



City Research Online

City St George's, University of London

Citation: Munshi, M. Z. A. (1981). A study of expander materials used in the cadmium electrode of ni-cd batteries. (Unpublished Doctoral thesis, The City University)

This is the accepted version of the paper.

This version of the publication may differ from the final published version. To cite this item please consult the publisher's version.

Permanent repository link: <https://openaccess.city.ac.uk/id/eprint/36939/>

Copyright and Reuse: Copyright and Moral Rights remain with the author(s) and/or copyright holders. Copies of full items can be used for personal research or study, educational, or not-for-profit purposes without prior permission or charge, unless otherwise indicated, provided that the authors, title and full bibliographic details are credited, a hyperlink and/or URL is given for the original metadata page and the content is not changed in any way. For full details of reuse please refer to [City Research Online policy](#).

A STUDY OF EXPANDER MATERIALS
USED IN THE CADMIUM ELECTRODE
OF Ni-Cd BATTERIES

A THESIS SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

by

M.Z.A. MUNSHI

at the

Department of Chemistry
The City University
Northampton Square
London EC1V OHB

October 1981

These investigations were supported
by Chloride Alcad Ltd., and were
carried out under the joint supervision
of Dr. A.C.C. Tseung and Mr. J. Parker.

ACKNOWLEDGEMENT.

I would like to sincerely thank my academic supervisor Dr. A.C.C. Tseung and my industrial supervisor Mr. J. Parker for their most valuable help and guidance given to me throughout the duration of the project.

I am indebted to my student colleagues in the Electrochemical Research Group for many valuable discussions relating to the project, to the Physics Department and to Chloride Alcad for their sponsorship of the project.

Many thanks are due to [REDACTED] of UMIST for allowing me to use the a.c. impedance facilities in his laboratory.

Finally I would like to express my gratitude to [REDACTED] and [REDACTED] for the typing of this thesis.

SUMMARY.

In Chloride Alcad Nickel-Cadmium pocket-plate flooded cells, iron oxide ($\alpha\text{-Fe}_2\text{O}_3$) and PVA are used as expanders in the cadmium negative plate to prevent crystal growth, thus retaining capacity. The use of these expanders in the negative electrode has two advantages. They increase the efficiency of the cadmium electrode and are cheap to buy commercially. Unfortunately, the iron-oxide may find its way to the positive plate where it acts as a poison and reduce the capacity of the plate. It is desirable, therefore, to find alternative expanders and to study the basic mechanism of inhibition of crystal growth in the battery electrodes.

Alternative expanders investigated included TiO_2 and Mg(OH)_2 and these showed extremely promising results when incorporated in the negative cadmium electrode, particularly magnesium hydroxide. The capacities obtained were almost as good as the iron-oxide incorporated electrode but the amount of magnesium hydroxide added to the electrode was less than $\frac{1}{10}$ that of the iron-oxide.

Mechanistic studies showed that iron underwent dissolution but the amount was very minute. The use of a planar-microelectrode in conjunction with linear sweep voltammetry, limiting current measurements, a.c. impedance and potential step techniques was found to be a cheap and efficient means of organic expander assessment. The major function of PVA appeared to be to increase the surface area/porosity of the electrode by acting in a number of ways and may be a means of improving the active material

utilisation.

α -Fe₂O₃ probably provides nucleation centres or spaces for cadmium hydroxide and acts in combination with the organic material in increasing the surface area for cadmium hydroxide formation. This makes the cadmium hydroxide film thinner and therefore much easier to reduce.

CONTENTS.

ACKNOWLEDGEMENT	i
SUMMARY	ii
LIST OF SYMBOLS	x
LIST OF TABLES	xiii
 <u>CHAPTER 1 HISTORY OF THE Ni-Cd CELL.</u>	
1.1 <u>INTRODUCTION.</u>	1
1.2 History of Chloride Alcad and Development of High Performance Batteries.	6
1.3 Characteristic of Vented Pocket Plate Alkaline Cells.	8
a) EP Range	8
b) MP and MS Range	8
c) UHP and UHS Range	10
1.4 Sealed Pocket Plate Alkaline Type.	15
1.5 Manufacturing Processes of Pocket Plate Ni-Cd Batteries.	18
a) Preparation of Active Material	18
b) Positive Active Material	18
c) Negative Active Material	19
d) Electrolyte	20
1.6 a) Production of Ni-Cd Pocket Plates.	21
b) Cell Assembly	24
c) Formation Cycle	28
 <u>CHAPTER 2 LITERATURE SURVEY AND OBJECTIVE OF THE PROJECT.</u>	
2.1 Electrochemical Reactions.	29
2.2 Soluble Intermediates.	31
2.3 Phases Formed on the Cd Electrode and the CdO Film Question.	35
2.4 Passivation of Cadmium.	46
2.5 Ageing of Porous Cadmium Electrodes.	51
2.6 Charge and Discharge Behaviour of Porous Cadmium Electrodes.	53
2.7 Benefits from Prevention of Crystal Growth by the Inclusion of Additives.	62

2.8 Objectives of the Project.	67
 <u>CHAPTER 3 SURFACE ENERGY CONSIDERATIONS.</u>	
3.1 <u>INTRODUCTION.</u>	70
3.2 Theoretical Principles.	70
3.3 Experimental - Materials.	73
3.4 Contact Angle Measurement.	74
 <u>CHAPTER 4 SYNTHETIC IRON OXIDES AND PVA.</u>	
4.1 Synthetic Iron Oxides.	78
4.2 PVA.	86
 <u>CHAPTER 5 BACKGROUND TO THE PROJECT.</u>	
 <u>CHAPTER 6 METHOD TO ACCELERATE CRYSTAL GROWTH BY MEANS OF</u> <u>LOW RATE AND HIGH TEMPERATURE.</u>	
6.1 <u>INTRODUCTION.</u>	95
6.2 Mechanism of Crystal Growth	97
6.3 Experimental.	98
6.4 Electrode Structure.	99
6.5 Electrochemical Oxidation.	100
6.6 Electron Microscopy Examination.	104
6.7 X-Ray Crystallographic Analysis.	104
6.8 Results and Discussions.	105
6.9 Conclusions.	119

CHAPTER 7 EFFECT OF ADDITIVES ON THE PERFORMANCE OF THE NEGATIVE
PLATE.

7.1	<u>INTRODUCTION.</u>	120
7.2	Experimental.	121
7.3	Results and Discussions.	129
7.4	Electron Microscopy Examination.	
a)	Structure of Electrodes containing neither PVA nor α -Fe ₂ O ₃ .	133
b)	Structure of Electrodes containing only PVA as additive.	136
c)	Structure of Electrodes containing only α -Fe ₂ O ₃ as additive.	139
d)	Structure of Electrodes containing both PVA and α -Fe ₂ O ₃ .	141
e)	Structure of Electrodes containing only precipitated Fe ₂ O ₃ as additive.	146
f)	Structure of Electrodes containing only TiO ₂ as the additive.	150
g)	Structure of Electrodes containing CaO as additive.	153
h)	Structure of Electrodes containing BaO.6Fe ₂ O ₃ as additive.	155
i)	Structure of Electrodes containing BN as additive.	155
7.5	Conclusion.	157

CHAPTER 7a EFFECT OF Mg(OH)₂ ON THE PERFORMANCE OF THE NEGATIVE
PLATE.

7a.1	<u>INTRODUCTION.</u>	162
7a.2	Experimental.	162
7a.3	Specific Surface Area.	163

7a.4 Results and Discussions.	168
-------------------------------	-----

CHAPTER 8 THE DISSOLUTION OF IRON FROM THE NEGATIVE ACTIVE
MATERIAL IN POCKET-PLATE Ni-Cd BATTERIES.

8.1 <u>INTRODUCTION.</u>	172
8.2 Experimental.	177
8.3 Results and Discussions.	181
8.3.1 EDAX and Coulometric Studies.	181
8.3.2 Cyclic Voltammetric Studies.	184
8.3.3 X-ray Studies.	192
8.4 Conclusions.	193

CHAPTER 9 EFFECT OF A GROWING Cd(OH)₂ FILM ON THE ANODIC BEHAVIOUR
OF CADMIUM IN KOH SOLUTION.

9.1 <u>INTRODUCTION.</u>	194
9.2 Experimental.	198
9.3 Results and Discussions.	200
9.4 Cyclic Voltammetry Measurement - Experimental.	206
9.5 Results and Discussions.	208

CHAPTER 10 DOUBLE LAYER AND FARADAIC IMPEDANCE.

All figures in this chapter are present: numerical error only.

10. <u>INTRODUCTION.</u>	213
10.1 Theoretical Principles.	213
10.2 The Randles' Method.	222
10.3 The Sluyters' Method.	223
10.4 Previous Work of Impedance on the Cadmium Electrode.	227
10.5 Experimental.	229

10.6 Results and Discussion.	232
------------------------------	-----

CHAPTER 11 AN INVESTIGATION OF EXPANDER ACTION AT THE PLANAR

Cd/Cd(OH)₂ ELECTRODE INTERFACE USING THE PULSE

TECHNIQUE.

11.1 INTRODUCTION	247
11.2 Theoretical Principles	247
11.2a Forms of Polarisation	247
11.2b Electrochemical Kinetics.	249
11.3 Previous work on the Kinetics of Passivation of Cadmium.	254
11.4 Experimental.	257
11.5 Results and Discussion from Potentiostatic Pulse Technique.	258
11.6 Conclusions.	267

CHAPTER 12 ELECTROCRYSTALLISATION.

12.1 <u>INTRODUCTION.</u>	268
12.2 The Thermodynamic Theory of Nucleation.	271
12.3 The Growth of Discrete Centres.	274
12.4 The Overlap Problem of Growth Centres.	276
12.5 Background Work.	281
12.6 Experimental.	283
12.7 Results and Discussions.	284

CHAPTER 13 FINAL DISCUSSION, CONCLUSION AND RECOMMENDATION

FOR FUTURE WORK.

13.1 The Cadmium Electrode of the Nickel-Cadmium Battery.	293
13.2 Alternative Expanders.	294
13.3 Expander Function.	297

APPENDICES

REFERENCES

LIST OF SYMBOLS.

a_i^j	activity of species i in position or phase j
dA	change of surface area
A	nucleation rate constant
C_i	concentration of species i
C_O^S, C_O^R	surface concentrations of species O and R (at $x = 0$)
C_O^b, C_R^b	bulk concentrations of species O and R
C	capacity of an electrode or cell <u>OR</u> capacitance
C_{DL}	double layer capacitance
d_{AV}	mean particle diameter
D_i	diffusion coefficient of species i
e	electric charge
E	electrode potential
E°	standard electrode potential
F	the Faraday
g	acceleration due to gravity
dG	change in free energy
ΔG_{ads}	free energy of adsorption
h	height of capillary rise, <u>OR</u> height of nucleus
i	current density
i_o	exchange current density
j	$\sqrt{-1}$

k	rate constant for a chemical process (see text for exact meaning) <u>OR</u> Boltzmann constant
k_{sh}	forward rate on the surface
L	inductance
MW	molecular weight
n	number of electrons transferred in overall electrode process <u>OR</u> number of particles
N	number of nuclei
P	pressure
q_i	charge density of species i
q_m	charge density on metal
r	radius of nucleus
R	gas constant <u>OR</u> resistance (see text for exact meaning)
S	surface area of electrode <u>OR</u> spreading coefficient
S_{AV}	aggregate specific surface area
t	time
T	absolute temperature
V	Volume
W	Warburg impedance
X	reactance
Z	impedance
$\bar{Z}_{(s)}$	transform of impedance
α	transfer coefficient <u>OR</u> as superscript indicates phase α
β	as superscript indicates phase β

γ	surface tension <u>OR</u> with subscript interfacial tension
δ	Nernst diffusion layer thickness <u>OR</u> tamped density
η or ξ or ϕ	overpotential ($E - E_{rev}$)
θ_i	surface coverage by species i, <u>OR</u> contact angle
μ	chemical potential
$\bar{\mu}$	electrochemical potential
v	potential sweep (scan)
ρ	density
σ	ionic conductivity <u>OR</u> surface free energy.
τ	transition time
ϕ_1	potential at the inner Hemholtz plane
ϕ_2	potential at the outer Hemholtz plane
ϕ_m	potential at the electrode surface
ϕ	phase angle in a.c. method <u>OR</u> overpotential
ω	frequency of a.c. modulation
Ω	volume of oxide produced per coulomb of electric current
Γ_i	surface excess of i

LIST OF TABLES

	Page
Table 1	80
Tables 2, 3, 4	106
Table 5	123
Table 6	124
Table 7	125
Table 8	130
Table 9	167
Table 10	168
Table 11	192
Table 12	201
Table 13	287
Table 14	288

CHAPTER 1

HISTORY OF THE Ni-Cd CELL

CHAPTER 1

HISTORY OF THE NICKEL-CADMIUM CELL.

1.1 INTRODUCTION.

Nickel-cadmium pocket plate batteries have been produced on a commercial scale since 1912. The fundamental investigations were carried out by the Swedish scientists Walden Jungner and Axel Estelle and independently by Thomas Edison in the U.S.A.¹ The initial part of this chapter deals with the investigations that led to the discovery of the nickel-cadmium couple, its basic electrochemistry and the development of the cell.

At the turn of the century, Sweden was heavily dependant on paraffin before the development of her hydroelectric power for her long northern winters. However, the paraffin was a major cause of many heavy fire losses and while Jungner was experimenting with electrically operated fire warning systems, the lack of reliable low-voltage power supplies for his fire-alarm first turned his mind toward electric batteries. It had always been Jungner's intention to obtain patent protection for a system and was intrigued by cells with what he called "unchangeable electrolyte". The patent by Lalande of 1882 (American Pat. 274, 110) involving a copper-cupric oxide cell with an unchangeable alkaline electrolyte and the Pollak patent of 1898 (German Pat. 107, 727) with iron in both the positive and negative plates were regarded as important ones in Jungner's collection. He was, however, impressed by the Dun Patent of 1835 and by the Darrieus Patent of 1893. The Dun cell had soluble negative electrodes and all the possible metallic oxide

positives were also named. Darrieus undoubtedly made the first suggestion for an accumulator with insoluble electrodes combined with, at least, the possibility of an unchangeable electrolyte. However, none of these inventors seemed to have any idea of the importance of the unchangability of the electrolyte. It has been quoted by Estelle that Jungner was the first to state the exact conditions for a practically complete unchangeability of the electrolyte in his application filed in 1899. He spent the next few years in a detailed and logical evaluation of all the possible couples in association with his principle of "unchangeable electrolyte". He spent much time on nickel-zinc, silver-zinc, nickel-cadmium and silver-cadmium couples.

With slender resources and his interests spread over so many systems he has no chance of bringing any of them to a satisfactory conclusion. However, he persevered with the cadmium electrode in the nickel-cadmium and silver-cadmium cells but was unable to overcome the caking and loss of porosity which occurred after a few cycles. Attempts with cadmium/graphite mixtures and copper and graphite rods as additional conductors proved failures. The struggles with cadmium continued, but under the necessity of producing commercial batteries, Jungner was reluctantly forced to turn to iron as his negative material. The cadmium electrode as we know it today was developed successfully by Axel Estelle and emerged successfully in 1912. Estelle solved the problem by using a mixture of iron and cadmium, which was electrolytically precipitated from a solution to form a very intimate mixture. In the Estelle

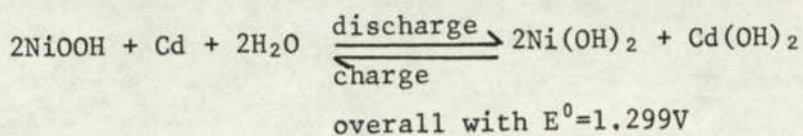
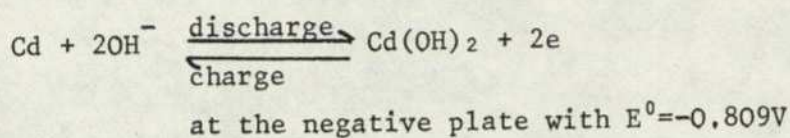
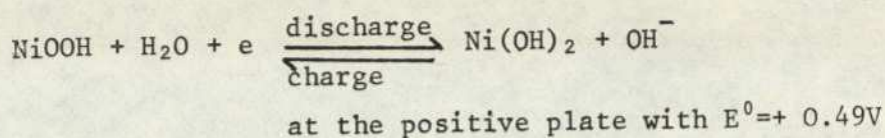
cell, the main electrochemical activity comes from the cadmium, while iron in the form of FeO is a dead 'grid' material. He found that a more positive metal cadmium, which stands next to iron in the absolute potential series of the metals can be used together with iron to advantage.

By this time Jungner and Estelle, having established a public company, the new Jungner Akkumulator Co., after additional finance was obtained in 1906, merged with K.L. Berg, an inventive engineer from the Swedish General Electric Co.

While Berg continued to improve the pocket manufacture, Estelle, in addition to his negative electrode difficulties was encountering, in his positive plate, those electrochemical problems which wrecked the first Edison battery in 1904. Thin flakes of nickel and cobalt were tried instead of graphite as a conductor because of early difficulties, but in anode electrolysis these were covered with an oxide layer. He returned to graphite and established the importance of graphite purity and the point that it must resist as far as possible the effect of anode electrolysis in alkali. The positive active material finally consisted mainly of nickel hydroxide containing up to about 5% of cobalt hydroxide and up to 20% of graphite generally in the form of both powder and flake in the ratio of about 2.1. The addition of cobalt had been found to improve both the capacity and the life of the active material.

After solving the major problems associated with the electrodes the first useable nickel-cadmium battery emerged in 1909 but not commercially until three years later.

The basic electrochemical reactions are as follows:-



These equations indicate that 1g of nickel hydroxide should give a capacity of 0.289 Ahr, and 1g of cadmium a capacity of 0.48 Ahr. In practice, at normal rates of discharge at room temperatures, the efficiency of use of the positive plate is about 70% and that of the negative active material is about 75%.

In the early days of the nickel-cadmium battery manufacture, there was no oxyacetylene welding, no reliable separator, and no means of reliably plating steel; because of inability of nickel plate onto steel ribbon, a pure nickel ribbon had to be used to enclose the positive material. The cost was enormous and first attempts to perforate this ribbon was made using a sewing machine. The first separators were glass rods, but later a crude form of perforated ebonite was tried. This gave trouble, both on account of excessive sulphur in the ebonite and because active material escaped from the crudely made pockets and lodged in the separator holes.

In 1909, however, the battery was still a long way from acceptable commercial usage and the new Jungner Co. had now come to the end of its resources. In 1910, still another company, the Swedish Jungner Ackumulator Co., was formed to take over the assets, and for the first time adequate funds were available.

Towards the end of World War I, the battery had, in spite of many difficulties, been brought to the stage where it was commercially and technically successful on shallow-cycle applications only, but had severe limitations on deep-cycle work.

From 1919 onwards, saw the whole design, development concept split into two separate but interlinked approaches which were to lead to two widely differing types of battery:

a) The improvement of the charge-discharge characteristics on shallow-cycle, high-performance batteries to make it comparable to that of the lead acid battery.

b) The improvement of the life characteristics on deep-cycle batteries to make it comparable with that of the Edison tubular positive nickel iron battery. Both these objectives were achieved by the end of World War II.

1.2 History of Chloride Alcad and Development of High-Performance Batteries.

In 1919, Jungner established a subsidiary company in England called Batteries Ltd., located at Hunt End, Redditch, which at that time only acted principally as selling agents for the parent company.

During the 1920's however, Batteries Ltd., began to prosper and in 1929, it broke away from its parent company to form a new company called Nife Batteries Ltd. This company continued to prosper and develop rapidly during the war period.

At the end of the war, Britannia Batteries situated at Redditch, which were German owned, were taken over and combined with Nife Batteries Ltd. The new company, Alkaline Batteries Ltd, became permanently situated at Redditch one reason being the ready supply of needles used to perforate the pocket plate strips. In 1973, the company which is part of the Chloride Group was renamed Chloride Alcad.

Shallow-cycled batteries were used for engine starting, switchgear and standby. In these markets, the life and reliability factors remained admirable and service lives of 20 years plus were becoming commonplace. It was this type of performance which gradually enabled the pocket positive nickel-cadmium battery to become commercially established in spite of the difficulties in the deep-cycle field. However, both life and high rate performance of lead-acid batteries were constantly being improved, and these factors were a constant threat to the competitive position. The best markets in the early

nineteen-twenties were in the lighting of public service vehicles, but self-starters became a standard fitting and batteries as then designed were unable to provide the heavy currents at an acceptable voltage. With the high market, Lucas organisation, themselves substantial makers of lead acid batteries, obtained the sole rights for nickel-cadmium batteries for heavy vehicle lighting and starting.

Among the many special battery developments of World War II, one in particular was to have substantial consequences. To meet the need for a small, high-output and shockproof cell to operate inside an anti-aircraft shell, W.S. Thomson developed the first miniature cells in 1942. The extent of gas recombination was not fully understood at this time and the containers were designed to resist some pressure on recharge. In 1941, the Ministry of Supply called for a 50V, 25 mAhr high tension battery to deliver up to 15 cycles on recharge in a sealed condition. This was met and the first sealed, rechargeable battery was produced. Arising from these and other developments, sealed cells are now in regular commercial supply. The next few sections deal with the range of Alcad's batteries and their methods of manufacture.

1.3 Characteristics of Vented Pocket Plate Alkaline Cells.

Alcad batteries are manufactured in three standard ranges, each designed to give optimum performance under specified conditions of operation.

1.3a EP Range. Ep cells in plastic containers are primarily designed for floating applications where the battery is subjected to:

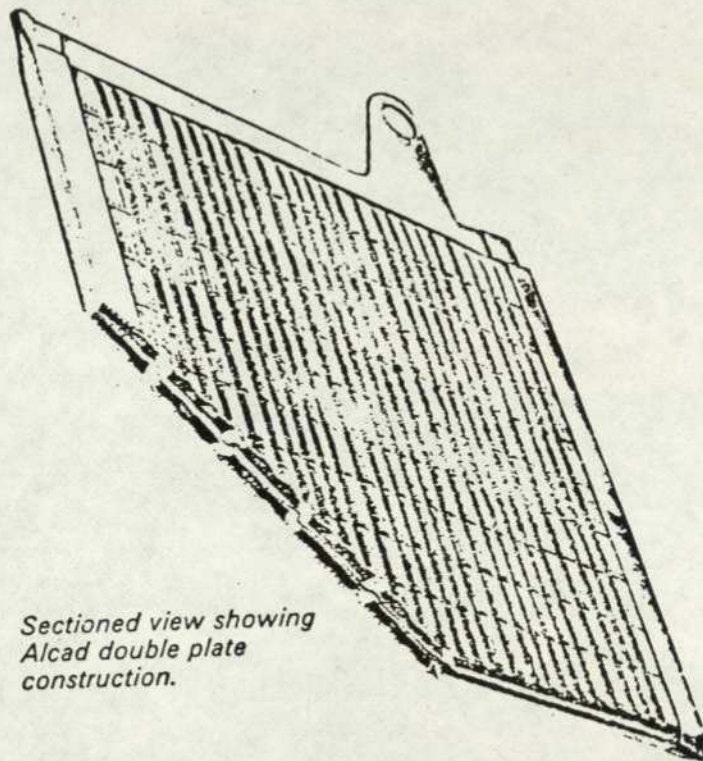
- a) Frequent shallow discharge,
- b) Occasional deep discharges.

The cells are employed on applications calling for a very wide range of discharge rates, but mostly between 1 hr and 20 hrs. They are, however, capable of providing satisfactory performance at higher rates for such applications as switch tripping, where other considerations often determine the choice of cell type and where the high voltage recovery rate, which is a feature of all nickel-cadmium cells is a decisive factor. (Capacity range EP 5-315 Ahr).

1.3b MP and MS Range.

MP and MS cells are suitable for medium period discharge between 30 minutes and 3 hours. They are primarily designed for uninterruptible power supplies and other standby power requirements in the 1 hour to 2 hour range. They can be relied on for low maintenance, excellent charge retention and efficient operation in extreme physical and electrical conditions. The unique Alcad double positive plate construction (Fig 1.1) is available when cycling performance is the main factor. This

Figure 1.1 Alcad Double Positive Plate used in the
MP/MS Range for Heavy Duty Applications



*Sectioned view showing
Alcad double plate
construction.*

has been proved over many years to enhance the life and performance of batteries operated on cycling duties.

MP cells embody polypropylene containers having high impact resistance and excellent mechanical and electrical properties.

MS cells have steel containers where conditions of shock, vibration or temperature extremes require that the strongest container be used.

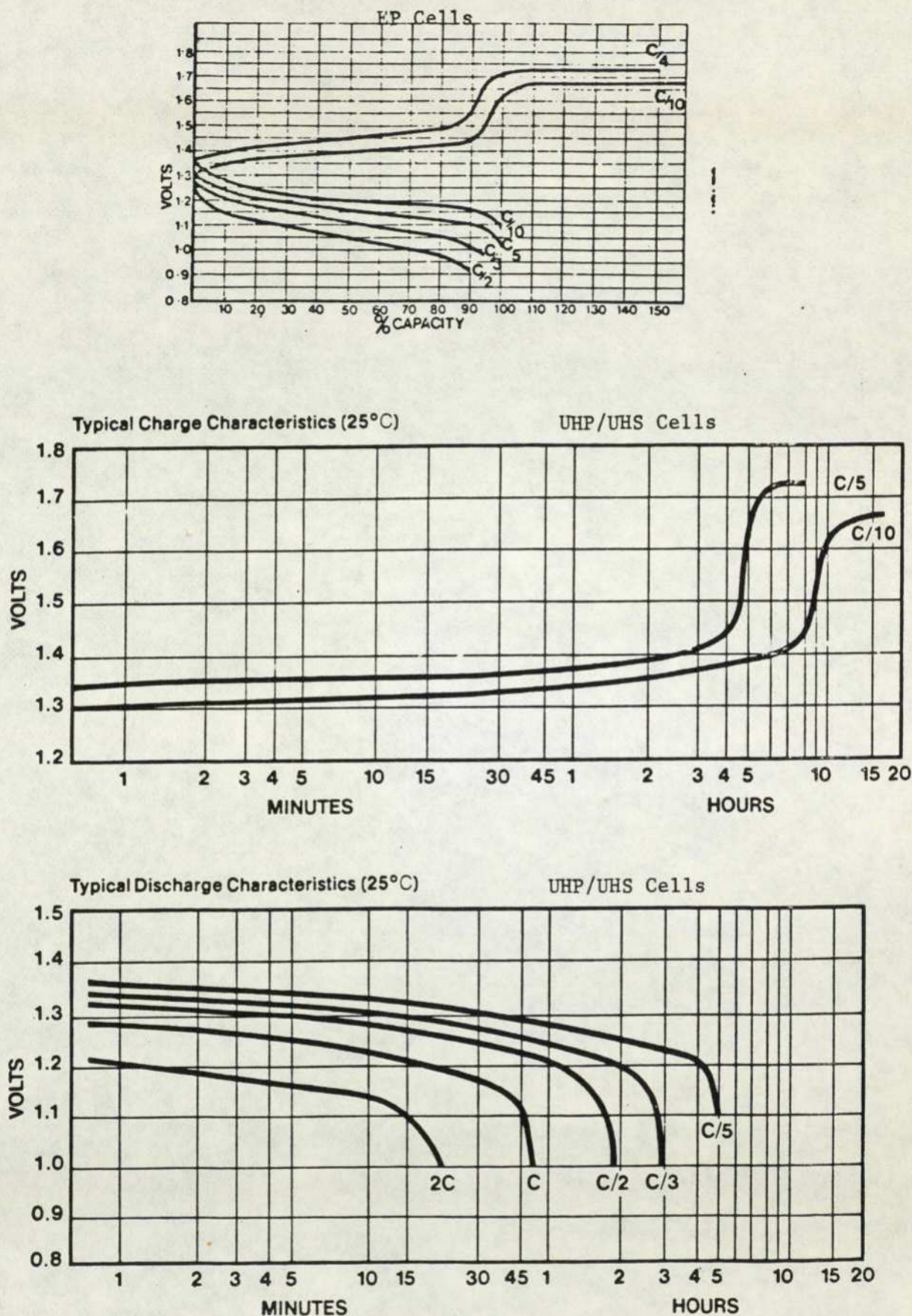
Their voltage characteristics lie between the general purpose EP type and the high performance UHP/S type (Fig 1.2)

1.3c UHP and UHS Range.

These cells are designed for duties calling for high rates of discharge between 1 second and 15 minutes. Alcad UHP and UHS cells are widely employed for applications such as engine starting, switch closing and standby power applications in which the battery has to provide a rapid discharge over very short periods. Currents of $20 \times C$ (Note: C refers to the capacity of the battery in amp-hrs) or more are available for engine starting making possible great economies in the size of battery which need to be fitted.

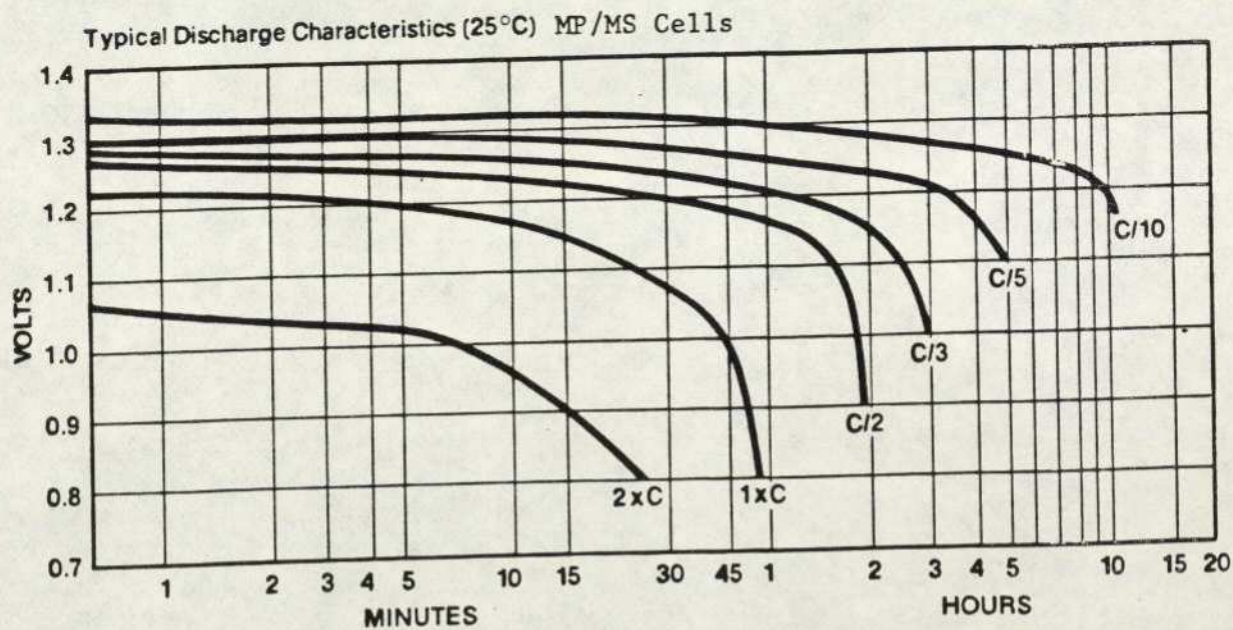
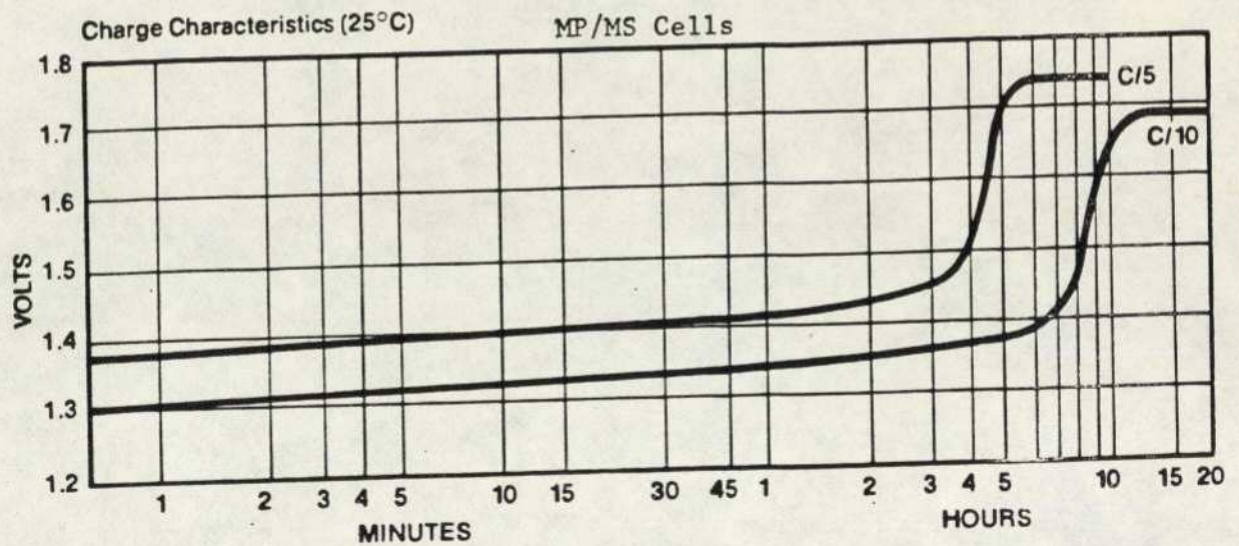
The ultra high performance of this range has been achieved through the further development of a new plate design which increases the exposure of the active material. The improved plate construction combines great mechanical strength with very low electrical resistance.

Figure 1.2 Charge and Discharge Characteristics at 25°C
for the EP and UHP/UHS Types of Vented Cells



Nominal discharge voltage is 1.2 volts per cell.

Figure 1.2 (cont.) Charge and Discharge Characteristics
at 25°C for the MP/MS Type of Vented
Cell



Nominal discharge voltage is 1.2 volts per cell

These cells are normally left on open circuit or floated across a constant voltage supply which maintains them permanently in a near fully charged condition.

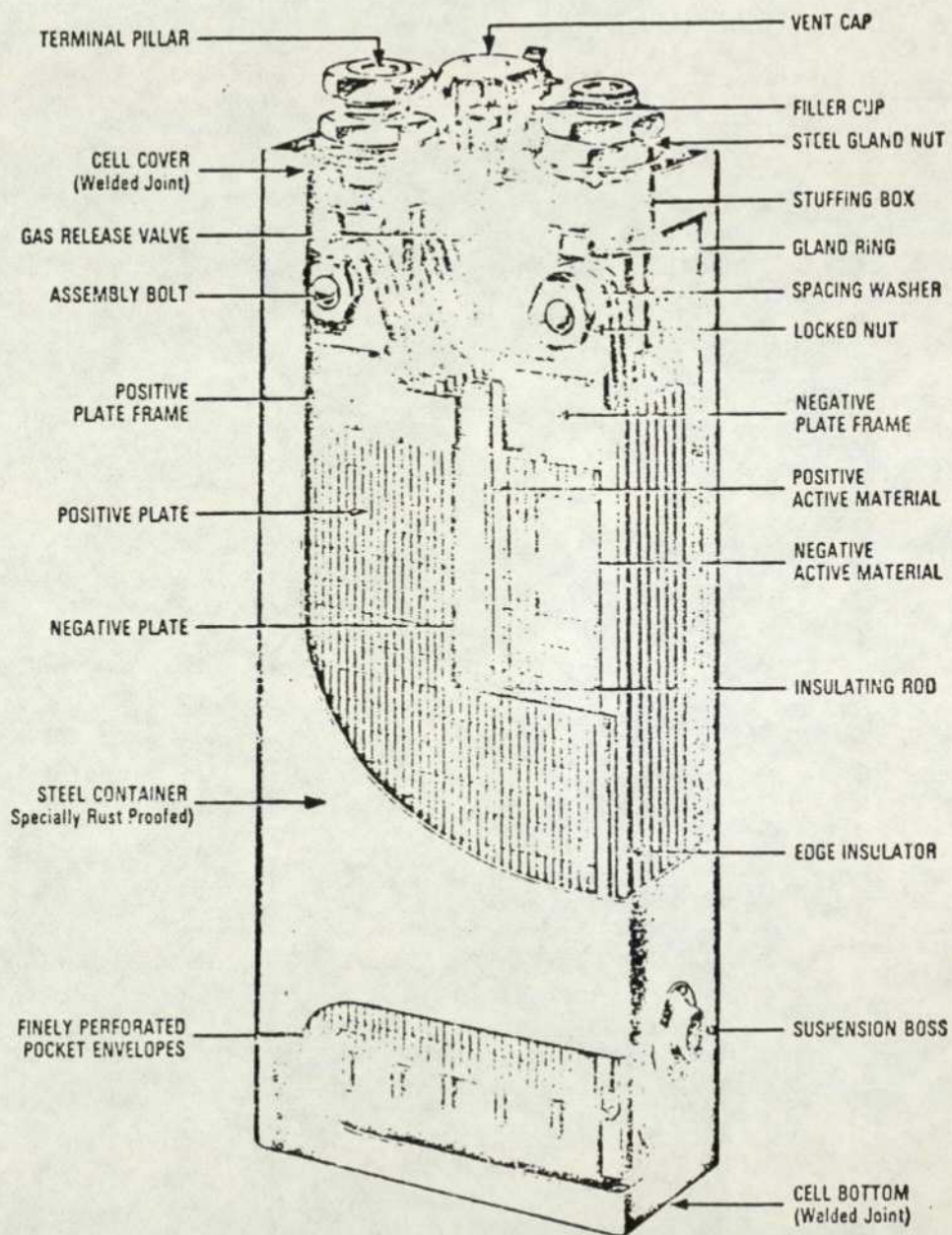
The above range of vented cells, MS and UHS designate steel containers and EP, MP and UHP plastic containers. The choice of whether a particular cell has a steel or plastic container depends on the application.

All the above nickel-cadmium cells are provided with a vent (Fig. 1.3). This is necessary to make it possible for the gases formed during the charge period to escape from the cell, and to provide an opening for filling the cells with water and electrolyte. Cell vents are constructed to prevent excessive evaporation of water from the electrolyte, eliminate the escape of electrolyte spray during charge and minimise the entry of carbon dioxide from the air into the electrolyte, and more recently they have incorporated a sintered ceramic disc to prevent explosion of cell gases.

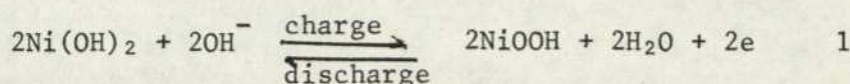
All vented cells have an excess of electrolyte (flooded cells) which must be topped up periodically with distilled water. This is mainly because on overcharge of the cell, oxygen is evolved at the positive (nickel electrode), and hydrogen at the negative (cadmium electrode). The water thus dissociated has to be replaced by periodic topping up to maintain the electrolyte concentration fairly constant and to ensure that the electrolyte level is above the plates.

The cell reactions on charge and discharge may be written as follows:-

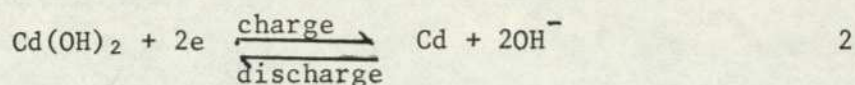
Figure 1.3 Sectional View of a Typical Alcad Steel
Vented Cell



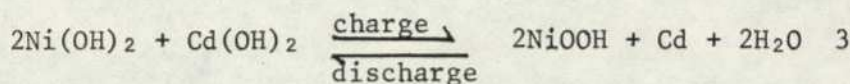
Positive electrode.



Negative electrode



Overall cell reaction.

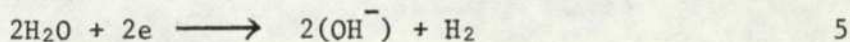


On Overcharging the Cell

Positive electrode



Negative electrode



Overall overcharge reaction.



1.4 Sealed Pocket Plate Alkaline Type.

The sealed pocket plate type is manufactured in one standard range (PS cell. Capacity 8-30 Ahr)

The advantages of the sealed cell over the vented cell types are:-

- i) splashing and spilling of the electrolyte is eliminated
- ii) refilling with water eliminated, therefore maintenance free,
- iii) they can be operated in any position.

The idea of the sealed cell is based on the following principles:

The negative electrode (cadmium) have a surplus of uncharged active material so that the positive plate starts to produce oxygen before the negative plate is fully charged. Because this oxygen reacts with the negative active material, to form cadmium hydroxide, the negative electrode never becomes fully charged and consequently never evolves hydrogen (therefore no requirement for an open cell). However, it is important not to overcharge this cell at high charge rates.

The negative active material is formulated to contain 12% more cadmium than in the vented cell negative. The cells consist of a series of interleaved positive and negative plates insulated by porous felted separator.

There is no free electrolyte in the cell, the total amount of electrolyte being confined to that retained in the highly absorbent separator. This enables the cell to be operated in any position and facilitates the transfer of oxygen from the positive to the negative plates, since this transportation to a certain extent is carried out in the gaseous state.

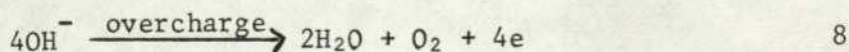
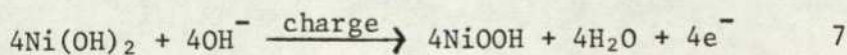
Only steel containers are used to withstand the pressures associated with recombination and they prevent diffusion of gases through the walls as in some plastic containers. The cells are of the robust rectangular shape (see Fig 1.3).

A safety valve is fitted to eliminate any possibility of high gas pressures > 60psi, building up inside the cell;

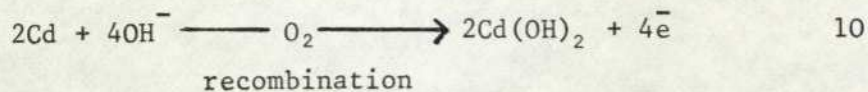
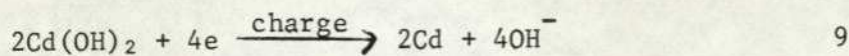
connected with the evolution of gases on overcharge or the unintentional reversal of the cell (i.e. - overdischarge).

The sealed cell is more costly and has a shorter life than the vented alternative. Thus the higher costs of the sealed cell must be balanced against the total elimination of routine maintenance. The cell on charge and discharge may be written as follows:-

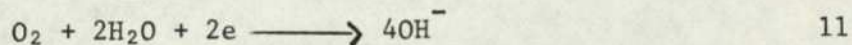
Positive electrode



Negative electrode

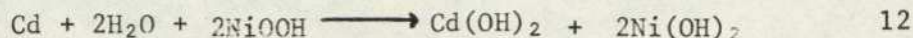


Having an excess of negative material results in oxygen being formed at the positive before H₂ is evolved at the negative. The oxygen migrates to the negative plate where it is reduced by the following reaction:-



Thus a continuous cyclic reaction is achieved between the negative and positive plates on charge, hydroxide being supplied for recombination following the reduction of oxygen.

Overall cell reaction



i.e. as in the flooded electrolyte cell.

1.5 Manufacturing Processes of Pocket Plate Ni-Cd Batteries.

1.5a Preparation of Active Materials.

The positive electrode incorporates nickel and cobalt compounds together with graphite and the negative electrode consist of cadmium and iron compounds in the Ni-Cd pocket type cell. The quality of the active material is of the utmost importance for the cell performance.

1.5b Positive Active Material.

The starting material is nickel sulphate, which is purchased to a specification permitting less than 0.2% impurities.

Cobalt in the form of cobalt sulphate is added to the nickel sulphate solution in such an amount that the Ni:Co is approximately 40:1 on a weight basis. It was discovered¹ in 1925 that the addition of cobalt improves both the capacity and the life of the positive active material.

Stock solutions of caustic soda and nickel sulphate are fed, via a vortex type mixing vessel, into the reaction tank and the mixture recirculated until the precipitation of the nickel hydroxide is complete. The slurry formed is pumped into open settling tanks and the supernatant liquid removed. The deposit in the tank is then pumped to a filter press to remove as much liquid as possible.

After pressing, the material is withdrawn in the form of a green cake and loaded into ovens for air-drying at 80-90°C, from which it emerges as dark green crystals.

Nickel hydroxide has a low electrical conductivity and flake graphite is added to improve the conductivity.

In the final form the positive plate active material consists of nickel hydroxide, containing up to about 5% of cobalt hydroxide and up to 20% of graphite, generally in the form of both powder and flake in the ratio of about 2:1. The physical condition of the material is critical, both the precipitation of the hydroxide from the sulphate solution and the subsequent operation are devised to produce a material with the correct flow and cohesive properties for electrode manufacture and to ensure a large surface area. Strict control is exercised over the various conditions e.g., purity of the solutions, temperatures and concentration.

1.5c Negative Active Material.

The preparation of the negative active material is usually carried out by the dry-mixing method.

The old method originated by Estelle² was the co-precipitation reaction and in this the active material was electrolytically precipitated in a spongy form, in a series of electroplating baths, from a solution containing Cd, Fe and some Ni ions

In the dry-mixing method the starting material is cadmium oxide. This then undergoes a hydration reaction to form the

hydroxide via a number of solution and solid phase reaction stages. The cadmium hydroxide slurry is extruded on a moving belt and dried in an oven for 1 hour at 120°C.

Finally the dried "cake" is transferred to a sifter grinder where it is ground. Iron oxide, graphite and PVA are then added in the required proportion to improve the physical and electrochemical properties. The iron oxide is added to prevent agglomeration of cadmium-cadmium hydroxide during cycling with a similar effect from PVA. Small amounts of graphite and paraffin are added to assist briquetting as well as initial conductivity.

The final formulation contains some 80% cadmium hydroxide, 16% iron oxide, 2% graphite and the rest PVA and paraffin. The particle size is designed to suit electrode manufacture with good flow properties.

1.5d Electrolyte.

The electrolyte is a 26.67% solution of potassium hydroxide (80%) and lithium hydroxide (55%). The proportion of KOH and LiOH are varied according to the type of cell.

a) Vented cell - KOH - 25%; LiOH - 1.67%

b) Sealed cell - KOH - 23.4%; LiOH - 3.33%

As the overall charge and discharge reactions result in the transfer of a relatively small amount of water between the electrolyte and the active materials of the plate, there is no significant change in specific gravity related to the state of charge of the battery.

Vented cells are not damaged by continuous overcharge, but unnecessary high rates of charge increases the water consumption and therefore maintenance in keeping the electrolyte level topped up.

The electrolyte normally has a density of 1.2g/ml. It is based on the knowledge that the cells become sluggish when the density is below 1.15g/ml and above 1.3g/ml the cycle life of the cells is impaired.

Electrolyte with a density of 1.2g/ml freezes at -27°C . Therefore for the Ni-Cd batteries used at low temperatures the density is increased to 1.25g/ml.

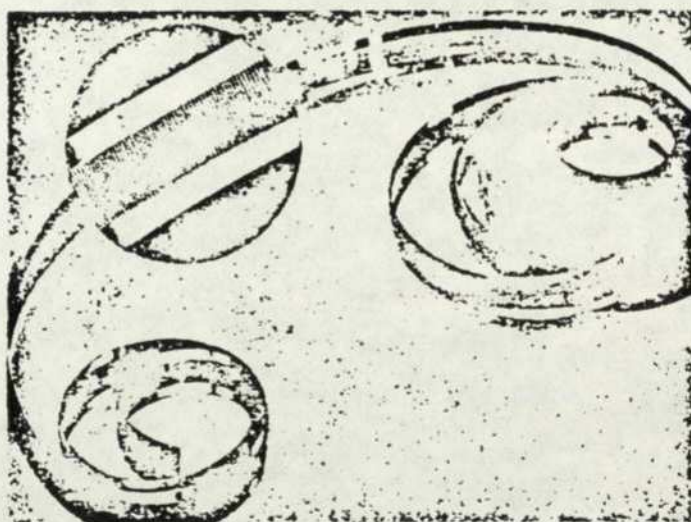
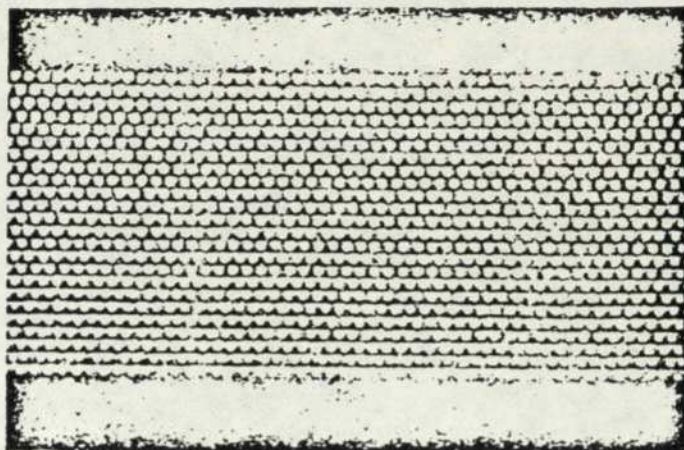
LiOH is added to improve the cycle life of the positive active material especially at high working temperatures.

1.6a Production of Ni-Cd Pocket Plates.

The basic principle³ of plate construction is the same for both positive and negative plates. They consist of pockets made from finely perforated steel strip, filled with the appropriate active material.

The first stage in plate making is to perforate the steel strip. This strip is made of low-carbon mild steel, 0.1mm thick and either 16mm or 24mm wide. The ribbon is perforated by passing it through a machine where rows of hardened steel needles punch small, circular holes in the ribbon. Only the centre part of the strip is perforated, leaving two plain edges, as shown in Fig.1.4.

Figure 1.4 The Finely Perforated Steel Strip From Which
the Pockets Containing the Active Materials
are Built Up



A plate used for high performance duties would have a larger open area than one used for low rate duty. The open area is generally about 12-18%. Moreover the new UHP range has an area of 25%.

After perforating, the steel ribbon is nickel plated, in order to avoid attack on the iron, which otherwise takes place when the ribbon is subjected to anodic oxidation during overcharge, which produces ferrate ions (detrimental effect on the positive electrode).

The next step in the manufacture is that two coils of the ribbon are attached to the platemaking line for filling the pocket with the active material. The platemaking line is equipped with either;

Briquetting machine - this presses briquettes (rectangular shaped strips of active material) with a length of normally 125mm, or

A powder filling machine - this continuously feeds active material between the strips.

As the first coil of ribbon is fed into the machine it is formed into a channel section by rollers. Passing under a hopper the loose powder is fed into the ribbon, or the briquettes formed continuously by the briquetting machine are placed accurately in the strip by an operator.

The second coil of ribbon is also formed into a channel section, which is now fed on top of the first to enclose the active material. Passing between further forming rolls, the

edges of the two strips are crimped together to form long, continuous pocket.

The crimping is not completely closed so that the required number of filled strips can be laced together by means of the partly open crimped edges (Fig 1.5).

The band of laced strips are then passed through a roller which partially compresses the filled strips and the newly pressed plate piece is then cut into the required lengths.

Both cut edges of the plate piece are enclosed by beading (steel strips formed into a U-section). The top corners of the beading are joined to a plate lug by spot welding (see Fig 1.6).

After spot welding, the plates are taken to a press of 800 tons capacity which, apart from pressing the plate into a homogeneous whole, imparts a profile onto the plate which not only strengthens the plates but provides locations for separator pins.

1.6b Cell Assembly.

The first operation of cell assembly is to group together the required number of plates of the same polarity onto a bridge or group bolt with spacing washers in between them. The bridge or group bolt also carries the pole bolt. Negative and positive plates are then interleaved so that plates of opposite polarity are adjacent to one another. The insulating rod separators are inserted by hand together with edge separators which fit on the beading of the plates to prevent short circuits.

