electrolysis.

1.2.1. Separation of Air

A oxygen plant is illustrated schematically in Figure 1.1. At the heart of the plant is the so called "cold box", including heat exchangers, condensers etc., where the actual fractionation of air takes place. To carry out the distillation the air must first be compressed, and this costs, in energy terms, for 98% purity at slightly more than one atmosphere pressure, 350 KW hr/ton for a 400 ton/day plant². Virtually all commercial oxygen, for convenience of transportation and storage, is liquified and this requires a further 750 KW hr/ton expenditure of energy².

Higher purity can only be achieved by further energy expenditure. There is a 7% drop in power requirement per ton for every 5% reduction in oxygen purity from 99.5%.

However, the apparatus needed for such production is complex and the energy requirements are substantial.

1.2.2. Electrolysis

The cell for the production of gaseous hydrogen and oxygen by the electrolysis of water, consists of an electrolyte (usually an aqueous basic solution), circulating between two electrodes, separated by a membrane which permits ion transfer between the two electrodes while preventing mixing of the product gases. The early electrolysis cells were "unipolar" in which

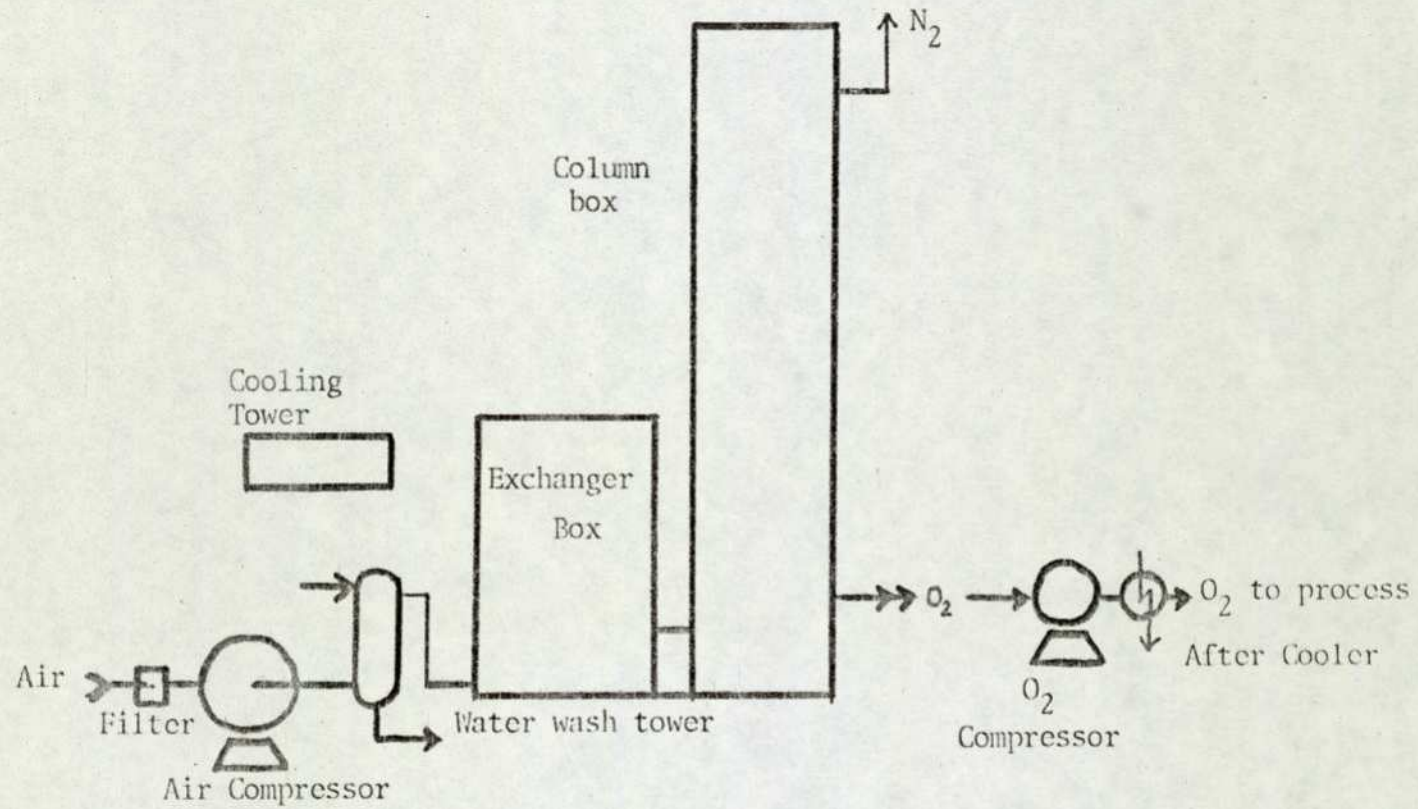


Fig. 1.1 PRINCIPAL COMPONENTS OF AN OXYGEN PLANT

a single cell could contain several electrodes, each of a fixed polarity. This type is considered out dated since it has a lower efficiency and requires more space than the "bipolar" type, which is the most common present day cell. In this arrangement, the cells are stacked in series such that the anode of one cell is the cathode of the adjacent cell and also the dividing cell wall. These cells are joined together to form a pack and pressed together between end electrodes, which are charged by a direct current source.

The "bipolar" arrangement reduces the internal resistance thus the power requirement.

The circulating electrolyte serves to remove the heat generated, facilitates the replenishment of the electrolyte and carries the evolved gas away from the electrode surfaces.

A recent report³ describes many types of electrolyzers and gives a review of previous work. Table (1.1), from that report, summarises the electrolysis cell performance of the systems discussed.

Currently the most advanced electrolysis system is that devised by General Electric⁴, which will become commercially available by 1980. It is claimed that this system eliminates both the alkaline electrolyte and the asbestos membranes by using a solid polymer electrolyte (S.P.E.), such as perfluorinated sulphonic acid. The S.P.E. when wetted with distilled water, becomes an excellent ionic conductor. The electrodes are pressed on to the SPE to give a cell capable of high current density

Table 1.1³

SUMMARY OF ELECTROLYSIS CELL PERFORMANCE

Manufacturer	P atm	T C°	Amp/cm ²	KOH conc. %	E volts	Efficiency %
Electrolyser	1	70	0.16	28	2.04	74
Teledyne	6.8	82	0.43	25	1.84	82
Lurgi	30	95	0.19	25	1.84	82
Bamag	1	80	0.25	26	1.92	78
Norsk Hydro	1	80	0.15	25	1.87	81
Life system	1	93	0.65	35	1.84	82
G.E.	200	82	1.06	-	1.85	81

operation at low over voltage.

Typically the electrode potentials are -0.25 V and $+1.5$ V vs hydrogen electrode for the cathode and anode respectively at $1\text{A}/\text{cm}^2$, 80°C . Despite the expensive materials used in construction, the S.P.E. system represents a dramatic decrease in capital cost compared with current alkaline pressurized cells. This is primarily due to the much greater current densities which are achievable in the S.P.E. system. However the use of noble metals could still prove to be a limiting factor in the adoption of this system. Also, the polymer itself is highly corrosive to the metals with which it comes in contact and is extremely sensitive to water purity.

1.2.3. Different Methods for Oxygen Production

An electrolytic process for the separation of oxygen from air, without application of external current, was claimed⁵. In this process two electrolytic cells were employed with electrodes in each one and electrolyte circulating between them. Air was introduced in to the first cell at a pressure of 10 atm. and oxygen was removed from the other at a pressure of 1.5 atm. Coupling of the differential partial pressure electrodes produced a flow of electrons from the oxygen electrode to the air electrode, resulting in oxygen being separated from air at the high pressure cell, carried by the electrolyte to the low pressure cell and liberated. The types of electrodes used in this method and the experimental data for the cell performance were not given, hence the comparison between such method and those mentioned earlier

is difficult.

Another process for the production of oxygen has also been reported⁶. In this method air is mixed with the alkali solution of a compound to form a peroxide. This peroxide can in turn decompose to give H_2O_2 and the oxidized form of the compound. The H_2O_2 is electrochemically oxidized to liberate oxygen and the oxidized form of the compound is electrochemically reduced to give the reduced form of the compound. The preferred form of this compound is an alkali metal anthraquinone -2, 7-disulfonate.

1.3. PROBLEMS IN OXYGEN UTILIZATION

The use of oxygen can cause many difficulties. If oxygen is produced centrally and distributed, the questions of storage and transportation arise.

Oxygen storage involves fire hazards, in addition to the need for space. Transportation will involve additional expense due to the need to liquify the oxygen to facilitate bulk transportation. These factors make the on-site production of oxygen more desirable under most circumstances.

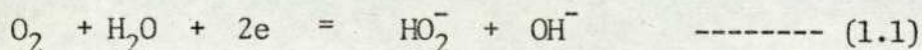
Instances in which on-site oxygen production by means of a portable unit is highly desirable can be found in medical applications and life support systems, such as field hospitals for the military or during emergency situations (e.g. in disaster areas) where transportation could be difficult or cause delay. Another example can be found in life support systems for high altitude flying in which the mass and bulk of

a cylinder is unsatisfactory. At present liquid oxygen or water electrolyzers are used, the electrolyzer is quite hazardous because of the hydrogen evolution.

The above examples illustrate the need for a variable capacity oxygen production unit capable of being manufactured for either a permanent installation or as a portable unit.

1.4. A POSSIBLE EFFICIENT METHOD FOR OXYGEN PRODUCTION

Berl⁷ showed that the electrochemical reduction of oxygen on graphite or carbon is a two electron process which goes through the perhydroxyl ion route:



If such electrodes were to be used in an oxygen extraction cell, the fact that the reduction of oxygen on carbon surfaces proceeds via a two electron step would be beneficial, provided that the HO_2^- could be chemically decomposed and the resultant oxygen collected in the anode compartment together with the oxygen evolved on the anode.

In this way, the number of coulombs required per mole of oxygen gas would be halved, leading to a significant reduction in power consumption.

In this study the practicability and the efficiency of this approach was investigated.

The approach to the study was as follows:-

- (a) Selection of suitable and efficient materials for the reduction and evolution of oxygen and for the chemical decomposition of the hydrogen peroxide.

- (b) The evaluation of the activity of the materials chosen and the study of the reactions involved.

CHAPTER TWO
EXPERIMENTAL TECHNIQUES

In this chapter the preparation, characterization and electrochemical testing of the materials used in this study will be described.

2.1. PREPARATION METHODS

2.1.1. Preparation of High Surface Area Graphite

The surface area of graphite powder supplied by B.P. Chemicals (Sunbury) Ltd. was increased by means of a vibrational ball mill. The graphite was of reasonably high purity

Carbon	99.5%
Iron	0.01%
Ash	0.01%
Hydrogen	0.35%
Nitrogen	0.02%

Batches of graphite powder weighing 20g were ground in a Mega pact Laboratory Mill (Pilamec Ltd., Gloucestershire) spherically shaped, 99.9% pure nickel shots were used as the grinding elements. After loading the nickel chamber (figure 2.1) with the graphite and nickel shots, it was evacuated using a rotary pump and the sample ground for 14 hours. There is inherent contamination of the final product, in a mill of this kind, due to frictional wear of the grinding elements and the chamber walls during use.

For this reason nickel was chosen as grinding media, as it is inert towards strong alkaline solution at oxygen reduction potentials. In addition nickel is a very poor catalyst for the decomposition of hydrogen peroxide. For these same reasons

nickel screen was chosen as current collector of the graphite electrode.

As the graphite was ground under vacuum, care had to be taken when admitting air into the mill chamber after the grinding operation. If admitted too rapidly the energy released due to the adsorption of oxygen on the graphite could cause the sample to ignite. To prevent this occurring the chamber was first cooled in air for several hours and then under running water. Even then air was admitted to the chamber only very slowly. The graphite was slowly collected by shaking the mill-chamber violently up and down, so as to eject the graphite out via the evacuation out-let.

2.1.2. Freeze drying

Freeze drying technique developed by Tseung and Bevan⁸ was used for the preparation of cobalt-nickel oxide catalysts used in the present work.

A mixed solution of cobalt and nickel nitrates was sprayed into liquid nitrogen using a high pressure white spot nitrogen cylinder connected to the flask containing the solution.

The high degree of dispersion present in the original solution was therefore maintained by rapid freezing of the fine spray and subsequent prevention of the recurrence of a liquid phase. This was achieved by subliming the ice under a vacuum of approximately 0.1 torr in the apparatus shown in figure (2.2). The frozen nitrate solution, contained in flasks, was maintained under vacuum until all the water had been removed; this point

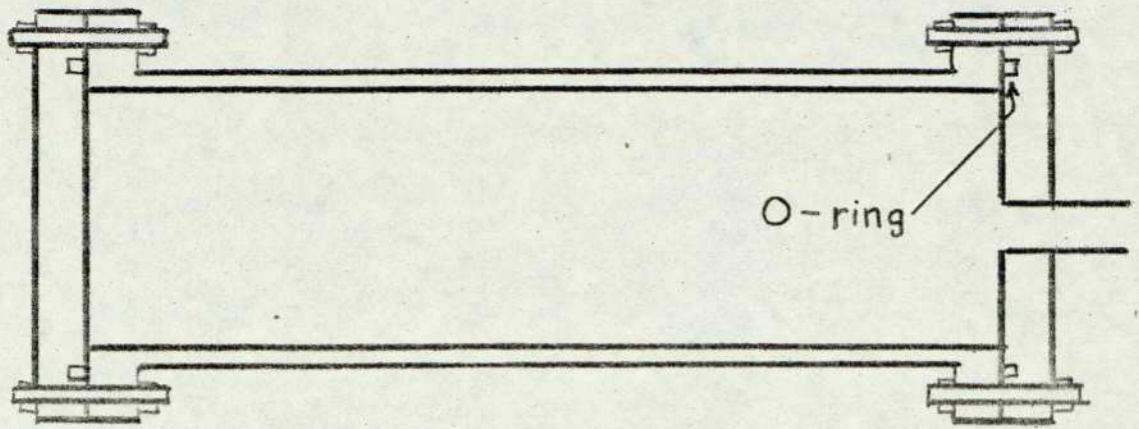


Fig. 2.1 THE NICKEL MILL

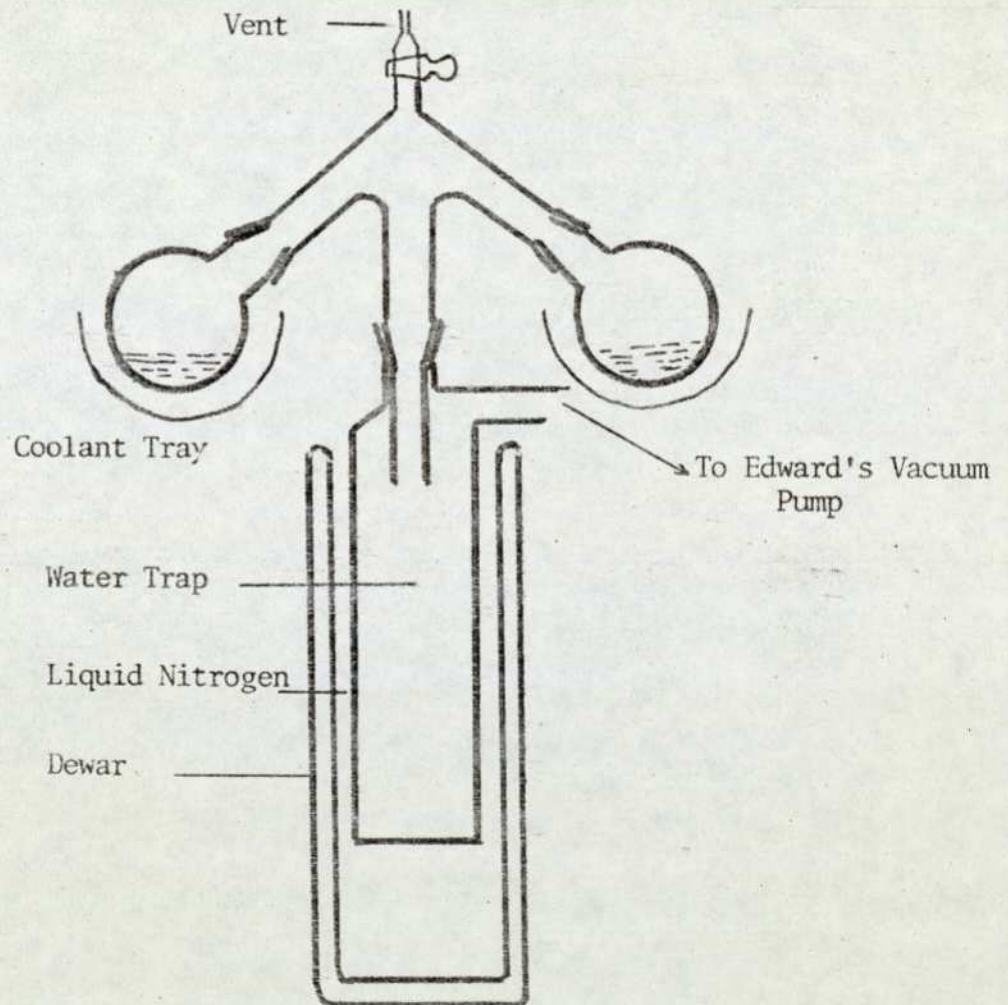


Fig. 2.2 FREEZE DRYING APPARATUS

was detectable due to a corresponding pressure drop to about 10^{-3} torr.

The samples had to be maintained at liquid nitrogen temperature in the initial stages of the process, at least until the pressure was better than about 0.5 torr.

The dried nitrates were subsequently decomposed whilst still under vacuum for one hour at 300°C . This was accomplished by heating the sample flasks with an "Electro-thermal" heating mantle. The temperature was gradually increased, as some salts have a tendency to dissolve in their own water of crystallisation if heat is applied too rapidly. Finally the powder was cured in air for 10 hours at 400°C in order to obtain the desired spinel structure..

Freeze drying assures atomic mixing of the constituent reactants⁸ and is thus applicable as a high surface area preparation route for spinels generally, as it permits lower curing temperatures.

2.2. CHARACTERIZATION TECHNIQUES

2.2.1. The B.E.T. Technique for Surface Area Measurement

Brunauer, Emmet and Teller⁹ applied a modified Langmuir treatment of adsorption to the case of multi-molecular layer formation, and derived an equation for this type of isotherm. This technique has been described else where^{10, 11} and could be summarised as follows:

By equating the rate of condensation of gas molecules on to an adsorbed layer to the rate of evaporation from that layer,

and summing for an infinite number of layers, it can be shown that:

$$\frac{P}{V_a(P_0 - P)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \cdot \frac{P}{P_0} \text{-----(2.1)}$$

where

V_m is the volume of gas (ml at S.T.P.) able to cover the whole surface of the adsorbent with a unimolecular layer of the gas.

V_a is the volume of gas adsorbed (ml at S.T.P.) (at a given value of P).

P_0 is the saturation pressure of the adsorbate.

P is the equilibrium pressure.

C is a constant (involving the heats of adsorption of successive layers).

The constant C is given by $C = \exp \frac{E_1 - E_2}{RT}$, the energy term being the difference between the heat of adsorption of the first layer and the heat of adsorption of the second and subsequent layers.

By plotting the function $\frac{P}{V_a(P_0 - P)}$ against $\frac{P}{P_0}$ the so-called B.E.T. plot a straight line is obtained. From the slope, $\frac{C - 1}{V_m C}$, and the intercept, $\frac{1}{V_m C}$, the monolayer capacity can be obtained $V_m = \frac{1}{\text{slope} + \text{intercept}}$.

In the original B.E.T. work the volume of the monolayer was measured, but in practice this involves the difference

between very large volumes, and unless the entire apparatus is calibrated for "dead space" with great care, errors are easily introduced. A great simplification to the B.E.T. technique proved to be the introduction of a gravimetric modification¹², the weight rather than the volume of the adsorbate is measured using a micro-balance. V_a and V_m are replaced by M_a and M_m respectively and the mass of the monolayer determined as above.

Figure (2.3) illustrates the apparatus used in this work. A (CI Electronics Mark III) micro-balance with a sensitivity of 10^{-6} g was used. The sample was weighed in to an aluminium crucible, suspended from one arm of the balance, and then counter-balanced. The apparatus was evacuated using rotary pump and then the sample was heated to 300°C with continuous evacuation using both rotary and diffusion pumps until the sample was at constant mass. The adsorption studies were carried out at liquid nitrogen temperature (77K) using N_2 gas as adsorbate. The pressure over the sample was increased in approximately 40 torr increments and the corresponding mass increment noted. In this manner a linear B.E.T. plot was obtained for pressures upto about 300 torr.

From the slope and intercept of the B.E.T. plot the monolayer mass was obtained in the manner previously described and the specific surface area (S.S.A.) of the sample calculated as follows

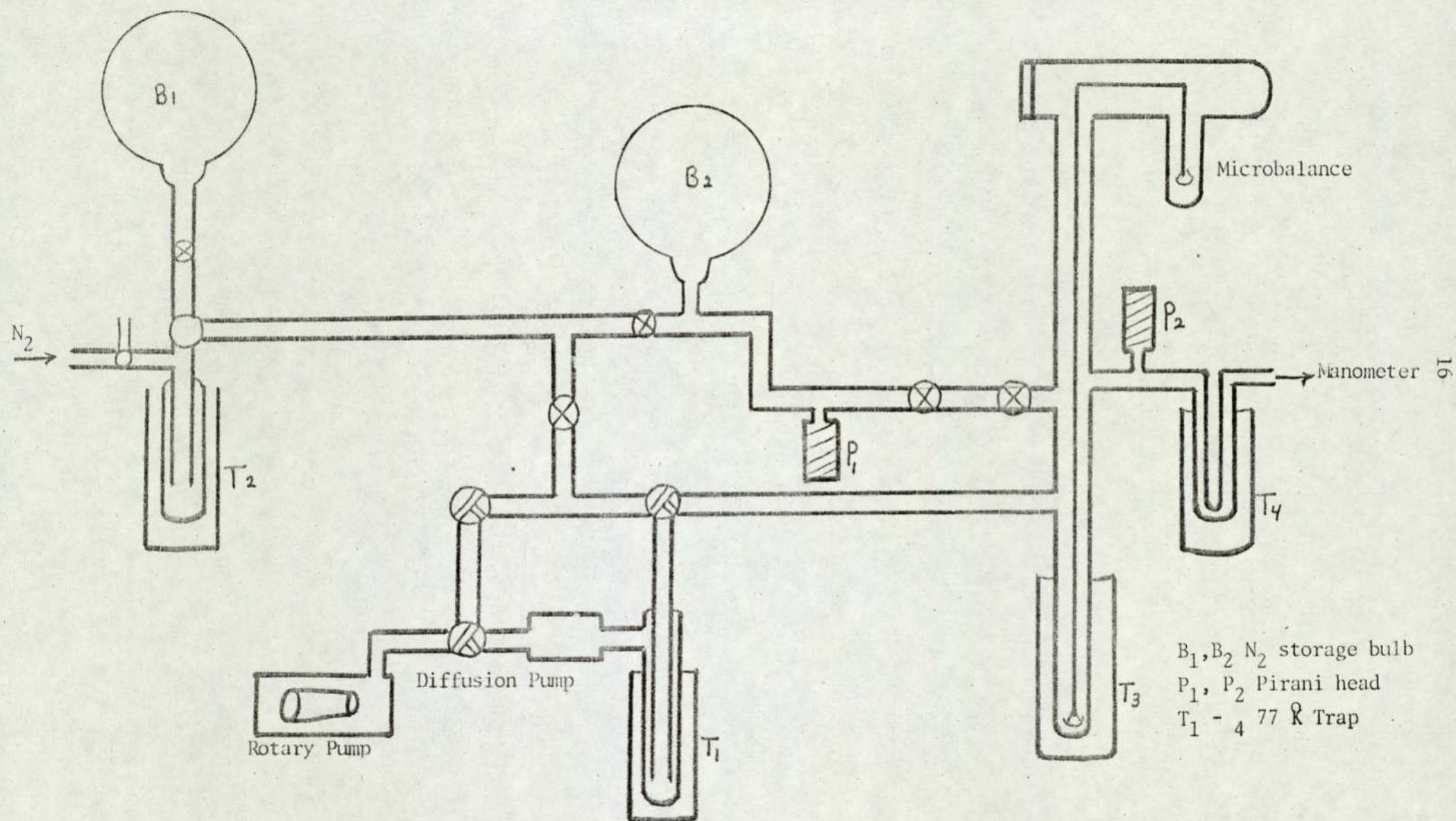


Fig. 2.3 B.E.T. APPARATUS

$$\text{S.S.A.} = \frac{aNM_m}{MW} \text{-----} (2.2)$$

where M is the molecular weight of adsorbate gas.

N is Avogadro number (6.023×10^{23}).

W is the mass of powder in the sample pan.

a is the cross-sectional area of an adsorbed molecule.

The cross-sectional area of an adsorbed nitrogen molecule was taken as $16.2 \text{ \AA}^2$, thus

$$\text{S.S.A. M}^2/\text{g} = 3.48 \times 10^3 \frac{\text{Mass of monolayer}}{\text{Mass of sample}}$$

2.2.2. X-ray Analysis

All samples were subjected to X-ray analysis using Debye-Scherrer powder technique¹⁴, so as to ascertain that the spinel or the other phases had been formed.

The work was carried out on a Phillips PW 1010 x-ray generator using an analytic camera of diameter 11.46 cm. Molybdenum K_α radiation was used at an anode voltage of 40 KV and 16 mA current. The samples were mounted in Lindemann glass tubes of internal diameter 0.5 mm and exposure times were 3 hours and 6 hours for the cobalt nickel oxide and cobalt iron oxide catalysts respectively. In analysing the resultant powder photographs the lines intensities were estimated visually and the lines were indexed assuming a cubic spinel unit cell. The lattice plane spacings could be obtained using the Bragg equation:

$$2d \sin \theta = n \lambda \text{-----} (2.3)$$

where

d is the lattice spacing of the crystal planes.

θ is the angle of the x-ray beam on the crystal planes.

n is an integer

λ is the wave length of the radiation used

(0.7106 Å for Mo K α x-rays)

For a cubic unit cell the relationship between the cube edge length, a_0 , and the plane spacing, d , is given by:

$$a_0 = d (h^2 + K^2 + I^2)^{\frac{1}{2}} \quad \text{-----}(2.4)$$

where h , K , I are integers (Miller Indices) corresponding to the d values.

If Miller Indices for a particular d value are known, a value for a_0 may be calculated. a_0 given in this work was the average of several d values and their corresponding Indices, giving the final value for the lattice parameter for the particular composition.

The values obtained for the plane spacings and their relative intensities of reflection were compared with those given for the same materials in the ASTM Powder Data File in order to determine the major phases present.

2.2.3. Electron Microscopy^{15,}

Scanning Electron Microscopy (S.E.M.) and (EDAX) analysis were carried out on cobalt nickel oxide samples in order to determine particle size distribution, particle shapes and the relative proportions of cations in the samples.

The work was conducted on a Japanese Electron Optics Ltd., JEM 100 B microscope with EDAX attachments.

Scanning secondary electron microscopy employs a scanning beam of electrons, focussed to a point on to the specimen. The secondary electrons emitted when the scanned primary beam impinges on the specimen are accelerated on to an electron multiplier and the signal generated is amplified and used to modulate the beam of a cathode ray tube whose raster is synchronised to that of the primary electron beam.

The secondary electron intensity is dependent upon specimen surface topology and composition, and thus, the image on the cathode ray tube is closely related to the specimen surface. Two kind of information could be obtained from the x-ray spectrum emitted by the specimen when primary beam electrons excite x-ray transitions.

From measurement of the wave length (or energy) of each characteristic x-ray that is emitted, the elements present in the specimen could be identified.

If the information output is suitably processed quantitative analysis is also possible. There are, however, many complications. The x-ray intensity emitted depends upon many factors, such as primary beam energy; x-ray photon energy, topology x-ray escape depth in addition to elemental concentration.

2.2.4. Electrical Conductivity Measurements

The electrical conductivity of the powder samples were measured using a Wayne-Kerr A.C. Bridge, operating at 1592 Hz,

and a conductivity cell similar to those employed by Bevan¹⁰ and Goldstein¹¹. The cell consisted of a P.T.F.E. ring in which a powder sample was compressed between two stainless steel discs. As powder was compressed, its conductivity rised to a maximum, as mutual contact among particles increased. The powder was compressed until further compression did not affect its conductance, which was measured between the two discs. The geometry of the cell permitted the conductivity to be calculated from the conductance.

Powder conductivity measurements are not very reliable as a guide to absolute conductivity, however some reproducibility could be achieved using a similar compression treatment and a fixed mass of specimen.

2.2.5. Atomic Absorption Spectroscopy¹⁶

A Perkin Elmer Model 290 spectrometer was used for the cation concentration analysis of cobalt nickel oxide samples. Samples were dissolved in aqua regia.

This method was also used in the corrosion tests, which were carried out on the KOH solution after prolonged polarisation of the nickel cobalt oxide electrodes. The sensitivity of apparatus is 2 p.p.m.

2.3. ELECTROCHEMICAL TESTING

2.3.1. Fabrication of Hydrophobic Electrodes

The method of Giner et al¹⁷, later improved by Tantram and Tseung¹⁸ was used in this work for the fabrication of graphite, platinum black and the different compositions of

nickel cobalt oxides electrodes.

Weighed quantities of electrocatalyst powder and aqueous polytetra fluoro ethylene (P.T.F.E.) dispersion were slurried either in methanol in the case of graphite or in distilled water in the case of the other catalysts used in this work. The mixture was then dispersed in an ultrasonic bath for five minutes and finally painted on to 100 mesh nickel or platinum screen previously degreased using acetone.

The electrode was then dried at 100°C for one hour, and cured at 300°C for another hour. It is important that the slurry is rapidly transferred to the screen in order to prevent the partial separation of the slurry especially in the case of heavy catalysts, such as platinum black. If partial separation occurs the Teflon/Catalyst ratio will be higher than intended as catalyst settles in the dispersion. It is also important to coat both sides of the screen equally, in order to prevent the Teflon ratio being higher on one side of the electrode than the other.

The curing removes the wetting agent (Triton X100) from the P.T.F.E. and causes partial sintering between the P.T.F.E. and the catalyst particles, thereby increasing the hydrophobic character and strength of the catalyst layer.

The temperature of curing is fairly critical; below 265°C the Teflon does not sinter, while above 330°C the Teflon transforms to glassy state, which produces highly inactive electrode.

The electrocatalyst loading is calculated from the weight change of the screen before and after fabrication assuming that the components of the electrocatalyst/P.T.F.E. dispersion are transferred on to the screen in the same ratio as in the original dispersion.

A nickel foil strip of dimensions 0.1 x 1 cm was spot welded onto the end of the nickel screen and a nickel wire was spot welded onto the nickel foil strip. The spot welds were then scraped in order to remove traces of copper left by the welder electrodes.

2.3.2. The Floating Electrode Cell System

The floating cell rig used for the study of oxygen reduction is shown in figure (2.4).

The cell consists of two compartments separated by glass frit. The 5 x 5 cm nickel screen counter electrode was contained in one compartment and the working and reference electrodes in the other. Teflon rings were used to clamp the working electrode to the hollow central pillar of the upper assembly, inside of which the reference electrode could be mounted.

The U-shaped Luggin Capillary, at the base of the central pillar, enabled potential measurements to be made between the reference and the working electrode. The working electrode compartment could easily be equilibrated with oxygen, or nitrogen using the sliding Teflon tube, which could be pushed into the electrolyte for purging, or simply used to sweep gas through the compartment.

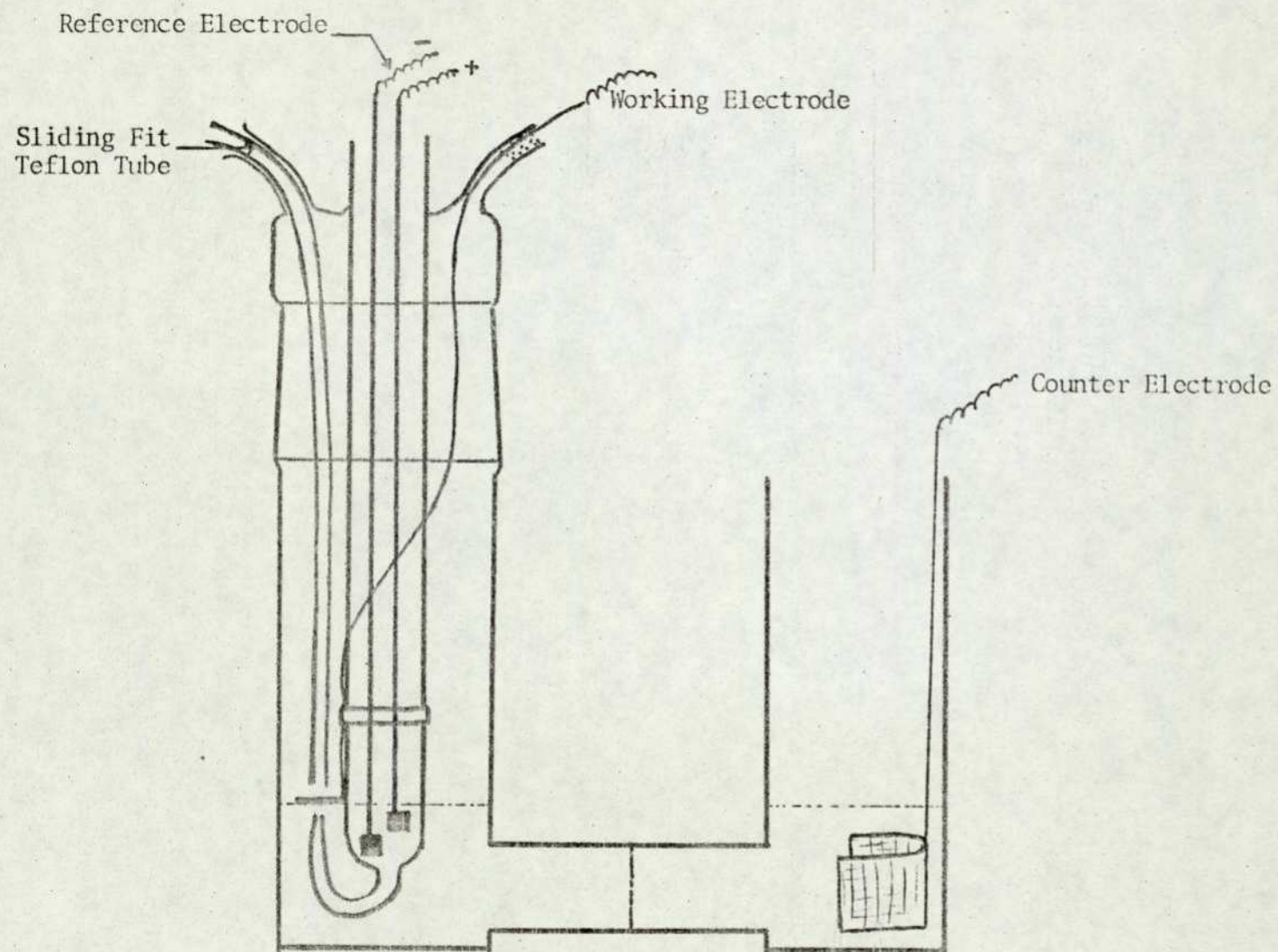


Fig. 2.4 THE FLOATING ELECTRODE CELL.

2.3.3. The Reference Electrode System

Dynamic Hydrogen Electrode (D.H.E.) was used as a reference electrode in this work.

The electrode designed by Giner¹⁹, consists of two platinized platinum electrodes, each 1 cm^2 in total geometric area, between which a constant current of (2 mA/cm^2) is passed. Figure (2.5) illustrates the electrode system, the lower electrode, connected to the negative terminal of a battery evolves hydrogen gas, which sweeps away the oxygen gas evolved on the upper electrode, thus preventing it from interfering with the lower electrode potential.

The potential of (D.H.E.) electrode was measured against a reversible-hydrogen electrode in 5N KOH at 25°C . It was found to remain constant at $(-31 \pm 1 \text{ mv})$ for several hours.

D.H.E./reversible-hydrogen electrode cell voltage was checked periodically through out the experiments. When the potential shifted from its value due to deposition of impurities, both chemical and electrochemical cleaning procedures were carried out. The impurities were oxidized by treatment with nitric acid, and anodic/cathodic polarisation cycles.

The final cathodic process serving to reduce the oxide film formed during the previous oxygen evolution step.

2.3.4. Steady State Polarization

In order to obtain current-voltage curves for steady state potentiostatic polarization, a constant electrode potential was maintained by means of a potentiostat. The potentiostat

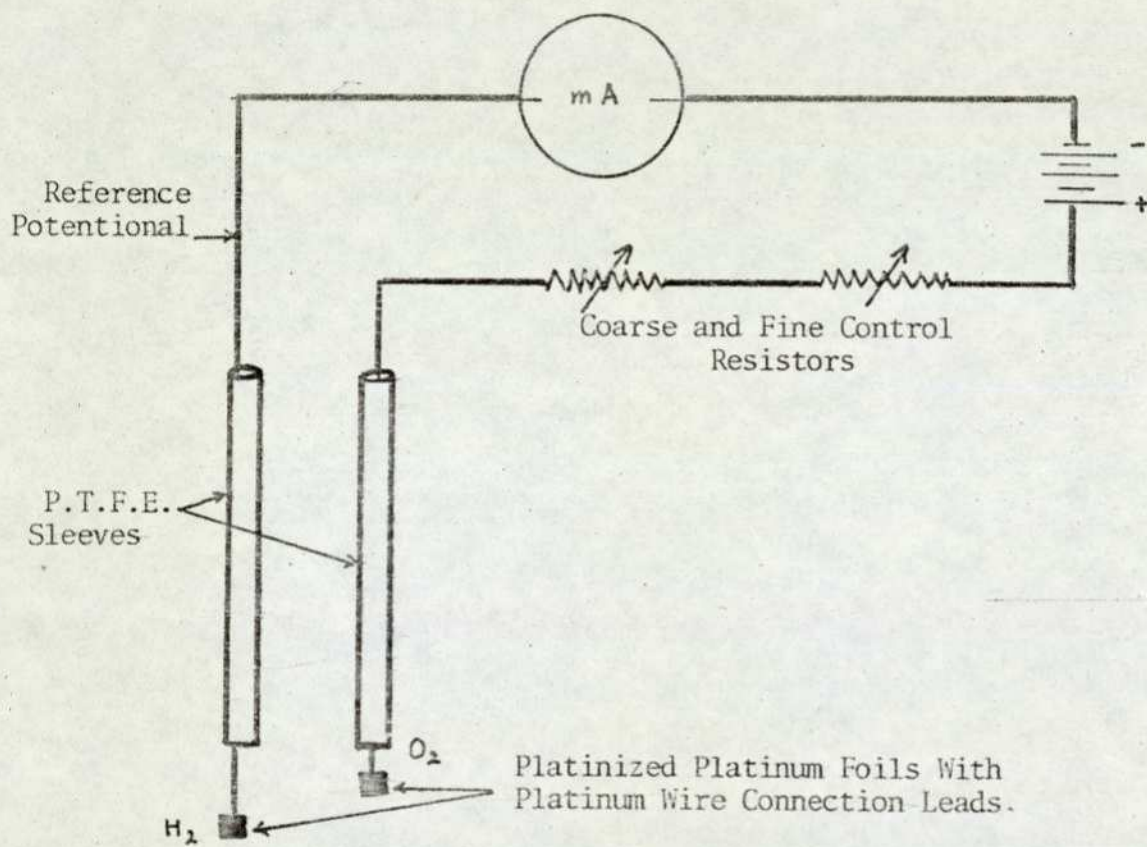


Fig. 2.5 DYNAMIC HYDROGEN ELECTRODE (D.H.E.)

continuously compares the adjustable internal voltage with the potential difference between the working and reference electrodes. Any imbalance is amplified and passed in to a feed back system, which adjusts the current flowing between the working and counter electrodes until the compared voltages are equal. The circuit has a very high input impedance in order to minimise the current drawn from the reference electrode, which thus remains virtually unpolarized.

The potentiostatic circuit is shown schematically in figure (2.6). In some of the experiments conducted in the course of this work galvanostatic polarization was used. In this method a constant current is applied and the potential between the working and reference electrodes is monitored. The galvanostatic circuit is shown schematically in figure (2.7).

2.3.5. Ohmic Correction of Polarization Curves

The main ohmic losses occur due to the electrolyte resistance, and, to a lesser extent there is a contribution from the resistance of the catalyst layer and the cell connections. A Luggin Capillary was used to minimize the gap between the reference and the working electrode. The interrupter technique²⁰ was applied to measure the ohmic polarization. In this method, a steady d.c. polarising current is interrupted at mains frequency (50 Hz) by means of a fast acting, mercury-wetted relay, producing a train of square current pulses through the cell. The circuit diagram for the interrupter is shown in figure (2.8). The over voltage components can then

be separately measured as a result of their differing time dependence of decay or growth. Thus, ohmic polarization is instantaneous, whereas activation and mass transfer effects require finite time intervals in which to become apparent. If then, the potential between the working and reference is displayed on an oscilloscope against a suitable time base, a trace similar to that shown in figure (2.9) will be displayed. From the current flowing and the vertical portion of the voltage/time trace, the resistance at that current can be evaluated using Ohm's law, and from evaluation of the resistance at different current density levels, the polarization curve could be corrected for ohmic losses.

As can be seen from figure (2.9) when the current is interrupted, a steep drop in potential is observed, followed by a more gradual potential drop. The initial vertical drop in potential is due to the instantaneous removal of ohmic polarisation. The slower potential drop is due to the slower removal of activation and concentration polarisation.

In porous electrodes, points within the electro catalyst layer are located at varying distances from the current collector. The equivalent ohmic circuit could be therefore represented as a stack of resistors in parallel¹¹, representing the electro-catalyst layer. This stack is in series with the cell connections and iR drop resistors (figure 2.10). The value of each parallel resistor increases as the distance from the current collector increases.

Anodic polarisation (oxygen evolution) usually involve bubbles formation, which introduce errors in the iR drop value. The iR drop determined at low current density level may not be applicable to higher current density, when appreciable changes in electrolyte concentration/resistivity occur in the electrode vicinity as a result of polarisation. Therefore, it was necessary to determine the iR drop for a series of current density levels.

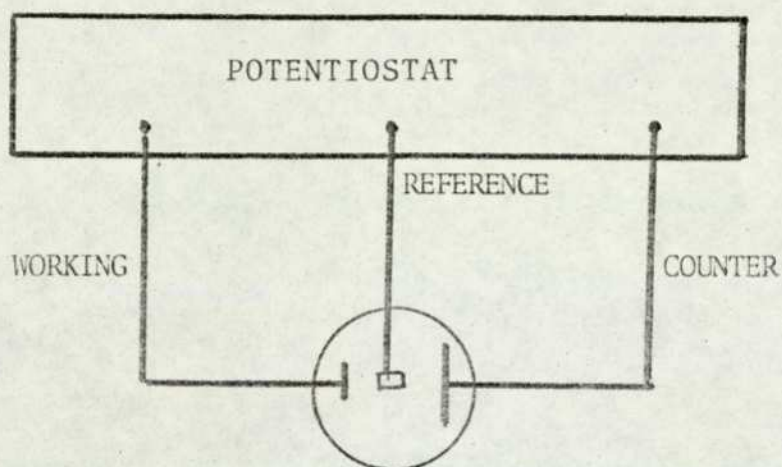


Fig. 2.6 SCHEMATIC CIRCUIT FOR POTENTIOSTATIC POLARIZATION STUDIES

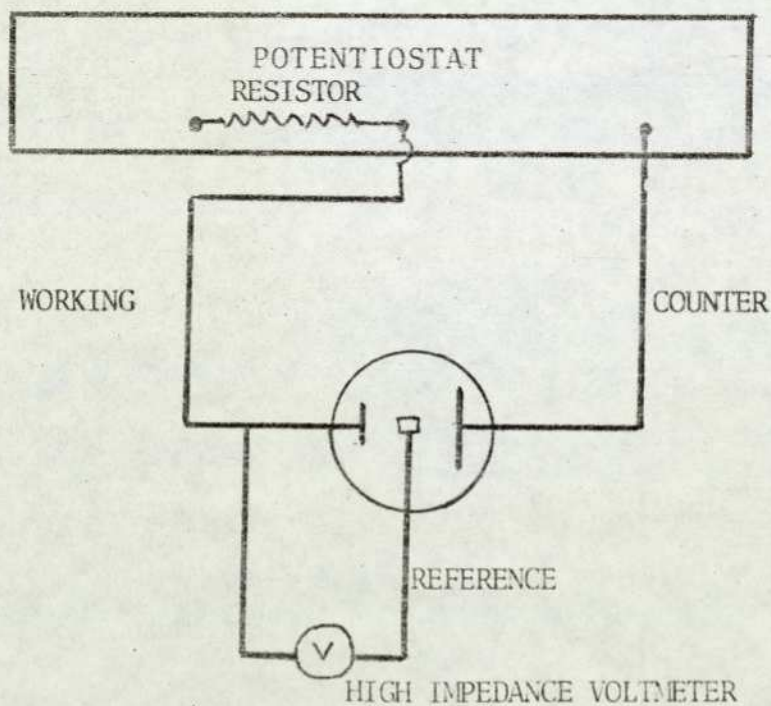


Fig. 2.7 SCHEMATIC CIRCUIT FOR GALVANOSTATIC POLARIZATION STUDIES

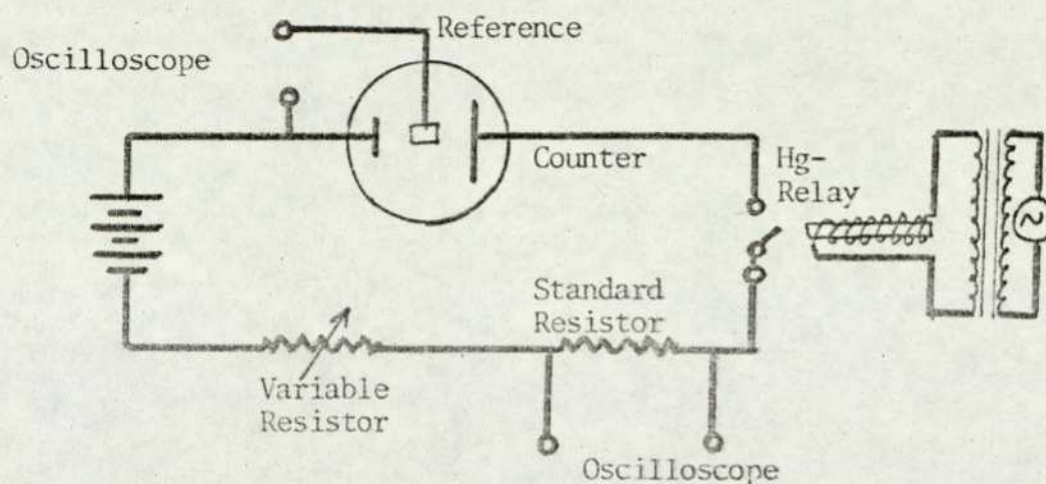


Fig. 2.8 CIRCUIT DIAGRAM FOR INTERRUPTER MEASUREMENT

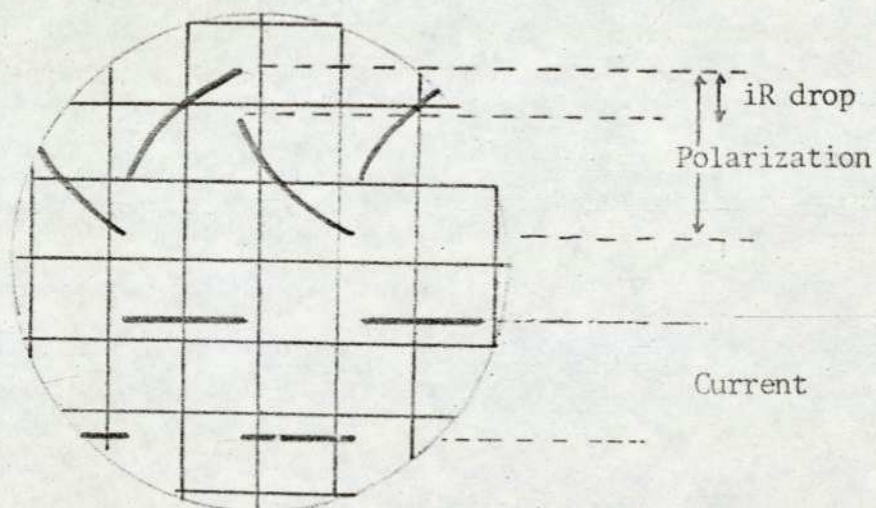


Fig. 2.9 TRACES OF ELECTRODE POTENTIAL AND CURRENTS OBTAINED USING THE INTERRUPTER CIRCUIT

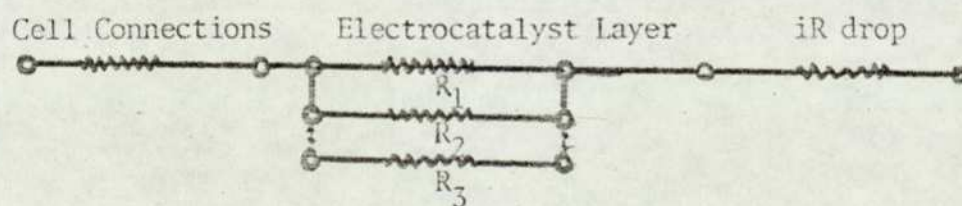


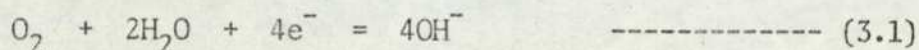
Fig. 2.10 POROUS ELECTRODE EQUIVALENT OHMIC CIRCUIT

CHAPTER THREE
OXYGEN REDUCTION

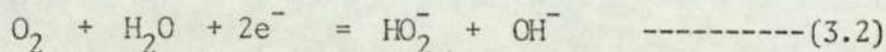
3.1. REVIEW OF PREVIOUS WORK

3.1.1. Electrode Materials for Oxygen Reduction

The electrochemical reduction of oxygen in alkaline solution ideally should take place according to the equation (3.1).



The standard reduction potential for reaction (3.1) is 0.401 V²¹. On most known materials, however reaction (3.1) is slow and irreversible at room temperature. This causes serious performance limitations in power sources, such as fuel cells and metal air batteries, in which oxygen reduction is the cathodic reaction. The review of previous work has indicated that high current densities for oxygen reduction could only be provided using costly electrocatalysts such as platinum and silver, but the potential would still fall well below the reversible value for reaction (3.1)²². On these electrodes the four electron process (reaction 3.1) does not proceed directly²³. On many electrocatalysts, oxygen reduction in alkaline solution occurs via a two-electron process⁷; producing hydrogen peroxide, present in solution as the perhydroxyl ion, HO₂⁻.