Figure 1.5

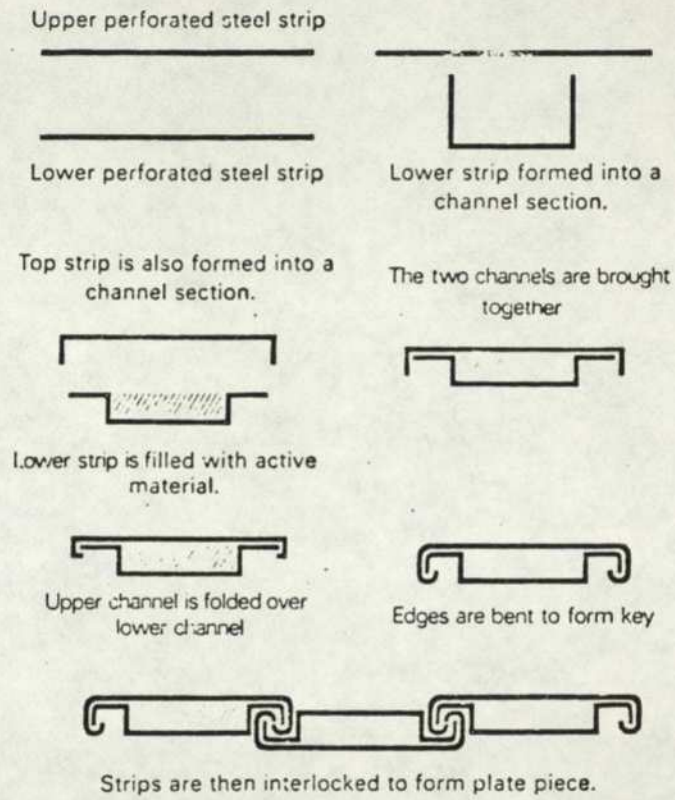
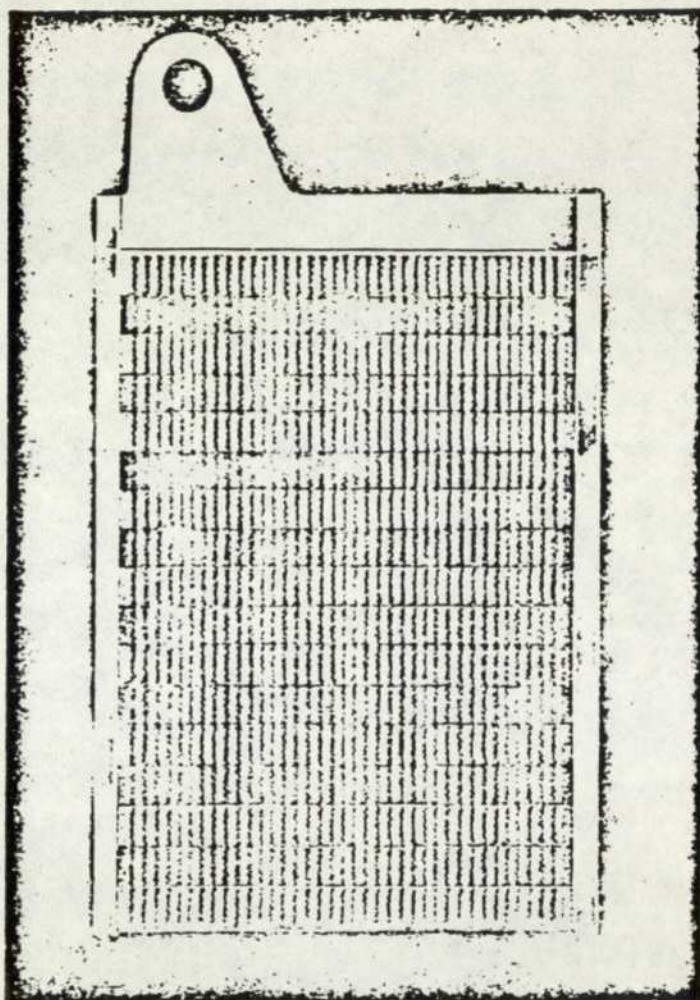
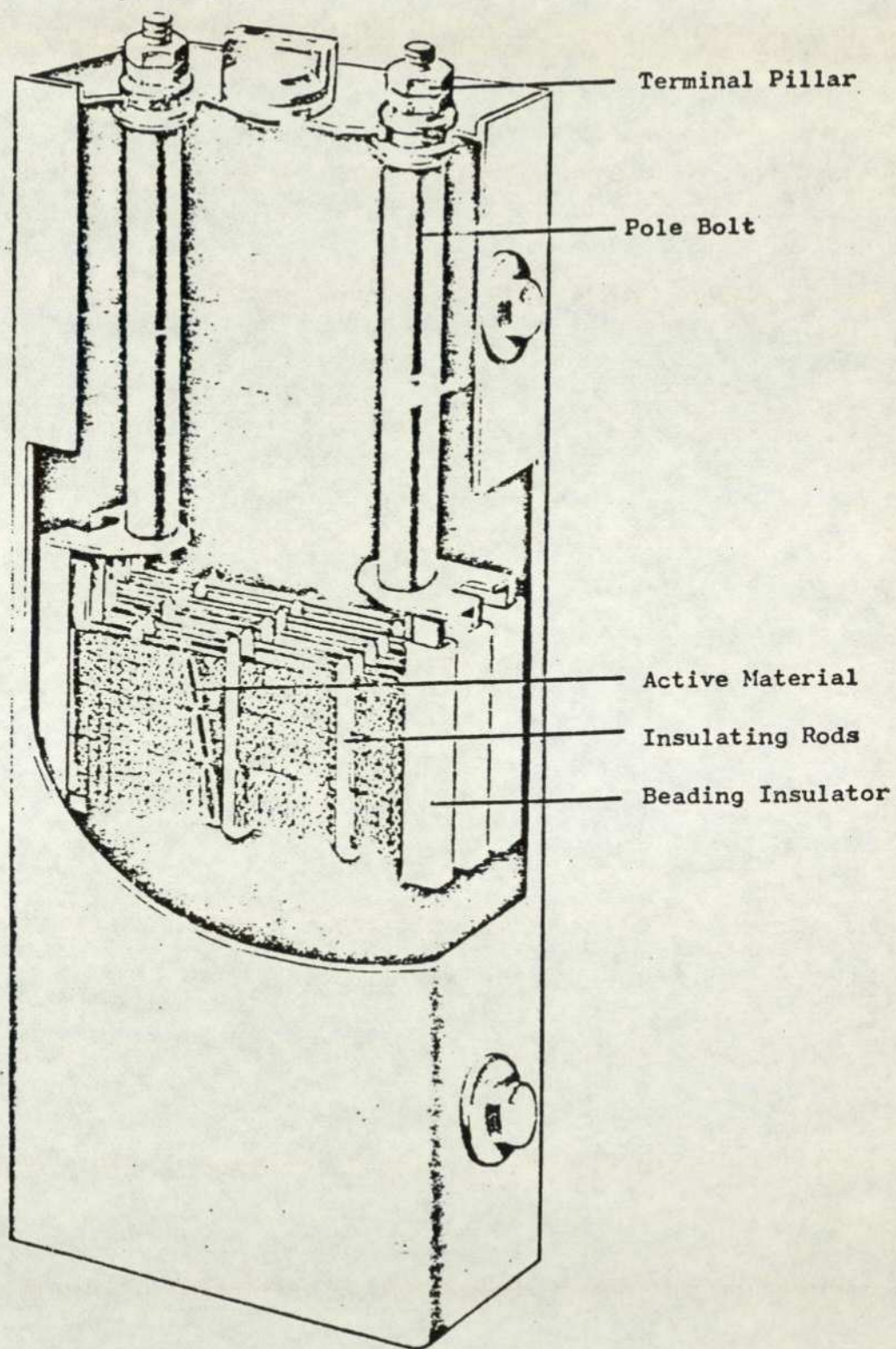


Figure 1.6 A Typical Plate Showing the Finely Perforated Envelope which Completely Encloses the Active Material



Above. A typical plate showing the finely perforated envelope which completely encloses the active material.

Figure 1.7 Cut-Away Section of a Typical Alcad Vented
Steel Cell.



(Where the internal resistance of a cell is not critical, perforated sheet separation is used). The plate complex, referred to as a group is then formed.

1.6c Formation Cycle.

The formation cycle consists of submerging the cells into 1.200 s.g. KOH electrolyte solution and subjecting it to several charge/discharge cycles.

The formation procedure is carried out for the following reasons:-

- a) It removes unwanted impurities e.g. SO_4^{2-} , CO_3^{2-} etc.
- b) The active materials in the plates are brought to a fully active condition during the formation process.
- c) The correct charge balance, which is especially important in the sealed cells, between the negative and positive plates is produced during the formation cycle (this involves a reversal after the third discharge) and ensures that there is a charge surplus on the negative electrode.

After formation, the group is then assembled by inserting into the cell container which may be steel or plastic material and the terminal glands, nuts and lids fitted (see Fig 1.7).

It is then filled with lithiated electrolyte. Cells are then given a C/5 capacity check, followed in selected cases by a quality assurance performance check.

CHAPTER 2

LITERATURE SURVEY AND OBJECTIVE OF THE PROJECT

LITERATURE SURVEY AND OBJECTIVE OF THE PROJECT.

2.1 Electrochemical Reactions.

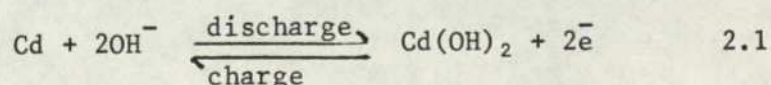
The mechanism of reactions of the cadmium and nickel hydroxide electrodes have very different characteristics.

The nickel hydroxide electrode operates via a solid phase mechanism, involving divalent (discharged)nickel and higher valencies than three (charged form). As no metallic phases are involved in the reaction, the mechanism differs intrinsically from that of the cadmium electrode.

The cadmium electrode reaction consist basically of an active-passive transition mechanism, with a passivation film, $\text{Cd}(\text{OH})_2$ being formed on the surface at more anodic potentials.

The mechanism of anodic oxidation of cadmium metal and cathodic reduction of the oxidation product in strongly alkaline solutions is of interest in understanding the behaviour of the cadmium electrode in nickel-cadmium batteries. In spite of much effort in recent years by a number of investigators, the reaction mechanism is still incompletely understood. For example, two radically different mechanism have been proposed in the literature for the anodic reaction: the dissolution-precipitation mechanism⁴⁻¹¹ and the solid-state oxidation mechanism involving ionic transport through the $\text{Cd}(\text{OH})_2$ film¹²⁻¹⁴.

The overall reaction at the cadmium negative electrode is:-



The theoretical equilibrium potential¹⁵ is -0.809V at 25°C in unit activity OH^- , when measured from a standard hydrogen electrode (S.H.E.). At 30% KOH concentration, the equilibrium potential calculated from vapour pressure measurements was found to be -0.851V vs S.H.E.¹⁶ or -0.899V vs Hg/HgO .¹⁷ Actual measured values are within 10mV of those predicted by theory. The isothermal temperature coefficient of the reaction is $-1.014\text{mV}/^{\circ}\text{K}$ ¹⁵.

It is interesting that the nickel positive and cadmium negative potentials partially compensate for changing electrolyte concentration, although the cadmium negative electrode is more sensitive changing 12mV between 20 percent and 30 percent KOH concentration.¹⁶

The potential of the nickel positive electrode changes significantly with state-of-charge. The cadmium negative electrode potential, on the other hand changes little, being quite flat for both charge and discharge. Thus under typical conditions, most of the potential change with state-of-charge is caused by phenomena at the nickel positive electrode, rather than at the cadmium negative electrode.

Overpotential at the cadmium negative electrode is relatively small, being around 60mV during charge and 15mV during discharge at $C/2$ rate, plus small overshoots at the beginning of both charge and discharge¹⁷. By contrast, the total overpotential at the nickel positive electrode is about twice that at the cadmium electrode. One reason for this difference is that the nickel electrode reaction requires water absorption during discharge and water release during charge, resulting

in significant concentration polarisation, whereas no water is exchanged in the reaction at the cadmium negative electrode. Both electrodes have high exchange currents ($5\text{--}58\text{mA cm}^{-2}$) and thus have good high-rate capability¹⁸.

2.2 Soluble Intermediates.

The soluble intermediates generated in the transitions between cadmium and cadmium hydroxide have not been adequately determined. Metallic cadmium has essentially zero solubility as Cd^{+2} in KOH solutions¹⁹. However, cadmium does form hydroxide complexes which are slightly soluble. It is this solubility that makes the electrode function, but as a result of it, the electrode undergoes morphological changes that reduce cycle life of cells.

Cadmium hydroxide solubility has been measured by many investigators^{20,21,22,23,24,25}. This solubility is small, being only about 15 milligrams per litre at 20°C , 6M KOH. Solubility increases with temperature, concentration and carbonate ion content. Harivel's transient data on solubility²⁰ shows that at 6M and 20°C the time constant (63% complete) is about $1\frac{1}{2}$ hrs.

Attempts to identify the species in the electrolyte have not produced clear answers. One important discovery was that after passivation by the underlayer and the onset of oxygen evolution, the radicals $\text{O}_2^{\cdot -}$ (superoxide) and O_3^- (ozonide) appear²⁶. It is hypothesized that these radicals are derived from the underlayer, perhaps CdO , during oxygen evolution, while the underlayer dissolves into a soluble complex which then forms

cadmium hydroxide. Precisely what all the species and intermediate reactions are is not known. One unidentified species was found in solution by ESR analysis²⁶.

The predominant soluble complex is generally thought to be either $\text{Cd}(\text{OH})_3^-$ or $\text{Cd}(\text{OH})_4^{2-}$. Ryans et al.²⁷, using a colorimetric method based on the measurement of fluorescence, tested the solubility of cadmium hydroxide with changing hydroxide ion concentration. They found that $\text{Cd}(\text{OH})_4^{2-}$ predominated at high electrolyte concentrations, and CdOH^+ predominated at low concentrations. They also found $\text{Cd}(\text{OH})_2$, soluble $\text{Cd}(\text{OH})_2$ and very little Cd^{2+} .

In tests with cadmium amalgams using a sitting-drop electrode and a hanging drop electrode, Armstrong et al. obtained $\text{Cd}(\text{OH})_4^{2-}$ early in anodization before passivation occurred²⁸. Further proof that there is a dissolved intermediate species was produced by Okinaka²⁹ who used a ring-disk method. He thought that the intermediate is $\text{Cd}(\text{OH})_3^-$, agreeing with the arguments of Milner and Thomas¹⁷.

Gilman and Sangermano collected absorbed cadmium ions on a platinum-catalysed oxygen electrode in 1M KOH³⁰ even though Ryans et al. had shown that there are very few free cadmium ions in solutions having such concentration²⁷.

Visco and Sonner, using a polarographic technique, concluded that $\text{Cd}(\text{OH})_3^-$ is the principle soluble species²⁵.

Hampson and Latham, in testing cadmium electrodes in NaOH solution using a.c. impedance and double pulse galvanostatic techniques, found that the charge transfer is very

rapid¹⁸. They also determined that the active area of the surface is reduced with time during anodization, and suggested that their observed impedance increase is caused by blockage.

Armstrong et al. in testing sintered-plate cadmium electrodes, found no electrochemical differences between them and smooth cadmium plated electrodes³¹. The dissolved species they obtained during the initial part of the anodization was $\text{Cd}(\text{OH})_4^{2-}$, in agreement with their previous work²⁸.

MacArthur, in experiments in which mass transfer was by linear diffusion only³², found that the anodization of cadmium occurs by dissolution, followed by a homogeneous reaction in competition with precipitation. His KOH concentration was only 3.3 molal, however.

Lake and Goodings¹⁹ have pointed out that the data of Latimer³³ show that no appreciable concentration of cadmium can exist as Cd^{2+} in basic solutions. These authors determined the concentration of cadmium ion in solutions of cadmium hydroxide and potassium carbonate in contact with solid CdO , $\text{Cd}(\text{OH})_2$ and CdCO_3 , using a polarographic technique. The amount of cadmium ion in solution was shown to be strongly dependent on the concentration of the complexing agent and the temperature of the solutions. The co-ordination number of the cadmium ion was determined by studying the dependence of the half-wave potential, $E_{\frac{1}{2}}$, on the activity of the complexing ion and the data were consistent with the major cadmium - containing species being $\text{Cd}(\text{CO}_3)_3^{4-}$ in solutions of potassium carbonate and $\text{Cd}(\text{OH})_4^{2-}$ in potassium hydroxide solutions. In mixed

hydroxide-carbonate solutions, it was clear from the data that the hydroxide complex would predominate.

The work of Lake and Goodings is difficult to interpret rigorously since saturated calomel was used as the reference electrode in the polarographic wave determination and, although estimates were made of the resulting liquid-junction potentials, the possibility of large errors in these estimates makes the data less satisfactory.

Dryssen and Lumme³⁴ have studied the extraction of Cd^{2+} from aqueous solutions using long-chain amines in benzene. The data they obtained suggest that the cadmium - containing species is $\text{Cd}(\text{OH})_4^{2-}$ over the pH range 9-13.

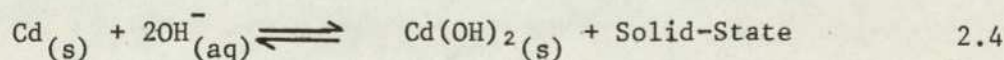
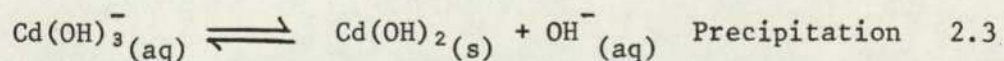
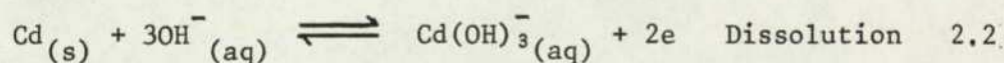
Gayer and Woontner²⁴ studied the solubility of $\text{Cd}(\text{OH})_2$ in dilute perchloric acid and sodium hydroxide solutions by spectrophotometric method. These authors found that the solubility of $\text{Cd}(\text{OH})_2$ showed a minimum for solutions between 10^{-4} and $10^{-2} \text{ mol l}^{-1}$ in sodium hydroxide. This effect was attributed to the production of the species $\text{Cd}(\text{OH})^+$ at low hydroxide concentration.

In a study of the hydrolysis of Cd^{2+} using a potentiometric method, Marcus²⁵ showed that a polynuclear species was formed and thus, from the evidence available, it must be taken that Cd^{2+} exist in the form of the four - co-ordinated hydroxy - complex $\text{Cd}(\text{OH})_4^{2-}$ in solutions containing an appreciable concentration ($>1 \text{ mol l}^{-1}$) of hydroxide ion.

2.3. Phases Formed on the Cd Electrode and the CdO Film Question.

The question of whether or not passivation is caused by a film of CdO is not entirely academic, for a better understanding of how the electrode works will help to improve the electrode efficiency. If a CdO film is found to be responsible, then research might emphasize more the chemical aspects, including detailed reactions and effects of impurities. If passivation is caused by Cd(OH)₂ blocking the underlying cadmium metal, then more emphasis would be expected on optimisation of electrode structure and on impregnation or forming methods that give the desired geometry of active material.

Much effort has gone into studying the detailed electrochemical reactions at the cadmium electrode. However, the intermediate reactions for equation (2.1) are still obscure, and our knowledge of the mechanisms for the formation of anodic films on solid cadmium is inadequate. The electrode does passivate on oxidation (discharge) due to some type of film formation in which a soluble intermediate is clearly involved, with solid-state reactions also occurring (2.2 - 2.4).



The main questions are:(1) What is the mechanism by which cadmium metal ceases to be anodically oxidizable after a period of active oxidation? Possibly CdO forms between the metallic cadmium and the cadmium hydroxide. (2) What are the important soluble intermediates? Answers to these questions, especially the first one, are important, for if the onset of passivation can be delayed, then the negative plates can be more efficiently utilized. The literature gives conflicting answer to both questions.

The idea that a cadmium oxide film is formed, possibly as a precursor of the dissolved species, occurred in 1900 to Edison who suggested the existence of Cd₂O film (British Pat 20960). The CdO film was postulated in 1928³⁶. Cadmium suboxide Cd₂O is green, and this colour has not been observed on cadmium electrodes, whereas the brown colour of CdO has occasionally been observed. No recent mention has been made of either Cd₂O on electrodes nor of the other oxides - Cd₄O or cadmium peroxide which has a composition ranging from Cd₅O₈ to Cd₃O₅^{37,38}.

If a CdO layer does exist, it appears to be limited to only a few monolayers. The following are the results from major investigations on the existence of a CdO film.

i) Falk obtained x-ray diffraction patterns from cadmium electrode, at various states of charge, immersed in electrolyte³⁹. He observed no CdO diffraction patterns, indicating that if CdO were present it would have been in its amorphous conditions. He also heated a cadmium electrode to create CdO, then added

KOH, while monitoring with x-ray diffraction. Prior to adding KOH, the electrode colour was yellowish brown, the acknowledged colour of CdO and CdO diffraction lines were seen. Adding KOH changed the colour to the greyish-white colour of Cd(OH)₂, and the CdO diffraction lines weakened within a few seconds. He concludes that if CdO is present as the original anodic species, it is transferred directly into Cd(OH)₂ by the electrolyte. Thus, Falk proposes that cadmium is transformed directly to cadmium hydroxide during anodization.

ii) Yoshizawa and Takehara x-rayed cadmium electrodes and, like Falk, found no indications of CdO in the diffraction patterns^{10,40,41}. With electron diffraction, however, they observed diffuse lines from CdO. It has been pointed out, however, that since solutions saturated with CdO were used in this work, there is a reasonable possibility for the CdO to crystallise out prior to the electron diffraction measurements²³. Repeating Falk's experiment, adding electrolyte to an electrode covered with CdO, they obtained similar results with the added finding that it takes a long time for CdO to change to Cd(OH)₂ if the electrolyte is weak in concentration. Their conclusion, not fully substantiated, was that cadmium oxidises anodically to cadmium hydroxide through an intermediate believed to be cadmium oxide, which is very unstable in KOH solution.

iii) Lake and Casey, based on the analysis of overpotential decay curves, proposed a model of an oxidising cadmium electrode with a CdO layer covering the cadmium metal^{42,7,8} the model consisting of cadmium metal, a layer of CdO, a highly

polarised inner double-layer in which the reaction $\text{OH}^- \rightarrow \text{O}^{2-} + \text{H}^+$ takes place, and then the Hemholtz double layer next to the free electrolyte. Their evidence indicates that the CdO film converts to $\text{Cd}(\text{OH})_2$ during open circuit.

iv) Armstrong, et al., formed anodic coatings on single-crystal and polycrystalline cadmium and electropolished single-crystal cadmium. They examined the coatings by glancing-incidence electron diffraction and by electron microscopy. They found no evidence of CdO and concluded that if it is present, it must occur as a thin amorphous layer⁴³

v) Breiter and Vetter studied smooth cadmium electrodes at constant potential⁴⁴, the investigation being aided by electron microscopy, infra-red spectroscopy, and x-ray diffraction. They found that the total amount of hydroxide decreases with potential and that at overpotentials of over 0.1V the amount of hydroxide is smaller than what would correspond to 100 per cent efficiency of cadmium hydroxide formation. This deficit is attributed to the simultaneous formation of amorphous CdO. X-ray diffraction patterns of the film did show traces of CdO lines, so they concluded that the oxide must be present in a largely amorphous form, and that the nature and growth of the amorphous CdO is controlled by a solid-state transport process. They also concluded that thick films of CdO, when anodically formed, convert into β -type cadmium hydroxide only very slowly.

vi) Devanathan and Lakshmanan, in experiments on smooth cadmium foil, determined that $iT^{\frac{1}{2}}$ varied linearly with i at low discharge current densities, and was constant at high current

densities¹¹. T is time for passivation at constant discharge current i . This relationship is consistent with a dissolution-precipitation mechanism in which the passivation step is the formation of an electronically conducting monolayer of oxide. The active intermediate in the passivation reaction is proposed to be Cd(OH)^+ .

vii) Croft, using cyclic voltammetry and constant potential, found that the rate of oxidation was a monotonically increasing function of the overpotential, and after a sufficient time has elapsed, the rate of oxidation follows a parabolic growth law¹². His results did not require postulation of a cadmium oxide phase, but could be explained by a mechanism in which the growth of the Cd(OH)_2 film was controlled by transport of mass and charge through the hydroxide layer.

viii) Okinaka, using a rotating ring-disk electrode, found evidence indicating that passivation is not the result of complete blocking of the cadmium metal surface with Cd(OH)_2 crystals, but rather is due to the formation of a thin, continuous film of CdO over metallic cadmium²⁹. His microscopic observation of the passivated surface showed the coverage with crystalline products to be incomplete. With an oxygen-saturated electrolyte at potentials that are normally passive to the anodic process, he observed reduction of oxygen actually occurring. This could not happen if the surface were completely covered by Cd(OH)_2 , but it can be explained by a thin film of CdO of high electrical conductivity next to metallic cadmium with Cd(OH)_2 crystals imbedded in the CdO film. He considered this CdO film

responsible for passivation, and it appeared to be insoluble or only very slowly soluble in an alkaline electrolyte.

ix) Ohse experimented with interrupter measurements, concluding that $\text{Cd}(\text{OH})_2$ is formed first and later partially dehydrated to form a CdO layer between the cadmium metal and the hydroxide⁴⁵.

x) Huber, in test with sodium hydroxide electrolyte, found CdO indications in X-ray diffraction patterns, accompanied by a brown colour characteristic of CdO ⁵. He claimed even stronger evidence of CdO in a sodium carbonate electrolyte. If in fact CdO film forms more easily with carbonate present, then an important discovery has been made, for commercial nickel-cadmium cells always contain carbonate.

xi) Jost claims experimental evidence for CdO ²¹. If in a galvanostatic technique the electrode is held at the hydrogen potential, then under certain circumstances, the zeta potential rises to the cadmium oxide potential and then drops.

xii) Will obtained a passivation film with a brown colour suggesting CdO , but had no special evidence for specifying either $\text{Cd}(\text{OH})_2$ or CdO as the cause of passivation⁴⁶.

xiii) Casey and Gardner withdrew samples of electrolyte from near the cadmium anode and quickly froze them in a liquid nitrogen to stop any hydrolysis, hydration or protonation which could occur after anodic treatment ceases and during manipulation of the wet sample. After anodic oxidation, they found O_2^- predominating at 25°C and O_3^- predominating at 40°C ²⁶. Thus,

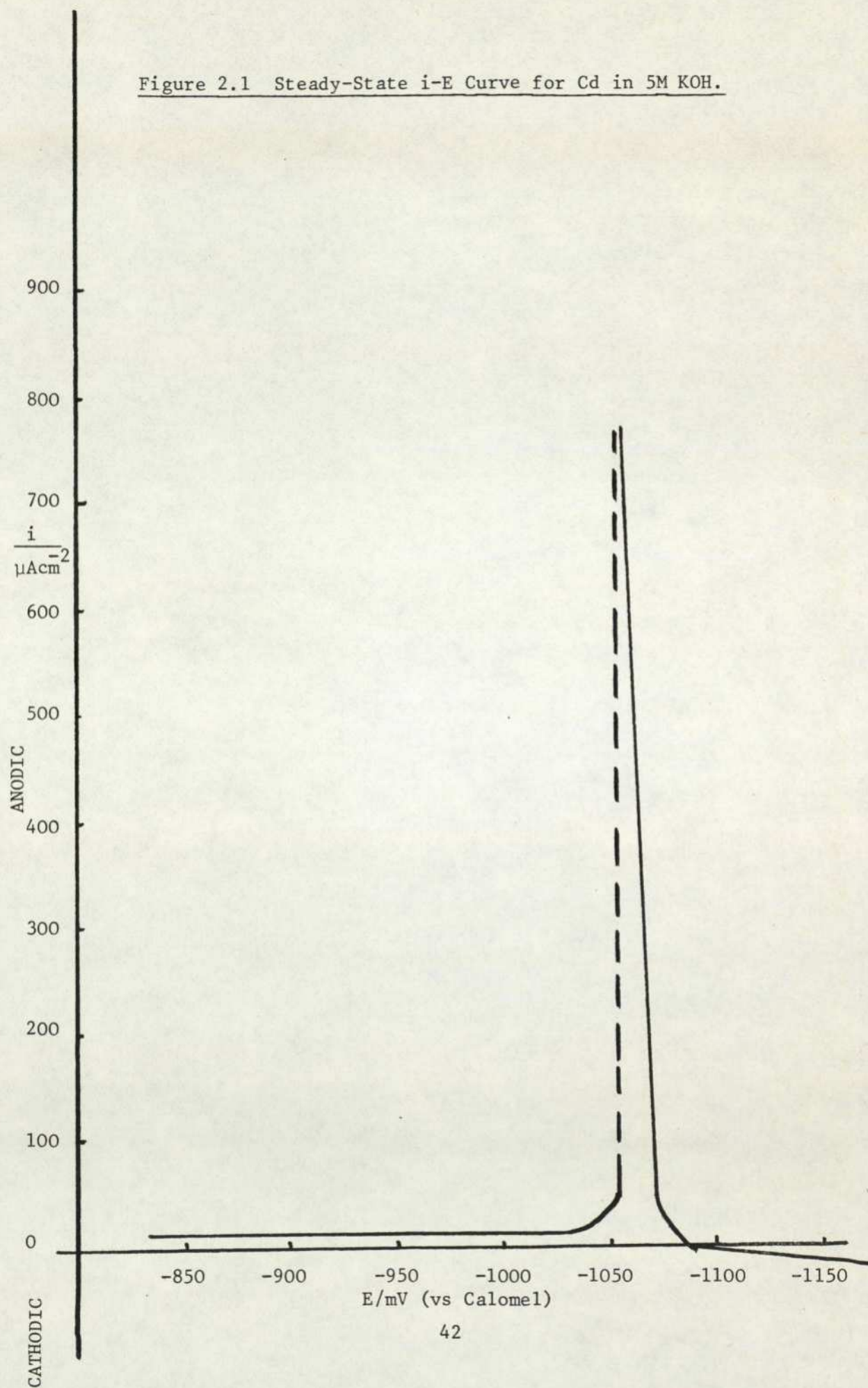
the glassy underlayer appears different at different temperatures. Furthermore, they found an absorption peak representing a second anodic reaction product of cadmium, but the species is not defined. They argue that the appearance of $\beta\text{-Cd(OH)}_2$ at high temperature and $\gamma\text{-Cd(OH)}_2$ at lower temperature is coincidental, and that it is the character of the surface states of the elusive and dynamic "CdO" underlayer beneath the Cd(OH)_2 that determines which of the two oxide species is produced.

xiv) Armstrong and West view passivation as caused by the formation of a layer of $\beta\text{-Cd(OH)}_2$ since there is only one discontinuity in the voltage-current curve (Fig 2.1), and this occurs close to the $\text{Cd}/\beta\text{-Cd(OH)}_2$ potential where it is thermodynamically "impossible" for CdO to be present on the electrode surface⁴⁷. They conclude that active dissolution occurs prior to film formation, which occurs through a solid-state mechanism.

xv) Milner and Thomas calculate that an overpotential of at least 36mV is needed to produce CdO¹⁷. Since such high departures from the reversible potential do not happen often, they claim that it is thermodynamically impossible for CdO to form under conditions that occur in the operation of cells. It should be noted that Ohse has presented a thermodynamic argument concluding that the formation of CdO is possible by a chemical process⁴⁵. Casey also claims CdO may be thermodynamically possible⁴⁸.

xvi) Azim and El-Sobki investigated anodic passivation of cadmium in NaOH ⁴⁹. At sufficiently high overpotentials, they obtained a film growth on exposed metal parts which they

Figure 2.1 Steady-State i -E Curve for Cd in 5M KOH.



took to be CdO. They consider the Flade potential to be the important threshold for formation of CdO.

xvii) Breiter and Weininger⁵⁰ have suggested the existence of a thin amorphous layer of CdO, formed next to the electrode, on the basis of results obtained by voltammetric measurements with superimposed a.c. This suggestion is difficult to check, although it should be noted that the work of Armstrong et al.,^{4,3} shows that at low anodic overpotentials, both Cd and Cd(OH)₂ could be seen by electron diffraction measurements, which necessitates that any amorphous layer must be thin, otherwise the Cd diffractions would be obscured.

Therefore, it is clear that some type of thin, passivating film is formed during discharge of the cadmium electrode, but it cannot be positively identified as CdO. One possible reason why experimental proof of CdO has been elusive is the evidence that the passivating film quickly converts to Cd(OH)₂ during open circuit⁷. Experimental techniques that permit in situ examination of composition, structure, and properties of the film are required to settle this point.

As discussed in the review by Armstrong et al.^{2,3}, β -Cd(OH)₂, γ -Cd(OH)₂, and CdO can be present in anodic films on Cd and these materials have different structures. The term β -phase is commonly used to describe both the poorly crystalline α -phase^{2,3,51}, precipitated initially in alkaline solution, and also the well crystallised β -phase having defined lattice parameters ($a_0 = 349.6$ and $c_0 = 470.2\text{pm}$)⁵¹. Both α - and β -Cd(OH)₂ belong to a hexagonal layer lattice system of the C6 type

(Brucite). It is in principle possible for the unstable α -phase to have a greater degree of hydration than β -Cd(OH)₂ and to exhibit a variable and increased interlayer spacing due to the presence of H₂O between the OH⁻ anion planes. Such structures are analogous to those of α - and β - Ni(OH)₂.xH₂O⁵².

Because of the inherent tendency of layer lattices to show differences in the stacking sequence between the layers a variety of secondary structures can be exhibited by the β -phase which shows differing conductivity and electrochemical properties, as discussed by Appelt^{53,54}. On the other hand, γ -Cd(OH)₂ has a crystal structure entirely different from the Brucite type^{51,55}. According to de Wolff⁵⁵, the γ -phase is monoclinic with four molecules per unit cell with lattice parameters of $a_0 = 567$, $b_0 = 1025$ and $c_0 = 341$ pm. Water is not required as an integral part of the structure as in α -Cd(OH)₂.

Bianchi⁵⁶, studied the anodic films formed on single crystals using a glancing-incidence electron-diffraction technique. The β -Cd(OH)₂ was found, in general, to be randomly orientated, though in a few cases weak spot patterns were obtained and were interpreted in terms of Cd(OH)₂ orientated such that its crystallographic axes were coincident with those of the Cd substrate. He was unable to correlate his electron-diffraction measurements with a simultaneous electron - microscopy study of the film.

Fleischmann, et al.,⁵⁷ in an investigation of the anodic behaviour of cadmium amalgams in alkaline hydroxide solutions, showed that the solid anodic phase formed is Cd(OH)₂, one-degree oriented with (0001) basal plane parallel to the substrate.

Armstrong, et al.,^{4,3} in a potentiostatic investigation of both polycrystalline and single-crystal cadmium, found evidence for the production of only β -Cd(OH)₂.

Both Breiter and Vedder^{4,4} and Okinaka and Whitehurst^{5,8} have demonstrated, using x-ray diffraction, the presence of monoclinic γ -Cd(OH)₂ in addition to the normal hexagonal β -phase in anodic products. The γ -phase is found to be most stable at low temperatures but appears to reduce more readily at both ambient and low temperatures.

Galushko, et al.,^{5,9} have re-examined the conditions under which CdO can be formed on a cadmium surface. It was shown that the colour of the anodized layer changed from light grey to black and then to yellowish black with increase in temperature, electrolyte concentration and current density. X-ray diffraction measurements were claimed to indicate that the yellow layer consisted of Cd(OH)₂ whilst the black layer contained both Cd(OH)₂ and CdO.

Continuing their previous investigations, Galushko and co-workers^{6,0} studied the reduction of heavily anodized films on Cd and concluded that the reduction process proceeded by a solid-state mechanism because of the invariance of the charging curves to stirring of the electrolyte.

Huber^{5,6,6,1} has identified the β -Cd(OH)₂ phase in thick anodic films on cadmium, but for thin films the existence of CdO is suggested. It should be noted, however, that Huber identified only two spacings due to CdO, one of which, the (200) plane with $d = 234.9\text{pm}$, lies very close to the (002)

plane of $\text{Cd}(\text{OH})_2$ and the (1011) plane of Cd^{43} .

The experiments of Winkler⁶² using a weighing technique, were repeated and extended by Falk³⁹, and it was suggested that the original data could just as well indicate the formation of the $\beta\text{-Cd}(\text{OH})_2$ phase rather than the CdO phase suggested by Winkler. It should be noted, however, that both authors ignore the possibility of a simultaneous dissolution reaction and assume 100% efficiency for film formation.

The i.r. spectroscopy work of Breiter and Vedder⁴⁴ shows traces of CdO only, but discrepancies between charge determinations and x-ray measurements lead these authors to suggest the existence of an amorphous layer of CdO . These discrepancies could well be due to the dissolution of cadmium.

To conclude, the presence of $\beta\text{-Cd}(\text{OH})_2$ in the anodic film is well established. There is also evidence that $\gamma\text{-Cd}(\text{OH})_2$ is simultaneously present to some extent. The evidence for CdO is much less satisfactory, and it is very doubtful from a thermodynamic point of view that formation of CdO rather than $\text{Cd}(\text{OH})_2$ would be favoured^{17,63}.

2.4 Passivation of Cadmium.

Passivation is the phenomenon by which a metal undergoing anodization does not continue to be oxidised even though the potential is adequate and the metal is not depleted. When cadmium is being oxidised at constant current, only a very small overpotential is required until the oxidation layers reach a depth of 100 to 1000 angstroms⁴², at which time the potential will

rise sharply in the negative direction and the current will go over almost completely into oxygen evolution. Then the metal is said to have then become passivated.

If the oxidation is carried out at constant potential, the electrode behaviour depends on whether or not the potential exceeds the potential of passivation. At potentials lower than the potentials of passivation, current density is low, but the discharge capacity is high⁶⁴. At potentials greater than the potential of passivation, current density is high and capacity is low, and the current decay with time is close to the theoretical $I = f(t^{\frac{1}{2}})$, which is indicative of film growth according to a parabolic growth law^{12,64}. Current-voltage sweeps always produce a high anodic peak^{7,64,47,12,29,49} showing an active region and a passive region due to film formation.

The fact that cadmium passivates on anodization (discharge) is important because it means that the electrode capacity limit is reached before all the active material is fully discharged. In a normally operating nickel-cadmium cell, the cadmium electrode is not fully discharged and so the passivation point would indicate the amount of cell capacity that is not being used and hence available as reserve. In some battery applications passivation occurs regularly, for example in a cell designed to be negative limited⁶⁵, in a cell that has unintentionally become negative limited, in a cell operating at low temperature, in high discharge rate applications and during cell reversal. If passivation could be delayed, then more of the active material could be utilised, and the energy density of the cell would be higher.

When cadmium is anodized (discharged) at constant current, the potential rise indicative of passivation precedes the evolution of oxygen. The overpotential gradually increases to about 0.9 volts, followed by oxygen evolution which typically is in the range of 80 to 100 per cent of theoretical gasging efficiency⁷.

The time to passivate is reported variously as (a) the time elapsed before an abrupt voltage change^{6,6}, (b) the time for a potential change of 0.4 volts¹⁴, or (c) the time to reach a relatively constant oxygen evolution potential⁷. The product of passivation time and discharge current is proportional to the amount of cadmium oxidised, and hence the discharge capacity of the plate. The discharge efficiency of the plate can be calculated from a comparison of the mass of the oxidised cadmium with the theoretical maximum.

The discharge capacity when passivation occurs is greatest under these conditions: (1) low current density, (2) optimum KOH concentration (or near-zero KOH concentration), (3) high temperature, (4) electrolyte contains K_2CO_3 and (5) optimum plate pore size and porosity.

The reason why CO_3^{2-} ions delay passivation is not understood but may be related to the fact that the product of discharge contains cadmium carbonate in addition to cadmium hydroxide. No explanation has been reported for the delay in passivation at high temperature^{14,66}. Gravity appears to have no significant effect on the passivation process, based on tests on planar electrodes in which electrode position was changed¹⁴.

If the discharge of a cadmium electrode is interrupted by open-circuiting before passivation, and later the discharge is continued, the net result is the same as if there had been no open-circuit period¹⁴. However, if a passivated electrode is open-circuited, it becomes depassivated and can sustain a small additional discharge. Apparently some of the passivating film is removed or changed to non-passivating film during stand⁷. Analysis suggests that the passivating CdO layer was converted during open-circuit to Cd(OH)₂, explaining why CdO has been detected only under carefully chosen conditions.

The capacity of a porous electrode depends upon the pore volume that is accessible to the electrolyte⁶⁷. Test of porous cadmium electrodes made by compressing cadmium dendrites⁶⁶ showed that with below-optimum porosities, passivation occurs when the void fraction reaches a critical minimum. This minimum void fraction increases with current density, being 0.32 for 8mA/cm² and 0.44 for 40mA/cm². The apparent cause is poor mass transfer in pores^{67,68,69,70}. Anodes with above-optimum porosities passivate when the volume fraction of metallic cadmium decreases to a critical value, this being apparently caused by low electronic conductivity of disruptions of structure, and by decreased surface area of cadmium particles.

Kang measured passivation time for planar cadmium electrodes at temperatures down to -60°C⁷¹. He correlated his data at low current densities by a linear dependance of $iT^{\frac{1}{2}}$ with i , where T is the passivation time at constant current density i . His correlation suggests that the low temperature limit is at the vitreous point, 165°K.

Insight into the passivation process internal to porous cadmium electrodes can be gained from experiments by Bro and Kang⁷². They examined the reaction profiles in compressed Cd powder electrodes at various current densities and have proposed an empirical equation to describe the polarisation behaviour. The overpotential was found to be very strongly dependent on current density.

Przybla, et al.⁶⁶, have similarly developed empirical equations relating discharge efficiency of the cadmium electrode at various temperatures to the current density, electrode thickness and anode porosity.

A passivation and electrode-inefficiency explanation that does not require the concept of a CdO film, proposes instead a film of $\text{Cd}(\text{OH})_2$ ³¹. Cadmium metal is first postulated to dissolve as $\text{Cd}(\text{OH})_4^{2-}$ which then precipitates as solid $\text{Cd}(\text{OH})_2$. As the discharge proceeds, the area of active cadmium is reduced both by its dissolution and by blocking of the electrode surface by $\text{Cd}(\text{OH})_2$. The overpotential increases until it is high enough for $\text{Cd}(\text{OH})_2$ to grow directly onto the cadmium. This film grows, and oxygen evolution starts when further film growth cannot be sustained.

Another possible explanation of passivation is that the cadmium hydroxide formed near the end of discharge has a high resistivity structure which hinders further discharge. This structure is hexagonal, but has no bridged OH^- groups, whereas the normal active cadmium hydroxide form has bridged OH^- groups⁵³. The high resistive form could occur locally where the OH^- ion concentration is low as a result of reduced porosity during discharge.

In summary, a rigorous explanation of passivation is not yet possible. Much of the evidence on passivation is indirect and can have more than one interpretation. A better understanding of passivation is important, for it is now a fundamental limiter of the efficiency of the cadmium electrode. Many of the experiments reported in the literature were based on cadmium electrodes that had been fully charged and fully discharged. Future investigations might well focus on the realistic operating regime of the cadmium electrode.

2.5 Ageing of Porous Cadmium Electrodes.

On charging sintered plate nickel-cadmium cells after storage for a few years, evidence of electrolyte leakage occurs⁷³. This had been due to premature hydrogen evolution from the electrode.

Scanning electron microscopy has been used to detect crystal growth of cadmium hydroxide negative active material which probably resulted in a decrease in active surface area. The difference in the crystal structure of a new cell and an aged cell has been quite marked. These changes appear to take place at the cadmium electrode and here recrystallisation has been found to occur such that the submicron particles of cadmium hydroxide in a fresh cell have enlarged to become rhombic crystals of greater than 10 μ m size in the stored defective cell. The crystal growth, though not homogeneous over the whole of the cadmium electrode, is sufficient to reduce the available electrochemically-active surface area.

Bramham, et al.⁷⁴, have examined the recharge behaviour

of both cadmium and nickel hydroxide electrodes removed from nickel-cadmium cells after storage (up to 5 years) in the discharged state. Scanning electron microscopy revealed considerable growth of hexagonal platelets of $\text{Cd}(\text{OH})_2$ on the electrode surface which increased in size progressively with time. In spite of this pronounced growth, galvanostatic measurements showed that little deterioration in charge acceptance at 20°C had taken place for partial charge inputs at the 1C rate. A decline in capacity at 20°C was noted however at very high charge rates (10 C). As expected the most noticeable deterioration in charge acceptance was exhibited where the $\text{Cd}(\text{OH})_2$ had been aged at 70°C and attempts were made to recharge the material at low temperatures (-20°C). The galvanostatic charge curves at 20°C for $\text{Cd}(\text{OH})_2$ showed little change after ageing apart from a less distinct demarcation between the end of charging and the onset of hydrogen evolution. At low temperatures (-20°C) pronounced cadmium nucleation overpotentials were observed such that electrodes reached H_2 evolution at the start of charge. Potentiostatic pulse experiments revealed no fundamental change in the mechanism of operation of the electrode.

Studies concerning the ageing of cadmium electrodes in silver-cadmium cells have been conducted by Papazova, et al.⁷⁵ According to these workers, after 12 months' storage at 20°C the metallic cadmium particles had increased in size by at least an order of magnitude from $10^{-4} - 10^{-5}\text{cm}$ to 10^{-3}cm . It is claimed that the same relative increase in size could be induced after only six month's storage at 50°C .

Further studies⁷⁶ at different temperatures showed that the cadmium metal content increased in size after $2\frac{1}{2}$ and 4 years, whereas the $\text{Cd}(\text{OH})_2$ crystallites showed no significant increase in size in the electrode interior.

The inclusion of antimony in the electrode structure leads to a reduction in the growth of cadmium during long periods of storage⁷⁷. Cyclic voltammetric studies concerning the presence of antimony in the electrolyte were considered to show improvements in reversibility of the charge-discharge processes (cf. studies by Kadnikova, et al.⁷⁸).

2.6 Charge and Discharge Behaviour of Porous Cadmium Electrodes.

Interest has been renewed concerning the cause of capacity loss by porous cadmium electrodes during cycling. Earlier studies, in particular those by Harivel, et al.⁷⁹, Salkind, et al.⁸⁰, Lifshin and Weininger⁸¹ and Breiter and Weininger⁶⁴ have indicated the importance which growth and redistribution of active material play in determining cycle life.

Harivel, et al.⁷⁹ in an extensive galvanostatic study of the sintered negative electrode discussed the efficiency of the electrode with reference to charge rate, electrolyte concentration and temperature. These authors suggested that the inefficiency on discharge was due to a limiting of the ionic diffusion by precipitated cadmium hydroxide. Crystals of non-oxidised cadmium metal existed within the pores of the sinter, the size of these crystals being a function of the previous charge-discharge history of the electrode. The area of the fully loaded sinters was estimated using an x-ray

technique as $8.3\text{m}^2\text{g}^{-1}$ of active material ($\text{Cd}(\text{OH})_2$). This was compared with an estimate of $7.8\text{m}^2\text{g}^{-1}$ of active material from a BET adsorption method.

Salkind, et al.⁸⁰ used a BET adsorption method to estimate the area of sintered plate electrodes. The authors obtained areas ranging from 1 to $13\text{m}^2\text{g}^{-1}$ of active materials for uncycled discharged electrodes. The large variation in area was found to decrease with cycling and was attributed to a redistribution of active material through the sinter. This redistribution was later shown by Breiter and Weininger using an x-ray technique⁶⁴, and these authors proposed that this redistribution was due to the existence of some soluble-soluble hydroxy-complex of cadmium.

Reed and McCallum⁸² have made a detailed investigation of sintered-plate cadmium electrodes cycled to various depths of discharge. Electrodes were examined by metallographic techniques and chemical analysis and capacity measurements in flooded electrolytes were made⁸³ to assess the relative charge and discharge efficiencies of active material. Greater loss of capacity were found at greater depths of discharge and greater cycle number and these were related to growth and redistribution of active material within the pore structure.

Barnard, et al.⁸⁴, using sintered plate electrodes have shown by chemical analysis that where the discharge rate is high (1C) the loss in capacity during cycling was due largely to inefficient utilisation of cadmium metal rather than to an inefficient charge process.

Later studies showed that when low discharge rates were used, thereby increasing the cycle time, recrystallisation of cadmium hydroxide could take place leading to a marked lowering in charge efficiency as determined by chemical analysis. The apparent independence of overall cycle efficiency on discharge rate, at a fixed high charge rate, observed previously⁸⁴ was due to an unexpected cancellation between the relative changes in charge and discharge efficiencies.

A failure mechanism, in line with that proposed earlier³¹ was considered to involve coverage of the cadmium surface by precipitated cadmium hydroxide which later induced a change in potential such that a passivating film formed directly on the surface by a solid state process.

The influence of the nickel structure on the performance of the cadmium electrode were investigated by Luksha, et al.⁸⁶ Sinters having a controlled pore diameter were prepared using a pore former. The best performance were from electrode having a pore diameter of $80\mu\text{m}$ and porosity of 80%. No correlation could be made between the sizes of the $\beta\text{-Cd(OH)}_2$ crystals at the electrode surface ($1\text{--}20\mu\text{m}$) and the pore diameter. This observation contrast sharply with that claimed by Will and Hess⁴⁶ for a simulated pore electrode where growth of $\beta\text{-Cd(OH)}_2$ is considered to be the main cause of capacity loss

Barnard, et al.⁸⁷ studied the growth and redistribution of cadmium and cadmium hydroxide in sintered plate electrodes as a function of charge rate and cycle number, using optical and scanning electron microscopy. The size of both cadmium and cadmium hydroxide was found to increase with increasing

cycle number and decreasing charge rate. On the other hand, high charge and discharge rates promoted greater aggregation and redistribution of active material towards the electrode edge. This was presumably caused by the greater non-uniformity of the reaction zones in the electrode at higher current densities.

Further studies⁸⁸ revealed that cadmium metal deposition can take place on top of conducting $\text{Cd}(\text{OH})_2$ (or CdO) crystallites confirming this process as a possible mechanism of active material occlusion.

Marek, et al.^{89,90} have similarly combined capacity, surface area, chemical analysis and electron microscopy measurements to study the influence of the impregnation process on the long-term cycling efficiency of sintered-plate cadmium electrodes. The electrodes were prepared by thermal decomposition of cadmium formate and their behaviour was compared with those obtained by impregnation with cadmium nitrate. Electrodes prepared via cadmium formate alone gave poor reproducibility on charge - discharge cycling owing to poor charge efficiencies arising from large CdO crystallites and shedding of the active material. Using scanning electron microscopy, electrodes prepared via the cadmium nitrate method showed that there was less tendency for $\text{Cd}(\text{OH})_2$ growth, suggesting a large number of nucleation sites.

Papazova, et al.⁹¹ have investigated the influence of the initial charge current density (formation process) on the subsequent cyclic charge - discharge behaviour of pressed CdO

electrodes for use in silver-cadmium cells. Chemical analysis revealed that the quantity of Cd produced during charging was about 95-98% after 2 cycles for changes in charge current density by over an order of magnitude. The utilisation of active material on discharge after the first cycle was in the range 57-63% and was relatively insensitive to discharge rate. After 15 charge-discharge cycles it was found that electrodes 'formed' at 0.2Adm^{-2} gave capacities of $\approx 50\%$ whilst those 'formed' at 0.8Adm^{-2} gave capacities of $\approx 70\%$. It was concluded that the improvements were related to the production of a more finely divided cadmium at high rates of charge, in agreement with other researchers.^{85,84,79} It is interesting to note that the changes in capacity after the initial fall are much less over 15 cycles than those observed by Barnard, et al.^{84,85}, and could reflect the obvious difference in electrode structure.

Casey and Vergette⁶⁷ have discussed the constant-current performance of a negative sintered electrode in terms of a physical model. The total charge delivered by the sinter was split into components, including charge available from the surface cadmium, charge available from cadmium lining larger pores and charge available from cadmium deeply buried inside the sintered matrix. These authors suggest that the capacity due to the deeply buried active material is not utilised except at the lowest discharge rates and thus the efficiency of the sinter could be explained in terms of the free pore volume available to the electrolyte. The pores of a sinter were characterised by defining a "choking index" which was small when the free pore volume was large and large when the free pore

volume was small. It was suggested that the amount of active material available for reaction decreased rapidly with increasing loading of the sinter.

In a more recent series of papers Dunning, et al,⁹²⁻⁹⁵ have developed a detailed model for the operation of electrodes involving sparingly soluble reaction products such as $\text{Cd}/\text{Cd}(\text{OH})_2$. Both solid-state (continuous-film) and dissolution-precipitation modes of electrode failure are considered. The dissolution-precipitation model takes into account the mass transfer limitations of soluble species and the changes in volume between the cadmium and cadmium hydroxide. The solubility of active material is shown to impose a practical limit on the mass transfer parameters. A mass transfer coefficient is defined which depends on diffusion rates and rates of crystallisation or nucleation of active material as well as the fraction of free cadmium surface. These workers also attempted the difficult task of taking into account the redistribution of active material within the pores during charge - discharge, a feature neglected in previous treatments.

Selanger⁶⁹ developed a model to describe the behaviour of porous electrodes at very high current densities. A one-dimensional pore model as used by previous workers was used to predict the shape of the overpotential - time transients at various current densities and the influence of electrode thickness and porosity. Electrode failure at low current densities was considered to be caused entirely by blockage of pores whilst at high rates mass transfer limitation was considered to predominate.

Armstrong, et al.⁹⁶ have studied sintered plate cadmium electrodes in alkaline solution using potentiostatic and galvanostatic techniques. The experimental measurements on the sintered plate electrode indicated that the behaviour is in many ways similar to that of the flat plate electrode. A mechanism for the discharge was proposed where firstly the active material dissolves as solution-soluble hydroxy-complexes ($\text{Cd}(\text{OH})_4^{2-}$) which may be reprecipitated within the body of the sinter as solid $\text{Cd}(\text{OH})_2$. As the dissolution proceeds the area of active cadmium is reduced either by direct dissolution of cadmium crystallites or by blocking of the surface by solid $\text{Cd}(\text{OH})_2$. Polarisation within the sinter increases until a potential is reached at the surface when a new reaction, the direct growth of a layer of $\text{Cd}(\text{OH})_2$ onto the cadmium becomes possible. This film grows at a rate determined by the current until sufficient current can be drawn from the reaction and then oxygen evolution must occur. The author suggest that the formation of this continuous insoluble film is the direct cause of the inefficiency on constant-current discharge of the porous electrode.

Because of the importance of the passivation during discharge, most of the research on the cadmium electrode has been related to the anodic processes. The cathodic charging process, by contrast, has received less attention even though the user usually has more control of charging conditions than he has of discharging.

One basic question is: Does the cathodic reduction occur

by a solid-state mechanism or is a solution phase involved? Okinaka showed that both mechanisms occur, the solid-state mechanism predominating at the start of the charge when there is little cadmium metal, and the solution - reduction mechanism predominating at the end of charge when there is much cadmium²⁹. This was confirmed by Will⁹⁷. Experiments in reducing cadmium oxide showed that electrolyte concentration plays a rôle, with solid-phase reactions predominating at low concentrations and combined solid-phase/solution phase reactions occurring at high concentrations as solubility increases²⁹.

The physical condition of the cadmium electrode, especially crystal size, is particularly important to electrode behaviour during charge. At the start of charge, with little exposed metal area for cadmium deposition, current density is high and overpotential can be high. During mid-charge, overpotential is low because there is plenty of cadmium metal surface area and cadmium hydroxide surface area available for the reaction. At the end of charge, the overpotential again increases because of less available $\text{Cd}(\text{OH})_2$. A high charge rate during most of the charging period, which can be accompanied by high overpotential, is advantageous in that it generates many nuclei, and hence many small cadmium crystals. At extremely high rates there is a risk of premature hydrogen evolution.

High charge and discharge rates and low temperature are effective in promoting small crystals^{79,58,98}, but cycling generally makes crystals bigger^{79,10,99}. Some cadmium hydroxide crystals crack at the surface⁹⁹, breaking down into smaller

ones during charge. Charge acceptance is highest if the cadmium hydroxide crystals are small at the start of charge, and if the preceding discharge was at a high rate and low temperature^{98,58}.

Low-temperature discharge produces $\gamma\text{-Cd(OH)}_2$ in addition to the usual $\beta\text{-Cd(OH)}_2$ ^{58,100}. The γ -form, having needle like crystals, is much more easily charged than is the β -form⁵⁸. "Inactive" and "active" forms of cadmium hydroxide have been reported at low temperature by Rubin¹⁰¹. These probably were the β - and γ -forms, respectively. Different potential plateaus reported for these two forms¹⁰¹, have not been observed by others⁵⁸. There is a possibility, however, that Rubin's "inactive" form is related to the high resistivity form noted by Appelt⁵³.

The fact that the γ -form is more easily charged is very significant⁵⁸. Discovering a way to generate $\gamma\text{-Cd(OH)}_2$ during room temperature discharge would substantially improve the performance of nickel-cadmium cells.

A low temperature effect not to be neglected is the high efficiency of the nickel positive plate, which reduces the effective negative-positive ratio. For example, the capacity of the cadmium electrode at -7°C is about 77 percent of its capacity at 21°C ⁷⁹. The nickel positive electrode, in contrast, has about 30percent more capacity at -7°C , making the negative-positive capacity ratio less for the lower temperature. Cells designed for low temperature require a greater amount of negative active material, and when properly designed have operated successfully

at -40°C and colder¹⁰²,

2.7 Benefits from Prevention of Crystal Growth by the Inclusion of Additives.

Though much of the experimental work on crystal growth at negative plates has been done with sintered-plate, the results apply also to pocket plates or any system in which cadmium is in contact with alkaline solution.

Many researchers have tried to improve the performance of the cadmium electrode by introducing foreign substances into the cell. However, the scope of their experiments and documentation of their results often was not complete enough for rigorous evaluation of the diverse effects of such additions. The added impurities may be gases, liquids or solids and the method of their incorporation can significantly affect the results.

Some additives or expanders as they are generally termed are beneficial, although they may also have undesirable effects. In general the beneficial additives are those that reduce the size of crystals formed on the cadmium electrode providing large area for the reaction. A useful additive must not increase polarisation or retard the reactions in any way, however.

Indium has been a successful expander in cadmium electrodes. It can be added during processing either as indium nitrate¹⁰³ or indium hydroxide¹⁰⁴. It improves high-rate performance at low temperature, and also somewhat at room temperature. The effectiveness of indium as an expander comes in part from its low solubility in KOH and its similarity to cadmium in axial ratio, ionic radius and electrode potential¹⁰⁴. Other research shows

that indium can be incorporated in the crystal lattice of cadmium oxide¹⁰⁵. Sweeping potential studies show that indium additions suppress the initial current peak associated with passivation, but introduce additional peaks of greater anodic potentials, thus delaying passivation¹².

Indium addition has also improved the energy density in nickel-cadmium cells. By improving the efficiency of the negative electrode during cycling, it has been possible to use relatively thick electrodes¹⁰⁶. On the other hand, one investigator said that he found no benefit from adding indium¹⁰⁷

Cobaltous ions increased the capacity of cadmium electrodes⁵³. The Co^{2+} ions form on the surface of cadmium hydroxide complex semiconductor - like compounds which show a catalytic activity between the positive and negative electrode during charge due to a redox reaction.

A french patent¹⁰⁸ relates to the addition to the negative plate of a sealed nickel-cadmium cell of "another body, potentially a metallic one, this body chosen in such a manner that its potential" is lower than the potential of the active material, but that preferably, its overvoltage with hydrogen in alkaline solutions is at least equal to and preferably higher than the overvoltage of the main metals of the electrode. The use of copper in a powder form or in amalgam with mercury is advised. Oxygen evolved on collapse of the negative would oxidise this addition of an auxillary metal.

Addition of nickel sulphate¹⁰⁹ to the cadmium electrode regenerate the electrode and reduce capacity loss. The addition

may be made to pure cadmium electrodes or cadmium with up to 1.5 percent iron, graphite and nickel flakes added.

The inclusion of nickel hydroxide, cobalt hydroxide or copper powder to cadmium electrodes in sealed cells¹¹⁰ enhances the anti-polar mass effect and undergo an electrochemical reaction which suppress the evolution of gas after the reversal of cells.

Many other inorganic and organic substances are used in various battery negatives. Most of them are patented and a list of some of them are given in Appendix 1.

Very little information is available concerning the use of organic additives to control the morphology of the cadmium electrode. Recently Udupa, et al.¹¹¹, have found that the discharge efficiency of the sintered-plate cadmium electrode is improved when quaternary ammonium compounds such as cetyltrimethylammonium halides are incorporated in the active material at the time of impregnation. The improvement in discharge behaviour was considered to be due to the smaller size of the active material present in the plate.

Gossenberger¹¹², made an evaluation of the behaviour of various cellulose and starch derivatives on the capacity of the cadmium electrode. It was tentatively suggested that growth of cadmium metal was inhibited by the additives.

Fleischer¹¹³ subsequently patented the use of cellulose ethers and derivatives such as CMC for reducing the fall in capacity of the cadmium electrode on cycling. More recently Solo'eva and Ryzhok¹¹⁴ mention the use of CMC and sunflower

oil. This paper deals mainly with the preparation of samples from porous cadmium electrodes suitable for transmission electron microscopy.

Acetate salts, when impregnated into both positive and negative plates, are claimed to improve charge retention¹¹⁵. This may result from lowered nitrate impurity levels or from different morphology because cadmium is precipitated as a metal in this process. It should be noted that cadmium electrodes impregnated in either cadmium chloride or cadmium acetate have lower utilisation and higher charging voltage than plates made from cadmium nitrate¹⁰².

Organic additives frequently interfere in the determination of surface area (c.f. difficulties encountered by Gossenberger¹¹²) and scanning electron microscopy provides a valuable method for assessing separately the growth of both cadmium and cadmium hydroxide.

Another important additive to the negative electrode is polytetrafluorethylene (Teflon)¹¹⁶. When added as a dispersion without sintering, it improves oxygen recombination, reducing the rate of cadmium migration and, based on information available so far, increases cell life. The faster oxygen recombination apparently results from improved three-phase interface reaction zones¹¹⁷.

Cenek, et al,¹¹⁸ have investigated the behaviour of plastic-bonded cadmium electrodes incorporating oxalic acid and a polyethylene binder on an iron substrate. It is claimed that the service-life of such plates is about 1900 cycles before the

capacity falls to $\approx 46\%$ of its theoretical value. In order to obtain acceptable cycle life it is claimed that the plastic content should not exceed 30-35% by volume. The oxalic acid appears to be used mainly as a pore forming agent, being leached out into the electrolyte on discharge.

Further studies by Cenek, et al.¹¹⁹, confirmed that incorporation of oxalic acid into the active mass increased the efficiency of utilisation by about 10-20% by minimising active material aggregation.

Thus it is generally agreed by many researchers that two principle types of modifiers have been described in the literature, one acting because of the nature of its crystal habit in the solid-state (inorganic) and the other depending on its adsorption onto the growing crystal from solution (organic).

Wagner¹²⁰ detailed the beneficial effects of ferric oxide on the reduction of cycling down and also stated that titanium dioxide included in the active material had the same results. Wagner believes that the function of this so-called expander is to provide lattice sites for the formation of cadmium hydroxide and metallic cadmium via the soluble cadmate species. By increasing the number of potential growth sites, the tendency to form a finely-divided deposit should be greater. It is postulated that any electrochemically inert, insoluble oxide could serve as an expander provided it possesses crystal lattice dimensions similar to those of cadmium hydroxide.

The action of expanders and a large range of expander materials have received extensive investigations for the lead/

lead sulphate system¹²¹⁻¹²⁸. However, very little work has been carried out on expanders in any detail for the cadmium electrode.

In summary, the solubility of reaction intermediates has been shown to be responsible for the growth of cadmium hydroxide crystals. However, as dissolution is vital to performance, particularly at low discharge rates, prevention of the formation of soluble species would not lead to improved characteristics. Therefore, the only logical solution to the problem of crystal growth, is to include within the cell some form of growth modifier.

This growth modifier is in the form of ferric oxide and polyvinyl alcohol (P.V.A.) in Chloride Alcad negative plates. More about the properties of iron-oxide and P.V.A. will be discussed in later chapters.

2.8 Objective of the Project.

The expanders function is thought to be to act as agents for the preservation of negative capacity throughout cell life. Unfortunately, the iron compound may find its way to the positive plate where it acts as a poison and reduces the capacity of the plate or deposit on the separator material where it may short-circuit the cell. It is desirable, therefore to find an inert substitute for the iron species, with resultant cost/performance benefits.

Other expander materials have been suggested in the literature, but there is no detailed long-term experience. The choice of such a material would be made easier if the operating principles

of expanders were understood. Such principles will probably apply to all aqueous electrolyte cell negatives and will probably be related to those of crystal growth.

Previous¹²⁹ work on platinum supported electrocatalyst has demonstrated the importance of support surface energy in influencing the growth of Pt crystallites through solution and recrystallisation. Similar mechanism may apply for cadmium nucleation and growth in the presence of the iron-oxide expander. Other mechanisms are also possible such as inhibition of growth sites and promotion of nucleation. The objectives of the present studies are listed below:-

- (a) Elucidation of the importance of surface energy of various inorganic oxide materials compared with cadmium.
- (b) Investigation of the methods available to accelerate the growth of Cd/Cd(OH)_2 crystallites upon discharge so that,
- (c) Alternative and more efficient expander materials (including those used in surface energy work) as well as $\alpha\text{-Fe}_2\text{O}_3$ and P.V.A. can be investigated fairly quickly using cycling techniques and by the use of Scanning Electron Microscopy and X-ray crystallographic analysis.
- (d) Elucidation of the mechanism whereby the iron-oxide migrates from the cadmium hydroxide electrode mixture.
- (e) Elucidation of any adsorption phenomenon occurring on a planar cadmium electrode by P.V.A. in KOH solutions by the use of a.c. impedance techniques.
- (f) Investigation of the effect of thin film growths of Cd(OH)_2

on a planar cadmium electrode in KOH solutions containing
P.V.A.

- (g) Investigation of the effect of thick film growths of $\text{Cd}(\text{OH})_2$
on a planar cadmium electrode in KOH solutions containing
P.V.A.

CHAPTER 3

SURFACE ENERGY CONSIDERATIONS

CHAPTER 3

SURFACE ENERGY CONSIDERATIONS.

3.1 Introduction.

An extensive literature survey¹³⁰⁻¹⁴⁸ showed that numerous methods were available for the determination of surface energy of solids. However, a method which was easy to use and reasonably fast was necessary¹⁴⁸ and this chapter describes the attempt to determine the surface energies of various substrates indirectly by the use of contact angle measurements¹⁴⁸ of molten cadmium. The substrates chosen were C; BaO.6Fe₂O₃; Fe₂O₃; TiO₂; pyrolytic C; SiO₂ in the form of a crucible and α -Al₂O₃.

3.2 Theoretical Principles.

On the surface of a solid, there are unsymmetrical and unbalanced forces present and that these forces are stored on the surface of a solid as surface energy. When liquid is in contact with the surface of solid, work must be done in order to form a new surface. This work function, called the surface energy can be defined as the free energy of formation of a new surface.

$$\gamma = \frac{dG}{dA} \qquad 3.1$$

where dG is the change in free energy and dA is the change of surface. The unit of surface energy, γ , appears to be an energy per unit area and it may either be erg.cm⁻² or dyne cm⁻¹. When a drop of liquid does not wet the solid surface, it will remain as a drop having a definite angle of contact between the liquid

and the solid surface,

Fig. 3.1 illustrates the equilibrium contact angle at a solid liquid gas interface¹⁴⁹.

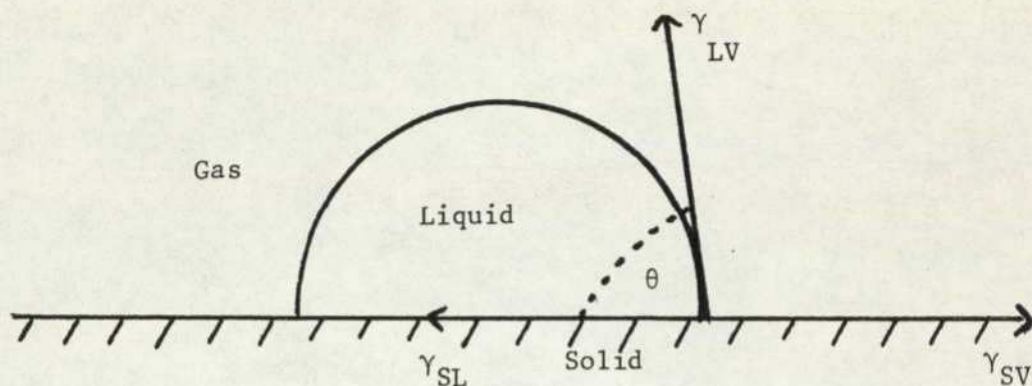


Figure 3.1

γ_{SL} = interfacial energy between solid and liquid,

γ_{SV} = interfacial energy between solid and vapour,

γ_{LV} = interfacial energy between liquid and vapour,

θ = contact angle

The relationship between the contact angle of the liquid and the interfacial energies can be defined quantitatively by the use of Young's equation¹⁵⁰:

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL} \quad 3.2$$

The liquid does not wet the solid when the contact angle θ is greater than 90° . When this occurs, the drops of liquid tends to ball up and move about freely on the solid surface and also does not enter the capillary pores. If θ is less than 90° , then the liquid wets the solid. On the otherhand, if the contact angle is zero, complete wetting occurs and the liquid

spreads freely over the solid surface at a rate depending on the liquid viscosity and the surface roughness.

The value of $\cos \theta$ will be positive if wetting occurs. Thus in the case of a finite contact angle, the imbalance of surface free energies is now given by a spreading coefficient, $S_{L/S(V)}$,

$$S_{L/S(V)} = \gamma_{SV} - (\gamma_{SL} + \gamma_{LV}) \quad 3.3$$

Thus $S_{L/S}$ is positive if spreading occurs. A corresponding necessary, but not sufficient, condition for spreading is that the liquid-vapour interfacial energy be less than the solid-vapour interfacial energy i.e. $\gamma_{LV} < \gamma_{SV}$. This condition is sometimes useful for screening purposes, since the values of γ_{LV} and γ_{SV} are usually available from standard handbooks, but not the γ_{SL} value

In the case of the wetting of a porous body, it is required for the liquid to penetrate into the porous body through capillary rise. From the Laplace equation¹⁵¹ it follows that

$$\Delta P = 2\gamma_{LV} \cos\theta/r \quad 3.4$$

where ΔP is the pressure difference required to force entry of the liquid, and r is the radius of the capillary.

If h denotes the height of the capillary rise above a flat liquid surface, ΔP can be expressed as

$$\Delta P = \Delta\rho \cdot g \cdot h. \quad 3.5$$

where $\Delta\rho$ is the density difference between the liquid and gas phase and g is the acceleration due to gravity.

If Θ is not zero, i.e. the liquid does not completely wet the capillary wall, then

$$\Delta P = 2 (\gamma_{SV} - \gamma_{SL}) / r \quad 3.6$$

so that a large ΔP can be obtained when γ_{SV} be made as large as possible, since for practical reasons it is not usually possible to choose γ_{SL} .

Thermodynamically, the most stable state of any system is that which results in the lowest free energy. Thus whether a liquid wets a solid is dependent on whether the total surface energy of the system will be decreased. Therefore if $\gamma_{LV} > \gamma_{SV}$, then from equation 3.3, S_{LS} will definitely be negative and no wetting occurs, i.e. $\Theta > 90^\circ$. This prediction will be valid provided there is no chemical reaction between the liquid and the solid¹⁴⁸

3.3. Experimental

Materials

Contact angle measurements were used to determine the wettability of molten cadmium on the surface of various substrates. In this study, Cd and pyrolytic graphite were used as a model system, since the surface properties of these materials can be easily found from literature. The carbon atoms in graphite crystal are strongly held together by covalent bonds in the hexagonal basal plane but the bonds between the layers are weak Van der Waals bonds. Thus a

small amount of energy is sufficient to bring about an increase in surface area of graphite since the hexagonal arrays could easily be moved by rupturing the weak bonds.

$\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ possess similar layer-like hexagonal structures. The structure of the unit cell is built up of spinel blocks each of which consist of four horizontal planes containing four oxygen atoms with nine ferric ions distributed between these planes. Between the spinel blocks are intermediate phases each of which contains a barium ion, three ferric ions and three oxygen ions. Therefore, slip will occur more readily between the planes cutting the 'c' axis, analogous to the layer-like graphite.

$\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ was prepared by pressing the appropriate amounts of Analar grade BaO and Fe_2O_3 in a lin. steel die at 5tsi and sintering at 1000°C for 24 hours. The $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ pellets had an average apparent density of 3.74 g cm^{-3} i.e. 69.5% dense. Using Archimedes principle the apparent density of the other substrates were also measured. TiO_2 (3.99), Fe_2O_3 (3.98), c (1.72), Pyrolytic C (2.18).

3.4 Contact Angle Measurements.

The sessile drop method¹⁵² was used for the contact angle determination. The contact angle can be obtained from the measurements of a sessile drop as shown in Fig. 3.2.

Providing the drop is small enough to be treated as a spherical segment, the contact angle can be calculated from the following equation.¹⁵³

$$\tan \frac{\theta}{2} = \frac{2h}{\Delta}$$

3.7

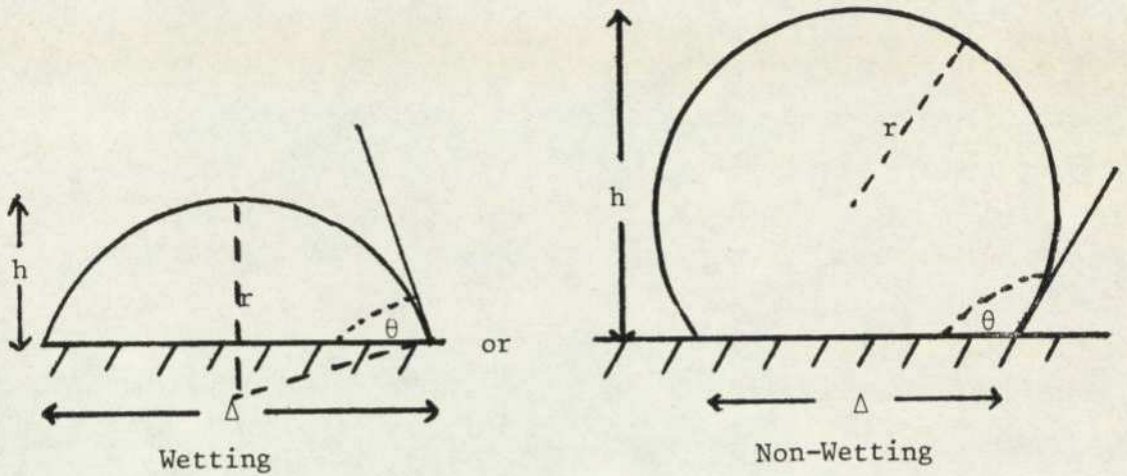


Figure 3.2 Use of a Sessile Drop for Contact Angle Determination

where Δ is the diameter of the base of the drop. However the ratio of h/Δ is independent of the radius of drop, for it is difficult to measure directly from the segment of a circle.

Fig. 3.3 shows a schematic diagram of the experimental facility used for contact angle measurements.

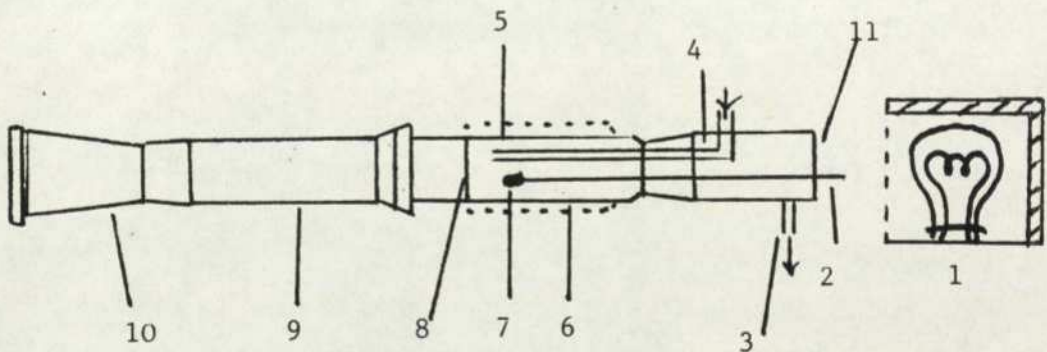


Figure 3.3 Apparatus for Measuring Contact Angles.

1. Illumination lamp; 2. Thermocouple wall; 3. Gas outlet into H_2S solution; 4. gas inlet; 5. Thermotape; 6. Tube furnace (silica glass with quick fit joint); 7. Specimen support; 8. and 11. windows; 9. Telescopic sight; 10. Camera.

Because of the highly poisonous character of molten cadmium, the whole unit was placed in a fume-cupboard. The experiment was performed in an atmosphere of argon to prevent aerial oxidation of cadmium, the exit gas being passed through a hydrogen sulphide solution to precipitate out any cadmium vapour to cadmium sulphide.

The drop of molten cadmium on various substrates was photographed at different temperatures and the result indicated that cadmium on graphite and barium hexaferrate does not wet the solids as expected, (the surface free energy of cadmium is about 600 dyne cm^{-1} at 450°C whereas the surface free energy value for a graphite single crystal is only 119 dyne cm^{-1} at room temperature). The results for TiO_2 (although showing that it wets), Fe_2O_3 and $\alpha\text{-Al}_2\text{O}_3$ were inconclusive because some chemical reaction on the surface was observed. At first it was thought that there may be some oxygen in the argon as impurity and so to investigate this possibility, the argon gas was passed over heated copper turnings before being passed into the sealed unit.

However the result did not differ very much except that in the case of iron (III) oxide it was not known whether the molten cadmium wetted it or not because the angle was so close to 90° . Surface reaction was indicated in all cases by a definite discoloration on the substrates as well as a thin film of cadmium oxide (brown) being formed on the cadmium beads.

The above experiment, although of great research interest did not prove to be quite as successful as we originally thought simply because of interferences from side reactions. However it must be remembered that surface energy is a valuable tool in interpreting any catalytic reactions and a knowledge of the relative magnitudes or effects would have been very useful.

Surface free energy plays an important rôle in all processes associated with a phase boundary: catalysis, adsorption, dispersion etc. Unfortunately, as pointed out by Bikerman¹⁵⁴ "none of the methods proposed so far for measuring (the surface energy of solids) can stand critical scrutiny". Without a knowledge of this quantity it is impossible to determine quantitatively the influence of various factors on the mechanism of surface processes.

CHAPTER 4

SYNTHETIC IRON OXIDES AND PVA

CHAPTER 4

SYNTHETIC IRON-OXIDES AND PVA USED IN ALCAD NEGATIVE PLATES.

4.1 Synthetic Iron-Oxides.

The synthetic iron-oxides used in the negative electrode active material have varying compositions. They are produced by precipitation methods and for the Red grades, calcination. They are all stable, and are used where high chemical and heat resistance are of importance. They most successfully resist the influences of light, industrial atmosphere, acids, alkalis and severe weather conditions. They are not affected by lime and cement and are inert to most of the paint and coating materials in common use. They are entirely harmless. Their application are not only in battery negatives but paints, concrete, coatings, plastics, rubber etc. etc. Scanning electron micrographs of three of the grades (Figure 4.1) show them to be acicular.

The grade used in the cadmium hydroxide active material is the MM15 (red type), and a typical analysis is given in Table I. Although the oxide is predominantly Fe_2O_3 (about 98%), the manufacturers specify that the rest is adsorbed water and traces of impurities.

Ideally, for battery uses, the synthetic oxides should be inert, but cyclic voltammograms of four of the grades manufactured (including a blank), show varying degree of activities (Figures 4.2-4.6). The hydrated iron-oxide which has not been heat treated was expected to be more soluble and active than the red heat treated oxide, but the reverse occurred indicating that conductivity may be the critical factor determining activity. The MM15 grade is of

Figure 4.1 Electron Micrographs of Synthetic Iron-Oxides



SYNTHETIC IRON OXIDES



Electron Microscopic
photographs 10,000 times
enlarged show that the
particle shape of these
"DEANOX" Synthetic
Iron Oxides are acicular.

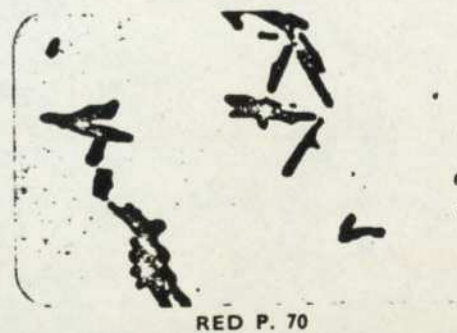
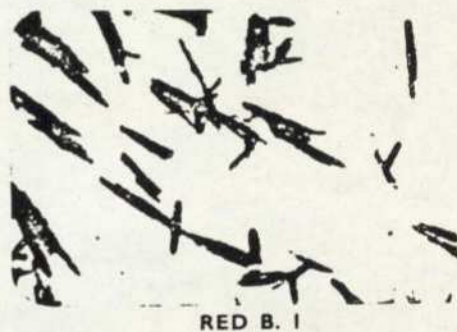


TABLE I

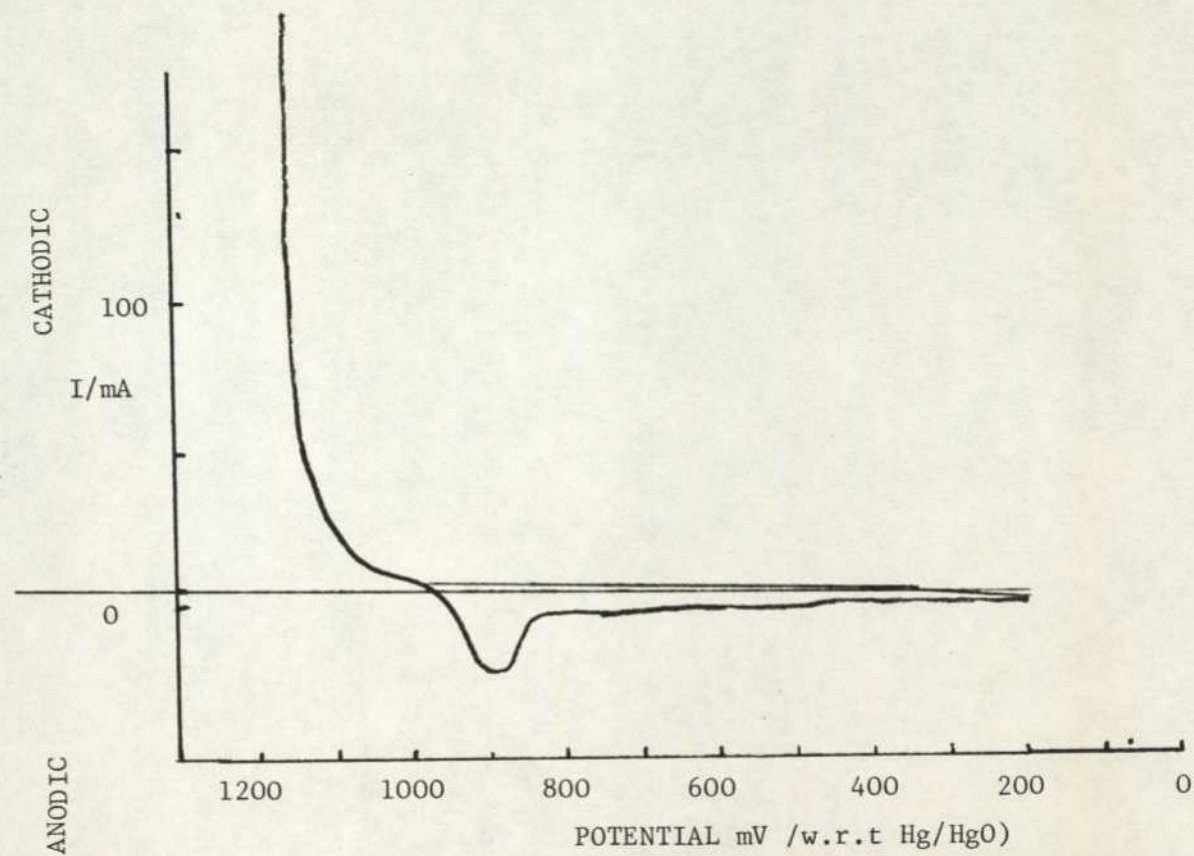
" DEANOX " SYNTHETIC IRON OXIDE TYPICAL ANALYSIS

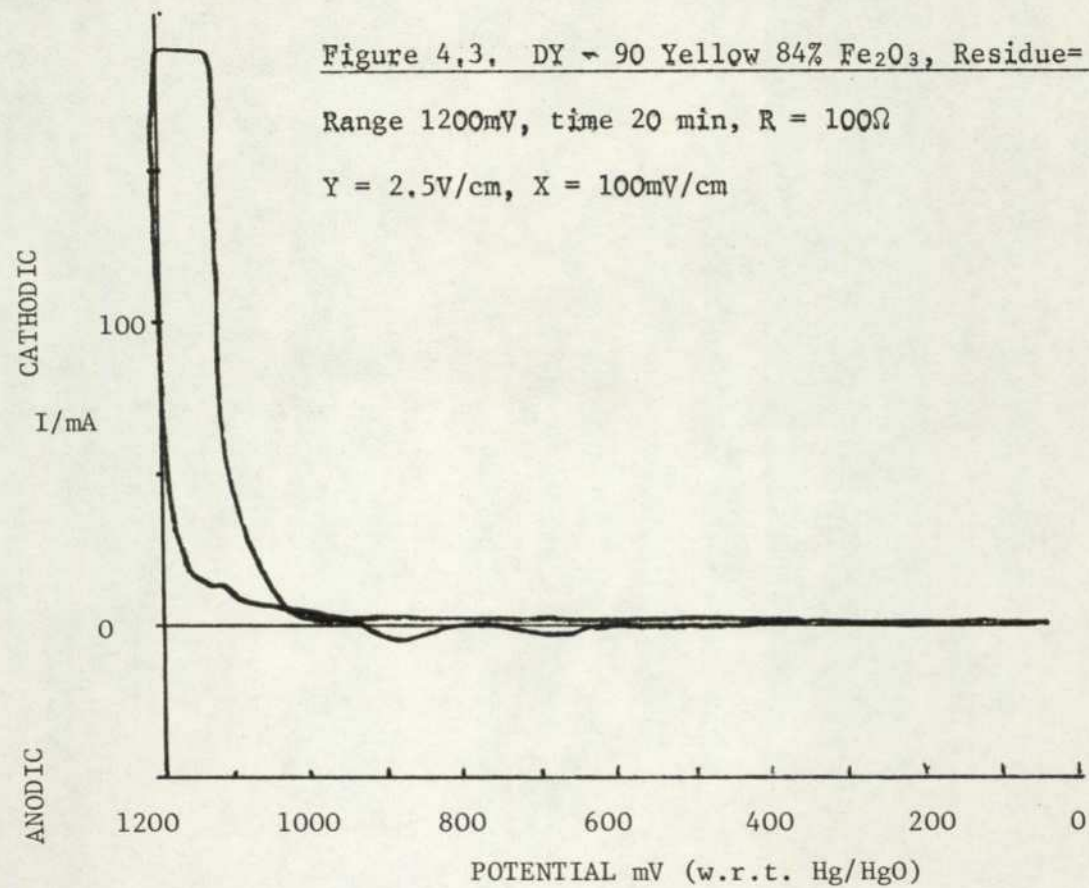
	<u>MM, 15</u>
	about
	%
Fe ₂ O ₃	97.5
SiO ₂	0.06
MnO ₂	0.07
PbO	No Trace
SnO ₂	No Trace
CaO	0.1
CuO	0.09
ZnO	0.1
TiO ₂	0.1
NiO	0.05
Tap Weight	1.05-1.15 g/ml
Bulk Density	0.65 g/ml
Particle Size	0.2-1.5 μ
Particle shape	Fused irregular shapes.

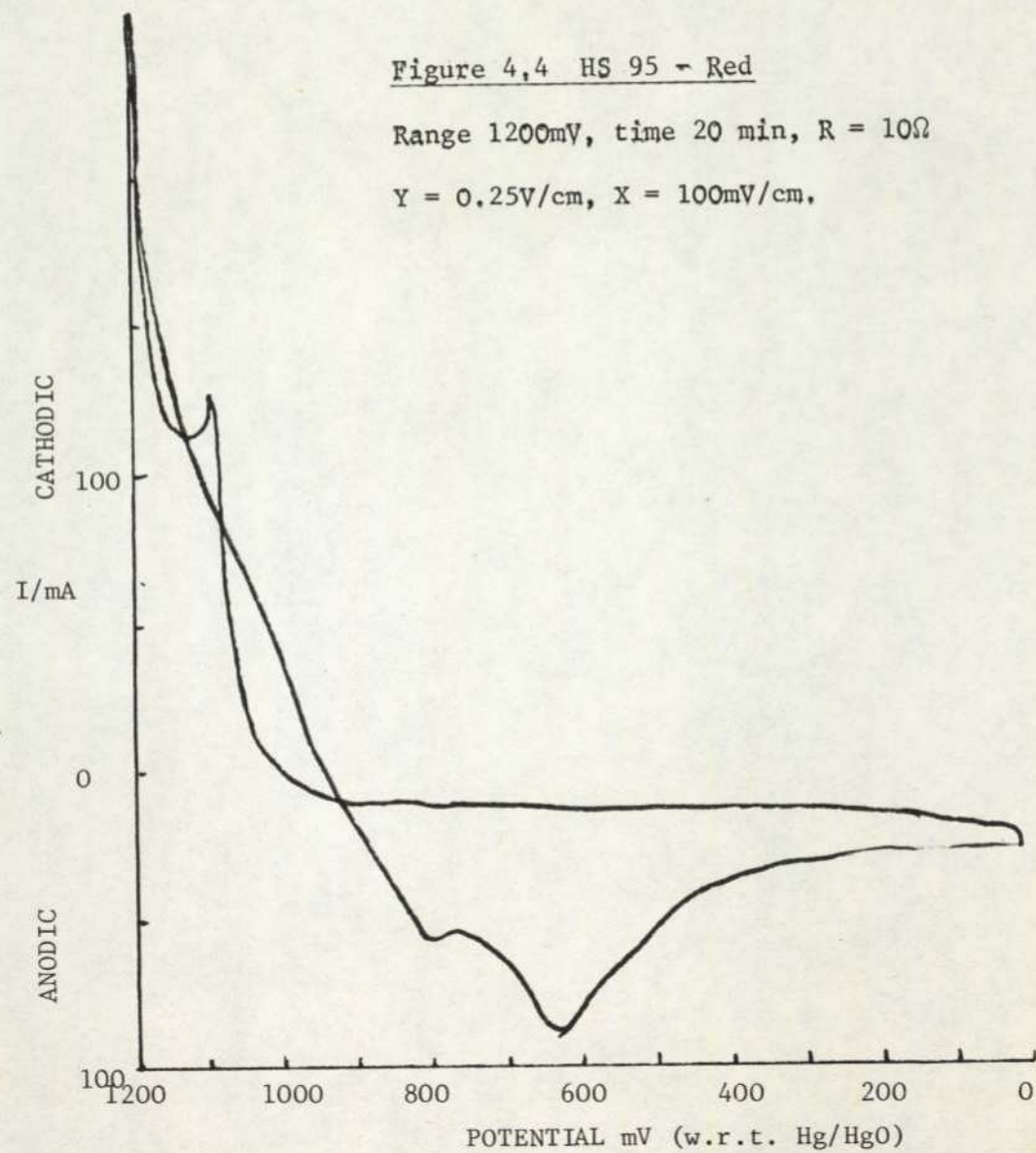
Figure 4.2 MYL $\rightarrow$ Orange, 87% Fe_2O_3 , Residue = combined water

Range 1200mV, time 20 min, $R = 100\Omega$

$Y = 2.5\text{V/cm}$, $X = 100\text{mV/cm}$







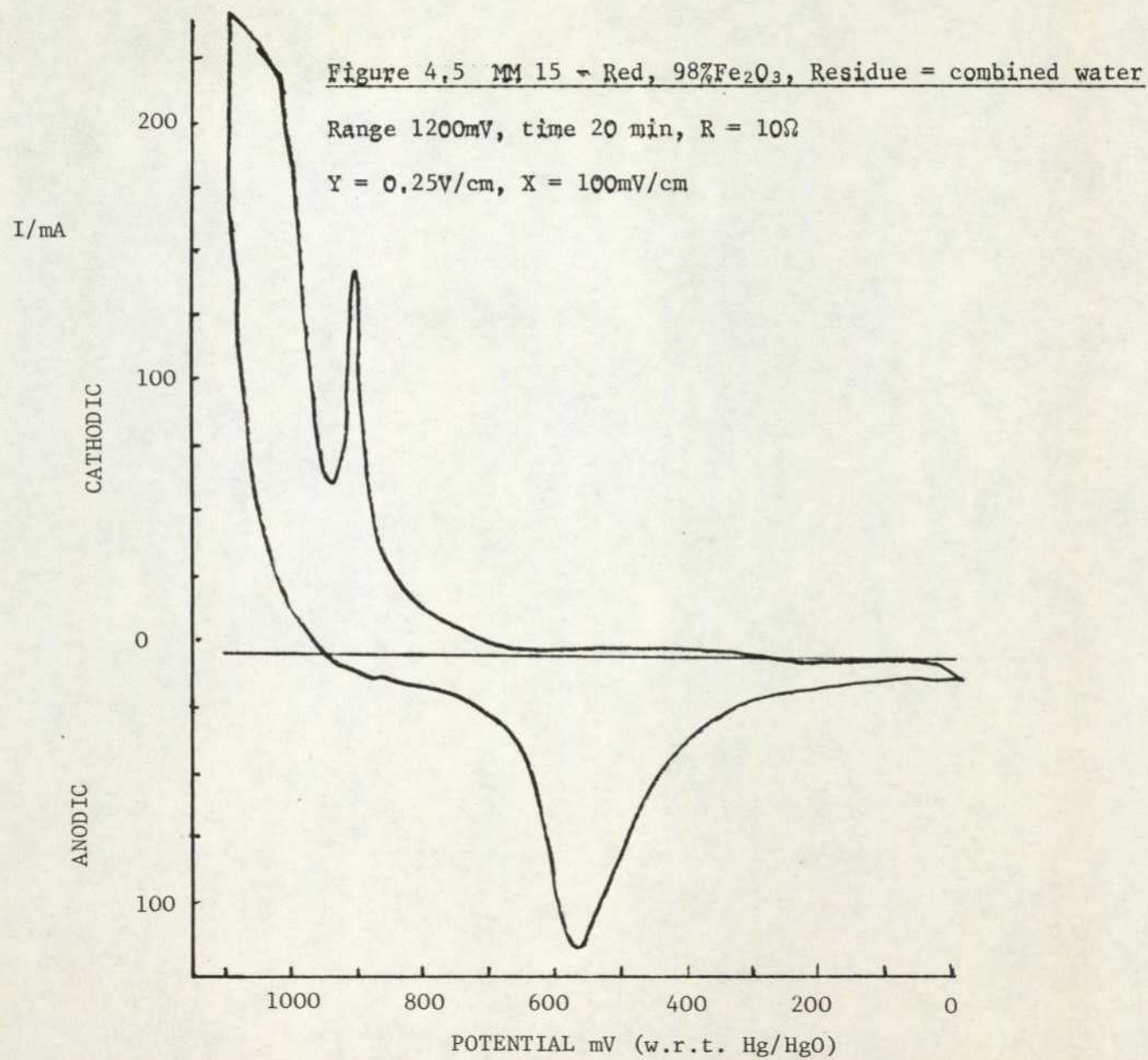
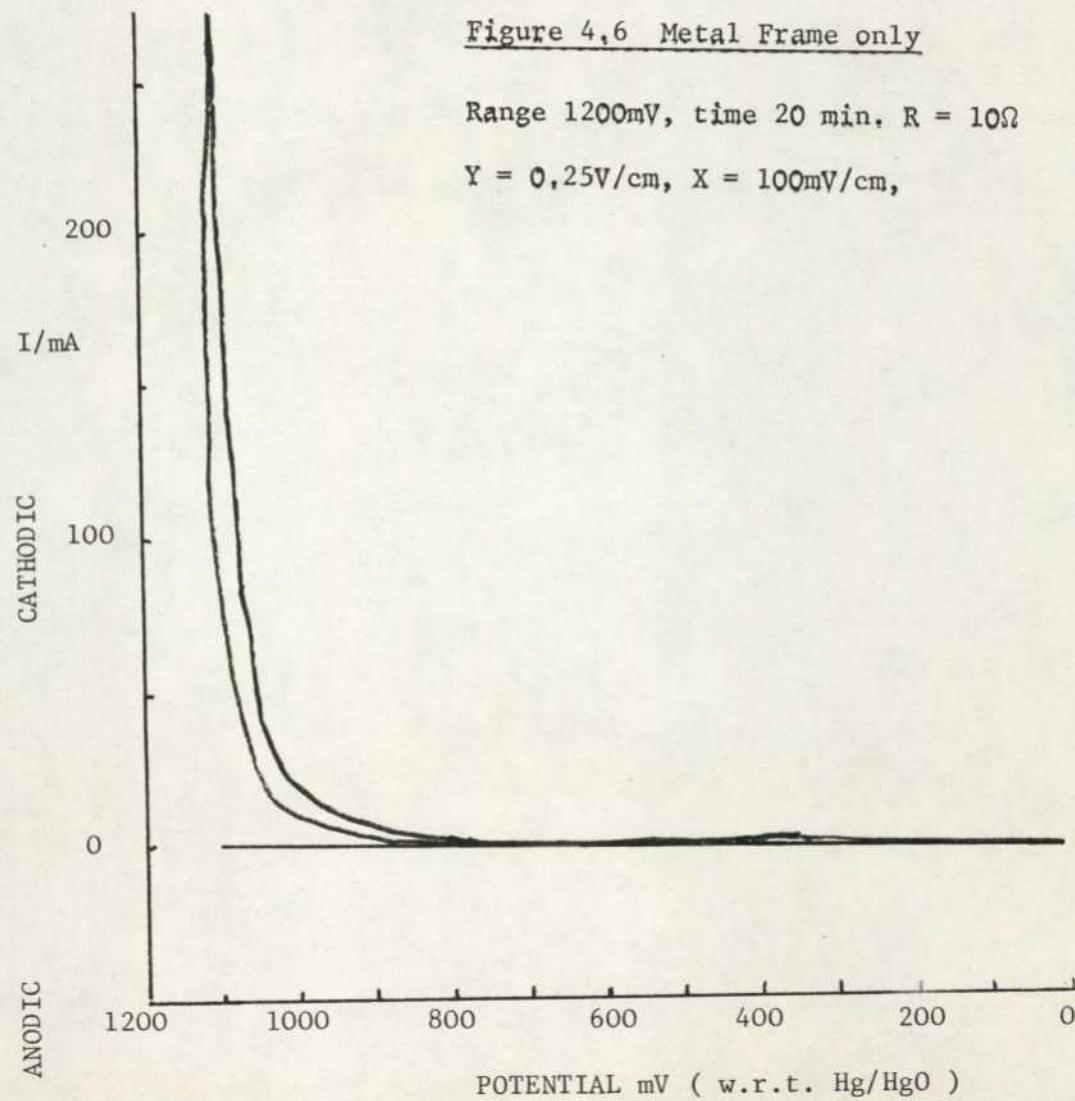


Figure 4,6 Metal Frame only

Range 1200mV, time 20 min, $R = 10\Omega$

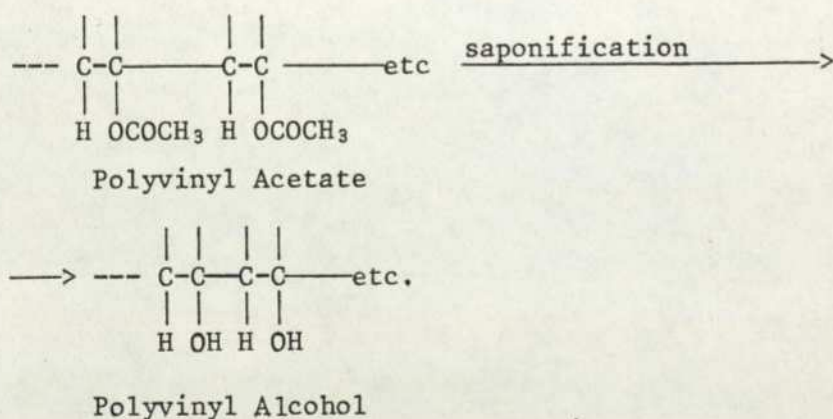
$Y = 0,25V/cm$, $X = 100mV/cm$,



the α - form and scanning electron micrograph (Figure 4.7) again shows this to be acicular. In the above experiment the graphite was added to impart some conductivity to the iron-oxide.

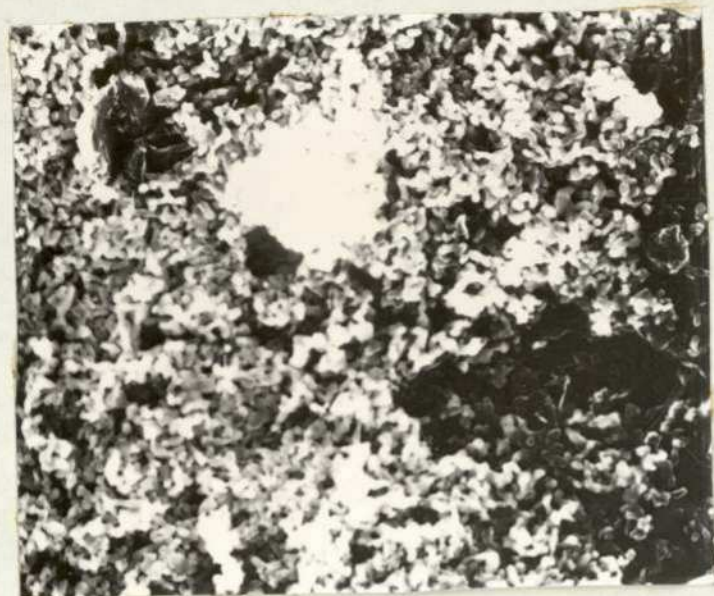
4.2 PVA

Polyvinyl alcohol (PVA) is produced by the hydrolysis of polyvinyl acetate with caustic soda (equation 4.1). The raw material acetylene adds acetic acid, forming vinyl acetate monomer. Vinyl acetate is polymerised under the influence of catalyst to produce polyvinyl acetate, which is hydrolysed to yield polyvinyl alcohol. In the 1950's when mass production of PVA was started, the source of the raw material, acetylene, was limited to the carbide obtained from limestone and coal. Since 1962, however, acetylene produced from natural gas has been used and since 1968, vinyl acetate produced from ethylene of petroleum has also been used. The following is a flow chart for the manufacturing process of polyvinyl alcohol (Figure 4.8).