For oxygen reduction in alkaline solution, platinum and palladium black give the highest performance levels²⁴. Porous carbon and graphite also show pronounced activity⁷. When carbon is activated with fairly low loadings of platinum, silver or

palladium, show performances in air not much less than that of platinum alone²⁵.

The task of finding a substitute for platinum as a highly active material for oxygen reduction has been difficult, because the material must also be conducting, corrosion resistant and easily prepared in a high surface area form. Novel electrocatalysts, such as Lanthanum-strontium cobalt oxide¹⁰ and carbon-cobalt phthalocyanine²⁶ have been reported, but show little, if any, improvement over conventional materials. On silver-graphite air electrodes²⁵ oxygen is electrochemically reduced on the graphite support, producing HO_2^- . This may be chemically decomposed by the impregnated silver, releasing oxygen for recycling.



King and Tseung^{27, 28} studied the reduction of oxygen on NiCo_2O_4 in alkaline solution and found that it possesses high activity at room temperature, but the performance of the electrode decreases sharply in few hours period. It has been suggested²⁸ that this decay could be attributed to substitution of OH^- in the lattice or the partial reduction of NiCo_2O_4 ²⁹.

Recent study³⁰ indicated that provided the electrode is held at 0.75V vs R.H.E., there is no decrease in performance over a test period of 140 hours. It was also found³⁰ that NiCo_2O_4 is irreversibly reduced below 0.70V vs R.H.E. at room temperature. In developing a low-cost oxygen electrocatalyst

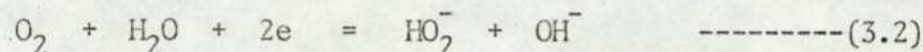
allowing high current density at lower voltages than those of the available materials, there have been two main approaches. The first, was adopted by Bevan and Tseung¹⁰, who studied the factors favouring "side-on" adsorption of an oxygen molecule. Studies by Tseung and Co-workers^{10, 31, 32} indicate that it is necessary to use paramagnetic oxides, such as $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ as electrocatalysts, in order to dissociatively chemisorb oxygen molecules, which are also paramagnetic. The reduction of oxygen then proceeds via four electron process and reversible behaviour is achieved, even at room temperature. The low performance of this catalyst below 100°C was attributed to the limited number of active sites and the slow rate of oxygen chemisorption^{31, 32, 33}. However the activity of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ for oxygen reduction at 170°C was higher than that of platinum black³². In a recent paper Conway³⁴ has reviewed the main achievements in electrode kinetics over the past twenty five years. He suggests that the main achievement in oxygen reduction process was the work of Tseung and Co-workers^{31, 35, 36} in which they investigated the possibility of catalyzing the reduction of oxygen using paramagnetic La-Sr-Cobaltites and other structures with which oxygen interacts magnetically. Conway also pointed to the work of Yeager^{37, 38} who investigated oxygen scission in relation to peroxide pathways in the reduction reaction.

The second approach was adopted by Goldstein³⁵, who used graphite/cobalt-iron oxide system. Oxygen was electrochemically reduced on the graphite, producing HO_2^- , which was then catalytically

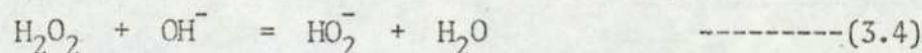
decomposed by the highly active catalyst, cobalt-iron oxide, yielding oxygen for recycling. This approach resulted in a general performance improvement compared to the performance of the graphite alone.

3.1.2. Oxygen Reduction on Carbon and Graphite in Alkaline Solution

On carbon and graphite the oxygen reduction process is fairly well understood. Oxygen is reduced by a two electron process

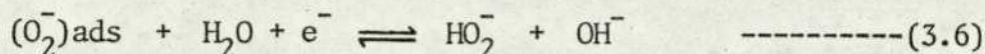
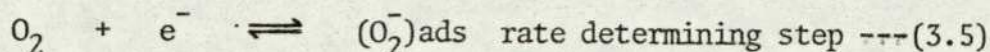


producing hydrogen peroxide. The hydrogen peroxide is fully ionized in alkaline solution³⁹, and present as HO_2^- .



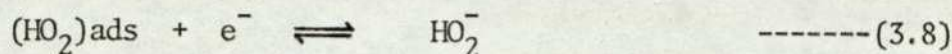
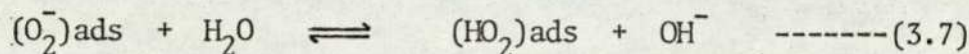
Berl⁷ has carried out the most thorough investigation of this system and proposed that reaction (3.2) is the only reversible and potential determining reaction. The thermodynamic standard potential expected for this reaction is $(-0.08\text{V})^{21}$ relative to hydrogen. Berl's findings have been confirmed by later workers, such as Weisz and Jaffe⁴⁰. In oxygen tracer studies using ^{18}O , Yeager⁴¹ showed that all the HO_2^- in the reaction came from oxygen molecules alone; thus the O-O bond in the oxygen molecule remained unbroken during the reduction process. Furthermore, a cathodic current efficiency of 100% for HO_2^- production from oxygen was also reported⁴¹. These results led Yeager^{37, 42} to propose a mechanism for oxygen reduction on carbon according

to



where the species $(\text{O}_2^-)_{\text{ads}}$ corresponds to an adsorbed radical.

Step (3.6) may occur in two steps; e.g.



It is difficult to interpret steady state polarization measurements on porous electrodes, on a kinetic basis, due to complications associated with mass transfer and the uneven distribution of ohmic drops within the pores of the electrode i.e. current densities are not uniform within porous media, because the diffusion and ohmic over voltages to the total is different at different points within the porous structure⁴³.

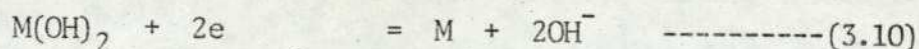
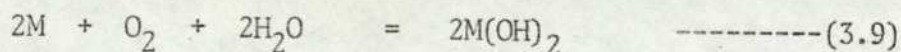
Yeager^{37, 42} avoided this problem by using two different electrodes, in the first the pore structure within porous carbon or graphite electrodes was completely filled by placing the porous electrode in molten paraffin at low pressure. In the second type of electrode, pyrolytic graphite was used, having very low porosity.

From the cathodic measurements for oxygen reduction on pyrolytic graphite rotating disc electrode, kinetic parameters, such as Tafel slope were determined and the above mechanism was suggested. It was also concluded⁴² that further reduction or decomposition of the peroxide on carbon or graphite proceeds

at very small rate in comparison to the two electron process (reaction 3.2).

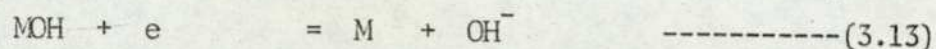
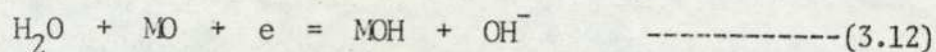
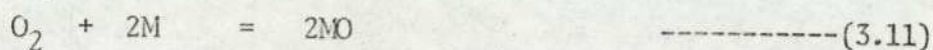
3.1.3. Oxygen Reduction on Nobel Metals in Alkaline Solution

Essentially two reaction routes have been proposed for oxygen reduction on silver and the noble metals. In the first, it is suggested that oxygen electroreduction proceeds by the formation and decomposition of surface oxides. Thus, for platinum, palladium and silver Sawyer and Day⁴⁴ proposed the following reaction path:-



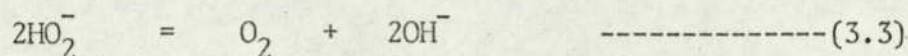
where M is the electrode metal.

Riddiford⁴⁵ proposed another path, in which chemical formation of metal oxides was followed by electrochemical reduction

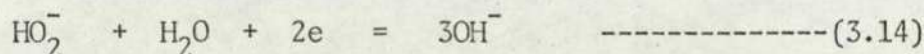


Reaction (3.13) was proposed as the rate determining step on platinum. In the second reaction route, it is suggested⁴⁶ that on silver and noble metals, oxygen reduction occurs via the two electron process to give HO_2^- as a reaction intermediate.

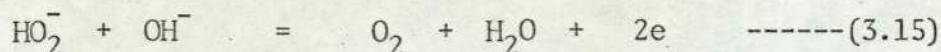
The HO_2^- in contrast to its behaviour on carbon, may undergo further reaction, direct chemical decomposition is



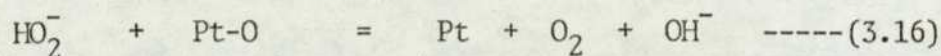
possible, since silver and platinum are amongst the best known catalysts for this reaction. Alternatively, the HO_2^- intermediate may be further reduced electrochemically,



The standard reduction potential for reaction (2.14) is (0.87 V)²¹. Gerischer⁴⁷ proposed the so-called "local cell" mechanism for oxygen reduction on platinum, when the metal surface is free of an adsorbed oxygen film. In this mechanism, he suggests that reaction (3.14) occurs at the cathodic sites of the electrocatalyst surface, and the reaction



at the anodic sites. The net result is a local cell process with the stoichiometry of equation (3.3). Bianchi and co-workers⁴⁸ have proposed that in the presence of Pt-O on the platinum surface, a reaction could occur between the Pt-O film and HO_2^-



This reaction continues until the film is destroyed, followed by the Gerischer mechanism⁴⁷. Ideally if reaction (3.2) and (3.14) proceeded reversibly the net effect would be reversible oxygen reduction by equation (3.1). This is not achieved in practice primarily, because of irreversibility

associated with reaction (3.14)⁴⁹.

This process occurs at a standard reduction potential even higher than that of reaction (3.1), and both reactions (3.14) and (3.1) require that the o-o bond is broken electrochemically. Oxygen reduction by this route will hence occur sluggishly, and the operating potentials will be determined by more rapid processes such as (3.2) in conjunction with (3.3).

Evans^{50, 51} suggested that oxygen reduction could occur, via four electron process (directly), but only at scarce, at favourable sites on the electrode surface. His mechanism is called "pseudo-splitting". In this mechanism it is assumed that some of the adsorbed oxygen molecules undergo partial electron transfer at the electrode surface, but do not fully dissociate. These adsorbed (pseudo-split) molecules can form hydrogen bonding with adjacent OH^- , and this hydrogen bonding spreads across the OH^- layer, which cover the electrode surface in alkaline solution. OH^- on the layer boundaries enter more easily into hydrogen bonding with nearby water molecules.

At this stage, completion of electron transfer, and breaking the o-o bond, is most likely, because such proton-switching lowering the activation energy for bond rupture. Finally reorientation of the OH^- layer will take place. The Kink Sites provide a break in the OH^- layer and also steric accessibility to water molecules; they are favourable sites for the reaction. For Evan's mechanism to take place the oxygen molecules have to adsorb in a side-on configuration (o-o).

However, Evans mechanism does not account for the occurrence of HO_2^- during the oxygen reduction process. HO_2^- is a predominant product on some materials such as carbon or graphite⁷. Goldstein and Tseung⁵² considered HO_2^- formation, and proposed a modification for Evans mechanism called "A joint pseudo-splitting/peroxide mechanism", in which they suggested that oxygen molecules could adsorb in an "end-on" configuration ($\begin{smallmatrix} \text{O} \\ | \\ \text{O} \end{smallmatrix}$) and a similar mechanism to "pseudo-splitting" could then operate.

Peroxide mechanism⁵² is shown schematically in figure (3.1).

3.2. SELECTION OF MATERIAL FOR OXYGEN REDUCTION

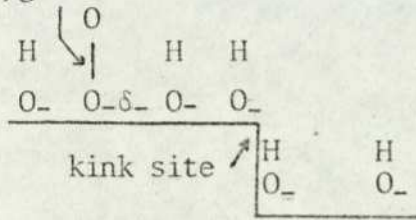
From the previous review, it became evident that carbon and graphite possess high activity towards oxygen reduction and they are suitable materials for hydrogen peroxide production. As mentioned earlier (Section 1.4), if such electrode used in an oxygen extraction cell, the fact that the reduction of oxygen on carbon surfaces proceeds via a two electron process could be beneficial, provided the HO_2^- was chemically decomposed and the resultant oxygen could be collected in the anode compartment together with the oxygen evolved on the anode.

Graphite is preferable to carbon, because it is purer and has a better electrical conductivity.

3.3. POROUS ELECTRODE

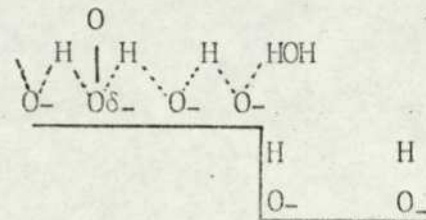
The use of porous, high surface area materials as electrodes for fuel cells and batteries has been studied for the case of gaseous dissolution reactions in the liquid phase^{53, 54} and

Oxygen molecule adsorbed end-on



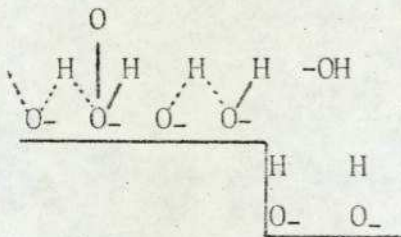
Electrode surface

(a) Partial electron transfer



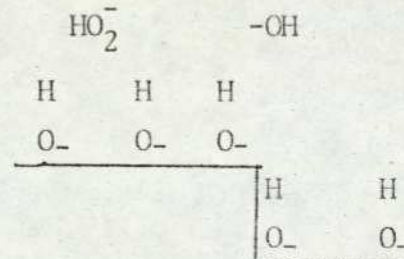
Electrode surface

(b) Hydrogen bonding



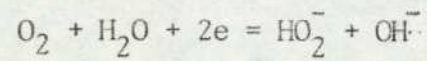
Electrode surface

(c) Completion of electron transfer



Electrode surface

Overall reaction



(d) Reorientation

Fig. 3.1 a-d STAGES IN THE PEROXIDE MECHANISM

it has been shown that this type of electrode gives a very much better performance than the equivalent weight of the same material in the form of a planar electrode. The main advantage of the porous electrode is, at a given potential it gives a much higher current than the planar electrode due to its higher surface area. High surface area powder used for gaseous dissolution reaction usually used with a hydrophobic binder, to increase the mechanical strength and facilitates the mass transfer of the gas to the active sites of the electro-catalysts. The use of Teflon bonded electrodes¹⁸ is a good method of reducing mass transfer problems, since the existence of a continuous, dry and porous network of Teflon in intimate contact with a continuous, electrolyte-soaked, porous catalyst network, ensures that gaseous reactants can diffuse into the electrode rapidly. Also provided the size of the individual electrocatalyst aggregates are small, the diffusion of the dissolved gases into the electrocatalyst pores will not be limiting. The three-phase interface is primarily a theoretical concept; only line contact can exist between a solid, liquid and gaseous phase so that in practice two phases must combine before any measureable reaction rate is possible. The gas molecules in fact diffuse through the liquid phase to the catalyst surface, so that most of the electrode reaction occurs within a very thin film of the electrolyte.

3.4. MATERIALS AND METHODS

3.4.1. Preparation of High Surface Area Graphite

The low surface area graphite ($5 \text{ M}^2/\text{g}$) was supplied by (B.P. Chemical Ltd., Sunbury). This graphite was of high purity (99.5% carbon). It was ground under vacuum in a vibratory ball mill as described in (section 2.1.1.). The grinding time of 14 hours chosen, was based on work carried out by Kent⁵⁵. He found that graphite surface area began to increase immediately when the mill was switched on and the rate of surface area increase fell off after about $350 \text{ M}^2/\text{g}$ had been reached and eventually tended towards a limiting surface area. This effect was attributed generally to aggregation among the very fine particles, as the forces of aggregation become greater than the grinding energy. Figure (3.2)⁵⁵ shows the relationship between grinding time and the surface area of graphite.

3.4.2. Fabrication of Teflon bonded Graphite Electrode

The general procedure is described in (Section 2.3.1). Weighed quantities of graphite powder and aqueous P.T.F.E. dispersion were slurried in methanol and dispersed using an ultrasonic bath for five minutes. The mixture then transferred by painting onto a nickel screen (100 mesh). After drying at 70°C for an hour in air, the electrodes are cured at 300°C in nitrogen for one hour.

3.4.3. The Electrolyte

The electrolyte used through out this study was 5N KOH,

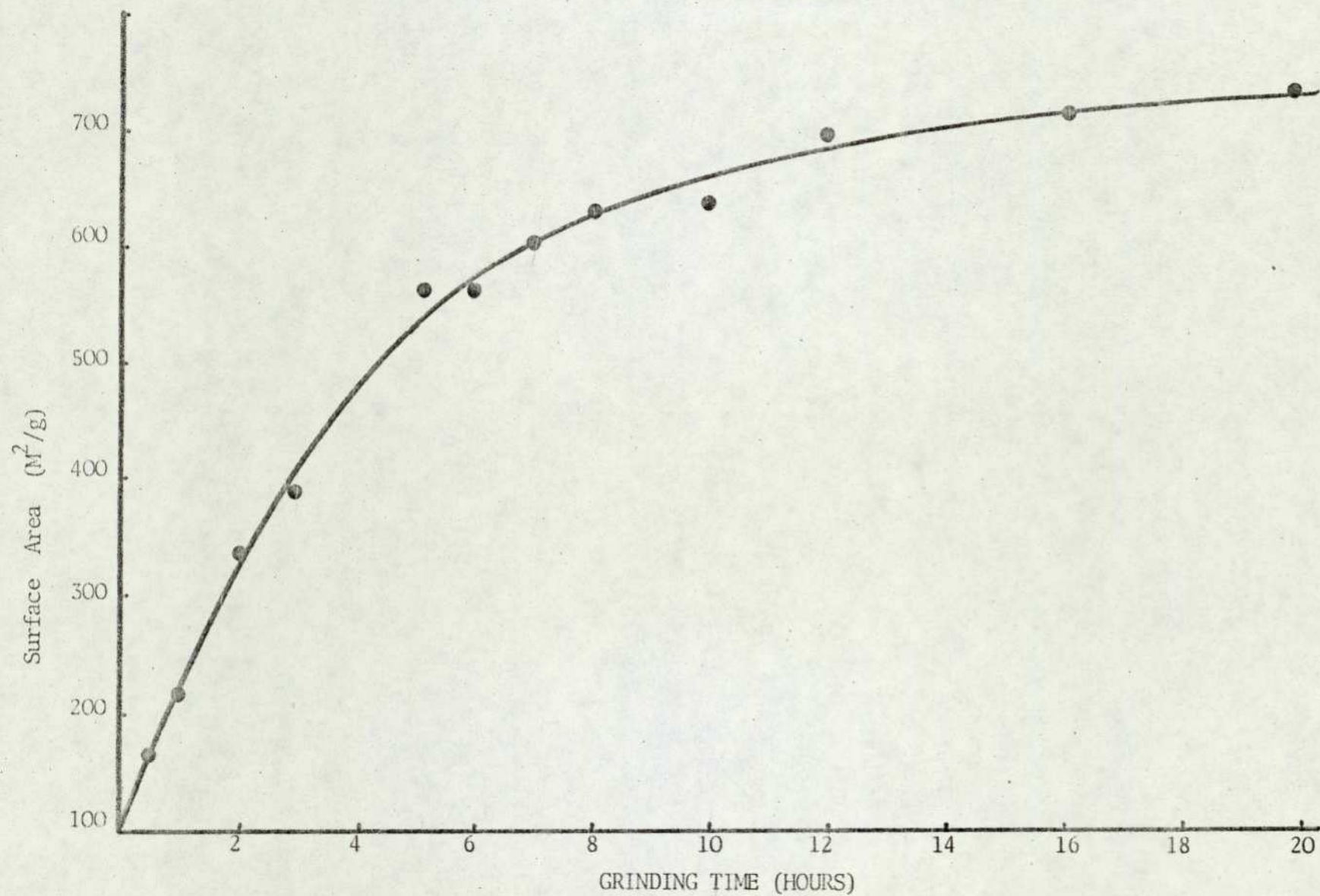


Fig. 3.2 RATE OF CHANGE OF SURFACE AREA WITH GRINDING TIME FOR GRAPHITE

made up from Analar pellets of potassium hydroxide and deionized, doubly distilled water. The electrolyte was prepared freshly before each experiment, in order to, eliminate the effects of carbonation. Air contains a small percentage of carbon dioxide and may slowly cause carbonation of alkaline electrolytes.

The oxygen electrode performance deteriorates as the K_2CO_3 concentration in the electrolyte rises, and, if highly porous electrodes are employed K_2CO_3 could precipitate in the pores and physically damage the electrode structure. For air electrodes, this problem could become serious only during long term use, however this problem could be avoided by removing CO_2 before the air enters the cell using an absorbent.

3.4.4. Polarization Runs

Steady state polarization curves were determined using the floating cell (described in section 2.3.2, and shown in figure 2.4) incorporated in a potentiostatic circuit. The potentiostat employed was a Chemical Electronics, TR 40-3A. The electrode was mounted and the cell assembled. After the electrode/electrolyte contact was established, the working electrode was supplied with oxygen or air, and the reference electrode (D.H.E. described in section 2.3.3) was equilibrated. The steady value of O.C.V. (Open Circuit Voltage) was measured using a digital voltmeter (D.V.M.) (Gould Advance, DMM 7) after 30 to 60 minutes of stability. The potentiostat was then switched to a value cathodic to the O.C.V. and switched to the cell. The current was recorded when it had reached a steady

value (after about three minutes). This procedure was repeated at 25 mV overvoltage increments (in the cathodic direction). The potentiostat was then disconnected and the ohmic correction carried out using the interrupter technique (described in section 2.3.5).

The errors in electrochemical testing were as follows:-

i) Current and Potential measurements:-

The current was measured to $\pm 2\%$ of full scale deflection and the potential to $\pm 0.5\%$, hence the error in these measurements is very small.

ii) The Correction for ohmic over voltage:-

Here, the main source of error was imposed by the inaccuracy inherent in reading from the oscilloscope grid. Measurement limits were to ± 0.2 cm.

3.5. RESULTS AND DISCUSSION

3.5.1. Steady State Performance

Figure (3.3) shows the iR -corrected performance of a Teflon bonded graphite electrode and a Teflon bonded platinum black electrode for the reduction of oxygen in 5N KOH in air, at room temperature. This shows that at any practical current densities, the platinum electrode is only about 150 mV better than the graphite electrode. The Teflon bonded Pt black was fabricated from platinum black (supplied by Johnson-Matthey), B.E.T. surface area of $10 \text{ M}^2/\text{g}$. Graphite B.E.T. surface area was $490 \text{ M}^2/\text{g}$ and the electrical conductivity was about $0.1 \text{ ohm}^{-1} \text{ cm}^{-1}$ at room temperature under 100 Kg/cm^2 compression.

The reason for measuring the activity of Teflon bonded platinum black for oxygen reduction was to establish a standard against which the performance of Teflon bonded graphite electrode could be compared. The reproducibility of polarization runs for repeated scans of a given electrode, and for tests on different graphite electrodes, was good, especially in the current density region below 200 mA/cm^2 , above that the reproducibility of repeated runs was less due to the flooding and sweating phenomenon of the hydrophobic electrode. As can be seen from figure (3.3) for oxygen reduction on both Teflon bonded graphite and platinum black electrodes, there is an initial steep drop of performance, attributable to high activation polarization, followed by a linear region with steady slope. There is no diffusion polarization region, which usually appear as a gradual tapering off as the limiting current is approached. This is in a good agreement with the observation of Goldstein¹¹ who noted the absence of a diffusion limited region for current density up to 2 A/cm^2 for oxygen reduction on Teflon bonded graphite electrodes. He concluded that diffusion limitations were insignificant at least upto 200 mA/cm^2 .

3.5.2. Effect of Graphite Loading and Teflon Ratio on the Performance of Teflon bonded Graphite Electrode for Oxygen Reduction

Tantram and Tseung¹⁸ found that the catalyst/Teflon ratio of 3:1 gives the best performance for oxygen reduction

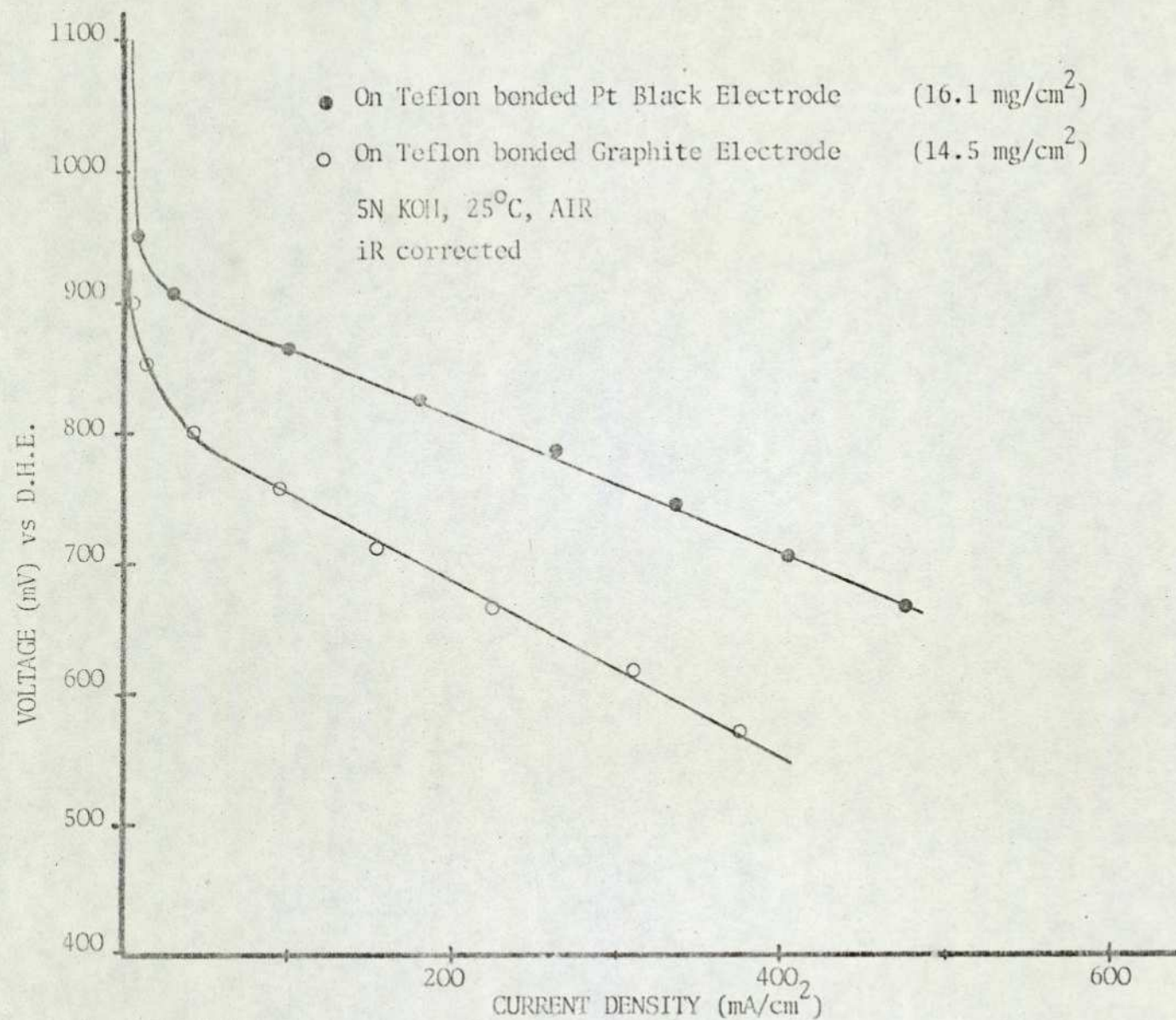


Fig. 3.3 STEADY STATE MEASUREMENTS OF OXYGEN REDUCTION

on Teflon bonded graphite electrode. A number of electrodes were prepared with different graphite loadings and catalyst/Teflon ratio of 3:1. Electrodes with graphite loadings ranging between 10 mg/cm^2 and 18 mg/cm^2 gave similar performance, whereas, electrodes with catalyst loading above 18 mg/cm^2 gave slightly lower performances. This could be attributed to the increase in the thickness of the electrode which lengthens the reactant diffusion path, therefore, increasing the mass transfer. The increase in the electrode thickness also increases the ohmic drop. Electrodes with catalyst loading less than 8 mg/cm^2 showed tendency towards flooding at current densities as low as 50 mA/cm^2 , which led to poor performance.

The comparison of performances involving different Teflon bonded electrodes could be inaccurate and proved to be difficult in practice, because there are many uncertainties associated with the electrode fabrication, such as the assumption that each component in the catalyst mix is transferred to the electrode in the same proportion. Also it is difficult to assess whether the catalyst/Teflon mix has been pasted evenly over the whole current collector surface. This depends largely on the skill of the maker. Therefore, in this work the average performance of several electrodes with similar loadings was taken for the comparison.

3.5.3. Corrosion Scans

Corrosion scans were carried out on graphite in the oxygen reduction potential region. The same procedure used in the normal polarization run was followed, but under nitrogen (white spot) atmosphere. The 5N KOH solution was purged with nitrogen gas for one hour to remove the dissolved oxygen in the solution. The nitrogen gas flow was subsequently maintained above the electrolyte during the period of the corrosion test.

It was difficult to remove traces of adsorbed oxygen from the graphite surface, but after several scans the current density at 500 mV vs D.H.E. was cathodic and below 0.3 mA/cm^2 . This current could be due to the oxygen in the nitrogen gas (maximum 5 p.p.m.) and the diffusion of some oxygen from the anode compartment. In conclusion the corrosion of graphite in 5N KOH, 25°C and in the potential region 0.9 to 0.5 volt vs D.H.E. is negligible and the presence of the impurities on the graphite is also negligible. Cyclic voltametry technique was also used under similar conditions in the oxygen reduction region at low scan rate (6.6 mV/sec) and the resultant voltammogram showed negligible corrosion current, less than 0.4 mA/cm^2 at 0.5 volt vs D.H.E.

Similar corrosion scans were carried out on nickel screen under similar conditions and the test revealed no sign of corrosion.

3.5.4. Current Stability of Oxygen Reduction on Graphite Electrodes

In short term test for current stability of oxygen

reduction on Teflon bonded graphite electrode (in 5N KOH, 25°C, in air), the electrode was held potentiostatically (at 0.7V vs D.H.E.). The current density decayed quickly from 121 to 95 mA/cm² in approximately 5 minutes. The decay was much slower for the following three hours. After the latter period the current reached a stable value (85 mA/cm²) and remained constant for the next three hours.

The major problem with carbon cathodes is their tendency to flood after prolonged use, especially at high current densities (greater than 100 mA/cm²).

Jindra and Mrha⁵⁶ attributed this phenomenon to oxidation of the carbon surface by the hydrogen peroxide.

This oxidation process produces mainly acidic carboxylic groups which render the carbon surface progressively more hydrophilic.

It has been reported⁵⁷ that carbons and graphites with basic surfaces make better electrocatalysts for the reduction of oxygen than the same materials with acidic surfaces. Kent⁵⁵ has suggested that the basic surface groups on graphite surface increase the performance of the graphite for the oxygen reduction reaction by catalysing the reduction of oxygen to HO₂⁻. He attributed the initial decay in the electrochemical activity of graphite for oxygen reduction to the oxidation of the basic groups on the graphite surface to acidic surface groups, probably by the hydrogen peroxide which is generated during the oxygen reduction.

The observed initial decay in the electrochemical activity of graphite electrode for oxygen reduction reaction could be explained in similar manner and could be attributed also to the flooding of the electrode, which lengthens the diffusion path for the reactant species (oxygen) and consequently increases the mass transfer.

3.6. HYDROGEN PEROXIDE PRODUCTION

Teflon bonded graphite electrodes were operated as air cathodes at fixed current densities for one hour. The cathode and anode were separated by a glass frit in a two compartment cell, thermostated at 25°C. A piece of 8 cm² Teflon bonded graphite electrode was used in the floating position in the cathode compartment (volume of electrolyte was 100 ml, distance from the centre of the cathode to the glass frit ~ 6 cm). An air pump supplied air to the cathode compartment. A 20 cm², 100 mesh nickel screen was used as the counter electrode. A Chemical Electronics potentiostat (TR 40-3A) was used in the Galvanostatic mode to feed current in to the cell.

After one hour, the concentration of H₂O₂ in the 5N KOH solution was measured by titrating the acidified, ice cooled solution with standard potassium permanganate solution. The self decomposition of hydrogen peroxide in 5N KOH in the same apparatus and under similar experimental conditions (but without passing current) was measured and found to be about 0.5 g/l-hr of HO₂⁻. Table (3.1) shows the amount of HO₂⁻ produced after the passage of a fixed amount of current for one hour. The

amount of HO_2^- in the cathode compartment was only about 74% of the total amount of HO_2^- produced.

This was mainly caused by the decomposition of HO_2^- on the nickel oxide anode surface. This loss was not measured in the blank correction. In addition, there was some additional decomposition of H_2O_2 during the pipetting of the solution and the titration operation. The catalytic activity of high surface area graphite towards the chemical decomposition of hydrogen peroxide was investigated by Goldstein¹¹. He concluded that graphite is quite inert for the decomposition of HO_2^- , $K_{f,m}$ at $25^\circ\text{C} = 6.7 \times 10^{-5} \text{ sec}^{-1} \text{ g}^{-1}$, where $K_{f,m}$ is the first order rate constant for the chemical decomposition of hydrogen peroxide.

The schematic diagram of the cell used for this set of experiments is shown in figure (2.4).

Table (3.1)

Hydrogen Peroxide produced from Oxygen reduction on a 8 cm^2
 Teflon bonded graphite electrode, current passed through
 the cell for 60 minutes.

Current mA	Theoretical gm HO_2^-	Experimental average gm HO_2^- (in 80 ml. electrolyte in the cathode compartment)	Experimental/ Theoretical %
200	0.1230	0.0917	74.55 (2)
400	0.2460	0.1866	75.85 (2)
600	0.3693	0.2675	72.40 (2)
800	0.4924	0.3575	72.6 ± 0.02 (4)

numbers between brackets show the number of experiments for
 each current density.

C H A P T E R F O U R

HYDROGEN PEROXIDE DECOMPOSITION

4.1. SELECTION OF CATALYST FOR HYDROGEN PEROXIDE DECOMPOSITION

Two factors were considered in selecting a catalyst for the decomposition of hydrogen peroxide, the first factor was the catalytic activity towards hydrogen peroxide decomposition. The second factor was the cost of the material.

Vielstich⁵⁸ reported that silver is superior to platinum in alkaline solutions and this was supported by Cota⁵⁹, who found silver to be the best available catalyst for peroxide decomposition.

Evaluation of a series of catalysts for their activity in H_2O_2 decomposition under similar conditions had been carried out by Cota and co-workers⁵⁹. In their study the initial rate of oxygen evolution at 22°C from 50 ml. 6.9 M KOH containing 5 ml. 1M H_2O_2 was measured gasometrically for a series of catalyst powders at constant weight. Their results together with the initial rates per unit total surface area, which have been calculated are shown in table (4.1).

Considering the initial rates on a weight basis, the results in table (4.1) confirmed the high activity of silver oxide and platinum black.

However, a non-noble metal catalyst, such as unsymmetrical cobalt ferrite, also has high activity, greater than Rany silver and palladium black. Transition metal oxides, such as MnO_2 and $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$ were much inferior.

In considering the initial rates on a surface area basis, it is evident from table (4.1) that silver possesses a high

*Table (4.1)

Activity of a series of catalysts for H_2O_2 decomposition at 22°C

Catalyst	Initial activity $K_{I,m} \times 10^4$, mole $\text{O}_2 \text{ sec}^{-1} \text{ g}^{-1}$ ($\pm 10\%$)	B.E.T. specific surface area $\text{M}^2 \cdot \text{g}^{-1}$ ($\pm 5\%$)	Initial activity normalized to unit B.E.T. specific surface area, mole $\text{O}_2 \text{ sec}^{-1} \text{ M}^{-2} \times 10^5$
Ag_2O	4.0	0.35	110
Pt black	3.6	14.7	2.4
unsymmetrical cobalt ferrite	1.3	16.8	0.77
Raney Ag	1.2	3.4	0.35
Pd black	1.2	7.6	0.15
Ag(Precip.)	0.76	0.13	58
MnO_2	0.42	0.35	1.2
$\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$	0.37	2.7	0.13
Fe_2O_3	0.25	7.3	0.034
Au	0.15	0.1	1.5
Ni black	0.15	8.5	0.018
Unsymmetrical nickel ferrite	0.12	0.79	0.015
Symmetrical nickel ferrite	0.07	0.65	0.011

The general formula for cobalt ferrite is $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$

Symmetrical cobalt ferrite $x = 1$

Unsymmetrical cobalt ferrite $x \neq 1$

* results obtained from ref. 59 and 11.

activity despite the low surface area. Platinum, unsymmetrical cobalt ferrite and palladium only show a comparable activity due to their high surface area.

Cota et al⁵⁹ did not specify the exact composition of their unsymmetrical cobalt ferrite.

Goldstein¹¹ has evaluated a large number of catalysts for their activity towards H_2O_2 decomposition using a similar approach to that of Cota et al⁵⁹. Some of these results are shown in table (4.2). The catalytic activities were compared using the parameter $K_{I,m}$, which describes the initial oxygen evolution rate, obtained at 25°C, with 5 ml. 1M H_2O_2 in 50 ml. 5N KOH, using 50 mg catalyst.

As can be seen from table (4.2), the two most active catalysts are Ag-graphite⁶⁰ and Pt black. These catalysts were followed in activity by cobalt-iron oxide prepared by the hydroxide method.

The best known catalysts which possess high activity for the decomposition of H_2O_2 , such as silver, platinum and palladium are very costly materials, therefore they were ruled out for this work. The remaining catalyst with high activity and low cost is the cobalt ferrite.

Goldstein and Tseung⁶¹ showed that the maximum activity and the lowest activation energy for H_2O_2 decomposition reaction on cobalt iron oxide ($Co_xFe_{3-x}O_4$) occurs at the composition with $x = 1$ i.e. ($CoFe_2O_4$), since the greatest availability of Octahedral Co^{II} occurs at this composition. Co^{II} ions can

Table (4.2)¹¹Comparison of catalyst activities for H_2O_2 decomposition

Catalyst	$K_{I,m} \times 10^6$ mole O_2 $\text{sec}^{-1} \text{g}^{-1}$ 25°C	B.E.T. specific surface area $\text{M}^2 \cdot \text{g}^{-1}$	Preparation method or pretreatment
5 at % Ag on Acheson graphite	1230	180	Freeze dried (AgNO_3 / graphite decomposed 120°C)
Pt black	990	30	Johnson-Matthey Fuel Cell Catalyst
5 at % Ag on Acheson graphite	850	9	Freeze dried (AgNO_3 / graphite decomposed 120°C) Treated 300°C , N_2 , 1 hour
$\text{Co}_1\text{Fe}_2\text{O}_4$	310	90	Hydroxide prepn., 1hr, hydro- thermal growth, treated 300°C , N_2 , 1 hour.
Pd black	205	4	Hopkin and Williams reagent
Ag	130	3	Hopkin and Williams reagent
MnO_2	95	7	Hopkin and Williams reagent
$\text{Co}_1\text{Fe}_2\text{O}_4$	80	40	Freeze dried (nitrates, 450°C , 3 hrs)
NiO	0.4	76	Freeze dried (acetates, 300°C , 3 hrs)
$\text{Co}_1\text{Fe}_2\text{O}_4$	0.4	<1	Solid state sintering (Oxides, 1400°C)

Test conditions, 50 mg catalyst, 5 ml. 1M H_2O_2 , 50 ml. 5N KOH,
 25°C , 1 atm.

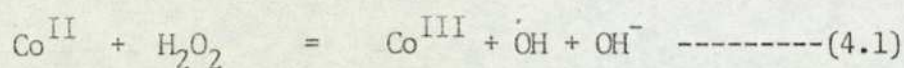
initiate a cyclic electron transfer process (redox reaction) on the catalyst surface.

The decomposition of H_2O_2 is defined as an acceptor reaction⁶², since it is catalysed by materials which can supply electrons to the H_2O_2 during the rate determining step.

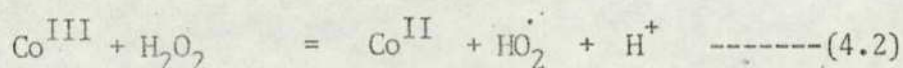
No work has been reported on the activity of nickel cobalt oxide for H_2O_2 decomposition, however the structure $(\text{Co}^{\text{II}})_t (\text{Ni}^{\text{III}} \text{Co}^{\text{III}})_o^{2-} \text{O}_4$ for NiCo_2O_4 has been proposed⁶³. Where the subscripts (t) and (o) refer to tetrahedrally and octahedrally coordinated cations respectively.

It was found²⁸ that the highest availability of Co^{II} occurs at the composition NiCo_2O_4 . The occurrence of Co^{II} on lattice sites, with its easy conversion to Co^{III} , allows a highly effective redox system to be set up initiated by Co^{II} centres.

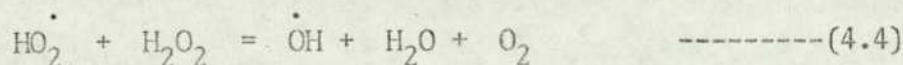
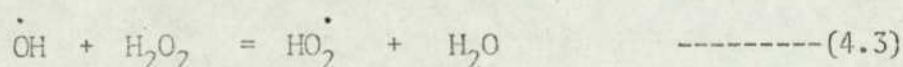
In the acceptor mechanism⁶², the over all process is a cyclic electron transfer reaction between the catalyst and successive H_2O_2 molecules.



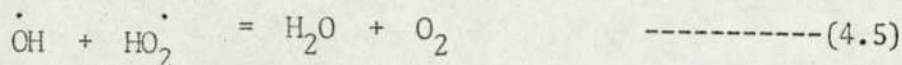
The catalytic centre then return to the divalent state by the reaction



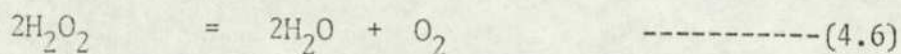
The free $\cdot\text{OH}$ and $\cdot\text{HO}_2$ radicals may set up chain reactions



before the terminating reaction.



The overall stoichiometry during catalysis is accordingly,



The catalyst NiCo_2O_4 can be prepared in high surface area form by freeze drying. This factor and the fact that NiCo_2O_4 possesses the highest availability of Co^{II} suggests that NiCo_2O_4 could be a very active material for H_2O_2 decomposition.

Therefore, it was decided to adopt the two types of catalysts (CoFe_2O_4 and NiCo_2O_4) for the decomposition of H_2O_2 and to carry out an evaluation of the catalytic activity of NiCo_2O_4 towards H_2O_2 decomposition.

4.2 EXPERIMENTAL

4.2.1. Preparation of CoFe_2O_4 and NiCo_2O_4

Since the catalytic properties are significantly enhance by increasing the surface area, it is of interest to prepare high surface area catalyst.

Goldstein and Tseung⁶⁴ investigated different preparation methods for the preparation of cobalt iron oxide catalysts, such as freeze drying, high temperature sintering and co-precipitation (oxalate and hydroxide routes). Of all the methods used, the hydroxide co-precipitation method offered the best chance of success in achieving high surface area catalyst, since the temperature required for decomposition is only 100°C . Therefore this method was adopted in this work

for CoFe_2O_4 preparation.

The procedure of the preparation of CoFe_2O_4 by hydroxide co-precipitation is as follows:

Analard grade cobalt chloride, ferric chloride and sodium hydroxide was used. The mixed metal salt solution was prepared by dissolving the appropriate amounts of metal chlorides in distilled deionized water. The solution was rapidly added with continual stirring to a known volume of freshly prepared 6N NaOH solution at room temperature. This volume of NaOH was ideally the quantity necessary to give pH. 12.5.

In practice, the mixed salt solution was added to 50 ml. of 6N NaOH, then the pH was adjusted to pH. 12.5, using a Vibret pH-meter (E.I.L. Ltd) by addition of more 6N NaOH. The resultant mixture was heated on a steam bath for an hour to dehydrate the gel. After cooling, the mixture was filtered, the precipitate was washed with distilled water until alkali free, and after air drying over night at 100°C , was ground to a fine powder in an agate pestle and mortar.

NiCo_2O_4 powder was prepared by the freeze drying technique (described in section 2.1.2 and 5.4.1a).

4.2.2. Determination of Catalytic Activity

The gasometric technique was used to determine the activity of the catalysts towards H_2O_2 decomposition, and the kinetic investigation of the reaction. The technique has been described by Cota et al⁵⁹ and Goldstein¹¹.

4.2.2a. H₂O₂ Decomposition Apparatus

The apparatus used in this work is based on that devised by Cota et al⁵⁹ and shown in figure (4.1).

It consists of the reaction vessel, which is a 250 ml. 3-necked flask. The flask side arms are fitted with a thermometer, stopper and the injection device, (figure 4.2).

The catalyst was held between two dumbbell-shaped Teflon plugs in a precision bore glass tube, joined to a B.19 cone fitted with a gas outlet tube and a Teflon stopper. A Teflon push rod pressing against the plugs, served to introduce the catalyst into the reaction vessel. The remaining part of the apparatus served to collect the evolved oxygen gas.

The use of the injection device led to practical difficulties such as loading of the catalyst, its introducing to the reaction mixture and loosening of the push-rod device.

Therefore another method of delivering the catalyst was devised for this work. All the experiments which were carried out with the injection device were repeated with the new design. Identical results were obtained, but with much less effort and practical problems. The new design, shown in figure (4.3), consists of a flask with an arm having a spoon-like shape. The arm could be rotated around its axis to deliver the catalyst.

Experiments, carried out under very low pressure (0.1 torr), proved the absence of leakage during the rotation.

4.2.2b. Analysis of Hydrogen Peroxide

Hydrogen peroxide is unstable with respect to

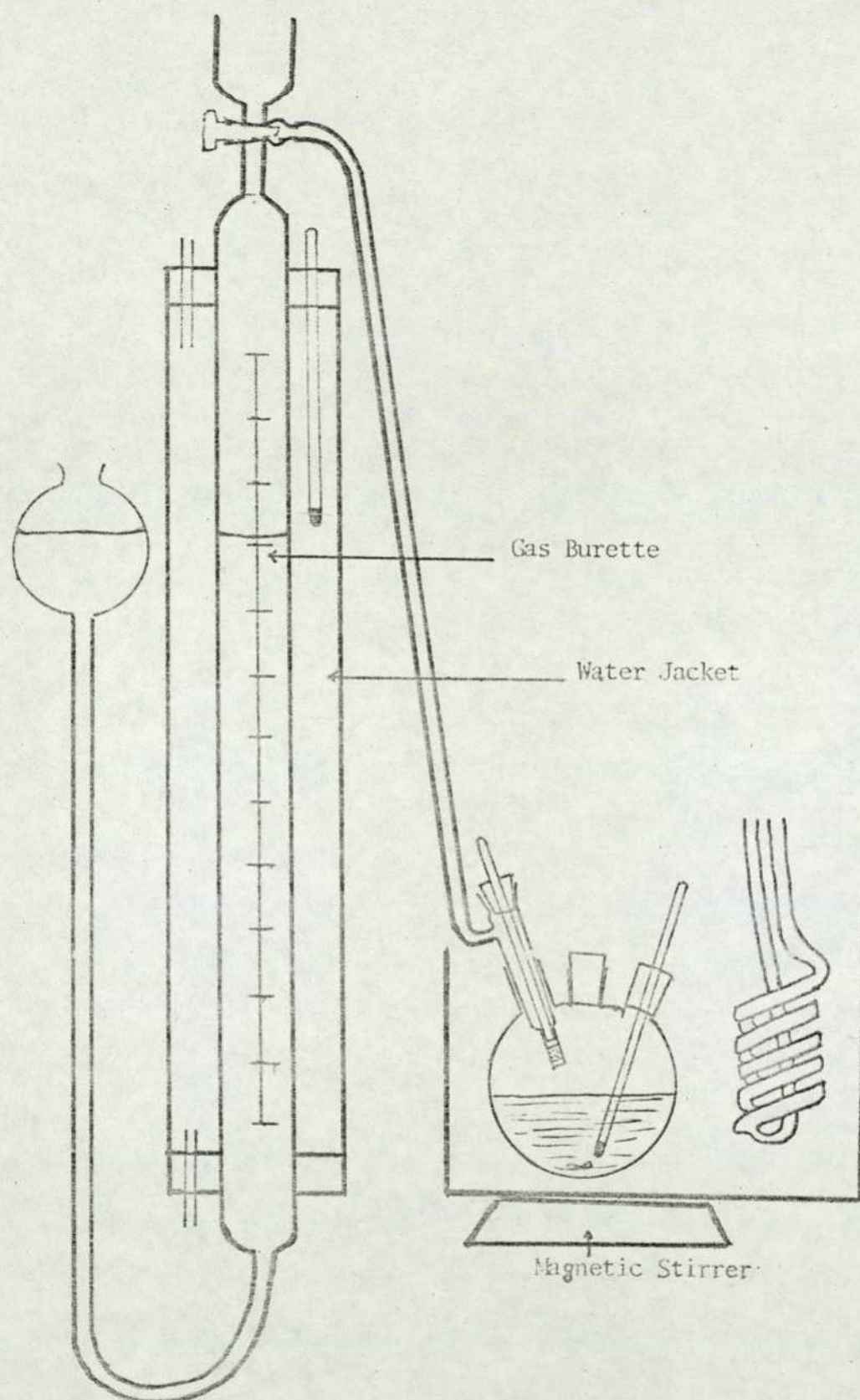


Fig. 4.1 THE HYDROGEN PEROXIDE DECOMPOSITION APPARATUS

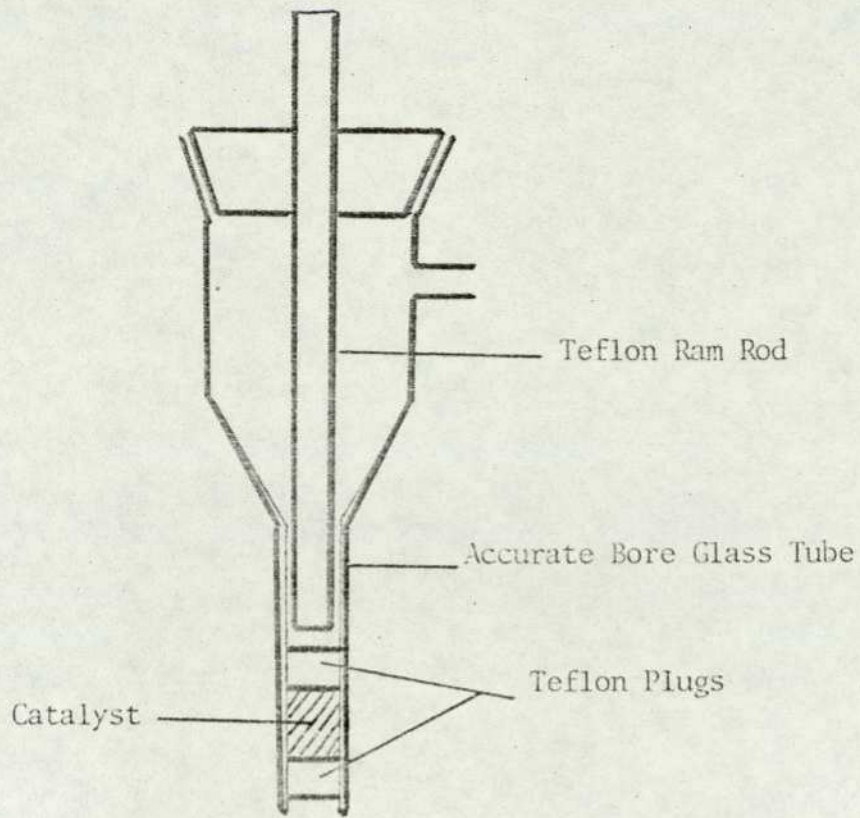


Fig. 4.2 THE INJECTION DEVICE

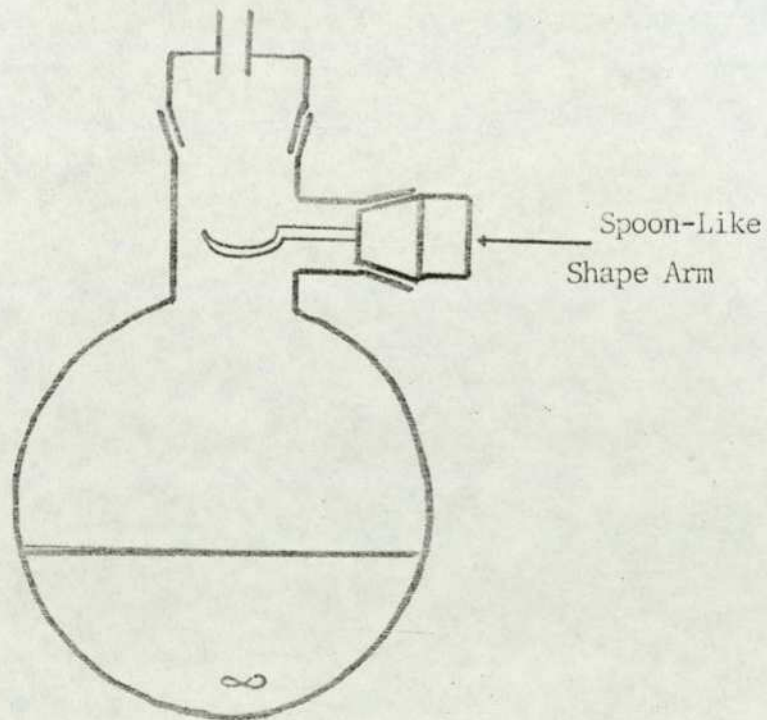


Fig. 4.3 THE NEW METHOD OF DELIVERING THE CATALYST

decomposition, however, the instability was found to be almost entirely due to impurities which catalyze the decomposition even when present in trace amounts. Absolutely pure H_2O_2 kept in inert containers does not decompose at ordinary temperatures, because of the high activation energy for the reaction.



$$\Delta G = -25.4 \text{ Kcal/mole}^{65}$$

Commercial H_2O_2 supplies often contain added stabilizers, such as sodium stannite or 8-hydroxy quinoline to inhibit the self decomposition reaction. These additives, although only present in the p.p.m. range, can profoundly modify the effect and activity order of decomposition catalysts. Since the H_2O_2 resulting electrochemically from oxygen reduction is additive free, a stabilizer free hydrogen peroxide was chosen for this study. This was Laporte Stabilizer - free peroxide, supplied at 35% w/w in polythene carboys.