The manufacturing process of PVA has the following advantages:

- a) Sodium acetate and methyl acetate, which are by-products of

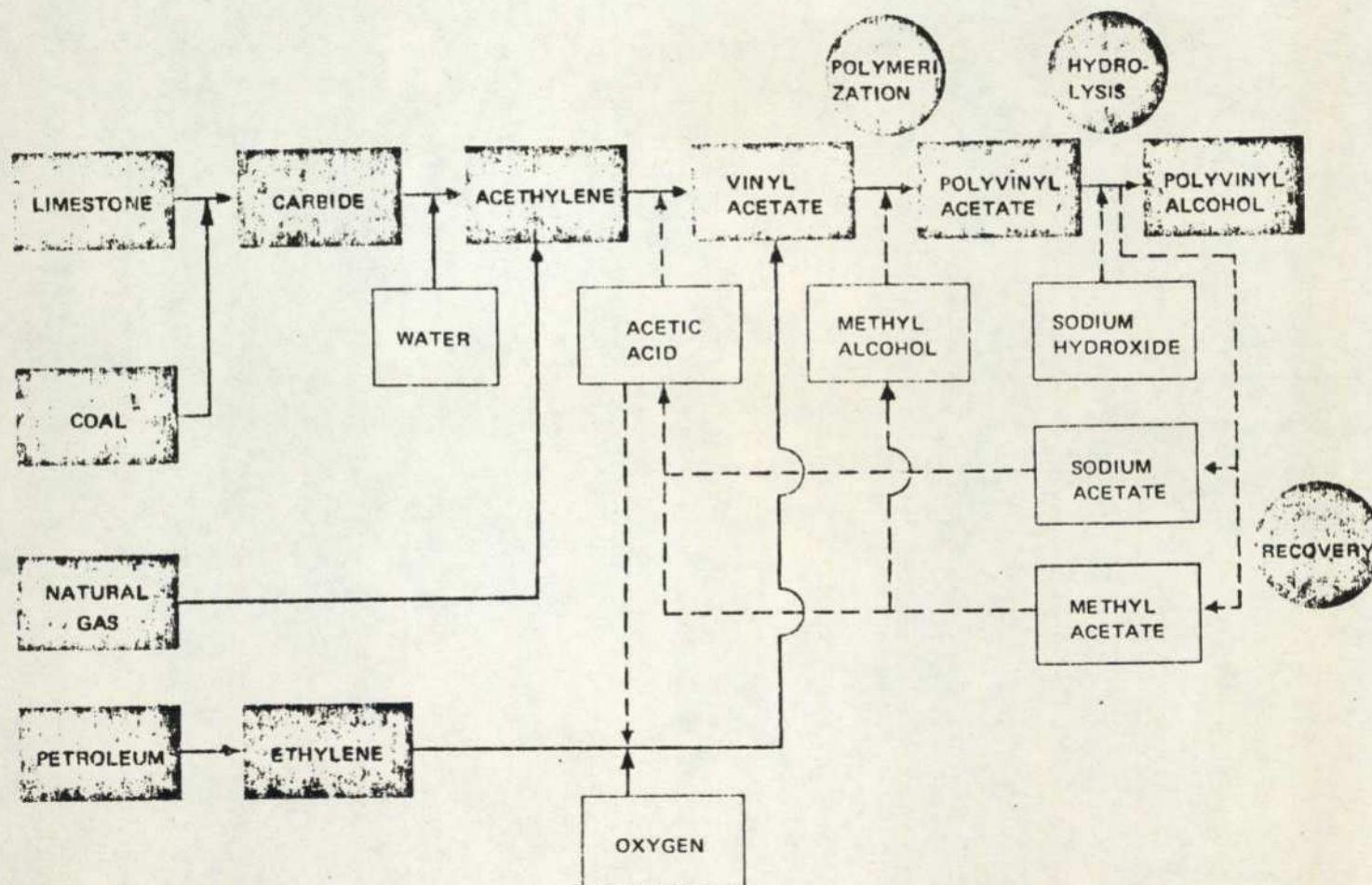


MAGNIFICATION

3000x

5μ

Figure 4.7 Deanox α - Fe_2O_3



the hydrolysis reaction, are recovered into acetic acid and methanol at an extremely high recovery rate and are reclaimed. This economises the consumption of raw materials and minimises manufacturing costs.

b) There is a continuous mass production system using the most advanced automation, line and equipment. Therefore, easy yet strict management and control of manufacturing conditions are assured making it possible to produce PVA of highly uniform and good quality.

The PVA used in the cadmium hydroxide active material is a white granular powder and its aqueous solution is colourless and clear, and has a pH value of around 6. It is available with highly uniform molecular weight and saponification number distribution and it contains very few impurities such as alkalies, iron, sodium acetate etc. In alkali it has a tendency to form gels and it is believed that it behaves as an anionic species.

CHAPTER 5

BACKGROUND TO THE PROJECT

CHAPTER 5

BACKGROUND TO THE PROJECT.

5.1 Iron-rich deposits on separator pins and on other parts of the cell were first reported and confirmed in 1972. These deposits caused early failure of cells due to short circuits across the separator and/or low positive group capacities. The latter is more likely to have been caused by iron poisoning of the positive active material. Although such deposits have been commonly observed in the U.K., including cells on open-circuit stand at Redditch, most drastic failures appear to be related to low float voltages and high temperature applications (i.e. in warmer climates). These observations were explained by the theory¹⁵⁵ that steel corrosion is enhanced in alkaline solution when it is electrically connected to the cadmium/cadmium hydroxide couple (i.e. as on the negative plate).

It has been pointed out¹⁵⁶ that the protective oxide film on steel, and iron-oxides, generally, are unstable at the potential of the cadmium negative electrode in alkaline solution. The reason that the problem of iron deposit seems to have increased in the 1970's may be that the relative stability of the oxide film on steel, as supplied, has decreased.

Corrosion of steel results after removal of the oxide film and can occur on open-circuit stand, where reduction of oxygen dissolved in the electrolyte acts as the driving force at the potential of the negative electrode. In a similar manner, iron-oxide present in both new and old negative active material can also be reduced with resultant corrosion or dissolution of the

products. This would be expected to be more difficult since it requires reduction of a bulk oxide, as compared with a relatively thin oxide film for the case of steel.

Corrosion with resultant iron-rich deposits can therefore be easily explained on open-circuit stand and on floating applications, where oxide film reduction is accelerated by charging, whereas subsequent discharge increases the corrosion reaction itself. The most common causes of failure — low float voltage and high temperature — also tend to produce easier film reduction and corrosion, respectively.

Steel corrosion can be prevented by a continuous, non-porous coating of nickel and it is believed that the iron deposit problem can be minimised by this means.

Previous potentiostatic work¹⁵⁵ clearly demonstrated the difference in corrosion behaviour, in alkaline electrolyte, of steel, nickel-plated and nickel surfaces respectively. In order to explain the variability of iron-rich deposition between cells, it was necessary to show that steel with different surface appearance showed variable corrosion characteristics.

Anodic polarisation curves¹⁵⁵ of steel could be made reproducible from one cycle to the next by cathodic activation treatment at 0.5 amps constant current (about $5\text{mA}\cdot\text{cm}^{-2}$) for 20 minutes. Using this treatment and a voltage scan speed of $50\text{ mV}\cdot\text{min}^{-1}$ a series of steel samples of different surface appearance were compared. All samples were of the standard mild steel strip, but had varying amounts of black-speckled deposits which could not be removed by standard cleaning methods.

A clear tendency emerged that the corrosion current densities increased with increase in blackened area. Because all steels were otherwise of the same composition and specification, this suggests that the relative ease of activation (i.e. removal of the protective, passive film) varies with the surface condition.

To demonstrate that all steel surfaces will ultimately activate, given a sufficiently long activation time, several samples were held cathodic for about 8 days. The resultant anodic polarisation curves for both blackened and 'clean' steel surfaces were now sufficiently similar to show that the passive film had been removed in each case by the prolonged treatment.

Other potentiostatic work has included holding steel samples at constant potential in the active region or cycling between potentials particularly encountered in cell applications. There is evidence of the formation of a black deposit on the steel surface under these conditions.

Examination of the nickel-plated samples of varying plating thickness/quality has confirmed the fact that a continuous, non-porous nickel surface was necessary to avoid iron contamination from steel corrosion.

Of the cells tested in this work, those standing on open-circuit in an oven at 50°C showed a clear indication of the origin of iron-rich deposits on separators. Pins from all cells containing negatives with unplated steel strips/components showed heavy brown deposits of a similar nature, if not colour, to those found in practice. Those plates made with pure nickel perforated strips and iron-containing active material (i.e. as in

standard flooded cell material) also showed deposits but at a very much lower weight per unit length than in the former groups.

No deposition was found from plates with nickel pockets and sealed cell active material (not containing iron) but where nickel-plated pockets were employed, a slight deposition at discrete points on the pin was observed. These spots were adjacent to the lacing of the pockets and were thought to originate from steel exposed by cracking of the plating as a result of deformation in manufacture.

Thus the main contribution to iron-rich deposition is corrosion of steel, with a minor amount from dissolution of iron-oxide from the active material. Adequate plating eliminates the major source as long as the coating is continuous and non-porous.

Radiotracer work at Harwell and laboratory examination at Redditch proved beyond any doubt that corrosion of steel is the major cause of iron poisoning of the positive plate.

Thus the results in the various areas of work show that corrosion of steel from the negative components is the principal source of iron-rich deposits in cells. The incidence of cadmium in the deposit is easily explained either by the solubility of cadmium hydroxide in alkali (solubility $10^{-4} \text{ mol l}^{-1} \text{ Cd}$) or by electrophoretic migration of the hydroxide particles!⁵⁷ Experiments as above have shown that there is a small contribution towards the iron-rich deposits from the dissolution of the iron-oxide in the negative active material. Whether this contribution is significant has not been established; however, with the possibility that the iron-oxide may have to be excluded from the cell

an alternative expander material would be necessary. These can only be screened if quick and reliable methods are readily available otherwise it would take many years to show whether or not an expander is beneficial if normal cycling regime is employed.

When an alkaline cadmium electrode is continuously cycled on a deep discharge regime, it loses capacity by a phenomenon referred to as fade-out,^{120a} due to the cells becoming cadmium limiting on discharge. This loss in capacity is due also to a decrease in the surface area of the active material.

Chloride Alcad have demonstrated that this fade-out test is quite valid with the normal cycling operations of a nickel-cadmium battery. Hence if the capacity of the negative plate can be gradually decreased, with various expanders included separately, then this provides a useful means of screening different expanders. Besides Wagner's method of accelerating crystal growth by low-rate discharging there is also Harivel and co-workers method⁷⁹ in which low rate charging but high rate discharging mode is used to decrease the capacity of a negative electrode. The next Chapter describes the above techniques to find the most optimum method of reducing the capacity of a standard new negative electrode so that this method can then be used to screen various expanders in the the subsequent chapters.

CHAPTER 6

METHOD TO ACCELERATE CRYSTAL GROWTH BY MEANS OF
LOW RATE AND HIGH TEMPERATURE

CHAPTER 6

METHOD TO ACCELERATE CRYSTAL GROWTH BY MEANS OF LOW RATE CYCLING AND HIGH TEMPERATURE.

6.1 INTRODUCTION

Nickel-cadmium batteries are designed with an excess amount of active cadmium in order to prevent loss of capacity on cycling and in the case of sealed batteries to have the cells operate on an oxygen cycle. A phenomenon referred to as fade-out is applied when the capacity decreases due to the batteries becoming cadmium limiting. The loss in capacity is attributed to a loss in real surface area because of the massive recrystallisation of cadmium and cadmium hydroxide crystals and consequently by the blockage of the electrode pores.

Using a scanning electron microscopy technique, previous problems associated with loss in capacity^{1-5,8} has revealed the presence of large crystals on a sintered negative plate after several months storage. These hexagonal shaped crystals have been identified as cadmium hydroxide which are formed by the agglomeration of fine particles initially present on the plate after manufacture. It is likely, therefore, that the loss in charging capacity can be explained by the reduction in electrochemically active surface area of active material which such changes in morphology entail.

Further evidence of crystal growth at sintered-negative plates was provided by Harivel, et. al.^{7,9} X-ray examination showed that a low charge rate promotes the formation of cadmium crystals of

substantial size whereas finer crystals can be obtained at high charge rate. This occurs because a larger number of nucleation sites are used at the higher current density leading to the deposition of larger numbers of relatively smaller cadmium micro-crystals. They also introduced the concept that properties of a porous negative electrode depend on the depth or distance from the surface and consequently on the thickness of the plate. The electrochemical efficiency changes from the surface to the interior of the electrodes of high porosity. Among the parameters observed were crystal size (minimum at the surface), flattening of crystals and the residual cadmium content in the plate after discharge. In addition, included in a thorough investigation were the effects of temperature, and electrolyte strengths on crystal size, principally that of residual cadmium metal following discharge.

Since cadmium hydroxide is less dense than cadmium it has been stated⁷² that the product during discharge remains inside the electrode causing the eventual 'choking' of the pore structure. This illustrates the important effect which electrode structure exerts on the utilisation, morphological and performance capabilities of a sintered and pocket negative plate.

The examination of surface structure is obviously a useful tool in understanding battery performance and the mechanism of ageing and eventual failure.

The slow step reaction during charge and discharge of the alkaline cadmium anode at moderate and elevated temperature is believed to be the reaction between a soluble cadmate ion species $\text{Cd}(\text{OH})_3^-$ and the active lattice sites.¹⁵⁹ At low temperatures the main reaction of the cadmium anode is believed to be a solid

state mechanism reaction in the cadmium and cadmium hydroxide crystal lattices.

It has been well established that crystal growth is a process dependent on limited solubility of the crystalline substance, a requirement adequately satisfied by cadmium hydroxide in caustic solutions with a solubility product of $2 \times 10^{-14} \text{ mol}^3 \text{ l}^{-3}$ at 25°C .^{1,7} Therefore, morphological changes of negative-active material are inherent within the nickel-cadmium system. Hence, in principle, any condition which causes accelerated production of dissolved intermediate, especially with a small number of available growth sites, would be expected to increase the rate of crystal growth.

6.2 Mechanism of Crystal Growth

To understand fully the causes of crystal growth and to take steps to minimise or prevent such behaviour, it is necessary to examine the mechanism of electrode reactions.

From work on planar cadmium electrodes it has been shown that the discharge reaction involves a solution - soluble complex which is probably $\text{Cd}(\text{OH})_4^{2-}$ though $\text{Cd}(\text{OH})_3^-$ has also been suggested.^{2,8,29,47,64}

The question of the charge-discharge mechanism has been a matter of debate over the last few years with both a dissolution-precipitation^{7,8} and a solid-state transportation mechanism being proposed.^{1,2}

It seems established that only the dissolution-precipitation mechanism can lead to subsequent crystal growth of cadmium hydroxide (on discharge) or cadmium metal (on charge).

Breiter and Weininger⁶⁴ suggest that both mechanism are operative at potentials below that of cadmium passivation (i.e. during normal discharge of the negative).

Armstrong, et al.³¹ have stated that active dissolution and precipitation alone takes place below the passivation potential, the solid-state process producing the deposit beyond this point.

The latter mechanism would appear to be the more acceptable, since it is in agreement with the universally recognised theory of the corrosion of metals which show an active-passive transition. In the active region, dissolution occurs freely unless limited by the solubility of products (as is the case with cadmium in alkaline solution), whereas in the passive region nucleation and film growth occurs via a substantially solid-phase process.

Conclusions which substantiate Armstrong's theory have come from several sources.^{58,98} In general, they have shown that high currents and low temperatures produce precipitates with small grain size, whereas low currents and elevated temperatures exhibit larger grain size and consequently reduce the electrochemically-active surface area. Thus at low discharge rates, the dissolved intermediate is involved leading to crystal growth, a mechanism which is accelerated by an increase in temperature.

6.3 Experimental

The problem of loss of capacity can be largely overcome by adding $\alpha\text{-Fe}_2\text{O}_3$ and PVA into the active cadmium constituent and by the removal of CO_2 from the cell. However since the function of iron oxide in the negative active material has to be investigated, it is necessary first to find a quick and reliable method

of accelerating the growth of cadmium and cadmium hydroxide crystals in the presence of the iron oxide.

6.4 Electrode Structure.

All tests were made on the electrodes that had been obtained as follows:-

The negative mixture was made from compacted cadmium hydroxide (β -form), α - iron(III) oxide, PVA and graphite obtained from Alcad. The mixture used was:-

Cd(OH) ₂	1kg	80.32% Cd(OH) ₂
Fe ₂ O ₃	200g	11.24% Fe
Graphite	25g	2.01% graphite
PVA	20g	1.61% PVA

and these were appropriately scaled down and mixed in a coffee blender. Then 2x4g of the negative mix were pressed in a special die (1.2x5.5cm) at 5 t.s.i. and carefully placed between the perforated nickel-plated strips which were crimped together. The pocket produced were pressed to obtain the correct overall thickness. Thin nickel strips were spot-welded with appropriate beading at the end for current take-off.

The characteristics of these electrodes were as follows:-

Width	1.2 cm
Length	11 cm
Overall thickness	3.2 mm

Weight of Negative	8g
Active Material	
Packing Density	2.5gcm^{-3}

6.5 Eletrochemical Oxidation.

A galvanostatic method was used for charging and discharging in all cases using a Chemical Electronics 0.5A - 20V potentiostat. The cells were made of a negative electrode of the above described type and of two nickel counter electrodes.

The distance between these electrodes was 4mm, the plates of both polarities being wholly immersed in a boiling tube containing 150mls of 1.200 specific gravity KOH and formed.

After charging i.e. after reduction of the active material, the cells were discharged by applying a constant current in the opposite direction.

Alcad's utilisation factor (K factor) was 1.85 A.hr/8g of the negative active material. Therefore the total capacity of each pocket electrode was

$$2 \times 4 \times 1.85 / 8 = 1.85 \text{ A.hr}$$

The pockets were formed according to the Alcad laboratory schedule as follows. Each negative was formed against two nickel counter electrodes.

- (1) Soaked overnight in 1.200sp.gr. KOH (pure)
- (ii) Electrolyte discarded, refilled with fresh 1.200sp.gr. KOH
- (iii) Formed as follows:

Cycle 1: 7hrs charge @ C/10,
 discharge @ C/5 to -0.700V vs Hg/HgO electrode.

Cycle 2: 7hrs charge @ C/4,
 discharge @ C/5 to -0.700V vs Hg/HgO electrode.

Cycle 3: 7hrs charge @ C/4,
 discharge @ C/5 to -0.700V vs Hg/HgO electrode.

(iv) Renew electrolyte with lithium hydroxide doped KOH.

(v) Capacity Test,

(a) charged 10hrs @C/5

(b) discharged @ C/5 to -0.700V vs Hg/HgO ref. electrode.

For this particular system with nickel counter electrodes,
 the cell voltages at various stages of a cycle are given below.

The half cell voltages are with respect to Hg/HgO reference
 electrode.

CHARGE

Ni electrode = +0.6V O₂↑

Cd electrode = -0.9V

Cell volts = (Ni) - (Cd)

= +1.5V

END OF CHARGE

Ni electrode = +0.6V O₂↑

Cd electrode = -1.1V H₂↑

Cell volts = (Ni) - (Cd)

= + 1.7V

DISCHARGE

Ni electrode = -1.1V H₂↑

Cd electrode = -0.9V

Cell volts = (Ni) - (Cd)

= - 0.2V

END-POINT? FOR DISCHARGE

Ni electrode = -1.1V H₂↑

Cd electrode = -0.7V

Cell volts = (Ni) - (Cd)

= - 0.4V

Cd ELECTRODE IN REVERSAL (OVER-DISCHARGE)

Ni electrode = -1.1V H₂↑

Cd electrode = +0.6V O₂↑

Cell volts = (Ni) - (Cd)

= - 1.7V

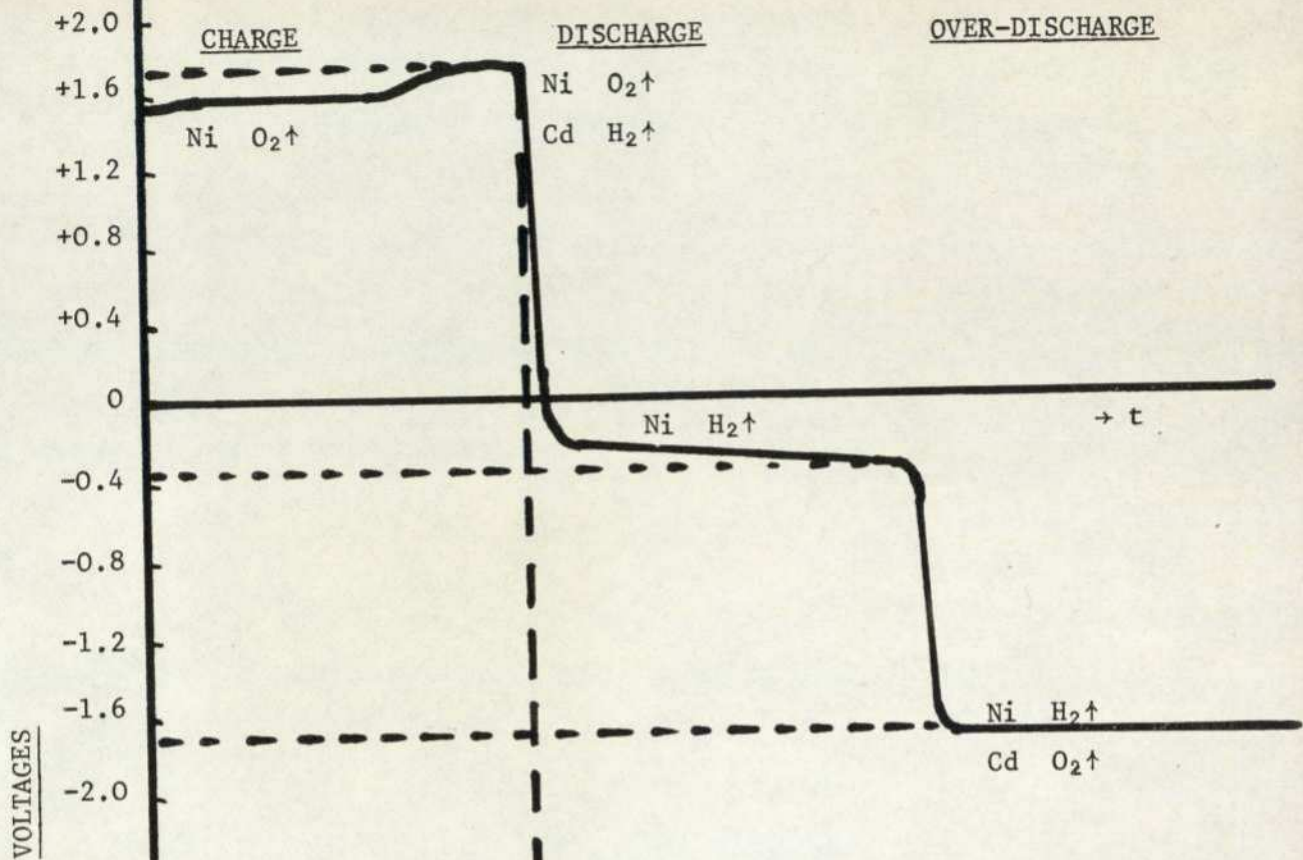
The profile for the cell voltages as well as for the cadmium electrode (w.r.t. Hg/HgO reference electrode) is shown in Figure 6.1.

The fade-out regime was adopted and the intensities of the charge and discharge currents as well as the temperature of operation is shown in Figure 6.2 for several sets of cells. Each condition of operation was done in triplicate and samples were obtained from the two best or reproducible electrodes for X-ray examination and electron microscopy.

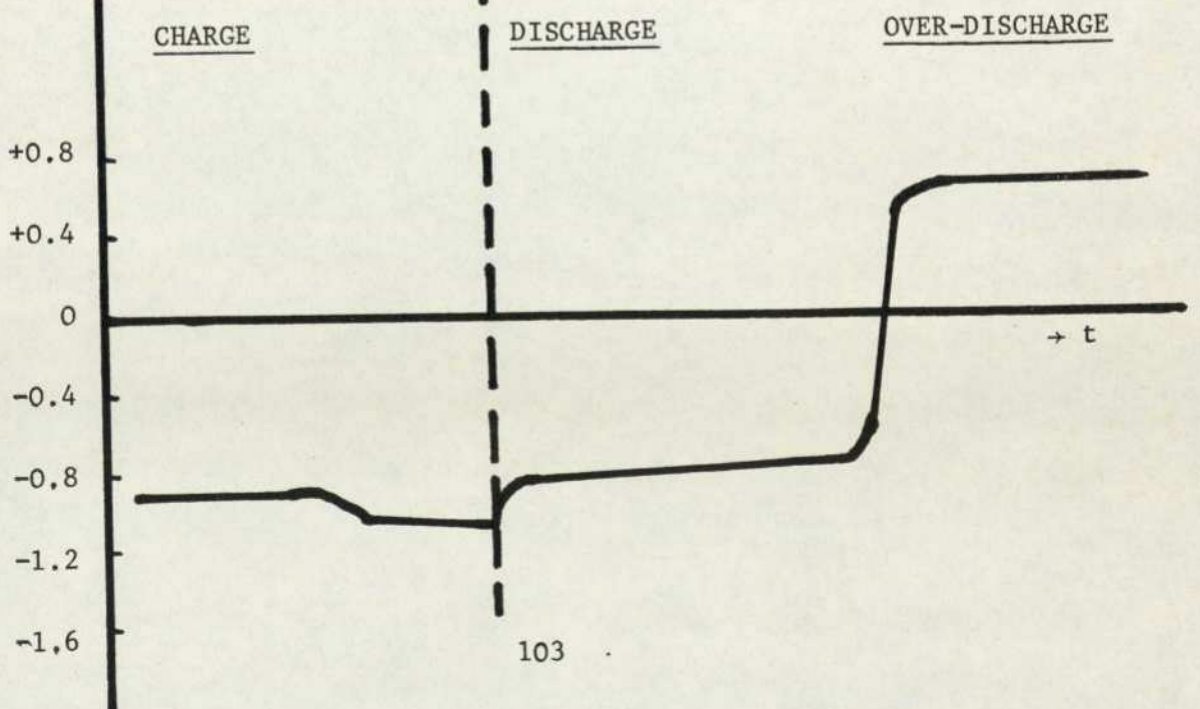
In all, fifteen cells were employed and the potential of each cadmium electrode, down to - 0.700V, was tabulated by comparison with a standard Hg/HgO electrode after each fade-out cycle.

Figure 6.1

VOLTAGE PROFILE--CELL VOLTS



VOLTAGE PROFILE—Cd PLATE VOLTS W.R.T. Hg/HgO REF. ELECTRODE



6.6 Electron Microscopy Examination

The selected samples for scanning electron microscope examination were prepared by washing the electrode material several times in deionised-distilled water until no trace of the caustic was left. The samples were taken at the end of the experiment and several scans of broken cross section at different magnifications were made. The most suitable magnification to work with was found to be that at 3000x. The conditions used on the microscope were 40 KV and high-resolution setting.

6.7 X-Ray Crystallographic Analysis

All selected samples were examined in the discharged state on a Phillips P.W.1010 X-ray diffractometer, using the $K\alpha$ radiation of Molybdenum. The patterns were taken from a ground mixture of the active material. The scanning speed of the goniometer was $1/8^\circ/\text{min.}$ for the 2θ angle with corresponding paper speed.

<u>Rate for charging and discharging</u>	<u>Temperature/$^\circ\text{C}$</u>	<u>No.</u>	<u>Charging time/hrs.</u>
C/40	37	1, 2, 3	56
C/40	21	4, 5, 6	56
C/80	21	7, 8, 9	112
C/80	50	10,11,12	112
C/50	50	13,14,15	70
C/50	37	16,17,18	70

Figure 6.2

6.8 Discussion and Results

The result of the effect of charging and discharging at various current densities in terms of the individual capacity obtained from each cell is given in Table 2 - 4.

It can be inferred from the results that the discharges at C/40 rates are not significantly affected at room temperature. The capacity does decrease but not as rapid as we would have hoped and a certain point is reached when the capacity levels off and subsequent low rate discharges has virtually no effect on reducing the capacity of the electrodes further and in some cases there is an increase in the capacity.

The ideal conditions required is such that at least ten cycles be obtained before the electrodes decreases to about 60% of their original capacities. This would then enable us to follow progressively the pattern of crystal growth of cadmium and cadmium hydroxide in the presence of iron oxide and later of other crystal habit modifier with the emphasis being kept on microscopic examination and X-ray analysis.

In the case of cells discharged at C/50 and C/80 rates and elevated temperatures, the capacity decreases considerably by the end of the second discharge and then begins to level off as before.

In all cases the first discharge of each cell seems to indicate the maximum capacity which can be attained by that cell at the various operating conditions.

The general trend however is that there is a loss in capacity the lower the charging and discharging rate and that this is greatly enhanced with increase in the temperature of operation.

TABLE 2

C/40 charge and discharge.

Capacity after	1/	2/	3/	4/	5/	6/
1st discharge/hrs	47.25	45.33	46.50	46.00	46.25	47.00
2nd "	47.25	45.33	46.50	45.50	45.75	47.00
3rd "	47.00	45.25	45.00	43.58	43.50	43.85
4th "	43.50	43.58	43.25	43.42	43.42	43.85
5th "	43.42	43.58	43.25	42.16	41.85	42.42
6th "	43.00	43.50	43.25	41.33	41.16	41.50
7th "	43.16	41.58	41.50	39.85	39.85	40.42
8th "	43.16	43.16	43.16	40.75	40.75	41.25

TABLE 3

C/80 charge and discharge.

Capacity after	7/	8/	9/	10/	11/	12/
1st discharge/hrs	92.58	91.50	91.92	98.50	94.00	92.75
2nd "	89.85	90.42	88.67	81.00	79.00	79.75

TABLE 4

C/50 charge and discharge.

Capacity after	13/	14/	15/	16/	17/	18/
1st discharge/hrs	63.00	64.75	64.75	65.50	65.50	64.16
2nd "	51.10	54.10	52.58	57.75	58.00	55.85
3rd "	51.58	54.00	53.00	56.00	56.00	54.00

The above result on the basis of capacity measurements alone is in agreement with Armstrong's theory that low currents and

high temperature reduce the surface area of the active material by increasing the grain size of the crystals, as shown later, thereby leading to a reduction in overall capacity.

A large number of electron photomicrographs (Figure 6.2-6.7) were taken in order to establish the effect of discharge rate and temperature on the size of the cadmium hydroxide crystals.

Although the crystal size varies over a wide range, it is clearly seen that the crystals formed at C/80 are much larger on the average than those formed at C/40 rate, especially at the higher temperature.

However, the result at lower temperature is not as distinguishable as we might have hoped probably because C/40 is in itself a very low discharge rate. Further, the individual capacity of each cell when compared with a C/5 standard rate indicates that there is very little difference between them. A closer examination of the photomicrographs shows that the heat treated cells had crystals which were much more crystalline or sharper in appearance than those at room temperature. The structure of the crystals were not distinctively evident from the photomicrographs but in some cases (C/80 and C/50 Figure 6.4-6.7), there did appear to be some rhombic-like and hexagonal like crystals.

A comparison of these photomicrographs with those of a cell having had three standard C/5 charge and discharge cycles after formation clearly indicates the amount of recrystallisation that had taken place in the low rate discharged cells (Figure 6.8,6.9). The crystals in the standard new negative cells consisted of fluffy, finely-divided grains with a few rhombic-like variety



No. 5
MAGNIFICATION
3000x

5μ

Figure 6.2 New Negative after the 8th C/40 discharge Cycle and Room Temperature.



No. 2
MAGNIFICATION
3000x

5μ

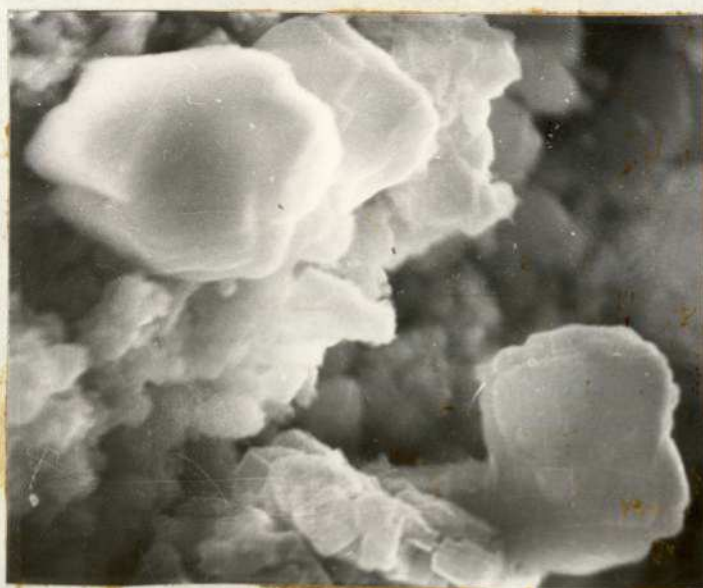
Figure 6.3 New Negative After the 8th C/40 discharge Cycle and 37°C.



No. 9
MAGNIFICATION
3000x

5μ

Figure 6.4 New Negative after the 2nd Discharge
C/80 Cycle and Room Temperature.



No. 10
MAGNIFICATION
3000x

5μ

Figure 6.5 New Negative after the 2nd C/80 Discharge
Cycle and 50°C.



No. 16
MAGNIFICATION
3000x

5μ

Figure 6.6 New Negative after the 3rd C/50 Discharge Cycle and 37°C.



No. 13
MAGNIFICATION
3000x

5μ

Figure 6.7 New Negative after the 3rd C/50 Discharge Cycle and 50°C.



MAGNIFICATION
3000x

5 μ

Figure 6.8 Discharged New Negative after 3
Standard Cycles.



MAGNIFICATION
3000x

5 μ

Figure 6.9 Discharged New Negative after 3
Standard Cycles.

of sizes much less than $2\mu\text{m}$ whereas those of the low-discharged cells often exhibited larger crystals of dimensions of the order of $10\mu\text{m}$ and above.

The crystals of a standard new negative electrode in the reduced state, 3 cycles after formation (Figure 6.10) were similar in size and appearance to the original $\alpha\text{-Fe}_2\text{O}_3$ (Figure 6.11), but an EDAX scan indicated that they were made up of a mixture of cadmium and iron oxide with a magnitude of around $1\mu\text{m}$.

If these photomicrographs are compared with discharged cells that had been similarly cycled but made up of straight cadmium hydroxide and graphite only then it is clearly seen that the crystal growth in this case is much more uniform in size and shape (Figure 6.12, 6.13), than those of the low-rate cells. The crystallite size without any expander has been increased almost four or five folds and also they are much more distinct in appearance and rhombic-like. In contrast the charged state of a similar cell is similar in appearance but has a much smaller grain size ($2\mu\text{m}$, Figure 6.14).

An EDAX scan study of the standard negative active material in its cycled state has shown that in most cases the iron oxide cannot be detected on its own but has cadmium or cadmium hydroxide covering its surface. Very few cadmium hydroxide crystals can be detected on their own but the iron oxide is used up in providing lattice sites for the deposition of cadmium and cadmium hydroxide via the soluble cadmate ion species $(\text{Cd}(\text{OH})_3^-)$.

To eliminate any possibilities of error arising from neighbouring crystallites when carrying out an EDAX study, a



MAGNIFICATION
3000x

5 μ

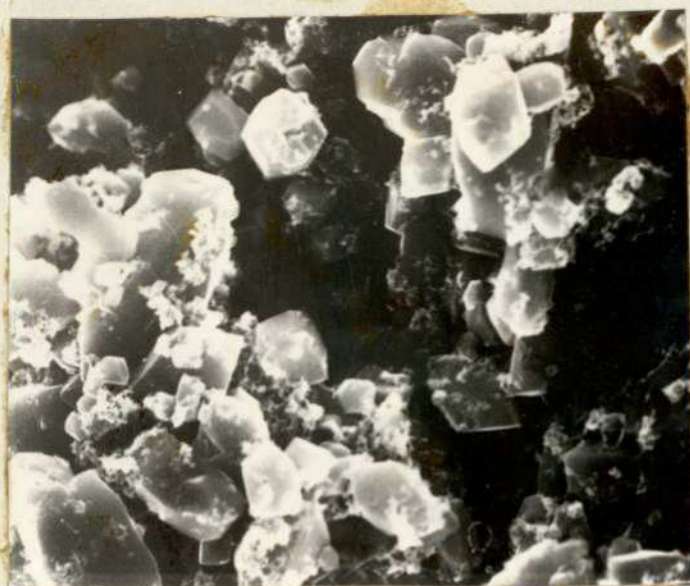
Figure 6.10 Charged New Negative after 3
Standard Cycles.



MAGNIFICATION
3000x

5 μ

Figure 6.11 Deanox Iron-Oxide.



MAGNIFICATION
3000x

5μ

Figure 6.12 Discharged $\text{Cd}(\text{OH})_2$ Electrode after
3 Standard Cycles.



MAGNIFICATION
3000x

5μ

Figure 6.13 Discharged $\text{Cd}(\text{OH})_2$ Electrode after
3 Standard Cycles.



Figure 6.14 Charged $\text{Cd}(\text{OH})_2$ Electrode after 3 Standard Cycles.

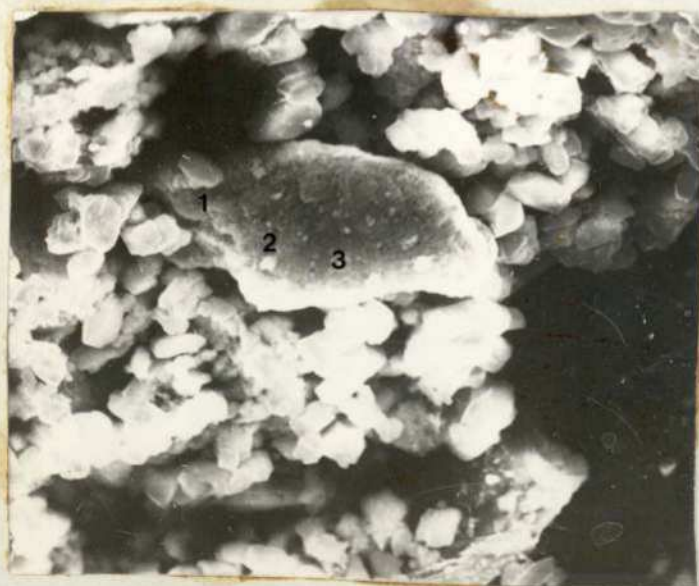


Figure 6.15 Mixture of $\text{Cd}(\text{OH})_2$ and New Negative Electrode Active Material from above in the Discharged State.

scan was made on a mixture containing a straight cadmium hydroxide electrode material and a standard new negative active material, both in the discharged state having had three standard cycles after formation.

In this way individual crystals of cadmium hydroxide alone and iron-oxide covered with cadmium hydroxide can be detected. Figure 6.15 shows a scanning electron photomicrograph of a typical mixture containing a large agglomerate with smaller aggregates surrounding it. The smaller crystallites are typical of the cadmium hydroxide crystals from Figure (6.12, 6.13) and as such only gave cadmium signals on the EDAX oscilloscope. The larger crystal was scanned at three different points as shown on the photomicrograph and the signals on the oscilloscope photographed to demonstrate the distribution of iron-oxide in the agglomerate. Point 1 showed virtually no iron signals and point 2 gave a slight signal but still not significant. However, point 3 in the centre of the crystal gave the normal intensity for the iron signal at around 6.5eV as shown in Figures 6.16-6.18, the other high signal being due to cadmium.

X-ray diffraction analysis of the low rate discharged negative active material showed conclusively that the cadmium hydroxide in all the photomicrograph was of the normal 'hexagonal' β -form and there was no γ -forms present.

However the structure of α -Fe₂O₃ from a normal rhombohedral form changed to γ -Fe₂O₃ which was cubic.

Typical X-ray diffraction intensity diagrams are shown in Figure 6.19. It is seen that no major lines corresponding to

EDAX Photographs of a Typical $\text{Cd}(\text{OH})_2/\text{Fe}_2\text{O}_3$ Mixture

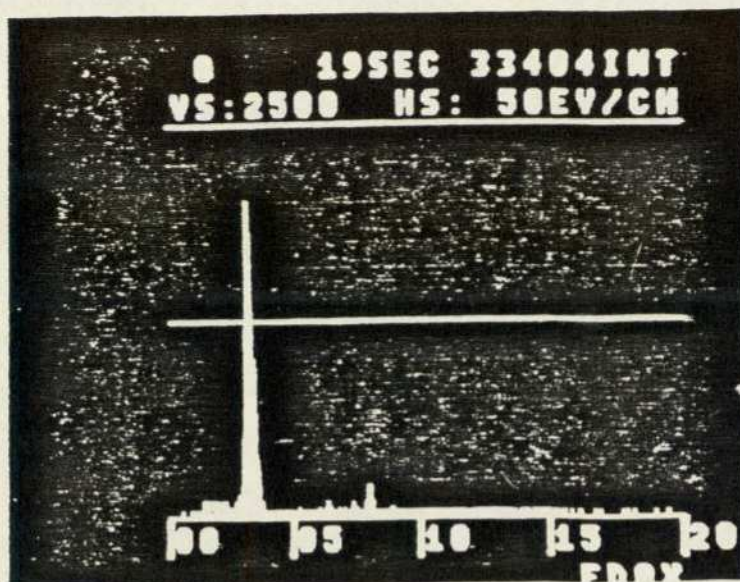


Figure 6.16

Point 1

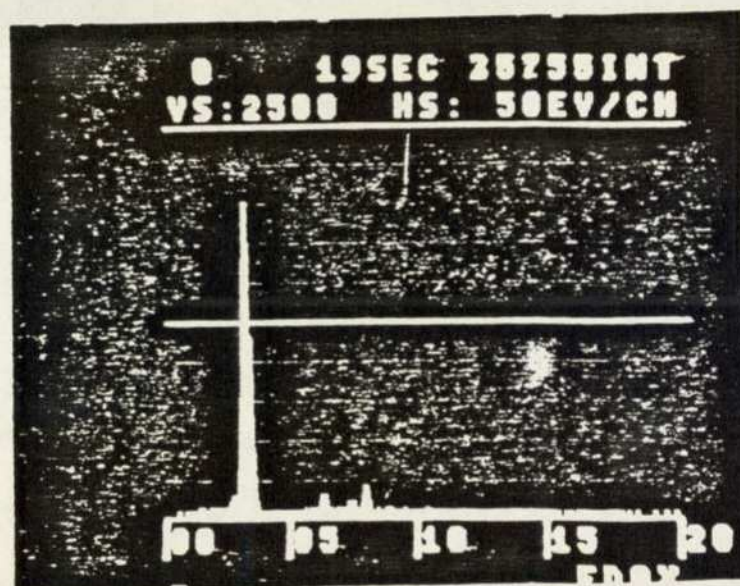


Figure 6.17

Point 2

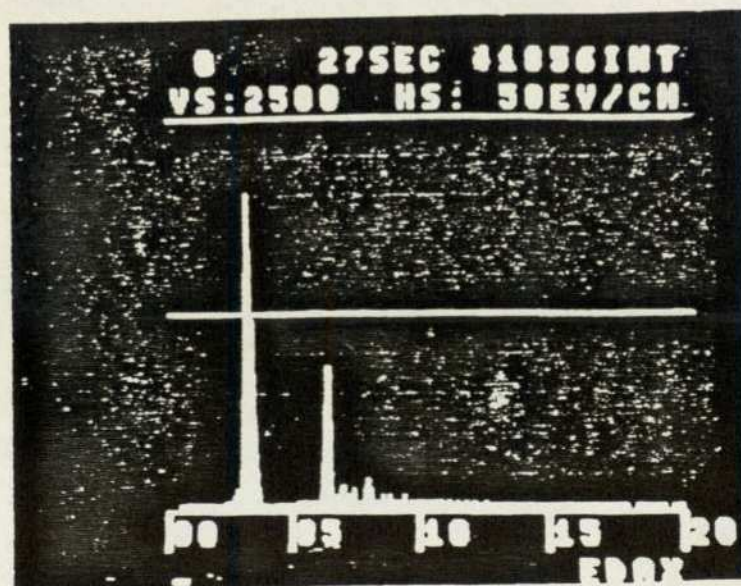
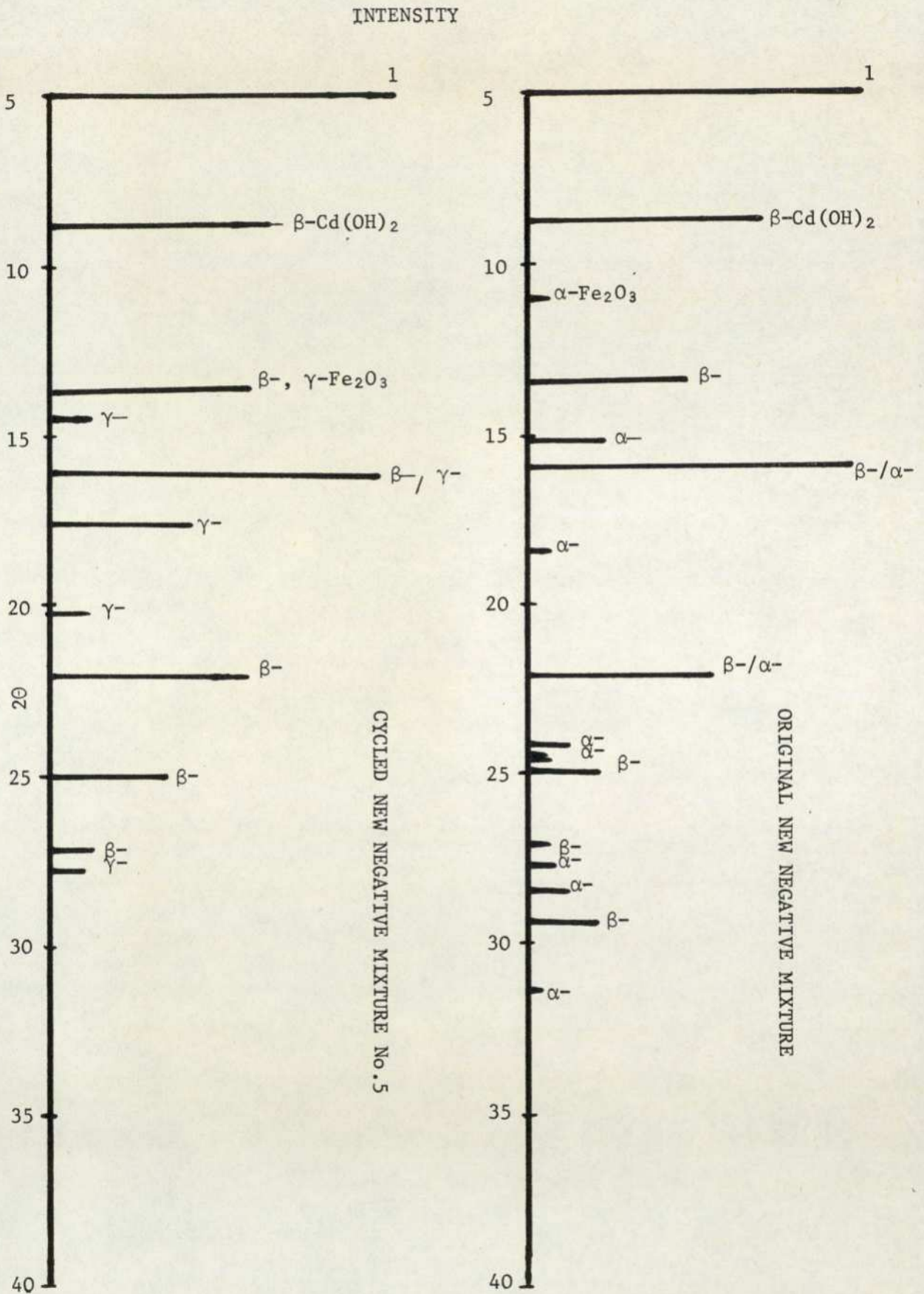


Figure 6.18

Point 3

Figure 6,19



α -Fe₂O₃ appeared in the pattern obtained with the cycled discharged electrode material while the electrodes that had not had any cycle whatsoever showed many distinct lines corresponding to α -Fe₂O₃.

It is postulated that this conversion from the α - form to the γ - form can only occur via a dissolution-precipitation mechanism. This could be an important factor in both establishing the mechanism of iron-oxide as an expander as well as pointing out the significance of poisoning of the positive plate in Alcad cells.

6.9 Conclusions

The effect of the low charge and discharge rates and high temperature on the negative cadmium electrode showed massive recrystallisation of the cadmium hydroxide with consequent loss in active surface area and thus of charging capacity. Scanning electron microscopy result indicated this to be the case and X-ray analysis showed the presence of γ -Fe₂O₃ with the exclusion of the α - form.

The accelerated crystal growth test^{120a} used within this project proved a quick and efficient method of accelerating crystal growth of the active material.

To study the full effects of the additives in the negative plate, the capacity of a plate needs to be decreased gradually and it is more feasible to use Harivel's method⁷⁹ (Chapter 7).

CHAPTER 7

EFFECT OF ADDITIVES ON THE PERFORMANCE OF THE

NEGATIVE PLATE

CHAPTER 7

EFFECT OF ADDITIVES ON THE PERFORMANCE OF THE NEGATIVE PLATE.

7.1 INTRODUCTION

Recrystallisation of active material is one of the most important processes in the cadmium negative electrode. The cadmium species are partly soluble and also the crystal ripening process tends to transform a lot of small, high surface area crystals into fewer larger ones having much less surface area. This phenomenon occurs in all cadmium electrodes, more intensely in some designs, and less in others. Recrystallisation is believed to be more severe with low porosity plates than with high porosity plates, but comparative data are not available on this point. Available data do show, however, that recrystallisation is promoted by low charge rates, high operating temperatures, repetitive cycling to low depths of discharge, and some conditions of storage, especially open circuit storage in the charged condition.

In a new cell, large hexagonal platelets of $\beta\text{-Cd(OH)}_2$ have been observed during the early stage of discharge. These platelets gradually enlarge during the discharge, then during the last part of the discharge there is an accelerated enlargement.

Nucleation and growth of $\beta\text{-Cd(OH)}_2$ apparently dominate during the early part of discharge, followed by crystal growth and dissolution of small crystals, with simultaneous growth of larger crystals.

The differences between a new cell and an Alcad's defect cell are extreme.¹⁶⁰ All changes appear to take place within the

cadmium electrode and here recrystallisation is found to occur such that the submicron particles of $\text{Cd}(\text{OH})_2$ in a fresh cell enlarges to become rhombic crystals of greater than 10μ size in the stored defective cell.

With the development of the scanning electron microscope, SEM, it has become possible to actually study the effect of various additives on the basic structure of the $\text{Cd}/\text{Cd}(\text{OH})_2$ electrode. Several attempts have been made to look at the oxidised or reduced negative electrode with SEM,^{6,84} but no systematic study of the effect of expanders on cycled electrodes has been reported.

There have been very few studies pertaining to the effect of PVA and iron-oxide on the negative electrode performance and crystallogenic modification during the discharge and virtually none on pocket type-electrodes. The present investigation was undertaken primarily to study the effect of additives on the structure of the cadmium-cadmium hydroxide electrode during its oxidation.

7.2 Experimental

Harivel, et al.⁹ showed by X-ray examination that a low charge rate promotes the formation of cadmium crystals of substantial size whereas finer crystals can be obtained at high charge rates. This occurs because a larger number of nucleation sites are used at the higher current density leading to the deposition of large numbers of relatively smaller cadmium micro-crystals.

Preliminary work at City University established that the

decrease in capacity by this method was gradual when using the C/40 charging and C/5 discharging mode. The effect of increase in the temperature of operation was found to be unimportant (Table 5).

Surface area measurements of several materials were made at Chloride Technical Limited (Research Centre) that were thought to be useful additives to investigate. Good expanders were thought to be the iron-oxides, titanium dioxide, magnesium hydroxide and PVA and barium hexa iron-oxide, calcium oxide, lead hexa iron-oxide, boron nitride and graphite as bad expanders.

The result of the surface areas of most of the materials are shown in Table 6. With the surface areas known, different negative mixtures were made by adding a surface area equivalent of the $\alpha\text{-Fe}_2\text{O}_3$ that was already added in Alcad's manufacture of the new negative active material.

The new negative mixture was made from compacted cadmium hydroxide, $\alpha\text{-Fe}_2\text{O}_3$, PVA and graphite, all obtained from Chloride Alcad. The blend of the active material was kept to Alcad's specification (Chapter 6) and is shown in Table 7 along with the weight ratios of all other mixtures.

In addition to the new negative mixture made in the laboratory, the standard new negative mixture obtained from the plant was also used to make plates.

Negative plates with twelve pockets containing different expanders were then prepared on the Alcad experimental plate making line. A negative plate containing the normal amount of PVA was made as well as one without any expander. In the case of calcium oxide, the normal weight% of iron-oxide that was added

TABLE 5

C/40 charge and C/5 discharge

1, 2 at room temperature,

3, 4 at 50°C.

Capacity after	1/	2/	3/	4/
1st discharge/hrs	5.58	5.67	5.25	5.25
2nd "	5.25	5.33	4.67	4.67
3rd "	5.00	5.00	4.41	4.41
4th "	4.58	4.58	4.16	4.16
5th "	4.33	4.33	4.00	4.00

TABLE 6

Sample	Gas used for Adsorption	Specific Surface Area/m ² g ⁻¹
Deanox Fe ₂ O ₃	Argon	3.34
Calcined Fe ₂ O ₃	"	4.56
BaO.6Fe ₂ O ₃	"	0.70
PbO.6Fe ₂ O ₃	"	2.07
Precipitated Fe ₂ O ₃	Nitrogen	6.07
TiO ₂	"	9.05
BN	"	10.08
Graphite	"	9.06

TABLE 7

Weight ratios of the various active material mixtures.

*Additives were added with respect to their surface areas compared with that of Deanox iron-oxide surface area.

The figures in bracket indicates the filling weight with respect to the cadmium hydroxide content in comparison to the std. new negative active material.

New negative and standard new negative electrode.

	<u>wt/g</u>	<u>%wt</u>	
Cd(OH) ₂	150.00	80.32% Cd(OH) ₂	(5g)
Deanox Fe ₂ O ₃	30.00	16.06% Fe ₂ O ₃	
Graphite	3.75		
PVA	3.00	1.61% PVA	
<u>Deanox Fe₂O₃ Electrode.</u>			
Cd(OH) ₂	150.00	81.63% Cd(OH) ₂	(4.92g)
*Deanox Fe ₂ O ₃	30.00	16.33% Fe ₂ O ₃	
Graphite	3.75		
<u>PVA Electrode</u>			
Cd(OH) ₂	150.00	95.69% Cd(OH) ₂	(4.2g)
PVA	3.00	1.91% PVA	
Graphite	3.75		
<u>Straight Cadmium Hydroxide Electrode.</u>			
Cd(OH) ₂	150.00	97.56% Cd(OH) ₂	(4.12)
Graphite	3.75		
<u>Calcined Fe₂O₃ Electrode</u>			
Cd(OH) ₂	150.00	77.04% Cd(OH) ₂	(5.21g)
*Calcined Fe ₂ O ₃	40.96	21.04% Fe ₂ O ₃	
Graphite	3.75		
<u>BaO.6Fe₂O₃ Electrode.</u>			
Cd(OH) ₂	150.00	50.52% Cd(OH) ₂	(7.95g)
*BaO.6Fe ₂ O ₃	143.14	48.21% BaO.6Fe ₂ O ₃	
Graphite	3.75		

TABLE 7 (cont.)

<u>*TiO₂ Electrode.</u>	<u>wt/g</u>	<u>% wt</u>	
Cd(OH) ₂	150.00	91.01% Cd(OH) ₂	(4.41g)
*TiO ₂	11.07	6.72% TiO ₂	
Graphite	3.75		
<u>Precipitated Fe₂O₃ Electrode.</u>			
Cd(OH) ₂	150.00	88.10% Cd(OH) ₂	(4.56g)
*pptd. Fe ₂ O ₃	16.51	9.70% Fe ₂ O ₃	
Graphite	3.75		
<u>CaO Electrode.</u>			
Cd(OH) ₂	150.00	81.63% Cd(OH) ₂	(4.92g)
CaO	30.00	16.33% CaO	
Graphite	3.75		

in Alcad cell negatives was substituted by calcium oxide.

The filling weight on the plate making line was varied for different mixtures so as to keep the amount of cadmium hydroxide added constant. For the standard new negative active material, the filling weight was 5g per 125mm length of pocket and was varied as such for different additives.

The negative and the positive plates were bolted to the pole bolts which acted as cell terminal posts. The plates were assembled in a plastic nickel-cadmium battery container containing a vent plug at the top to allow gases to pass out but not allow gases such as carbon dioxide to pass in.

For the lead hexa iron-oxide, boron nitride and graphite additives, because these materials were considered at a much later date, only pocket type cells were made as described previously.

The cells were first given a soaking process in the caustic electrolyte followed by the formation process according to the Alcad laboratory schedule.

Galvanostatic method was used for charging in all cases using a Chemical Electronics 0.5A- 20V potentiostat. The discharge of the plate type cell was made through a resistor at constant current whereas with a single pocket type cell the potentiostat was used.

After the formation cycle, the electrolyte from each cell was discarded and replaced by a lithium hydroxide doped KOH. The capacity cycle was then carried out at C/5 charge and discharge rates and the potentials of each cadmium electrode down to $-0.700V$ were tabulated by comparison with a standard Hg/HgO electrode

after each cycle.

Following the capacity cycle, low rate charging at C/40 and relatively high rate discharging modes at C/5 were employed throughout the rest of the experiment. At the end of certain discharge cycles, a pocket was removed from each plate type cell and a small amount of the active material examined under the electron microscope.

The selected samples for scanning electron microscopy examination were prepared by washing the electrode active material several times in deionised-distilled water until no trace of the caustic was left. The most suitable magnification to work with was found to be 3000x and the condition on the electron microscope was kept at 40KV and high resolution setting. In some cases lower magnification was used when good resolution could not be obtained at the higher magnification, due possibly to oxidation of the microscope filament or even due to uneven surfaces of the active material.

Some of the active material from selected cells was used for X-ray crystallography analysis. The samples were examined in the discharged state on a Phillips 1010 X-ray diffractometer, using the $K\alpha$ radiation of Molybdenum. The patterns were taken from a ground mixture of the active material and the scanning speed on the goniometer being $1/8^\circ/\text{min.}$ for the 2θ angle with corresponding paper speed.

One-half of the pocket was used for cyclic voltammetry but only the microscopic examination, capacity tests, and X-ray analysis proved of much value in the examination of the oxidised

negative electrode, which consisted almost entirely of cadmium hydroxide. Therefore, only the capacities, microscopy and X-ray examination of the cadmium-cadmium hydroxide electrode are considered.

7.3 Results and Discussion.

The result of the effect of low charging and high discharging rates in terms of the individual capacities obtained from each cell is given in Table 8.

The cycling test indicated that the standard new negative mixture had greater capacity than PVA or $\alpha\text{-Fe}_2\text{O}_3$ mixture on their own.

The general trend on the plate type cell is shown below:-

Std. New Negative > PVA > iron-oxides > TiO_2 > Straight $\text{Cd}(\text{OH})_2$ > $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ > CaO

The calcium oxide mixture gave the poorest performance with virtually no capacity at all whereas with the low surface energy substrate barium hexa iron-oxide, the performance was about 20% that of the standard new negative mixture initially with gradual increase in the capacity later on with cycling.

The calcium oxide result was explained by the fact that calcium hydroxide had deposited on the surface of cadmium hydroxide thus preventing any charge take up. This reaction was also thought to be happening with the barium hexa iron-oxide electrode, but X-ray analysis could not detect any barium hydroxide even though there were indications that the expander might have broken down in the form of the original mixture. The slight increase in the

TABLE 8

(1) New Negative (2) Deanox Fe_2O_3 (3) PVA (4) Straight $\text{Cd}(\text{OH})_2$ (5) Calcined Fe_2O_3 (6) $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ (7) TiO_2
 (8) Precipitated Fe_2O_3 (9) CaO (10) Standard New Negative (11) BN (12) $\text{PbO} \cdot 6\text{Fe}_2\text{O}_3$ (13) Graphite, electrode mixtures.

Normal mode of operation after C/5 charge and discharge formation cycle is:- C/40 charge and C/5 discharge.

	1/	2/	3/	4/	5/	6/	7/	8/	9/	10/	11/	12/	13/
Initial capacity after formation cycle/hrs.	5.25	5.17	4.92	4.67	5.25	1.33	4.67	5.08	0.08	6.00	4.00	4.30	4.25
Capacity after													
1st discharge/hrs.*	4.83	4.67	4.75	4.33	4.58	1.42	4.42	4.92	-	5.25	3.50	4.00	-
2nd "	4.92	4.42	4.83	4.50	4.33	1.33	4.17	4.58	-	5.17	-	-	-
3rd "	4.92	4.42	4.83	4.25	4.17	2.25	4.00	4.25	0.25	5.00	-	-	-
4th " *	4.75	3.92	4.42	3.92	3.67	2.50	3.50	3.83	0.45	4.75	-	-	-
5th "	4.67	3.75	4.42	3.75	3.42	2.17	3.50	3.67	0.18	4.67	-	-	-
6th "	4.50	3.58	4.08	3.42	3.33	1.92	3.42	3.67	-	4.50	-	-	-
7th " *	4.33	3.42	3.75	3.25	3.25	1.92	3.25	3.58	-	4.33	-	-	-
+	82.50	66.00	76.00	69.50	62.00	144.00	69.50	70.50	-	72.00			

* Pocket removed for SEM analysis

+ % of initial capacity after the 7th cycle.

capacity of the barium hexa iron-oxide and calcium oxide cells could possibly have been due to the substrates being leached out of the negative plate on continuous cycling.

The result on lead hexa iron-oxide, graphite and boron nitride expander cells also gave lower capacities than the standard new negative cell and considerable emphasis must not be placed on this fact since only one cycle was carried out. However, the trend was there that the low surface energy substrates were bad expanders.

The titanium dioxide, classed as a good expander before the start of the experiment gave a very encouraging result in the negative electrode. The capacities that were obtained were just as good as the iron-oxides even though the amount of TiO_2 added to the negative plate was only $1/3$ that of deanox iron-oxide.

Up to the 5th cycle the straight cadmium hydroxide cell gave performances which matched the iron-oxides and titanium dioxide expander cells, but subsequent cycling resulted in a steady decline in the capacity.

In the case of the three iron-oxide cells, the precipitated iron-oxide plate appeared to give a slightly better performance than the Deanox or calcined iron-oxides, although overall there was very little difference between them. The general trend between the iron-oxides and the titanium dioxide substrate was that, intrinsically, the higher surface area material gave the better performance. Since lower weight ratios were used in the case of the titanium dioxide and precipitated iron-oxide expander it can be stated theoretically anyway, that these materials

could have given much higher capacities than the Deanox iron-oxide had the cell contained more of the substrate.

The capacities obtained by using only PVA as the expander were far greater than any of the solid inorganic expanders. This immediately gives rise to the question as to whether or not the inorganic materials are actually expanders. One might ask is it the PVA or the iron-oxides that controls the crystal growth of the cadmium hydroxide or is it a combination of both.

However, the best result in terms of capacity measurements was obtained when a mixture of Deanox iron-oxide and PVA were added as the substrates. In this case the standard new negative cell as well as the new negative cell gave equally good performances.

The above results on the basis of capacity measurements alone indicates that expanders such as a high surface area inorganic additive, i.e. iron-oxide or titanium dioxide and an organic material like PVA are useful additive in the negative plate of a nickel-cadmium battery to improve cycle life. Also a combination of an inorganic and an organic additive give an even better performance than when used singly.

Table 8 also gives the percentage of the initial capacity retained after the 7th cycle and the general trend is that the new negative is superior to PVA and this in turn to the iron-oxides and titanium dioxide electrode mixtures.

7.4 Electron Microscopy Examination.

At the end of the 1st, 4th and 7th discharge cycle, a pocket

was removed from the negative plate of each cell and a cross-section of the active materials examined under the electron microscope. The magnification was 3000x in most cases, but on some materials, good resolution could not be obtained and so a lower magnification was used.

7.4a Structure of Electrodes containing neither PVA nor Fe_2O_3

Figures 7.1, 7.2, and 7.3 depicts the SEM examination of the structure of electrodes in which the nucleation and growth of the cadmium hydroxide crystals has not been altered by additives. Figure 7.1 at a magnification of 3000x, illustrates that after the end of the 1st discharge cycle, the size of the cadmium or cadmium hydroxide crystals are already so great that further cycling appears to have no drastic effect on their enlargement. It can be seen from the last chapter that the discharged state of the cadmium hydroxide electrode after three standard cycles have microstructures which are similar in shape and size to that electrode which have been cycled by the above mode. Thus low rate charging appears to have relatively small effect, initially anyway, on the electrode structure of the straight cadmium hydroxide negative electrode.

Figures 7.2 and 7.3 are photomicrographs taken at the end of the 4th and 7th discharge cycle and the size of the cadmium hydroxide particles have increased from an average of $5\mu\text{m}$ to $8\text{--}10\mu\text{m}$ in diameter.

It is very important in this discussion that the extensive nature of the massive growth process in the plates containing neither PVA nor Fe_2O_3 be realised as otherwise the large



MAGNIFICATION
3000x

5μ

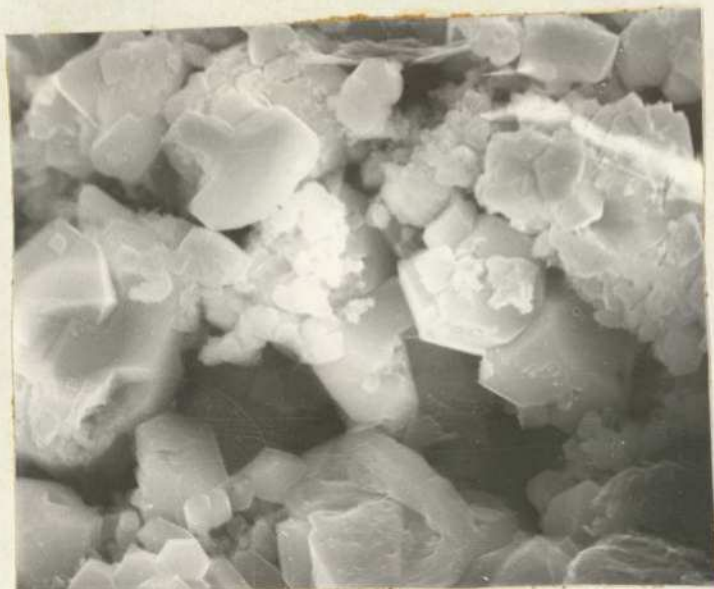
Figure 7.1 Straight $\text{Cd}(\text{OH})_2$ Electrode Material,
1st Cycle.



MAGNIFICATION
3000x

5μ

Figure 7.2 Straight $\text{Cd}(\text{OH})_2$ Electrode Material,
4th Cycle,

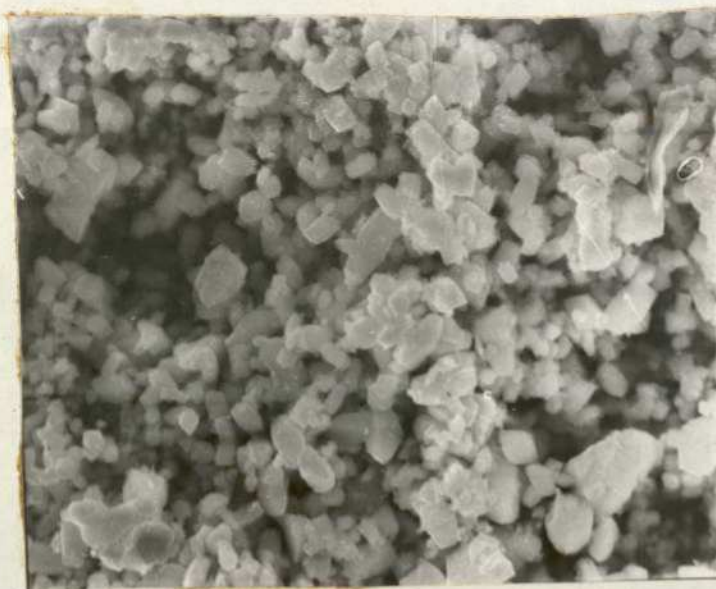


MAGNIFICATION

3000x

5μ

Figure 7.3 Straight $\text{Cd}(\text{OH})_2$ Electrode Material,
7th Cycle.



MAGNIFICATION

3000x

5μ

Figure 7.4 PVA Expander Electrode Material,
1st Cycle.

inhibiting effect of the expanders on this growth process will not be fully appreciated. The particles of Figure 7.1 are fairly large and uniform in size on surface but appears to be much smaller internally. Figure 7.3 shows them to be more rhombic-like and some of the smaller ones hexagonal like. The rhombic structures are associated with the defect Alcad cells as mentioned before. The hexagonal crystals could possibly be the cadmium particles whereas the much larger crystals be the cadmium hydroxide but this is not quite certain. Also the smaller internal crystallites appears to have been replaced by the much bigger rhombic-like crystals.

7.4b Structure of Electrodes containing only PVA as additive.

The presence of PVA in the negative electrode has a marked effect on the cadmium hydroxide structure as well as the capacity. The larger agglomerates such as shown in Figure 7.1 almost entirely disappear and are replaced by more uniform particles of about 1-2 μ m in diameter (Figure 7.4).

It is difficult to resolve this structure because of the fine, looseness nature of the particles, but from examination at a higher magnification (Figure 7.5), however, it was concluded that the particles consisted of many small platelets, growing sideways in two dimensions only, from some common nucleus. This growth resulted in the production of roughly spherical particles with a large electrochemical surface area and a very rough and porous surface.

Figures 7.6 and 7.7 are photomicrographs taken at the end of the 4th and 7th discharge cycles respectively and indicates



MAGNIFICATION

10,000x

2.5 μ

Figure 7.5 PVA Expander Electrode Material,
1st Cycle.



MAGNIFICATION

3000x

5 μ

Figure 7.6 PVA Expander Electrode Material,
4th Cycle.



MAGNIFICATION
3000x

5 μ

Figure 7.7 PVA Expander Electrode Material,
7th Cycle.



MAGNIFICATION
10,000x

2.5 μ

Figure 7.8 Deanox Fe₂O₃ Expander Electrode
Material, 1st Cycle.

that there has been an overall increase of only two-fold in size during cycling. The smaller crystallites have been replaced by larger agglomerates and the structure appears to resemble the photographs taken from the PVA - free electrode, but of much smaller size.

It is clear that the modification produced by the PVA is many times more effective than would at first appear. The structure of the cadmium hydroxide in the presence of the additive is similar in shape but much smaller in size and thickness and have been replaced by simpler structures. It is also likely that the total surface area presented by the particles of Figure 7.4 is many times larger than that of the particles of Figure 7.1 and this is also reflected in the relative capacities.

7.4c Structure of Electrodes containing only Deanox Fe_2O_3 as additive

The SEM examination of the structure of electrodes in which only Deanox iron-oxide was the additive indicated that the structure was essentially similar to the one produced when PVA was added but more rhombic-like and possibly growing in three dimensions, Figure 7.8. There were very fine grainy areas in some places and an EDAX scan revealed a relatively high iron signal in these regions than on the flatter areas. These grainy areas were also clearly visible in the photomicrographs taken at the end of the 4th and 7th discharge cycles (Figures 7.9 and 7.10 respectively).

The majority of particles of Figure 7.8 were 1-2 μm in diameter increasing to 2-3 μm after the 7th cycle, with the shape of the crystals becoming more non-uniform and spherical.



MAGNIFICATION

3000x

5μ

Figure 7.9 Deanox Fe_2O_3 Expander Electrode Material, 4th Cycle.



MAGNIFICATION

3000x

5μ

Figure 7.10 Deanox Fe_2O_3 Expander Electrode Material, 7th Cycle.

Careful examination of plates with and without Deanox iron-oxide showed no appreciable differences in particle structure in most areas after the 1st cycle, although later on, whereas the cadmium hydroxide electrode crystals enlarged to produce rhombic particles of 10 μm in diameter, the iron-oxide doped electrode changed from probably rhombic-like, but much smaller crystals to small spherical agglomerates.

The Deanox iron-oxide seems to have a delayed effect on altering the crystal structure of the cadmium hydroxide but nevertheless it does take part in changing the morphology of the cadmium hydroxide crystals as well as the surface area.

7.4d Structure of Electrodes containing both PVA and Deanox Fe_2O_3 .

As mentioned before, the new negative blend is one that has been made in the laboratory using conventional mixtures and so the uniformity of the mixing cannot be expected to be very high. Hence the behaviour of the electrode initially, in terms of the capacity and electron micrograph structures should be expected to be different from that of the standard new negative active material that has been mixed on the plant scale.

Figures 7.11, 7.12 and 7.13 are photomicrographs of the new negative plate active material at the end of the 1st, 4th and 7th discharge cycles respectively.

Figure 7.11 shows that the particles are very similar in shape and size to those of Figure 7.4 containing only PVA as the additive but further cycling produces crystals (Figure 7.12) which resembles the Deanox iron-oxide electrode crystal structures.



MAGNIFICATION
3000x

5 μ

Figure 7.11 New Negative Electrode Material,
1st Cycle.



MAGNIFICATION
3000x

5 μ

Figure 7.12 New Negative Electrode Material,
4th Cycle.



MAGNIFICATION

3000x

5 μ

Figure 7.13 New Negative Electrode Material,
7th Cycle.



MAGNIFICATION

3000x

5 μ

Figure 7.14 Standard New Negative Electrode
Material, 1st Cycle.

Figure 7.13 is a photomicrograph of randomly oriented rhombic as well as much smaller granier-like crystals of high surface area.

Figures 7.14, 7.15 and 7.16 depicts the photomicrographs of the standard new negative electrode active material after the 1st, 4th and 7th discharge cycles respectively.

It can be seen from Figure 7.14 that the granier crystals have already begun to form from the 1st cycle and continue to produce much smaller aggregate crystals of 1-2 μm in size on continuous cycling. The result of the capacity measurement clearly indicates that initially, the standard new negative mixture is superior to the new negative made in the laboratory possibly due to more uniform mixing on the plant scale but gradual cycling causes the performance to level out. This non-uniform mixing is also demonstrated perhaps in the photomicrograph of Figure 7.11 where it would seem that only PVA is functioning in modifying the crystal growth in the initial stage and the iron-oxide playing a part later on.

It is fairly well established then that PVA and Deanox iron-oxide are more effective when used together than when either is used alone. As has already been stated, iron-oxide tends to produce granier as well as rhombic-like crystals and the effect of PVA was to decrease the size of the individual platelets to almost two dimensions. These platelets undoubtedly increase the total surface area, but are usually found to be so tightly packed in agglomerates that the porosity appears to be small.

When iron-oxide and PVA were used together the structure



MAGNIFICATION

3000x

5 μ

Figure 7.15 Standard New Negative Electrode Material, 4th Cycle.



MAGNIFICATION

3000x

5 μ

Figure 7.16 Standard New Negative Electrode Material, 7th Cycle.

of the cadmium hydroxide was different from either that of the expander free electrode or from that of the electrode containing only the PVA additive. The type of structure that was typical when PVA and iron-oxide were both present was found to be a cluster of granier-like particles with the appearance of a high surface area and also of higher porosity than the latter.

It is generally agreed that the granier structures have a higher surface area than the plate-like structures of the PVA additive electrode and this alone may explain the better performance obtained when the additives are used together.

7.4e Structure of Electrodes containing only precipitated Fe_2O_3 as the additive.

Precipitated iron-oxide, obtained from Hopkin and Williams was added as the expander in the amount dependent upon its surface area (Table 6). Since the surface area was relatively high, only about half the amount to that used in the Deanox iron-oxide plate was necessary.

Careful examination of the negative plate with and without precipitated iron-oxide showed remarkable differences in shape and size of the individual particles.

The particles containing the iron-oxide expander consisted of much smaller, granier aggregates of high surface area and porosity (Figure 7.17) than the one without any additive (Figure 7.1).

Figures 7.17, 7.18 and 7.19 are photomicrographs taken at the end of the 1st, 4th and 7th discharge cycles respectively and shows that progressive cycling causes the crystals to grow



MAGNIFICATION
3000x

5μ

Figure 7.17 Ptd. Fe_2O_3 Electrode Material,
1st Cycle.



MAGNIFICATION
3000x

5μ

Figure 7.18 Ptd. Fe_2O_3 Electrode Material,
4th Cycle.



MAGNIFICATION
3000x

5μ

Figure 7.19 Pptd. Fe_2O_3 Electrode Material,
7th Cycle.



MAGNIFICATION
3000x

5μ

Figure 7.20 Calcined Fe_2O_3 Electrode Material,
1st Cycle.

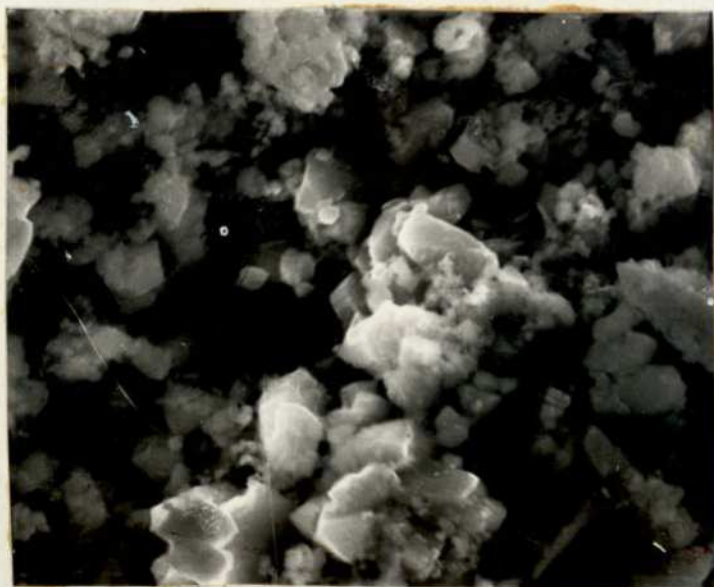


MAGNIFICATION

1500x

5 μ

Figure 7.21 Calcined Fe_2O_3 Electrode Material,
4th Cycle.



MAGNIFICATION

3000x

5 μ

Figure 7.22 Calcined Fe_2O_3 Electrode Material,
7th Cycle.

in a much similar way to the one containing only Deanox iron-oxide. An indication is that the precipitated iron-oxide probably produces more fluffier type crystals but there is not much to choose between them in terms of capacity measurements.

Similar results were obtained when calcined iron-oxide was used as the expander and Figures 7.20, 7.21 and 7.22 show this to be the case.

7.4f Structure of Electrodes containing only TiO_2 as the additive.

The amount of TiO_2 that was added was approximately 1/3 that of the Deanox iron-oxide and yet the photomicrographs of Figures 7.23, 7.24 and 7.25 taken after the 1st, 4th and 7th discharge cycles indicates that modification of the crystal structure can also be obtained using TiO_2 as the expander.

Figure 7.23 show that the shapes and sizes of the particles resemble the electrode structure containing only PVA.

On further cycling, the electrode structure begins to form rhombic-like crystals and eventually goes to the granier-like form as seen in the iron-oxide doped electrode. However, these granier structures, although of a high surface area, appear to be much more aggregated resulting in perhaps a decrease in porosity. This is not shown in the performance when compared with the iron-oxide cells, but the agglomeration could be due to the way TiO_2 behaves in strong alkaline media by having a tendency to form gels on the microscale. It is difficult to say at this stage whether or not this gel formation, if it happens at all, is beneficial or detrimental. On one hand it may behave like PVA



MAGNIFICATION
3000x

5μ

Figure 7.23 TiO_2 Expander Electrode Material,
1st Cycle



MAGNIFICATION
3000x

5μ

Figure 7.24 TiO_2 Expander Electrode Material,
4th Cycle.



MAGNIFICATION

3000x

5μ

Figure 7.25 TiO_2 Expander Electrode Material,
7th Cycle.



MAGNIFICATION

3000x

5μ

Figure 7.26 CaO Expander Electrode Material,
1st Cycle.

as a surface acting agent or otherwise be harmful by forming agglomerates. If it behaves like a gel, then a much lesser amount in the active material would be more useful to the battery capacity. The only way to prove this is to have cells containing TiO_2 and PVA and cycle them using the normal rates and conditions of operation.

It seems therefore that the behaviour of TiO_2 and Fe_2O_3 as battery expanders are totally different. Whereas, it is believed that iron-oxide dissolves (as seen later) and reprecipitates and forms a more or less homogeneous mixture with the cadmium hydroxide, TiO_2 probably forms a gel and acts as a surface acting agent as well as a nucleating agent.

7.4g Structure of Electrodes containing CaO as the additive.

Although cycling tests gave virtually no capacity with CaO as the expander, the photomicrographs obtained were quite interesting. Figures 7.26 and 7.27 were taken at the end of the 1st and 7th cycle respectively.

Figure 7.26 showed that the surface of the electrode was completely coated with a white deposit, most likely, calcium hydroxide, thus preventing any charge take up of the cadmium hydroxide. Further cycling appeared to have no effect on producing any reasonable capacity but the calcium hydroxide flakes began to crystallise out to form dendritic-needle-like crystals (figure 7.27).



MAGNIFICATION
3000x

5μ

Figure 7.27 CaO Expander Electrode Material,
7th Cycle,



MAGNIFICATION
3000x

5μ

Figure 7.28 Ba_{0.6}Fe₂O₃ Expander Electrode
Material, 1st Cycle.

7.4h Structure of Electrodes containing $\text{BaO}, 6\text{Fe}_2\text{O}_3$ as the additive.

Barium hexa iron-oxide doped electrode gave very little capacity initially and later on increased to a steady value, but was still less than that of the new negative electrode.

The photomicrograph of Figure 7.28 taken after the 1st cycle clearly indicated why the capacity was so low. The electrode active material appeared to be one mass with very few pores left for electrochemical reactions to take place.

Further charge and discharge cycles probably had the effect of breaking up this mass creating more pores to give an increase in the capacity (Figure 7.29). Figure 7.30 taken at the end of the 7th cycle indicated that the structure by now was very porous and granular and an EDAX scan resulted in the signals due to iron, barium and cadmium as expected (not shown). But it did not indicate whether the cadmium hydroxide was depositing on the barium hexa iron-oxide or vice-versa. It seems most likely that the barium hexa iron-oxide was covering the major part of the active material and preventing any charge take up in a similar manner to CaO , although the presence of barium hydroxide films remained undetected.

7.4i Structure of Electrodes containing BN as the additive.

BN was added as the expander using the single pocket type cell and so only one test could be done on the cell as the pocket once cut up and disturbed, could not be used again. The capacity obtained was not quite as bad as the barium hexa iron-oxide electrode and the crystal structure at the end of the 1st cycle showed very interesting results. Two parts of the electrode were



MAGNIFICATION
3000x

5μ

Figure 7.29 $\text{Ba}_{0.6}\text{Fe}_2\text{O}_3$ Expander Electrode Material, 4th Cycle.



MAGNIFICATION
3000x

5μ

Figure 30 $\text{Ba}_{0.6}\text{Fe}_2\text{O}_3$ Expander Electrode Material, 7th Cycle.

examined under the electron microscope. The first one at 1000x magnification was that of the surface (Figure 7.31) and the other at 3000x of a broken up cross-section (Figure 7.32).

The surface specimen gave a very high cadmium signal on the EDAX indicating that the extensive growth of the skeletal nature was predominantly cadmium hydroxide.

On the broken up specimen it was concluded that most of the internal particles were predominantly boron nitride with a small amount of cadmium hydroxide. It was difficult to say however, which particle was cadmium hydroxide or boron nitride because of the similarity of shape and size of both of them.

It was reasonable to expect the boron nitride crystals to be at the internal part of the electrode because with the material being electrochemically in-active and also inert in strong caustic solution, it could not take part in any reaction and hence could not migrate. Only the cadmium had the possibility of migrating outside the electrode to form cadmium hydroxide on discharge growing subsequently on the boron nitride particles.

Work was also done on other low surface energy expander materials such as lead hexa iron-oxide and even graphite and although single pocket cells were used and only the standard formation cycles carried out, there were signs that these materials were detrimental to the capacity (Table 8).

7.5 Conclusions.

From the above observations, it was evident that PVA produced a marked change in the microstructure of the oxidised



MAGNIFICATION

1000x

10 μ

Figure 7.31 BN Expander Electrode Material,
1st Cycle.



MAGNIFICATION

3000x

5 μ

Figure 7.32 BN Expander Electrode Material,
7th Cycle,

Cd/Cd(OH)₂ electrodes. In other words, the presence of PVA changed the growth behaviour of the cadmium hydroxide crystals that was formed during the discharge process. The nature of the change produced by the PVA reduced the extensive growth of the large rhombic-like crystal formation with a low surface area to one of plate-like crystals of relatively high surface area.

All type of iron-oxide expanders seemed to provide granier type crystals with high surface area although the shape of the crystals were of a three dimensional kind. The result on the iron-oxide cells also showed that the important factor in the expander addition was not the amount that was added but upon its surface area. Since it was believed that the iron-oxides had a tendency to dissolve it was important to realise the precipitated product that was obtained with cadmium hydroxide was on a microscale, and therefore, its surface area would be considerably enhanced.

When iron-oxide and PVA were used together additional changes in the structure of the cadmium hydroxide crystals took place, beyond that produced by PVA or iron-oxide alone. These additional changes acted to cause a further increase in the surface area and increased porosity.

It seems highly likely then that PVA appears to be the inhibitor of crystal growth and the presence of the iron-oxide in very fine particles provide the nuclei on which the cadmium hydroxide crystallises.

The behaviour of TiO₂ as a potentially good expander appeared to be different to the iron-oxide expander. Although

titanium dioxide modified the crystal structures of the cadmium hydroxide and gave capacities which matched those from the iron-oxide cells, the mechanism of its operation could not be understood.

The above work has shown that high surface energy substrates such as the iron-oxides and titanium dioxide are beneficial expanders and that low surface energy substrates like barium hexa iron-oxide, calcium oxide, boron nitride and even lead hexa iron-oxide and graphite can be harmful additives even though their individual mechanism may be entirely different to one another depending upon their behaviour in strong alkaline media.

Previously our thinking was such that high surface energy oxides would be useful additives in the negative plate but in the light of the present work it seems that it is not the oxide that is playing a role in crystal growth inhibition, but the hydrated oxide or hydroxide. In alkaline solution the surface of the oxide material is generally covered with a few angstrom thick of hydroxide and it is thought that this creates a higher surface area than the oxide.

In the case of titanium dioxide the formation of a gel seems highly likely from the chemistry of titanium dioxide in alkaline media and this gel also provides a greater surface area. Although this gel is not a true hydroxide or oxide of titanium, it is nevertheless a hydrated oxide.

Even though the trend is that high surface energy materials are better expanders as is indicated by titanium dioxide and the iron-oxides, the fact that it is mainly the hydroxide surface

layer that is playing a part in the growth inhibition of cadmium hydroxide causes a break down in the concept of high surface energy oxides. It is possible that a high surface energy oxide would be considered to be a good expander but the mechanism that the cadmium hydroxide deposits on this substrate to stabilise the system is no longer valid as it is the hydroxide that the cadmium hydroxide deposits on and not the oxide.

More work would have to be carried out in this field to investigate this mechanism and it is thought that starting with the hydroxide as the initial expander material might be more beneficial to the capacity of the negative plate than the oxide.

CHAPTER 7a

EFFECT OF $\text{Mg}(\text{OH})_2$ ON THE PERFORMANCE
OF THE NEGATIVE
PLATE

CHAPTER 7a

EFFECT OF $\text{Mg}(\text{OH})_2$ ON THE PERFORMANCE OF THE NEGATIVE PLATE.

7a.1 INTRODUCTION

The last Chapter described the effect of good and bad expanders using the technique of galvanostatic charging and discharging, SEM, and surface area measurements.

Magnesium hydroxide was thought of as a possible good expander from the literature because of its extremely low solubility in KOH and high chemical inertness, like ferric oxide. It was relatively cheaper than titanium dioxide and could be obtained commercially as a very high surface area powder. However, although the material was considered in the last few months of the investigation, we still felt it was useful to carry out, at least, capacity and scanning electron microscopy measurements on a pocket-electrode scale. With the availability of Coulter Counter in the laboratory and the feeling that instead of surface area measurements on the dry powder, aggregate size in KOH solution might be more important, we decided this time to use the Coulter Counter to measure the aggregate surface area in solution.

7a.2 Experimental.

Initially the Coulter Counter was used to measure the particle size distribution of the $\alpha\text{-Fe}_2\text{O}_3$ and commercially obtained magnesium hydroxide from BDH. The instrument was Model D Industrial, designed for particle sizing techniques over the range 1 μm to 75 μm . The theory and principle of operation

of the Coulter Counter is given in Appendix 2.

After the counts at various size levels are made, the data is set out in the form shown in Figure 7a.1 for magnesium hydroxide in 4.5M KOH and Figure 7a.2 for iron-oxide in the same electrolyte, column 4. Calibration is obtained and noted together with all relevant information, including dilution factor if used. These are the main information needed from the Coulter Counter and the results can then be processed.

For a number distribution, column 5 gives the number of particles above diameter (d) in column 8.

For a volume (weight) distribution a simple integration of this data must be performed (columns 9-13).

Column 12 is the sum of values in 11. Starting at the coarse (top) end it gives the cumulative volume (weight) above each size level. The final value, if there are few or no particles left uncounted, is the 100% value.

Column 13 is obtained by continual division of this 100% value into each of the $\Sigma \Delta n \cdot \bar{V}$ values in 12. This, for particles of uniform density, is also the cumulative weight % oversize distribution since the density term cancels out.

7a.3 Specific Surface Area.

Although the results will not be accurate in the case of porous or non-spherical materials since the calculation involves the assumption that the particles are solid spheres, it is a good guide nevertheless.

COMPLETE TECHNIQUE

Figure 7a.1
INDUSTRIAL MODEL D
COULTER COUNTER DATA AND WEIGHT CONVERSION

Sample <u>Mg(OH)₂</u>	Source _____	Electrolyte <u>4.5M KOH</u>	Dispersant <u>glycerol</u>	Date _____
Aperture Diameter <u>140μ</u>	Manometer Volume <u>0.5</u>	Calibration Factor, k <u>9.241</u>	Calibration Date _____	Operator _____
Aperture Resistance _____	Coincidence Factor, P <u>6.86</u>	Notes _____		

[illegible]

Figure 7a.2

INDUSTRIAL MODEL D

COULTER COUNTER DATA AND WEIGHT CONVERSION

COMPLETE TECHNIQUE

Sample $\alpha\text{-Fe}_2\text{O}_3$ Source Z. munshi Electrolyte 4.5M KOH Dispersant glycerol Date _____
 Aperture Diameter 140/50 μ Manometer Volume 0.5/0.05 Calibration Factor, k 9.583/3.857 Calibration Data _____ Operator _____
 Aperture Resistance _____ Coincidence Factor, P 6.86/3.125 Notes sieve factor = 0.4, manometer factor (m.f) = 10, two-tubes used.

t	I	A	n' (raw counts)				$\bar{n}'$	$P\left(\frac{\bar{n}''}{1000}\right)^2$	B	$n = \bar{n}' + n'' - B$	$V = t.I.A$	$d = k \cdot \sqrt{V}$ (μm)	Δn	$\bar{V}$	$\Delta n \cdot \bar{V}$	$\Sigma(\Delta n) \bar{V}$	Wt. %
80	1	8	0,0	0,0	0,0		0			0	640	82.51	0	-	-	-	
40	1	8	0,0	0,0	0,0		0			0	320	65.55	0	480			
20	1	8	1,2	3,2	2,2		2			2	160	51.94	1	240	480	480	37.83
"	0.5	"	3,4	4,1	3,3		3			3	80	41.30	1	120	120	600	47.28
"	0.25	"	3,3	4,4	4,5		3.83			3.83	40	32.77	0.83	60	49.8	650	51.22
"	0.13	"	5,7	9,10	5,5		6.83			6.83	20.8	26.16	3.0	30.4	91.2	741	58.39
"	0.066	"	10,7	8,9	10,10		9.0			9.0	10.56	20.99	2.17	15.68	34.0	775	61.07
"	0.033	"	18	22	13	15	17.0			17.0	5.28	16.67	8.0	7.92	63	888	66.04
"	0.017	"	26	27	25	27	26.25			26.25	2.72	13.42	9.25	4.0	37	875	68.95
"	"	4	52	52	49	55	52			52	1.36	10.62	25.75	2.04	53	928	73.13
20	0.130	8	13	13	15	14	13.75			55	20.8	9.16	3	1.125	3.375	931	73.36
"	0.066	"	25	31	19	25	25.0			100	10.56	7.35	45	0.67	30	961	75.73
"	0.033	"	32	42	42	58	43.5			134	5.28	5.84	74	0.34	25	986	77.70
"	0.017	"	119	93	100	112	106			424	2.74	4.70	250	0.174	44	1030	81.17
"	"	4	256	325	304	290	294	.3		1177	1.36	3.72	753	0.088	66	1096	86.37
"	"	2	519	580	503	487	522	.9		2092	0.68	2.951	915	0.0435	40	1136	89.52
"	"	1	893	872	835	873	868	2.4		3482	0.34	2.343	1390	0.022	31	1167	91.96
25	0.093	"	1258	1220	1232		1237	4.8		4967	0.233	2.066	1485	0.0125	19	1186	93.46
20	"	"	1516	1462	1394		1457	6.6		5854	0.186	1.917	887	0.0090	8	1194	94.09
30	0.053	1	1630	1701			1666	9		6700	0.159	1.819	846	0.0075	6	1200	94.56
20	0.053	"	2280	2354	2396		2343	17		9440	0.106	1.588	2740	0.006	16	1216	95.82
10	"	"	4366	4220	4466	4212	4316	58		17496	0.053	1.262	8056	0.0036	28	1244	98.03
10	0.033	"	8287	8156	8224		8222	211		38732	0.033	1.078	16236	0.0015	24	1268	99.92
																	100

9942047

For 50 μ tube $n = (\bar{n}' + n'' - B) \times \text{sieve factor} \times \text{manometer factor}$.

$$\text{The net outer surface of particle} = \Sigma \pi d^2 n \quad 7b.1$$

$$\text{Net mass of particle} = \Sigma (\pi/6) d^3 \delta n \quad 7b.2$$

where δ is the tamped density.

Hence mean aggregate specific surface area S_{av}

$$= \frac{6 \Sigma d^2 n}{\delta \Sigma d^3 n} \quad 7b.3$$

$$\text{Whilst mean particle diameter } d_{av} = \frac{6}{\delta \cdot S_{av}} \quad 7b.4$$

The tamped density of the magnesium hydroxide powder was calculated as 0.184 g.cm^{-3} , whilst that of the Deanox iron-oxide was 1.183 g.cm^{-3} .

From the Coulter Counter weight conversion and data distribution charts of magnesium hydroxide and iron-oxide, and using equation 7a.3, the mean aggregate specific surface area S_{av} for iron-oxide was calculated as $0.09 \text{ m}^2 \text{ g}^{-1}$, whilst that of magnesium hydroxide was $0.70 \text{ m}^2 \text{ g}^{-1}$. Therefore, since 16% of $\alpha\text{-Fe}_2\text{O}_3$ is normally added to the standard new negative active material only one-eighth of this percentage of magnesium hydroxide, i.e. 2%, should suffice to give the same overall specific aggregate surface area as that of $\alpha\text{-Fe}_2\text{O}_3$.

However, to save any further unnecessary optimisation, several other weight % of magnesium hydroxide were also used, and are tabulated in Table 9 together with the cadmium hydroxide and the iron-oxide mixes as well as their filling weights. The graphite was included in all mixes for initial conductivity.

TABLE 9

(A) New Negative Electrode.

	<u>% weight</u>	<u>filling wt.</u>
Cd(OH) ₂	80.32% Cd(OH) ₂	(5g)
α-Fe ₂ O ₃	16.06% Fe ₂ O ₃	
Graphite	2.00% Graphite	
PVA	1.61% PVA	

(B) α -Fe₂O₃ Electrode.

Cd(OH) ₂	81.63% Cd(OH) ₂	(4.92)
α-Fe ₂ O ₃	16.33% Fe ₂ O ₃	
Graphite	2.04% Graphite	

(C) Straight Cd(OH)₂ Electrode.

Cd(OH) ₂	98.00% Cd(OH) ₂	(4.10)
Graphite	2.00% Graphite	

Magnesium Hydroxide Electrodes.

(D)

Cd(OH) ₂	96.00% Cd(OH) ₂	(4.18)
Mg(OH) ₂	2.00% Mg(OH) ₂	
Graphite	2.00% Graphite	

(E)

Cd(OH) ₂	97.00% Cd(OH) ₂	(4.14)
Mg(OH) ₂	1.00% Mg(OH) ₂	
Graphite	2.00% Graphite	

(F)

Cd(OH) ₂	97.50% Cd(OH) ₂	(4.12)
Mg(OH) ₂	0.50% Mg(OH) ₂	
Graphite	2.00% Graphite	

(G)

Cd(OH) ₂	96.50% Cd(OH) ₂	(4.16)
Mg(OH) ₂	0.50% Mg(OH) ₂	
PVA	1.00% PVA	
Graphite	2.00% Graphite	

Therefore the various mixtures were prepared and pocket-type electrodes of these mixes made as before with their appropriate filling weights. The formation procedure was the same as described in Chapter 6.

After formation the electrolyte was replaced with lithiated electrolyte and galvanostatic C/5 charges and discharges were carried out up to the 20th cycle and then a C/40 charge followed by a C/5 discharge was carried out.

7a.4 Results and Discussion.

The result of the effect of cycling in terms of the individual capacities obtained from each cell is given in Table 10 below.

TABLE 10

<u>Type</u>	<u>Capacity (hrs/min)</u>				
	<u>1st</u>	<u>5th</u>	<u>10th</u>	<u>20th</u>	<u>C/40char./C/5disch.</u>
(A) New Negative.	5.55	5.50	5.50	5.35	5.15
(B) α -Fe ₂ O ₃	5.25	5.40	5.40	5.25	5.05
(C) Cd(OH) ₂	5.00	5.00	4.50	4.30	4.10
(D) 2%Mg(OH) ₂	5.35	5.20	5.20	5.10	4.50
(E) 1% Mg(OH) ₂	5.35	5.30	5.20	5.15	5.05
(F) 0.5% Mg(OH) ₂	5.35	5.30	5.20	5.20	5.05
(G) 0.5% Mg(OH) ₂ /1%PVA	5.25	5.30	5.25	5.20	5.10

It is clear that the result of adding magnesium hydroxide to the negative electrode has some beneficial effect. Also by the end of the 20th discharge the capacities of the magnesium

doped electrodes holds in comparison to the iron-oxide electrode. However, both the magnesium hydroxide and the iron-oxide electrodes on their own are still not as good in performance as the new negative electrode. The effect of adding 1% of PVA to one of the magnesium hydroxide electrode (G), has little bearing on its performance. The addition of 2% Mg(OH)_2 to the cadmium hydroxide had detrimental effect on the capacity but a lower weight per cent as in the case of (E) and (F), (1.0% and 0.5% Mg(OH)_2 respectively) improved the performance.

Scanning electron microscopy was only carried out on the F type of negative electrode, (i.e. containing 0.5% magnesium hydroxide), and on magnesium hydroxide powder itself.

The negative electrode for SEM study was prepared in exactly the same way as those of other expander mixtures in Chapter 7 and the condition on the microscope was as before (i.e. 40 KV, high resolution setting and 3000x magnification).

Figure 7a.3 shows the electron micrograph of the electrode containing 0.5% magnesium hydroxide additive taken at the end of the C/40 charge-C/5 discharge cycle. It is seen that the particles were similar in shape to that of the Deanox iron-oxide negative electrode (Figure 7.8-7.10). The size of the particles varied from 1-3 μ . There were some grainy areas which were reminiscent of the iron-oxide electrode together with the usual solid particles associated with either cadmium or cadmium hydroxide.

There did not appear to be any massive recrystallisation at this stage and the electrode seemed to be fairly porous.

Electron micrograph of the magnesium hydroxide powder (Figure 7a.4) showed that the aggregates were made up of flake-like particles.

Thus the Coulter Counter result used would have been incorrect since spherical particles were assumed in the original aggregate size calculation. It is reasonable therefore to expect better performance from electrodes containing less magnesium hydroxide than the 2% obtained from the Coulter Counter, since thin flake-like particles would be expected to give a higher surface area than spherical particles.

Magnesium hydroxide thus appears to beneficially modify the crystal growth behaviour of cadmium hydroxide. Although the work is only in the infancy stage, better performance could be obtained using better mixing techniques, more proper optimisation and plate-type electrode used.



MAGNIFICATION
3000x

5μ

Figure 7a.3 $\text{Mg}(\text{OH})_2$ Expander Electrode Material,
after the 21st Low-Rate Cycle.



MAGNIFICATION
3000x

5μ

Figure 7a.4 Magnesium Hydroxide.

CHAPTER 8

THE DISSOLUTION OF IRON FROM THE NEGATIVE ACTIVE
MATERIAL IN POCKET-PLATE Ni-Cd BATTERIES

CHAPTER 8

THE DISSOLUTION OF IRON FROM THE NEGATIVE ACTIVE MATERIAL IN POCKET-PLATE NICKEL-CADMIUM BATTERIES.

8.1 INTRODUCTION

In Chapter 6 X-ray crystallographic analysis of the negative active material showed that iron oxide underwent a structural change from the α -form to the γ -form. We believed this was via a soluble intermediate stage and this Chapter attempts to demonstrate that this was so.

Iron rich deposits on separator pins and on other parts of the cell were reported and confirmed in 1972 at Chloride Alcad.

Two common modes of failure of these cells are the poisoning of the positive active material by iron compounds and by the deposition of iron compounds on the separator material which results in short circuits in the cell.¹⁶¹

Previous work¹⁶² has shown that the main part of the iron transferred to the positive active material originates from the perforated steel strips containing the active material and secondly that the main part of the iron deposited on the separator originates by the corrosion of the steel strip containing the negative active material; the potential of this strip is in the corrosion region indicated by the Pourbaix diagrams.

It has been demonstrated¹⁶³ that the corrosion can be reduced by nickel plating of the negative steel strips. However it is possible that some transfer of iron from the Fe_2O_3 if this is used as an additive in the negative active material, may also take place.

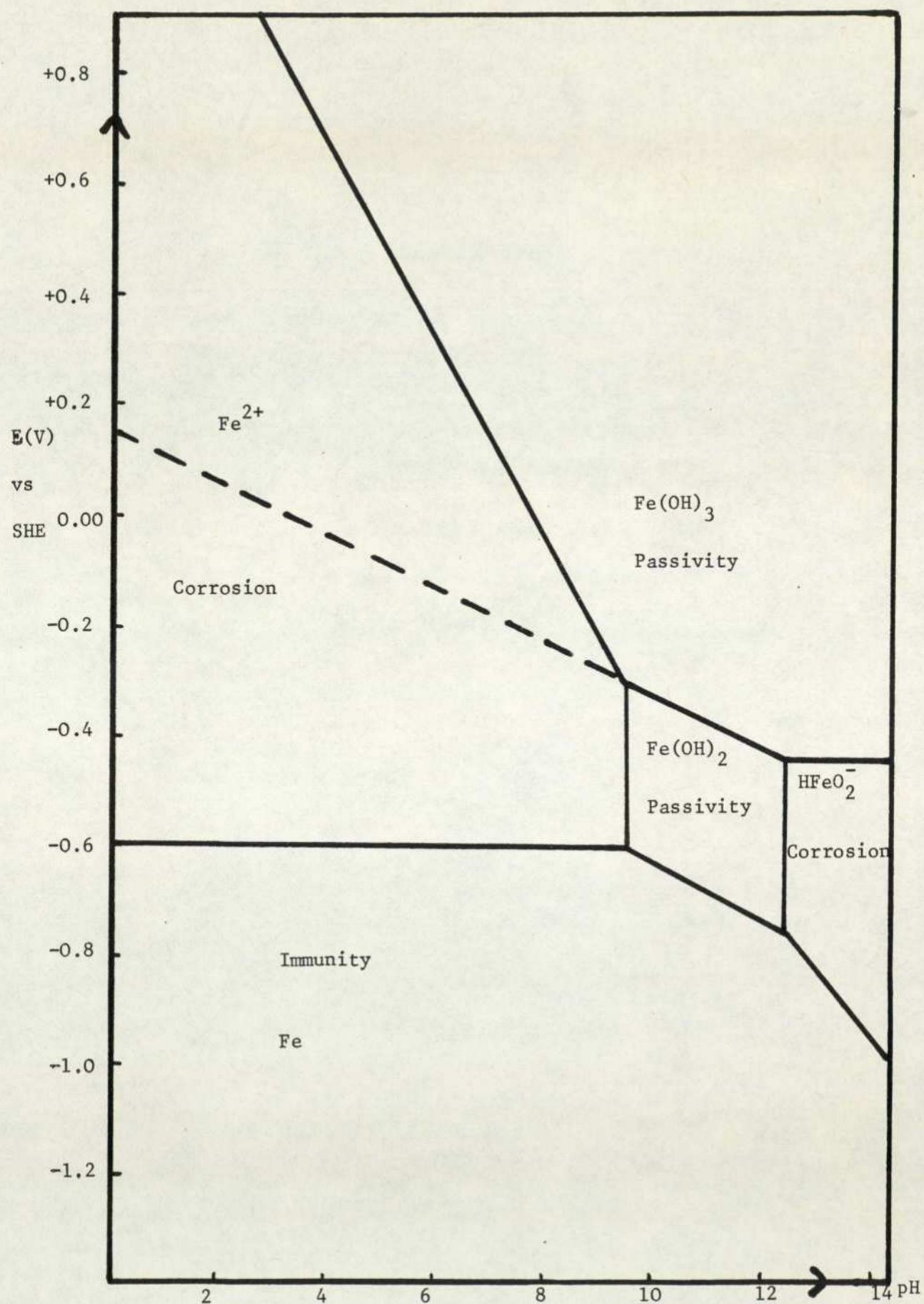


Figure 8.1 Potential-pH Diagram for Fe/Fe(OH)₂/Fe(OH)₃/H₂O System at 25°C.