A volumetric method was chosen for the analysis of H_2O_2 since it combines accuracy with rapidity.

In the permanganate method the KMnO_4 solution was standardized using the primary standard sodium oxalate, following a method introduced by Fowler and Bright⁶⁶. The standardized solution of KMnO_4 was then used to standardize the H_2O_2 solution in ice cooled acidic ($1\text{M H}_2\text{SO}_4$) solution.

For greatest accuracy a $1\text{M H}_2\text{O}_2$ solution was made for each run, and its strength determined.

4.2.2c. Description of a Typical Run

5 ml of a 1M H_2O_2 solution was pipetted in to a thermostated reaction flask containing 50 ml., 5N KOH and the Teflon coated magnetic stirrer. The injection device was fitted and the magnetic stirrer started. The gas burette reading at zero time was taken by equalizing the levels of the distilled water in the reservoir and the gas burette. The catalyst was immediately injected in to the reaction vessel and a stop clock started simultaneously.

Oxygen was evolved from the hydrogen peroxide and displaced liquid from the gas burette. Care was exercised to equalize burette and reservoir levels for each reading. The barometric pressure was recorded. After about an hour the burette reading become constant and was taken to be the reading at infinite time.

In a similar run, by omitting the catalyst, a measure of the self-decomposition rate of H_2O_2 could be obtained.

This decomposition is due to heterogeneous catalysis by glass walls of the reaction vessel⁶⁷, the Teflon items⁵⁹, and base catalysis by the reaction medium⁶⁸.

The self-decomposition rate was a small blank correction to the Time - Volume Curves.

4.3. RESULTS AND DISCUSSION

4.3.1. X-Ray Analysis

The technique was described in (Section 2.2.2).

CoFe_2O_4 prepared by hydroxide co-precipitation method gave d- values slightly lower than the corresponding d-values of the ASTM data, however little trace was found of d-values corresponding to other phases, showing that the hydroxide co-precipitation method produce single phase product (CoFe_2O_4 possesses a spinel structure). The accuracy in d-values depends essentially on measurements with the Vernier film reader, and these are limited by the sharpness of lines on the film. Very fine powder produce rather blurred lines.

X-ray powder data for CoFe_2O_4 and the possible impurities in cobalt iron oxide are presented in Table (4.3).

4.3.2. The Initial Rate Constant

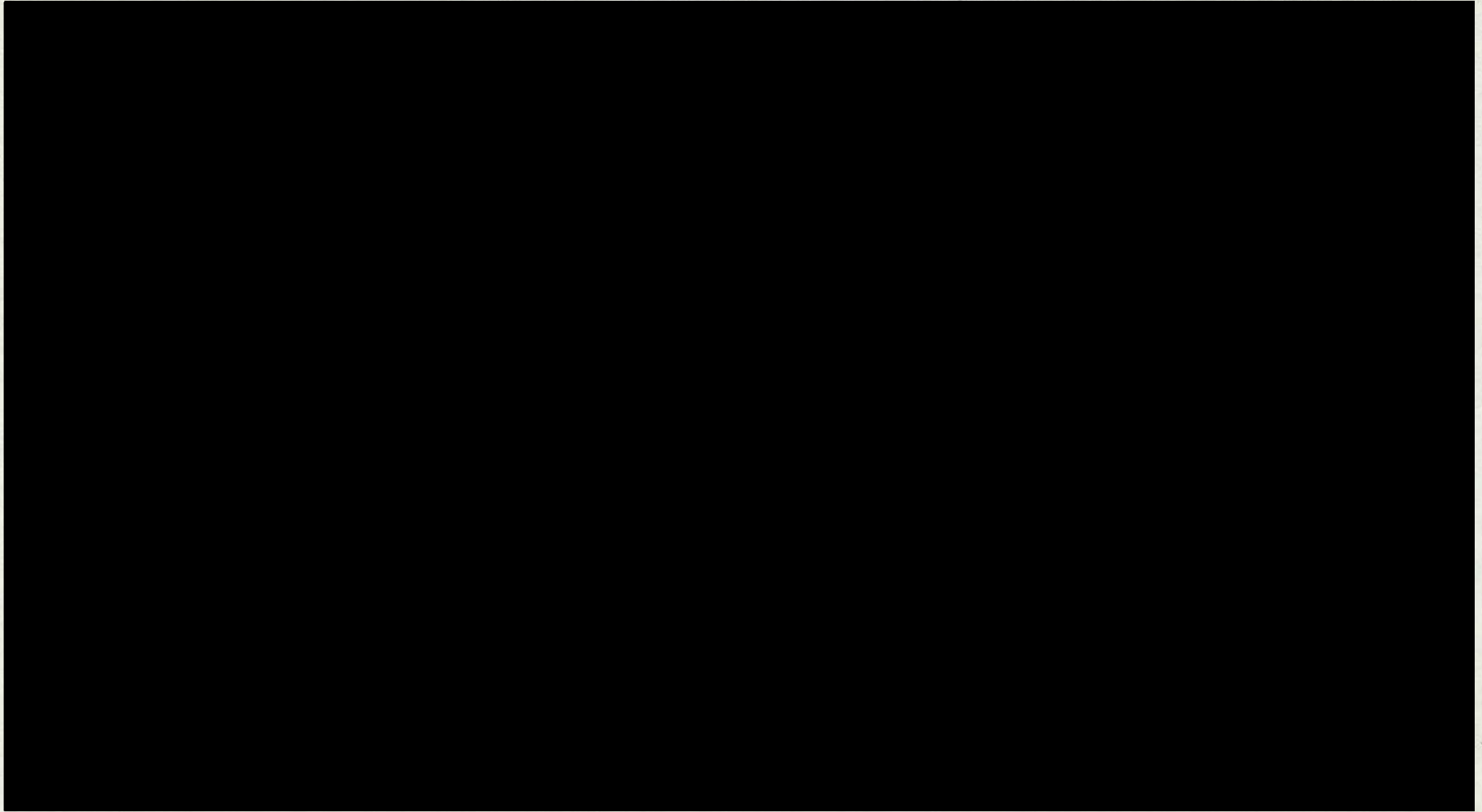
Cota et al⁵⁹ found that a useful parameter for expressing the catalytic activity for H_2O_2 decomposition was the initial rate of oxygen evolution at (N.T.P.) per unit mass of catalyst ($K_{I,m}$).

Figures (4.4) and (4.5) show plots of burette reading versus time for CoFe_2O_4 (prepared by hydroxide co-precipitation) and NiCo_2O_4 (prepared by freeze drying) respectively. A tangent at zero time was drawn on the graph and its gradient gave the initial rate of oxygen evolution on each catalyst.

$K_{I,m}$ is dependent on the initial concentration of H_2O_2 , pH and

Table (4.3)

X-RAY ANALYSIS OF $\text{Co}_1\text{Fe}_2\text{O}_4$ AND A.S.T.M. X-RAY POWDER DATA FOR $\text{Co}_1\text{Fe}_2\text{O}_4$ AND THE POSSIBLE IMPURITIES IN CoFe_2O_4
(PREPARED BY HYDROXIDE CO-PRECIPITATION)



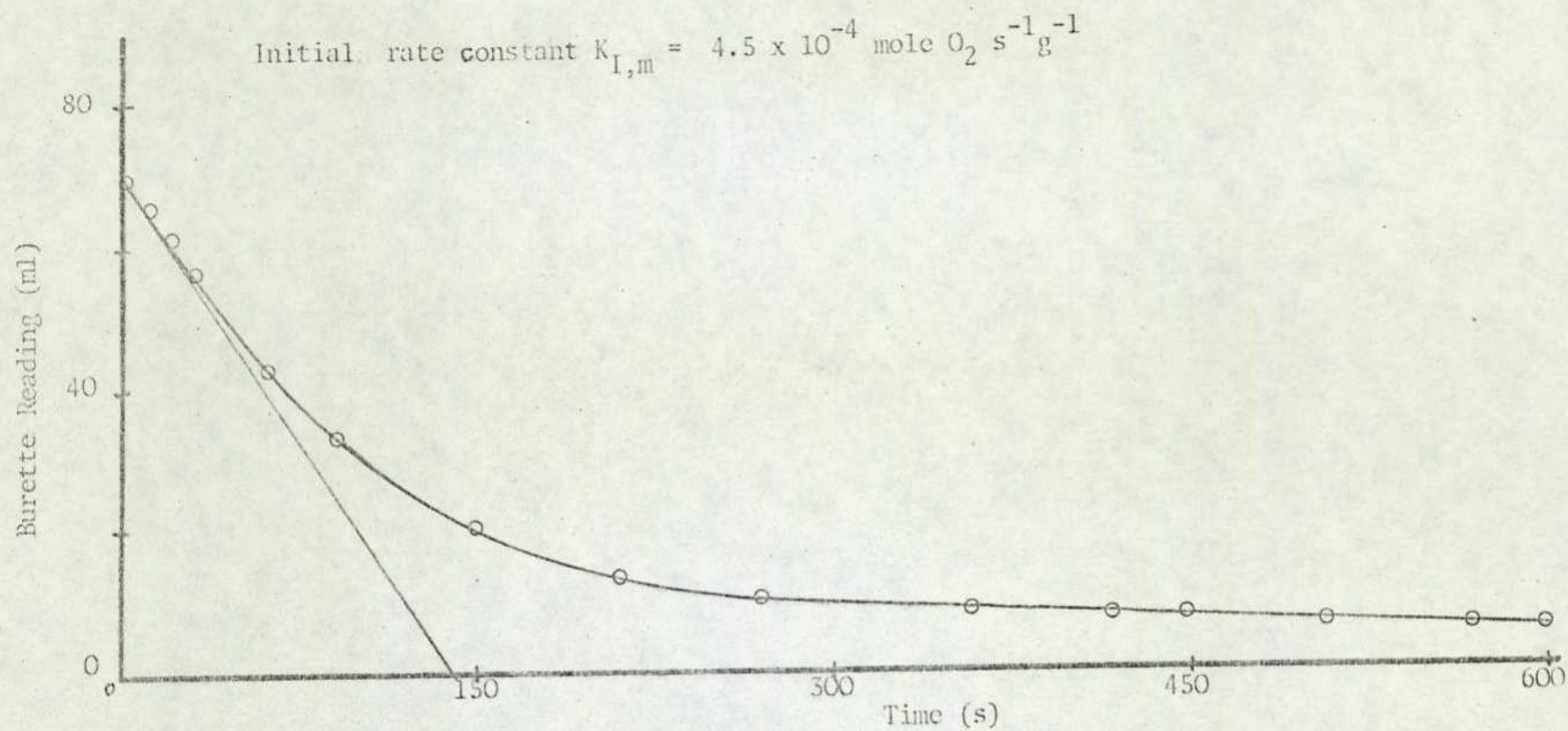


Fig. 4.4 VOLUME OF OXYGEN EVOLVED VERSUS TIME, FOR H_2O_2 DECOMPOSITION AT 25°C , BY CeFe_2O_4 (HYDROXIDE CO-PRECIPITATION)

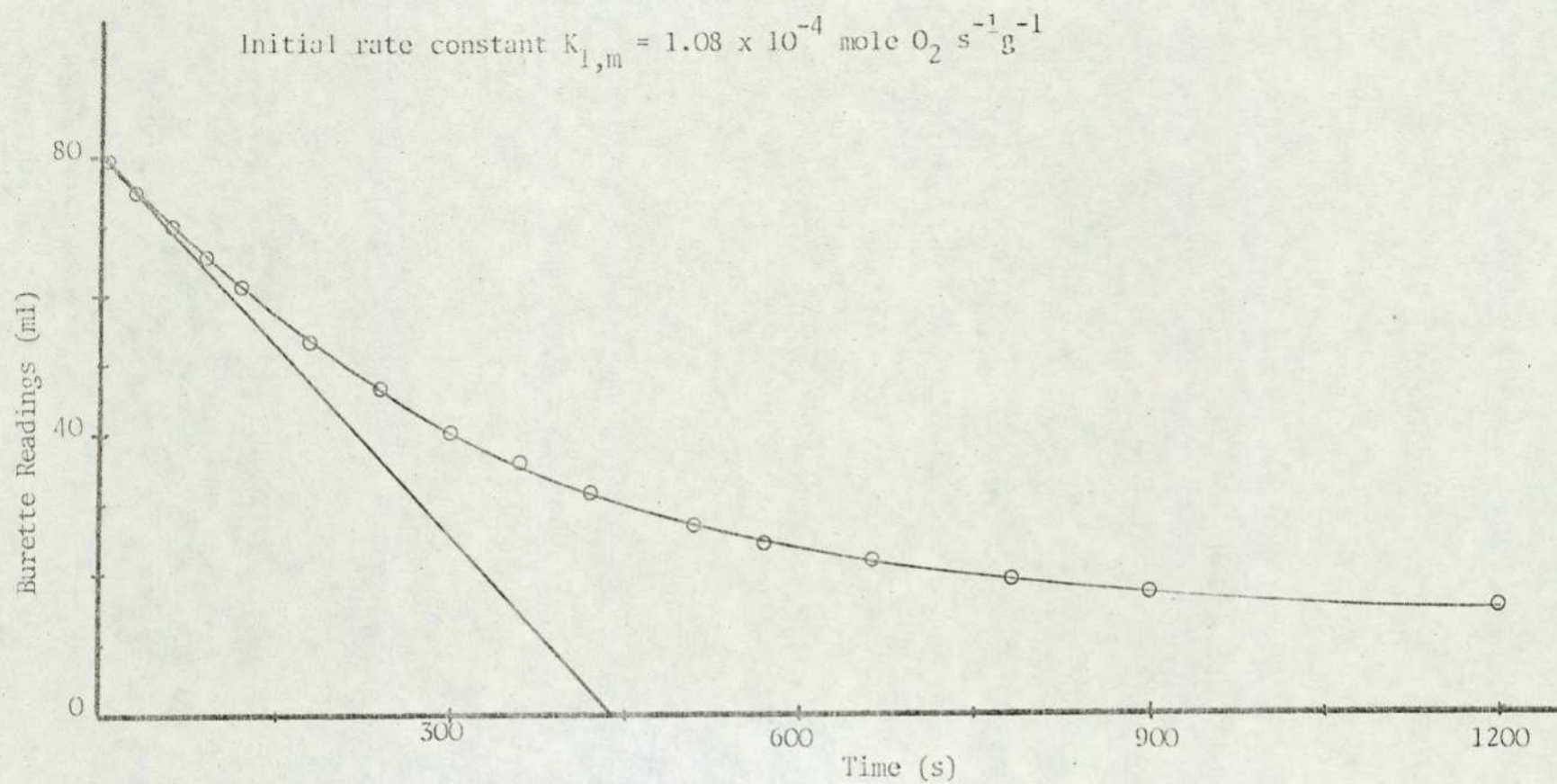


Fig. 4.5 VOLUME OF OXYGEN EVOLVED VERSUS TIME, FOR H_2O_2 DECOMPOSITION AT 25°C ,
BY NiCo_2O_4 (FREEZE DRYING)

and temperature⁵⁹. Therefore, the utmost care was exercised in measuring the H_2O_2 concentration accurately and in keeping the temperature steady within $\pm 0.1^\circ\text{C}$. The pH change was negligible due to the large volume (50 ml.) of 5N KOH.

However the main error in the $K_{I,m}$ measurement was the inaccuracy in drawing the tangent on the graph, since the tangent has to be drawn at the extremity of the curve.

The initial rate constant, $K_{I,m}$, is effectively independent of the kinetic order of the decomposition reaction⁵⁹.

Secondary phenomena such as diffusion control and side-reactions are thus largely excluded.

4.3.3. The reaction order and reaction rate constant

The following kinetic treatment for H_2O_2 decomposition on NiCo_2O_4 is similar to that conducted on CoFe_2O_4 ¹¹.

If (a) is the initial concentration of H_2O_2 , and (c) the amount of H_2O_2 which has reacted at time t, then (a-c) is the concentration present at time t. For first order kinetics

$$-\frac{d(a-c)}{dt} = K(a-c) \quad \text{-----}(4.8)$$

where K is the first order rate constant for the reaction.

To obtain the variation in the concentration (c) as a function of time the differential equation must be integrated

$$\int \frac{dc}{a-c} = K \int dt \quad \text{-----}(4.9)$$

Since $c = 0$ at $t = 0$

$$\therefore Kt = \ln \left(\frac{a}{a-c} \right) \quad \text{-----}(4.10)$$

Thus, if $\log_{10}(1 - \frac{c}{a})$ is plotted as a function of t , a straight line results, of slope $\frac{-K}{2.3}$.

The oxygen evolved at a given time is directly proportional to the H_2O_2 decomposed, thus (a) is the difference between the burette reading at zero time (V_0) and that at infinite time (V_∞).

Similarly (c) is ($V_0 - V_t$), V_t being the burette reading after t sec.

Figures (4.6) and 4.7) show a $\log_{10}(1 - \frac{c}{a})$ versus t plots for $Co_1Fe_2O_4$ (prepared by hydroxide co-precipitation, B.E.T. surface area $120 M^2/g$) and $NiCo_2O_4$ (prepared by freeze drying, B.E.T. surface area $69.7 M^2/g$) respectively.

Both plots are linear over 95% of the total reaction time, showing that no secondary processes occur during the decomposition reaction. The straight line in both graphs passing through the origin is good evidence for first order kinetics. Moreover, the reaction rate constants were shown to be independent of the initial H_2O_2 concentration but directly proportional to the catalyst mass in the reaction mixture. These results are also characteristic of first order kinetics⁶⁹.

The obtained results on $CoFe_2O_4$ are in good agreement with the previous results of Goldstein⁶¹.

4.3.4. Activation Energy for H_2O_2 Decomposition

It has been shown⁶¹ that provided diffusion effects

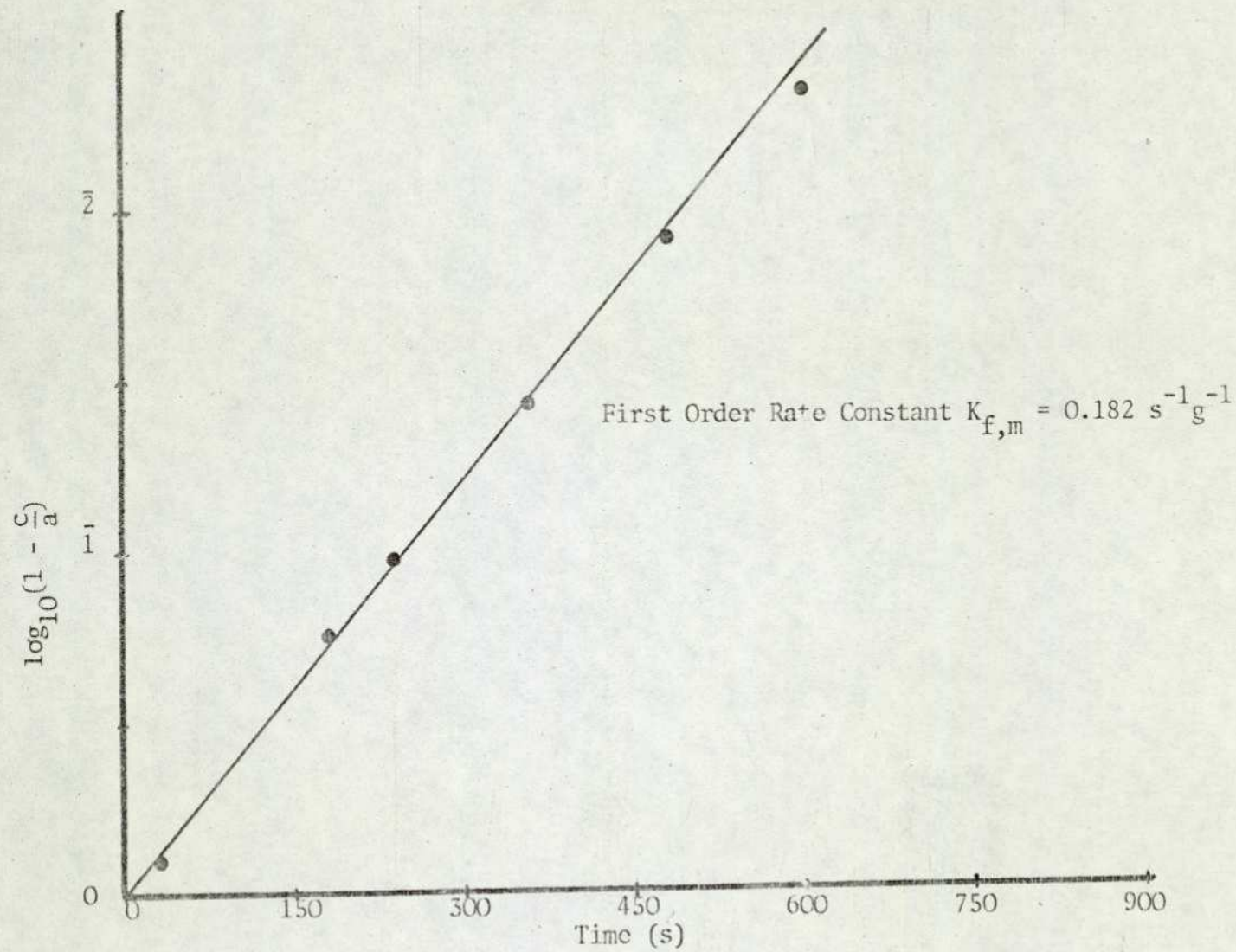


Fig. 4.6. $\log\left(1 - \frac{c}{a}\right)$ VERSUS TIME PLOT SHOWING FIRST ORDER KINETICS, FOR H_2O_2 DECOMPOSITION AT 25°C , BY CoFe_2O_4 (HYDROXIDE CO-PRECIPITATION)

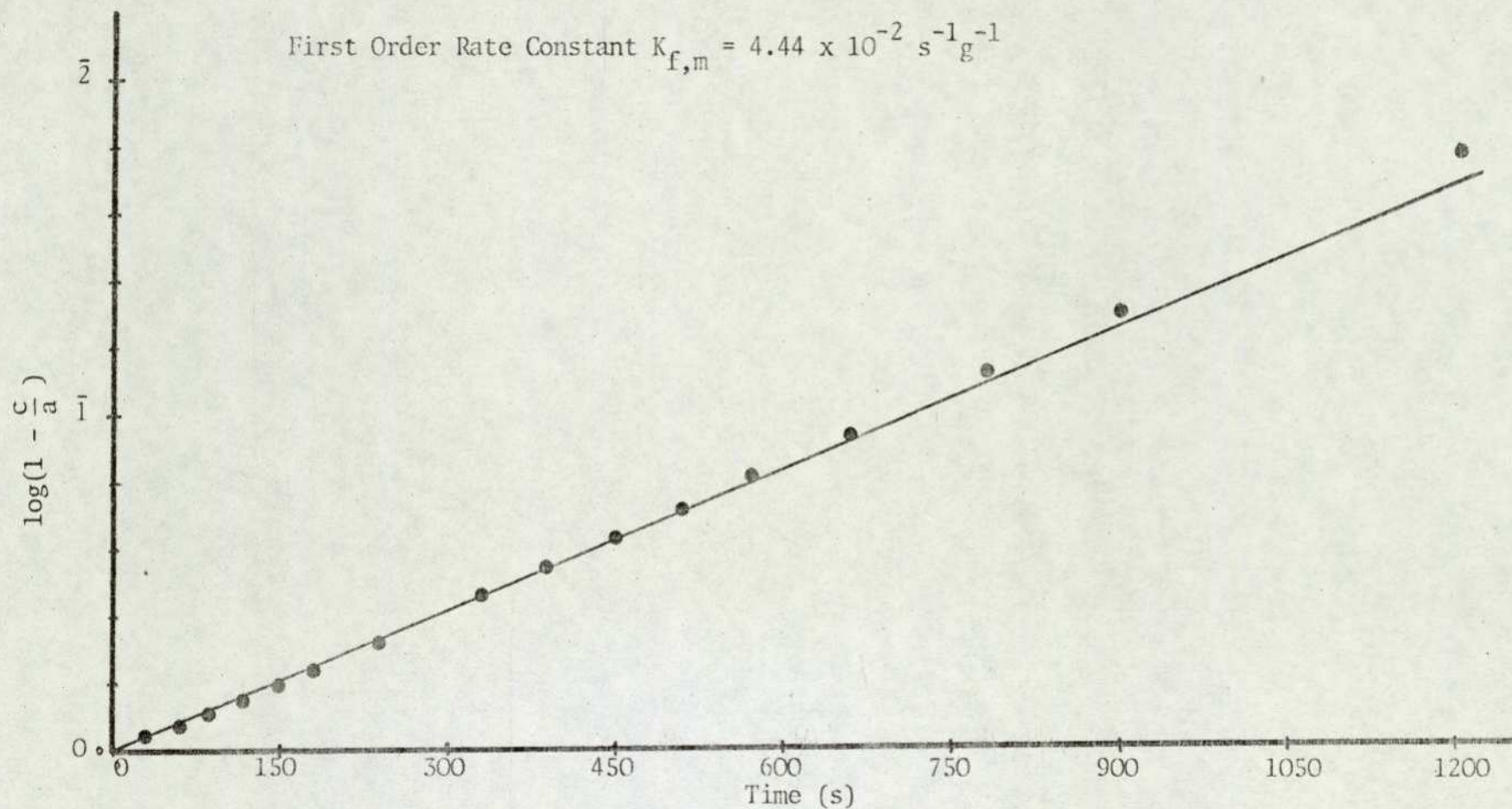


Fig. 4.7 $\log(1 - \frac{c}{a})$ VERSUS TIME PLOT SHOWING FIRST ORDER KINETICS FOR H_2O_2 DECOMPOSITION
AT 25°C , BY NiCo_2O_4 (FREEZE DRYING)

can be assumed to be negligible, catalytic activity in the H_2O_2 decomposition reaction may be the result of two main factors:

1. The intrinsic catalytic activity of the catalyst which depends on its chemical composition and electronic structure.
2. The microstructure of the catalyst, which depends on total available surface area, aggregate surface area and the pore size distribution.

To ascertain the intrinsic activity order for different catalysts, a kinetic parameter which is independent of the catalyst microstructural effects has to be employed.

Activation energy is largely independent of the catalyst microstructural effects and is much more affected by its chemical composition and electronic structure⁶¹.

Arrhenius showed that the dependence of the rate constant for a reaction on the temperature could be described by the equation

$$\frac{d \ln K}{dT} = \frac{E}{RT^2} \quad \text{-----}(4.11)$$

where K is the reaction rate constant

T is the absolute temperature

E is the activation energy of the reaction

R is the gas constant

equation (4.11) becomes on integration

$$K = A \exp (-E/RT) \quad \text{-----}(4.12)$$

where A is the constant of integration.

A plot of $\log K$ versus $1/T$ should hence be linear with a slope of $(-E/2.3R)$.

Experiments were conducted at 25, 30, 35 and 40°C.

Figures (4.8) and (4.9) show the activation energy plots for the decomposition of H_2O_2 on $NiCo_2O_4$ powder (prepared by freeze drying).

Figure (4.8) is obtained by plotting the first order reaction rate constant ($K_{f,m}$) against $1/T$ K, whereas figure (4.9) was obtained by plotting the initial rate constant ($K_{I,m}$) against $1/T$ K.

The activation energy for the decomposition of H_2O_2 over $NiCo_2O_4$ obtained from figure (4.8) was 10.98 Kcal/mole, similar to the value of 10.6 Kcal/mole obtained by Goldstein and Tseung¹¹ for the decomposition of H_2O_2 on $CoFe_2O_4$.

$K_{I,m}$ is less diffusion controlled than $K_{f,m}$, because it is measured at zero time and should, to approximation, represent the H_2O_2 decomposition kinetics before the diffusion layer begins to control the supply of H_2O_2 to the catalyst surface.

Therefore, the activation energy obtained using $K_{I,m}$ should be diffusion free and represent the intrinsic catalytic activity of the catalyst. This may explain the lower value (10.8 Kcal/mole) obtained for the activation energy of H_2O_2 decomposition on $NiCo_2O_4$ using $K_{I,m}$ instead of $K_{f,m}$.

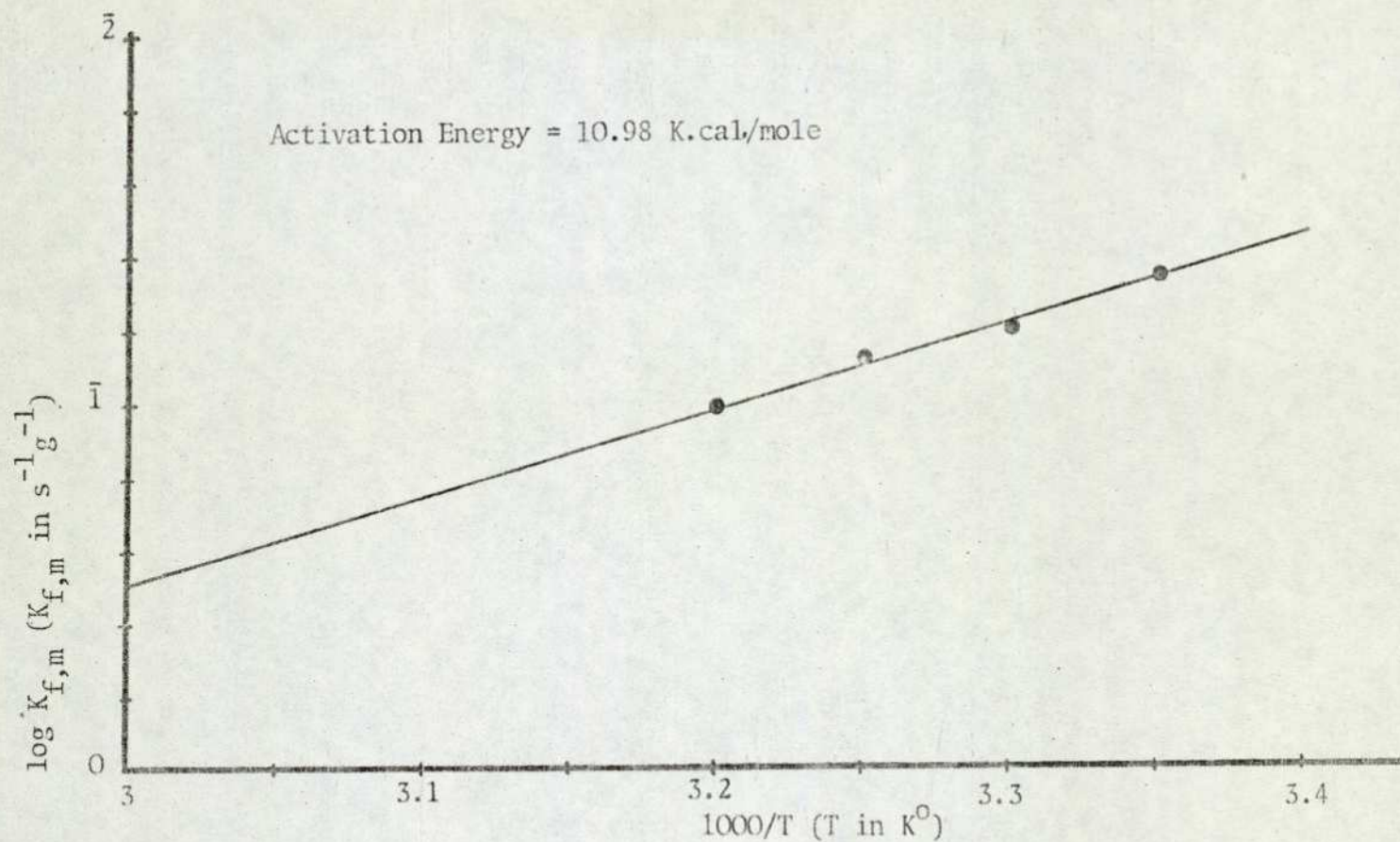


Fig. 4.8 ACTIVATION ENERGY PLOT FOR H_2O_2 DECOMPOSITION USING FIRST ORDER RATE CONSTANT FOR UNIT MASS CATALYST $K_{f,m}$, FOR $NiCo_2O_4$ (FREEZE DRYING).

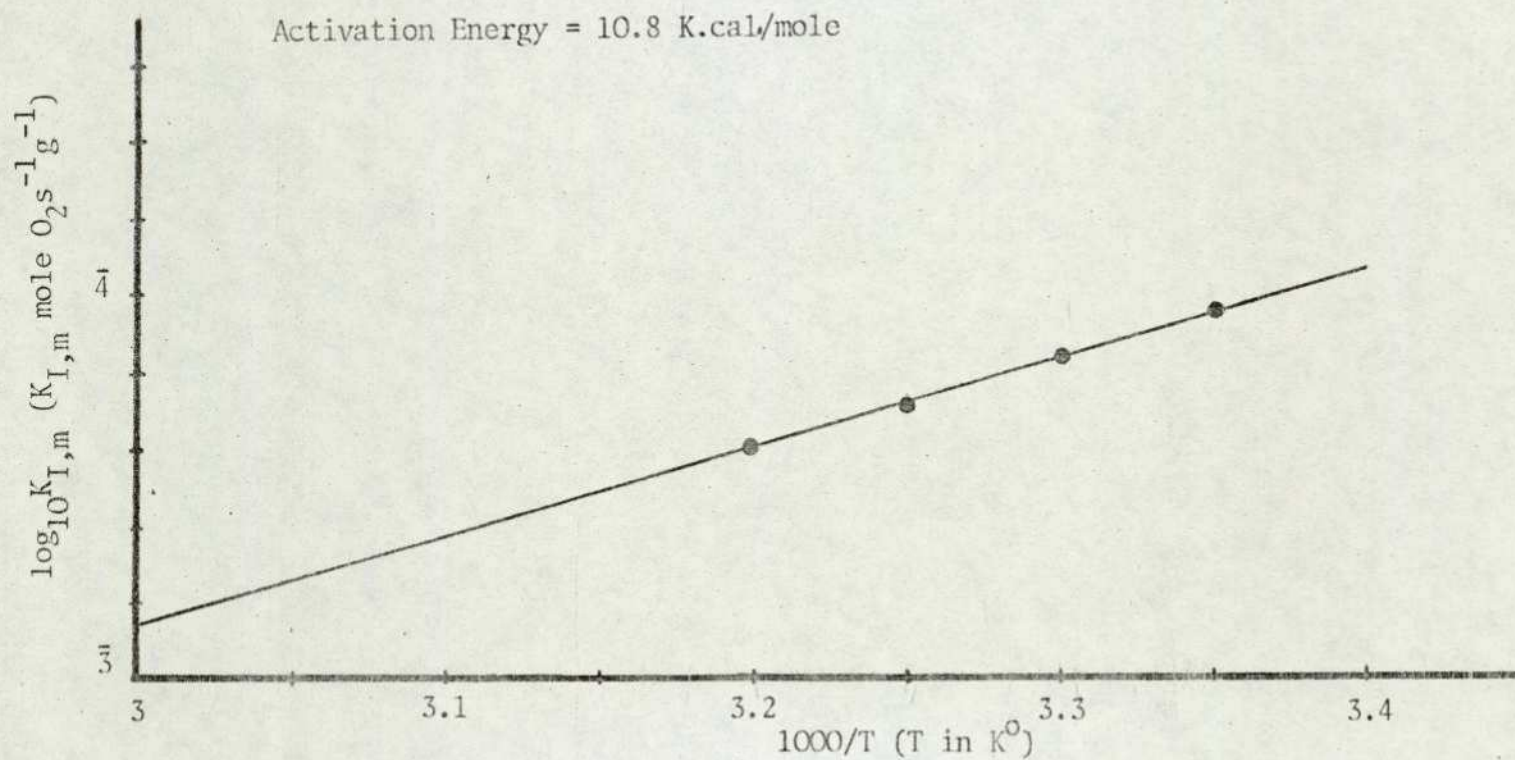


Fig. 4.9 ACTIVATION ENERGY PLOT FOR H_2O_2 , DECOMPOSITION USING INITIAL RATE PER UNIT MASS CATALYST, $K_{I,m}$, FOR NiCo_2O_4 (FREEZE DRYING).

4.3.5. The Stability of The Catalysts (Storage Effect)

Both catalysts (CoFe_2O_4 and NiCo_2O_4) showed negligible decrease in activity (for H_2O_2 decomposition) after standing for a period of three months in 5N KOH in a sealed sample bottle. This is mainly a result of the high insolubility of the oxide phase and the stability of the spinel lattice. Storage in air for a period of three years showed no effect what so ever on the catalytic activity of both catalysts towards H_2O_2 decomposition.

CHAPTER FIVE

OXYGEN EVOLUTION

5.1. REVIEW OF ELECTRODE MATERIALS FOR OXYGEN EVOLUTION

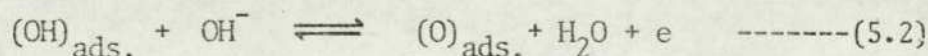
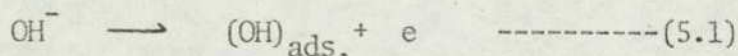
The oxygen evolution reaction is of particular importance in secondary metal-air batteries, water electrolysis plants and the oxygen extraction device proposed in this work. A literature review of a number of metals and alloys as electrocatalysts for the evolution of oxygen suggests nickel for the anode material in alkaline solutions, and noble metals and their alloys in acid solutions. Among the noble metals, the performance of Ru, Ir and their alloys has been found to be far superior to that of a pure Pt anode⁷⁰. Ajanasoski et al⁷¹ studied Pt/Ir alloys in acid and alkali media and found that their activities are superior to those of the pure metals, Pt, Ni, Ru and Co. In an attempt to find a better electrode material for oxygen evolution, Lu and Srinivasan⁷² have investigated the performance of Ni based alloys in alkaline solutions at 80°C. They found that Ni and Ni-Ir alloys are better electrocatalysts than pure Ir, and Ni-Ir alloys to be slightly better than pure Ni. It was suggested⁷² that iridium oxide formed on the electrode surface of Ni-Ir alloys probably tends to dissolve at oxygen potentials. Consequently, the oxide film formed on the surfaces of these alloys on which the oxygen evolution takes place, will be predominantly composed of nickel oxide, despite the bulk composition of the alloys themselves. Therefore, the Ni-Ir alloys would be expected to exhibit approximately the same electrochemical activities for oxygen evolution as that of pure nickel. For

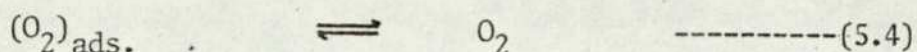
the Ni-Ru system⁷², Ru tends to dissolve anodically in KOH solution due to the formation of soluble ruthenate RuO_4^- . Ni-W alloys⁷² showed low activity for oxygen evolution, this is due to the low electronic conductivity of tungsten oxide formed on the surface. Fiori and co-workers⁷³ have studied the evolution of oxygen on the mixed oxides (NiLa_2O_4 and NiNd_2O_4), using porous electrodes (prepared by thermal decomposition of mixed nitrates on Pt sheet). They claimed an anodic performance of $0.5\text{A}/\text{cm}^2$ (at 1.6V vs R.H.E.), 30% KOH, 80°C for these electrodes. However, most of the earlier work has been on precious metals and there are no guide lines for selecting materials for the evolution of oxygen. Hence, it was decided to investigate the possibility of replacing the costly noble metals by more economical materials, which also possess high activity for oxygen evolution. Criteria for the selection of suitable electrocatalysts for the oxygen evolution reaction have been suggested⁷⁴ as a result of the present work.

5.2. CRITERIA FOR SELECTING A MATERIAL FOR OXYGEN EVOLUTION

5.2.1. Metal/Metal Oxide and Lower metal oxide/Higher metal oxide Couples

Hoare⁷⁵ suggested that the mechanism of oxygen evolution in alkaline media could involve





However, this does not indicate whether such reaction occur on a metal oxide surface. In the case of oxygen evolution on Pt⁷⁵, it has been shown that unless the Pt electrode is anodically polarized beyond the equilibrium potential of the PtO/PtO₂ couple, oxygen evolution cannot proceed. Similar arguments apply to all other metals, that is, oxygen evolution may only proceed when the potential of the electrode is higher than the potential of the metal/metal oxide couple or the lower metal oxide/higher metal oxide couple, in the case of more than one form of oxide. Hoare⁷⁵ found that in all the metals he studied, the oxygen produced initially reacts with the bare metal surface to form oxides and hence the potential at which oxygen can start to evolve from the oxide surfaces is related to the metal/metal oxide couple, or if there is more than one form of oxide, the lower metal oxide/higher metal oxide couple.

Thus, the ideal couple will be one which has a potential lower than, or similar to, the theoretical potential of the oxygen electrode. The data for the various oxide couples can easily be obtained from the Pourbaix Diagrams⁷⁶.

5.2.2. Electrical Resistivity

It is impractical to use solid semiconducting oxide electrodes since the ohmic losses will be too high. However,

it has recently been shown⁷⁷⁻⁷⁹ that Teflon bonded porous electrodes, supported on nickel screens, are far more efficient than solid electrodes for oxygen evolution. Since the catalyst/Teflon mixture is in close contact with conducting nickel wires, the likely ohmic losses in such electrodes can easily be estimated if we assume that almost all the ohmic losses occur in the catalyst/Teflon mixture⁸⁰. If we assume that current is being collected on four sides of the square holes in the nickel mesh, we have

$$I R = \frac{\rho i L^2}{16t} \quad \text{-----} \quad (5.5)$$

(See Appendix A)

where I is the total current, Amps; R is the total resistance of the electrode, ohm; i, current density, A/cm²; L, length of each side of the square hole in the nickel mesh, cm; ρ , resistivity of the catalyst/Teflon layer, ohm-cm, t, thickness of catalyst/Teflon layer. Taking the typical case of Teflon bonded porous electrode supported on 100 mesh nickel screen, L is 0.04 cm and t is 0.025 cm. Hence if the catalyst/Teflon layer has a resistivity of 100 ohm cm. and operating at 0.5A/cm², the IR loss will be about 0.2V. However, if the resistivity, ρ is 10³ ohm cm, the IR loss will be 2V. Hence the resistivity of the catalyst/Teflon layer should be below 100 ohm-cm. In actual practice, taking into account the increased resistivity due to the presence of Teflon particles and contact resistance between the catalyst powder, the maximum allowable bulk

resistivity of the semiconducting oxide for use in such electrodes will be about 10-15 ohm-cm.

5.2.3. Corrosion Resistance

It is important to know the stability of the candidate oxide materials under the operating conditions (i.e. pH 14, 1.3-2V). In the absence of detailed experimental data, the best guide is the Pourbaix diagram⁷⁶, whereby stability is defined as when the equilibrium concentration of the metal ion in solution is less than 10^{-6} g ions/l.

5.2.4. Catalytic Properties of Semiconducting Oxides

It is difficult to be certain which of the available data on semiconducting oxides would be of relevance in predicting which oxides are of interest in oxygen evolution reactions. In any case, it should be able to desorb the oxygen molecule from the surface relatively easily. Since the oxygen reduction on most of the common oxides has been studied, their activity could be used as a guide - high activity implies that oxygen is not too strongly chemisorbed on the surface.

5.2.5. Electrocatalyst Microstructure

In order to maximize the area available for oxygen evolution reaction, it is necessary to use Teflon bonded porous electrodes⁷⁹. Therefore, the electrocatalyst aggregates must be strong enough to withstand the gas pressure built up inside the pores; hence, the semi-conducting oxides should be prepared by chemical methods to ensure there are solid bonds between the particles inside each electrocatalyst aggregate⁷⁸.

Of the numerous methods available for the preparation of high surface area semi-conducting oxides, freeze drying⁸ and co-precipitation methods⁶⁴ are particularly useful.

5.3. LIST OF CANDIDATE MATERIALS

Table (5.1) lists the conductivity, corrosion resistance, oxygen reduction performance as well as the equilibrium potential of metal/metal oxide or lower metal oxide/higher metal oxide couples of a selected number of candidate materials. The physical properties listed are for the higher metal oxides. Obviously, if the oxides whose equilibrium potential is lower than, or close to that of the oxygen electrode potential; possess adequate conductivity, corrosion resistance and ability to reduce oxygen (implying low heat of oxygen adsorption), they will start to evolve O_2 sooner than other oxides and be expected to give higher anodic current at a given over-potential. An examination of Table (5.1) shows that it is difficult to get suitable oxides which can satisfy all the above requirements, but the oxide couples on Ni and Co seem to satisfy most of the requirements except for their high electrical resistivity. However, the spinel $NiCo_2O_4$ ⁸¹, possess relatively low resistivity ($\sim 10 \text{ ohm cm}$) and is therefore chosen for detailed study.

RuO_2 - TiO_2 would seem to be the next best candidate material. This was substantiated by recent studies of Srivinsan et al²⁹.

Table (5.1)

Properties of Semiconducting Oxides

Oxide	Electrical Conductivity	Corrosion Resistance at pH = 14	Oxygen Reduction	Potential vs NHE volt
La/La ₂ O ₃	Poor	Good	Poor	- 2.069
Ti ₂ O ₃ /TiO ₂	Poor	Good	Poor	- 0.556
V ₂ O ₄ /V ₂ O ₅	Poor	Poor	Poor	- 0.666
Cr ₂ O ₃ /CrO ₂	Poor	Poor	Poor	+ 1.284
MoO ₂ /MoO ₃	Poor	Poor	Poor	- 1.09
W ₂ O ₅ /WO ₃	Poor	Poor	Poor	- 0.029
Mn ₂ O ₃ /MnO ₂	Fair	Doubtful	Fair	+ 1.014
Co ₂ O ₃ /CoO ₂	Poor	Good	Poor	+ 1.447
Lower Co ₂ NiO ₄ / Higher Co ₂ NiO ₄	Good	Good	Good	+ 1.4
Ni ₂ O ₃ /NiO ₂	Poor	Good	Poor	+ 1.434
RuO ₂ /RuO ₄	Good	Poor	Good	+ 1.387
Rh ₂ O ₃ /RhO ₂	Good	Doubtful	Good	+ 1.73
PdO ₂ /PdO ₃	Good	Good	Good	+ 2.03
OsO ₂ /OsO ₄	Good	Poor	Good	+ 1.00
Ir ₂ O ₃ /IrO ₂	Good	Poor	Good	+ 0.93
PtO/PtO ₂	Good	Good	Good	+ 1.7
Cu ₂ O/CuO	Poor	Doubtful	Poor	+ 0.667
AgO/Ag ₂ O ₃	Good	Poor	Good	+ 1.57
Au ₂ O ₃ /AuO ₂	Good	Doubtful	Poor	+ 2.63

5.4. MATERIALS AND METHODS

5.4.1. Preparation of Catalysts

5.4.1a. Nickel-Cobalt Oxides

Five different compositions of nickel cobalt oxides ($\text{Co}_x\text{Ni}_y\text{O}_4$, where $0 \leq x \leq 3$, $0 \leq y \leq 2$) were prepared by the freeze drying technique⁸ (described in section 2.1.2). The weights of nickel and cobalt nitrates used for each composition are given in table (5.2).

The dry mixed nitrates were decomposed in vacuum at 300°C for one hour and cured at 400°C for 10 hours in air.