Figure 8.1 shows that iron at high pH values is in the passive region at potential above -0.400V vs the standard hydrogen electrode (S.H.E.). On open circuit in alkaline media, iron demonstrates considerable stability due to the formation of a passive oxide film which affords protection. The potential of the iron under these condition is -0.877V vs S.H.E. When connected to a high surface area cadmium, as in the case of a negative plate, the potential of iron is maintained in the active potential region of -0.809V vs S.H.E. (i.e. where corrosion can occur). The degree of corrosion will depend on how easily any protective oxide present is reduced to bare metal.

Careful consideration of the potential- pH^{164} (Fig. 8.1) diagram for iron indicates that iron in cell electrolyte at the potential of about -0.809V vs S.H.E. (i.e. that of cadmium on open circuit) is unstable and will corrode forming a soluble iron ion, HFeO_2^- . Salkind et al¹⁶⁵ have also stated that at this potential, iron has a tendency to corrode at a much faster rate in the presence of cadmium.

However when the additive involved is $\alpha\text{-Fe}_2\text{O}_3$, at potentials more negative than -0.877V vs S.H.E., it is possible that some of the active $\alpha\text{-Fe}_2\text{O}_3$ could become reduced to elementary iron via the HFeO_2^- complex. This potential is exceeded during the over-charge of cadmium electrodes. As the Potential- pH diagram of Figure 8.2 shows, there is a region in the $\text{Fe} - \text{Fe}_2\text{O}_3 - \text{Fe}_3\text{O}_4$ system at $\text{pH } 14$ in which HFeO_2^- is present and the iron oxide has to pass through this intermediate phase before reduction to iron.

During the oxidation of cadmium, as in the case of discharge in the nickel-cadmium cell, there is a decrease of the pH in the

matrix of the negative mass due to the depletion of OH^- ions to form $\text{Cd}(\text{OH})_2$. At the same time, the electrode potential of iron produced from the Fe_2O_3 will become less negative due to the lowering of the pH.

Ojefors¹⁶⁶, using cyclic voltammetry has shown with sintered iron electrodes that iron exhibits a distinct corrosion region over the potential range of -0.900V to -0.650V. Increase in temperature causes the active region to be shifted to more negative potentials.

The fact that iron has a detrimental effect on the capacity of the positive plate has been shown by Jungner and Edison.³⁶ Jungner proposed an inactive barrier of nickel-iron-oxide complex. Tichenor¹⁶⁷ noted that ferric hydroxide additions to the nickel hydroxide decreased the electrode capacity. The effects were attributed to growth of insulating barrier layers of one form or another thereby limiting electronic conduction processes.

Tuomi¹⁶⁸ concluded this reduction in the capacity to be due to the low oxygen overvoltage from the ferric hydroxide which reduced the internal potential below the value necessary to oxidise the active material properly. The effect was localised depending upon a distribution of low oxygen overvoltage centres rather than the incorporation of iron into the active material.

Work carried out by Parker¹⁶⁹ on two sets of Ni-Cd cells having 100% capacity showed that one set had an iron content in the positive plate of 0.4% and the other 1.0%. Another set of cells with 0.4% iron only gave 64% capacity. His conclusions were that the actual amount of iron incorporated into the positive active material bears no real significance to its failure in capacities but that

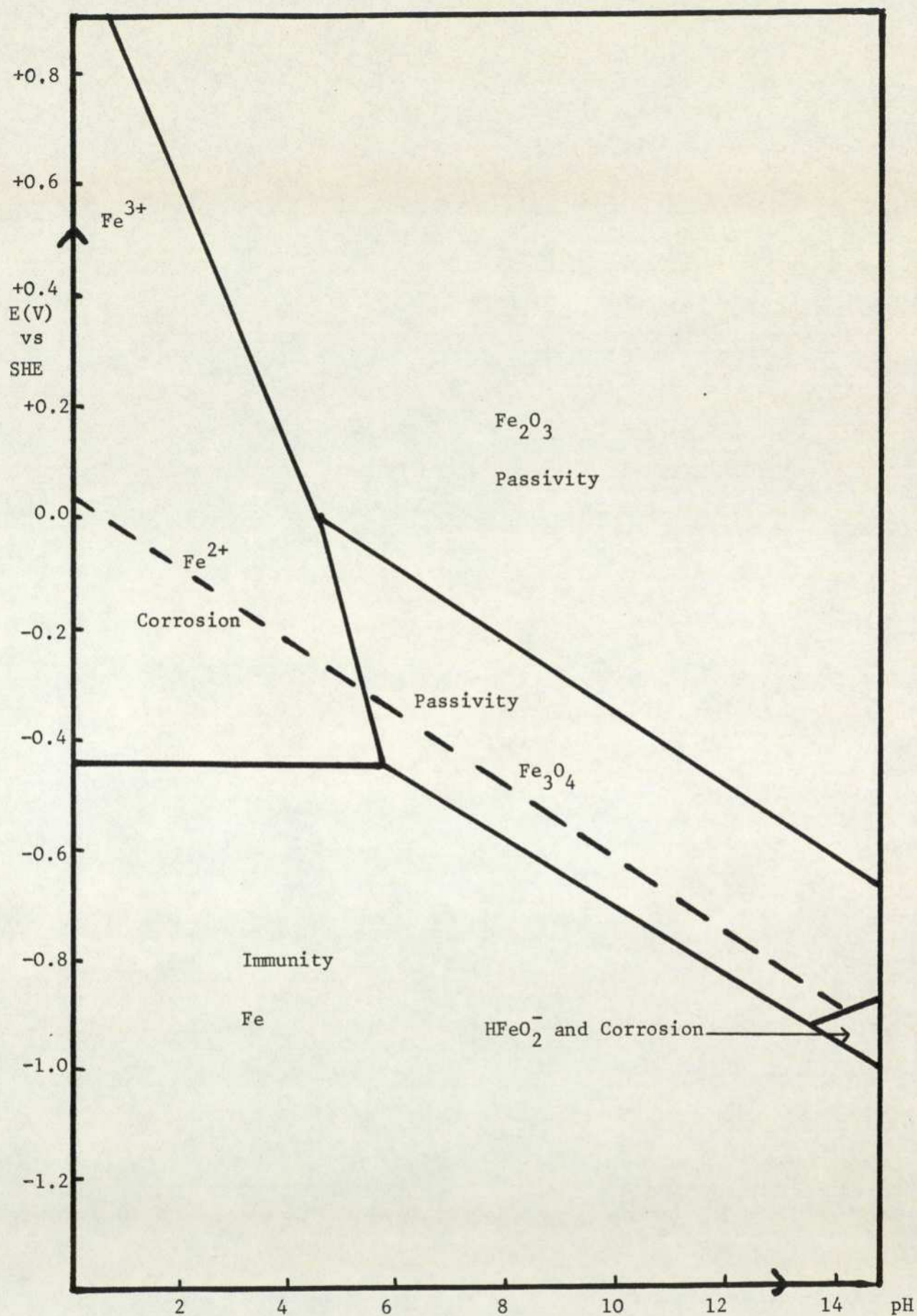


Figure 8.2 Potential-pH Diagram for Fe/Fe₂O₃/Fe₃O₄/H₂O System at 25°C.

its position is probably more important as outlined by Tuomi.¹⁶⁸

Although it has been shown that the poisoning of the positive plate is due mainly to iron corrosion of the cell components and consequent incorporation into the positive active material, it is believed that there could be a small contribution towards the iron-deposits from the dissolution of the iron-oxide in the negative active material.

The main purpose of this chapter is to present experimental evidence supporting this assumption.

8.2 Experimental

Cycling tests were carried out on a single pocket electrode in 4.5M KOH and any dissolved species were electroplated onto a pure nickel counter electrode and examined under an electron microscope using an EDAX technique, X-ray Diffraction and by cyclic voltammetry. The amounts were measured by coulometric measurements.

The experimental cell used for cycling is shown in Figure 8.3.

The negative electrode mixture had the following composition:-

β - $\text{Cd}(\text{OH})_2$	48%
α - Fe_2O_3	48%
Graphite	4%

It was enclosed in a pocket made from a thin perforated pure nickel ribbon and its characteristics were as follows:-

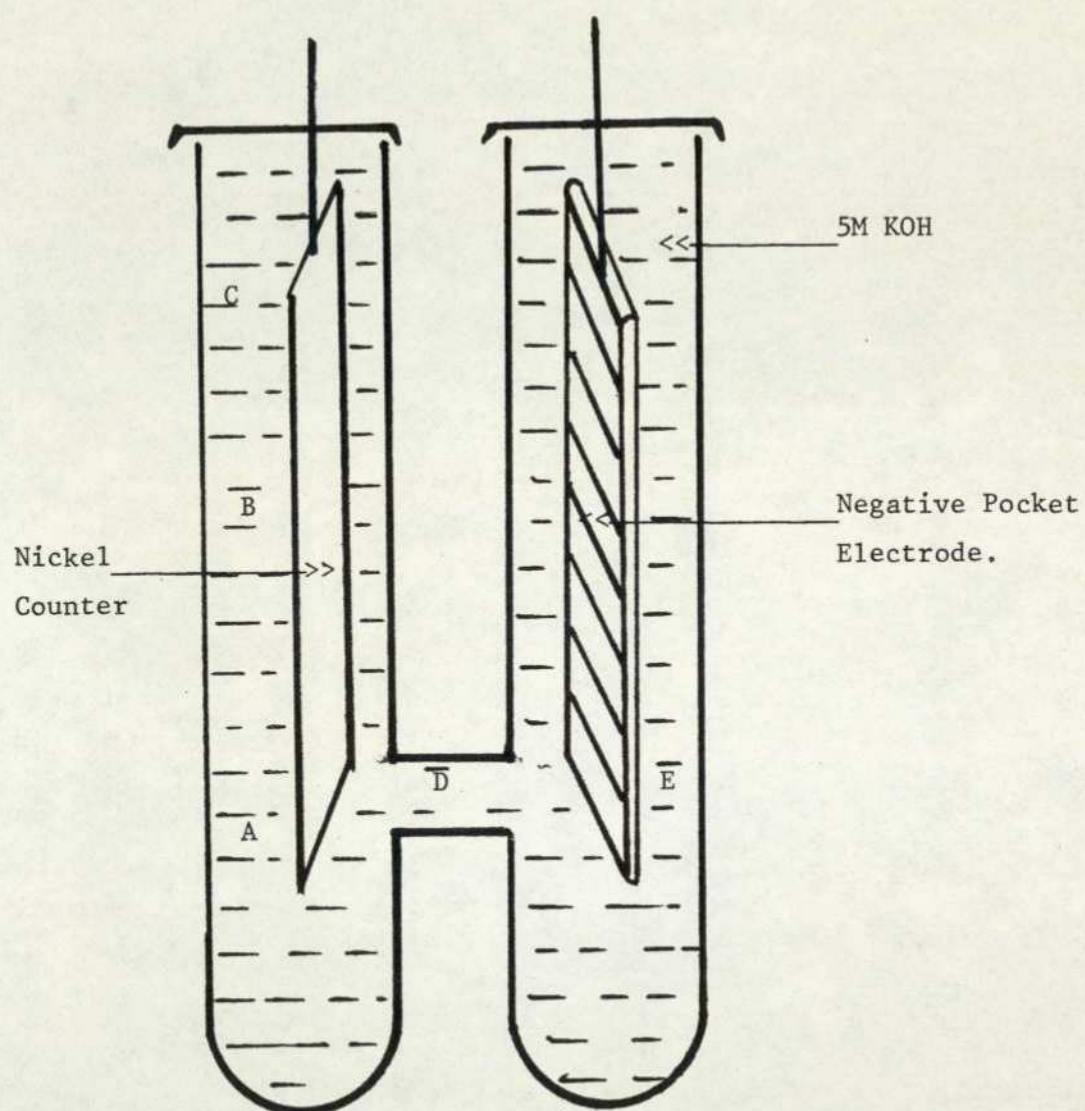


Figure 8.3 Experimental Cell.

Theoretical capacity	0.696A.hr
Width	1.2 cm
Height	5.5 cm
Overall thickness	3.2 cm
Weight of active material	2.5 g

The counter electrode consisted of a thin perforated pure nickel ribbon, 5.5 x 1.2 cm in dimension, the distance between the working negative electrode and the counter electrode was 3 cm. Physical agitation was carefully avoided and electrochemical agitation was minimised by using a low current and also by switching the circuit off at the onset of gas evolution from the cadmium electrode.

The electrolyte was made from BDH Aristar KOH, and the specific gravity of the electrolyte adjusted to 1.200. The iron content of the electrolyte was determined by atomic absorption and was found to be 1.4 ppm. A Chemical Electronics Potentiostat was used in the galvanostatic mode for the charging and discharging of the electrode. The negative electrode was first subjected to eight forming charge-discharge cycles in the following manner:-

1st 4 cycles

charge at c/10 rate for 14 hr.

discharge at c/10 rate to -0.700V vs Hg/HgO ref. electrode

2nd 4 cycles

charge at c/5 rate for 7 hrs.

discharge at c/5 rate to -0.700V vs Hg/HgO ref. electrode.

This lengthy formation procedure was adopted to ensure that there was no further visible shedding of the active material from the cadmium electrode. The cycling operations were carried out in a

separate cell and at the end of each cycle, the electrode was washed, using deionised-distilled water and fresh electrolyte was added to the cell. The negative electrode was then charged in the same cell. After transferring to the test cell, it was discharged at c/10 rate to -0.700V vs Hg/HgO Reference electrode using a pure nickel perforated foil as the counter electrode. This charge - discharge procedure in separate cells was carried out to prevent any removal of electrodeposited material from the nickel ribbon in the test cell and was repeated fifteen times at room temperature.

The polarisation curves on the nickel electrode were measured under cyclic voltammetric conditions using the Chemical Electronics 0.5A-20V Potentiostat in conjunction with a sweep generator and a J.J. PL4 recorder. All solutions were deaerated by bubbling with nitrogen before each experiment.

EDAX photographs were taken on the nickel counter electrode from the test cell at the A, B and C position at a magnification of 300x. The electron beam of the electron microscope was generated at 40KV and a high resolution setting was used.

X-ray powder diffraction measurement were also carried out on the active material in the charged and discharged state. The samples were examined on a Phillips P.W. 1010 X-ray diffractometer using the $K\alpha$ radiation of Molybdenum. The patterns were taken from a ground mixture of the active material and the scanning speed on the goniometer was kept at $1/8^\circ/\text{min}$ for the 2θ angle with corresponding paper speed.

In addition to the above examinations on the nickel cathode deposits, Atomic Absorption analysis of the solution was carried out on a Perkin Elmer 370 type spectrophotometer.

In order to measure the relative participation of the $\alpha\text{-Fe}_2\text{O}_3$ additive and mild steel pockets normally used to contain the active material in a pocket cadmium electrode the experiment were repeated using a thin perforated unplated mild steel ribbon in place of the nickel ribbon to make the negative electrode. The amount of iron transferred was compared with that from the pure nickel ribbon electrode under the same experimental conditions.

8.3 Results and Discussion

8.3.1 EDAX and Coulometric Studies: To determine the distribution of iron that may have corroded from the anode and deposited as a metal on the cathode, EDAX scans were performed at the A, B and C positions of the unwashed nickel electrode. Figure 8.4 - 8.6 shows the distribution of iron along the electrode. Figure 8.7 shows a scan on unused nickel which did not show any iron to be present. The iron $K\alpha$ signal appear at 6230eV, the nickel $K\alpha$, $K\beta$ at 7060eV and 7800eV respectively and the potassium $K\alpha$ from the caustic solution at 3312eV. The cadmium signal occurs at 3313eV and careful examination on the microscope eliminated any question of cadmium being present and the line in that region was due to potassium. The EDAX scans were carried out on a 10eV/Channel for 520 seconds. The scans showed that iron was not present on unused nickel but present in increasing quantities on the treated nickel from positions A to C.

EDAX is essentially a qualitative technique. The actual quantities of iron deposited was determined coulometrically from a potential-time curve obtained on charge and discharge of the nickel electrode. This is shown in Figure 8.9 together with the curve obtained on the

Figure 8.4 Position A

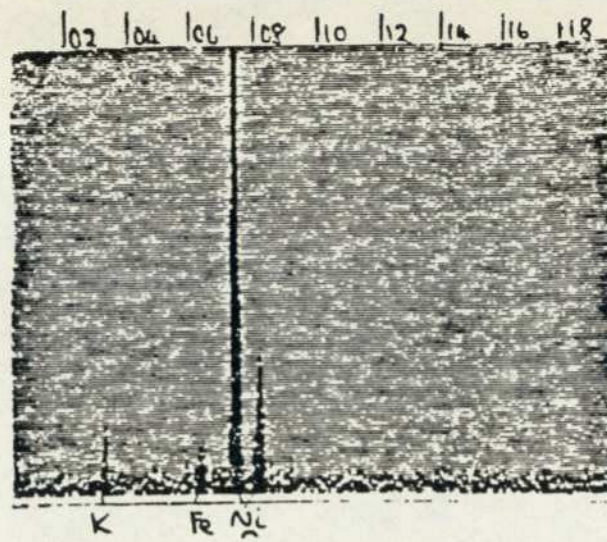


Figure 8.5 Position B

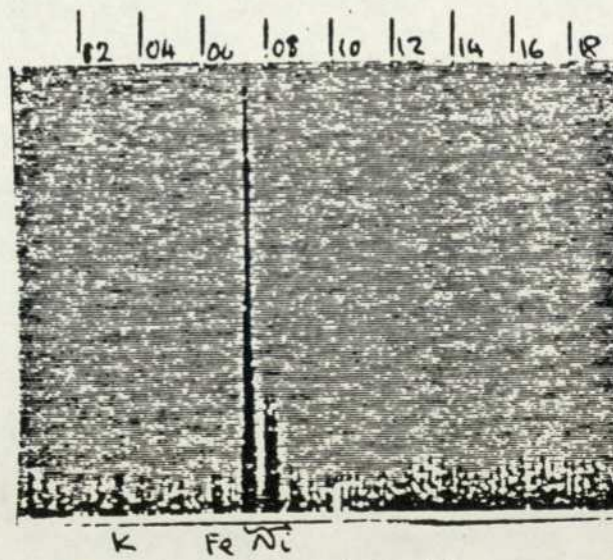


Figure 8.6 EDAX Photograph of Position C

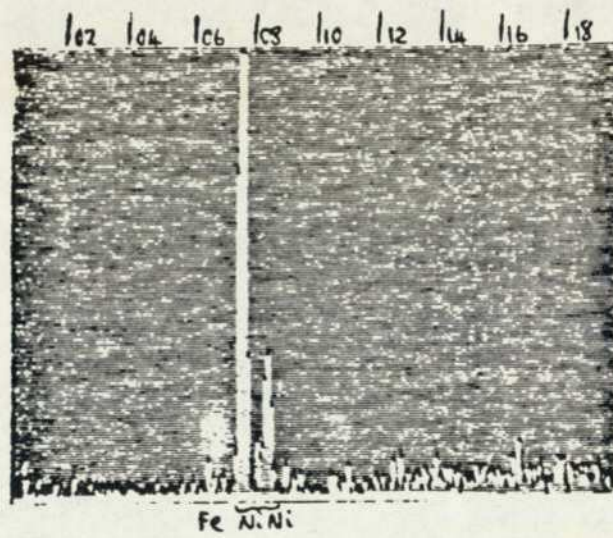
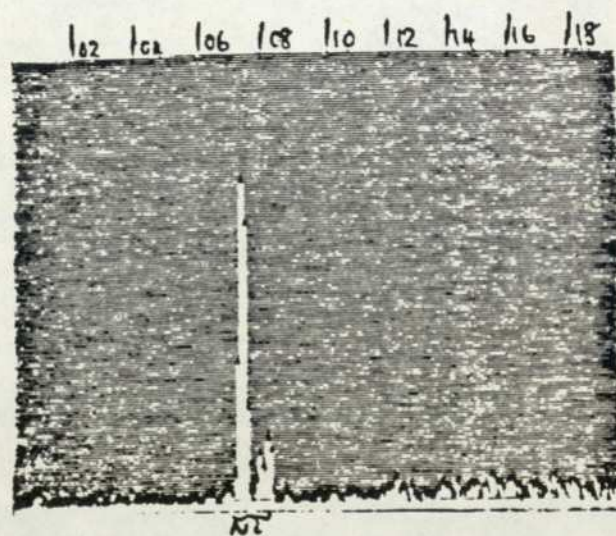


Figure 8.7 EDAX Photograph of the Unused Nickel



unused nickel ribbon. Both curves were obtained at a constant current of 1mA and it is seen that the electrodeposited nickel had a capacity of about 8 minutes and 20 seconds but the unused nickel ribbon produced negligible capacity.

Analysis of the electrolyte using Atomic Absorption spectroscopy before and after the experiment on samples taken from the counter electrode compartment revealed that the level of iron had increased from 1.4 ppm to 2.1 ppm by the end of the experiment. The reproducibility of the low atomic absorption analysis for iron at such concentrations was found to be within 0.1 ppm over four samples.

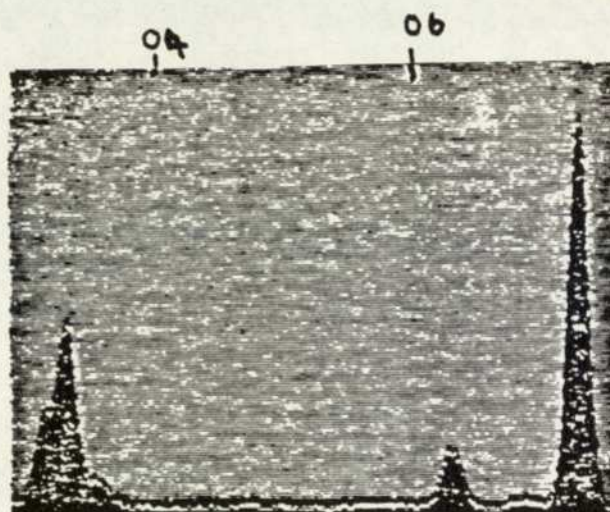
Experiments using a low porosity sintered glass disc in the bridge D of the test cell to prevent any carriage of active material from the anode to the cathode gave similar results to those obtained above indicating that there had been no shedding of the active material from the pocket. An atomic absorption analysis on the caustic electrolyte that had a sintered glass disc soaking for 2 months did not show an increase in the level of iron indicating that there had been no dissolution of iron from the disc.

In the experiment using the mild steel ribbon, a magnified EDAX photograph (Figure 8.8) taken from position B of the nickel counter electrode again demonstrated the presence of iron. Coulometric analysis showed that at a constant current of 1mA the capacity was 64 minutes (Figure 8.10).

Atomic absorption analysis of the electrolyte after the experiment showed an increase in the level of iron to 2.7 ppm.

8.3.2 Cyclic Voltammetric Studies: Figure 8.11 shows a typical voltammogram for the nickel counter electrode with the electro-

Figure 8.8 EDAX Photograph of Position B
From the Mild Steel Ribbon
Experiment



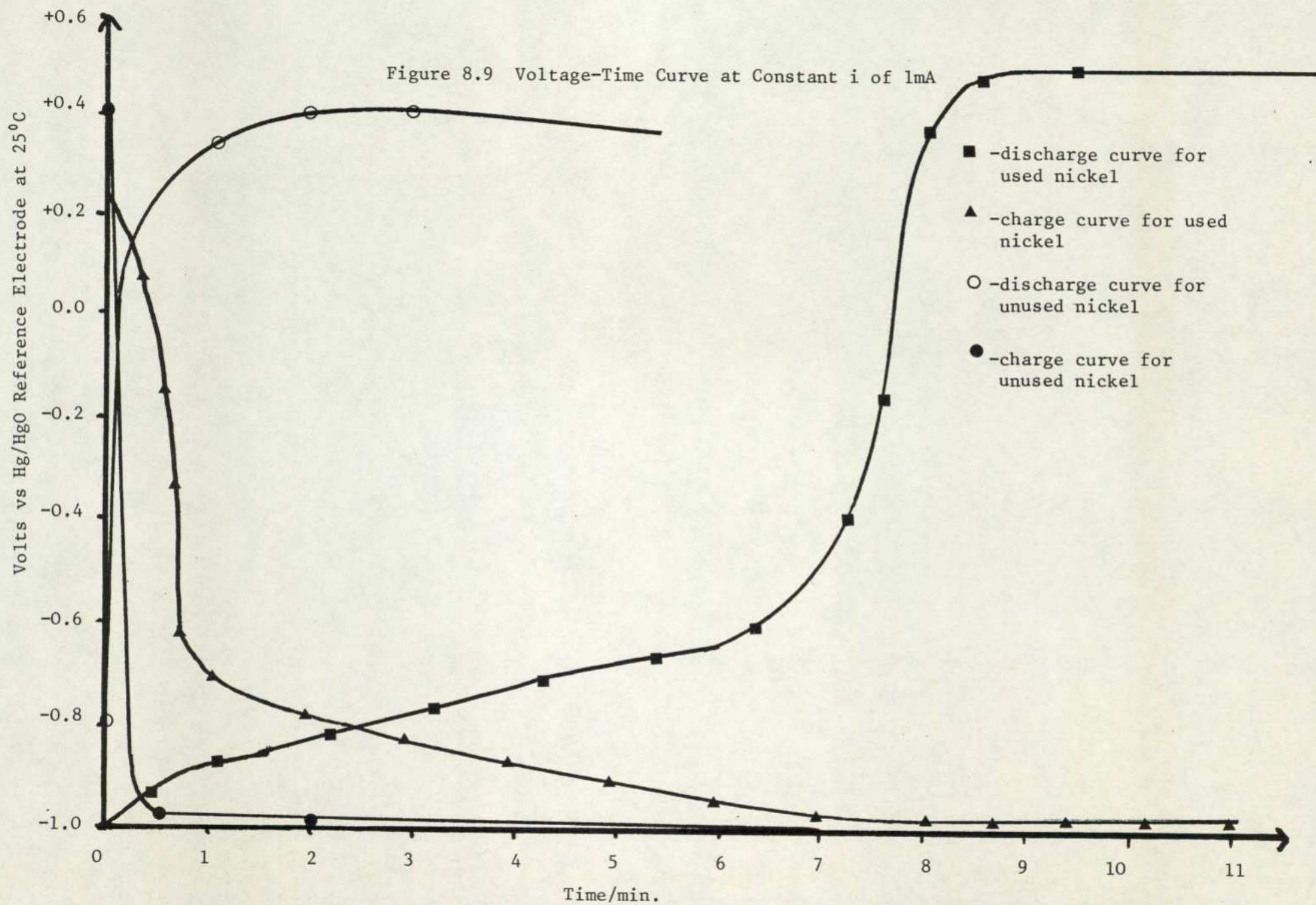
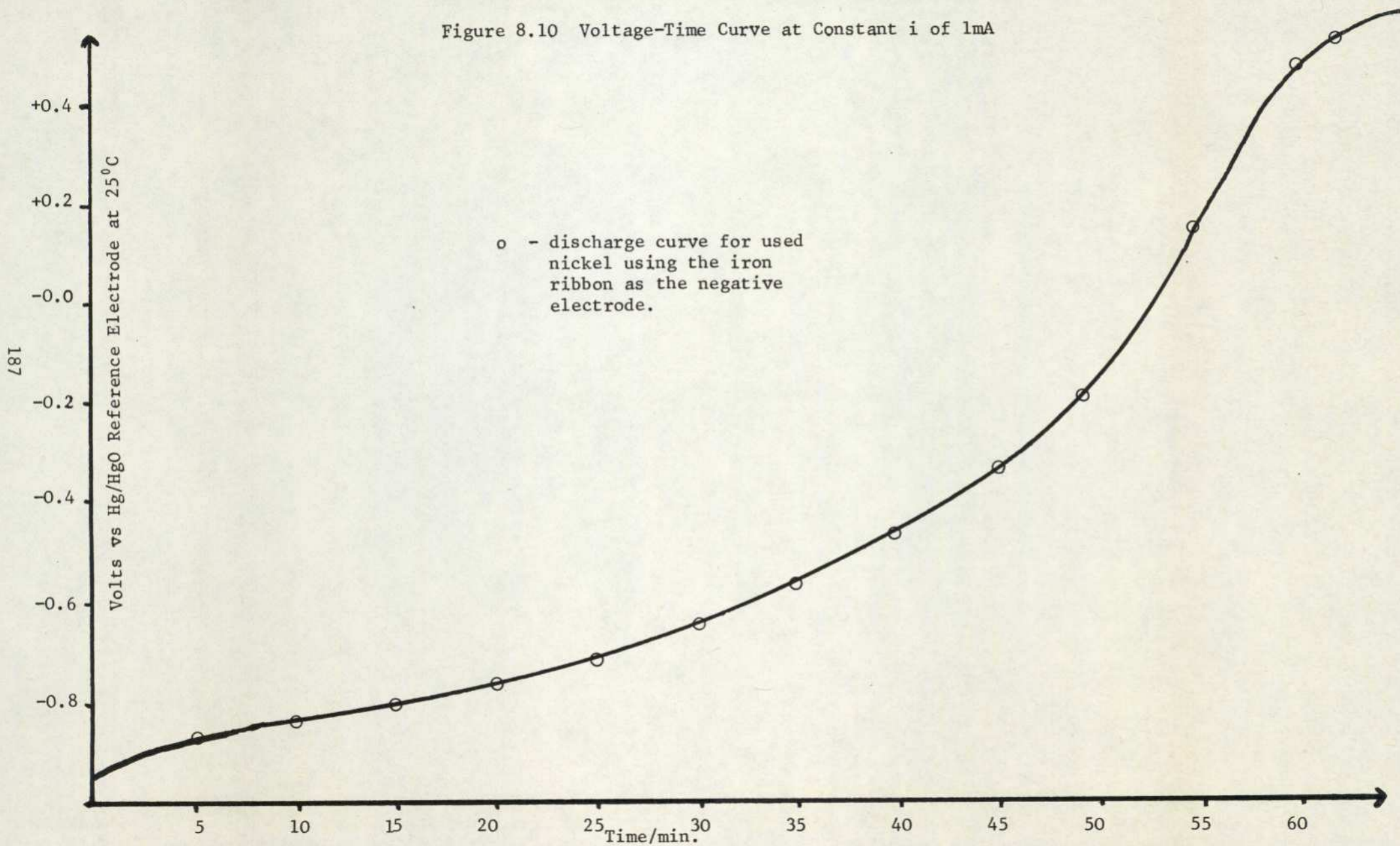
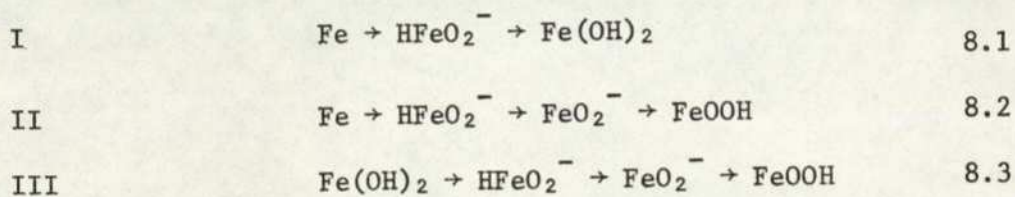


Figure 8.10 Voltage-Time Curve at Constant i of 1mA



deposited material obtained from the experiment using the pure nickel ribbon as the negative component. The potential was scanned between -1.000V and -0.400V (with reference to Hg/HgO electrode). The general shape of the curve in both sets of experiments were very similar. Peaks I, II and III occur at -837mV, -755mV and -595mV respectively. Only one reduction peak appears as expected, that at about -860mV.

As demonstrated by Ojefors¹⁶⁶ on the iron electrode, the process occurring as shown in Figure 8.11 are as follows:-

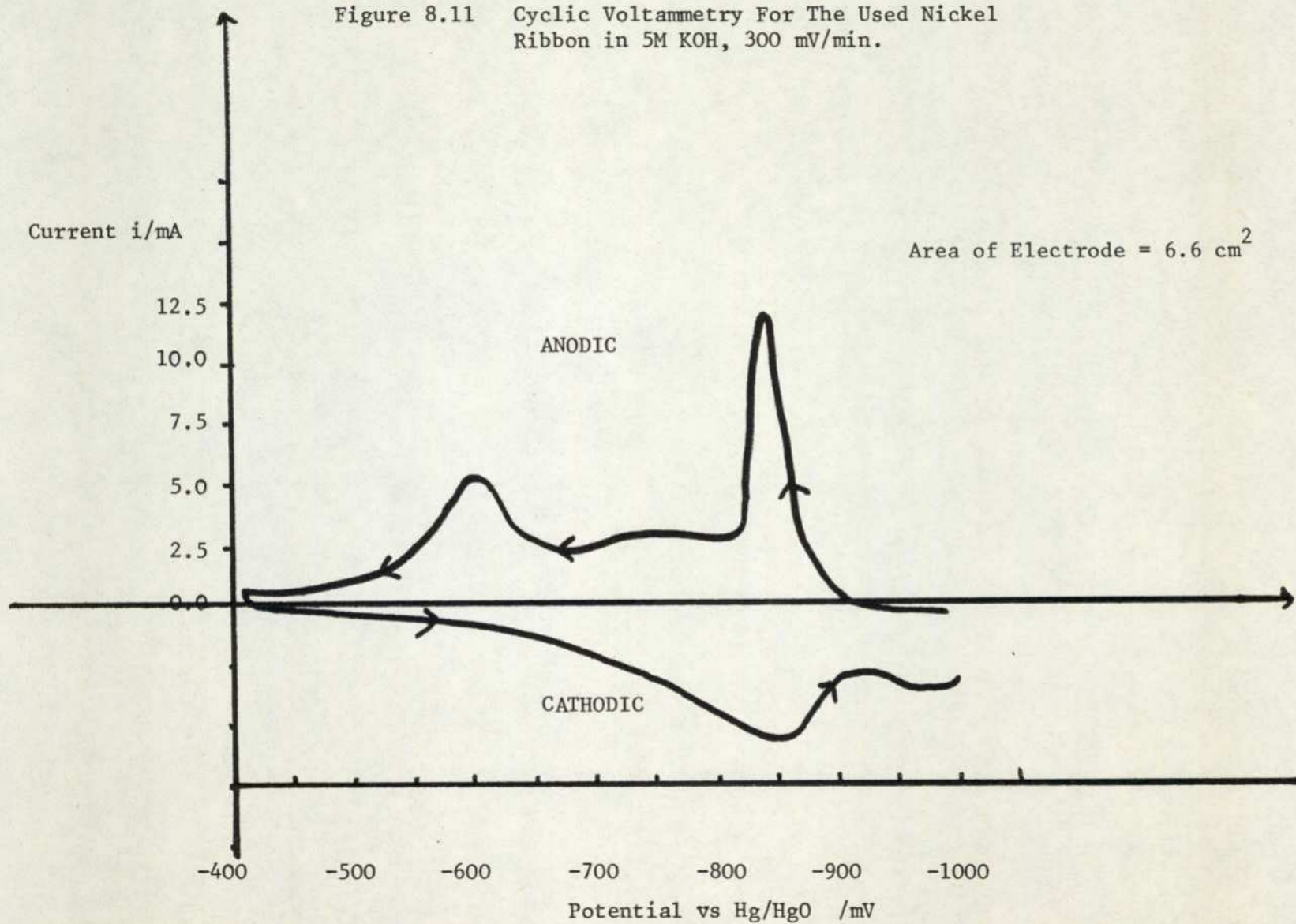


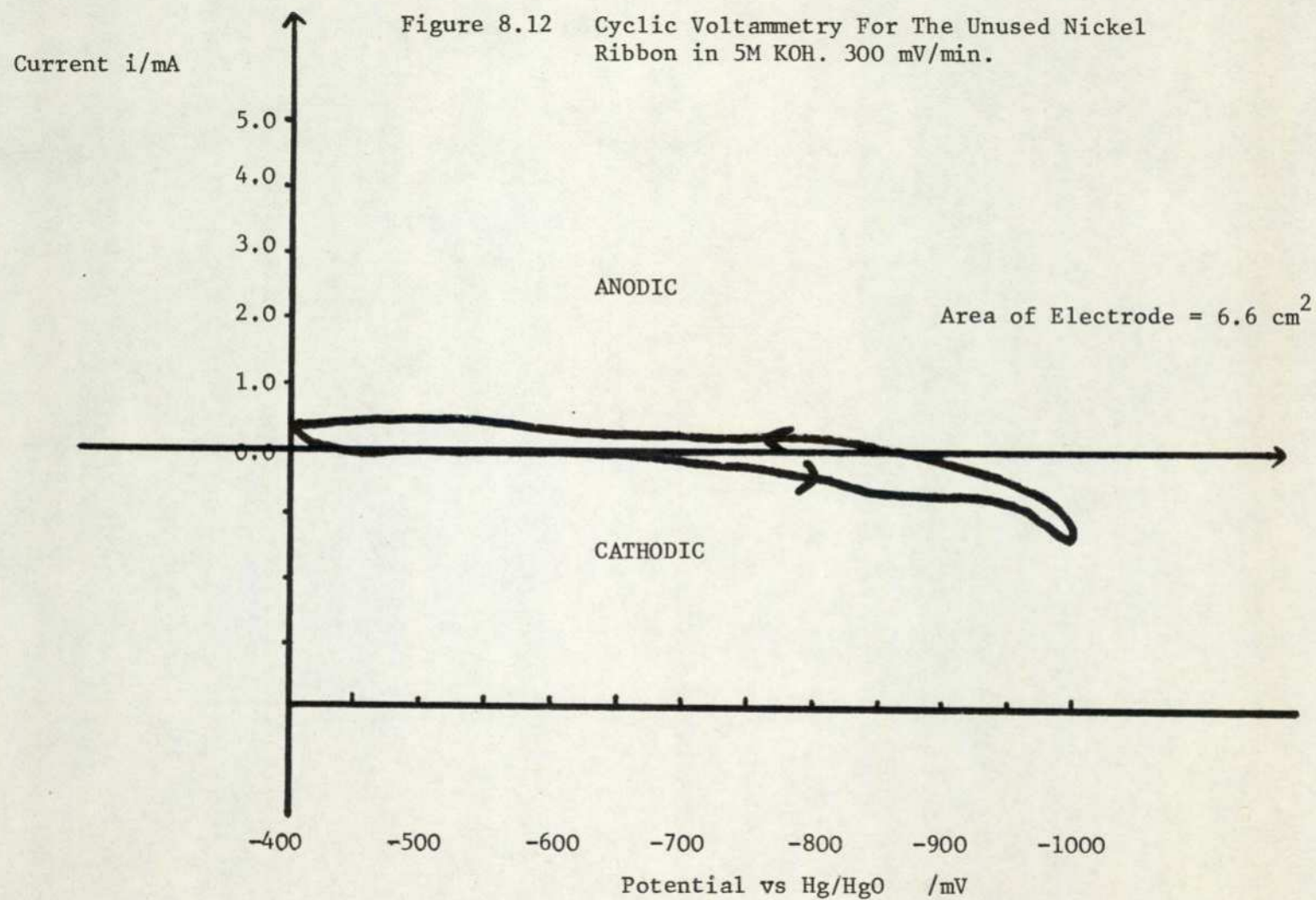
Process I occurs in the active (corrosion) potential region of iron and the first peak results from complete surface coverage with hydroxide, resulting in a partial passivation.

Process II occurs at potentials more positive (on the Hg/HgO scale) than about -595mV, when conversion of ferrous ions to ferric ions can take place. This results in a second sparingly soluble ion (FeO_2^-) which rapidly forms the solid FeOOH, leading to the second, more complete, passivation. It is in this secondary passive region that steel lies in equilibrium in alkali, but when connected to a source of negative potential (e.g. cadmium or a potentiostat), it will lie in region I with the resulting tendency to corrode.

By comparison the unused pure nickel ribbon (Figure 8.12) has very low electrochemical activity between -0.400V and -1.000V vs Hg/HgO.

Figure 8.11 Cyclic Voltammetry For The Used Nickel Ribbon in 5M KOH, 300 mV/min.

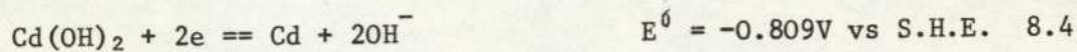




The voltage of the peaks coincide with the voltage expected for reactions I and III above and therefore the cyclic voltammetry is confirmation that the deposit responsible for the coulometric capacity is iron.

From observation of the potential and current scales it is seen that the iron peaks are readily distinguishable from that of nickel. The reason for the relative stability of nickel in alkali are that the anodic current densities are lower than for iron and when connected to cadmium (i.e. in a negative plate), nickel is negative to its reversible potential (-817mV) and is therefore cathodically protected under normal conditions.

The basic electrochemical reactions for iron and cadmium are as follows:-



and



indicating that iron is cathodic to cadmium by about 70mV.

These equations also indicate that 1g of cadmium should give a capacity of 0.477 A.hr and 1g of iron a capacity of 0.960 A.hr. Assuming that the reaction occurring is as above and that all of the iron oxide can be converted to iron, then a rough estimate of the amount of iron transferred over 15 cycles is about 0.013% of the iron oxide. Over 2000 cycles, as in the normal case of operation of a nickel - cadmium battery and assuming continuous transfer, this could increase to about 2% of the iron oxide. This figure is from

the iron oxide alone, but if unplated steel ribbons are used to make the pockets, then the actual amount could increase by about 7 - 8 folds as shown by the cycling test.

8.3.3 X - Ray Studies: As it was difficult to get clear X-ray powder patterns using the diffractometer on the nickel ribbon, they were obtained on the active material in the charged and discharged state. Table 11 shows the various phases that are present in the two state.

Table 11- X-RAY DIFFRACTION ANALYSIS OF THE ACTIVE MATERIAL IN 5M KOH AT ROOM TEMPERATURE.

<u>State of Active Material</u>	<u>Phases Present</u>
As received	$\alpha\text{-Fe}_2\text{O}_3$, $\beta\text{-Cd(OH)}_2$
Charged	$\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ $\alpha\text{-Fe}$, $\gamma\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$, $\beta\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$, Cd, $\beta\text{-Cd(OH)}_2$,
Discharged	$\alpha\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$, $\gamma\text{-Fe}_2\text{O}_3$, $\beta\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$, Cd, $\beta\text{-Cd(OH)}_2$.

The result indicates that during the cycling, the original $\alpha\text{-Fe}_2\text{O}_3$ undergoes a structural change with the formation of various phases. The phases that are shown in the X-ray pattern include $\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$. There is, however, no consistency as to the products formed during the charging and discharging modes and this is in agreement with the results of other researchers.^{165, 170, 171} The

fact that $\gamma\text{-Fe}_2\text{O}_3$ and other forms of oxides are observed shows that part or all of the $\alpha\text{-Fe}_2\text{O}_3$ must undergo reduction during the charging of the electrode to a lower state such as Fe and on oxidation it is this iron that dissolves and a minute fraction of it migrates to the nickel ribbon where it is deposited as iron.

8.4 Conclusions:

This present study shows that there is some dissolution of $\alpha\text{-Fe}_2\text{O}_3$ and that iron can be deposited in other parts of the cell though the amount is likely to be very much lower than the amount dissolved from the perforated mild steel ribbons used to enclose the active material.

CHAPTER 9

EFFECT OF A GROWING $\text{Cd}(\text{OH})_2$ FILM ON THE ANODIC
BEHAVIOUR OF CADMIUM IN KOH SOLUTION

CHAPTER 9

EFFECT OF A GROWING $\text{Cd}(\text{OH})_2$ FILM ON THE ANODIC BEHAVIOUR OF CADMIUM IN KOH SOLUTIONS.

9.1 INTRODUCTION

In the production of vented, flooded nickel-cadmium batteries, it is desirable to add to the negative plate cadmium hydroxide forming the active material, small amounts of additives such as Fe_2O_3 , $\text{Ni}(\text{OH})_2$, PVA, cellacol, phenol etc. These additives are generally termed expanders or extenders and are used in the negative electrode to prevent crystal growth, thus retaining capacity.

The porous cadmium electrode has the property of loss of capacity in the absence of any expanders. Investigations particularly on sintered cadmium plates have suggested that the fall in capacity is related to the growth of cadmium and cadmium hydroxide^{72,79,82,86,172,173} crystals and the redistribution of active material.^{64,81,84} It has been stated⁷⁹ that the effect of this crystal growth is more pronounced at low charge rates and at high temperature as might be expected.

Several researchers^{58,86,172} found that the cadmium hydroxide crystals which grow on cycling are not easily recharged and it has been suggested⁷² that the loss in capacity is due solely to this mechanism. However, Armstrong et al.³² prefer the mechanism whereby the failure is credited to the growth of a passivating film on the surface of the active material.

As the charge-discharge reaction proceed by a dissolution-precipitation pathways and the fact that crystal growths appear

to cause early failure of cadmium electrodes, a modification of the crystallographic environment by the addition of a suitable expander material should overcome the problem of crystal growth.

Two principle types of crystal growth modifiers (expanders) have been described in the literature; one affecting nucleation and the other depending on the adsorption onto the growing crystal (mainly organic compounds and soluble inorganic compounds). The action of expanders and a large range of expander materials have received extensive investigation for the lead / lead sulphate systems.^{121-128, 174-176} The well-known result of this process are to create a better high discharge rate at low temperatures, and also to effect improvements in the cycle life of the battery. Unfortunately, however, there appears to be no clear consensus as to the mode of action of expander materials for the cadmium electrode.

This is probably due to the expander functioning in more than one way and it is therefore difficult to asses the effect of PVA by using conventional battery negative electrodes because included in the negative active material are iron-oxide and other additives such as graphite and paraffin.

It was seen in Chapter 7 that even if we exclude the iron-oxide and paraffin we could still not perform the various techniques to study the PVA effect on the discharge of the cadmium electrode simply because there would be so many parameters to consider such as porosity, surface area, design and structure of the electrode etc. etc. and on top of this the mathematics valid for the various electrochemical techniques on a planar electrode would breakdown on a porous system.

Surface morphological effects of PVA on the cadmium hydroxide electrode during cycling can easily be monitored using SEM and X-ray crystallographic techniques but any adsorption phenomenon, changes in conductivity or changes in the electrocrystallisation are extremely difficult to infer from surface structures.

It is therefore the object of the next few chapters to examine the effect of PVA on the discharge of the planar cadmium electrode and finally to come to some conclusion as to how in conjunction with iron-oxide they help to maintain the crystallite size of the cadmium-cadmium hydroxide to a minimum, thus prolonging battery life.

When a planar cadmium electrode is polarised in strong alkaline solutions, the cadmium ions emerging from the metal react with the OH^- ions and settle on the electrode as a $\text{Cd}(\text{OH})_2$ film. Initially the $\text{Cd}(\text{OH})_2$ film is thin and so the dissolution current is high, but as it grows thicker, the rate of ion transport to the film/solution interface decreases as well as the limiting reaction current. The cadmium species move under the effect of concentration and potential gradients which become smaller as the film grows thicker. The reaction rate thus drops accordingly.

Croft¹² derived equations for the current as a function of time in the case where the driving force is an ionic concentration gradient.

$$i = \left(\frac{kT}{e} \frac{\sigma}{2\Omega} \right)^{\frac{1}{2}} (1 - \exp \{ - \frac{e\phi}{kT} \})^{\frac{1}{2}} t^{-\frac{1}{2}} \quad 9.1$$

and if the driving force is a gradient in the electrostatic

potential, then the current density is given by

$$i = \left(\frac{\sigma \phi}{2\Omega} \right)^{\frac{1}{2}} t^{-\frac{1}{2}} \quad 9.2$$

where ϕ is the overpotential, Ω is the volume of oxide produced per coulomb of electric current, σ the ionic conductivity, e the electric charge, k the Boltzmann constant, T is the absolute temperature and t is the time.

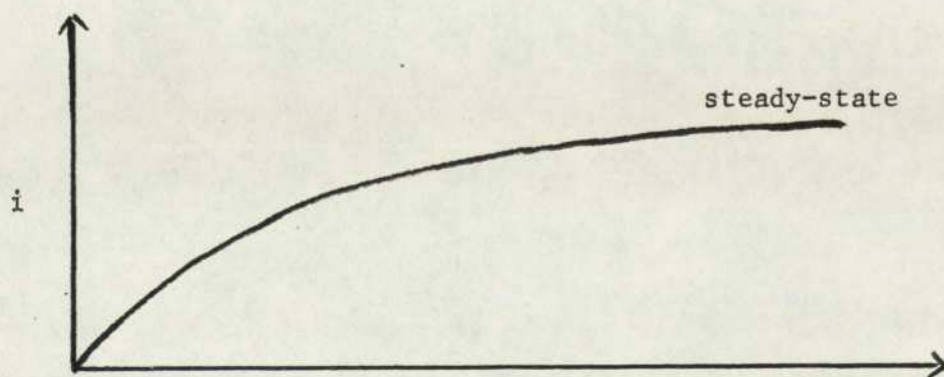
The work that was undertaken in this investigation describes the limiting current measurements on the anodic oxidation of a planar cadmium electrode as a function of time and at fixed potentials.

Cyclic voltammetry measurements were also made and here the electrode potential was scanned at a constant rate between two voltage limits and the current response to the potential sweep monitored.

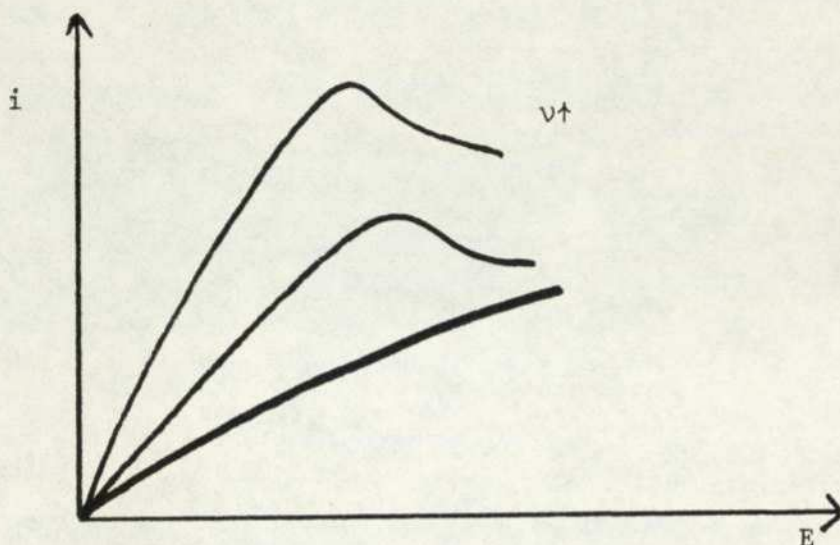
Consider the effect of a single potential sweep on the following electrode transfer reaction.



For a sufficiently slow potential sweep the current obtained can be said to correspond to a steady-state value.



However, as the scan rate (v) increases, a peak appears in the i vs E curve and becomes increasingly more prominent due to the combined effects of high mass transfer rate in the now non-steady state followed by the progressive depletion of the reactant concentrated in the diffusion layer.



Experiments were carried out on a planar cadmium disc electrode and also studying its effect in the presence of PVA.

9.2 Experimental

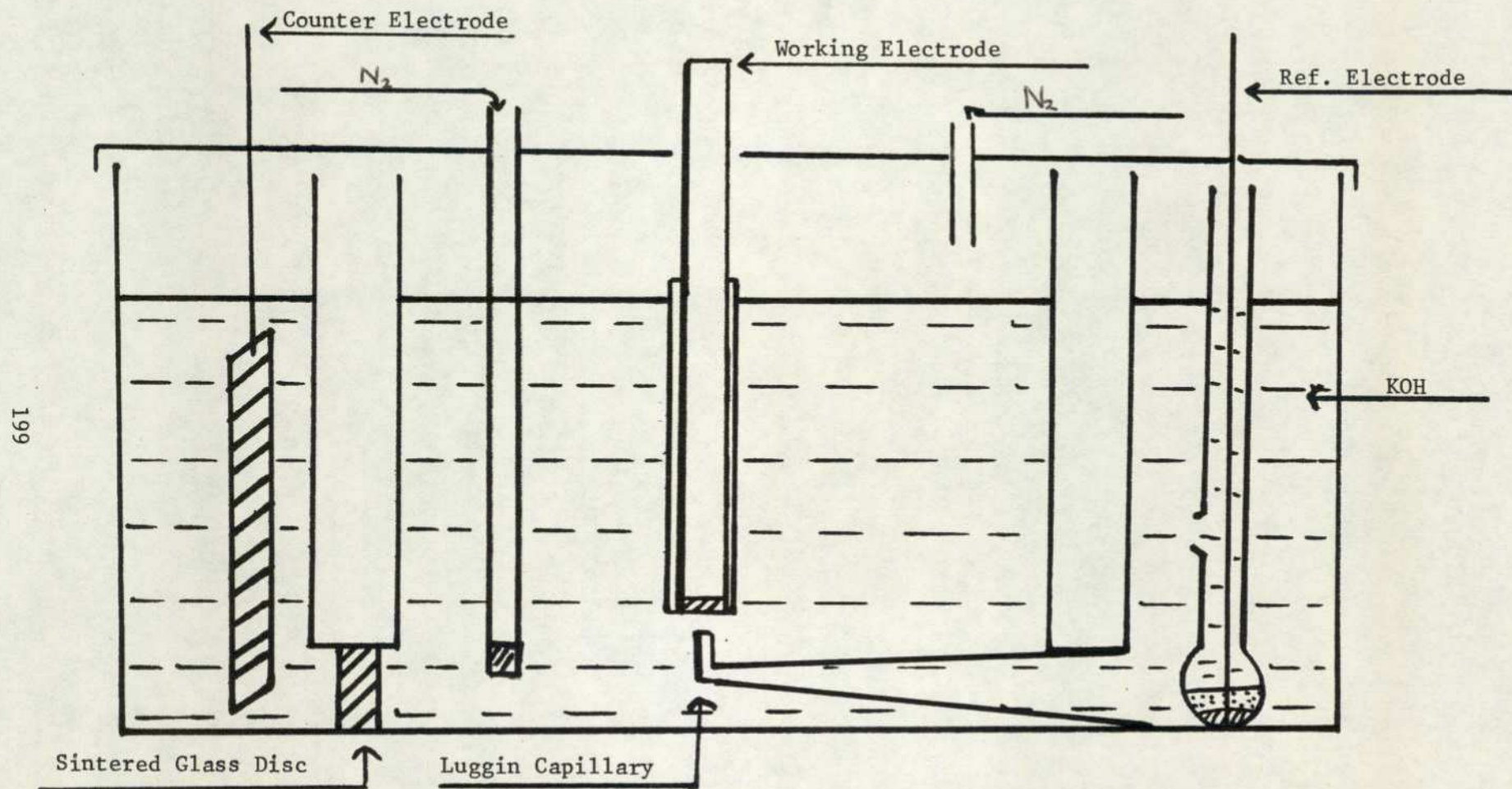
Limiting Current Measurements.

The cadmium used in this investigation was a disc, area 0.283 cm^2 cut from a rod supplied by BDH (99.9% pure).

It was set in an Araldite holder. Measurements were made in a conventional 3-electrode cell using Hg/HgO reference electrode and a Ni counter electrode as shown in Figure 9.1.

The solutions used were 1, 5 and 10M KOH made up from Analar pellets and deionised-distilled water. All solutions were deoxygenated with nitrogen and the experiment conducted at room

Figure 9.1



temperature ($25 \pm 2^{\circ}\text{C}$).

Prior to experiment the electrode was polished mechanically with 4/0 emery paper wetted with methanol, cleaned with methanol and water and then polished with diamond paste. It was finally cleaned with methanol again and held at a cathodic potential of - 1.000V with reference to the Hg/HgO electrode for $\frac{1}{2}$ hour.

Limiting current measurements were made using a Chemical Electronics 0.5A - 20V potentiostat. Additives that were looked at were PVA, sodium silicate and calcium hydroxide.

9.3 Results and Discussion

Plots of i against $t^{-\frac{1}{2}}$ calculated from the experimental i vs t curves for a number of KOH solution concentrations are reported in Figure 9.2. These plots are straight lines which would eventually approach the coordinate origin at $t = \infty$.

The slopes of the straight lines are given by $di/dt^{-\frac{1}{2}}$ and increases with the concentration of the KOH solution. The values of the gradient characterises the ionic conductivity of the film and to a certain approximation they are proportional to the logarithm of KOH concentration.

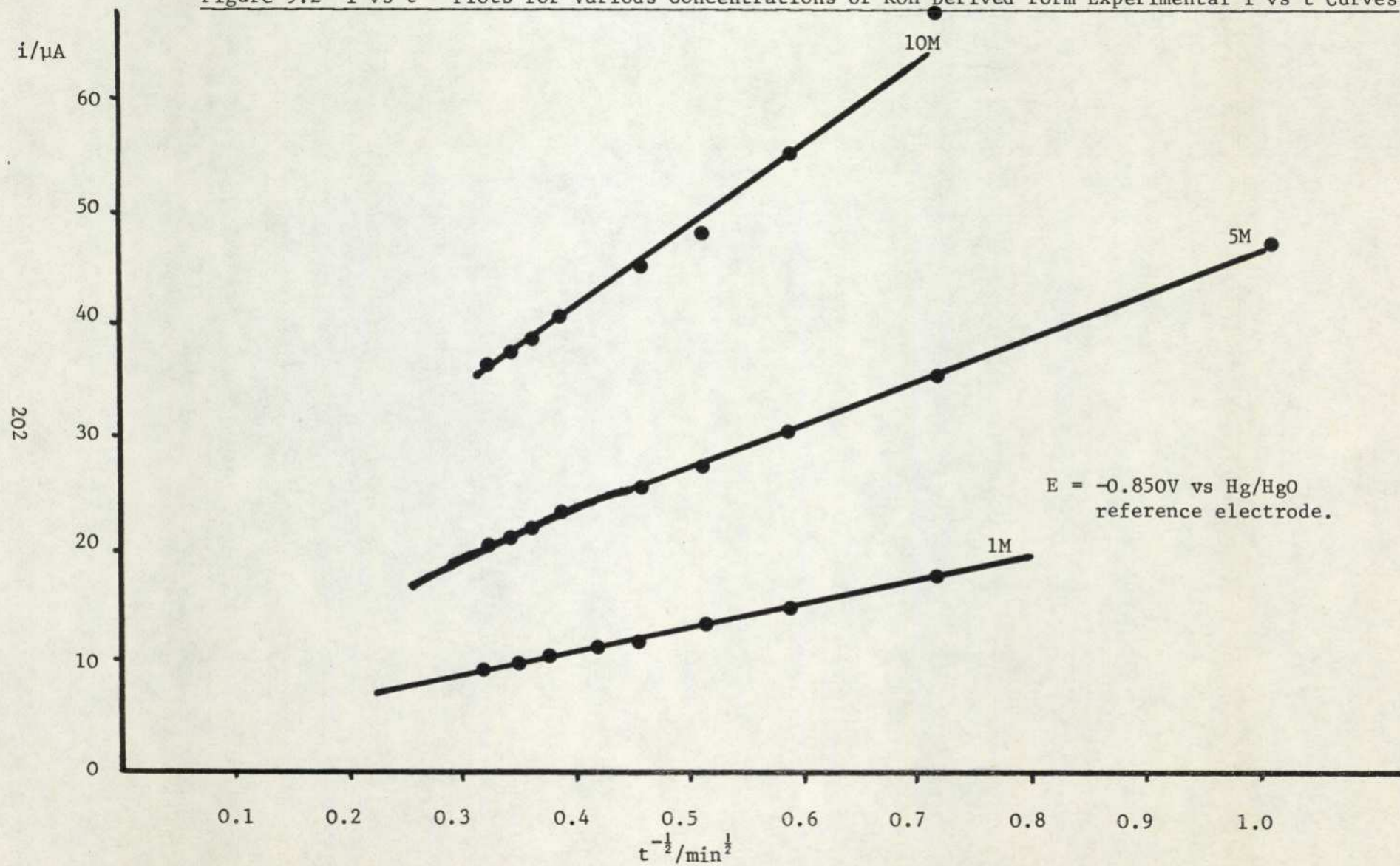
In some cases an increase in the anodic potential also leads to an increase in the slope of the i vs $t^{-\frac{1}{2}}$ curve which approach the coordinate origin (Table 12). The substantial effect of potential on the ionic conductivity and on the rate of film formation evidently must be attributed chiefly to the effect of an electrostatic field gradient on these reactions.

The effect of an organic additive such as PVA and inorganic

TABLE 12

-E/V	KOH/M		
	1	5	10
0.86	23	33.5	66.5
0.85	22.5	38.5	73
0.84	24.5	-	-

Figure 9.2 i vs $t^{-\frac{1}{2}}$ Plots for Various Concentrations of KOH Derived from Experimental i vs t Curves.



additives such as sodium silicate and calcium hydroxide were investigated on the current-time relationship and on the ionic conductivity of the cadmium hydroxide layer.

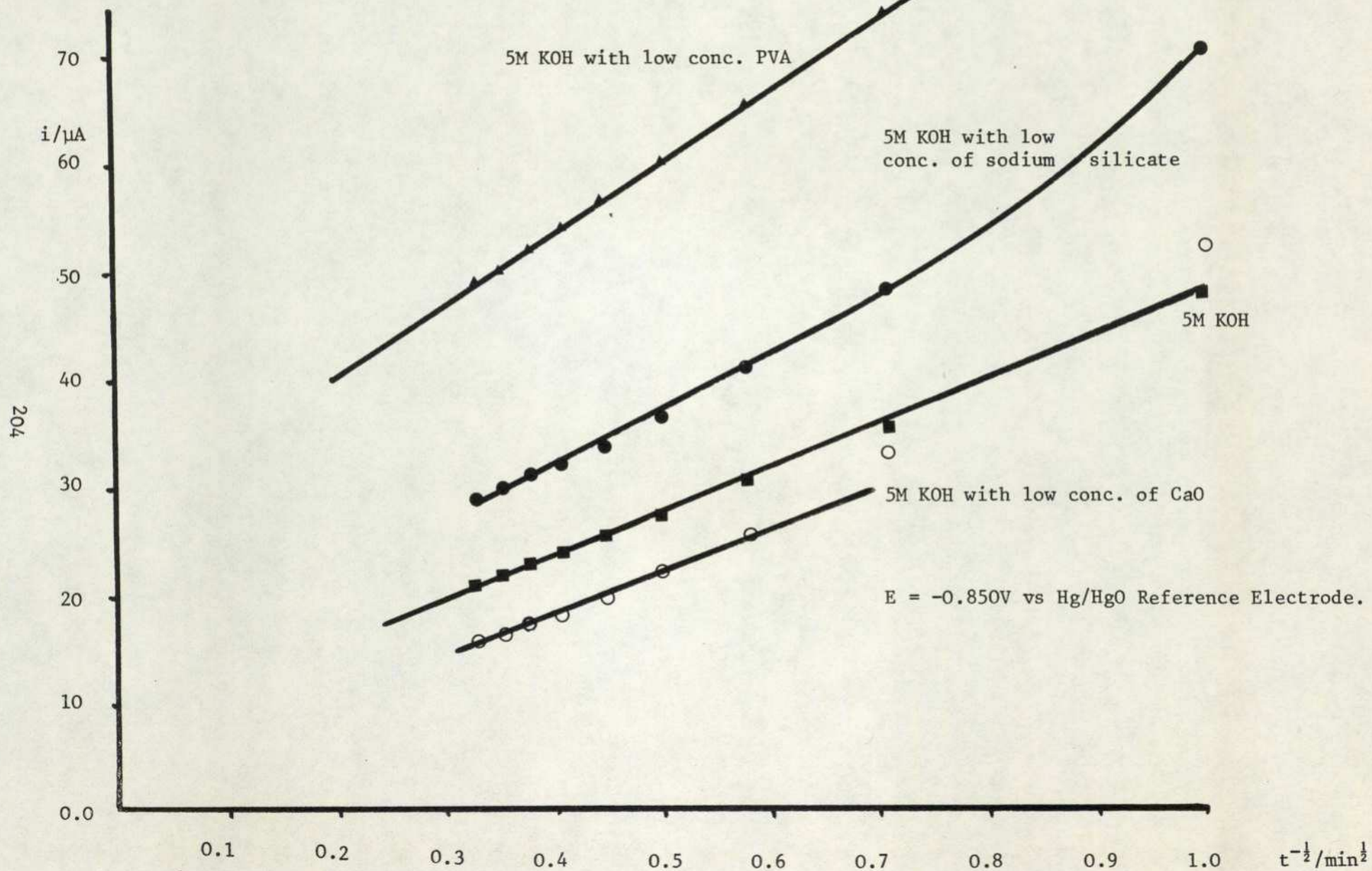
When a high concentration of calcium hydroxide was added to the 5M electrolyte, there was a decrease in the slope of the i vs $t^{-\frac{1}{2}}$ curve and this caused inhibition of current flow in the $\text{Cd}(\text{OH})_2$ layer ($E = -0.860\text{V}$).

However, very low concentrations of the organic and the sodium silicate increased the slope and hence caused an increase in the current flow through the $\text{Cd}(\text{OH})_2$ layer (Figure 9.3).

The fixed potential experiments indicated that after sufficient time had elapsed, the rate of oxidation followed a parabolic growth law. The law was consistent with at least two hypothesis:¹² The cadmium ions emerging from the metal reacts with the OH^- ions at the metal electrolyte interface and deposits on the metal as $\text{Cd}(\text{OH})_2$. The parabolic growth law would then come into operation when the metal was completely covered with cadmium hydroxide except for small pores. The ability of the cadmium to form the $\text{Cd}(\text{OH})_3^-$ species as postulated by Okinaka²⁹ then decreases at the metal electrolyte surface because of insufficient supply of electrolyte at the surface of the metal. Therefore as the cadmium hydroxide layer thickens, the $\text{Cd}(\text{OH})_3^-$ ion path increases, thus causing a current proportional to $t^{-\frac{1}{2}}$.

The other hypothesis is that the cadmium ion or OH^- ion moves through the cadmium hydroxide layer and the process of electron transfer reaction occurs at the metal hydroxide-electrolyte interface. Using this hypothesis, the parabolic growth

Figure 9.3 i vs $t^{-\frac{1}{2}}$ Plots for Various Additives in KOH Solution



law sets in when the exchange currents associated with the metal-hydroxide and hydroxide-electrolyte boundaries are large compared with the rate of growth so that the rate is limited only by transport through the hydroxide. As the hydroxide layer increases, the resistance increases and the current required to maintain the imposed potential decreases, thus yielding a parabolic growth law.

It is thought that the second hypothesis is more likely where reaction occurs at the cadmium hydroxide-electrolyte interface. Probably the cadmium ions appearing during the oxidation settle in sites of the $\text{Cd}(\text{OH})_2$ lattice. Under the effect of the concentration and potential gradient being set up, these ions acquire additional activation energy which is sufficient to lift them from the lattice sites and transfer them to interstitial sites where under the effect of these gradients, they move via defects or vacancies to the film/solution interface to form the required product.

The increase in the limiting current and also in the ionic conductivity found in the alkaline solution when PVA and sodium silicates had been used as expanders and also when the OH^- ion concentrations had been increased was probably due to the adsorption of these ions in the lattice sites. This increases the negative charge surrounding the cadmium ions and facilitates their transfer to interstitial sites thus leading to a higher concentration of cadmium ions in the interstitial sites and to a higher ionic conductivity of the film.

Cationic additives such as calcium hydroxide seemed to

inhibit the transfer of cadmium ions to the interstitial sites leading to a lowering in the ionic conductivity.

Therefore, if the ionic conductivity of the cadmium hydroxide can be increased by the addition of a suitable organic or soluble inorganic expander, then it is probable that the expander could be beneficial in the negative plate of the nickel-cadmium battery.

9.4 Experimental

Cyclic Voltammetry Measurements.

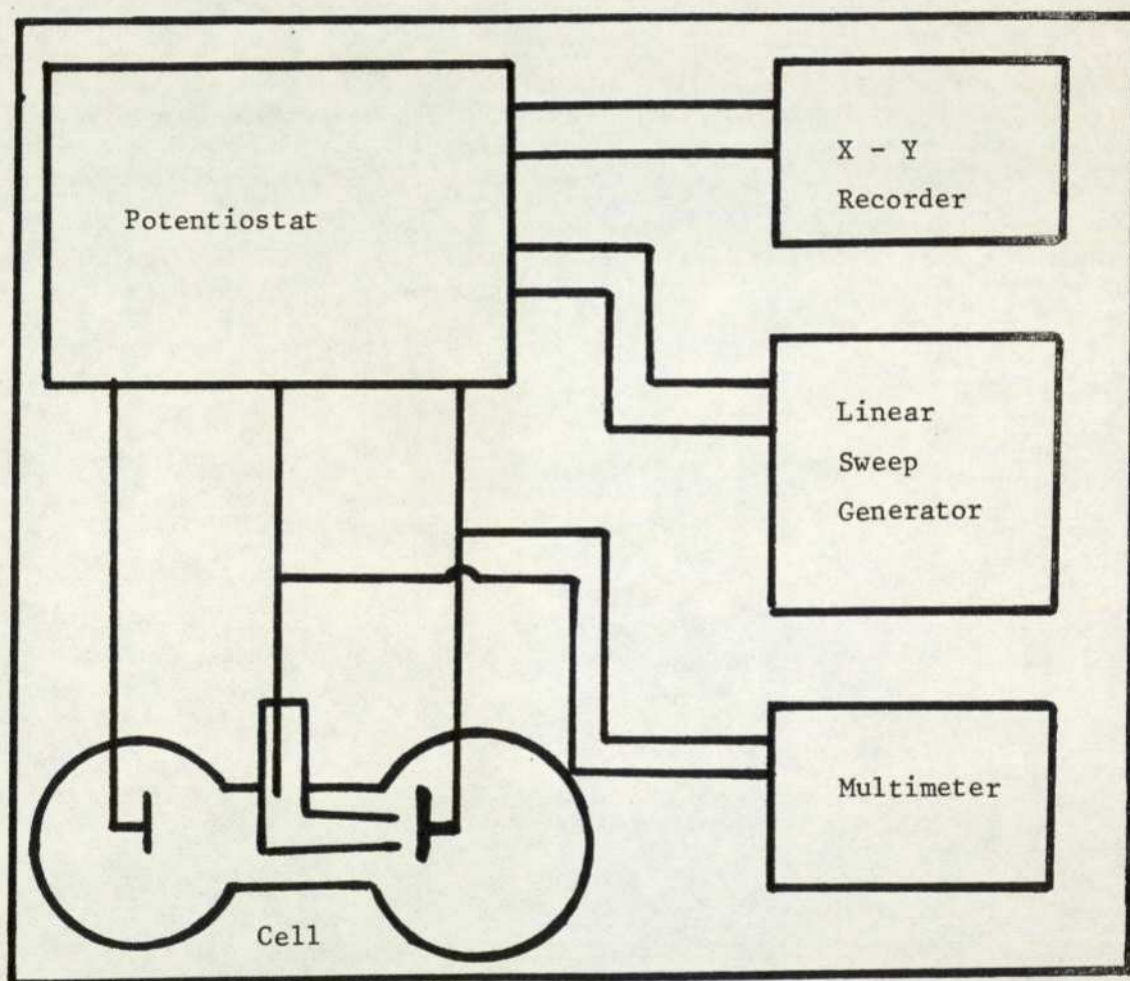
The cadmium disc electrode was treated in exactly the same way as for the limiting current measurement and the cyclic voltammetry measurements were made using the Chemical Electronics 0.5A - 20V potentiostat in conjunction with a sweep generator and a J.J. PL4 recorder (Figure 9.4).

All solutions were deaerated by bubbling with nitrogen before each experiment.

A saturated solution of PVA in 5M KOH electrolyte was made and three aliquots of 3mls, 5mls and 10mls of this solution added at each stage of the experiment. Prior to each experiment the cadmium electrode was polished and cleaned in the usual way and held cathodically at - 1.000V vs Hg/HgO reference electrode for $\frac{1}{2}$ hour in 600mls of KOH electrolyte. The sweep speed chosen was 400 mV/min.

It was recommended by Chloride Alcad, as a matter of interest to try tere-phthalic acid as a possible alternative organic expander. A saturated solution of tere-phthalic acid in 5M KOH

Figure 9.4 Circuit Diagram for Linear Sweep Voltammetry.



was prepared and aliquots of 3mls, 5mls and 10mls of this solution added to 600mls of the electrolyte in separate experiments. The rest of the experimental conditions were exactly the same as that for the PVA experiment.

9.5 Results and Discussion

Figure 9.5 shows linear potential sweep voltammograms under conditions of continuous cycling between -0.600V and -1.000V (vs Hg/HgO ref. electrode) showing the influence of the addition of various concentration of PVA to the electrolyte.

In the absence of the expander (curve 3), normal behaviour was exhibited, i.e. the dissolution of cadmium as a $\text{Cd}(\text{OH})_3^-$ or $\text{Cd}(\text{OH})_4^{2-}$ species and then multilayer formation upon repetitive cycling. The formation of the multilayer resulted in the passivation of the electrode surface at $\sim -860\text{mV}$ vs Hg/HgO reference electrode. The cathodic peak was at $\sim -970\text{mV}$ and a long 'tail' was exhibited whether or not an expander was used.

The addition of the expander to the electrolyte created a marked change in the polarisation curve. In the oxidative process, a greater amount of charge was required to passivate the electrode surface when 5mls (curve 1) of the saturated solution of PVA was added than say 10mls or 3mls of PVA solution (curves 2, 4). The anodic and the cathodic peaks diminished as they did with the electrode without any expander in the electrolyte. The amount of charge required to passivate the electrode increased by 3-fold when 5mls of PVA was used than in the case without any expander. This is the usual case that too much or

Figure 9.5 Cyclic Voltammetry of Planar Cadmium Electrode with Different Concentration of PVA Additive. Scan Rate = 400mV/min.

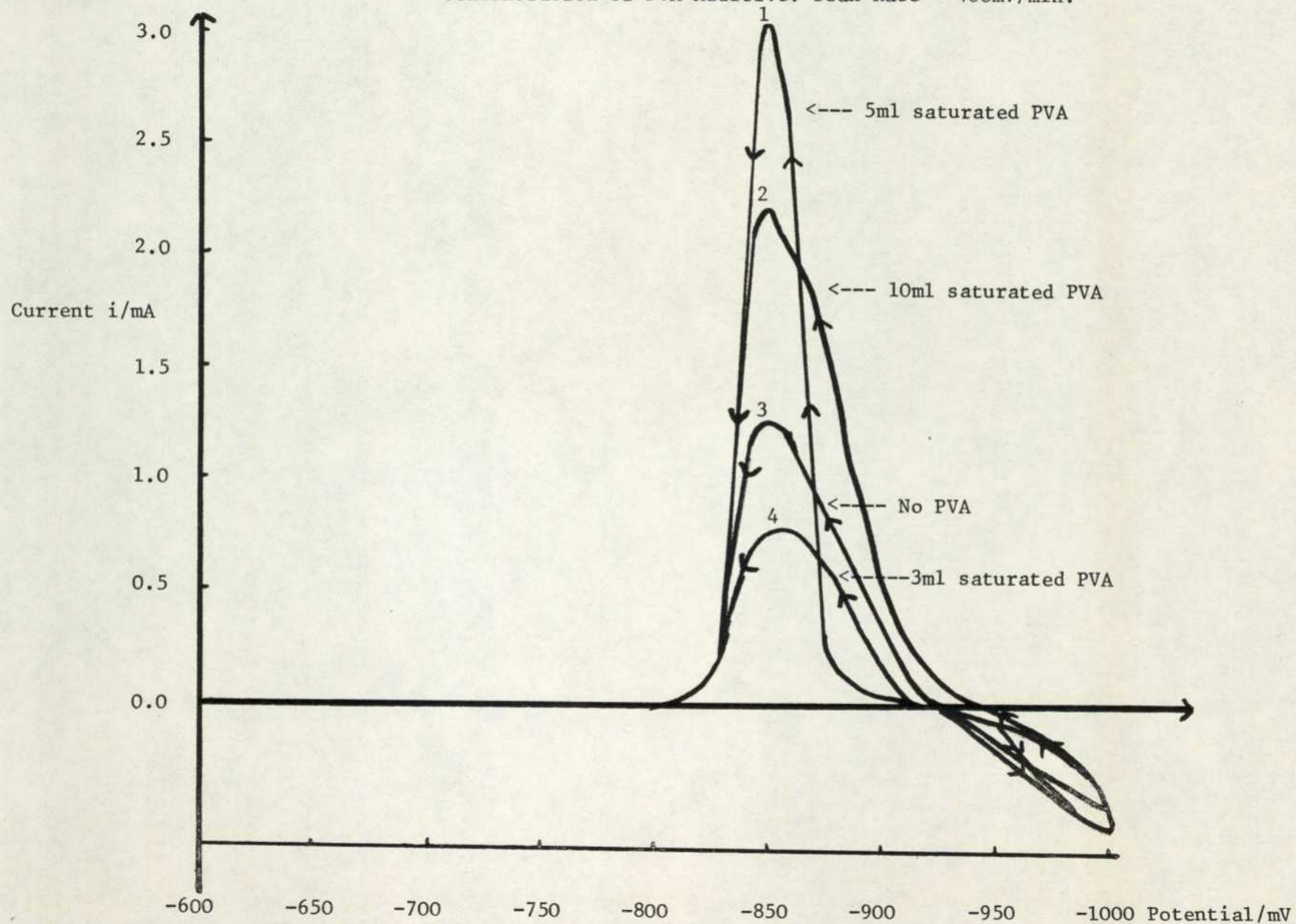


Figure 9.6 Successive Cyclic Voltammograms For The Stationary $\text{Cd}(\text{OH})_2/\text{Cd}$ System in 5M KOH. Scan Rate = 200mV/min.

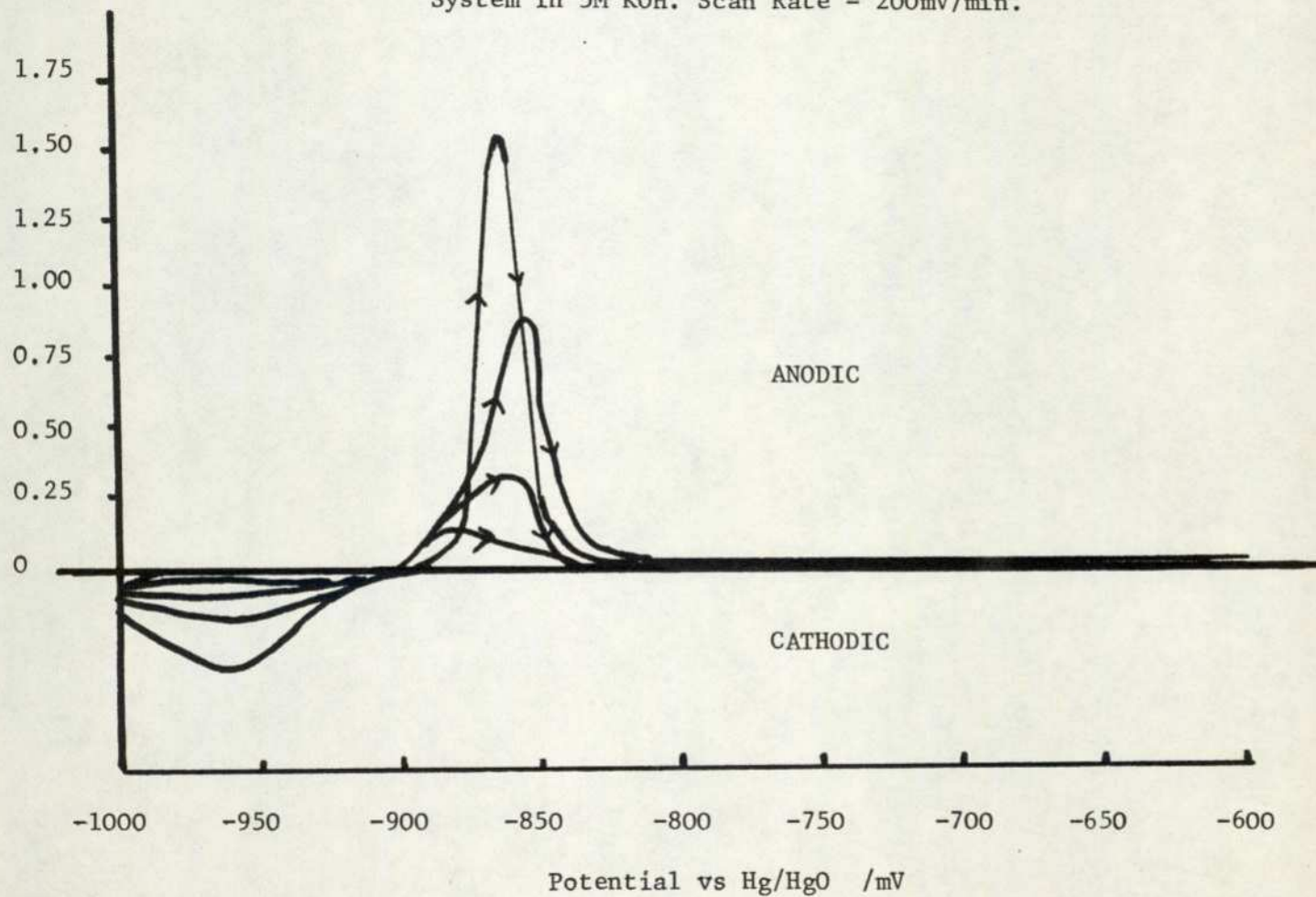
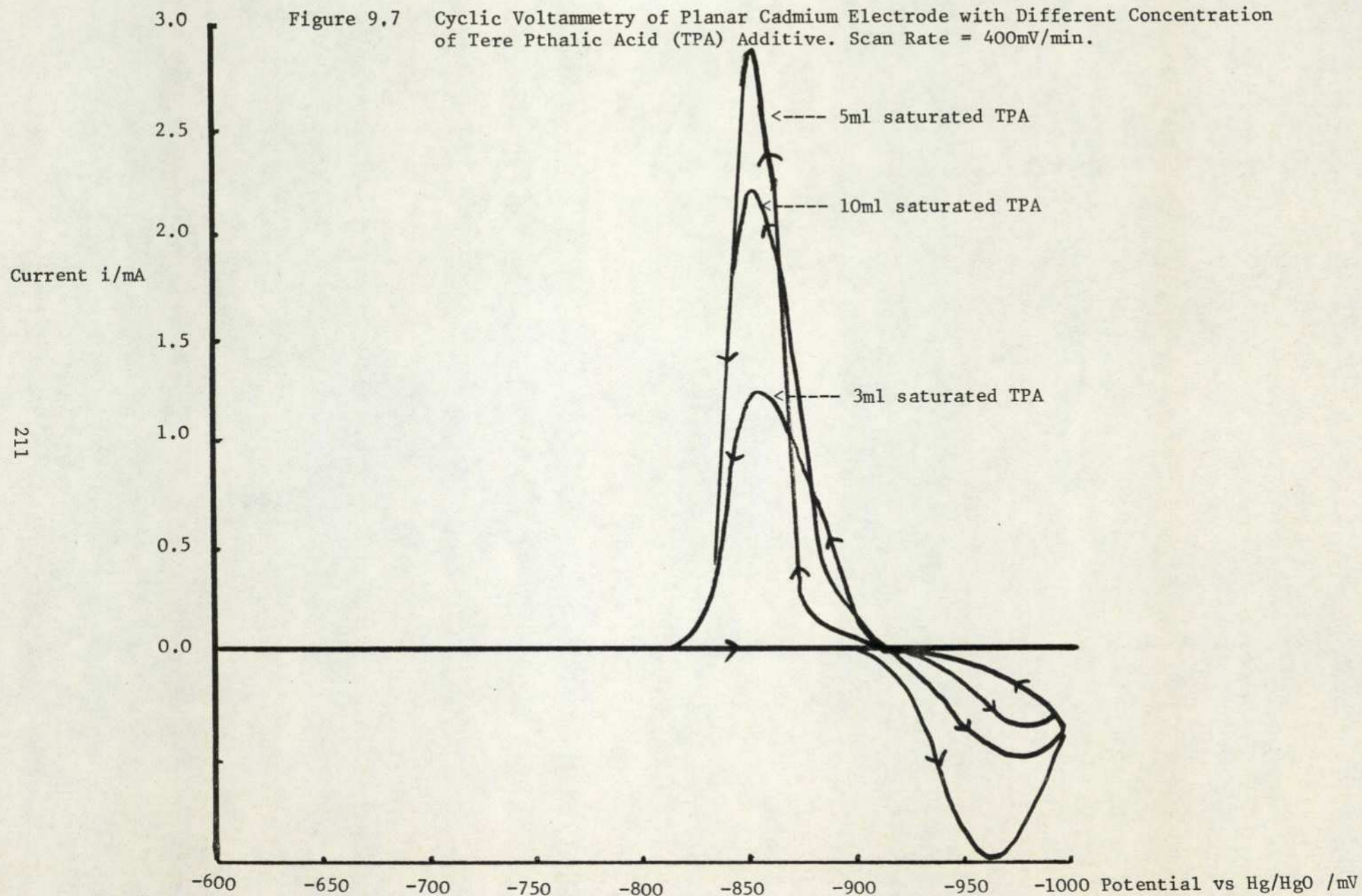


Figure 9.7 Cyclic Voltammetry of Planar Cadmium Electrode with Different Concentration of Tere Pthalic Acid (TPA) Additive. Scan Rate = 400mV/min.



too little of an expander can be harmful or not as efficient to the electrode performance and an optimum value has to be reached.

Figure 9.6 shows successive cyclic voltammograms on a fresh cadmium electrode with PVA added to the electrolyte. The anodic peak occurred at -865mV vs Hg/HgO and on subsequent cycles shifted to more cathodic potentials. With increasing time, a decreasing amount of charge was required to passivate the electrode showing that ultimately on a planar electrode even the PVA cannot increase the transport of ions through the cadmium hydroxide that is already formed on the electrode.

On a planar electrode, therefore, the PVA probably helps to maintain a highly porous deposit of cadmium hydroxide on the metal surface and this porous deposit provides channels for the migration of OH^- ions to react with the accessible metal thus resulting in a high limiting current and high charge density.

In the absence of PVA, the deposit is believed to be relatively non-porous, probably forming rhombohedral crystallites of cadmium hydroxide on the surface of the metal. This results in a relatively low limiting current and low-charge density.

Tere-phthalic acid provided similar results to those obtained with PVA (Figure 9.7).

It is believed that the mode of action of these additives are very similar and to study the full effect of the PVA expander under consideration we need to look at adsorption phenomenon and kinetics of electrocrystallisation and the next three Chapters deals with these aspects using the a.c. impedance and transient techniques.

CHAPTER 10

DOUBLE LAYER AND FARADAIC IMPEDANCE

DOUBLE LAYER AND FARADAIC IMPEDANCEINTRODUCTION

10

Impedance measurements were carried out to study the effect of any PVA adsorption on a planar cadmium electrode. Armstrong and co-workers¹⁹¹ had already studied the impedance of cadmium on a planar electrode but no studies pertaining to the effect of PVA on the cadmium electrode had been made. It was therefore necessary to carry out impedance measurements in the presence of this expander so that adsorption phenomenon could be studied as well as other properties such as double layer capacities.

10.1 Theoretical Principles

The surface of any electrode is a region of extreme heterogeneity which may extend into one or more of the phases. The electric field normal to the surface and the preferred orientation of adsorbed species will impose an additional, molecular anisotropy and the description of an electrode surface is therefore necessarily complex.

The major components of most electrode systems are the metal and the solvent, and they impart the main character of the interface. Dissolved species, perhaps present in only small concentration may accumulate in the interface either because of their intrinsic surface activity or, in the case of ionic species, because of an imposed electric field across the electrode surface. The degree of adsorption of a species will be the resultant effect of several competing forces, i.e. between the chemical and electrical forces attracting the species

to the metal and the solvation forces resisting that attraction. If the standard state of the adsorbed species is taken as that in the limit of zero coverage (equivalent to infinite dilution in the bulk), then the corresponding energy term will be the standard free energy of adsorption $\Delta G_{\text{ads}}^{\theta}$, i.e. the change in free energy for the adsorption of 1 mole of the species from its standard state in solution to its standard state in the interface. It follows that for the species i

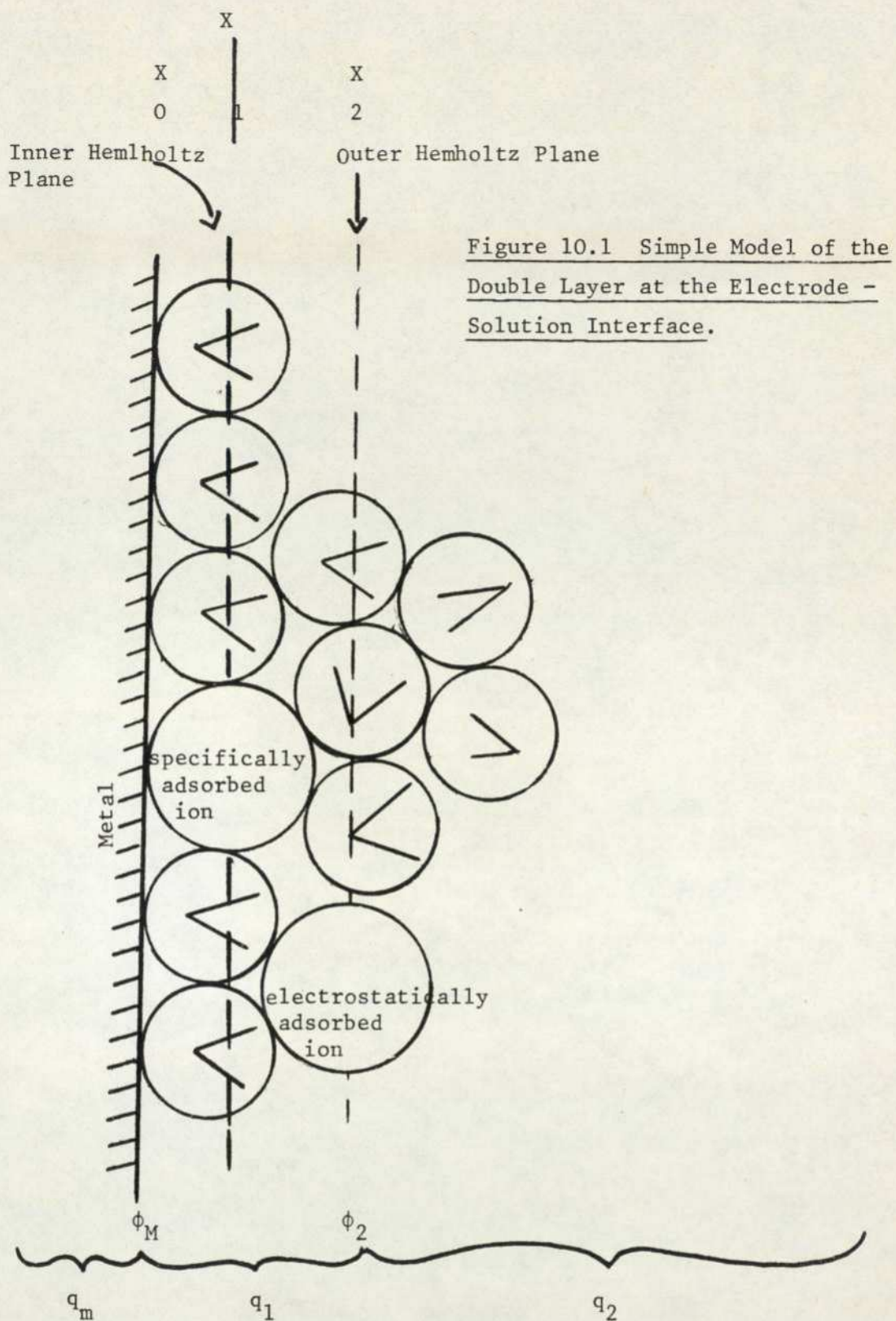
$$\Delta G_{\text{ads},i}^{\theta} = \bar{\mu}_i^{\beta} - \bar{\mu}_i^{\gamma} \quad 10.1$$

where $\bar{\mu}^{\gamma}$ is the electrochemical potential and γ and β denote respectively the solution phase and interphase. For all other compositions

$$a_i^{\beta} = a_i^{\gamma} \exp - \frac{\Delta G_{\text{ads},i}^{\theta}}{RT} \quad 10.2$$

where a_i^{β} is the surface activity yet to be operationally defined. If i is a charged species then $\Delta G_{\text{ads},i}^{\theta}$ and a_i^{β} will be potential dependent.

The simplest model for the distribution of ions at the interphase was first suggested by Helmholtz (Fig. 10.1): a plane layer of charges (excess adsorbed ions) confronts a plane layer of opposite charges in the electrode. The interphase, is therefore, equivalent to a parallel-plate capacitor, and electrodes which behave in this way are termed "ideally polarisable". The concept of a strict and rigid distribution of ions on a simple plane was oversimplistic because thermal agitation of ions in solution would affect their distribution over an appreciable distance into bulk solution.



The theories of the structure of the electrical double layer are several. The presently accepted theory is that of Devanathan, Bockris and Muller¹⁷⁷. According to this theory, the electrode is covered with strongly oriented adsorbed water molecules. These water molecules are bound to the electrode at least partly by electrostatic forces which are directly proportional to the charge on the metal. When this charge approaches zero, the water molecules are bound relatively poorly to the metal surface, hence specific adsorption of ions can take place by a replacement of some of these water molecules by some of partially desolvated ions. The locus of the centroids of these adsorbed ions is called the inner Hemholtz plane (IHP). Adjacent to this layer is a layer of water molecules which is not so oriented because these water molecules are under the influence of both the electric field and thermal fluctuation. They behave like a secondary hydration sheath of an ion. Some of these water molecules belong to the primary hydration sheath of the metal ions. The plane passing through the electrical centres of these metal ions is known as the outer Hemholtz plane (OHP). An important quantity which affects the calculation of the capacity of the double layer is the dielectric constant of the medium, which between the metal and the IHP is about 6 to 7, whilst between the IHP and OHP is about 30 to 40.

The structure of the ionic double layer may be investigated directly by measuring the interfacial tension or the differential capacity. The bulk of experiments in this field have been performed on mercury (or dilute amalgam) electrodes since both the interfacial tension (γ) and the differential capacity (C_{DL})

can be determined accurately. The two quantities are related by

$$\gamma - \gamma_{\max.} = - \int_{E_{pzc}}^E C_{DL} dE \quad 10.3$$

This equation is derived from the Gibbs adsorption isotherm and the equation of electrocapillarity. It is based on purely thermodynamic considerations as applied to an "ideally polarised" electrode. The quantity E_{pzc} is the potential of zero charge and it coincides with the electrocapillary maximum, i.e. the potential at which γ reaches its maximum value.

Equation 10.3 is more commonly used in its differential form

$$C_{DL} = - \frac{\partial^2 \gamma}{\partial E^2} \quad 10.4$$

in order to determine C_{DL} from interfacial tension measurement.

The relative surface excess Γ^1 is related to the surface tension by an equation of the form

$$\frac{\partial \gamma}{\partial \mu_i} \mu_j, E = - \tau_i^1 \quad 10.5$$

where all surface excesses are calculated with respect to the solvent, i.e. μ_j refers to all ionic or molecular species in the system except the solvent. Thus adsorption data can be derived from surface-tension or differential capacity data. τ^1 is an integral quantity and gives no information on the distribution of adsorbed species in the interphase, as a function of distance from the electrode for example.

When an ion is specifically adsorbed the values of γ and C are altered in a characteristic manner. For example in the case of anion adsorption, there is a marked increase in the value of C at each potential on the positive (anodic) branch of the capacitance curve and the p.z.c. is shifted in a negative direction. Equally when the cation is adsorbed, the increase in C is on the cathodic branch of the curve and the p.z.c. is shifted in a positive direction.

The adsorption of neutral organic molecules is restricted to a well-defined potential region on both sides of the p.z.c. Outside this region the measured curves coincide with those obtained in the absence of organic adsorbate. The limits of the adsorption region are bounded by two sharp "adsorption-desorption" peaks in the capacity-potential curve. Between them the capacitance has a low, essentially constant value. The potential region over which adsorption occurs increases with bulk concentration of the organic species.

Electrochemical interfaces, such as the surface of a corroding electrode, can be viewed as a combination of passive, electrical circuit elements, i.e. resistance, capacitance and inductance. If an alternating voltage is applied to these, the resultant current can be determined using Ohm's Law:

$$V = iR \quad 10.6$$

provided that R (resistance) is replaced by the appropriate expression for the reactance, X , of the passive element in question i.e.

$$V_{\text{peak}} = i_{\text{peak}} X \quad 10.7$$

The reactance of a capacitor or an inductor can be expressed in several forms, the most convenient to use probably being that using the complex number,

$$X_R = R \quad 10.8$$

$$X_C = \frac{1}{j\omega C} \quad 10.9$$

$$X_L = j\omega L \quad 10.10$$

where ω = angular frequency ($\omega = 2\pi f$) and L = inductance. This notation makes it possible to represent any reactance or the impedance of a combination of reactances, as a vector in the real-imaginary plane in the form of an Argand diagram (Fig. 10.2).

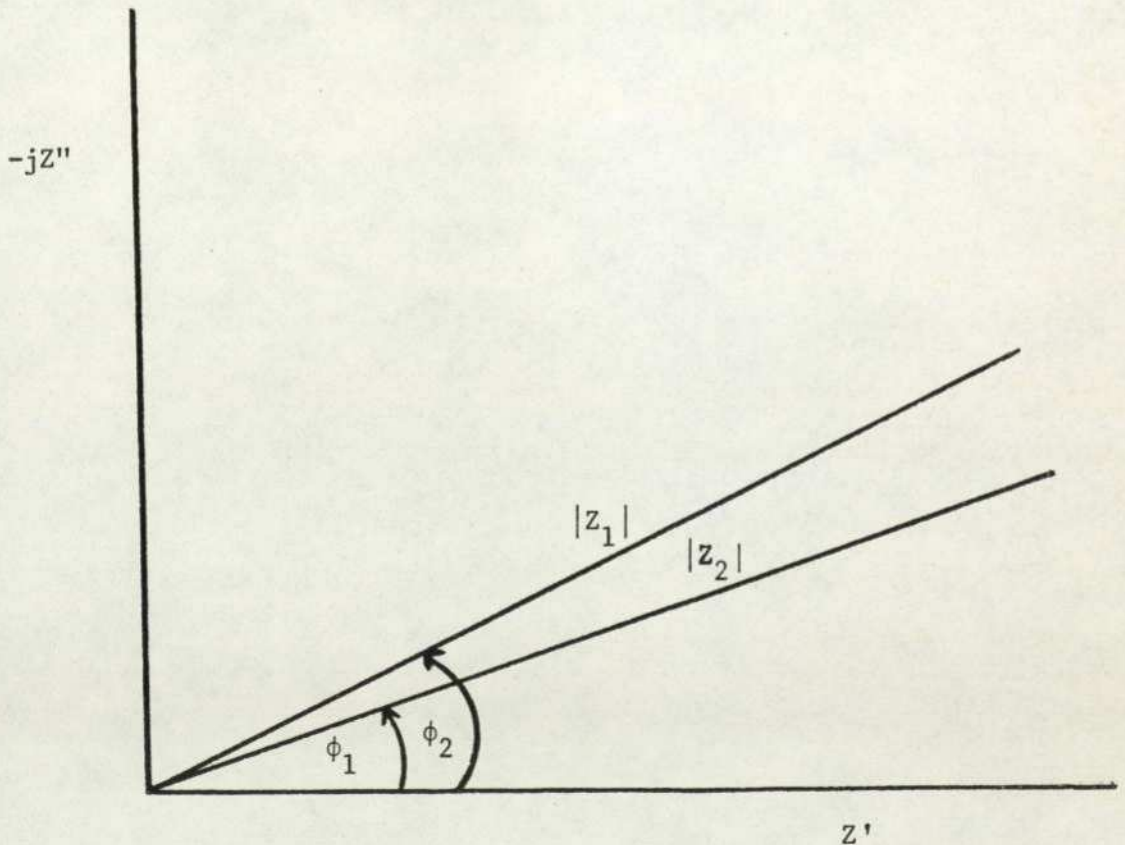


Figure 10.2 Argand Diagram Showing Impedance Vectors Z_1 and Z_2 .

An impedance, Z , can thus be completely defined by specifying the magnitude, $|Z|$, and the angle, ϕ its vector makes with the real positive axis or alternatively, by specifying the magnitude of its real, Z' and imaginary Z'' components.

The two notions are equivalent since:

$$Z'_s = |Z| \cos \phi \text{ real component} \quad 10.11$$

and

$$Z''_s = |Z| \sin \phi \text{ imaginary component} \quad 10.12$$

or in complex number notation

$$Z_s = Z'_s - jZ''_s \quad 10.13$$

Since the above reactance expressions contain ω , the angular frequency of the applied waveform, the magnitude and phase angle of the impedance vector representing the response of a circuit containing reactive elements will vary as ω varies.

A useful means of representing this variation with frequency is the Nyquist diagram. This is an extension of the Argand diagram using frequency as a variable. The diagram consists of a set of points, each representing the magnitude and direction of the impedance vector at a particular frequency.

As examples of the response, a series and parallel combination of a resistor and capacitor are shown in Figs. 10.3a and 10.3b together with their Nyquist diagrams.

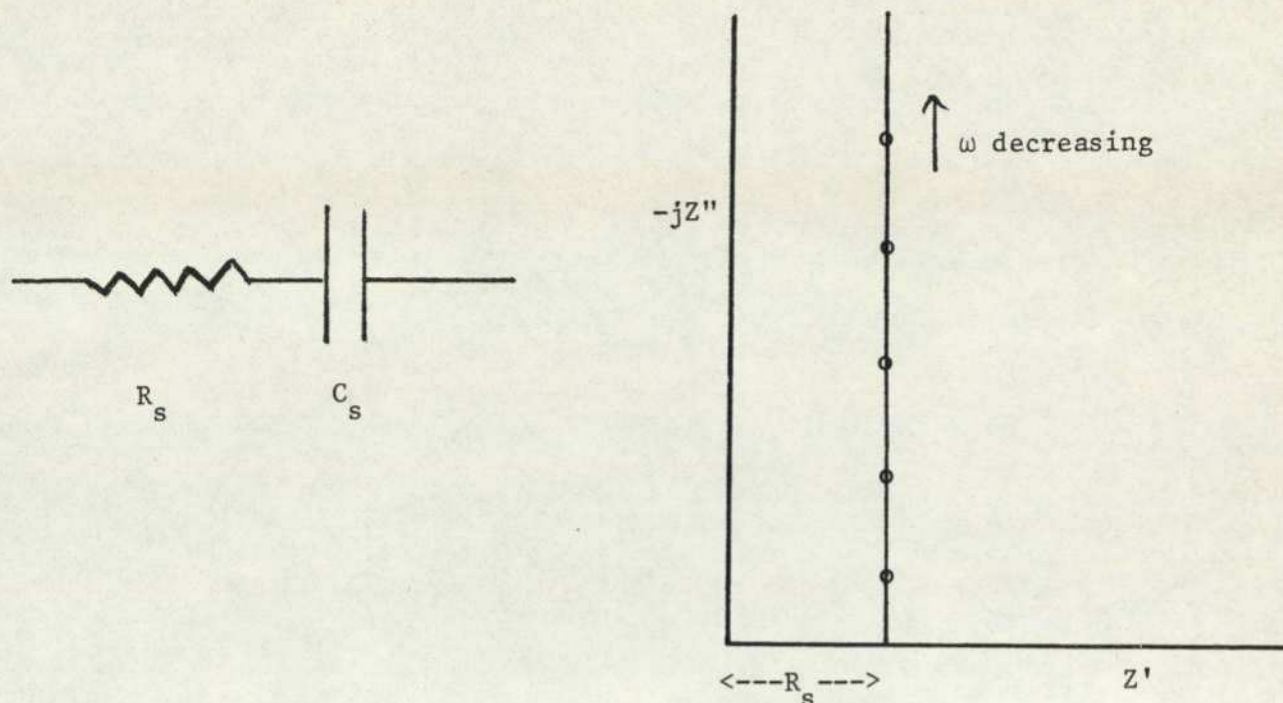


Figure 10.3a Series Resistor/Capacitor Combination and its Complex Plane Response.