5.4.1b. Lithiated Nickel Oxide

This catalyst was prepared by the Teichner method⁸² as follows:

Nickel hydroxide prepared by precipitation from nickel chloride with KOH was mixed with a solution containing enough LiOH to give nominal 5 atm.% Li. The resulting slurry was ultrasonically dispersed for one hour and finally completely decomposed under vacuum at 200°C . After leaching the resultant powder with water, the Li content of the sample was found to be about 1 atm.% by atomic absorption analysis. The powder resistivity was $100 \Omega\cdot\text{cm}$, and B.E.T. surface area $100 \text{ M}^2/\text{g}$.

5.4.2. Electrode Fabrication

The Teflon bonded electrode (described in section 2.3.1) and porous (non Teflon bonded) electrode were both used in the study of oxygen evolution.

Porous NiCo_2O_4 electrodes were prepared by dipping a

100-mesh nickel screen in to 2M Ni/Co nitrate solution (Ni/Co = $\frac{1}{2}$). The electrodes were dried and heated at 400°C for 15 minutes to decompose the nitrates. This was repeated several times until the desired catalyst loading was obtained. Finally the electrode was cured in air at 400°C for 10 hours. Formation of the spinel structure of NiCo_2O_4 was confirmed using x-ray powder diffraction (x-ray powder data are listed in Tables 5.3 and 5.4).

5.4.3. Steady State Potentiostatic Measurements

The technique and the circuit were described earlier (section 2.3.4). For all oxygen evolution experiments, the electrode was in an immersed mode. The three compartment Pyrex cell used for oxygen evolution experiments is illustrated schematically in figure (5.1). A piece of 5 x 5 cm Pt foil was used as the counter electrode. The potential of the working electrode was measured against a dynamic hydrogen electrode (D.H.E.) (described in section 2.3.3). 5N KOH was used as the electrolyte in all experiments. An interrupter technique (described in section 2.3.5) was used to measure the ohmic drop between the tip of the Luggin Capillary and the working electrode.

5.5. RESULTS AND DISCUSSION

5.5.1. Physical Properties of Nickel-Cobalt Oxide Samples

Cobalt has three well-defined oxides⁸³, CoO (cubic), Co_2O_3 (hexagonal) and Co_3O_4 (inverse spinel). Higher oxides have been claimed but appear to be stable only as hydrates,

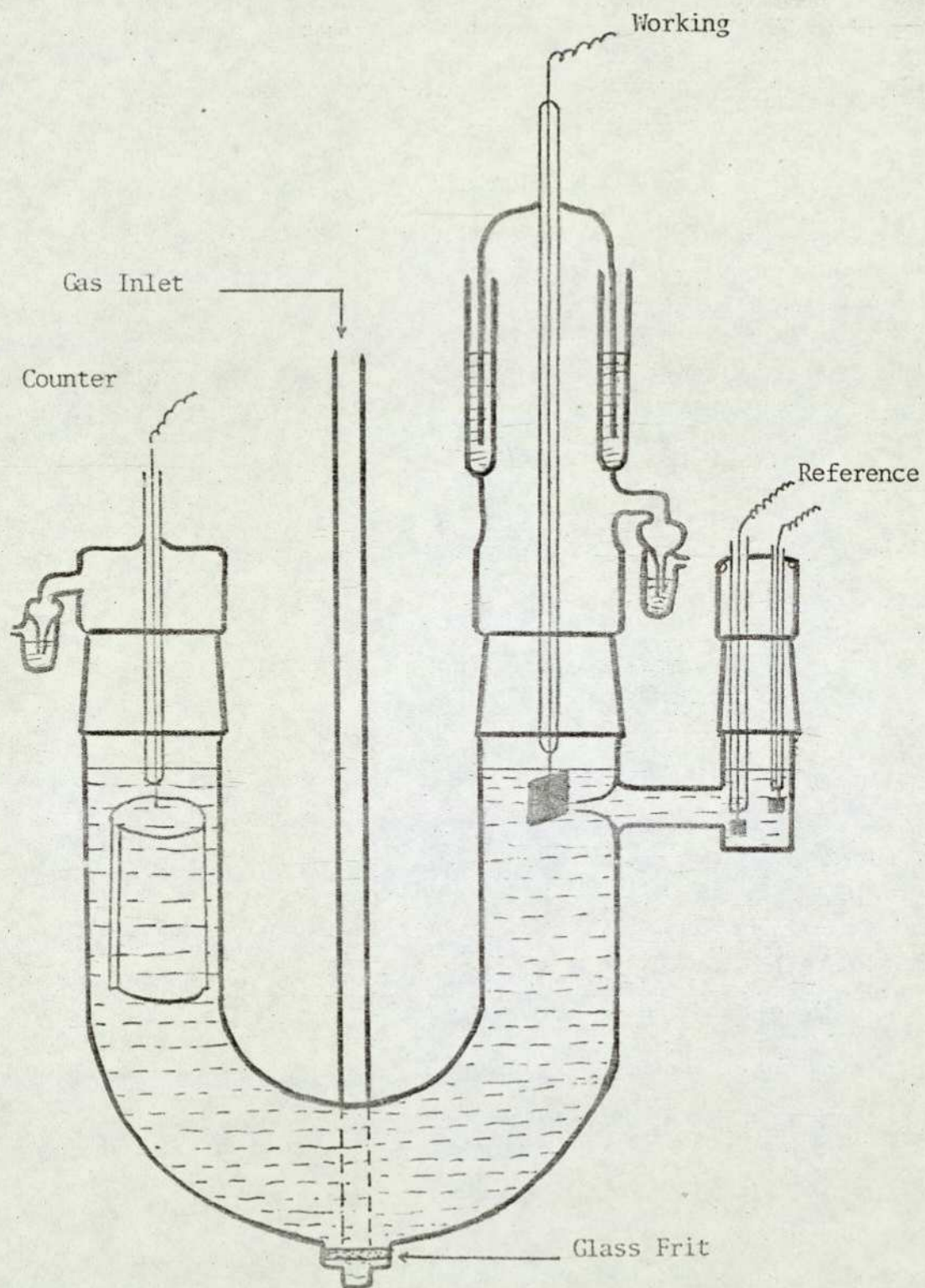


Fig. 5.1 THE CELL USED IN OXYGEN EVOLUTION STUDY

Table (5.2)

Weights of Cobalt/Nickel Nitrates Used for The Preparation
of (10 g) Nickel Cobalt Oxides ($\text{Ni}_y\text{Co}_x\text{O}_4$) By Freeze Drying.

Catalyst Composition	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ M.wt. 291.04 97.5% g	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ M.wt. 290.81 98% g
Co_3O_4	37.19	-
NiCo_2O_4	24.82	12.33
$\text{Ni}_{1.5}\text{Co}_{1.5}\text{O}_4$	18.62	18.51
Ni_2CoO_4	12.42	24.69
NiO	-	39.72

The total volume of the solution in each case = 150 ml.

Table (5.3)

X-ray Analysis of Cobalt Nickel Oxides Prepared by Freeze Drying

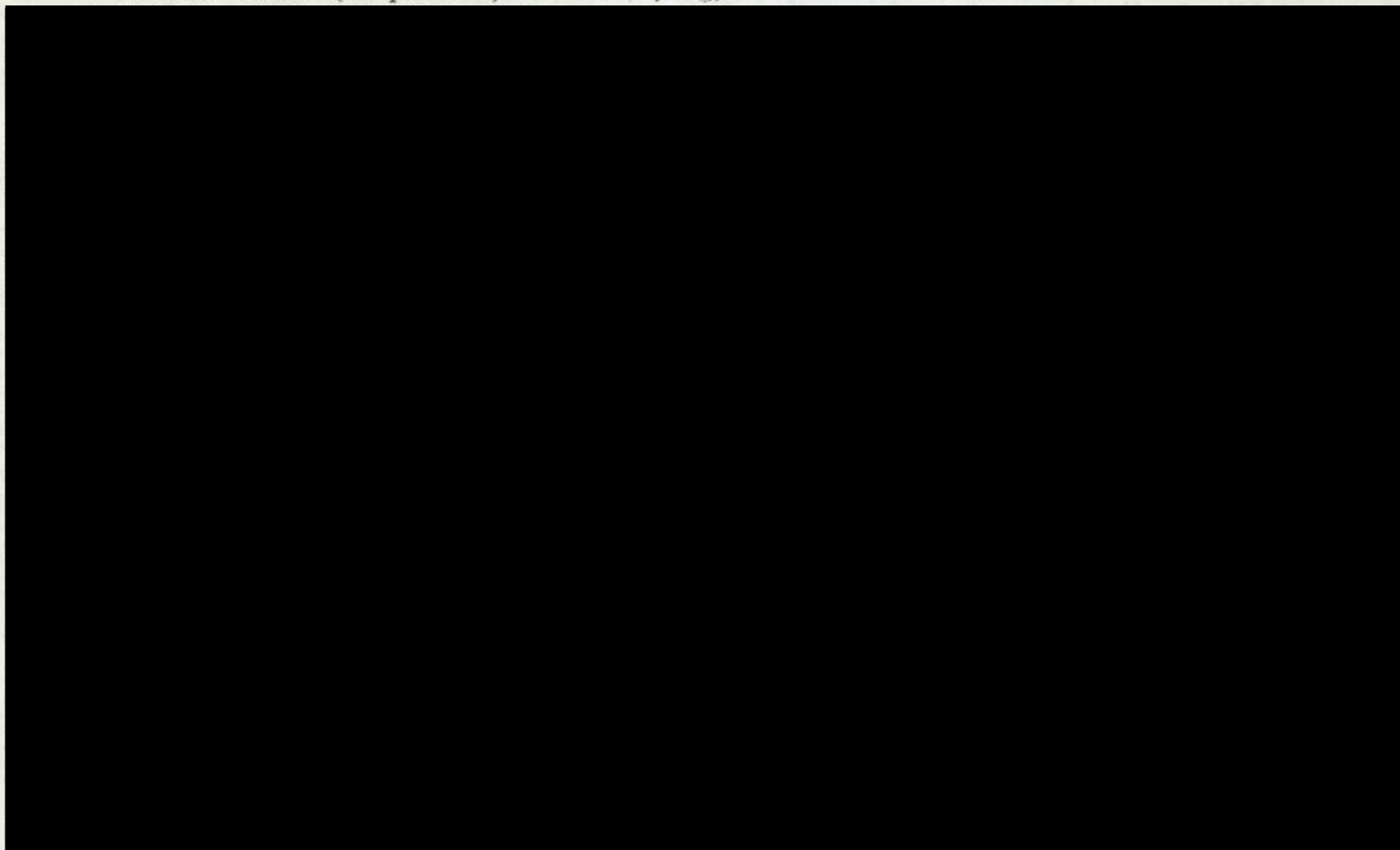
THERMAL DECOMPOSITION		FREEZE DRYING										PREPARATION METHOD
NiCo_2O_4		NiCo_2O_4		$\text{Ni}_{1.5}\text{Co}_{1.5}\text{O}_4$		Ni_2CoO_4		NiO		Co_3O_4		where vs = very strong s = strong m = medium f = faint vf = very faint
dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	
4.74	vf	4.61	vf	3.36	m	2.60	s	2.39	s	2.86	m	
2.62	s	3.2	vf	2.95	s	2.35	s	2.09	s	2.42	vs	
2.45	vs	2.7	s	2.60	vs	2.04	s	1.65	vf	2.31	vf	
2.04	m	2.45	vs	2.38	m	1.8	vf	1.48	m	1.65	vf	
1.71	vf	2.03	m	2.16	m	1.63	m	1.26	vf	1.55	f	
1.56	vs	1.73	f	1.98	s	1.46	m	1.19	vf	1.42	f	
1.44	vs	1.55	vs	1.81	s	1.24	f					
		1.43	vs	1.64	vs							
				1.40	m							
				1.33	m							
*8.12 Å		*8.13 Å		*8.17 Å		*8.15 Å		..		*8.08 Å		Lattice Parameter

I = Intensity estimated visually.

* = Calculated lattice parameter

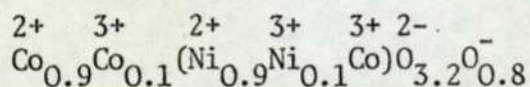
Table (5.4)

A.S.T.M. X-ray Powder Data for NiCo_2O_4 and The Possible Impurities in Nickel
Cobalt Oxides (Prepared by Freeze Drying)



such as $\text{CoO}_2 \cdot \text{XH}_2\text{O}$. Above 900°C the spinel structure of Co_3O_4 degrades sharply to that of the lower oxide CoO with loss of oxygen.

Nickel has only one well-defined oxide, the cubic NiO . Many claims exist for higher oxides, as in the case of cobalt, but again these appear to be stable only as hydrates, eg. $\text{Ni}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ and $\text{NiO}_{1.9} \cdot \text{XH}_2\text{O}$. The unit cell parameters of the cubic CoO and NiO phases are sufficiently similar ($4.26 \text{ \AA}$ and $4.18 \text{ \AA}$ respectively) to permit the formation of a solid solution throughout the whole composition range⁸⁴. In addition, there is a spinel-type mixed-oxide based on Co_3O_4 which is readily formed⁸⁵ provided the nickel content (cation fraction) is not greater than one-third⁸⁶. The spinel structure may be presented as $\text{A}(\text{B}_2)\text{O}_4$, where A represents tetrahedrally and B octahedrally coordinated ions. On the basis of crystallographic and electronic considerations of the spinel structure as well as thermogravimetric analysis results, King and Tseung²⁸ suggested that the distribution of nickel, cobalt and oxygen ions in the NiCo_2O_4 lattice is given by



where the ions outside the brackets are tetrahedrally coordinated and ions inside the brackets are octahedrally coordinated. The O^- ion exists in the form of loosely bound oxygen. Thermogravimetric studies⁸¹ showed that the NiCo_2O_4 spinel started to

break down to form the cubic NiCo_2O_3 (by oxygen loss) at about 450°C , compared to 900°C for its parent compound Co_3O_4 , suggesting that some of the lattice oxygen is loosely bound. This 'loosening' effect is maximized by introducing as much nickel as possible into the Co_3O_4 lattice. The maximum permissible amount is one-third of Co cations substituted by Ni cations. The semi-conducting properties of NiCo_2O_4 are governed by an electron hopping between the Ni^{+2} and Ni^{+3} in the octahedral sites⁸¹.

Table (5.5) shows the B.E.T. surface area, crystal structure and powder resistivity of the nickel cobalt oxide samples (prepared by freeze drying). The results showed that their surface area were similar but there was a significant difference in electrical resistivity. Apart from Co_3O_4 , only NiCo_2O_4 had the pure spinel structure, (x-ray powder data for these oxides are listed in table 5.3 and 5.4). The very high resistivity of the other oxide samples may significantly reduce their anodic performance. Since all these oxides are expected to form higher oxides whose resistivity may be significantly different, it is still worth while to study their activity.

5.5.2. The Importance of Aggregate Surface Area

For a very porous, high surface area catalysts the greatest contribution to the B.E.T. surface area arises from the pore walls of the developed internal structure. In fact, the outer surface of the catalyst aggregates probably represents

Table (5.5)

Physical Properties of the Nickel Cobalt Oxide Samples

Composition (cation% of cobalt)	Phases X-ray	B.E.T. surface area M^2/g	Resistivity ohm-cm
Co_3O_4 (100%)	spinel	75	10^4
$NiCo_2O_4$ (66.6%)	spinel	69	10
$Ni_{1.5}Co_{1.5}O_4$ (50%)	spinel + cubic	55	10^4
Ni_2CoO_4 (33.3%)	spinel + cubic	56	5×10^5
NiO (0%)	cubic	38	10^6

only a small fraction of the total surface. During gas evolution reactions on these catalysts, the gas bubbles formed may force the electrolyte out of the interior of the aggregates and only the external surface of the aggregate will be functioning⁷⁹, i.e. the smaller the aggregate size of the catalyst powder the larger the available surface area for the reaction. The average aggregate size of the powders can be measured by the Coulter Counter technique. This technique has been described in detail elsewhere⁸⁷.

Apparatus for this technique is not available in the author's Laboratory, hence, Scanning Electron Microscopy (described in section 2.2.3) was carried out on nickel cobalt oxide samples (prepared by freeze drying), in order to determine aggregate size distribution and the aggregate shape. This visual investigation showed that for the nickel cobalt oxide samples (but not for nickel oxide) there was a range of aggregate sizes present in each sample and that the aggregates possessed non-spherical (random) shapes. Therefore, it was not possible to assess, with any degree of accuracy, the average aggregate size. However, examination of Electron micrographs of nickel oxide reveals spherically-shaped aggregates of less than 6.6μ diameter to be present, but most of them are in the range $(36-50)\mu$ in diameter.

Electron micrographs (shown in figure 5.2) for the different oxides shows that the average aggregate size of nickel oxide is much larger than those of the rest of the oxides.

5.5.3. EDAX Analysis

X-ray fluorescence analysis for nickel cobalt oxide samples (prepared by freeze drying) was carried out using an EDAX analysis system. The concentration of each elemental component was estimated by peak height/background measurements corrected for atomic weight and specimen tilt. The Electron microscopy analytical results are listed in table (5.6).

Calculation of the quantity of each individual element from the peak height measurements in figure (5.3), were estimated according to the following equation:

$$\frac{\text{Number of counts} - \text{Background counts}}{\text{Correction factors} \times \text{Atomic weight}} = \text{Atoms}$$

where, correction factor for Ni = 0.93 and Co = 1.01.

Figure (5.3a) shows a typical EDAX analytical concentration count for cobalt and nickel in NiCo_2O_4 sample.

Figure (5.3b) shows EDAX analytical concentration count for cobalt oxide and nickel oxide (dotted line) to illustrate the overlap of Ni K_α peak (dotted line) and Co K_β peak, which makes the measurement of the concentration, by integration of the area under the peak, more complex for samples containing both nickel and cobalt.

EDAX analysis was used mainly to examine the homogeneity of nickel cobalt oxide samples. The atomic ratio of different areas of the specimen (for each sample) were compared. The atomic ratios were identical showing a high degree of homogeneity in the samples prepared by freeze drying.

Table (5.6)

EDAX Analysis of Nickel and Cobalt in Freeze Dried Nickel

Cobalt Oxide Samples

Oxide (freeze drying)	Ni conc. count	Co conc. count	Ni and Co back ground count	Atomic ratio	
				Ni atom	Co atom
$\text{Ni}_1\text{Co}_2\text{O}_4$	1995	4000	100	34.7	65.5
$\text{Ni}_{1.5}\text{Co}_{1.5}\text{O}_4$	4000	3990	100	71.4	65.3
$\text{Ni}_2\text{Co}_1\text{O}_4$	4000	2050	100	71.4	32.7
Co_3O_4	-	4000	100	-	65.5
NiO	4000	-	100	71.4	-

$$\text{Wt\% Ni in NiO} = 78.6$$

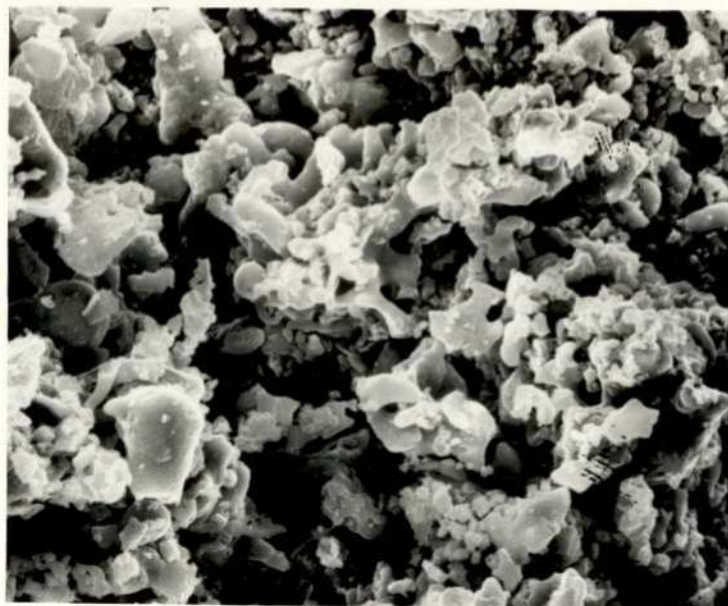
$$\text{Wt\% Co in Co}_3\text{O}_4 = 73.4$$

$$\frac{71.4}{78.6} = 0.9084$$

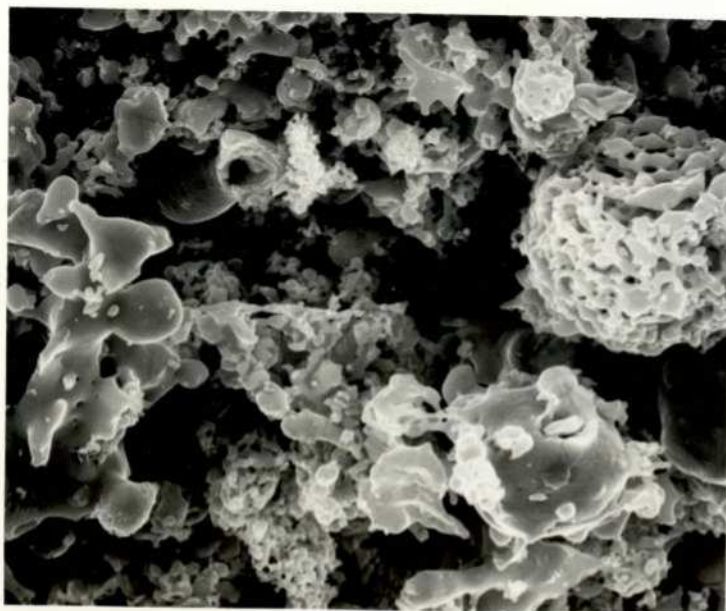
$$73.4 \times 0.9084 = 66.7 (\approx 65.5)$$

Thus the discrepancies in the figures are explained.

Fig. 5.2 ELECTRON MICROGRAPHS OF NICKEL-COBALT OXIDE
Samples, Prepared by Freeze Drying
Magnification = 300 times. 1 cm = 33 μ , 40 Kev



a - Cobalt Oxide (Co_3O_4)

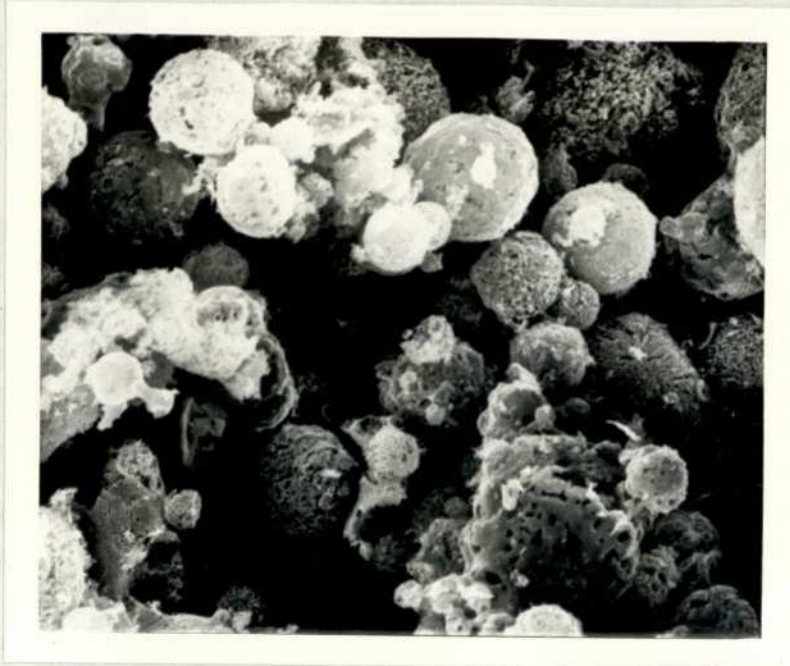


b - NiCo_2O_4

Fig. 5.2 (continued)

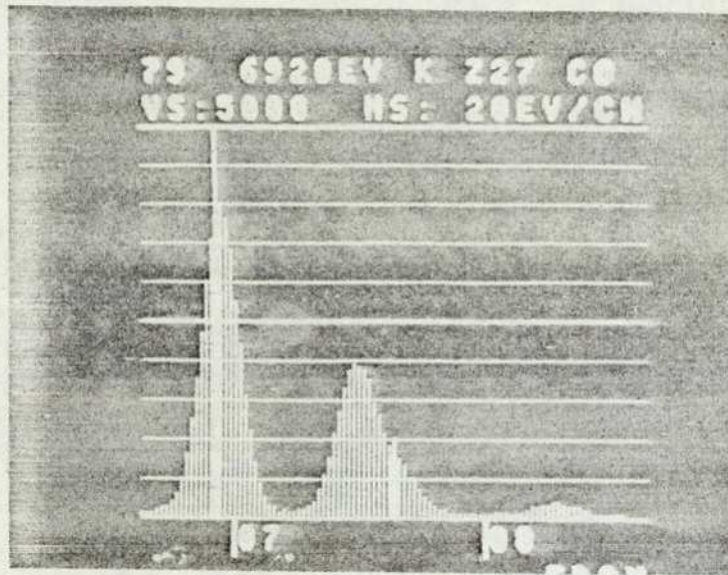
c - $\text{Ni}_{1.5}\text{Co}_{1.5}\text{O}_4$ d - Ni_2CoO_4

Fig. 5.2 (continued)

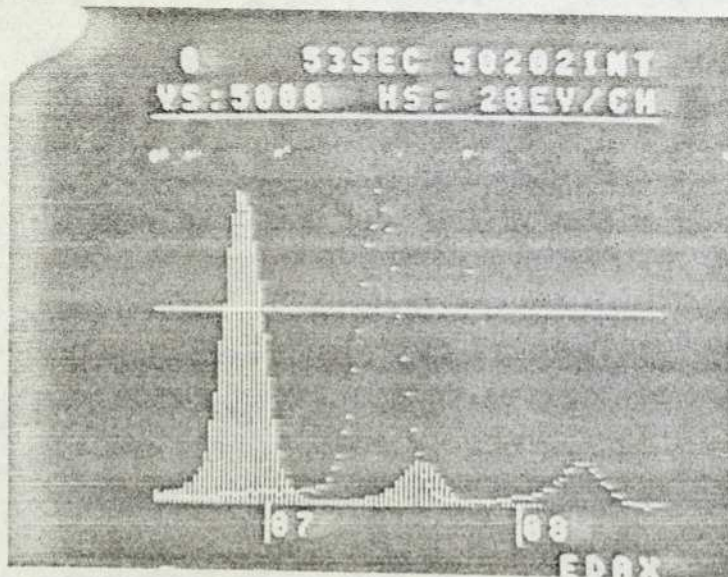


E - Nickel Oxide (NiO)

Fig. 5.3



5.3a. A TYPICAL EDAX ANALYTICAL CONCENTRATION COUNT FOR COBALT AND NICKEL IN NiCo_2O_4



5.3b. AN EDAX ANALYTICAL CONCENTRATION COUNT FOR COBALT AND NICKEL IN COBALT OXIDE AND NICKEL OXIDE (doted line) RESPECTIVELY.

5.5.4. Steady State Oxygen Evolution

Steady state oxygen evolution measurements were made at 25, 40, 50, 60 and 70°C on all the nickel cobalt oxide samples. The Teflon bonded electrodes were preanodized at 2V vs D.H.E. for one hour and the steady state readings of current density were recorded starting from the highest anodic potential (2V). The time given for each reading was five minutes. The results were corrected for iR-drop, using the interruptor technique.

All the oxide samples were tested as immersed Teflon bonded electrodes. 100 mesh nickel screen was used as the current collector and the catalyst/Teflon ratio was 10/3 in all these electrodes.

The results of these tests are shown in figures (5.4 - 5.8). The measured resistance (between the tip of the Luggin Capillary and the working electrode) (R) values increased with current density. At 25°C, the R value for a NiCo_2O_4 electrode changed from 0.07 ohm to 0.1 ohm as the current increased to about 500 mA/cm². The major contribution to the increased resistance was bubbles formation on the electrode surface.

V-i plots for all the compositions showed that very little current could be drawn until the equilibrium potential of the lower metal oxide/higher metal oxide couple (1.4 - 1.45 V vs D.H.E.) for the nickel cobalt oxide catalysts was reached.

Figure (5.9) shows the activation energy and current

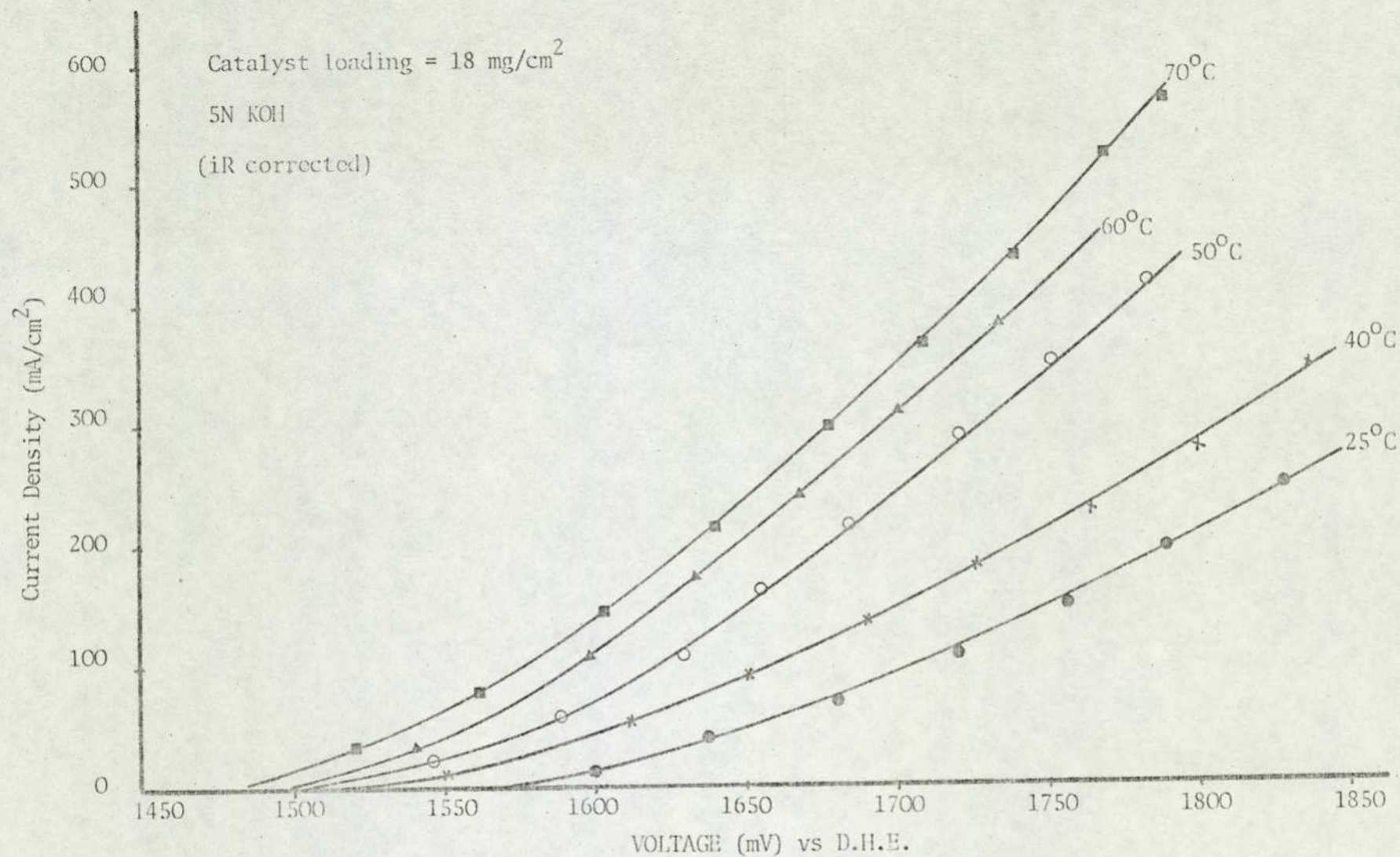


Fig. 5.4 OXYGEN EVOLUTION ON TEFLON BONDED Co_3O_4 ELECTRODE

The Electrode has been preanodized at 2V vs D.H.E. for 1 hr.

5N KOH, (iR-corrected)

Catalyst Loading = 9.8 mg/cm^2

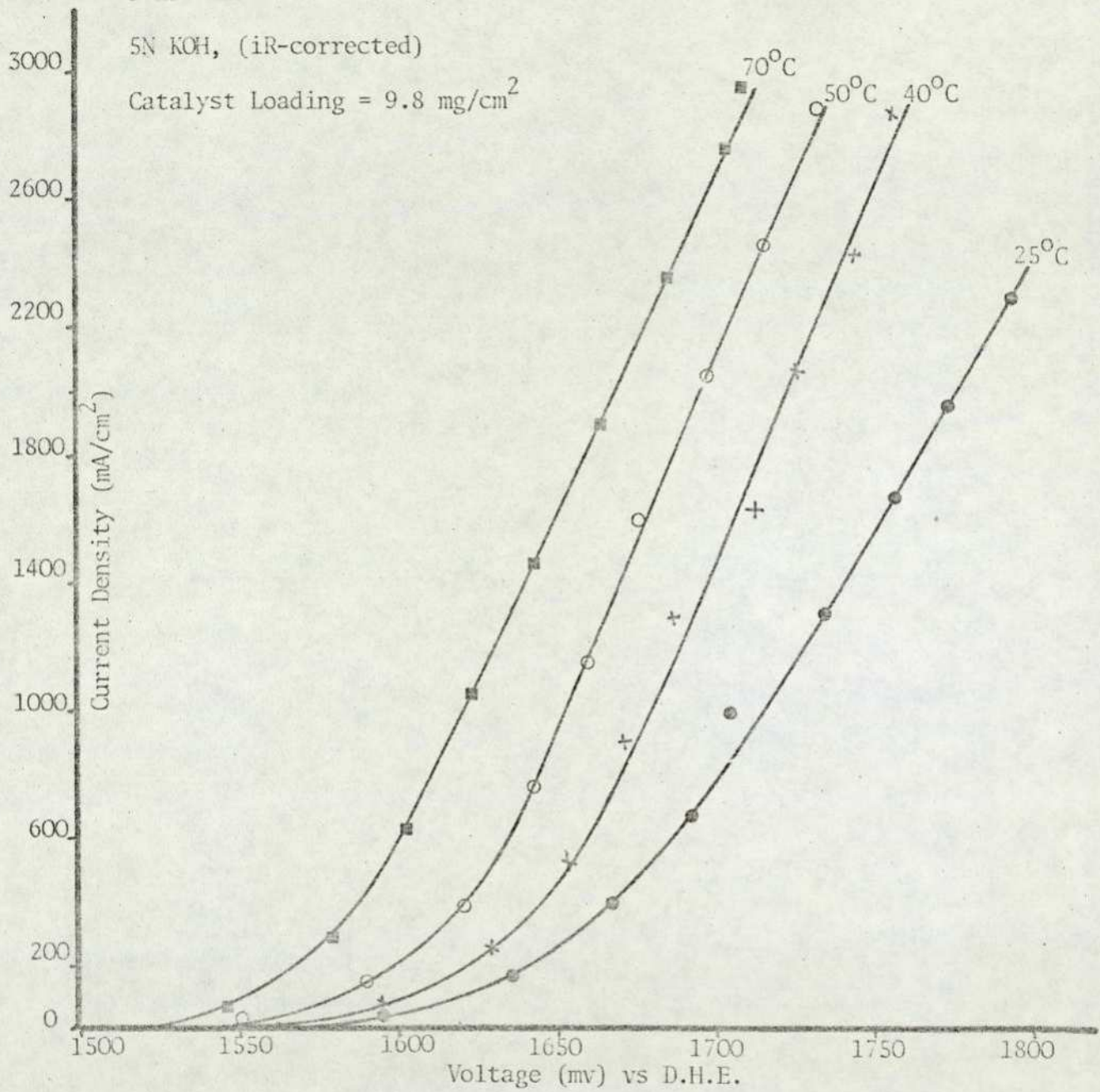


Fig. 5.5 OXYGEN EVOLUTION ON TEFLON BONDED NiCo_2O_4 ELECTRODE

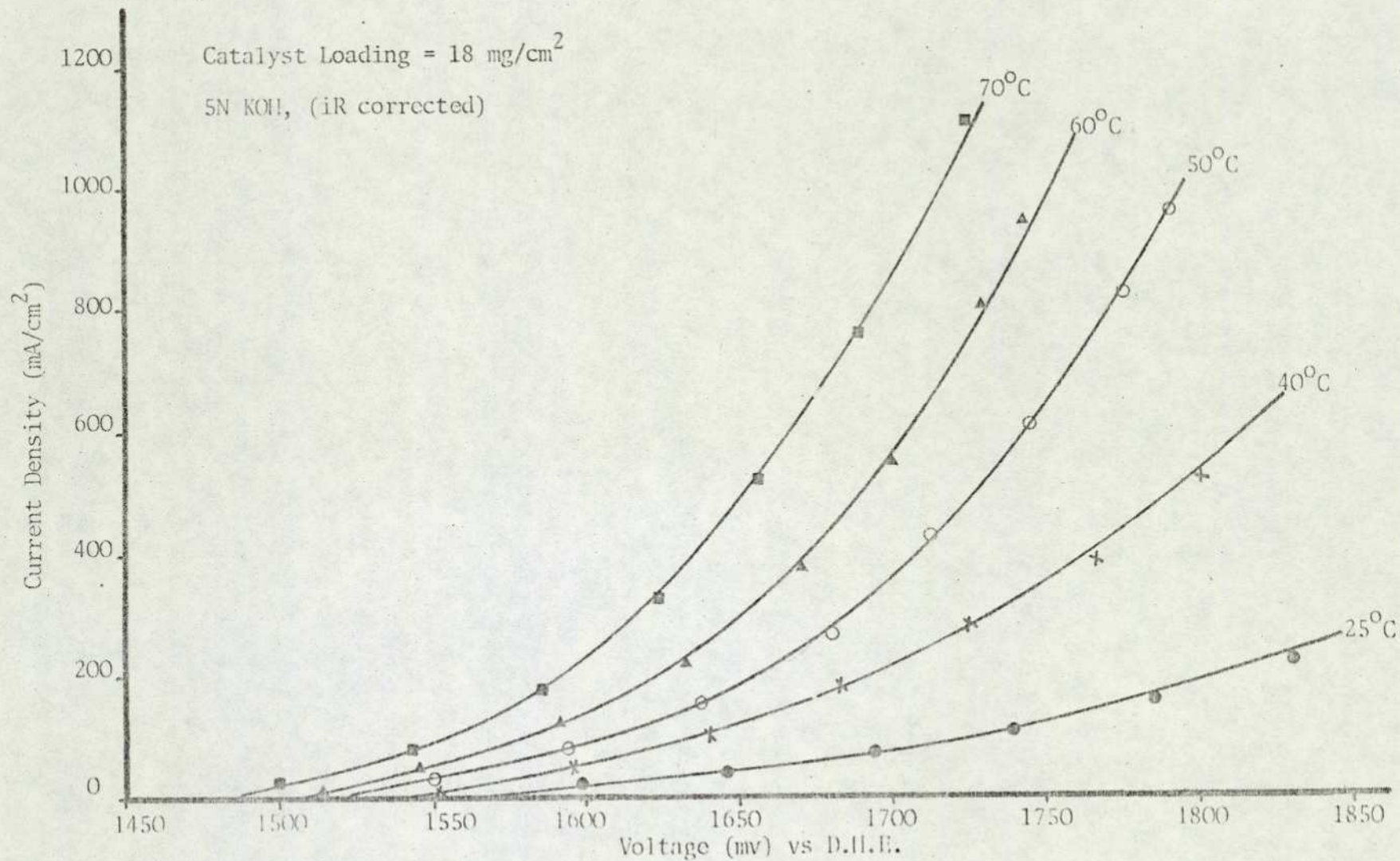


Fig. 5.6 OXYGEN EVOLUTION ON TEFLON BONDED $\text{Ni}_{1.5}\text{Co}_{1.5}\text{O}_4$ ELECTRODE

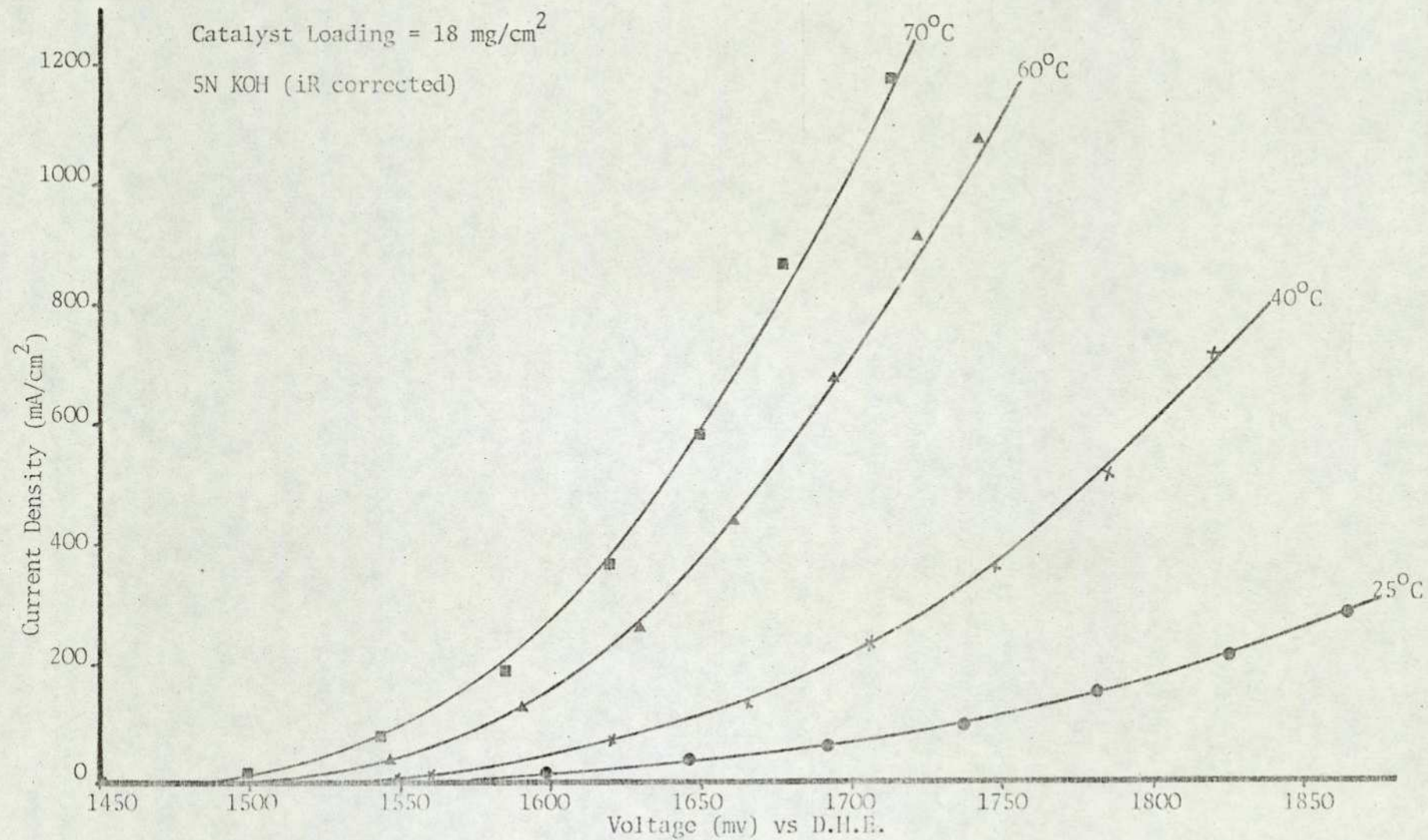


Fig. 5.7 OXYGEN EVOLUTION ON TEFLON BONDED Ni_2CoO_4 ELECTRODE

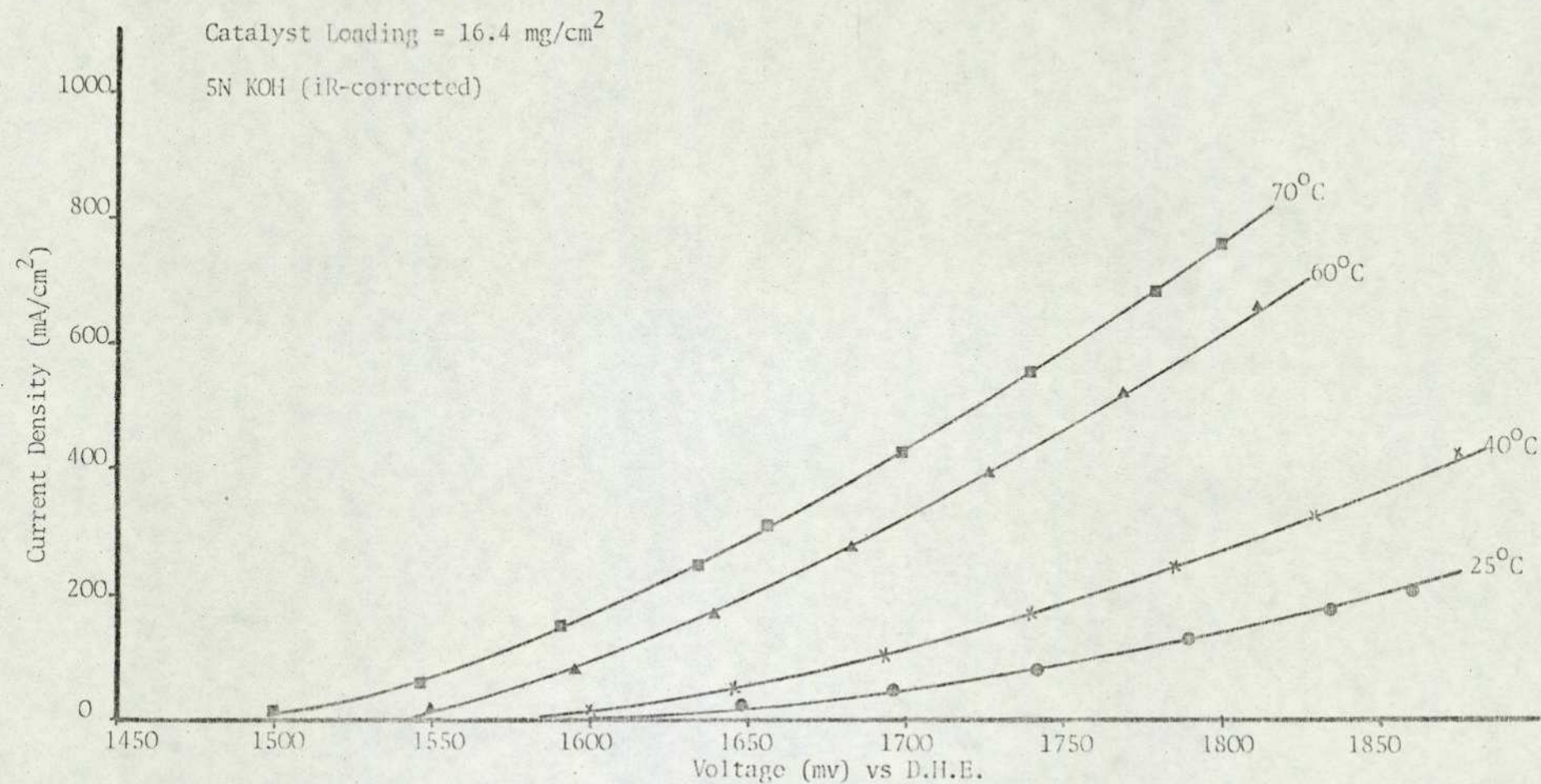


Fig. 5.8 OXYGEN EVOLUTION ON TEFLON BONDED NiO ELECTRODE

○ Activation Energy at 1.6V vs D.H.E.

● Current Density at 1.6V vs D.H.E., 5N KOH, 25°C

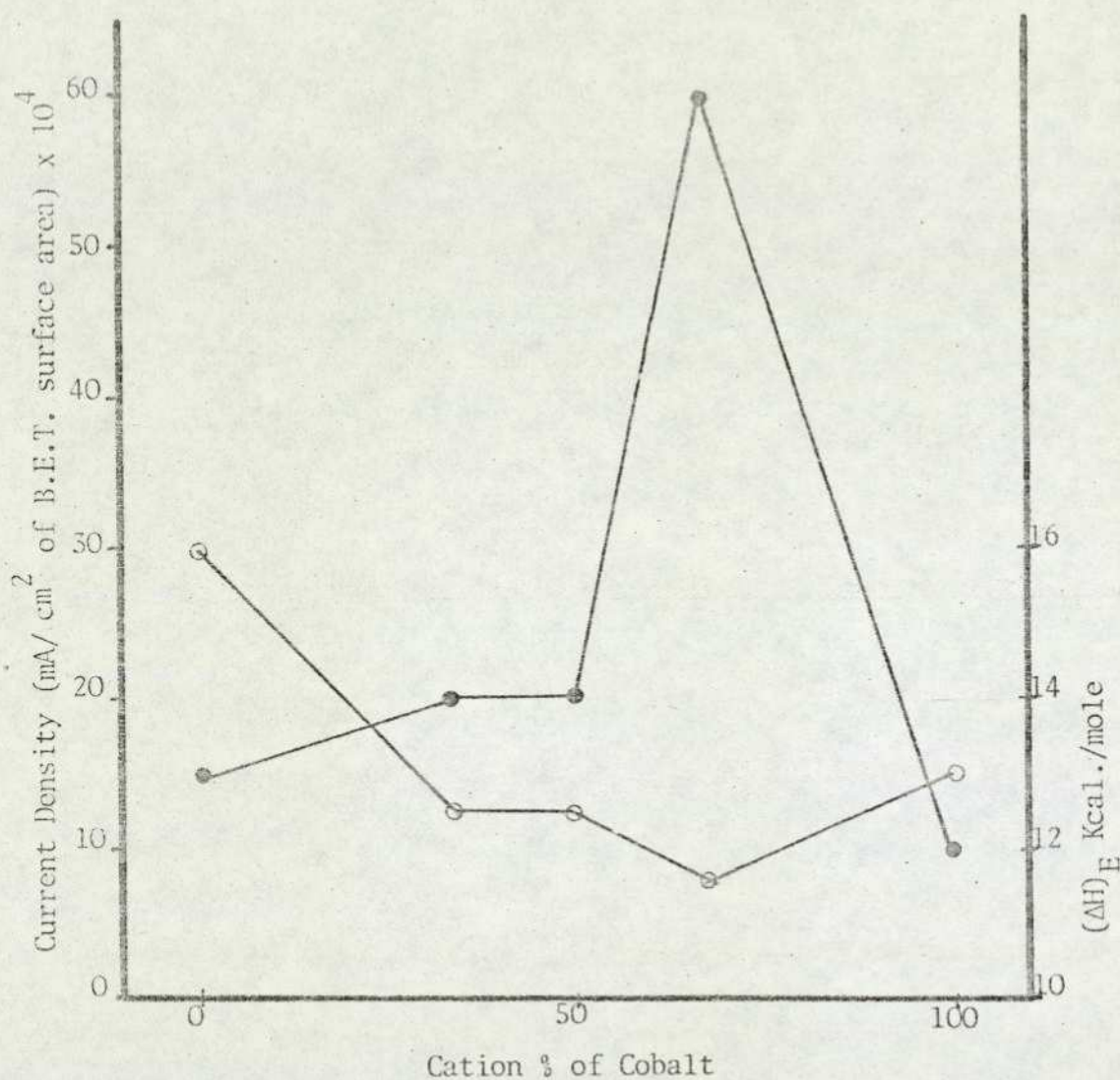


Fig. 5.9 VARIATION IN CURRENT DENSITY AND ACTIVATION ENERGY WITH COMPOSITION (FOR OXYGEN EVOLUTION ON NICKEL COBALT OXIDES)

density at 25°C of the oxygen evolution reaction on the various compositions of nickel cobalt oxides at 1.6V versus D.H.E.

The activation energy was calculated using the following equation⁸⁸:

$$(\Delta H)_E = -2.3R \left(\frac{\partial \log i}{\partial (1/T)} \right)_E \text{ ----- (5.6)}$$

The current density is expressed as mA/unit catalyst B.E.T. surface area (cm²). The results indicate that NiCo₂O₄ has the lowest activation energy and the highest current density in the nickel cobalt oxide series.

It was noticed that the Open Circuit Voltage (o.c.v.) for an unused electrode of NiCo₂O₄ on first contact with the electrolyte frequently approached the reversible oxygen potential. On anodic polarization after testing the electrode for oxygen evolution, the o.c.v. was about 1.5V vs D.H.E., decayed slowly to about 1.46V in five minutes and then the decay became much slower till it reached a steady value of 1.3V in few hours (~ 5 hours). The high value of o.c.v. after anodic polarization could be attributed to the formation of higher oxides. The decay of o.c.v. indicating the decomposition of the higher oxides. If the anodized electrode was held at a low potential, such as 1.1V for a few minutes, the o.c.v. returned to its original value ~1.15V vs D.H.E. indicating the reduction of the higher oxides at low potentials (~ 1.1V vs D.H.E.).

5.5.5. Effect of Preanodization on Teflon bonded Electrodes

Apart from the improvement in the reproducibility

of the polarization measurements, the anodic performance of the Teflon bonded electrodes at 25°C was also improved after the preanodization (at 2V, 1 hour).

The increase in performance was noticed particularly on Teflon bonded NiCo_2O_4 electrodes with catalyst loadings higher than 20 mg/cm². Figure (5.10) shows the anodic performance of Teflon bonded NiCo_2O_4 electrode at 25°C before and after the anodization.

The increase in performance could be partly attributed to greater utilization of the catalyst inside the structure of the Teflon bonded electrode due to the removal of the excess thin layer of Teflon which covers the electrode surface. This is based on visual observation of the Teflon bonded electrode surface which usually became less hydrophobic after prolonged polarisation (more than one hour).

No improvement in performance was observed at temperature greater than 25°C when the measurements were conducted on the same electrode. This could be due to a faster growth of the poor conducting nickel oxide on nickel screen which would result in a sharper drop in performance, or to the fact that the electrode had been preanodized already at 25°C. Furthermore, the improvement in reproducibility and performance of the preanodized electrode could be attributed to the formation of higher oxides, which could be dependent on polarisation time.

As a result of the present study, it is postulated⁷⁴

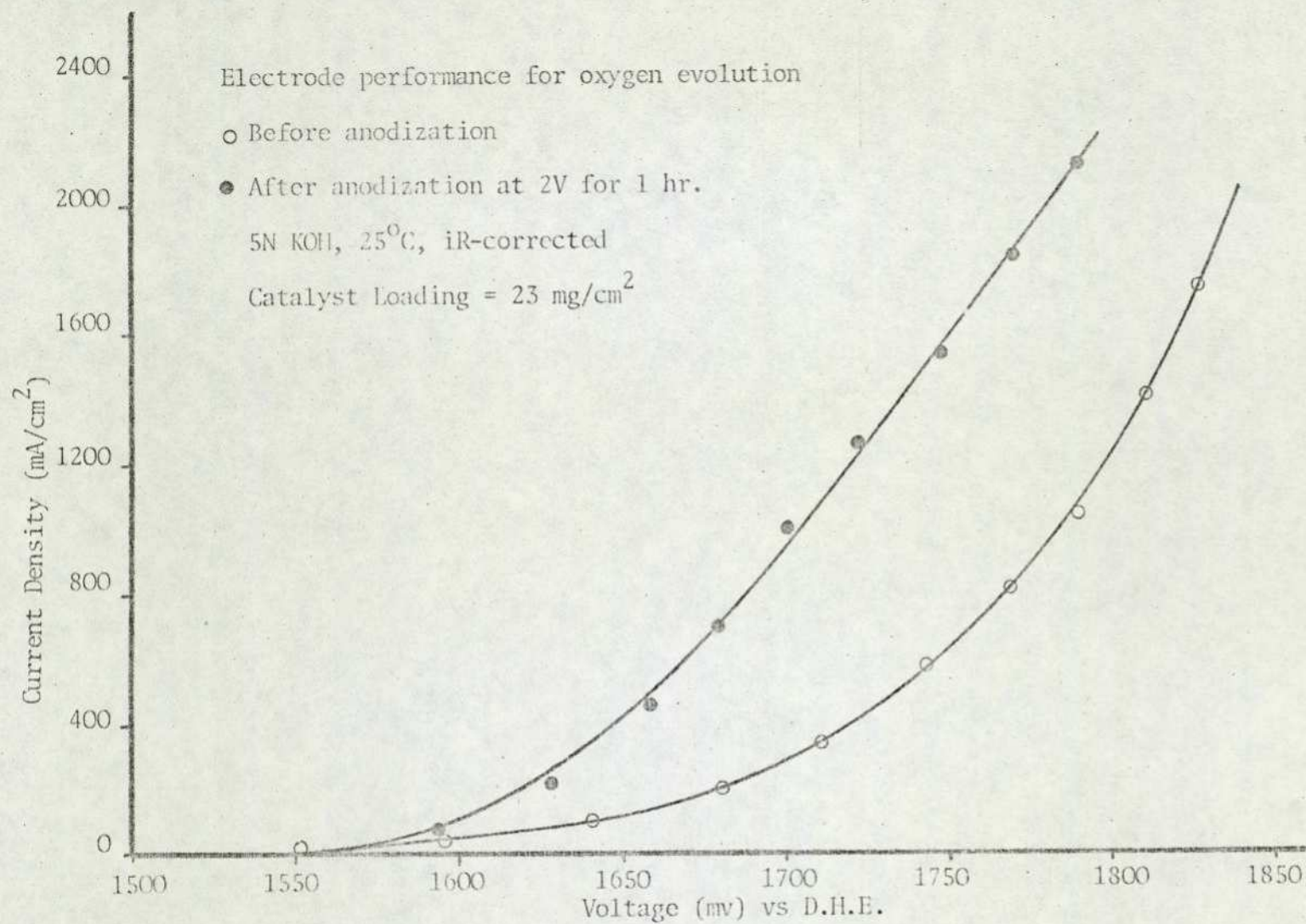
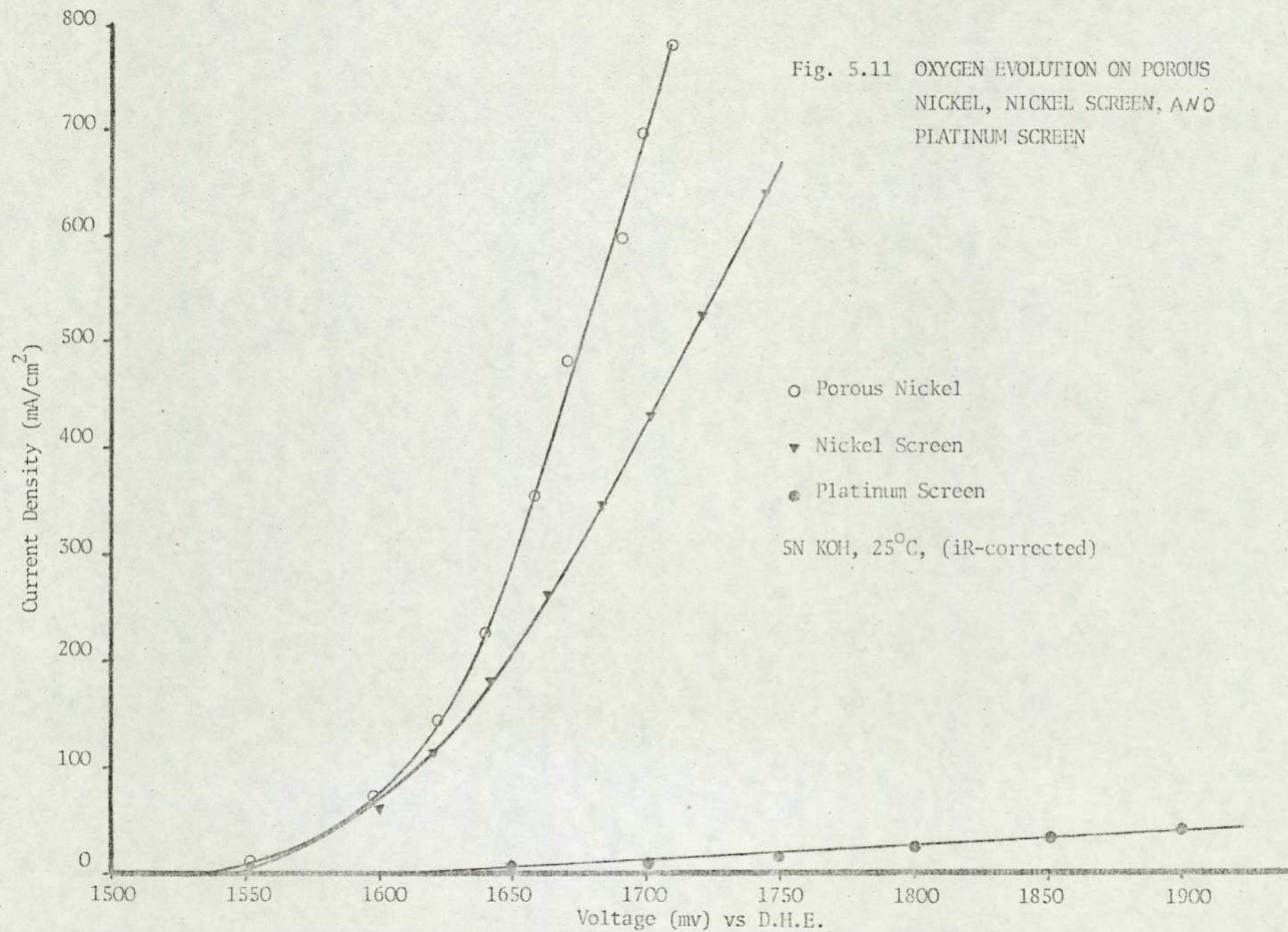


Fig. 5.10 OXYGEN EVOLUTION ON TEFLON BONDED NiCo_2O_4 ELECTRODE BEFORE AND AFTER ANODIZATION

that a good fit between the redox potential for the lower metal oxide/higher metal oxide couple and the thermodynamic potential for $\text{H}_2\text{O}/\text{O}_2$ couple in the same medium could be used as a criterion for the selection of a good oxygen evolution electrocatalyst, and that oxygen evolution can proceed only after the formation of higher oxides of the catalyst⁸⁹. This is supported by other workers in studies of oxygen evolution on Ni ⁹⁰ and Ir ⁷⁰. Their results strongly suggested that the "right type of oxide" for catalyzing the oxygen evolution reaction may be formed when the oxidation state of an existing surface oxide is increased prior to, or simultaneously with, the beginning of oxygen evolution. Moreover, Gottesfeld⁷⁰ suggested that an increase in the oxidation state of the oxide may have two effects: (a) to produce a mixed valence defect structure in the bulk of the oxide which allows a better electronic conductivity. (b) to produce active sites in the form of metal ions with a higher positive charge for the chemisorption of OH or O intermediates.

5.5.6. Oxygen Evolution on Metal Substrates

The anodic performances of 1 cm^2 nickel screen, porous nickel plaque and Pt screen electrodes are illustrated graphically in figure (5.11). It can be seen from figure (5.12) that the anodic performance of both nickel screen and porous nickel plaque electrodes decreased from 200 mA/cm^2 to less than 70 mA/cm^2 over a period of 40 hours, suggesting that the growth of high resistance nickel oxide films has greatly



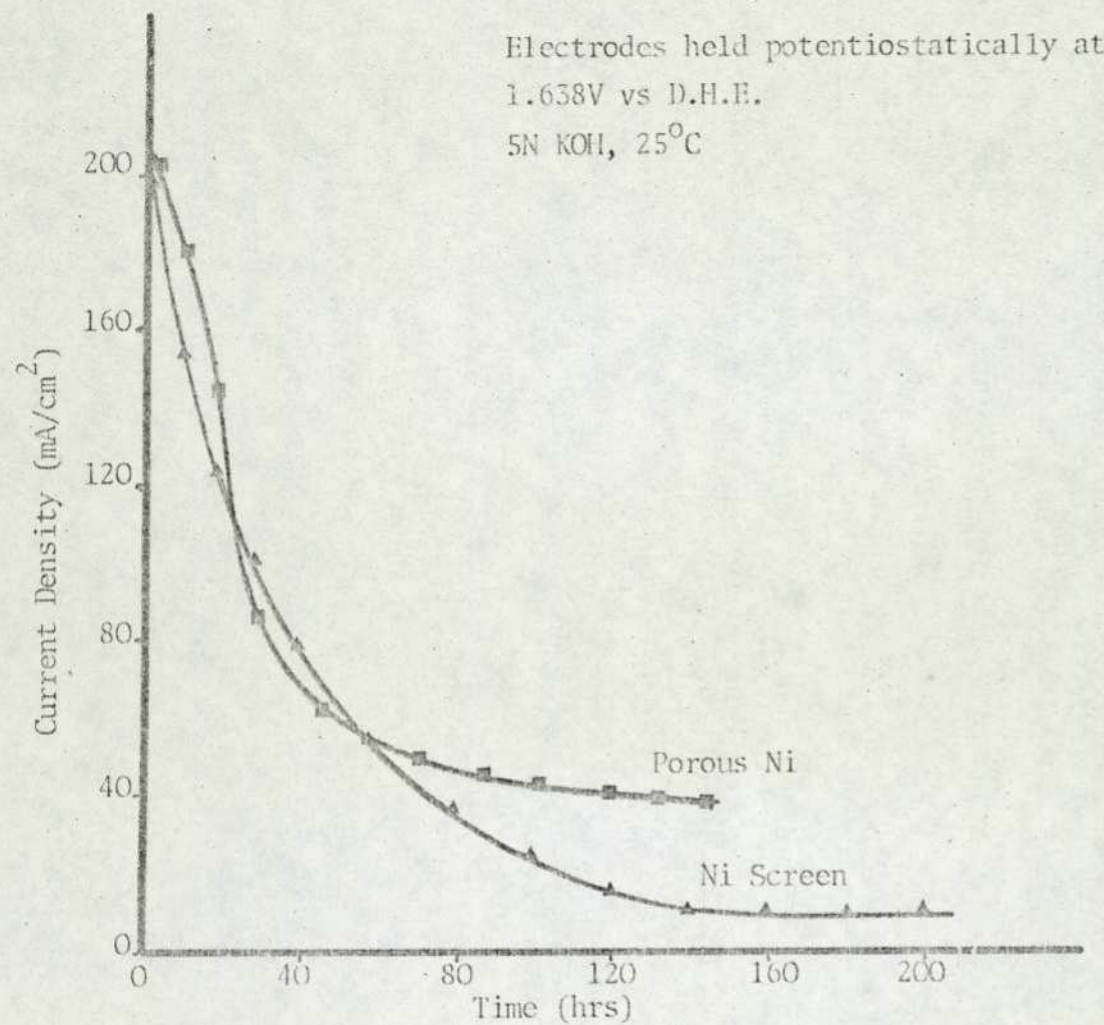


Fig. 5.12 OXYGEN EVOLUTION ON NICKEL SCREEN AND POROUS NICKEL
AS A FUNCTION OF TIME

reduced the activity of the electrodes. The above results, concerning the decay of current with time during oxygen evolution on nickel⁷⁴ have been investigated recently by Lu and Srinivasan⁹⁰. They suggested that the time variation of current density at constant potential, above 1.56V for oxygen evolution on nickel, is due to the continuous transformation of active (Ni^{3+} ions) to inactive (Ni^{4+} ions) sites. The latter are inert for oxygen evolution⁹⁰ and as a result of their creation there is a decrease in the electronic conductivity of the oxide film. Srinivasan also found that the period of time required for approaching a stable current is inversely proportional to electrolyte temperature and attributed this to an increase in the rate of conversion of Ni^{3+} to Ni^{4+} . It has been also reported⁹¹ that the ratio of $\text{Ni}^{3+}/\text{Ni}^{4+}$ ions in the oxide film is dependent upon the potential as well as the polarization time.

As can be seen from figure (5.11), despite the very much higher nickel area in the porous plaque, the activity is only marginally higher than that of the nickel screen electrode. This suggests that when oxygen is produced inside pores, it will have to build up sufficient pressure to expel the electrolyte from the pores before oxygen can escape; hence only the mouth of the pores could function⁷⁹. Thus it is necessary to use Teflon bonded porous electrodes to maximise the area available for oxygen evolution.

Furthermore, the results confirm our earlier hypothesis⁷⁴

that oxygen evolution on nickel would begin at about 1.45V, i.e. just above the potential of the lower nickel oxide/higher nickel oxide couple. Srinivasan et al.⁹⁰ found that the preanodized nickel electrodes at 1.5V are more active than untreated nickel for oxygen evolution. This was attributed to the presence of the so called "right type of oxide" i.e. β -NiOOH on the electrode surface. However, the same authors found that the increase of preanodization time at 1.5V causes an enhancement of the oxide film thickness, which in turn causes an increase in electrode resistance resulting in a drop in performance. Gottesfeld⁷⁰ found that the oxygen evolution currents obtained on Iridium electrodes (covered with a thick (2500 Å) layer of oxide, formed by potential multicycling) were 5-10 times higher than currents obtained at the same potential after the thick oxide has been removed (by applying anodic potential above 1.65V vs R.H.E.).

The removal of the thick oxide above 1.65V was attributed to the formation of a soluble Ir species of a higher oxidation state.

Gottesfeld excludes the possibility of an increase in surface area during the cycling being the only reason for the improvement in performance, and points to the special role that a mixed valence surface phase oxide (possibly with high defect structure) may have in the oxygen evolution reaction on iridium.

From the results for oxygen evolution on Pt screen

(illustrated in figure 5.13) it can be seen that the performance also decreased to a lower, steady level after only 20 minutes. These results indicate that initially some of the anodic current is used to build up the PtO_2 layer. Once the process has reached an equilibrium state, oxygen evolution proceeds on the PtO_2 surface. However, it is worth noting that the overvoltage is very much higher than on nickel, and this is in agreement with the postulate concerning the potential of the lower oxide/higher oxide couple, that of PtO/PtO_2 is higher than that of $\text{NiO}/\beta\text{-NiOOH}$.

Damjanovic et al^{92, 93}, also found that the performance of Pt anode for oxygen evolution decreases as the thickness of the oxide film increases, and suggested⁹² a model according to which a surface oxide film forms a barrier to charge transfer in series with the double layer barrier.

However, Gottesfeld^{70, 94} showed that a thick phase oxide, which can be formed on Pt under a specific polarisation scheme, improved the activity of the electrode for oxygen evolution and concluded that the formation of the "right type of oxide" may improve the activity of noble metal oxygen electrodes. This conclusion agrees with that of Srinivasan⁹⁰ on nickel electrodes.

Gottesfeld⁷⁰ also suggested that the defect (or mixed valence) structures of surface oxides are different in their

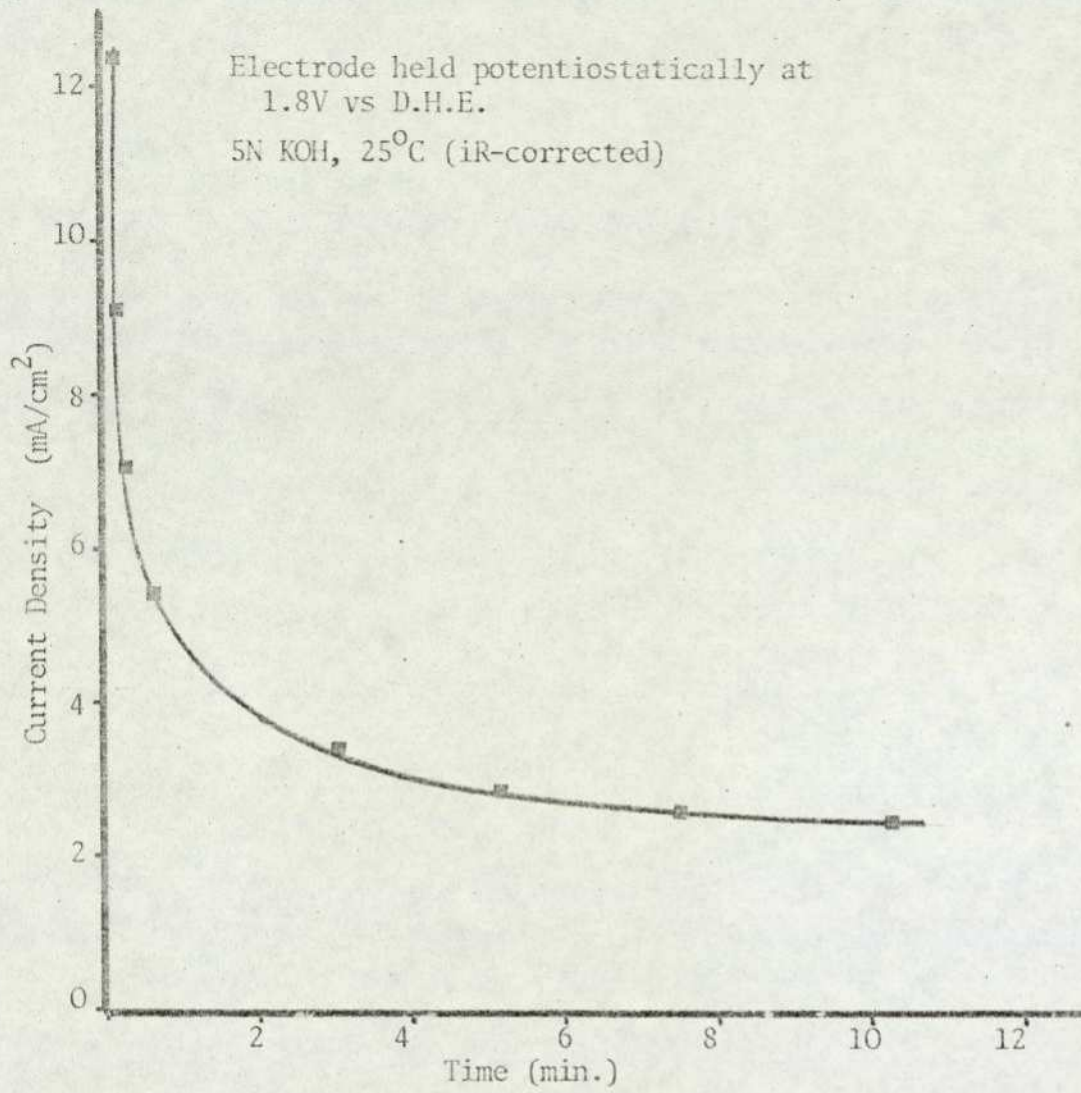


Fig. 5.13 OXYGEN EVOLUTION ON Pt SCREEN AS A
FUNCTION OF TIME

catalytic activity from the superficial (10-20 Å) oxide films formed on Pt under anodic polarisation. This could explain the apparent differences between the results obtained by Damjanovic et al⁹² and those obtained by Gottesfeld⁷⁰.

5.5.7. The Contribution of the Current Collector to the Overall Performance of the Teflon bonded Electrode

The results obtained on nickel screen suggest that, the screen itself can give a significant amount of current initially and cannot be neglected in our study.

On the other hand, Pt screen is far more passive and the oxygen evolution current reaches a steady value within 20 minutes. It is interesting to note that the iR-corrected results for oxygen evolution on Teflon bonded NiCo_2O_4 electrode supported on 100 mesh nickel screen, showed that at 70°C, over $1.2\text{A}/\text{cm}^2$ could be obtained at 1.63V vs D.H.E. (figure 5.5).

The corresponding results for oxygen evolution on Teflon bonded NiCo_2O_4 electrode supported on Pt screen is $0.95\text{ A}/\text{cm}^2$ (figure 5.14). It is difficult to determine accurately the screen contribution to the total current density of the Teflon bonded electrode, however the maximum contribution could be assessed from the oxygen evolution on the screen alone, under similar conditions. (figure 5.11).

The results presented in figures (5.5) and (5.14) clearly demonstrate that the contribution of the screen to the total current density of the Teflon bonded electrode is small

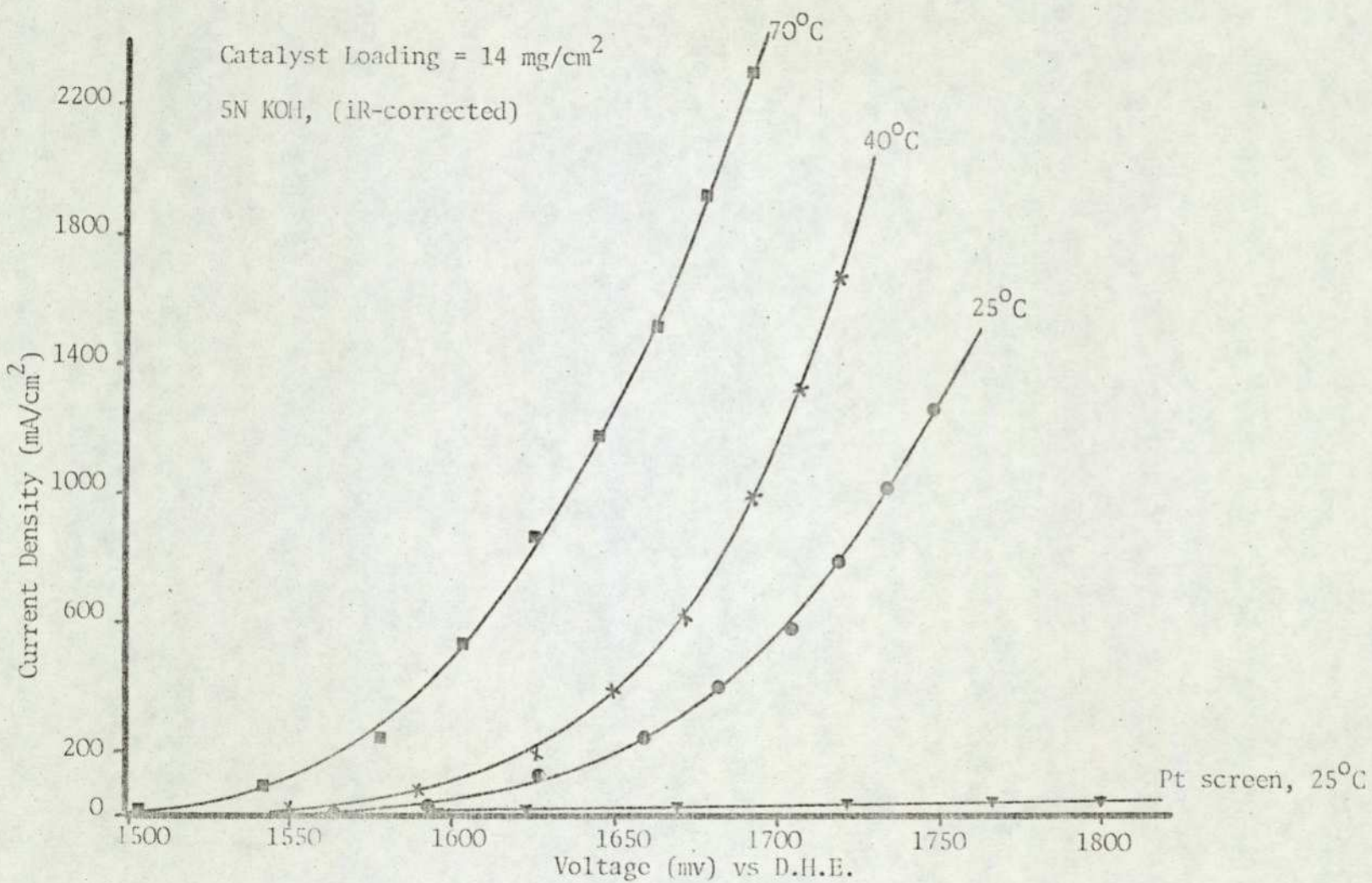


Fig. 5.14 OXYGEN EVOLUTION ON TEFLON BONDED NiCo_2O_4 ELECTRODE (SUPPORTED ON PURE Pt SCREEN)

and that the catalyst (NiCo_2O_4) is the major contributor to the performance of the electrode.

5.5.8. Effect of the Catalyst/Teflon Ratio on the Anodic Performance of Teflon bonded NiCo_2O_4 Electrodes

Figure (5.15) shows the effect of the catalyst/Teflon ratio on the anodic performance of Teflon-bonded NiCo_2O_4 (in 5N KOH, 25°C) at different potentials. In an optimized structure, ideally the total external area of the catalyst aggregates and the Teflon aggregates should be similar⁷⁷. Thus, the optimum catalyst/Teflon ratio should vary with the aggregate size of the catalyst. In the case of NiCo_2O_4 prepared by freeze drying, the results showed that beyond 30% Teflon, there was a sharp drop in performance, since a high Teflon content results in low electrical conductivity and severe non-wetting problems. In the range 20% to 30% there was no significant effect of the Teflon content on performance. It was not possible to study the effect of lower Teflon content below 15% as the structure was too friable.

5.5.9. Electrode Structure

Tseung and Vassie⁷⁹ compared the performance of porous Pt black and Teflon bonded Pt black electrodes in the hydrogen evolution reaction. They showed that more of the Pt surfaces in the Teflon bonded electrodes was available for the reaction since the H_2 gas bubbles could escape through the dry Teflon channels, thus ensuring higher performance. However, it is

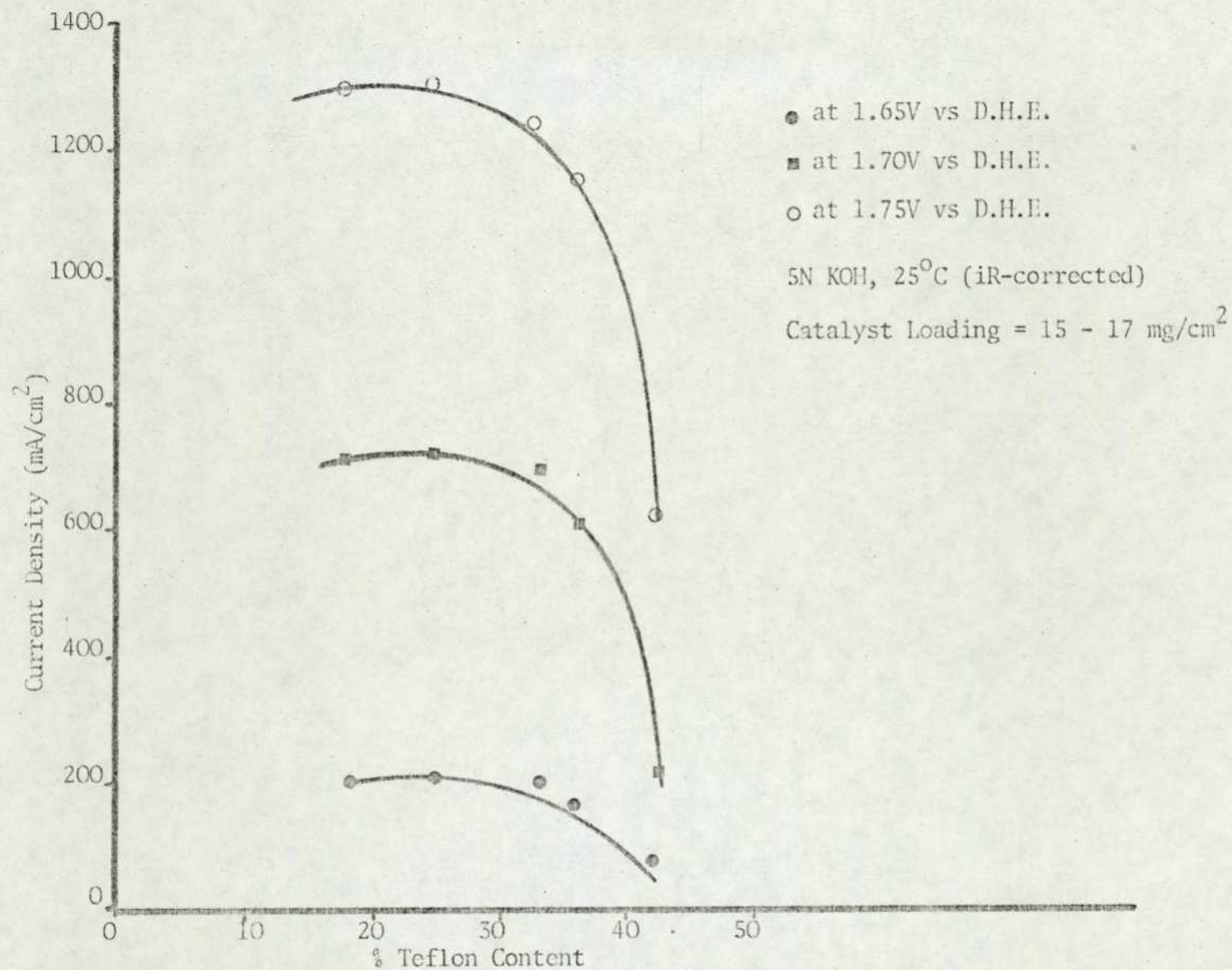


Fig. 5.15 EFFECT OF TEFLON CONTENT ON THE PERFORMANCE OF TEFLON BONDED NiCo_2O_4 ELECTRODE FOR OXYGEN EVOLUTION

not certain whether similar considerations are appropriate for oxygen evolution since the oxygen bubbles formed on Teflon bonded electrodes are larger than those formed on other (non Teflon bonded) porous electrode surfaces. The presence of large bubbles reduces the amount of surface available for oxygen evolution. The problem is further complicated by the fact that it is difficult to study the effectiveness factor of oxygen evolving porous electrodes by potentiostatic pulse techniques⁸⁹ since higher oxides are formed during the oxygen evolution reaction. Alternatively it was decided to study the effect of NiCo_2O_4 loading on performance in the two different electrode structures i.e. porous and Teflon-bonded electrodes. In this way, though there are differences in the surface area and aggregate size of NiCo_2O_4 catalysts prepared by freeze drying and thermal decomposition of nickel nitrate/cobalt nitrate solution, the variation of performance with loading in the two different structures should provide some insight into their relative effectiveness.

In the case of Teflon bonded NiCo_2O_4 electrodes, figure (5.16) shows that, between 1650-1750 mv vs D.H.E., the anodic performance increases almost linearly with loading ($4\text{-}20\text{ mg/cm}^2$). Beyond 20 mg/cm^2 , there is no further increase in performance. However, the performance of non Teflon bonded porous NiCo_2O_4 , figure (5.17), is lower and except within a limited range of loading ($4 - 6\text{ mg/cm}^2$) the anodic performance actually decreased

with increased loading, indicating that the utilization of the electrocatalyst surface is lower at increased loading. Visual examination of the porous NiCo_2O_4 electrodes revealed that at lower loadings (up to $10 \text{ mg NiCo}_2\text{O}_4/\text{cm}^2$) the nickel screen is not completely covered by the porous NiCo_2O_4 layer. The catalyst coats the nickel wires but there are still holes left at the centre of each mesh opening. As the loading is increased further, the holes are completely covered and the coating is much denser.

In Teflon bonded NiCo_2O_4 electrodes, because of the additional volume due to the Teflon, the nickel mesh is covered completely even at $5 \text{ mg NiCo}_2\text{O}_4/\text{cm}^2$ loading.

The results indicate that Teflon bonded electrodes are superior to non Teflon bonded electrodes. Basically, Teflon bonded electrodes are composed of a hydrophobic porous Teflon phase, intertwined with a porous hydrophillic catalyst phase¹⁸. When gas is evolved, at low current density ($\sim 20 \text{ mA}/\text{cm}^2$), the gas can diffuse out of the pores. At higher current densities, oxygen bubbles are formed and these eventually push the electrolyte out of the pores. In the case of Teflon bonded electrodes, the oxygen can then escape through the dry Teflon channels and therefore the interior of the electrode is not completely denuded of electrolyte. However, non Teflon bonded porous electrodes do not have dry channels and only the top surface of the electrode is electrochemically active, since the interior is depleted of electrolyte. At low

NiCo_2O_4 loadings, since there is only sufficient catalyst to coat the nickel wires, the total external surface area of the NiCo_2O_4 layer will be greater than when the nickel mesh is completely covered. Furthermore, since the higher NiCo_2O_4 loadings are prepared by repeated impregnation of nickel cobalt nitrates, the resultant NiCo_2O_4 structure is denser, again leading to reduced performance.

It is interesting to note that at the same Luggin Capillary to working electrode distance, the measured iR-drop is very much higher in the case of non Teflon bonded NiCo_2O_4 electrodes (~ 0.2 ohm instead of ~ 0.1 ohm for Teflon bonded NiCo_2O_4 electrodes). Since the amount of electrolyte in the interior of the non-Teflon bonded electrode is very much less, it is reasonable to expect a higher resistance.

5.5.10. Modification of the Surface of Teflon Bonded NiCo_2O_4 Electrodes

During the course of this work, it was noticed that the oxygen bubbles on the surface of the Teflon bonded electrodes were larger and detached less readily from the surface than on non Teflon bonded electrodes. This suggested that the hydrophobicity at the surface of the Teflon bonded electrode might be the responsible for the above phenomenon. Therefore Teflon bonded NiCo_2O_4 electrodes were dipped into a nickel nitrate/cobalt nitrate solution, dried and heated at 300°C for 5 hours. A thin layer of hydrophillic nickel cobalt oxide

($\sim 5 \text{ mg/cm}^2$) covered the surface of the electrode. In use, such electrodes gave significantly higher performance, 1.8 A/cm^2 at 1.7V vs D.H.E. (at room temperature, 5N KOH) instead of 1 A/cm^2 under the same conditions for standard Teflon bonded electrodes (see figure 5.18).

The oxygen bubbles evolved at the surface of the modified electrode were very much smaller and these detached far more readily from the surface. Since the total catalyst loading in both cases was 23 mg/cm^2 , the improved performance was more likely to be caused by modification at the electrode surface.

5.5.11. Mechanical Strength of Teflon bonded and Non Teflon bonded Porous NiCo_2O_4 Electrodes

Vassie⁷⁷ showed that the pressure generated inside a $100 \text{ \AA}$ catalyst pore is in the order of 100 atmospheres, rising to 1000 atmospheres for a $10 \text{ \AA}$ pore. Unless the electrocatalysts are prepared by chemical methods, such as decomposition of metallic salts, followed by solid state sintering to form semi-conducting oxides, the strength of the catalyst aggregates would not be strong enough to resist the pressure generated inside the pores. An additional function of the Teflon particles is to bind the catalyst aggregates together. In use, Teflon bonded NiCo_2O_4 electrodes are very much stronger than porous NiCo_2O_4 electrodes, since the latter tend to shed NiCo_2O_4 , especially at high loadings. Surface modification of the Teflon bonded electrodes by forming a layer of porous

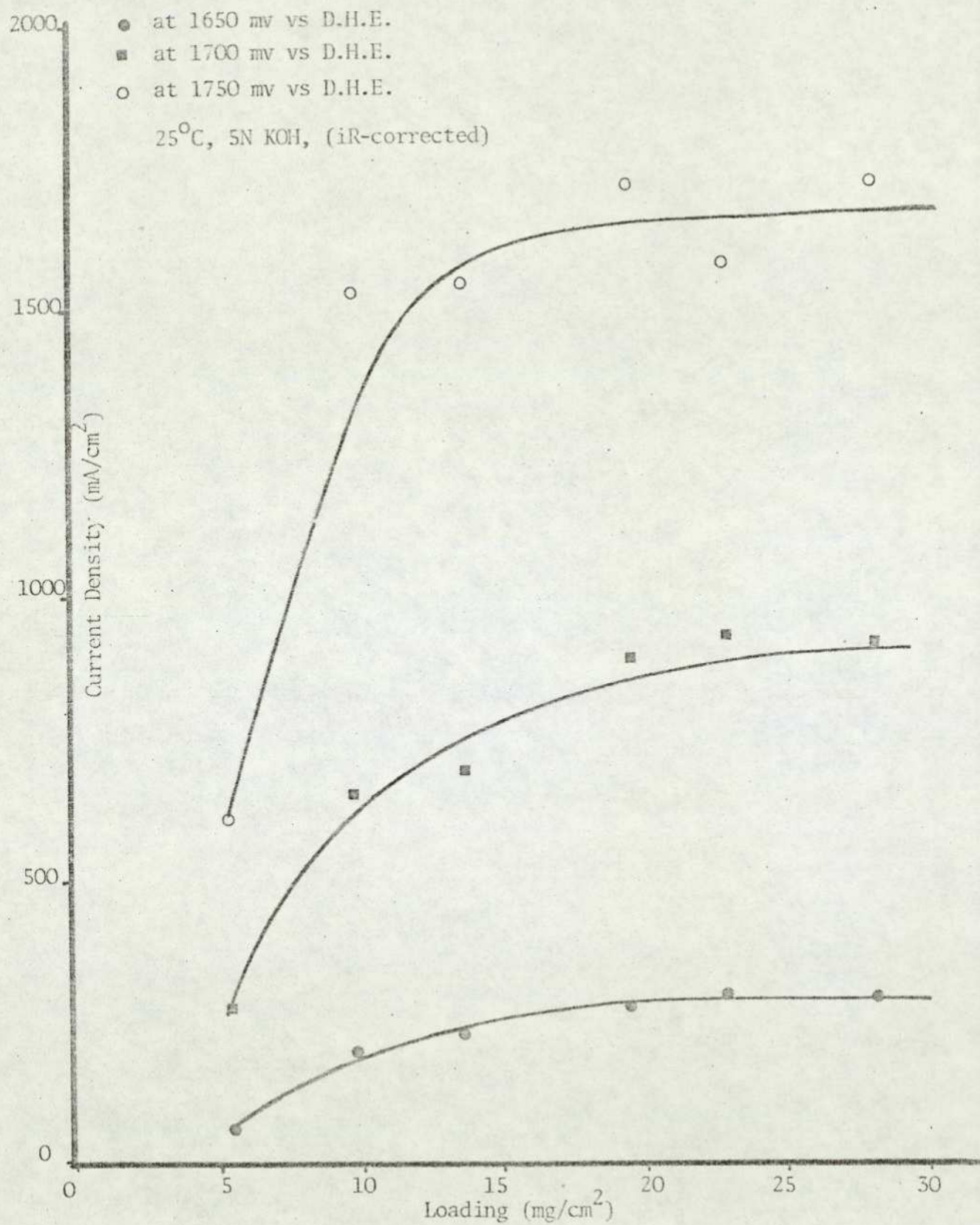


Fig. 5.16 OXYGEN EVOLUTION ON TEFLON BONDED NiCo_2O_4 ELECTRODES
(Ni SCREEN AS CURRENT COLLECTOR)

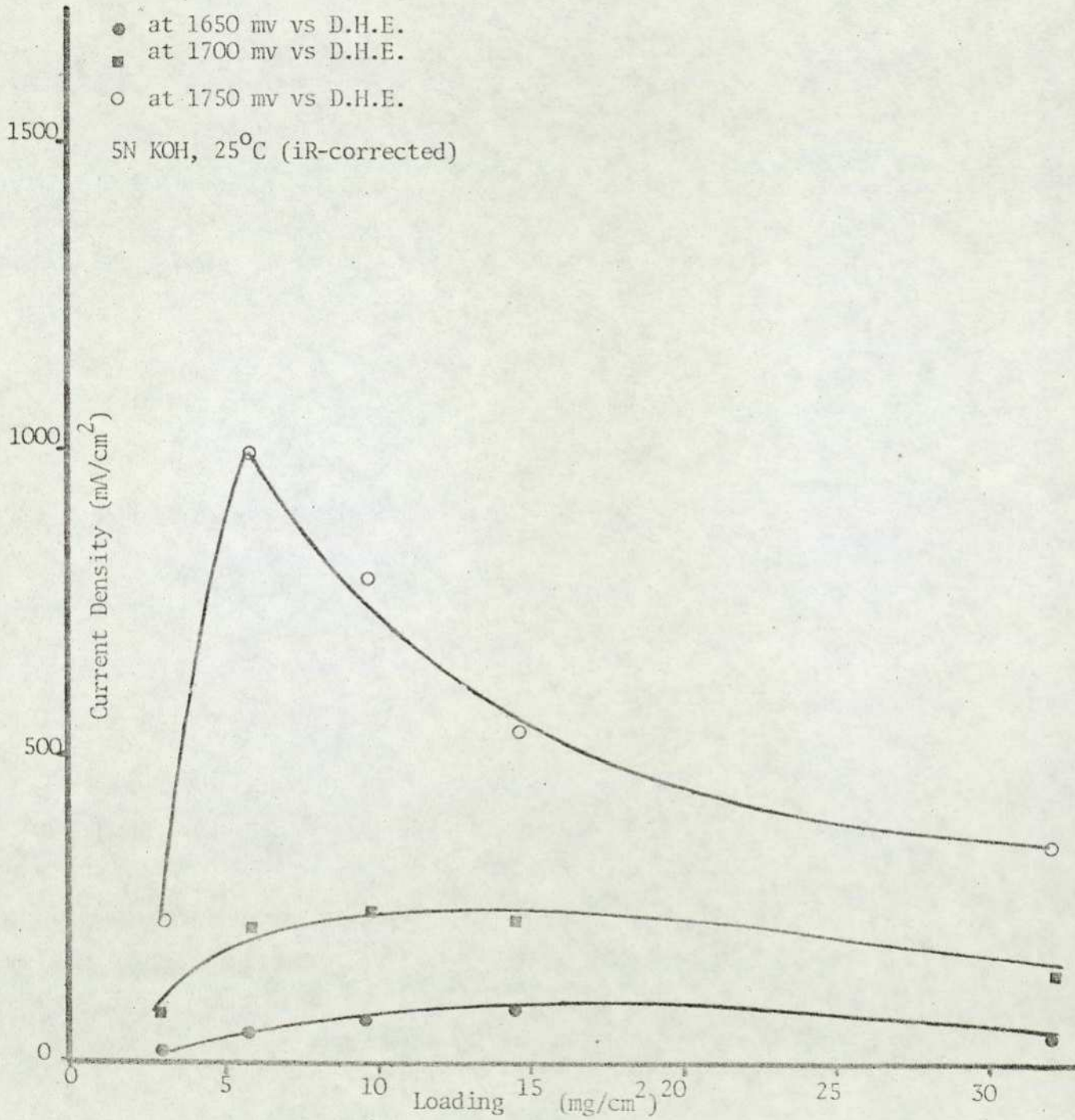


Fig. 5.17 OXYGEN EVOLUTION ON NON TEFLON BONDED POROUS NiCo_2O_4 ELECTRODES (Ni SCREEN AS CURRENT COLLECTOR)

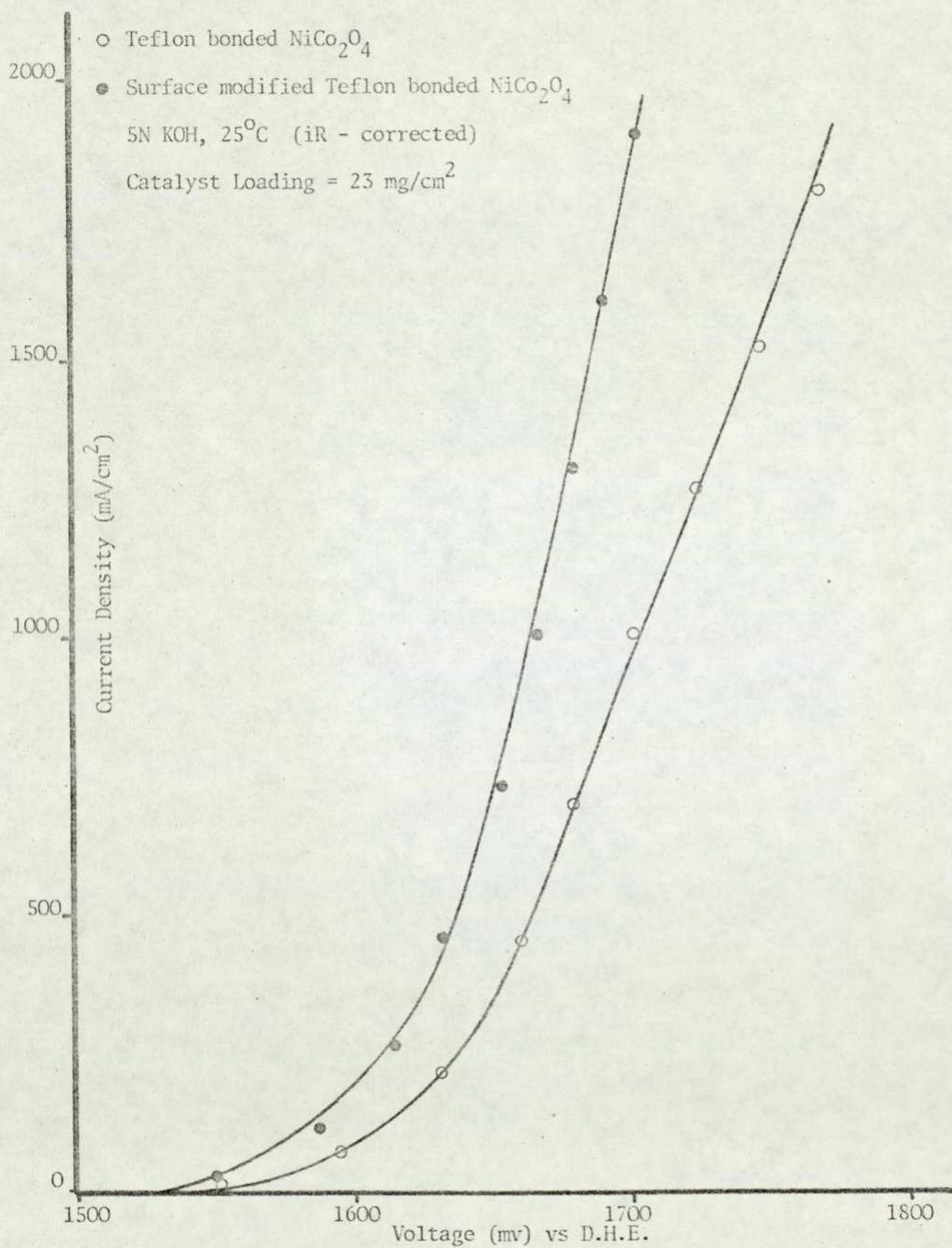


Fig. 5.18 OXYGEN EVOLUTION ON TEFLON BONDED AND SURFACE MODIFIED
TEFLON BONDED NiCo_2O_4 ELECTRODES

nickel cobalt oxides is not entirely satisfactory, because some of the oxides on the surface tend to drop off during prolonged testing at high current densities ($\sim 1\text{A}/\text{cm}^2$, > 100 hours).

5.5.12. Stability of Teflon bonded NiCo_2O_4 Electrodes

A long term test over a period of 250 hours was carried out on a Teflon bonded NiCo_2O_4 electrode supported on Pt screen, (figure 5.19), confirmed that the performance of this electrode did not change with time.

In practice, nickel screen would have to be used as current collector, on cost basis, and the electrode might be used at temperature greater than 25°C .

Figures (5.19) and 5.20) show that after an initial decay at both 25°C and 80°C , the performance of Teflon bonded NiCo_2O_4 electrodes, supported on nickel screen, remained stable and that the initial decay was attributed to the growth of poorly conducting nickel oxide films on the nickel screens.

Over a total test period of 300 hours, there were no visible signs of physical deterioration in the electrode and atomic absorption analysis of the KOH solution after the endurance test did not reveal the presence of nickel or cobalt ions (sensitivity of apparatus 2 p.p.m.).

Longer stability tests (over a period of three months) were carried out on our samples of Teflon bonded NiCo_2O_4 electrodes elsewhere⁹⁵, and the results confirmed the high electrochemical activity towards oxygen evolution and showed

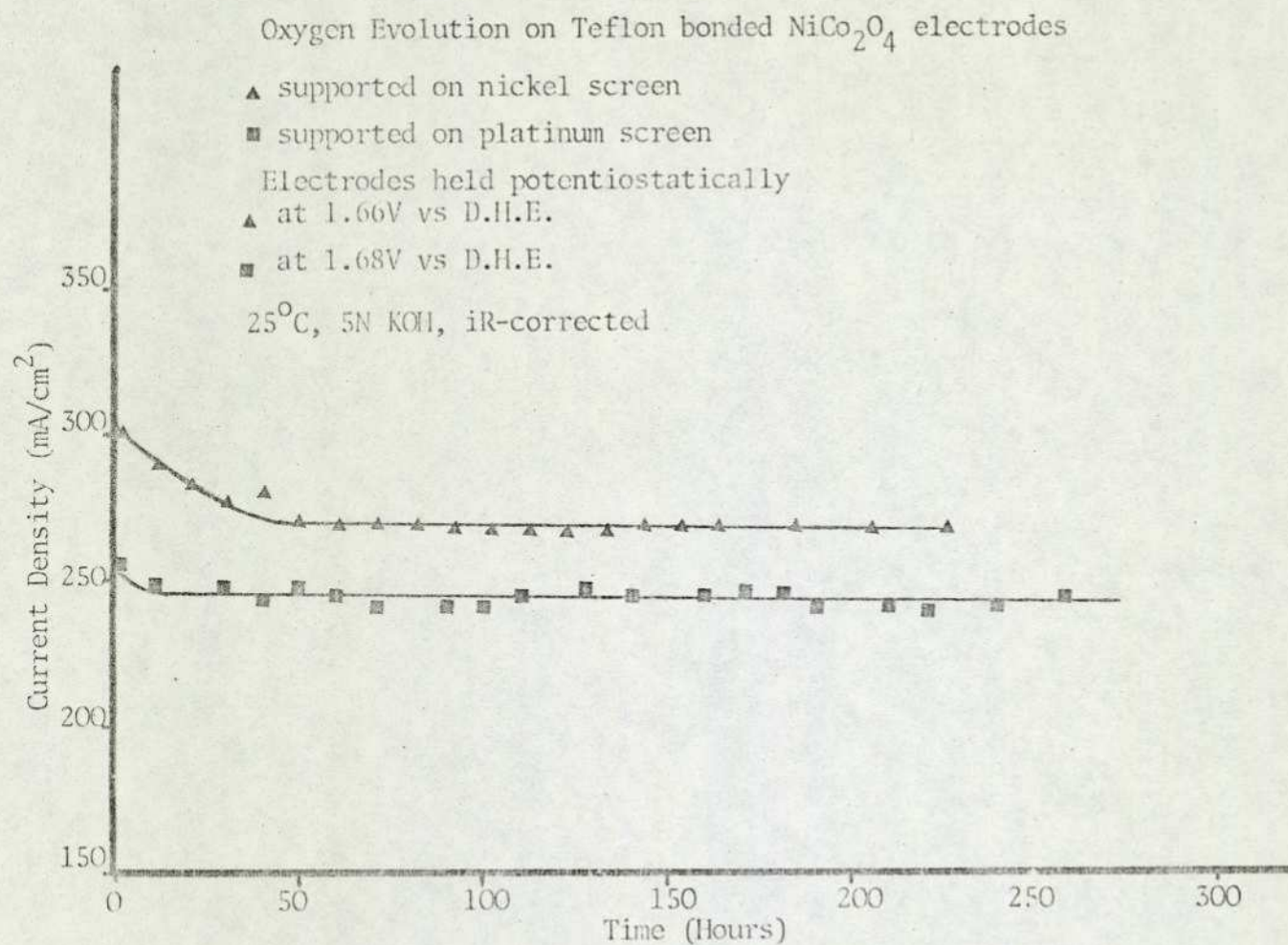


Fig. 5.19 OXYGEN EVOLUTION ON TEFLON BONDED NiCo_2O_4 ELECTRODES AS A FUNCTION OF TIME (AT 25°C).

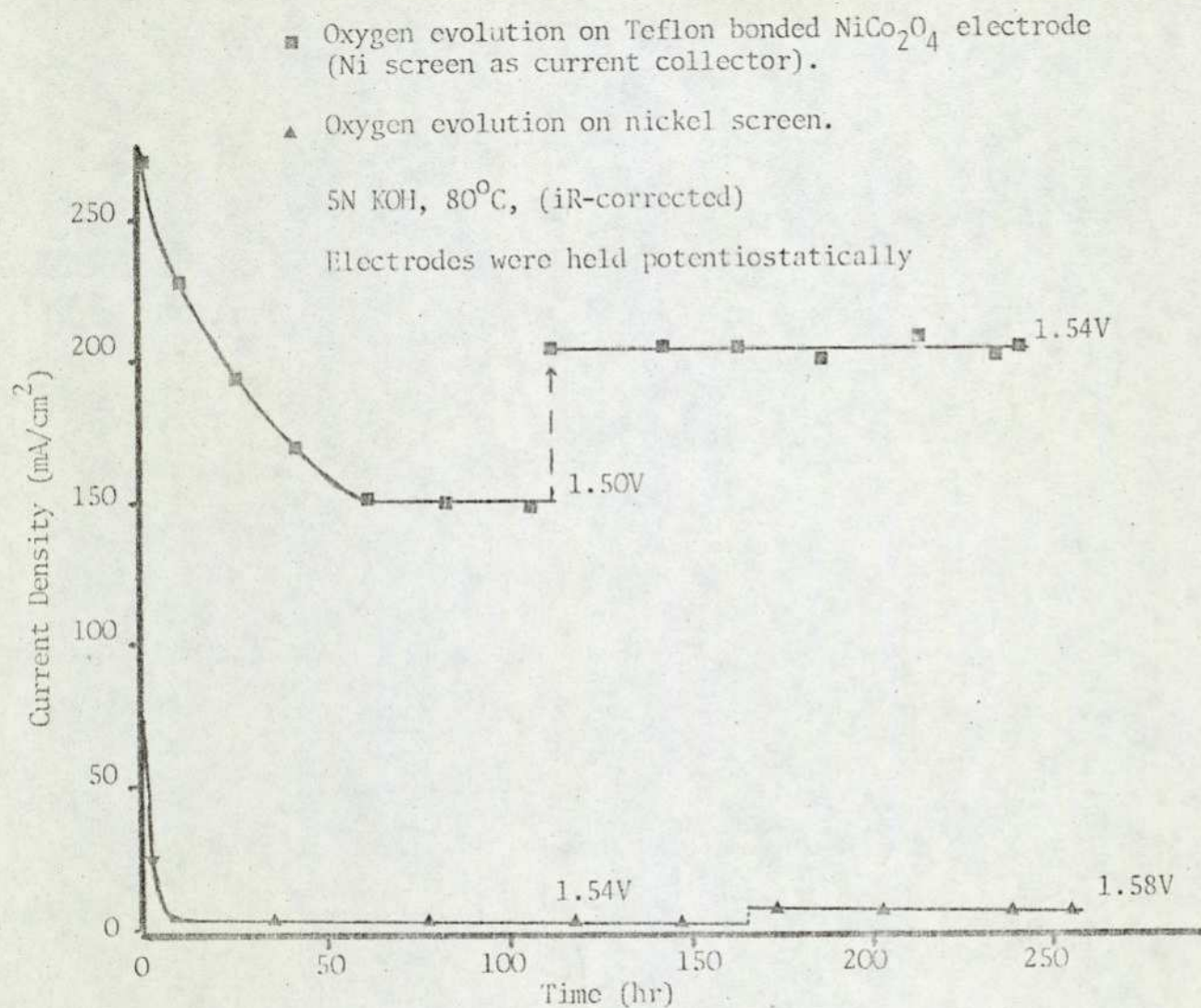


Fig. 5.20 OXYGEN EVOLUTION ON TEFLON BONDED NiCo_2O_4 ELECTRODE AS A FUNCTION OF TIME (AT 80°C).

an excellent stability.

5.5.13. Physical Disruption During Oxygen Evolution at High Current Density

No disruption was observed when current densities as high as 3A/cm^2 were imposed on Teflon bonded NiCo_2O_4 electrodes for more than 10 hours.

5.5.14. Storage Effect

The effect of storage under air in a sealed container was examined by retesting of the sample (NiCo_2O_4) for oxygen evolution after a period of 3 years. There was no deterioration in the catalyst activity.

5.6. ALTERNATIVE OXIDE SYSTEMS

It has been shown in this work⁷⁴ that the most important criterion governing the choice of oxides for oxygen evolution is the equilibrium potential of the metal/metal oxide or the lower metal oxide/higher metal oxide couple if there is more than one form of oxide. This should be lower or similar to the theoretical potential of the oxygen electrode. Apart from NiCo_2O_4 , NiO would seem to be a good candidate material, since the equilibrium potential of $\text{NiO/Ni}_2\text{O}_3$ is 1.434V, close to 1.4V for NiCo_2O_4 (versus R.H.E.). However, it is an insulator ($\rho > 10^6$ ohm-cm). By doping it with lithium⁹⁶ it is possible to reduce the resistivity to acceptable values, (i.e. below 100 ohm-cm)⁷⁴.

5.6.1. Anodic Performance of NiCo_2O_4 and Lithiated Nickel Oxide

Figure (5.21) compares the anodic performance of Teflon bonded lithiated nickel oxide and NiCo_2O_4 electrodes. This shows that NiCo_2O_4 is only marginally better than lithiated nickel oxide, though its activity per unit area is significantly higher. Nickel metal is also relatively active as shown in figure (5.11). However, it must be borne in mind that the performance of nickel anodes decay with time and the steady state performance, attained after 60-80 hours, is markedly inferior to the initial performance. The build up of relatively low conductivity NiO was suggested as the reason for this decay⁷⁴. Thus, lithiation of the nickel oxide formed on the nickel screen may be one possible solution to the problem.

5.6.2. Relative Activities of the Different Catalysts

Figure (5.22) illustrates the anodic performance of Teflon bonded platinum black (B.E.T. Surface area $\sim 10 \text{ M}^2/\text{g}$) supported on Pt screen, at different temperatures (25, 40, 70°C).

The main purpose of measuring the activity of Teflon bonded platinum black for oxygen evolution was to obtain a standard against which the performance of Teflon bonded electrodes which have been evaluated in this work could be judged. The results presented in this chapter clearly show that NiCo_2O_4 is the more active catalyst for oxygen evolution.

The high activity, the excellent stability and the low cost of NiCo_2O_4 make it the most favourable anode in alkaline solutions.

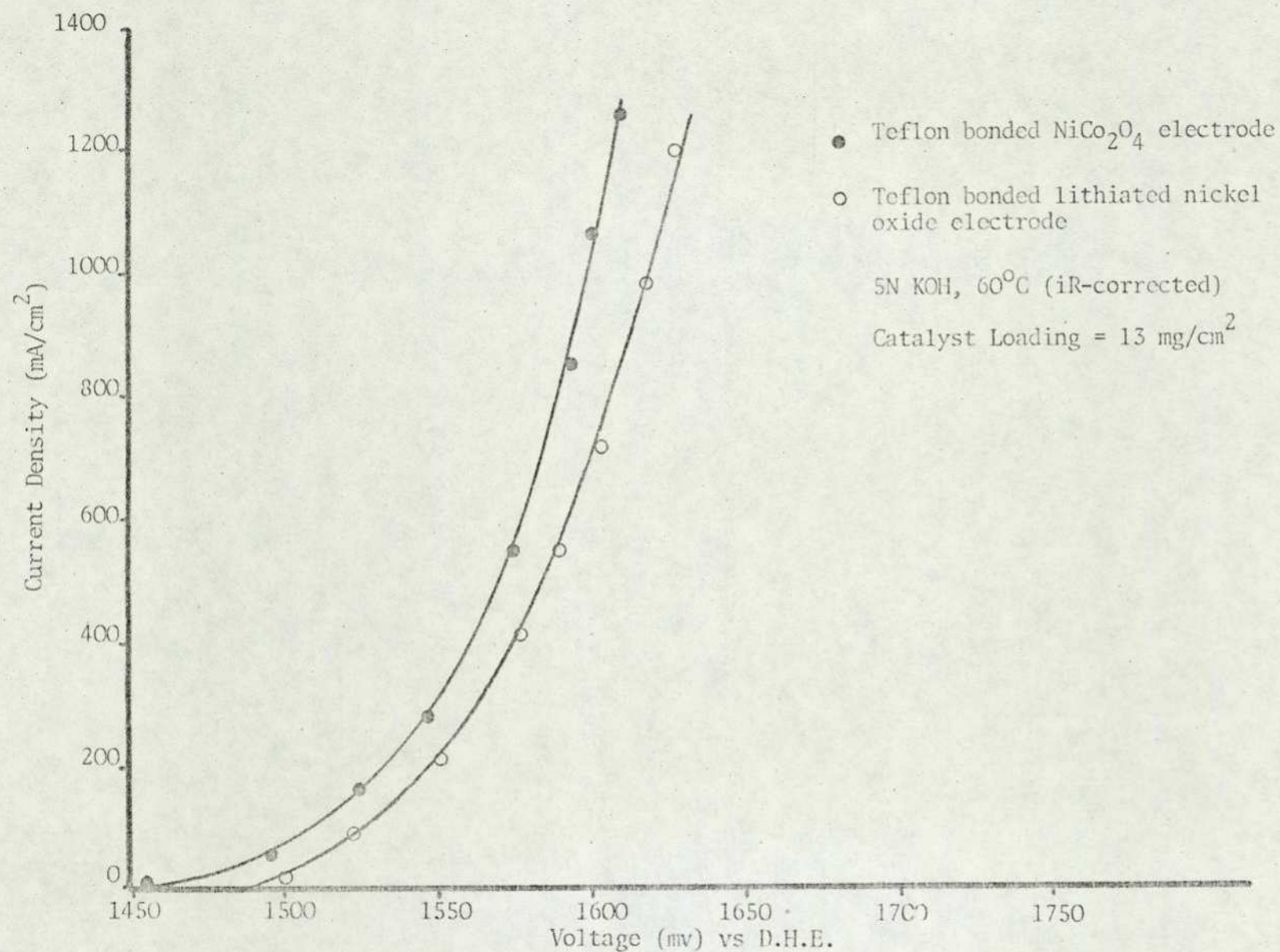


Fig. 5.21 OXYGEN EVOLUTION ON TEFLON BONDED NiCo₂O₄ AND LITHIATED NICKEL OXIDE ELECTRODES

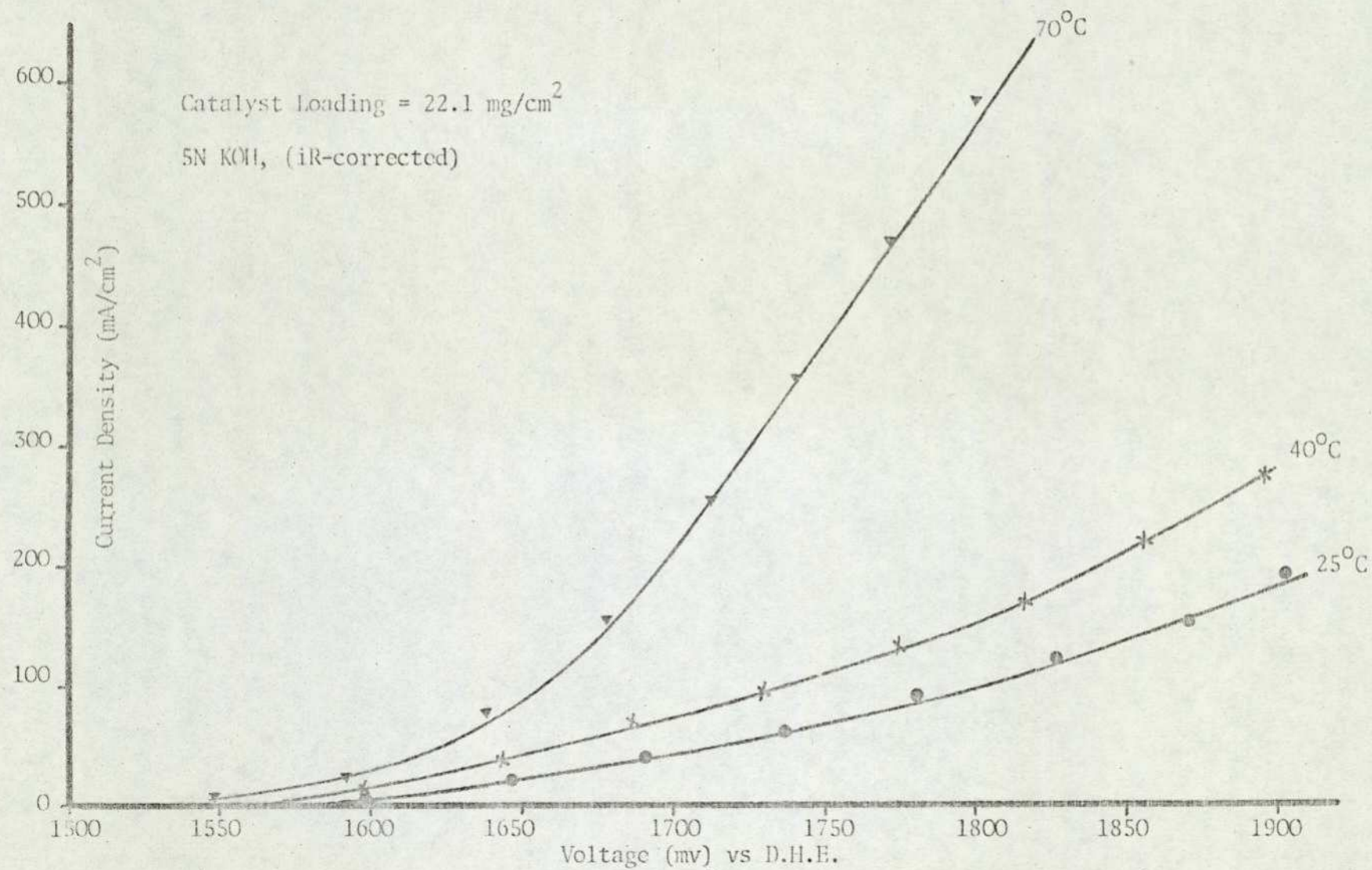


Fig. 5.22 OXYGEN EVOLUTION ON TEFLON BONDED PLATINUM BLACK ELECTRODE AT DIFFERENT TEMPERATURES

C H A P T E R S I X

A POTENTIOSTATIC PULSE STUDY OF OXYGEN EVOLUTION
ON TEFLON BONDED NiCo_2O_4 ELECTRODES

6.1. Kinetic Studies of Oxygen Evolution on Metals

The Kinetic studies of oxygen evolution on different metals such as Pt, Au, Ni, Pd, Ir, Rh and their alloys have been reviewed by Hoare⁷⁵ and more recently by Erdey-Gruze⁹⁷ and Appleby⁹⁸. Hoare⁷⁵ has shown that in all the metals studied the oxygen produced initially reacts with the bare metal surface to form surface oxides. Since the composition and state of the surface oxide layer strongly influence the electrode process as discussed in Chapter 5, it is difficult to compare the behaviour of different electrode metals as far as oxygen evolution is concerned.

The poor reproducibility of the measurements of kinetic parameters such as the Tafel slope for the oxygen evolution reaction was reported^{75, 97} and it was attributed to the strong dependence of the kinetics of oxygen evolution on the state of the electrode surface; this in turn is influenced by the pre-treatment of the metal and the presence of impurities. Hoare⁹⁹ has shown that in a purified system reproducible results over at least three complete cycles of polarisation are obtainable, if the electrode is anodized initially at the highest potential under investigation until a steady state value is obtained. In this way, a stable catalytic surface is formed on the electrode.

Damjanovic et al^{93, 100} have also stressed the importance of anodizing platinum in H_2SO_4 at high anodic potential (1.7-2V) for sometime before taking electrochemical measurements. Under

such conditions, it was possible to obtain V -log i relationships which were linear over several decades^{101, 102} and had slopes of 2.3 ($2RT/F$) and then only if the potentials in the subsequent process of measurement were lower than those used in the electrode pretreatment.

Bockris et al.¹⁰¹ have investigated the kinetics of oxygen evolution on platinum electrodes in acid and alkaline solutions, and reviewed 14 different possible paths, suggested by different workers for oxygen evolution reaction.

Bockris¹⁰¹ also found that for oxygen evolution on platinum in alkaline solution, the anodic Tafel line has a distinct break in slope at about 1.6V. At potential below 1.6V the Tafel slope was RT/F , whereas above 1.6V it was $2RT/F$.

The break in Tafel slope was attributed to a change in the rate determining step.

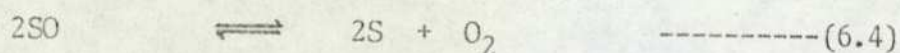
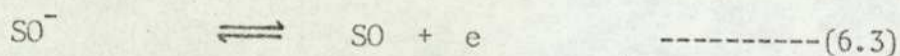
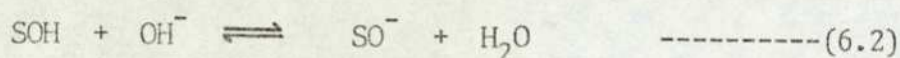
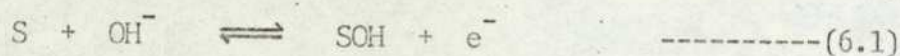
Evidence that an oxygen atom in the surface oxide film participates directly in oxygen evolution reaction was provided by Rosenthal and Veselovskii¹⁰³. These workers have found that, if the platinum surface oxide film is initially enriched with ^{18}O , (by anodic polarisation in ^{18}O enriched solution) the first portion of oxygen gas anodically evolved at platinum (in ^{18}O unenriched solutions) is enriched with ^{18}O . The participation of oxygen atoms in the oxide film in oxygen evolution has been supported recently by Damjanovic⁹² in study of oxygen evolution on Pt.

Iwakura et al.⁸⁸ recently studied the evolution

of oxygen on platinum oxide (PtO_2) in alkaline solutions.

The electrode was prepared by firing layers of chloro platinic acid on to titanium at 450°C for one hour to form PtO_2 layer. The formation of PtO_2 was confirmed by ion and x-ray diffraction analysis. However it was not certain whether the film still retained the PtO_2 structure after it had been subjected to anodic treatment.

They also suggested the most probable reaction path under Langmuir conditions was as follows:



where (S) is the surface sites.

A plot of η (0-500 mv) vs $\log i$ gave two Tafel regions. At lower η , the Tafel slope was 2.3 (RT/F), corresponding to step (6.2) being the rate determining step (r.d.s.) assuming $\alpha = 0.5$. At higher η , the Tafel slope was 2.3 (2RT/F), corresponding to step (6.1) being (r.d.s.).

They did not discuss the expected value of the Tafel slopes for steps (6.3) and (6.4). Since these steps represent the "oxide" decomposition path proposed by Krasilshchikov¹⁰⁴, (6.3) and (6.4) should correspond to 2.3(2RT/3F) and 2.3(RT/4F) respectively.

The results of Iwakura et al. also confirmed the importance

6.2. THE PROBLEMS OF KINETIC MEASUREMENTS ON POROUS ELECTRODES

It is difficult to interpret steady state polarization measurements for gas dissolution reactions on porous electrodes, due to complications associated with mass transfer and non-evenly distributed ohmic drops within the pores of the electrode i.e. current densities are not uniform within porous media because the diffusion and ohmic overvoltages vary throughout the length of the pores, hence the contribution of activation, diffusion and ohmic overvoltages to the total is different at different points within the porous structure⁴³. Moreover the study of oxygen evolution reaction on solid electrodes is complicated by the formation of oxides on the surface as well as the formation of gas bubbles which will block off significant amounts of the electrode surface. The amount of blockage will vary with current density. If porous electrodes are used, apart from the above problems, gases generated inside the pores will push the electrolyte out of the pores, reducing the amount of surfaces available for electrochemical reaction as the current increases⁷⁹. Thus, we have a situation whereby apart from concentration polarization, the amount of surface area available is continuously changing with overvoltage, rendering the application of the Tafel equation difficult. The considerations discussed in Chapter 5 and the results obtained suggested that NiCo_2O_4 spinel oxide was of particular interest.

Since the spinel NiCo_2O_4 breaks down at 450°C to form relatively inactive cubic NiCo_2O_3 ⁸¹, it is impossible to prepare solid NiCo_2O_4 spinel oxide by solid state sintering or melting and casting techniques for fundamental electrode kinetic studies.

Therefore, we have to confine our studies to porous electrodes.

Tseung and Vassie⁷⁹ showed that by measuring the potentiostatic transients of Teflon bonded Pt black and Pt foil electrodes, the exchange current density (i_0) values for hydrogen evolution in 5N H_2SO_4 , at 25°C were essentially the same, suggesting that the above problems may be solved by the potentiostatic pulse technique¹⁰⁶ provided allowances can be made for the formation of higher oxides⁷⁴.

6.3. EXPERIMENTAL

Most of the work in this Chapter is on NiCo_2O_4 powder (prepared by freeze drying).

The catalyst preparation and the electrode fabrication as well as the cell design have been described earlier (section 5.4). The 5N KOH used for the experiments conducted in this Chapter, was pre-electrolyzed at constant current of 5 mA/cm^2 for 48 hours in N_2 atmosphere, using two large platinum gauze of area 20 cm^2 to adsorb the impurities which could be present in the electrolyte.

The steady state techniques have been described in Chapter 5.

6.4. RESULTS AND DISCUSSION

6.4.1. Steady State Measurements for Oxygen Evolution on Teflon bonded NiCo_2O_4 Electrodes

Figure (6.1) shows the V vs log i plot for oxygen evolution on Teflon bonded NiCo_2O_4 electrode at 25°C , 5N KOH. The electrode was preanodized at 2V vs D.H.E. for one hour and the current density was measured with decreasing potential.

The plot gives two distinct Tafel slopes, below 1.7V Tafel slope is 0.03 V/decade, and above 1.7V Tafel slope is 0.1 V/decade.

The value corresponding to the theoretical Tafel slope for the reaction (6.1) is 0.119 V/decade and 0.059 V/decade for the reaction (6.2).

The results in figure (6.1) are different from those of Teflon bonded NiCo_2O_4 electrodes, at 25°C , which have not been preanodized (figure 6.2), since measurements of the current density were taken with increasing potential, (anodically), from the o.c.v. . Tafel slope at potential below 1.7V was 0.047 V/decade, $i_o = 8.7 \times 10^{-14} \text{ A/cm}^2$ of B.E.T. surface area and above 1.7V Tafel slope was 0.14 V/decade, $i_o = 3.4 \times 10^{-7} \text{ A/cm}^2$ of B.E.T. surface area.

Tafel slopes and the exchange current density for oxygen evolution on preanodized Teflon bonded NiCo_2O_4 electrode at different temperatures are given in Table (6.1).

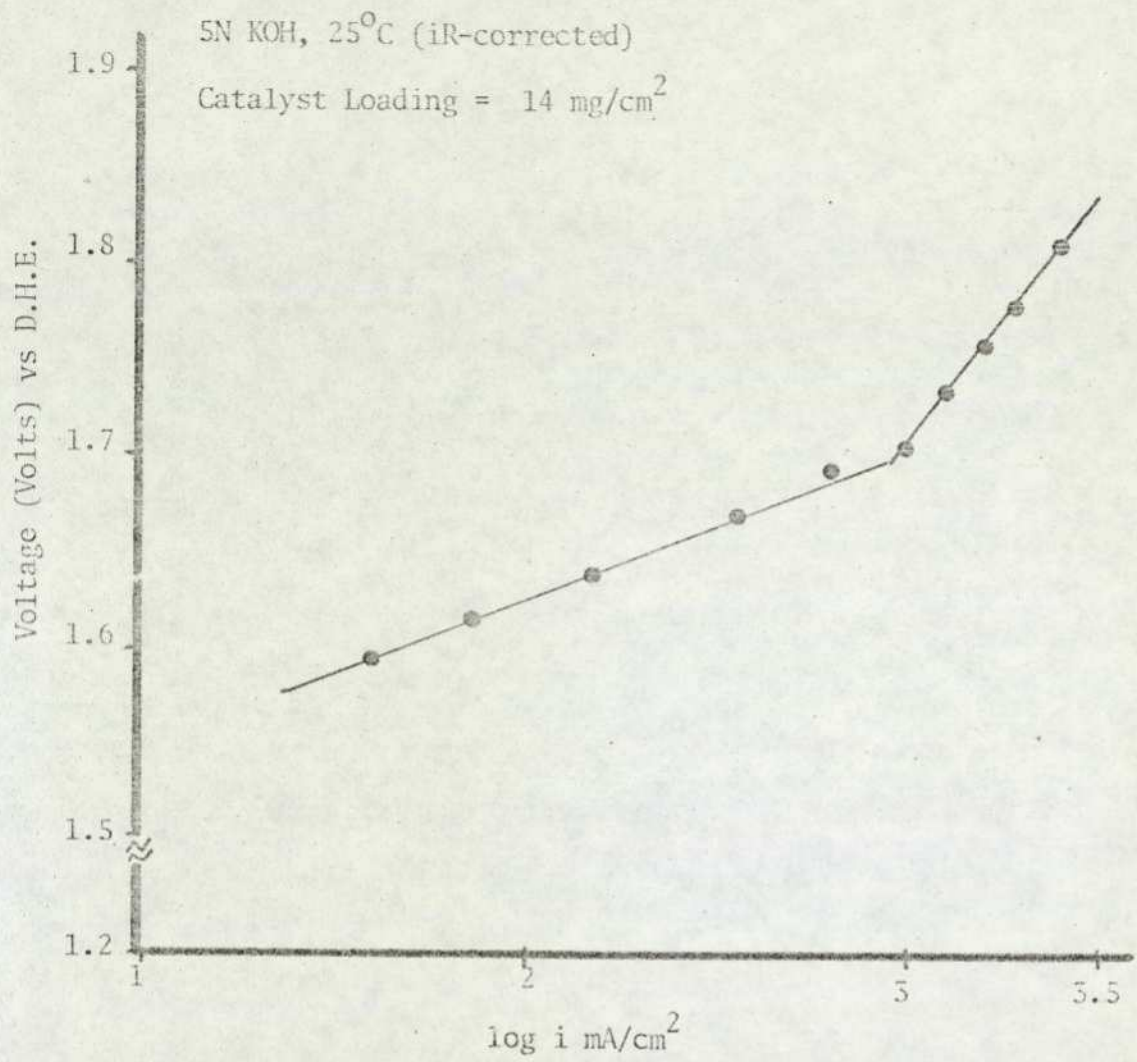


Fig. 6.1 STEADY STATE MEASUREMENTS FOR OXYGEN
EVOLUTION ON PREANODIZED TEFLON BONDED
NiCo₂O₄ ELECTRODE.

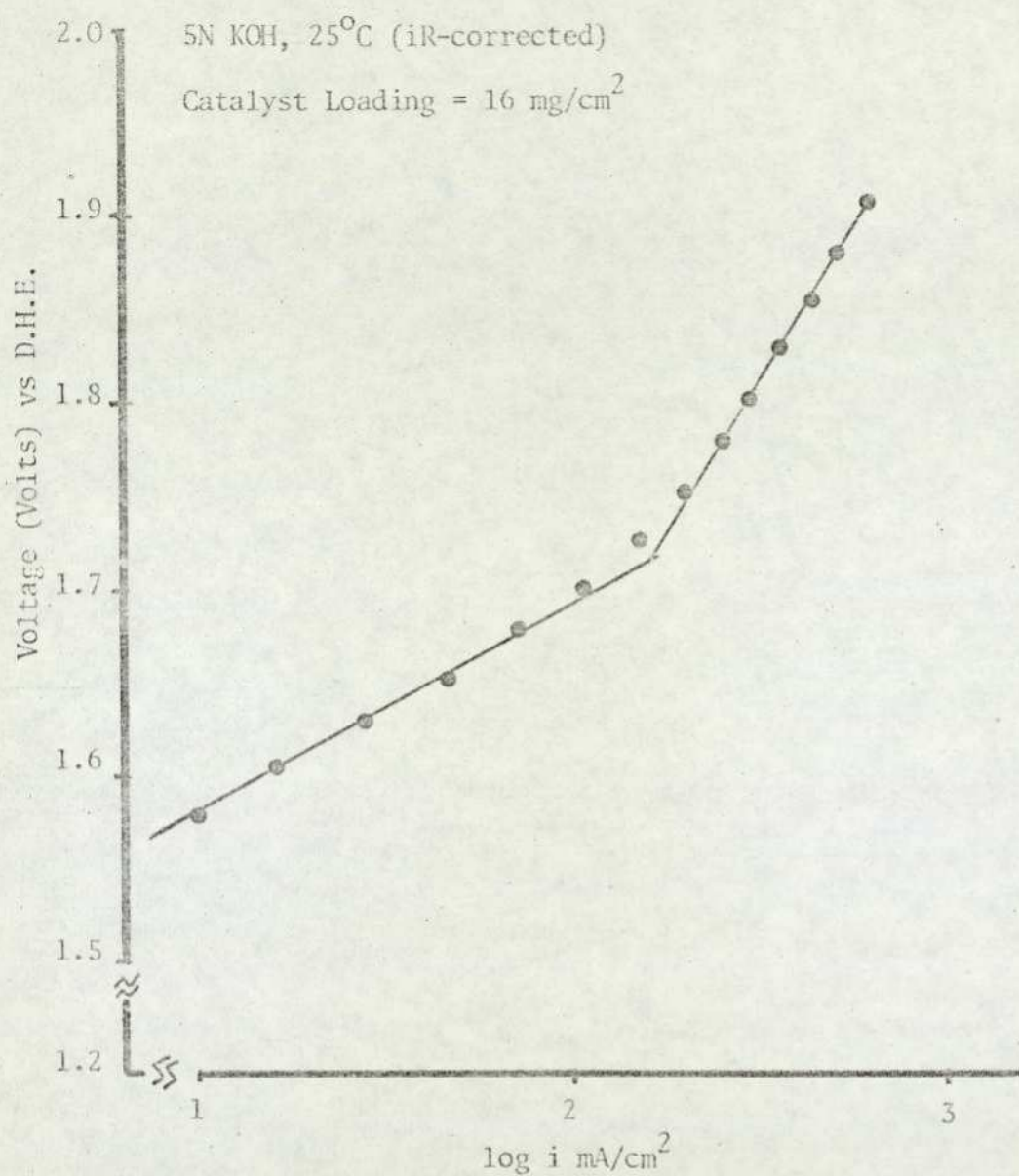


Fig. 6.2 STEADY STATE MEASUREMENTS FOR OXYGEN EVOLUTION
ON TEFLON BONDED NiCo_2O_4 ELECTRODE

Table (6.1)

T C°	i_o (A/cm ² of B.E.T. surface area)		Tafel slope (V/decade)	
	(low η) $\times 10^{16}$	(high η) $\times 10^7$	low η	high η
25	4.7	10.2	0.033	0.107
50	1.4×10^2	38.9	0.033	0.125
70	7.4×10^3	81.3	0.035	0.137

Identical steady state oxygen evolution experiments were performed on different Teflon bonded NiCo_2O_4 electrodes, in order to estimate the variation in Tafel slope value.

The results showed that, although, all the electrodes were preanodized and tested under similar conditions the Tafel slope values varied between 0.06 and 0.1 V/decade, at high overvoltage. This significant variation is not surprising considering the continuous change in the available surface area and the amount of concentration polarization caused by bubbles formation and emptying of pores.

6.4.2. Linear Sweep Voltammetry¹⁰⁷

In Voltammetry the potential continuously changing and the voltage output of power supply varies linearly with time. The resultant current potential plot (voltammogram) consist of a pattern of current maxima along the potential axis, whose heights and positions are characteristics of the electrode process. The occurrence of maxima for any given electrode process is a mass transfer effect; as the voltage varies, the rate of electron transfer at the electrode

increases, and the current increases accordingly. The reactants at the vicinity of the electrode are progressively removed, and this tends to decrease the current. This effect of depletion becomes progressively predominant and the current potential curve exhibits a maximum.

The exact profile of the voltammogram is affected by parameters such as temperature, voltage scan rate and the number of voltage cycles.

A linear sweep generator (Chemical Electronics) was used in conjunction with the potentiostat and the cell. The current voltage curves were plotted using x-y-t pen recorder (Bryans Model 29000A4).

In experiments where the scan rate was higher than 50 mv/s the ramp-section of a wave form generator (Chemical Electronics type 01) was used instead of the linear sweep generator. A schematic diagram of the system is shown in figure (6.3).

Since no studies have been made on the oxidation of NiCo_2O_4 at high anodic potentials, it is important to establish the anodic potential regions which may be of interest.

Figure (6.4) shows cyclic voltammogram for Teflon bonded NiCo_2O_4 electrode supported at 100 mesh nickel screen at scan rate 50 mv/s. (between 0.75 V and 1.9V vs D.H.E.).

As can be seen from figure (6.4) the anodic current starts to increase sharply at about 1.37V to give a peak current due to conversion of the oxide to a higher oxidation state at potential about 1.55V. The broad shape of the peak indicates

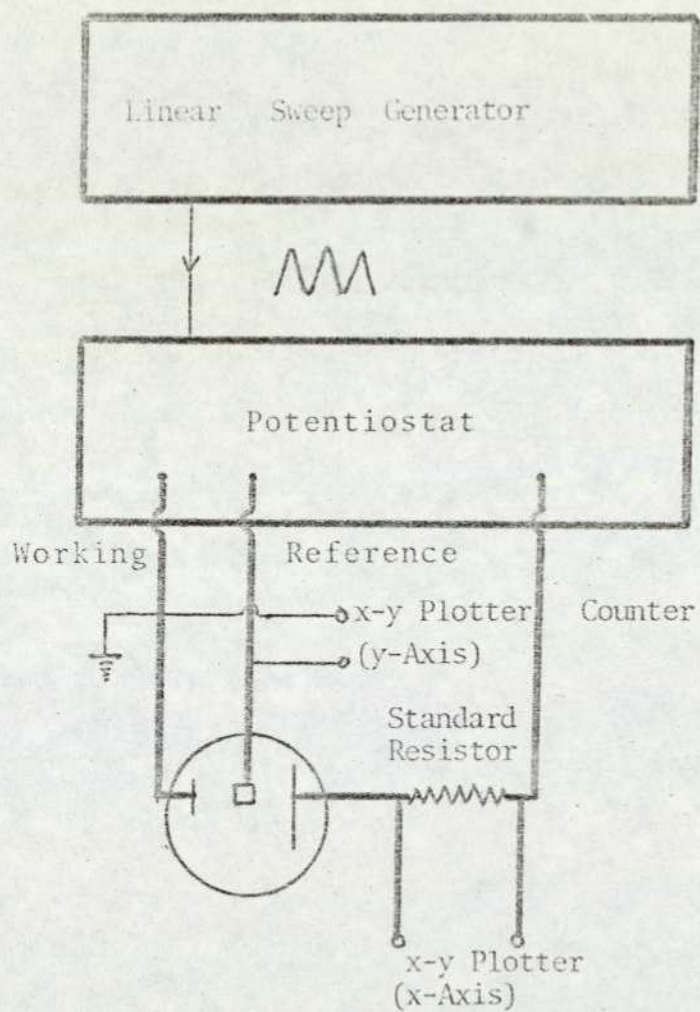


Fig. 6.3 CIRCUIT FOR LINEAR SWEEP VOLTAMMETRY

that sharp changes in oxidation state do not occur. It probably also reflects a high electrode resistance. At 1.7V, there is a sharp increase in current density, suggesting that the main process is the evolution of oxygen. On the cathodic sweep, there is a very little hysteresis and the higher oxides are only reduced below $\sim 1.6V$.

Recent work¹⁰⁸ has shown that $NiCo_2O_4$ is stable only at potentials above 0.75V vs D.H.E. and at 0.5V the $NiCo_2O_4$ spinel structure is destroyed completely and the resultant product is a mixture of nickel and cobalt oxides. Hence cyclic voltammetric studies were restricted to potentials above 0.75V.

Figure (6.5) shows the anodic polarization studies on nickel screen at 25 and 70°C. The anodic peak before oxygen evolution is the Ni^{+2}/Ni^{+3} oxidation peak i.e. the transformation of $Ni(OH)_2$ to $\beta-NiOOH$.

At 25°C the formation and reduction of $\beta-NiOOH$ on Ni took place at potentials of about 1.45V and 1.35V vs D.H.E., respectively.

From anodic polarisation studies on nickel, using cyclic voltammetry, at different temperatures (25, 40, 50, 60 and 70°C), it is clear that, independent of temperature, oxygen evolution never occurs until the higher oxide is present on the surface. This is direct evidence supporting our argument, discussed in Chapter 5, concerning the necessity of achieving the higher oxide before oxygen evolution can take

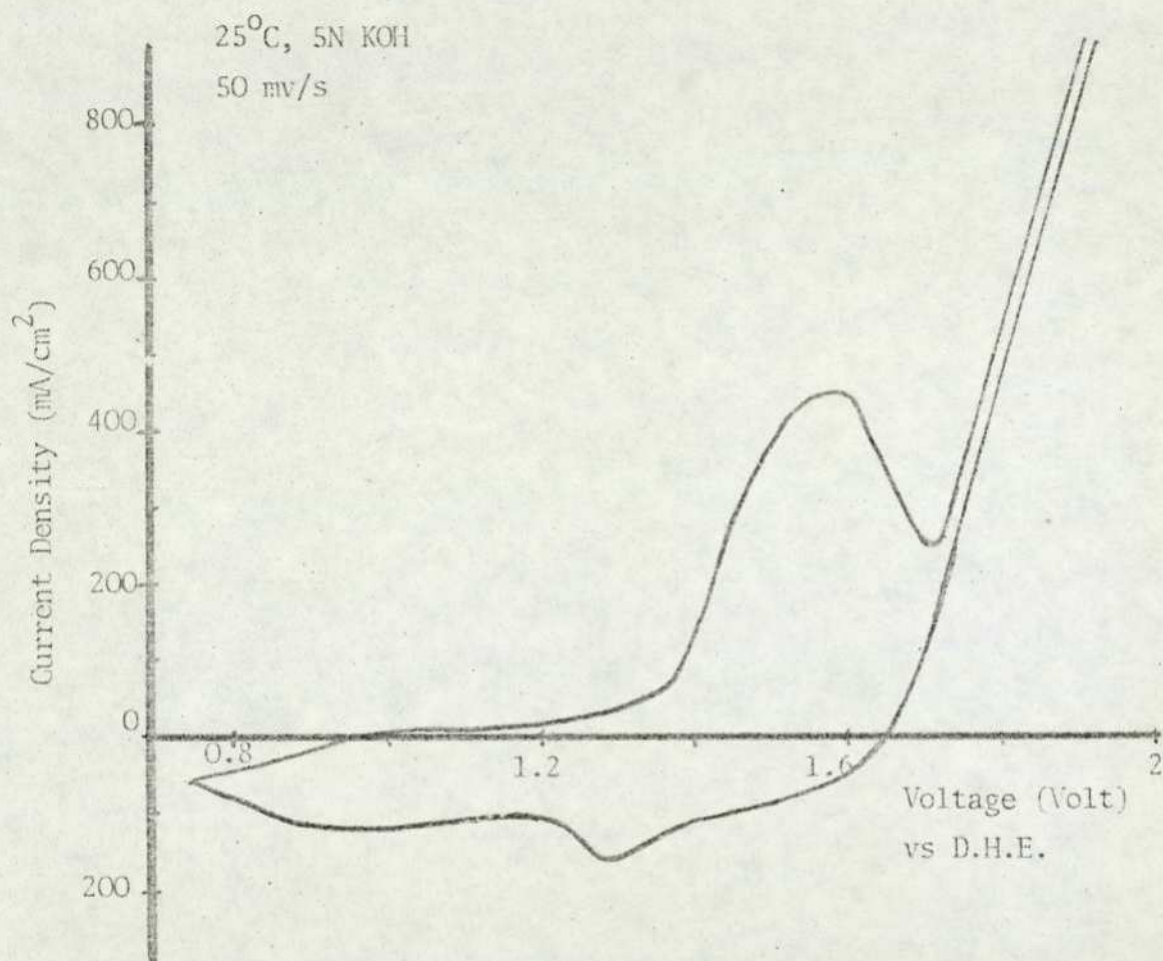


Fig. 6.4 CYCLIC VOLTAMMOGRAM FOR ANODIC POLARIZATION
REGION (ON TEFLON BONDED NiCo_2O_4 ELECTRODE)

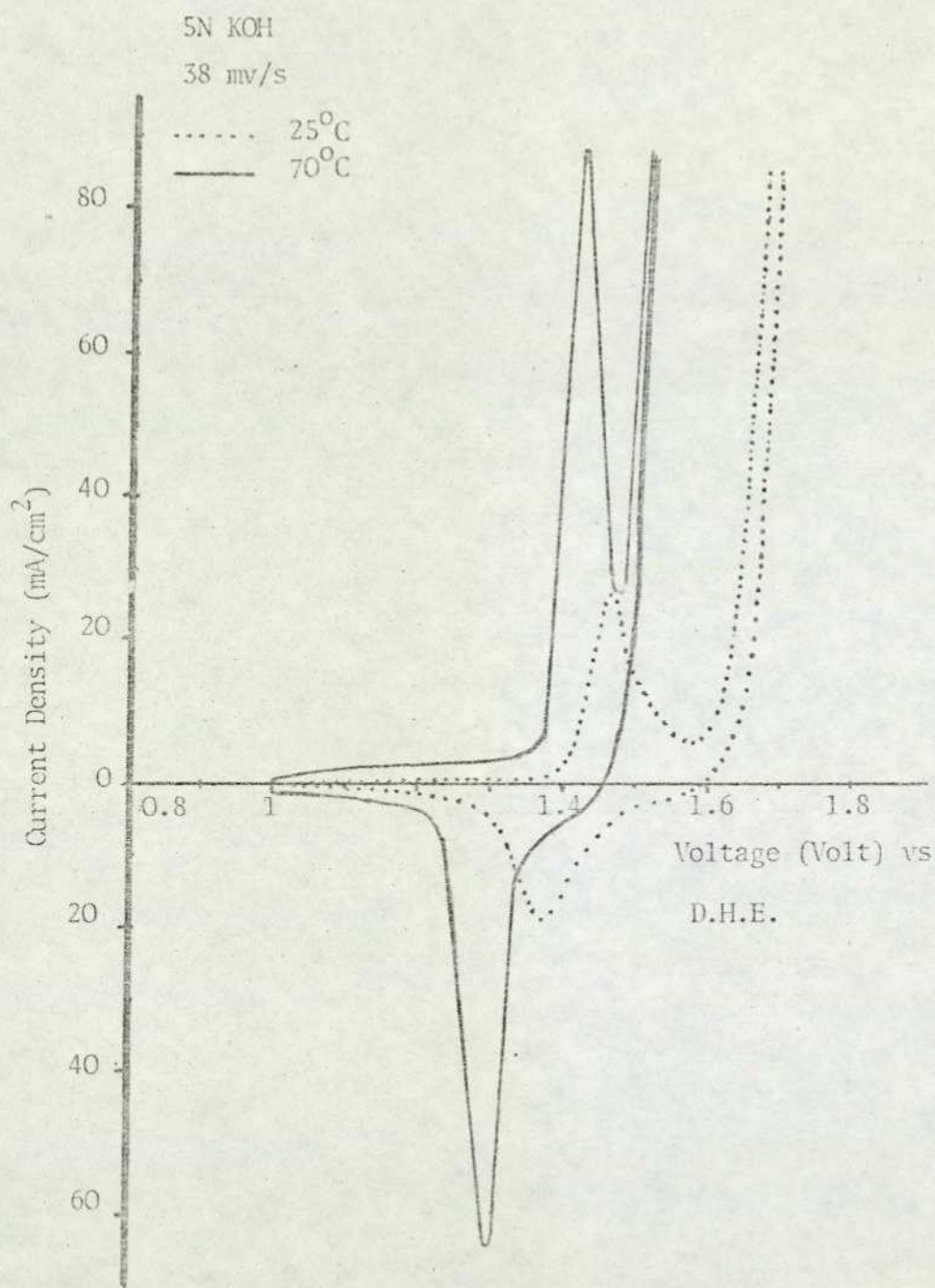


Fig. 6.5 CYCLIC VOLTAMMOGRAMS FOR ANODIC POLARIZATION
REGION (ON NICKEL SCREEN)

place. As the temperature increased the over voltage for oxygen evolution on nickel decreased.

6.4.3. Potentiostatic Pulse Technique

This technique has been discussed in detail by Hobbs, Vassie and Tseung¹⁰⁶ and used for the study of hydrogen evolution on Teflon bonded Pt black⁷⁹.

At the instant of applying an overvoltage to the electrode, the mass transfer effects are negligible, and the $i - \eta$ relationship will be governed solely by the charge transfer (neglecting ohmic and double layer charging effects). Mass transfer effects become more significant as the reaction time increases. After an infinite time the steady state conditions will be attained. The electrode behaves as a "leaky" condenser and at the instant of applying the potential a very small, but finite time, is required to charge the electrode. So it is not possible to take measurements at exactly zero time due to double layer charging effects. This time depends on the capacity of the electrode double layer and consequently, on the electrode surface area. For planar electrodes, the current transient can be predicted by mathematical analysis^{110, 111} assuming semi-infinite diffusion¹¹⁰. However, for porous electrodes, the situation is far too complex, because it is unlikely to obey the laws of semi-infinite linear diffusion¹⁰⁶.

It is more realistic to take measurements at the shortest time interval after the double layer charging is complete and

accept a small amount of concentration polarization. The experimental procedure was as follows:-

The electrode was left to equilibrate in the chosen test conditions until the open circuit voltage (o.c.v.) was steady. The potentiostat was set to this value and switched to the cell and a single potential jump applied to the electrode by means of a pulse generator (Chemical Electronics type - 01). The change in current with time was measured across a one ohm standard resistor in series with the cell, and the voltage-time trace was recorded on an x-y-t recorder (Bryans 29000 A4). The signal from the pulse generator was fed to the x-y-t recorder through a transient recorder (Data Lab. DL 901).

This procedure was repeated for varying values of potential jump. The potentiostatic transient currents were recorded after double layer charging had been completed (200 μ sec).

A schematic circuit diagram of the potentiostatic pulse system is shown in figure (6.6).

The transient currents were corrected for ohmic-drop using a galvanostatic pulse technique (at different current values). The traces were displayed on an oscilloscope (Rem scope type S01, Cawkell Ltd.) in which the storage facility was used. A schematic circuit diagram of galvanostatic pulse system is shown in figure (6.7).

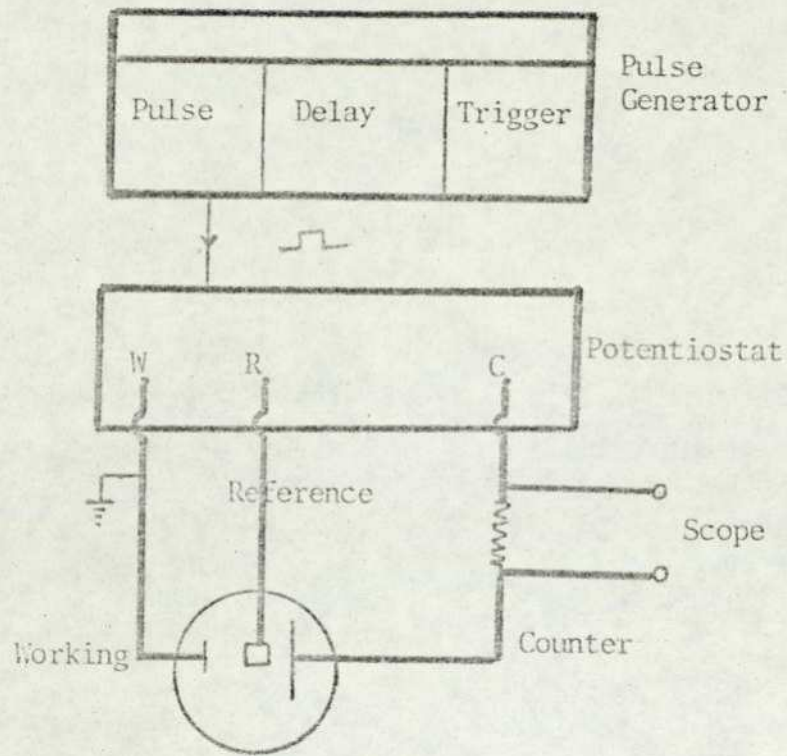


Fig. 6.6 SCHEMATIC CIRCUIT DIAGRAM FOR POTENTIOSTATIC PULSING

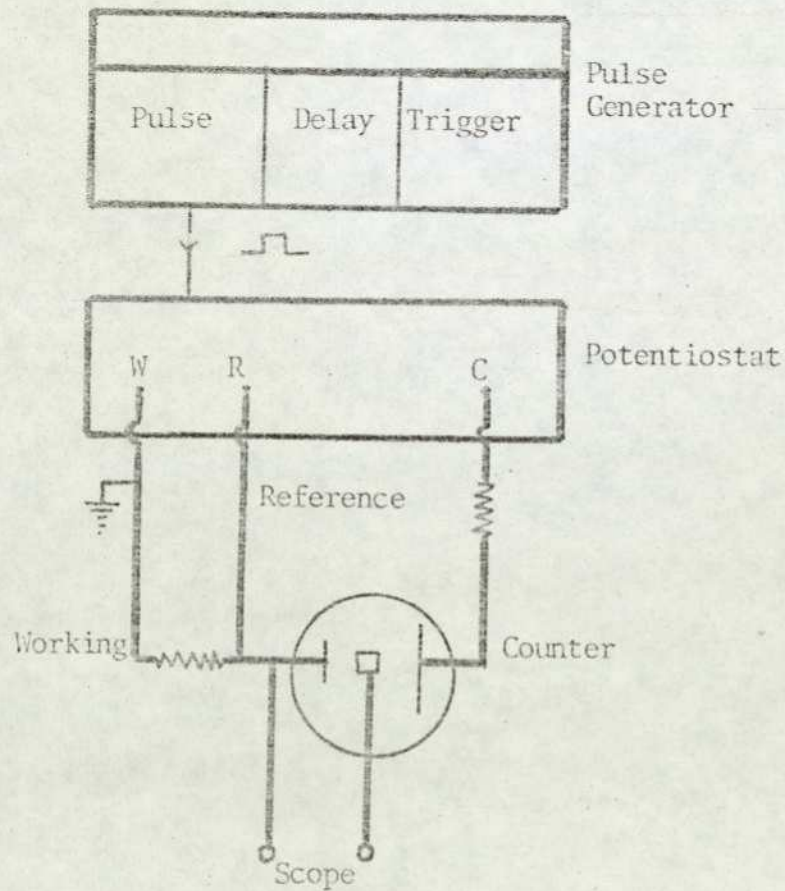


Fig. 6.7 SCHEMATIC CIRCUIT DIAGRAM FOR GALVANOSTATIC PULSING

6.4.3a. Possible Errors in the Pulse Measurements

i) The potential was measured with a digital voltmeter accurate to ± 1 mv in one volt i.e. 0.1%.

ii) An error which is less easily estimated is encountered when it is required to measure the current at very short time when the possibility exists that non-faradaic currents are present. This problem is likely to be significant for very high surface area porous electrodes, since for planar electrodes the non-faradaic double layer charging current is known to decay to zero very quickly.

6.4.3b. Measurement of Double Layer Charging Time

Cyclic voltammetric studies on Teflon bonded NiCo_2O_4 electrodes in 5N KOH (at 25°C , N_2 atmosphere) have shown that faradaic processes, such as the reduction of the nickel and cobalt oxides were at minimum at 0.8 - 0.9V vs D.H.E.

Hence, a Teflon bonded NiCo_2O_4 electrode was held at 0.8V vs D.H.E. in pre-electrolyzed 5N KOH in N_2 atmosphere and anodic pulses (50-100 mv) were applied (using pulse generator). A typical voltage time trace of the double layer charging process is shown in figure (6.8). The sharp spike is due to the charging of the double layer, whereas the minimum and the continuation of the trace to longer times could be attributed to a) an oscillatory effect in the potentiostat pulse generator and the cell circuit and b) a pseudo-capacity effect.

The double layer charging time (t_c) can be measured as

shown in figure (6.8). The effect of varying the applied pulse amplitude from 50 to 100 mv had the effect of doubling the value of the double layer charging current (Table 6.2). However, the double layer charging time remains the same (200 μ s).

$$t_c = C_D R$$

where, t_c = time constant

C_D = double layer capacity

R = electrolyte resistance between the Luggin Tip and the working electrode.

Table (6.2)

Electrode	t_c μ s	I_p mA/cm^2	Pulse amplitude mv
Teflon bonded NiCo_2O_4 Electrode	200	62	50
Catalyst loading = 14 mg/cm^2 B.E.T. surface area = 69.78 M^2/g	200	125	100

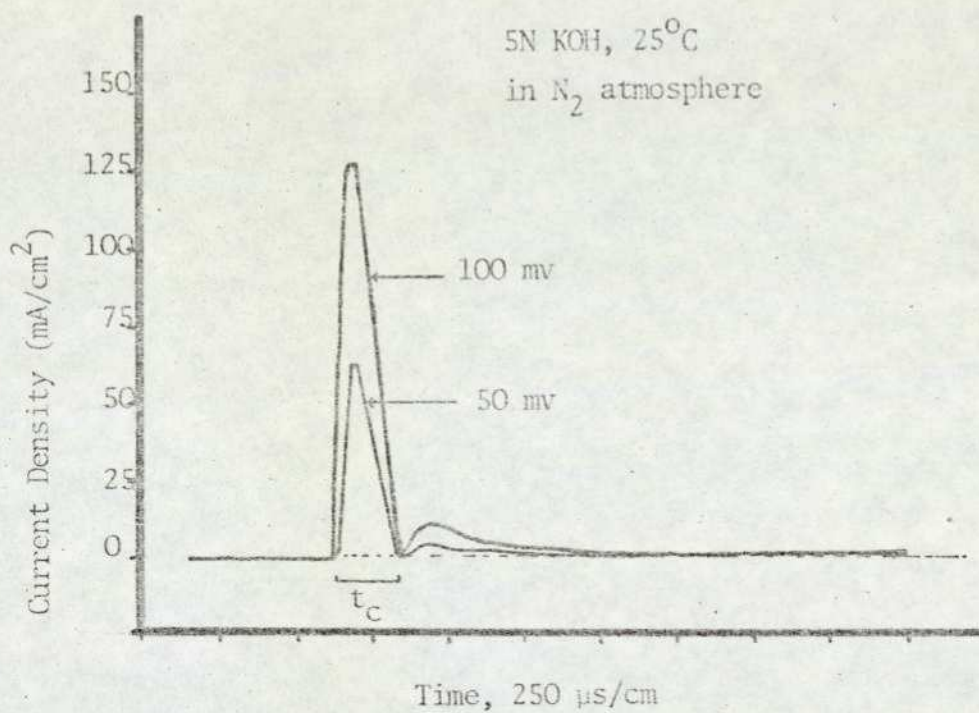


Fig. 6.8 DOUBLE LAYER CHARGING TRACE OF TEFLON
BONDED NiCo_2O_4 ELECTRODE

6.4.4. Effectiveness Factor

The effectiveness factor, or degree of utilization is defined⁷⁹ as the ratio of the actual reaction rate to that which could occur if all the surface through out the inside of the catalyst particle were exposed to the reactants at the same concentration and temperature as that existing at the outside surface of the particle.

Effectiveness factor could be determined experimentally as follows:

At a given overvoltage the current density is determined

- a) after a time, t_1 , when the value is steady and
- b) after a time, t_2 , when double layer charging is complete.

The ratio of the current density at t_1 to that at t_2 gives the effectiveness factor.

Figure (6.9) compares the potentiostatic pulse (A and B) and the steady state (C) current voltage curves for oxygen evolution on Teflon bonded NiCo_2O_4 electrode, at 25°C , 5N KOH. The electrode was preanodized at 2V vs D.H.E. for one hour in each experiment (A, B, C). The transient current in (A) (in which pulsing started from the o.c.v. i.e. 1.2V vs D.H.E.) is very high in comparison to that of the steady state (C).

At 1.5V vs D.H.E., the transient current in (A) reached about 1000 mA/cm^2 , whereas at the same potential under steady state polarization the current is negligible.

Moreover, the transient current at 1.68V gives 2150 mA/cm^2 as compared to $\sim 500 \text{ mA/cm}^2$ for the steady state measurement.

Thus, the utilization factor is 0.23.

Earlier studies by Tseung and Vassie⁷⁹ showed that the difference between the potentiostatic transient and steady state results for H_2 evolution on Teflon bonded Pt black electrodes was only about 50% at 500 mA/cm^2 .

The high utilization factor was due to the escape of gas with little expulsion of electrolyte from the interior of the catalyst pores on the Teflon bonded electrode.

Thus, if the only difference between the steady state and transient performance was due to mass transfer effects, a similar utilization factor of 0.5 for the evolution of oxygen on Teflon bonded electrodes would be expected.

The very high transient performance obtained on oxygen evolution in (A) suggests that a considerable portion of the current measured under potentiostatic pulse conditions is associated with the formation of higher oxides.

Therefore, it is necessary to form the higher oxides before a realistic mechanistic study of the oxygen evolution process can be undertaken.

Experiment (B) shows the significance of the starting potential (i.e. from which the pulsing starts). In this experiment (B) the Teflon bonded $NiCo_2O_4$ electrode was anodized at 2V

for one hour, then the potentiostatic pulse was applied anodically from 1.5V vs D.H.E.

The potential of 1.5V from which the pulse applied was chosen, because the iR -corrected potentials of the linear sweep results (shown in figure 6.4) indicate that the higher oxides are not reduced above this potential (1.5V).

The utilization factor obtained from the current density of experiments (B) and (C) at 1.7V was 0.47, which is very close to that obtained for hydrogen evolution on Teflon bonded Pt black electrode (~ 0.5). This suggests that the results of experiment (B) are more accurate than those of experiment (A) and that the anodizing of the electrode at high potentials to form the higher oxides is insufficient unless the electrode potential is maintained above that at which the higher oxides are likely to be reduced.

It is interesting to note that the steady state performances (C) at high current densities (above $1A/cm^2$) are closer to the transient performance figure (6.9). This could be attributed to the stirring effect of the high rate of gas evolution.

6.4.5. Tafel Slope and the Potentiostatic Pulse Measurements

V vs $\log i$ plots for experiments A, B and C are shown in figures (6.10), (6.11) and 6.1), respectively. Tafel slopes and the exchange current densities obtained from these experiments at 25°C are shown in Table (6.3).

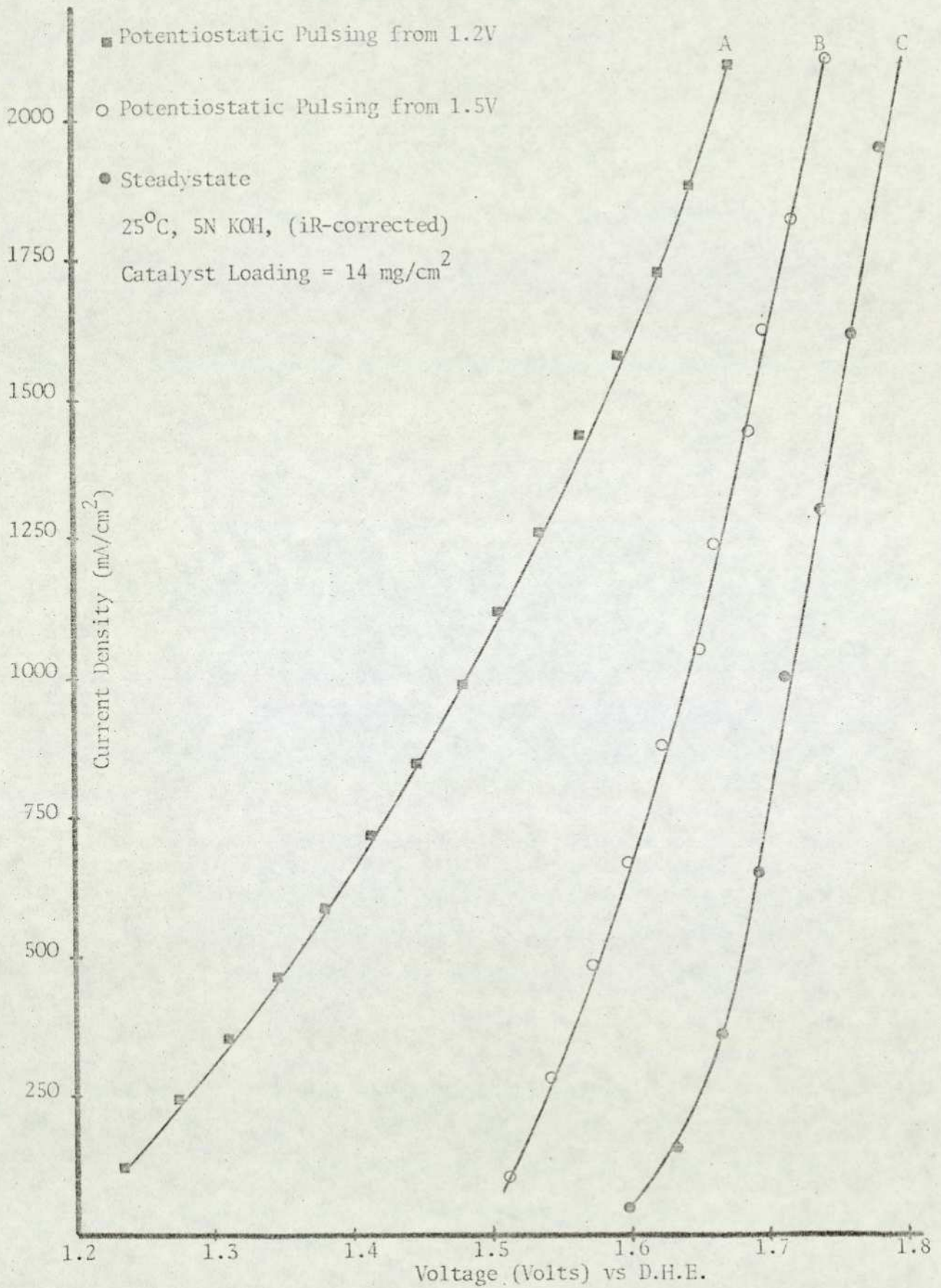


Fig. 6.9 STEADYSTATE AND POTENTIOSTATIC PULSE MEASUREMENTS FOR
 OXYGEN EVOLUTION ON PRE-ANODIZED TEFLON-BONDED NiCo_2O_4
 ELECTRODE

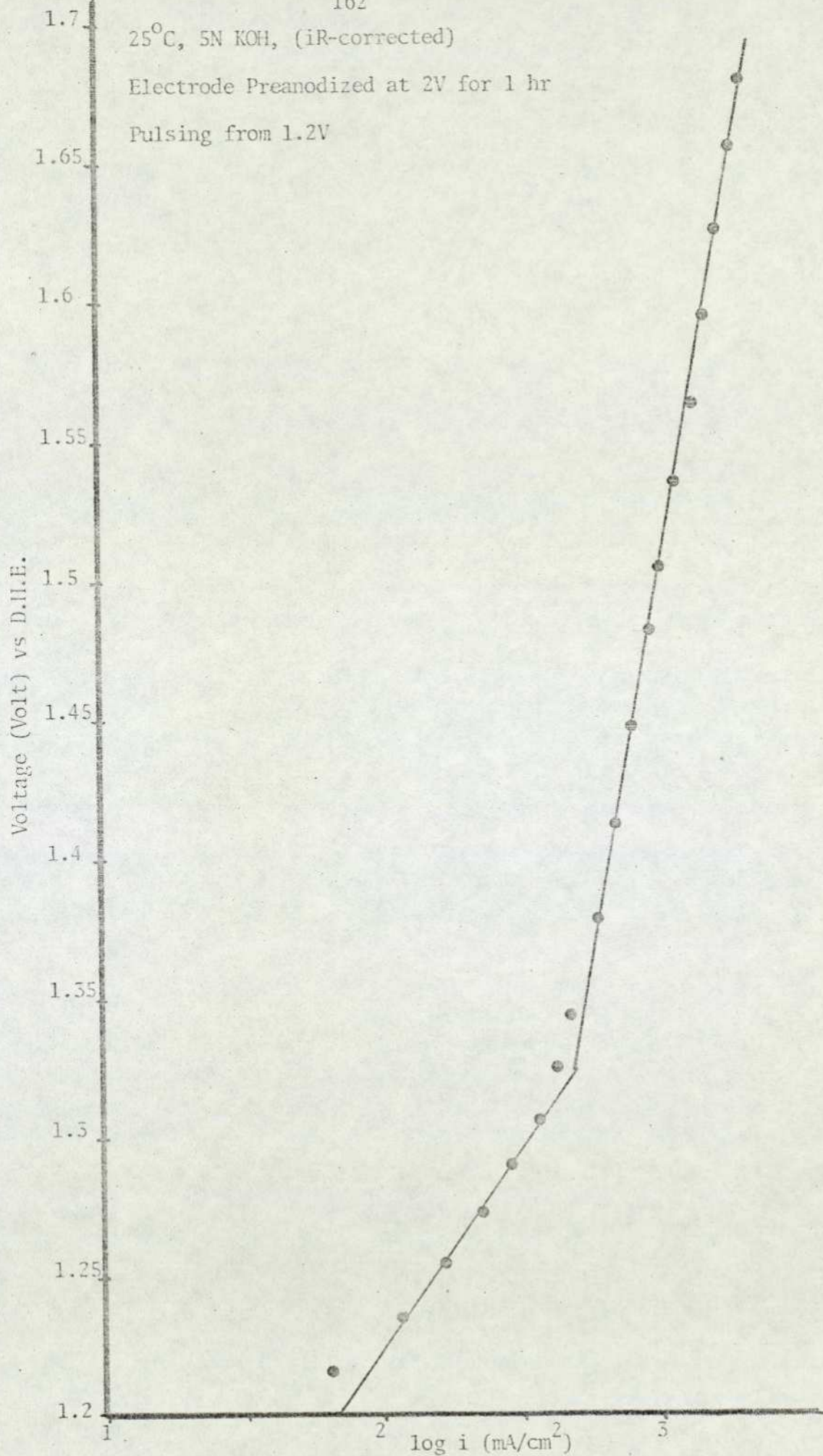


Fig. 6.10 POTENTIOSTATIC PULSE MEASUREMENTS FOR OXYGEN EVOLUTION
ON PRE-ANODIZED TEFLON BONDED NiCo_2O_4 ELECTRODE

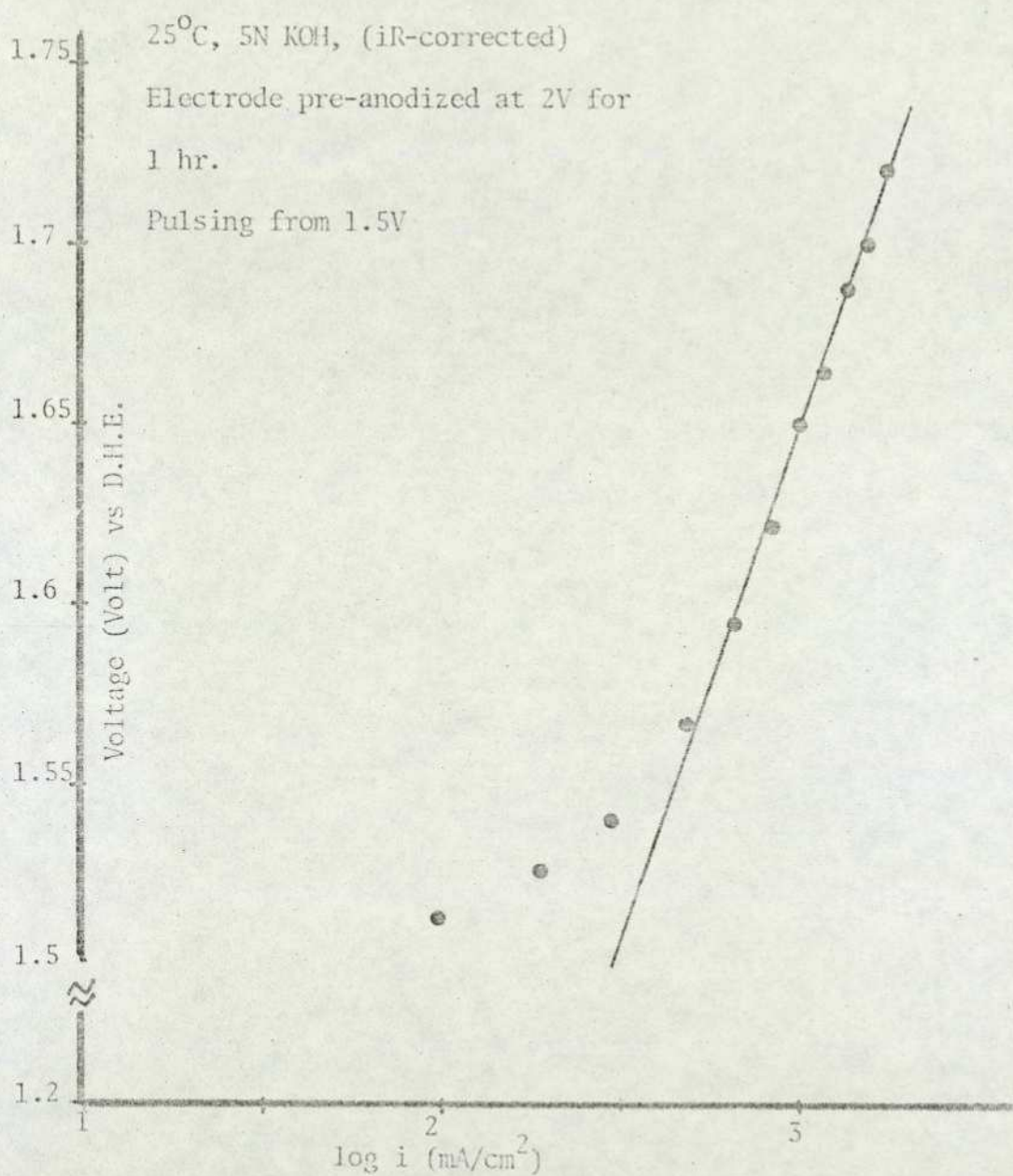


Fig. 6.11 POTENTIOSTATIC PULSE MEASUREMENTS FOR OXYGEN
 EVOLUTION ON PRE-ANODIZED TEFLON BONDED NiCo_2O_4
 ELECTRODE.

Table (6.3)

Experiment	i_o (A/cm ² of B.E.T. surface area) x 10 ⁷		Tafel Slope V/decade	
	low η	high η	low η	high η
A	67	309	0.06	0.23
B	-	29	-	0.12
C	4.7×10^{-9}	10	0.03	0.1

The exchange current densities for the experiments A, B and C are expressed in terms of Amper per unit of B.E.T. surface area (cm²). It was not possible to use oxygen stripping technique¹¹² to measure the electrochemical surface area of NiCo₂O₄ electrode, due to the instability of NiCo₂O₄ in the oxygen reduction region^{108, 29}. Identical experiments to (B) were carried out on different Teflon bonded NiCo₂O₄ electrodes to estimate the variation of Tafel slope value.

Tafel slope values obtained were similar to that of experiment (B), in contrast to the steady state experiments, where Tafel slope values varied significantly between 0.06 and 0.1 V/decade for different Teflon bonded NiCo₂O₄ electrodes under similar conditions.

Analyzing the anodic and the cathodic traces of the potentiostatic pulse, revealed that, in the case of experiment A (where pulsing started from the o.c.v.), the cathodic current of the cathodic pulse was very high indicating a reduction of large amount of the higher oxides formed during the anodic

pulse. This is shown in figure (6.12).

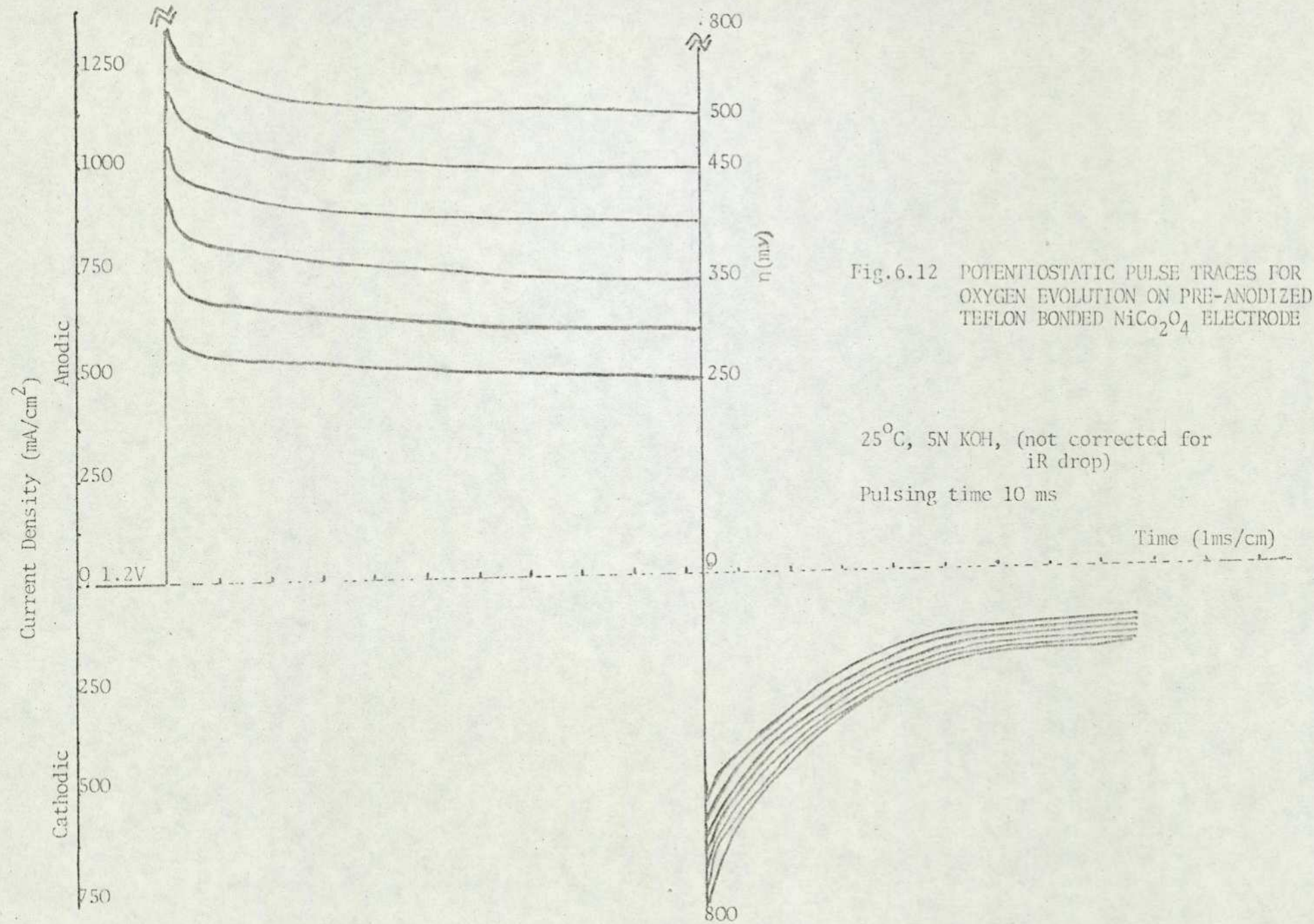
Changing the potential from which the pulsing was applied, towards more anodic potential in 25 mV increments revealed that the corresponding reduction current of the cathodic pulse become smaller and smaller until the potential was 1.5V.

Above this potential the reduction currents were the same ($\sim 50 \text{ mA/cm}^2$) (figure 6.13).

This indicated that the higher oxides were not reduced above 1.5V.

The small oxide reduction current ($\sim 50 \text{ mA/cm}^2$) compared to the very high anodic current ($\sim 2000 \text{ mA/cm}^2$) at 500mV over voltage, suggesting that the anodic current in experiment (B) is mainly due to the oxygen evolution, which must be the predominant reaction above 1.5V. Unlike experiment A where the anodic current is a combination of currents for higher oxide formation and oxygen evolution.

Different pulsing times were used (10 ms, 30 ms, 100 ms, 1s) for each potentiostatic pulse experiment (similar to B) and under similar conditions. No change in the anodic pulse performance was observed, indicating that the pulsing time of 10 ms was sufficient to complete the oxygen evolution reaction. 10 ms was chosen because, longer pulsing time (i.e. 30 and 100 ms) resulted in the formation of a large amount of oxygen bubbles, which adhered to the electrode surface, limiting the advantages of the pulse technique.



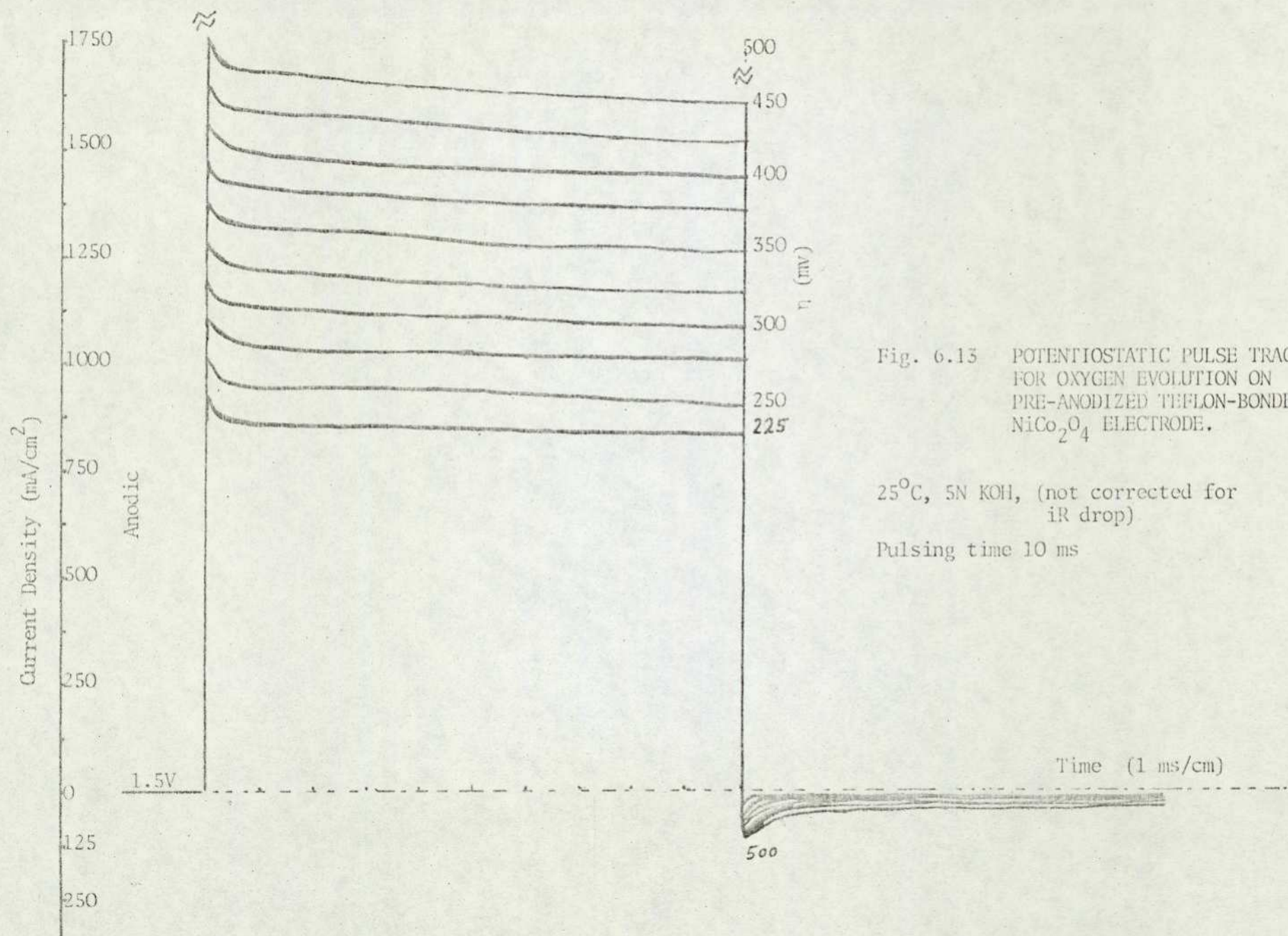


Fig. 6.13 POTENTIOSTATIC PULSE TRACES
FOR OXYGEN EVOLUTION ON
PRE-ANODIZED TEFLON-BONDED
 NiCo_2O_4 ELECTRODE.

25°C , 5N KOH, (not corrected for
iR drop)

Pulsing time 10 ms

CHAPTER SEVEN

AN INTEGRATED ELECTROCHEMICAL-CHEMICAL METHOD
FOR THE EXTRACTION OF OXYGEN FROM AIR

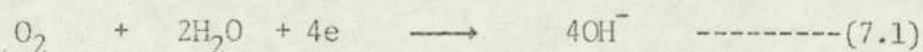
7.1. INTRODUCTION

Portable oxygen generators are finding increasing applications in field hospitals, village clinics in developing countries, welding and high altitude fighter aircraft. There are two basic types of oxygen generators: (a) chemical generators, which use expensive chemicals. (b) electrochemical generators, which either electrolyse water or extract oxygen from the air by using an oxygen reduction cathode coupled to an oxygen evolution anode^{113, 114}.

This chapter gives some preliminary results on an integrated electrochemical-chemical method which shows promise of significantly reducing the capital as well as the running costs of portable oxygen generators¹¹⁵.

7.2. OXYGEN GENERATION BY ELECTROCHEMICAL METHODS

The most common method is to electrolyse water to produce H_2 and O_2 . The theoretical voltage for electrolysing water at $25^\circ C$ is 1.23V but the high overvoltage at the anode and the cathode increases the operating voltage to about 2.2V at 100 mA/cm^2 . Moreover, the production of H_2 as the by-product, apart from increasing the power consumption, is a potential hazard in situations where portable oxygen generators are used. A more efficient method is to use a Teflon bonded Pt black fuel cell cathode to reduce the oxygen in the ambient air to form OH^- :

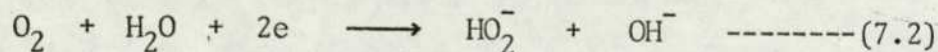


The OH^- diffuses through a suitable membrane, such as woven asbestos or glass fibre mat to an anode at which oxygen is liberated. At 25°C , the performance of a Teflon bonded Pt black air cathode in 5N KOH at 100 mA/cm^2 is 0.8V vs RHE (Reversible Hydrogen Electrode). The performance of a similar electrode when polarized anodically gives 100 mA/cm^2 at 1.9V vs RHE. Thus the working voltage of the cell described above, taking into account of the unavoidable iR losses, would be approximately 1.3 - 1.4V, significantly lower than the 2.2V (at 25°C) for electrolysis cells.

Though this type of oxygen extractor is an improvement over traditional water electrolysis cell for the production of oxygen, their capital and running costs are still relatively high and their use is limited to specialized applications.

7.3. AN INTEGRATED ELECTROCHEMICAL-CHEMICAL APPROACH TO THE PROBLEM

Berl⁷ showed that the reduction of oxygen on graphite or carbon is a two electron process which goes through the perhydroxyl ion route:



This means that when such electrodes are used in a fuel cell, it is not as efficient as cathodes which directly reduce oxygen to hydroxyl ions via a four electron process. Therefore, it is usual to add peroxide decomposition catalysts⁶¹ to the carbon cathode, so that the HO_2^- produced could be

decomposed, thus yielding O_2 for recycling, leading to higher efficiency³⁵.

On the other hand, if such electrodes were to be used in an oxygen extraction cell, the fact that the reduction of oxygen on carbon surfaces proceeded via two electron step would be beneficial, provided the HO_2^- was chemically decomposed and collected in the anode compartment. In this way, the number of Coulombs required for the oxygen extraction process will be halved, leading to significant reduction in power consumption.

7.4. EXPERIMENTAL

7.4.1. Selection of Materials

High surface area graphite powders ($\sim 500 \text{ M}^2/\text{g}$) prepared by vacuum grinding in a vibrating ball mill have been shown, (Chapter 3), to possess very high activity for oxygen reduction in alkaline solution. Graphite is thus suitable as the cathode catalyst. Fuel cell grade Pt black ($\sim 10 \text{ M}^2/\text{g}$) was also used as a cathode catalyst in some experiments for the reasons given in section 7.5.4. $CoFe_2O_4$ and $NiCo_2O_4$ have been evaluated (Chapter 4) as H_2O_2 decomposition catalysts, and the results indicated that these materials possess high activity and stability under the conditions used. $NiCo_2O_4$ was exclusively used as the anode catalyst, since it has been shown (Chapter 5) to be the most active and stable material for oxygen evolution.

On cost, activity and stability criteria the above materials

are the suitable catalysts for the proposed oxygen extractor¹¹⁵.

7.4.2. Preparation of Electrodes and Experimental Methods

The two types of electrodes used were of the porous electrode and the Teflon bonded electrode varieties described in Sections 5.4.2. and 2.3.1. respectively.

Figure (7.1) shows a schematic diagram of the oxygen extraction cell, which can be seen to consist of three glass compartments in all 5N KOH was used as the electrolyte.

In the first compartment a Teflon bonded cathode was used in the floating mode, the tip of the Luggin Capillary was placed about 1 mm below the floating electrode. A dynamic hydrogen reference electrode (D.H.E.) was used to monitor the potential of the working electrode. A piece of Teflon-bonded CoFe_2O_4 , supported on nickel screen or a NiCo_2O_4 coated screen, in the second compartment, served as the peroxide decomposition assembly. In the third compartment, a Teflon-bonded NiCo_2O_4 electrode was used as the anode. Potentiostatic or galvanostatic control was provided by a Chemical Electronics Potentiostat (TR 40-3A). A gas burette attached to the top of the second and the third compartment was used to measure the amount of oxygen produced.

7.5. RESULTS AND DISCUSSION

7.5.1. Steady State Performance

From figure (3.3) (Chapter 3), it can be seen that the performance of the Teflon bonded graphite electrode is only marginally less than that of a Teflon bonded Pt black

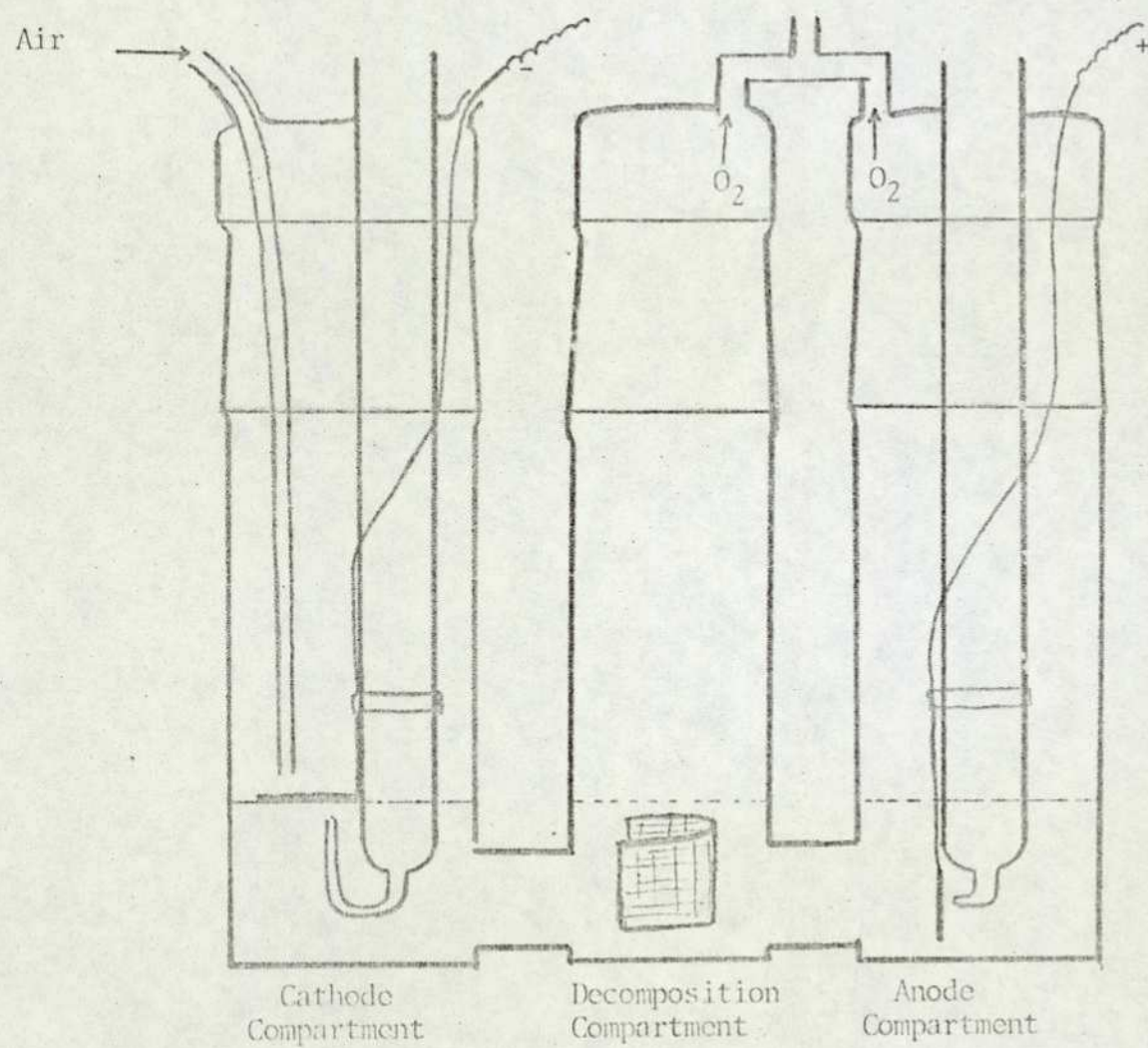


Fig. 7.1 SCHEMATIC DIAGRAM OF THE OXYGEN EXTRACTION CELL

electrode for the reduction of oxygen in 5N KOH, at 25°C in air.

Figure (7.2) compares the anodic performance of a Teflon bonded Pt black electrode and a Teflon bonded NiCo_2O_4 electrode in 5N KOH, 25°C. As expected NiCo_2O_4 is significantly more active than Pt black⁷⁴, since the redox potential of the lower NiCo_2O_4 /higher NiCo_2O_4 couple (~ 1.45 V) is far lower than the PtO/PtO_2 couple (~ 1.70 V).

7.5.2. Hydrogen Peroxide Production

The experimental procedure and the results obtained for the hydrogen peroxide production, (Table 3.1), are presented in (Chapter 3 Section 3.6). Table (3.1) gives the amount of HO_2^- produced after the passage of a constant current for one hour. The results confirm the Berl mechanism⁷, that is the reduction of oxygen on graphite surfaces proceeds via a two electron process.

7.5.3. Hydrogen Peroxide Decomposition

The study of the kinetics of hydrogen peroxide decomposition on NiCo_2O_4 and CoFe_2O_4 have been described in Chapter 4. If any of these two catalyst is to be used in an actual oxygen extraction cell, it must be either fired on to nickel screens or bonded with Teflon. Table (7.1) lists the first order rate constant ($K_{f,m}$) values of NiCo_2O_4 powder (prepared by freeze drying, B.E.T. surface area $69 \text{ M}^2/\text{g}$), Teflon bonded NiCo_2O_4 electrode, porous NiCo_2O_4 on nickel

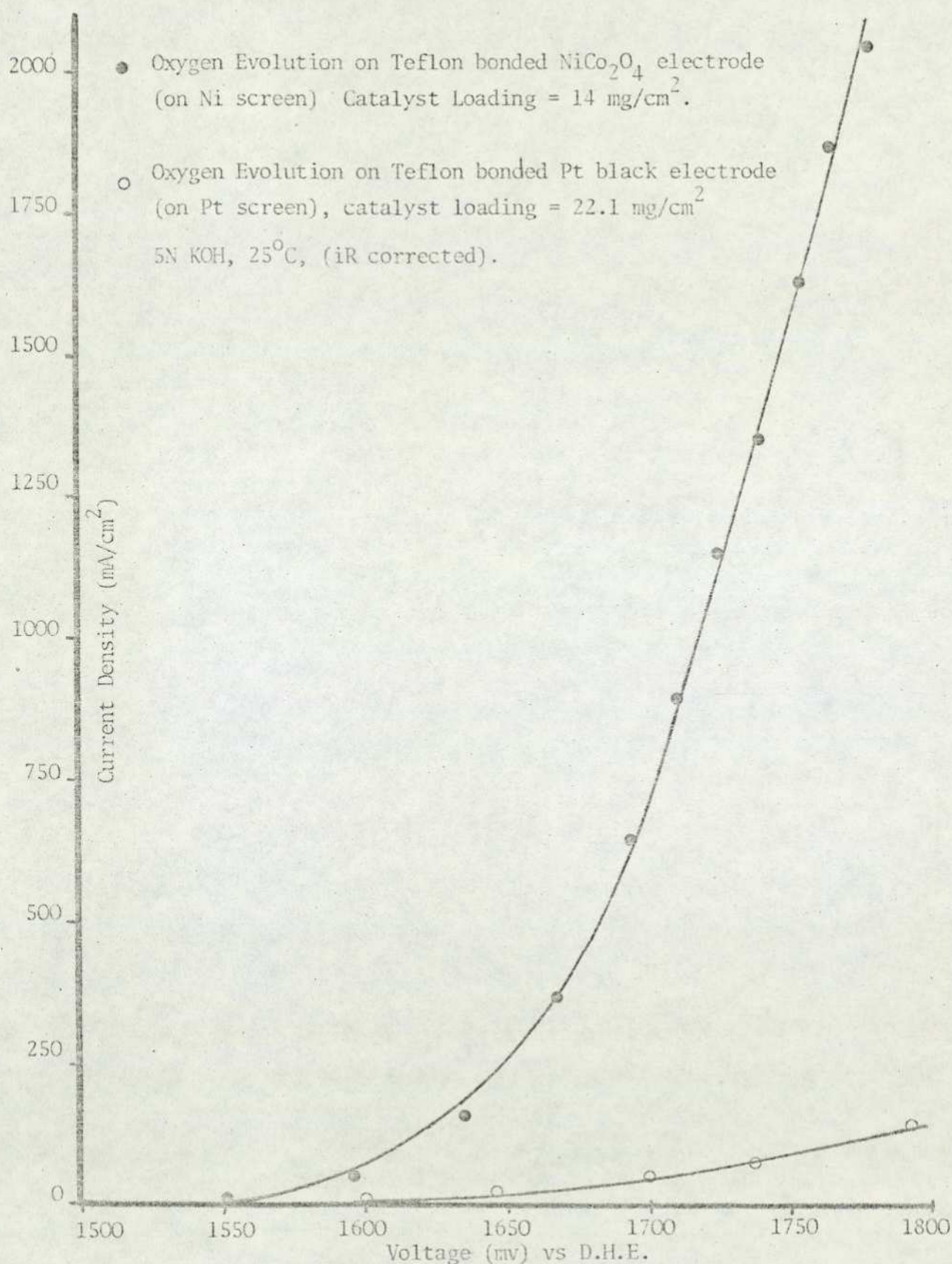


Fig. 7.2 STEADY STATE MEASUREMENTS OF OXYGEN EVOLUTION ON TEFLON BONDED Pt Black and NiCo_2O_4 ELECTRODES

screen (prepared by thermal decomposition of cobalt and nickel nitrates on nickel screen at 400°C for 10 hours) as well as CoFe_2O_4 powder (prepared by hydroxide co-precipitation, B.E.T. surface area 120 M^2/g).

Table (7.1)

Catalyst	$K_{f,m} \times 10^2$ $\text{sec}^{-1} \text{g}^{-1}$	$K_{I,m} \times 10^4$ mole O_2 $\text{sec}^{-1} \text{g}^{-1}$	Temp. $^{\circ}\text{C}$
1- NiCo_2O_4 powder (freeze drying)	4.44	1.08	25
	6.30	1.52	30
	7.40	1.95	35
	10.24	2.51	40
2- 4 cm^2 Teflon bonded NiCo_2O_4 electrode (on Ni screen)	0.24	-	25
3- 4 cm^2 porous NiCo_2O_4 electrode (thermal decomposition of nitrates on Ni screen)	4.89	-	25
4- CoFe_2O_4 powder (hydroxide co-precipitation)	18.28	4.57	25

The results presented in Table (7.1) suggest that CoFe_2O_4 is more active than NiCo_2O_4 . However after correcting for the difference in B.E.T. surface areas, it is apparent that their

performances are similar. It is interesting to note that the performance of porous NiCo_2O_4 electrodes for H_2O_2 decomposition is double that of Teflon bonded NiCo_2O_4 electrodes. This is not surprising since the oxygen produced inside the pores of the electrode pushes the electrolyte out of the pores and most of the catalytic reaction therefore occurs on the electrode surface. Approximately 50% of the Teflon bonded electrode surface is composed of Teflon particles and hence its activity for H_2O_2 decomposition would be expected to be lower. In addition the presence of hydrophobic Teflon particles reduces the rate of diffusion of the electrolytes. Therefore, porous NiCo_2O_4 on nickel screen was chosen for the H_2O_2 decomposition assembly.

7.5.4. Oxygen Extraction from Air

Table 7.2 shows that the best results were obtained when graphite was used as the cathode and a piece of NiCo_2O_4 supported on nickel screen was placed between the cathode and the anode (NiCo_2O_4) (Cells A & B). When no separate H_2O_2 decomposing assembly was used (Cell C), the power consumption was similar to a cell which used platinum black as the cathode (cell D). Even though the cathodic reduction of oxygen on graphite proceeded via a two electron process with the formation of HO_2^- , the peroxide ions which had diffused to the anode compartment was not fully decomposed; when the power was switched off in cell C, gassing continued slowly for a long time on the Teflon-bonded NiCo_2O_4 surface which is not as

active as the thermally decomposed NiCo_2O_4 used in the H_2O_2 decomposition assembly. This suggests that when the anode is functioning electrochemically, the oxygen bubbles evolved effectively blanketed a large part of the surface, making it unavailable for the HO_2^- decomposition reaction (cell C). On the other hand, when a H_2O_2 decomposition assembly was placed between the platinum cathode and the NiCo_2O_4 anode, there was no improvement. This is not surprising, since most of the HO_2^- produced at the platinum cathode surface would be decomposed, yielding O_2 for further cathodic reduction³⁵, (cell E). It is interesting to note that in all cases, the power consumption is significantly lower than a conventional water electrolyser (cell F). Moreover, cell B is significantly better than the results obtained by Wynveen and Montgomery¹¹⁴ (cell G), which used platinum black anode and cathode.

It is important to note that not all the HO_2^- produced by the graphite cathode was utilized in the experimental cell. This was mainly caused by the large separation between the cathode and the anode and not due to differences in the diffusion coefficients of HO_2^- ($\sim 9.3 \times 10^{-6} \text{ cm}^2/\text{s}$)¹¹⁶ and OH^- ($\sim 0.97 \times 10^{-5} \text{ cm}^2/\text{s}$)¹¹⁷. This can be remedied by decreasing the cathode/anode gap in future designs.

Though the basic concepts have been experimentally verified, it is necessary to undertake the more detailed studies suggested in Chapter 8 before a prototype oxygen extractor can be built. However, the integrated electrochemical-

Table (7.2)

Extraction of oxygen from air (400 mA passed through cell for 30 min)

Cell Temp. No.	Cathode	H ₂ O ₂ decomposer	Anode	Theoretical From H ₂ O ₂ decomposition ml (NTP)	Theoretical From O ₂ evolution ml (NTP)	Experimental ml (NTP)	Voltage iR free volt	Power Consumption KW hr/1000 litres of O ₂
A	25°C 4 cm ² Teflon bonded graphite on nickel screen	2 x 10cm ² NiCo ₂ O ₄ on nickel screen	4 cm ² Teflon bonded NiCo ₂ O ₄ on nickel screen (O ₂ evolving)	45.60	45.60	78.03±3.18(5)	1.34	3.46
B	40°C "	"	"	"	"	77.04±3.02(4)	1.04	2.69
C	25°C "	none	"	"	"	49.82±1.11(3)	1.34	5.41
D	25°C 4 cm ² Teflon bonded Plat- inum black on Pt screen (O ₂ reduction)	none	"	N/A	45.60	46.96±0.68(5)	1.26	5.36
E	25°C "	2 x 10cm ² NiCo ₂ O ₄ on nickel screen	"	N/A	45.60	47.77	1.26	5.26
F	25°C 4 cm ² Teflon Pt black on Pt screen (H ₂ evolving)		"	N/A	"	45.80	2.09	9.12
G	40°C Teflon bonded Pt electrode (O ₂ reduction)		Teflon bonded Pt electrode (O ₂ evolving)	N/A	45.60	45.60	1.0	4.38

chemical method for oxygen extraction from ambient air¹¹⁵, described above, has significant advantages over existing methods of oxygen production, such as, electrolysis and oxygen extractors^{113, 114}. These advantages could be summarised as follows:

- a) Low power consumption (2.92 Kwhr/1000 litre oxygen).
- b) Low capital cost, inexpensive components and catalysts required.
- c) No explosion hazards.
- d) Capable of continuous operation at variable loads and producing gas stream of variable oxygen content.

The brief review presented in Chapter (1) has outlined the importance and the potential market of oxygen gas in many industrial, medical and scientific areas.

The desirability of on-site oxygen production by means of a portable unit under certain circumstances was also mentioned.

Since the present oxygen extractor¹¹⁵ is based on inexpensive catalysts and standard Teflon bonded electrode structures, it may be possible to replace the present bottled oxygen (see Appendix B).

7.6. A POSSIBLE DESIGN FOR THE PRESENT OXYGEN EXTRACTION CELL

The cell designed by WynVeen and Montgomery¹¹⁴ could be adopted in the manner of figure (7.3) to suit the oxygen extractor presented in this work. A suitable membrane could be placed adjacent to the cathode, this would serve to separate

the cathode from both the anode and the H_2O_2 decomposition assembly (see figure 7.3).

In designing a practical cell the following factors should be considered. The air supplied to the cathode must be passed through a CO_2 absorber to remove the traces of CO_2 in air in order to prevent the carbonation of the electrolyte (KOH). To prevent the cell from desiccating, it is necessary for the net transfer of water into and out of the cell to be zero. This could be achieved by bubbling the air through a fixed temperature water bath, so the partial pressure of the water vapour in the air entering the cell would be equal to that over the electrolyte at the cell operating temperature. Control of the partial pressure of oxygen in the outlet gas could be achieved by mixing the oxygen stream with the exhaust gas stream from the cathode compartment. This facility is essential in some medical applications. The removal of KOH entrained in the oxygen gas stream is also essential.

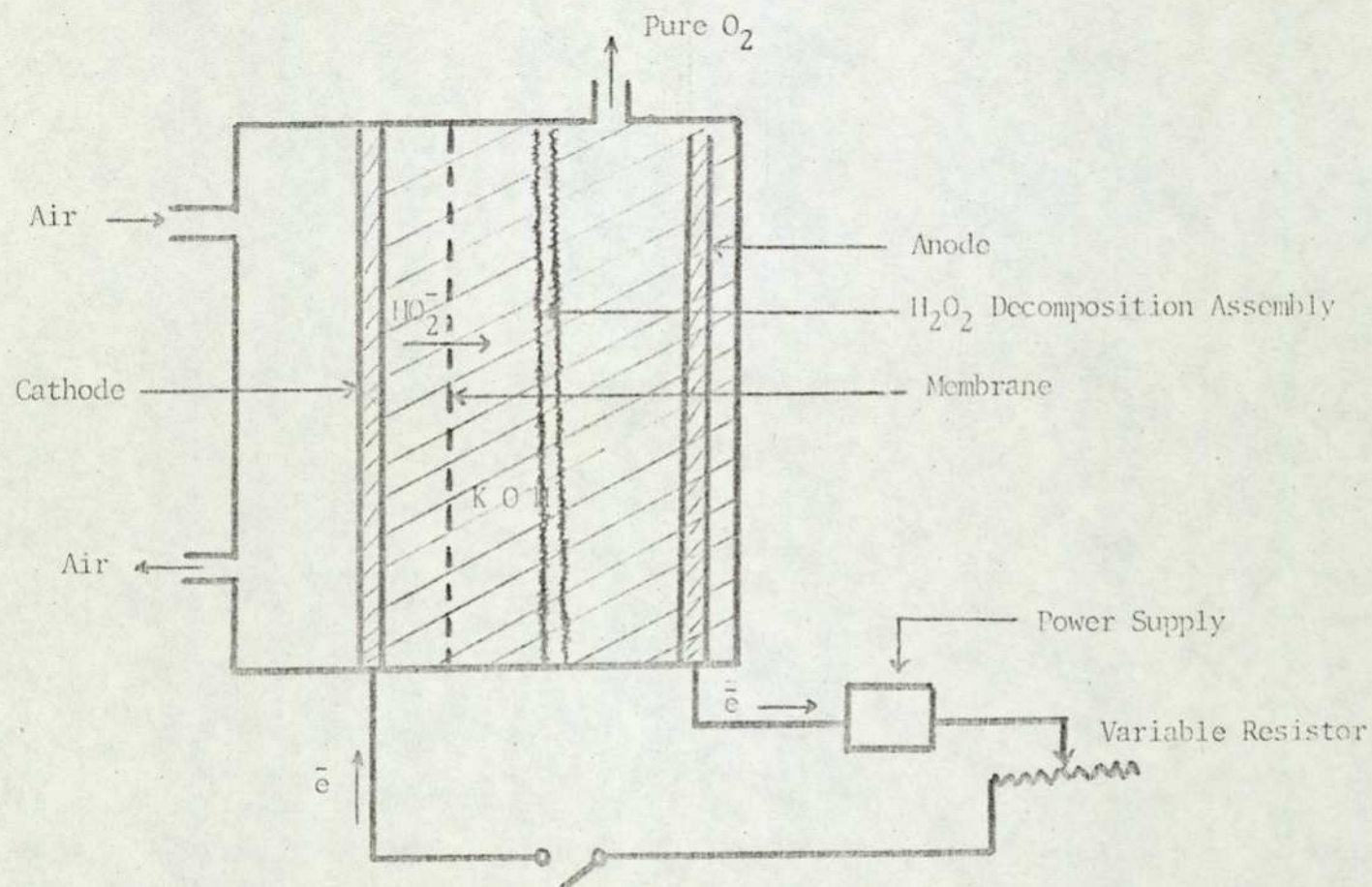


Fig. 7.3 DESIGN FOR THE PRESENT OXYGEN EXTRACTOR

C H A P T E R E I G H T

CONCLUSIONS AND SUGGESTIONS FOR FURTHER
WORK

8.1. CONCLUSIONS

8.1.1. Oxygen Reduction

The results presented in Chapter 3 for the hydrogen peroxide production have confirmed that the reduction of oxygen on a graphite surface proceeds via the Berl mechanism⁷ to produce HO_2^- and since carbon does not decompose hydrogen peroxide efficiently, the end product is hydrogen peroxide. These results also confirm the conclusion that the further reduction or decomposition of the peroxide on graphite proceeds very slowly in comparison to the two electron process⁴².

8.1.2. The Decomposition of H_2O_2

The hydroxide co-precipitation and freeze drying methods used to prepare CoFe_2O_4 and NiCo_2O_4 respectively, were successful in producing high surface area catalysts for the decomposition of H_2O_2 . A useful parameter for comparing catalytic activities was the initial rate of oxygen evolution, for a given H_2O_2 concentration and temperature. If the decomposition kinetics follow a known rate law, a more accurate measure of catalytic activity is the reaction rate constant. Since the activation energy proved to be a measure of the intrinsic catalytic activity and independent of catalyst microstructure⁶¹, it was a suitable parameter for comparison of the intrinsic catalytic activity of two different catalyst, (CoFe_2O_4 and NiCo_2O_4) which probably possess different microstructures (primarily due to the different methods used for their preparation). NiCo_2O_4 powder proved, as expected to be

a highly active catalyst for H_2O_2 decomposition reaction. The highest availability of Co^{II} occurs at the composition NiCo_2O_4 . The occurrence of Co^{II} on lattice sites, with its easy conversion to Co^{III} , allows a highly effective redox system to be set up initiated by Co^{II} centres.

On cost, activity and stability bases both CoFe_2O_4 and NiCo_2O_4 catalysts proved to be the best candidate materials to be used for the decomposition of H_2O_2 in the present oxygen extractor.

8.1.3. Oxygen Evolution

The criteria which have been suggested in this work, especially the role of the metal/metal oxide couple or lower metal oxide/higher metal oxide couple in determining the minimum voltage required for the oxygen evolution, together with other essential requirements such as low electrical resistivity and suitable electrode microstructure, for selecting an active material for oxygen evolution have been supported experimentally by the studies on NiCo_2O_4 and lithiated nickel oxide. The high activity, the excellent stability and the low cost of NiCo_2O_4 make it the most favourable material for oxygen evolution in alkaline solutions. Such a catalyst offers a great deal to the improvement of water electrolysis and metal-air batteries as well as oxygen extractors. In the case of metal-air batteries, the Teflon bonded NiCo_2O_4 electrode would make suitable rechargeable oxygen or air electrode, because oxygen reduction performance

on this electrode is equivalent to that of the silver/graphite electrode and is stable above 0.75V vs R.H.E. Moreover oxygen evolution on such an electrode results in no electrode degradation.

The experimental results of oxygen evolution on Teflon bonded NiCo_2O_4 electrodes demonstrate the importance of preanodization in improving reproducibility and performance of the electrode. This improvement could be attributed to the formation of higher oxides, which may possess better conductivity and catalytic activity.

Furthermore, the results also showed that Teflon-bonded electrodes offer the best electrode structures for oxygen (gas) evolution, because of the greater utilization of the catalyst surface area and the better mechanical strength.

The cyclic voltammetric studies of the anodic polarization, on NiCo_2O_4 and nickel electrodes (Chapter 6), provided further support to the suggestion^{74, 89} (Chapter 5 and 6) that oxygen evolution proceeds only after the formation of the higher oxides.

Considering the complexity of the higher oxides formation and gas evolution on porous electrodes, the potentiostatic pulse technique was useful in solving some of the problems, such as mass transfer and bubble formation, associated with the study of the oxygen evolution reaction on the oxide electrodes. The pulse technique is useful, particularly in determining the effectiveness factor and obtaining reproducible

and reliable measurements of some of the kinetic parameters such as the Tafel slope. However, for the potentiostatic pulse measurements to be reproducible, the electrodes must be preanodized sufficiently to form stable higher oxides and the potentials of the electrodes should be maintained above that of the higher oxides reduction.

8.1.4. The Present Electrochemical-Chemical Method for Oxygen Extraction

Oxygen gas is very important in many industrial, medical and scientific areas. An inexpensive and efficient oxygen extractor based on an integrated electrochemical-chemical method has been demonstrated. The experimental results shown in Chapter 7 (Table 7.2 A, B) supported our earlier suggestion (section 1.4), that using the two electron process of oxygen reduction on graphite would be beneficial, provided the HO_2^- produced was chemically decomposed and the resultant oxygen gas collected together with that evolved on the anode.

At 40°C , 5N KOH, the power consumption of this method was only 2.69 Kwhr/1000 litres of oxygen, significantly lower than the conventional electrochemical oxygen extractors and water electrolyzers. This oxygen extractor is particularly suitable for village clinics in developing countries where bottled oxygen is not readily available. Other specialized applications include oxygen supply for fighter aircraft pilots and military field hospitals.

8.2. SUGGESTIONS FOR FURTHER WORK

8.2.1. Oxygen Evolution

The high activity of NiCo_2O_4 for oxygen evolution make further investigation on this catalyst desirable.

In the nickel cobalt oxide series, NiCo_2O_4 has the highest activity and the lowest activation energy. Moreover, it has the lowest resistivity and the highest amount of loosely bound oxygen²⁸. If the resistivity is too high, only oxides adjacent to the nickel wire in the mesh current collector can function. Hence, it would be of interest to investigate the doping of the other compositions with lithium to decrease their resistivity. The role of the loosely bound oxygen in the NiCo_2O_4 lattice, in the oxygen evolution reaction remains to be investigated. A possible approach is to use H_2^{18}O to determine whether the higher oxides are decomposed at higher potentials to form oxygen using similar procedures outlined by Rozenthal and Veselovskii¹⁰³. Nickel screen is usually used as the current collector in the Teflon bonded electrodes. It has been shown earlier that the anodic performance of nickel screen drops significantly after a period of time. The build up of relatively low conductivity nickel oxide was suggested as the reason for this decay. This consequently causes a drop in the overall performance of the Teflon bonded electrode. However, it has been shown that lithiated nickel oxide possesses a high activity for oxygen evolution. Thus, lithiation of nickel oxide (on the nickel screen) may be one possible solution

to the problem. This could also contribute to a small extent to improve the overall performance of the Teflon bonded NiCo_2O_4 electrode for oxygen evolution. The correlation of physical properties, such as the electronic structure, of the nickel cobalt oxide series with their electrochemical behaviour needs further investigation. This should add another criterion to those suggested earlier for selecting an active material for the evolution of oxygen.

The potentiostatic pulse measurements, presented in Chapter 6, on preanodized Teflon bonded NiCo_2O_4 electrodes, could be verified by obtaining the potentiostatic pulse measurements in a different manner. The anodic pulse from the (o.c.v.) could be applied for a short time (~ 10 ms), followed by a cathodic pulse for longer time, i.e. sufficient to reduce all the higher oxides formed in the earlier anodic step. The net charge corresponding to oxygen evolution could be calculated by subtracting the charge of the reduction of the higher oxides from that of the anodic pulse, the latter being a combination of oxygen evolution and oxide formation. If the potentiostatic pulse measurements of this approach confirm those obtained earlier, the pulse technique could be considered as adequate to overcome many of the problems associated with electrochemical measurements, for oxygen evolution, on porous electrodes and hence kinetic parameters for the oxygen evolution reaction could be determined accurately and the elucidation of a mechanism would be possible.

It has been shown in this work that, for oxygen evolution, Teflon bonded electrodes allow a higher utilization of available electrocatalyst surface. Further work on the optimization of the electrode structure in terms of aggregate size, pore size as well as novel and more permanent methods of modifying the hydrophobicity of the Teflon bonded electrode surface could be very rewarding.

8.2.2. Oxygen Extraction

Wynveen and Montgomery¹¹⁴ found the performance of their "oxygen extractor" to be dependent upon the flow rate and the pressure of the air supply to the cathode, the power required to generate a given quantity of oxygen decreased as the flow rate or the pressure increased. Therefore these points need to be investigated in order to optimise the design of the present oxygen extraction device. Optimization will also demand studies of other parameters, such as operating voltage, current density and temperature ranges.

It is necessary to perform life testing on single cells. Life and performance testing of cell stacks upto 100 watt would also be required to provide the information necessary for the construction of the 1 kw prototype.

The heat and water balance of the oxygen extractor also require investigation.

During the oxygen extraction experiments (Section 7.5.4), using NiCo_2O_4 coated nickel screen for H_2O_2 decomposition, it was observed that when the power was switched off, and hence HO_2^- ions production on the cathode ceased, the

decomposition reaction continued for sometime (~ 10 min.). However the total volume of oxygen produced (after completion of HO_2^- decomposition) was found to be the same as in the earlier experiments using the more noble catalysts (platinized platinum or silver screen). It was therefore apparent that NiCo_2O_4 and CoFe_2O_4 are less efficient for the decomposition reaction and hence optimization of catalyst loadings and areas is essential in order that decomposition of peroxide ions matches their cathodic production. This must be achieved in order to supply the anode with the OH^- ions necessary for the oxygen evolution reaction.

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APPENDIX A

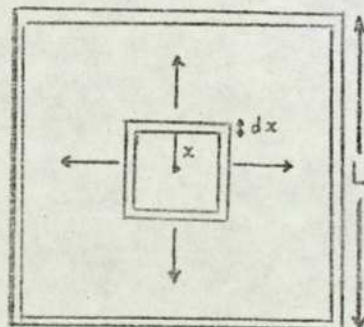
Ohmic Losses in the Teflon-bonded Electrode^{80,74}

The conductivity measurements of the catalyst powder (described in 2.2.4) were made on compressed samples, whereas in the electrode there is no such constraint and the particles are touching one another loosely, leading to high contact resistances. The presence of a non-conducting (Teflon) phase is a further complication.

Estimation of the resistivity effects in a porous, Teflon bonded electrode is very complex, but approximate values can be obtained if certain simplifying assumptions are made.

Consider a one cm^2 portion of 100 mesh nickel screen, there are a certain number of holes. The electrocatalyst could be considered to reside in the holes of the nickel screen, that is in "boxes".

Consider now a square element of side $2x$ whose centre is also the centre of the hole; assume that the current generated within each side of this element travels towards the adjacent current collector thus:



Let hole side = L cm , Current density = i A/cm²,
 specific resistivity = ρ ohm/cm and thickness = t cm

Current generated in central square (I) = $4x^2 i$

Resistance of square element (R) = $\frac{\rho x}{8xt}$

$$R + dR = \frac{\rho(x + dx)}{8xt}$$

$$dR = \frac{\rho dx}{8xt}$$

$$dV = IdR = 4x^2 i \frac{\rho dx}{8xt}$$

Assuming uniform current generation in all parts of the electrode,

IR drop in entire hole (and hence also that of the entire electrode)

$$V = \frac{i\rho}{2t} \int_0^{L/2} x \, dx = \frac{i\rho}{2t} \cdot \frac{x^2}{2} \Big|_0^{L/2}$$

$$V = \frac{i\rho L^2}{16t}$$

APPENDIX B

At present, commercial companies, such as Air Products and British Oxygen charge £30 initially for each oxygen cylinder, plus a rental charge of 90p per month. Each replacement cylinder costs £3. The standard oxygen cylinder contains 6.79×10^3 litres of oxygen at N.T.P. If we assume that 3 cylinders of oxygen are used per day, then the total cost based on 200 working days per year will be $= 3 \times £30 + 3 \times 12 \times £0.90 + 3 \times 200 \times £3 = £1922.40$.

The power consumption of the oxygen extractor is about 3 Kwhr/1000 litres of oxygen.

∴ To produce the same amount of oxygen in one oxygen cylinder (6.79×10^3 litre) will require $= 3 \times 6.79 = 20.37$ Kwhr

∴ Total electrical power required to produce the same amount of oxygen in 600 cylinders $= 12222$ Kwhr.

Total cost of electricity, if 1 Kwhr cost 3p will be £366.66.

Assuming the capital cost of oxygen extractor $\sim$ £400 (when it is produced on an industrial scale) and the maintenance of the extractor and replacement of electrodes $\sim$ £100/year, then the total cost will be about £866.

At present over 1.2 million cylinders of oxygen are sold every month in U.K. The use of the oxygen extractor in village clinics is extremely cost effective. On average, a 4 hours surgical operation requires 1000 litres of oxygen.

Thus, assuming the oxygen extractor is used continuously for

200 days per year, the amount of oxygen generated would be sufficient for 4200 operations i.e. only $\frac{£866}{4200} = 26\text{p}$ per operation.

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A.C.C. Tseung and S.M. Jasem, Electrochim.
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TEFLON BONDED NICKEL-COBALT OXIDE ELECTRODES"
S.M. Jasem and A.C.C. Tseung, Proc. Electro-
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Switzerland, Zurich, 21 Aug. 1978.
4. "AN INTEGRATED ELECTROCHEMICAL-CHEMICAL
METHOD FOR THE EXTRACTION OF OXYGEN FROM AIR"
A.C.C. Tseung and S.M. Jasem, Provisional
U.K. Patent application No. 14752, April 1978.

The publications listed above have been removed for
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ABEL & IMRAY,

CHARTERED PATENT AGENTS

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303-306 HIGH HOLBORN,
LONDON,
WC1V 7LH.

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19th April, 1978.

Attention: [REDACTED]
National Research Development
Corporation,

P.O. Box 236,
Kingsgate House,
66/74 Victoria Street,
London. SW1E 6SL.

Dear Sirs,

Re: British Patent Application No. 14752/78
Tseung/Jasem - "Gas Extraction"

Further to your letter of 6th March, 1978 and the various telephone discussions between your Mr. Neville and our Mr. Machin, we filed the above application on 14th April, 1978 and it has been given the number and date shown above. In accordance with your requirements we are enclosing two copies of the provisional specification and an informal drawing as filed together with the official filing receipt. Also enclosed is a photocopy of Form 1 as filed.

As you will realise, it will be necessary to file a new British Application under the provisions of the Patents Act 1977 if this case is to proceed to grant and you will receive a reminder from us concerning this and possible foreign applications in about nine months' time.

In the meantime please do not hesitate to contact us if you require any further work done on this matter.

Yours faithfully,

[REDACTED]
ABEL & IMRAY

Encs.

c.c. Dr. A.C.C. Tseung + enclosures.

AGENT

APPLICANTS REF.

INTERNATIONAL CONVENTION DATE



The Patent Office

25 Southampton Buildings

London, WC2A 1AY

The Comptroller acknowledges the receipt of documents purporting to be an application for a patent and an accompanying ~~provisional~~ ^{provisional} specification in the name(s) of

Alfred Chan Chung Tseung and

These documents have been numbered and dated as below.

Further acknowledgment:

Samuel Mahmood

DIV-DATE CLAIMED		FROM APPLN. NO.	
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		FORM 4	

No. **14752**
14 APR 1973

Sasem

[To be quoted on all correspondence]

FORM P. ACK 4

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PATENTS ACTS, 1949 to 1961

APPLICATION FOR PATENT

(To be accompanied by two copies of Patents Form No. 2
or of Patents Form No. 3)

APPLICANT'S OR AGENTS REF.

PCM

Note: This is a comprehensive form and parts inappropriate to a particular application should be cancelled. In the case of an application by the inventor, only parts 1, 4 and 6 of this form are appropriate, together with part 5 if a Patent of Addition is applied for.

(a) Insert (in full) name, address and nationality of applicant(s).

1. ~~I/We~~ (a) ALFRED CHAN CHUNG TSEUNG [REDACTED]

and

SAMEER MAHMOOD JASEM, [REDACTED]

(b) Delete the words which are not applicable.

~~are~~/are in possession of an invention which is described in the accompanying (b) ~~provisional~~ complete specification under the title (c)

(c) Insert title of invention.

"Gas Extraction"

(d) Insert name of inventor if included at (a).

(b) (X) Alfred Chan Chung Tseung and
(We Sameer Mahmood Jasem
(The said (d)

claim to be the true and first inventor of the invention.

or

(e) Insert (in full) name, address and nationality of inventor(s) if not included at (a).

2. I/We believe (e)

to be the true and first inventor of the invention.

and (b) (I
(we

(the said

(am (the assignee of the said inventor in respect of the right
(b) (are (b) (to make this application.
(is (the personal representative of the said inventor

3. (b) (The invention (A part of the invention) was communicated from abroad to (b) (me (us (the said

by (f)

(f) Insert (in full) name and address and nationality of communicator.

4. ~~I~~/We declare that to the best of ~~my~~/our knowledge and belief the statements made above are correct and there is no lawful ground of objection to the grant of a patent to ~~me~~/us on this application and ~~I~~/we pray that a patent may be granted to ~~me~~/us for the said invention.

Use of the invention in the United Kingdom before the date of the application for a patent is, in general, a lawful ground of objection.

5. And I/we request that the patent may be granted as a PATENT OF ADDITION to

(b) (patent No. (the patent to be granted on application No.

6. And ~~I~~/we request that all notices, requisitions, and communications relating to this application may be sent to Abel & Imray at (g) Northumberland House, 303-306 High Holborn, London. WC1V 7LH

(g) The address must be in the United Kingdom.

(h) who ~~is~~/are hereby appointed to act for ~~me~~/us.

(h) Delete if not applicable.

7. Signature(s) (i)

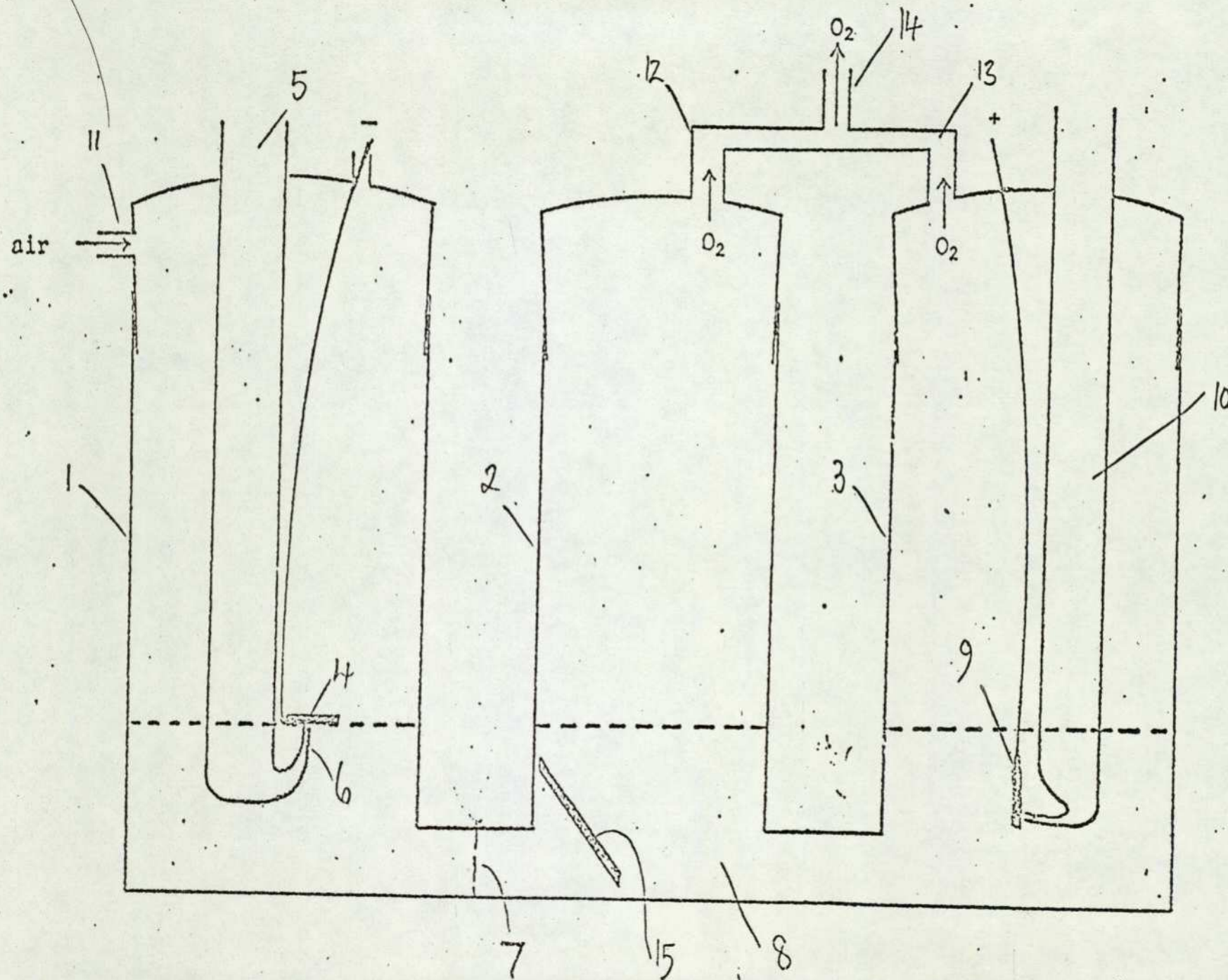
(i) To be signed by applicant(s).

Declaration to be signed by anyone named as inventor in part 2 who is not an applicant. I/We claim to be the true and first inventor(s) and assent to the making of this application.

To the Comptroller,
The Patent Office, 25 Southampton Buildings,
London WC2A 1AY.

NOTICE TO INVENTORS

Attention of applicants is drawn to the desirability of avoiding publication of inventions relating to any article, material or device intended or adapted for use in war (Official Secrets Acts 1911 and 1920). In such cases, after an application for a patent has been filed at the Patent Office, the Comptroller will consider whether publication or communication of the invention should be prohibited or restricted under Section 18 of the Act and will inform the applicant if such prohibition is necessary. Applicants are reminded that, under the provision of this Section, applications may not be filed abroad without written permit or unless an application has been filed not less than six weeks previously in the United Kingdom for a patent for the same invention and no direction prohibiting publication or communication has been given.

Fig 1.

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P R O V I S I O N A L S P E C I F I C A T I O N

"Gas Extraction"

WE, ALFRED CHAN CHUNG TSEUNG,

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and

SAMEER MAHMOOD JASEM,

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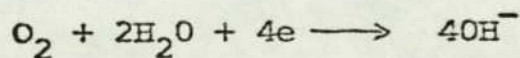
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do hereby declare this invention, to be described in the following
statement:-

This invention relates to the extraction of gases from gaseous mixtures and, more especially, to the extraction of oxygen from ambient air.

Portable oxygen providing equipment is finding increasing applications in military field hospitals, in the village clinics of developing countries, in oxy-acetylene welding and in high altitude fighter aircraft. Besides oxygen cylinders, such equipment comprises two basic types of oxygen generator; (a) chemical generators, and (b) electrochemical generators, which either electrolyse water or extract oxygen from the air by using an oxygen reduction cathode coupled to an oxygen evolution anode.

Chemical generators employ expensive chemicals and, to date, the most common method used to generate oxygen has been the electrolysis of water. However, the high overvoltage at the anode necessitates an operating voltage of about 2.2 volts at 100 mA/cm² and, the production of hydrogen as a by-product, apart from increasing the power consumption, is a potential hazard. Quite recently, therefore, there has been developed a more efficient electrochemical method in which a polytetrafluoroethylene (PTFE) bonded platinum black cathode is used to reduce oxygen in the ambient air to form hydroxyl ions in accordance with the following equation:



The hydroxyl ions diffuse through a suitable membrane, for example, a woven asbestos or glass fibre mat, to an oxygen evolution anode, usually a platinum electrode. The working

voltage of this cell, taking into account the unavoidable heat losses, is about 1.3 to 1.4 volts at 100 mA/cm^2 , which is significantly lower than the corresponding value for an electrolysis cell. However, the capital and running costs involved are still relatively high and the use of this type of oxygen extractor has been limited to specialised applications.

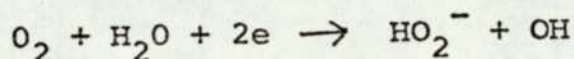
The present invention is based on our surprising observation that the efficiency of such electrochemical gas extraction and regeneration methods can be improved significantly in certain applications by employing an additional chemical step in which one or more substances formed in the electrochemical reaction is itself converted to the desired gaseous product, preferably by catalytic decomposition.

Accordingly, the present invention provides a method in which an electrochemical cell is used to separate a gas from a gaseous mixture by reduction of said gas at the cathode and regeneration of said gas at the anode, wherein one or more substances formed in the cathodic reduction or anodic regeneration is chemically converted to produce said gas and wherein the gas formed by both the anodic regeneration and the chemical conversion is recovered as the product. The present invention also provides apparatus for carrying out such a method.

In its broad aspect the present invention may be applied to the extraction of any gas from a gaseous mixture provided that said gas may selectively be cathodically reduced and anodically regenerated by electrochemical reactions which produce

a substance which can be chemically converted to said gas, preferably by catalytic decomposition. However, it will be appreciated from the foregoing remarks that the invention is especially applicable to the extraction of oxygen from ambient air and, for convenience, it will now be described in more detail with reference to such an application.

It is known that the reduction of oxygen on certain electrodes, especially graphite and carbon, is a two electron process obeying the equation



This means that when such electrodes are used in a fuel cell, they are not so efficient as electrodes which directly reduce oxygen to hydroxyl ions via a four electron process. It has, therefore, been proposed to add peroxide-decomposition catalysts to a carbon cathode in a fuel cell so that the peroxy ion is decomposed to yield oxygen for recycling, thus leading to a higher efficiency. In accordance with the present invention, however, the catalytic decomposition of the peroxy ion is used in an oxygen generator to provide an additional supply of oxygen as product.

In an especially preferred form of the present invention, therefore, there is provided an oxygen extraction apparatus comprising at least one cell which is provided with a cathode for the reduction of oxygen by an electrochemical reaction which produces peroxide ions and an anode which will regenerate oxygen, said cell being further provided, externally of the cathode

compartment, with means for the catalytic decomposition of hydrogen peroxide.

It will be appreciated that such apparatus will also be provided with means for the supply of ambient air at a suitable rate and also with means for collecting the oxygen produced by the electrochemical and chemical reactions. In practice the apparatus will typically comprise a plurality of such cells, for example from 10 to 20, and may advantageously be built to a moduli design for ease of replacement and repair of the cells. It will, in any case, be appreciated that the design of the apparatus will depend upon the particular application and, especially, upon the desired rate of production of oxygen.

Suitable physical constructions for the cell will be apparent to those conversant with fuel cell technology. For example it will, in general, be appropriate to provide means such as a porous screen made, for example, from asbestos or glass to separate the cathode compartment from the remainder of the cell in order to prevent back diffusion of oxygen bubbles to the cathode compartment and to prevent diffusion of air bubbles into the product stream. If the cell is compact in nature it may be necessary to provide means such, for example, as a net made from a plastics or other insulating material, to ensure that there is no electrical contact between the anode and the catalytic means.

Other constructional features which may prove advantageous or necessary in certain applications include means for removing

carbon dioxide, means for removing electrolyte, e.g. potassium hydroxide entrained in the oxygen product stream and means for controlling the oxygen content of the final outlet gas by admixture of the oxygen product stream with exhaust gas from the cathode compartment; this is essential in some medical applications. It will, in addition, in general be necessary to provide adequate means for controlling the voltage, current density, temperature and operating pressure of the cell and for monitoring the overall heat and mass balance of the apparatus.

In this preferred application of the present invention it is necessary for the cathode to reduce oxygen by an electrochemical route which produces peroxide ions, usually together with hydroxyl ions (generally via the two electron process described above or a near stoichiometric variation thereof) but which is made from a material which does not possess significant peroxide decomposition activity. For example, cathode materials such as fuel cell grade platinum black produce peroxide ions, but because they have a relatively high peroxide decomposition activity, will not, in general, be suitable for use in the present invention because the peroxide ion will be decomposed in the cathode compartment and the oxygen so produced cannot be collected with the oxygen produced at the anode.

In general it is preferred to use a high surface area graphite powder which has been found to possess a very high

activity for oxygen reduction in alkaline solution. A suitable graphite powder having a surface area in the range of 500 to 600 m²/g may be prepared by vacuum grinding of graphite in a vibrating ball mill; the cathode may be prepared from the graphite powder by bonding with PTFE. However, it will be appreciated that other materials may be suitable for the cathode in certain applications.

The main criterion for the oxygen evolution anode is that it should operate at a low oxygen overvoltage. Thus certain anodes such as PTFE-bonded platinum black and nickel screens will not, in general, be suitable for use in the present invention. However, amongst suitable materials there may be mentioned, for example, PTFE-bonded lithiated nickel oxide and, especially, PTFE-bonded nickel cobalt oxide (NiCo₂O₄) which has a lower redox potential than a platinum black anode.

Both the cathode and anode may, in some cases, advantageously be formed by depositing the active materials on a suitable support, such as a nickel screen.

The electrolyte itself is advantageously an aqueous solution of an alkali metal hydroxide, e.g. sodium hydroxide, or especially, potassium hydroxide, but it will be appreciated that other electrolytes may be useful in certain applications.

The essence of this preferred application of the present invention is to provide means for catalytically decomposing hydrogen peroxide (or, more correctly, the peroxy-

ion which it forms in the electrolyte) to produce an additional supply of oxygen for collection in the anode compartment. In this way, the effective current required for the oxygen extraction process is halved leading to a significant reduction in power consumption. In certain instances it may be appropriate to provide such means as a chemical substance in solution or dispersion in the electrolyte, but, in general, it will be preferred to provide the catalyst in the form of a solid member or, more especially, absorbed or coated on a suitable solid support. Amongst suitable materials there may be mentioned, for example, certain spinel oxides and silver which may be coated or absorbed on a graphite or carbon support. Preferred peroxide decomposition catalysts are CoFe_2O_4 and, especially, NiCo_2O_4 . These materials may be brought into suitable form by bonding with PTFE, but, in general, it will be preferred to coat them on a suitable porous or perforated support, e.g. a nickel screen. It has been found that their activity is considerably greater in the latter form because the catalytic reaction can more easily occur on the surface of the screen and because, in addition, the available surface of the screen is entirely composed of the catalyst whereas about 50% of a PTFE bonded member is composed of PTFE particles where no catalytic reaction can occur.

Both CoFe_2O_4 and NiCo_2O_4 are relatively cheap materials which can be produced in particulate form by freeze-drying methods or by thermal decomposition or double precipitation methods.

In summary, it may be stated that the electrochemical chemical method of oxygen extraction according to the present invention provides significant advantages in cost reduction and in other respects as compared with the conventional electro-chemical oxygen extractors at present available. At operating voltages of around 1 volt and at an operating temperature of 40°C with 5N KOH as the electrolyte the approximate power consumption of a cell constructed in accordance with the present invention is only about 2.7 to 3 kilowatt hours per 1,000 litres of oxygen produced whereas conventional extractors require about 4.4 kilowatt hours. Rough calculations indicate that if the cells of the present invention are used in an efficient manner they will be capable of producing oxygen in a relatively cheap manner and will lead to significant savings in cost in applications where oxygen cylinders are at present employed.

The following Examples illustrate the invention.

A three compartment cell was constructed as shown in Figure 1. It will be appreciated that the cell shown was constructed for experimental evaluation of various aspects of the present invention and is not to be considered as typical of a cell to be used commercially.

The cell generally comprises a cathode compartment 1, a catalytic decomposition compartment 2 and an anode compartment 3. The cathode compartment 1 is provided with a floating electrode 4 and, as shown, a Dynamic Hydrogen Reference

electrode (DHE) 5 was used to monitor the potential working electrode 4, the tip of the Luggin capillary 6 of the DHE electrode 5 being positioned about 1 mm below the floating electrode 4. If desired, the cathode compartment 1 may be separated from the remainder of the cell by the provision of a No. 4 glass frit 7. 5N KOH solution was used as the electrolyte 8. The anode compartment 3 was provided with a working anode 9 and with a DHE electrode 10. Air was passed into cathode compartment 1 via inlet 11 and the oxygen produced in compartments 2 and 3 was collected by means of outlets 12 and 13, respectively. As shown, outlets 12 and 13 led to a further combined outlet 14.

EXAMPLE 1.

In this Example a cell was used having two compartments separated by a No. 4 glass frit and provided with a 8 cm² PTFE-bonded graphite floating cathode and a 20 cm² nickel screen anode. Current was passed at the fixed densities shown using a Chemical Electronics Potentiostat (TR 40-3A). The 5N KOH electrolyte (80 ml) was thermostatted at 25°C and an air pump was used to supply air to the cathode compartment.

After 1 hour, the concentration of H₂O₂ in the electrolyte was measured by titration against standard potassium permanganate solution. The self decomposition of H₂O₂ in 5N KOH under the same condition (but without passing current) was measured and found to be 0.525 g/litre of HO₂⁻ per hour. The number of runs is shown in brackets.

Table 1 shows the amounts of HO_2^- produced at different current densities and confirms that the reduction of oxygen on graphite proceeds via the two electron process.

The 74% yield of HO_2^- as compared with theoretical was mainly one to decomposition on the nickel screen anode and losses during pipetting and titration.

TABLE 1

Current mA	Theoretical gm HO_2^-	Experimental average gm HO_2^- (in 80 ml. electrolyte)	Experimental/ Theoretical %
200	0.1230	0.0917	74.55 (2)
400	0.2460	0.1866	75.85 (2)
600	0.3693	0.2675	72.40 (2)
800	0.4924	0.3575	72.6 $\pm$ 0.02 (4)

EXAMPLE 2

Various electrode combinations were evaluated using the cell shown in Figure 1. A Chemical Electronics Potentiometer (TR 40 - 3A) was used to feed a 400 mA current to the cell for 30 minutes and a gas burette was attached to outlet 14 to measure the amount of oxygen produced (except that the glass frit 7 was omitted).

The PTFE-bonded electrodes were prepared in a conventional manner, the NiCo_2O_4 /nickel screen electrode and the PTFE-bonded NiCo_2O_4 /nickel screen screen electrodes were prepared as follows:

(a) NiCo_2O_4 /nickel screen electrodes. 100 mesh nickel screens were dipped into 2M Ni/Co nitrate solution (Ni : Co = 1 : 2) and the screens were heated in air at 400°C for 10 hours. The formation of NiCo_2O_4 spinel on the electrode surface was confirmed by X-ray powder diffraction.

(b) PTFE-bonded screen electrodes. The electrocatalyst NiCo_2O_4 (prepared by freeze drying) was mixed with GP1-Fluon dispersion (ex ICI). The catalyst : PTFE ratio was 10 : 3. The mixture was then painted onto a 100 mesh nickel screen and dried at 100°C for 1 hour. The results obtained with the various electrode combinations are shown in Table 2.

It will be seen that the best results were obtained when operating in accordance with the present invention (cells A and B) using a PTFE-bonded graphite/screen cathode and a PTFE-bonded NiCo_2O_4 /nickel screen anode with a NiCo_2O_4 /nickel screen catalytic decomposer.

When no catalytic decomposer was employed (cell C) the power consumption was similar to that with a cell using platinum black as the cathode (cell D). Even though, in cell C, the cathodic reduction of oxygen occurred by a two electron process, the peroxide ions diffusing to the anode were not fully decomposed and when the power was switched off gassing continued slowly for a long time on the PTFE-bonded NiCo_2O_4 anode surface (which is not so active as the thermally

decomposed NiCo_2O_4 /nickel screen catalytic decomposer). This suggests that when the anode is functioning electrochemically the oxygen bubbles effectively blanket a large part of its surface, making it unavailable for peroxide decomposition.

5 When a peroxide decomposer was placed between a platinum cathode and the NiCo_2O_4 anode (cell E) no improvement was noted. This is not surprising because any HO_2^- ions produced at the platinum cathode would be decomposed there, yielding oxygen for further cathodic reduction.

10 It will be seen that in all cases the power consumption was significantly lower than for a conventional water electrolyser (cell F) and that cell B, constructed in accordance with the present invention, gives significantly better results than the previously proposed
15 cell (cell G) using a platinum black anode and cathode.

 Finally, it will be noted that in the experimental cells A and B, not all the peroxy ions produced were decomposed. This is mainly because of the large distance between the anode and cathode and significant improvements
20 in peroxide conversion can be obtained by decreasing the anode/cathode gap.

TABLE 2

Extraction of oxygen from air (400 mA passed through cell for 30 min)

Cell No.	Temp.	Cathode	H ₂ O ₂ decomposer	Anode	Theoretical From H ₂ O ₂ decomposition ml (NTP)	Theoretical From O ₂ evolution ml (NTP)	Experimental ml (NTP)	Voltage iR free volt	Power Consumption KW hr/1000 litres of O ₂
	25°C	4 cm ² Teflon bonded graphite on nickel screen	4 cm ² NiCo ₂ O ₄ on nickel screen	4 cm ² Teflon bonded NiCo ₂ O ₄ on nickel screen (O ₂ evolving)	45.60	45.60	78.03±3.18(5)	1.34	3.46
	40°C	"	"	"	"	"	77.04±3.02(4)	1.04	2.69
	25°C	"	none	"	"	"	49.82±1.11(3)	1.34	5.41
	25°C	4 cm ² Teflon bonded Platinum black on Pt screen (O ₂ reduction)	none	"	N/A	45.60	46.96±0.68(5)	1.26	5.36
	25°C	"	4 cm ² NiCo ₂ O ₄ on nickel screen	"	N/A	45.60	47.77	1.26	5.26
	25°C	4 cm ² Teflon Pt black on Pt screen (H ₂ evolving)		"	N/A	"	45.80	2.09	9.12
	40°C	Teflon bonded Pt electrode (O ₂ reduction)		Teflon bonded Pt electrode (O ₂ evolving)	N/A	45.60	45.60	1.0	4.38

EXAMPLE 3

The catalytic activity of NiCo_2O_4 and CoFe_2O_4 catalytic decomposers was measured by a conventional gasometric technique.

5 In all cases the reaction rate constant was found to be independent of the initial H_2O_2 concentration but directly proportional to the catalyst mass, indicating first order Kinetics.

10 Experiments were conducted at 25°C , 30°C , 35°C and 40°C . By plotting the first order reaction rate constant against the reciprocal of the temperature (degrees kelvin) the activation energy for the decomposition of H_2O_2 over freeze dried NiCo_2O_4 (surface area $69.7 \text{ m}^2/\text{g}$ was calculated as 10.98 Kcal/mole . similar to the value of 10.60 Kcal/mole obtained for CoFe_2O_4 (prepared by coprecipitation of cobalt and iron hydroxides followed by dehydroxylation at 100°C)
15 having a surface area of $120 \text{ m}^2/\text{g}$.

Taking differences in surface area into account this shows the activity of NiCo_2O_4 to be approximately equivalent
20 to that of CoFe_2O_4 . However NiCo_2O_4 is easier to prepare and apply to a screen and is thus currently preferred for use in the present invention.

It will be apparent from the above description that the present invention is especially advantageous in that it
25 provides an oxygen generator which is highly efficient, which

has a lower power consumption than hitherto proposed cells and which can be constructed from relatively cheap materials. It will be understood, however, that the electrochemical/chemical process described is not limited to such an application and other applications, modifications and variations falling within the scope of the present invention will be apparent to those skilled in the art.

ABEL & IMRAY

Chartered Patent Agents,
Northumberland House,
303-306 High Holborn,
London. WC1V 7LH.

PCM/BJM