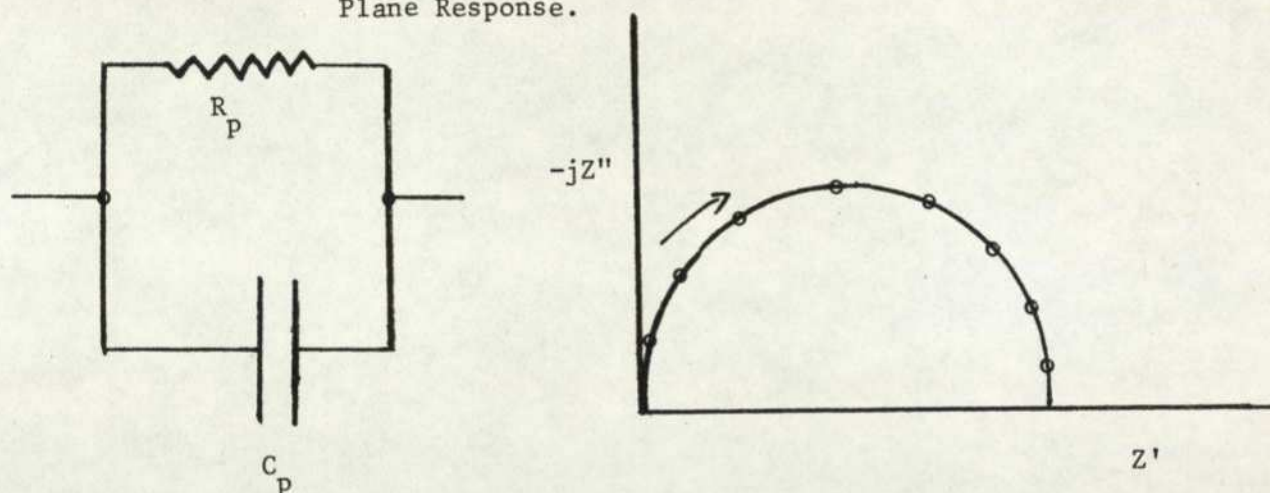


Figure 10.3b Parallel Resistor/Capacitor Combination and its Complex Plane Response.

The faradaic impedance at the working electrode thus arises from the electrochemical reactions taking place there. In the technique, a small-amplitude sinusoidal potential signal is imposed on the electrode. The interphasial response to this signal is compared to the components of an equivalent circuit containing a resistance and a capacitance connected in series.

Two principal methods have been developed to analyse the impedance data as a function of frequency.

10.2 The Randles' Method^{178,179.}

Randles proposed that the electrode impedance could be represented by the equivalent circuit shown in Fig. 10.4

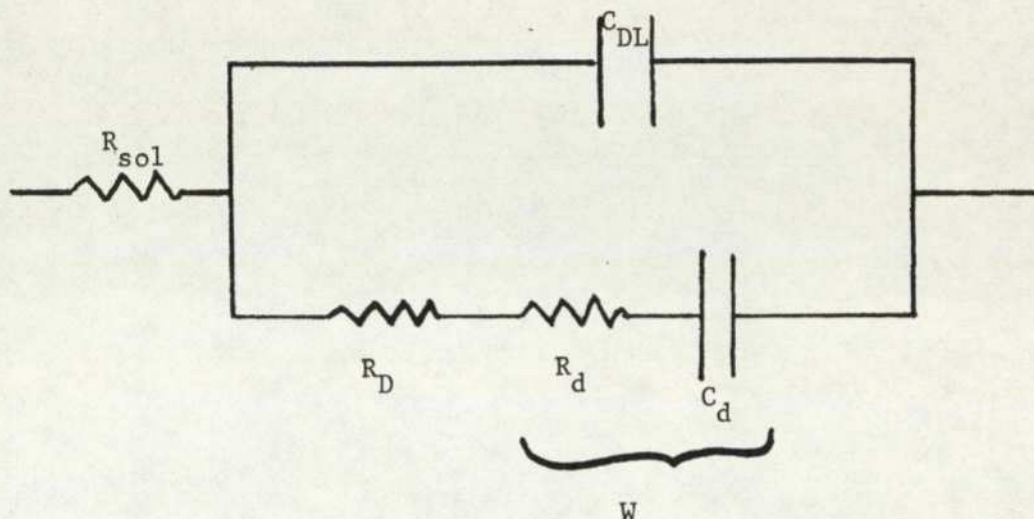


Figure 10.4

where R_{sol} is the ohmic resistance of the electrolyte and C_{DL} is the double layer capacitance (which varies with d.c. potentials depending on the concentration and nature of the electrolyte). R_D (or Θ) is the charge transfer resistance or activation polarisation and is related to the concentration C_{ox} and C_{Red} , reaction rate constant K_{sh} and the transfer coefficient α by the equation.

$$\Theta = \frac{RT}{n^2 F^2 K_{sh} C_{ox}^{s\alpha} C_{Red}^s 1-\alpha} \quad 10.14$$

The Warburg impedance (W) is a complex frequency-dependent quantity and is the impedance associated with the diffusional movement of charged species to and from the electrode. Randles derived the following expression for W

$$W = \sigma \omega^{-\frac{1}{2}} |1 - j| \quad 10.15$$

where σ is the Warburg coefficient, W the angular frequency and $j = |-1|^{\frac{1}{2}}$

The Warburg coefficient can be expressed as

$$\sigma = \frac{RT}{n^2 F^2 2^{\frac{1}{2}}} \cdot \frac{1}{C_{ox}^s D_{ox}^{\frac{1}{2}}} + \frac{1}{C_{Red}^s D_{Red}^{\frac{1}{2}}} \quad 10.16$$

In 10.14 and 10.16, C_{ox}^s and C_{Red}^s can be replaced by C_{ox}^b and C_{Red}^b if measurements are made at the equilibrium potential.

At potentials away from this value σ and Θ can be expressed in terms of bulk concentration provided that 14 and 16 are suitably modified.

A disadvantage of this method is that if C_{DL} is influenced by the concentration of one of the electroactive species the results may become erroneous.

Various methods have been proposed for the determination of Θ and σ from impedance measurements. Vector methods were used by Randles¹⁷⁹ and Delahay et al.¹⁸⁰. Gerisher¹⁸¹ has presented a treatment in which he neglected the imaginary part of the Warburg impedance and Vetter¹⁸² has corrected the cell impedance for the double layer capacitance and solution ohmic resistance.

11.3 The Sluyters' Method¹⁸³.

The Sluyters' method uses the same equivalent circuit as Fig. 10.4 but the impedance is displayed as a vector in a cartesian co-ordinate system - the so called complex plane plot or Nyquist diagram.

The components of the impedance vector are related to the

absolute value $|Z_s|$ and the phase angle ϕ of the impedance by the equations 10.11 and 10.12 previously mentioned.

From Fig.10.4 it follows that the cell impedance is

$$Z = R_{sol} + \frac{1}{j\omega C_{DL} + \frac{1}{\Theta + \sigma\omega^{-\frac{1}{2}} - j\sigma\omega^{-\frac{1}{2}}}} \quad 10.17$$

After separation of the real and imaginary parts of Z we obtain equation 10.13:

$$\text{i.e.} \quad Z_s = Z'_s - jZ''_s \quad 10.13$$

where Z' and Z'' are given by

$$Z'_s = R_{sol} + \frac{\Theta + \sigma\omega^{-\frac{1}{2}}}{(\sigma\omega^{\frac{1}{2}}C_{DL} + 1)^2 + \omega^2 C_{DL}(\Theta + \sigma\omega^{-\frac{1}{2}})^2} \quad 10.18$$

and

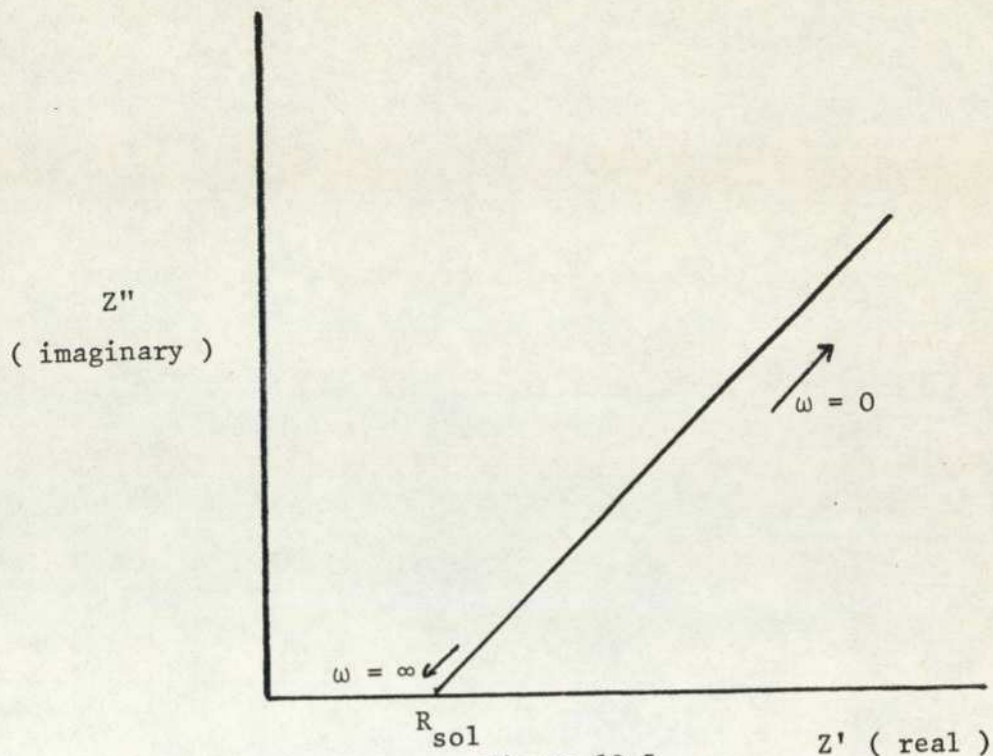
$$Z''_s = \frac{\omega C_{DL}(\Theta + \sigma\omega^{-\frac{1}{2}})^2 + \sigma\omega^{-\frac{1}{2}}(\sigma\omega^{-\frac{1}{2}}C_{DL} + 1)}{(\sigma\omega^{\frac{1}{2}}C_{DL} + 1)^2 + \omega^2 C_{DL}(\Theta + \sigma\omega^{-\frac{1}{2}})^2} \quad 10.19$$

Although equation 10.13 is complex, its two limiting cases (at low and high frequencies) yield important results.

1. If the activation polarisation term is neglected (i.e. Θ is small compared to W - usually at low frequencies) then 10.13 reduces to

$$Z_s = R_{sol} + \Theta + \sigma\omega^{-\frac{1}{2}} - j(\sigma\omega^{-\frac{1}{2}} + 2\sigma^2 C_{DL}) \quad 10.20$$

When the real and imaginary parts are plotted against each other, we obtain a straight line of unit slope as shown in Fig. 10.5



2. At higher frequencies, the concentration polarisation (W) can be neglected for a fairly irreversible reaction and equation 10.13 reduces to:

$$Z_s = R_{sol} + \frac{\Theta}{1 + \omega^2 C_{DL}^2 \Theta^2} - j \frac{\omega C_{DL} \Theta^2}{1 + \omega^2 C_{DL}^2 \Theta^2} \quad 10.21$$

If in this case, the real and imaginary parts are plotted against each other, a semi-circle is obtained. Values of R_{sol} , Θ and C_{DL} may be computed from those plots shown in Fig.10.6. At lower frequencies diffusion polarisation will give rise to a distortion of the semi-circle, as illustrated in Fig. 10.7, leading to a line of unit slope eventually. The extent of this distortion is dependent upon the relative values of Θ , σ and C_{DL} .

Figure 10.6 Complex Plane Display for a Charge Transfer Controlled Reaction

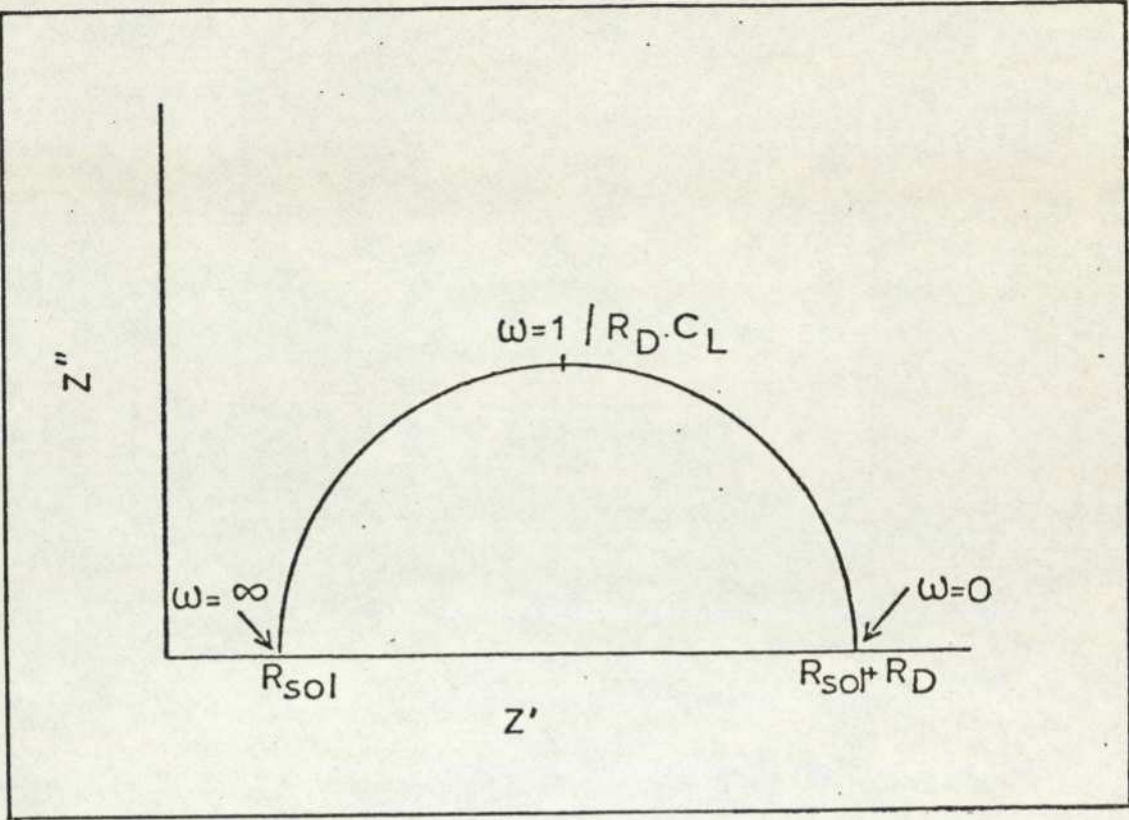
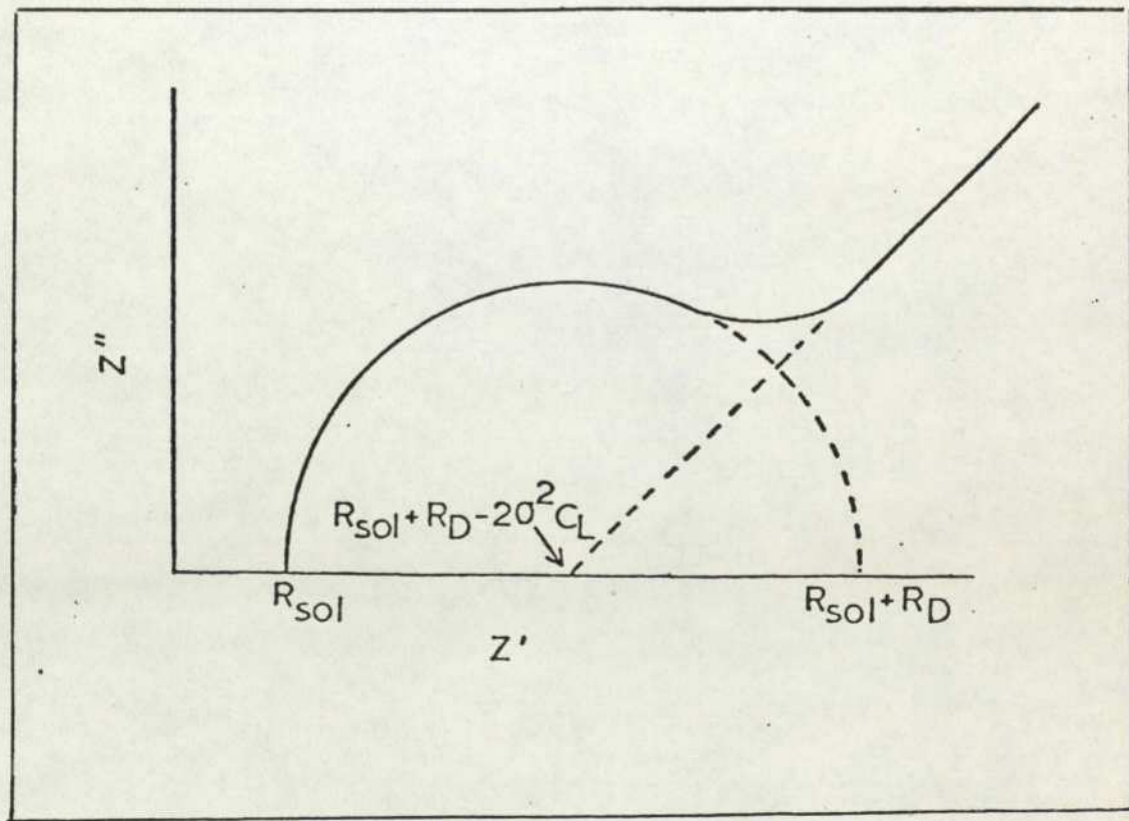


Figure 10.7 Complex Plane Diagram for a Reaction Under Mixed Control



Cadmium in alkaline solution shows some active dissolution prior to passivation. Both active and passive regions have been studied extensively using potentiostatic and galvanostatic measurements^{23,29,47,18,184,12,13,11,185,57,28,71,186,187}. Armstrong and Edmonson¹⁹¹ have made a detailed study of the impedance of planar Cd electrodes in alkaline solution. In the active dissolution region (-895 mV with respect to Hg/HgO) at frequencies 3Hz, a Warburg impedance is found due to diffusion of soluble Cd(OH)_4^{2-} species. At very low frequencies (1.5 to 0.005 Hz) deviation is observed due to interaction of the Nernst diffusion layer with the a.c. diffusion layer. The data are treated on the basis of a simple Randles' circuit. From plots of R_p and C_p vs $\omega^{-1/2}$ the solubility of Cd(OH)_4^{2-} in 10M KOH is estimated as $2-5 \times 10^{-1} \text{ mol dm}^{-3}$. A Nernstian slope of $30 \pm 5 \text{ mV}$ per decade for a 2 e reversible reaction was confirmed from plots of $\log i$ vs E . Estimates of the charge transfer resistance enabled the potential dependance of the exchange current to be reduced as $30 \pm 50 \text{ mV/decade}$. This value was considered to be consistent with a reaction involving two consecutive electron transfer, the first being in equilibrium, the second rate determining. These observations entirely confirm the earlier observations made by Armstrong and West using a ring-disc technique⁴⁷.

A potential just into the passive region (-870 mV) showed Warburg impedance at high frequencies which was also rotation speed dependent similar to the observations in the 'active' region. This was interpreted in terms of diffusion of soluble species in

the film. At very low frequencies a second Warburg impedance was found due to diffusion of species within the solid phase. At potentials further into the passive region (-700 mV) a marked change in the shape of the impedance diagrams was evident, showing mainly a low frequency Warburg impedance due to diffusion of species within the solid phase.

L'vova et al.^{188,189} analysed impedance measurements for Cd in KOH solution around the reversible $\text{Cd}/\text{Cd}(\text{OH})_2$ potential and claimed to find an impedance frequency dependence characteristic of diffusion. They proposed a mechanism for passivation involving electrochemical adsorption of hydroxide ions. These workers¹⁹⁰ also obtained impedance results for cadmium in the potential range where cadmium is in the passive state. At intermediate and low frequencies they considered a Warburg impedance to be the best approximation.

Armstrong et al.²⁸ studied the dissolution of cadmium amalgams prior to film formation and showed that the amalgams dissolved reversibly as $\text{Cd}(\text{OH})_4^{2-}$.

Hampson and Latham¹⁸ studied the charge transfer reaction at polycrystalline cadmium electrodes in NaOH solution and the complex plane impedance plot they obtained was a straight line of approximately unit slope deviation at lower frequencies. They interpreted the Warburg behaviour as indicative of a very fast charge transfer reaction with the deviation due to the presence of adsorption.

Hardly any information has been available concerning the effect of additives on the impedance plot and that which is

available has been in KF electrolytes^{192,193}.

The present work describes a study of the organic additive, PVA, on the impedance spectrum in the active-passive region.

10.5 EXPERIMENTAL

Impedance measurements were made on a planar cadmium disc electrode 0.283 cm^3 cut from a rod supplied by BDH (99.9%) pure and set in an Araldite holder. A conventional 3-electrode cell was used with a calomel reference and a large Ni counter electrode as shown in Fig. 9.1.

The solution used was 5M KOH made up from Aristar pellets and deionised water. All solutions were deoxygenated with nitrogen and the experiment conducted at room temperature.

Prior to experiment the electrode was polished mechanically with 4/0 emery paper wetted with methanol, cleaned with methanol and water and then polished with diamond paste until a mirror-like finish was obtained. Subsequent polishings were carried out on a rotating buff and finally cleaned with methanol and then deionised water before immersing into the KOH solution and held at the various potentials at which the impedance measurements were made.

The apparatus used was a Solatron 1170 Transfer Function Analyser consisting essentially of a programmable generator that provides the perturbing sinusoidal signal, a correlator to analyse the response of the system and a display of the results. The TFA has the advantage of rejecting all harmonics present in the output of the system and minimises the effect of random noise. The

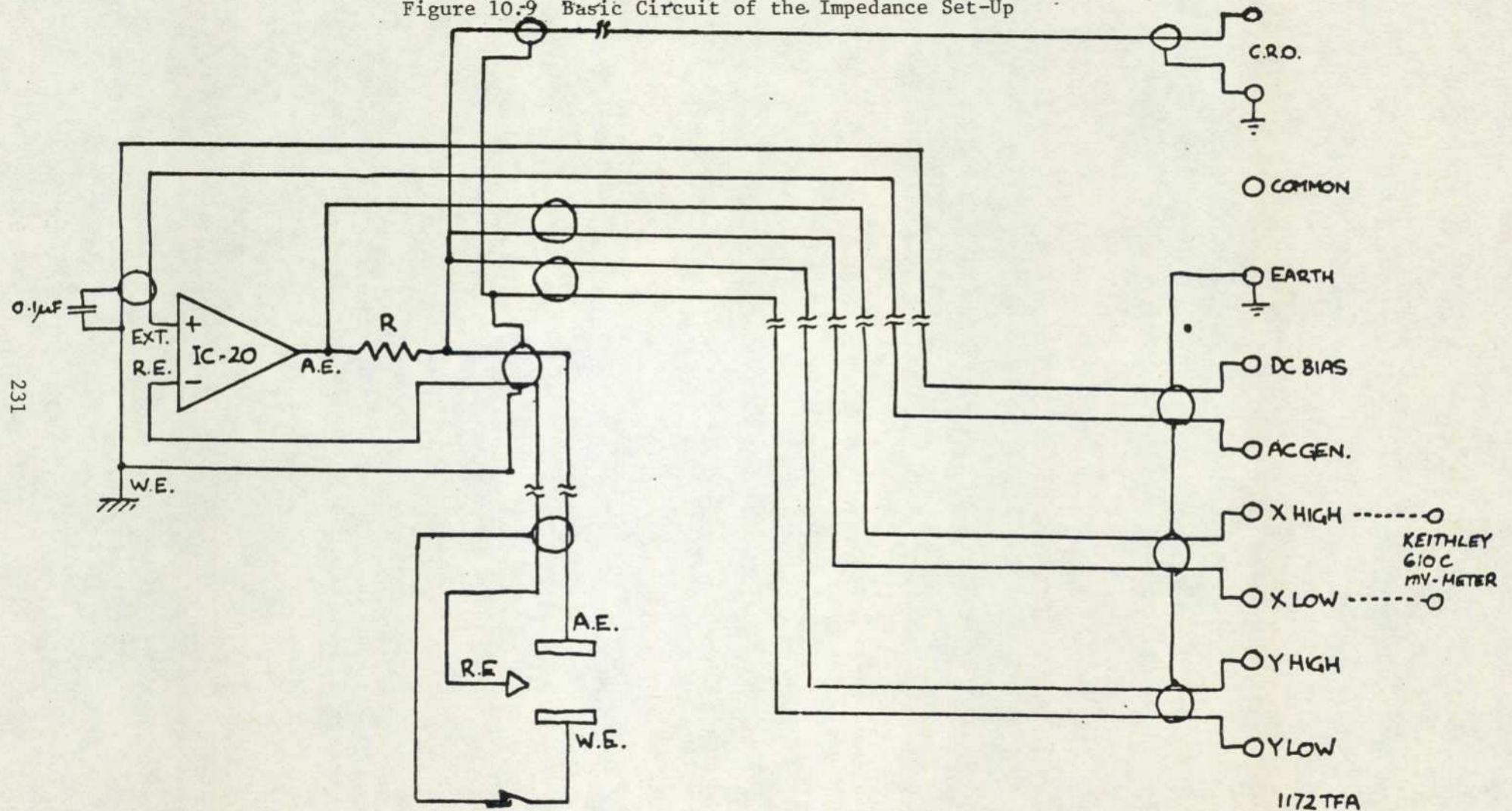
generator was programmed to sweep through a large frequency range from 9.999 kHz to 10.0 mHz.

The TFA generates small sinewave voltage perturbations of known frequencies and the input/output of the electrochemical cell is then correlated and presented in terms of phase shift and modulus of impedance. The results are first obtained as data lists of frequency, phase shift in degrees and modulus of impedance and these are then presented as complex plane plots of real and imaginary impedance in the normal manner using a P.V.D. -11/10 computer system and plotted on a X-Y recorder (Rikadenki).

The time required for the TFA to make a single measurement is equal to the period of the signal (i.e. 1 second at 1 Hz) and this becomes a major contribution to the total experimental time at low frequencies. Automated impedance measurements were carried out under potentiostatic conditions using a ministat supplied by Thompson and Associates and the basic circuit is shown in Fig. 10.9.

The cell impedance was measured as recommended by Sluyters¹⁸³. The a.c. current through the experimental cell was monitored in the usual way, as a voltage drop across a resistor in the potentiostat output (auxillary electrode) lead. The a.c. voltage across the cell was measured directly between the working and the auxillary electrode. The ratio of the cell voltage to the cell current gave the cell impedance and since the impedance of the auxillary electrode/electrolyte interface can be made negligibly small it is in effect the impedance of the working electrode/electrolyte

Figure 10-9 Basic Circuit of the Impedance Set-Up



interface that is measured. It should be noted that this arrangement eliminates the effects of phase shift occurring within the potentiostat itself. The potentiostat should however still have a sufficient bandwidth so that true potentiostatic control of the electrode interface is maintained even at high frequencies.

D.C. bias was applied to the system using the d.c. source provided by the 1170 TFA.

A Fenlow Electronics digital multimeter was used to measure the applied dc. potential and a Keithley 610^C electrometer was used to monitor the voltage drop across the counter resistor and hence the current through the cell.

The operating principle of the TFA is described in Appendix 3.

10.6 Results and Discussion

The steady-state current-voltage curve for cadmium dissolution in 5M KOH is shown in Fig. 2.1. This represents an active region at potentials cathodic to -1050 mV at which there is a sharp discontinuity to a passive region due to film formation. The open-circuit voltage occurs at ~ -1090 mV.

Automated impedance measurements were carried out in de-oxygenated 5M KOH solutions on planar electrodes in both the active and passive region from -1200 mV to -850 mV vs calomel reference electrode.

Since PVA is only sparingly soluble in KOH solution, three separate portions of a saturated solution (3 mls, 5 mls and 10 mls)

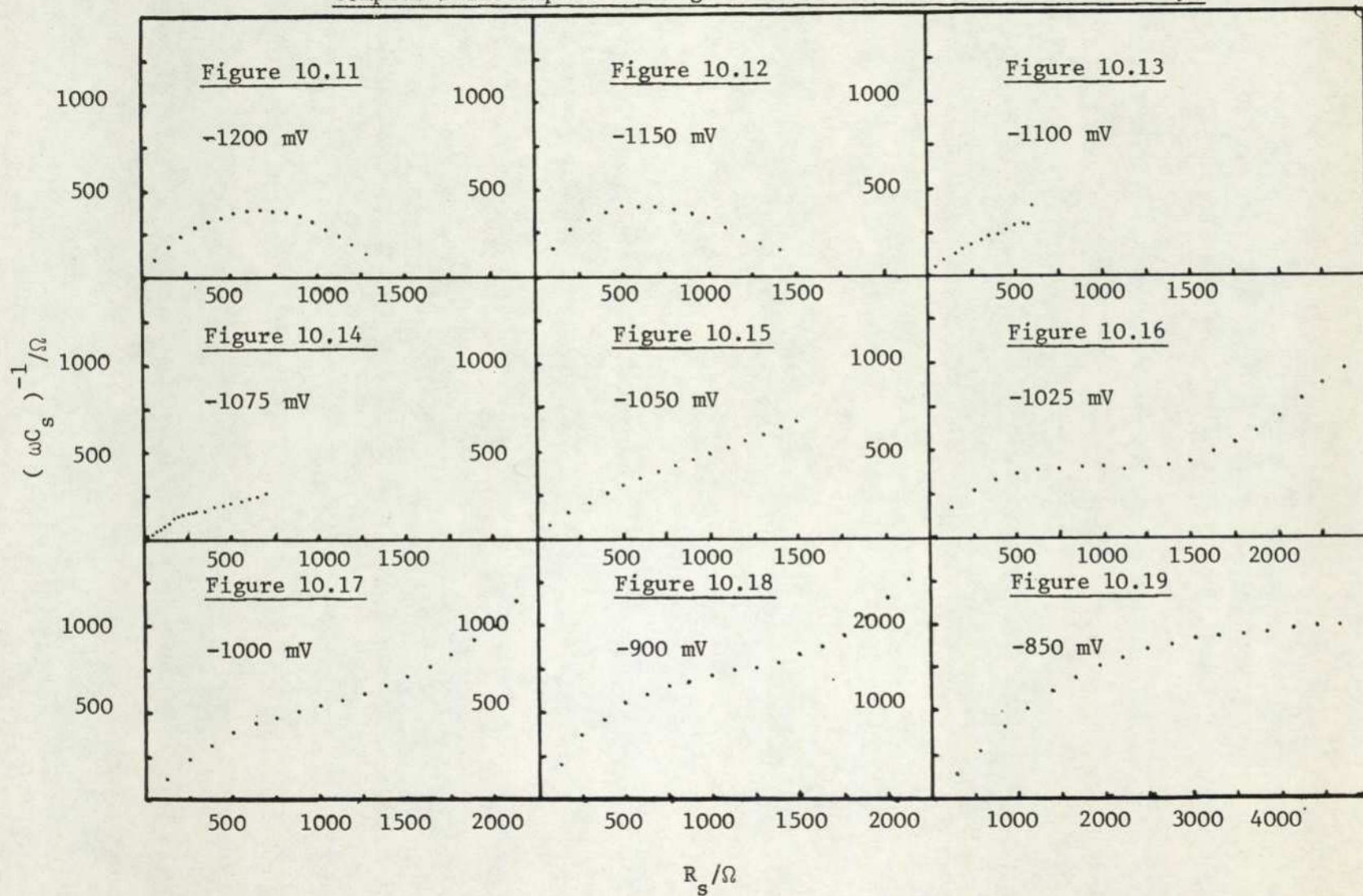
were added to 600 mls of 5M KOH to study the effect of variable concentration on the faradaic impedance of cadmium.

Figs. 10.11-10.19 show the complex plane impedance plots obtained for planar cadmium electrode in KOH solution only, in both the active and passive regions. At potentials cathodic to o.c.v., the impedance plots can be fitted to a semi-circle, whereas at potentials positive to -1050 mV, i.e. after passivation, the impedance plots correspond to a semicircle at high frequencies and at low frequencies to a straight line of unity slope.

Thus the shapes of the first and second spectrum obtained at potentials negative to the rest potential (-1090 mV) are simply large semi-circles. As at these potentials the current due to the faradaic reaction is small, these are analysed in terms of a combination of double layer capacitance and charge transfer resistance. The c.t. resistance will be large under these conditions.

As the potential is increased, these quantities become smaller and the distinct semicircle character disappears or is slightly distorted (-1100 mV). At -1075 mV the shape of the impedance spectrum changes from a semicircle to a semicircle with a Warburg character. However, a magnified complex impedance plot at this potential (Fig. 10.46) shows that another phenomenon might also be occurring. The sudden change up to the potential where passivation occurs must be due to OH^- adsorption prior to film formation. This seems to be confirmed since the possibility of a second semicircle appears to be inherent in the complex plot. The adsorption of OH^- on the

Complex Plane Impedance Diagrams for Planar Cd in 600mls KOH only.



planar cadmium has also been shown by Armstrong¹⁹¹.

At -1050 mV (Fig. 10.15), the impedance plot begins to form a definite shape again but this time it was necessary to include in the analysis an additional Warburg diffusion impedance to account for diffusion of species in the film present on the surface.

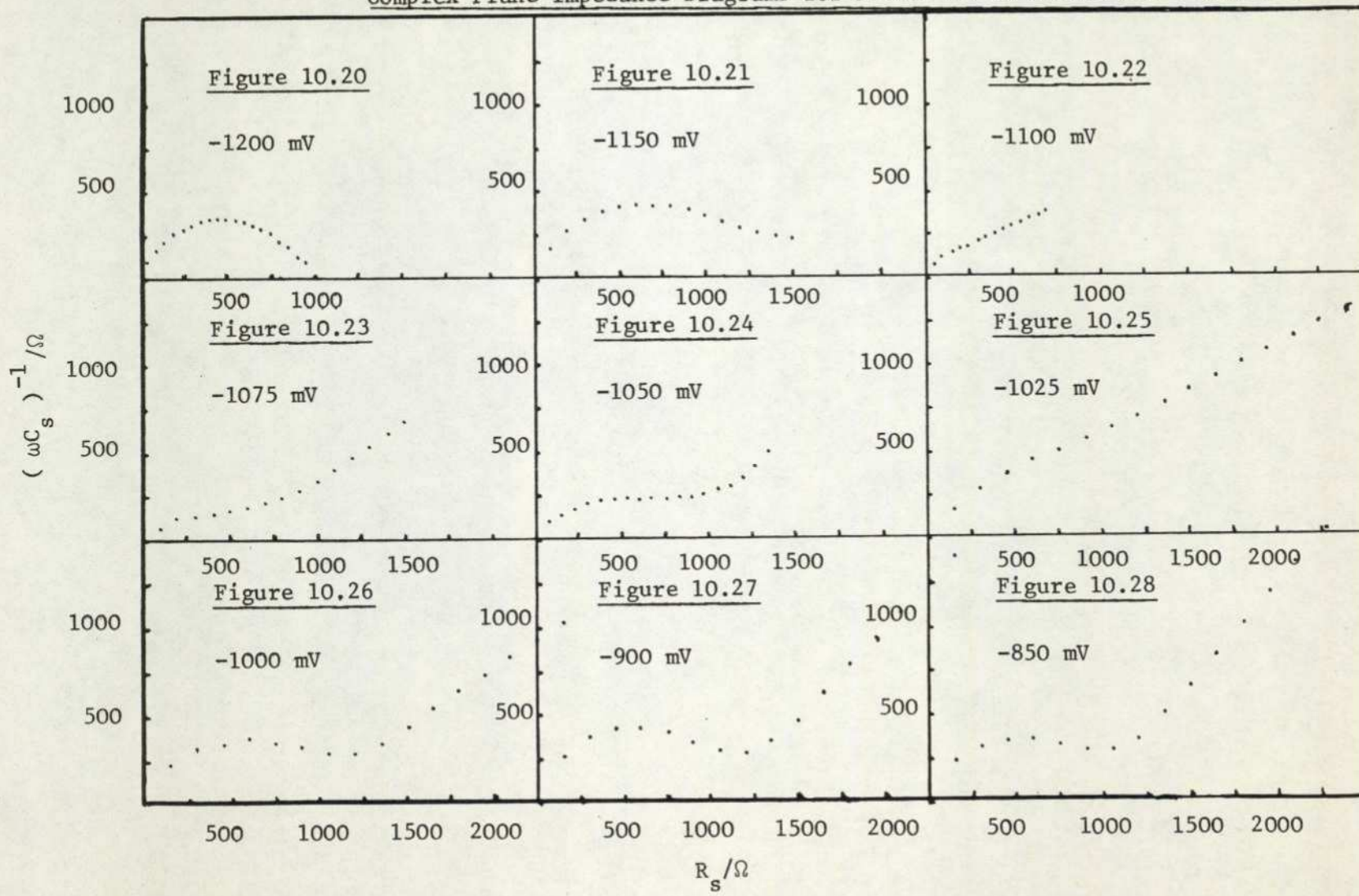
As over the whole potential range positive to the rest potential the cadmium electrode is covered with hydroxide layers due to passivation, this spectrum and subsequent ones which follow (Figs. 10.16-10.19) can be interpreted in terms of a variation in the stoichiometry of the film with potential. As the region in which the current does not vary with potential is reached, diffusion begins to take part in the reversible dissolution process and the circuit is, in the simplest case a Warburg impedance in parallel with C_{dl} .

The introduction of various concentrations of PVA to the electrolyte produces a change in the complex plane impedance plots.

However, the addition of 3 mls of a saturated solution of PVA to the electrolyte causes very little or no difference to the impedance spectra (Figs. 10.20-10.28) and semicircles with resistance R_p in parallel with the double layer capacity C_{dl} are observed in the active region. In the passive region reversible dissolution gives rise to an additional Warburg impedance. The absence of a possible second semicircle could not be explained (at ~ -1075 mV), but the semicircle that was obtained appeared to be flat at the top and the Warburg diffusion tended towards $22\frac{1}{2}^\circ$

Complex Plane Impedance Diagrams for Planar Cd in 600mls KOH + 3mls PVA

236



initially and then rising to one of unit slope (Fig. 10.47). This was probably due to a combined interaction of charge transfer and adsorption effects.

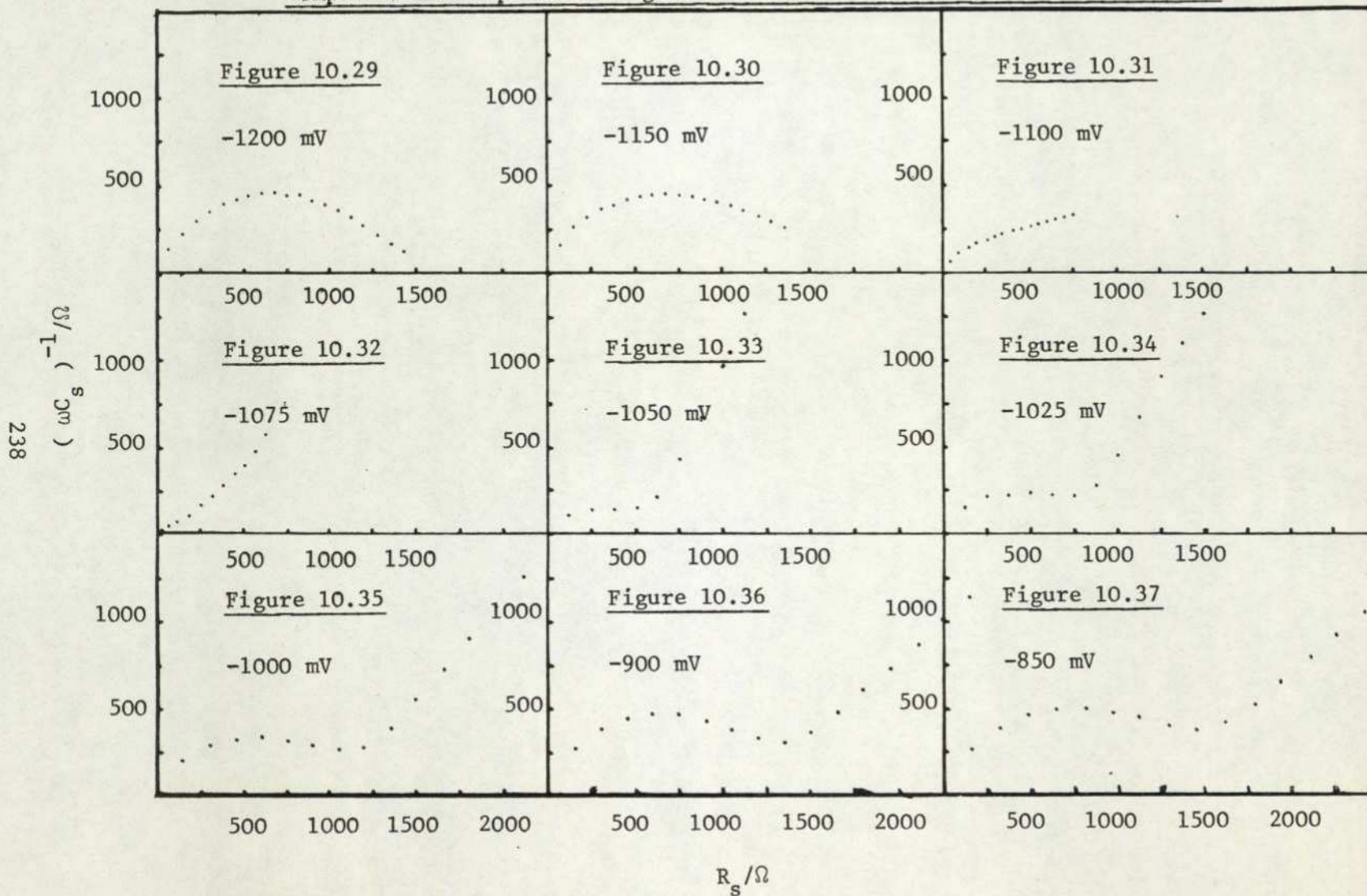
The complex plane impedance plots obtained when 5 mls of the PVA solution were added to the electrolyte showed very interesting results (Fig. 10.29-10.37).

In the active region, the impedance spectra were semicircles as in the case when there was no additive present. At about -1075 mV (Fig. 10.48), the complex plane plot again appeared to give a second semicircle. This start of the second semicircle was clearly distinguished from any Warburg behaviour in that the line was greater than 45° (Fig. 10.33). This prominent feature can only be attributed if the PVA is strongly adsorbed on the surface of the cadmium electrode. This can also be interpreted in terms of an equivalent circuit involving the series combination of two double layer capacitances and a resistance proportional to the conductivity of the electrolyte.

At potentials positive than -1025 mV, the familiar shapes of a semicircle followed by Warburg impedance begins to take place. The capacity currents in this set of experiments are much higher than in the case without PVA.

As the PVA concentration is increased to 10 mls, very similar shapes in the impedance spectra are obtained (Figs. 10.38-10.45) and match closely to those from 3 mls PVA and those without any PVA.

Complex Plane Impedance Diagrams for Planar Cd in 600mls KOH + 5mls PVA



Complex Plane Impedance Diagrams for Planar Cd in 600mls KOH + 10mls PVA.

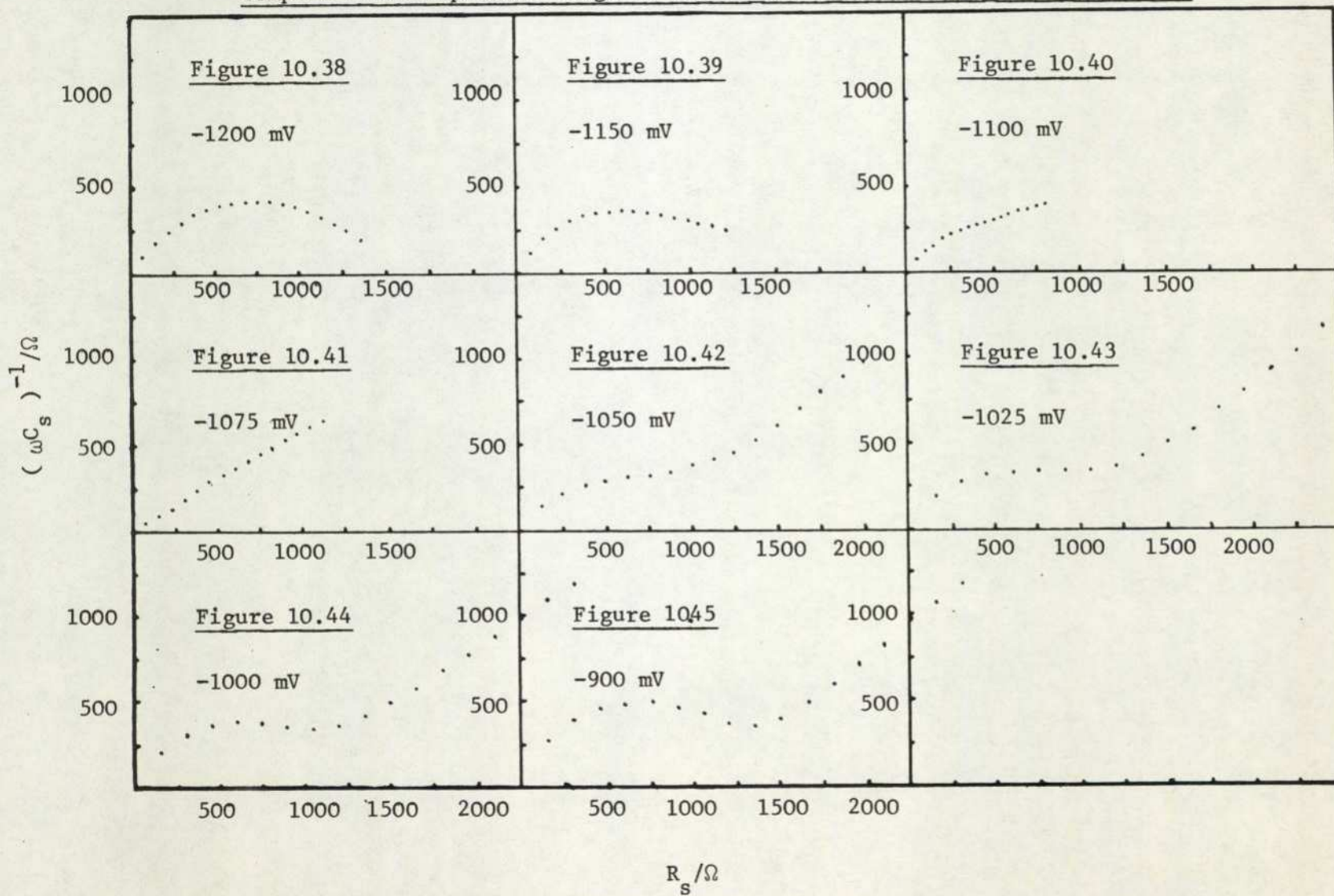


Figure 10.46 Complex Plane Impedance Diagram for Planar Cd Electrode in Deoxygenated 5M KOH, at a Potential of -1075 mV vs Calomel.

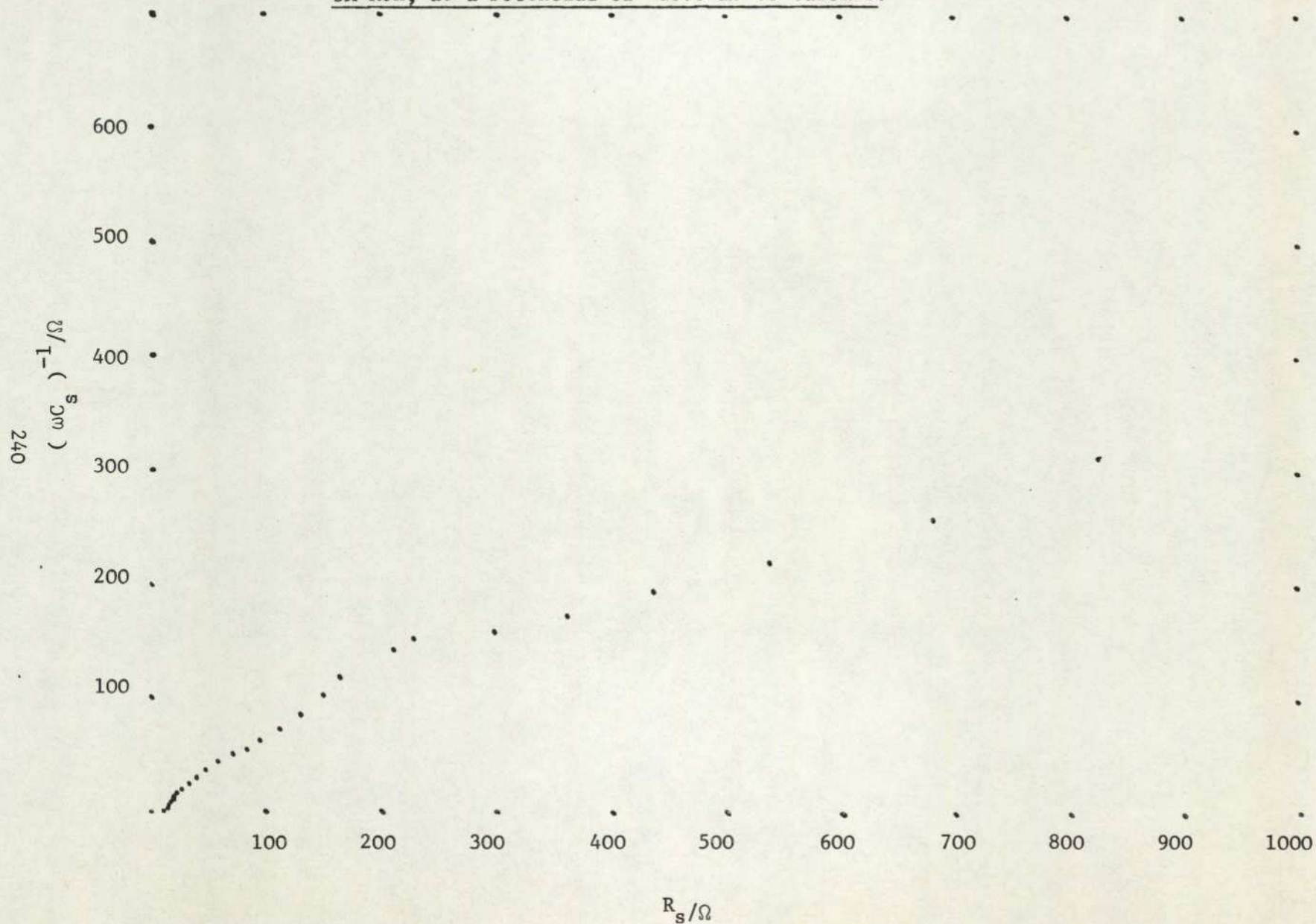


Figure 10.47 Complex Plane Impedance Diagram for Planar Cd Electrode in Deoxygenated 5M KOH + 3mls Saturated PVA, at a Potential of -1075 mV vs Calomel.

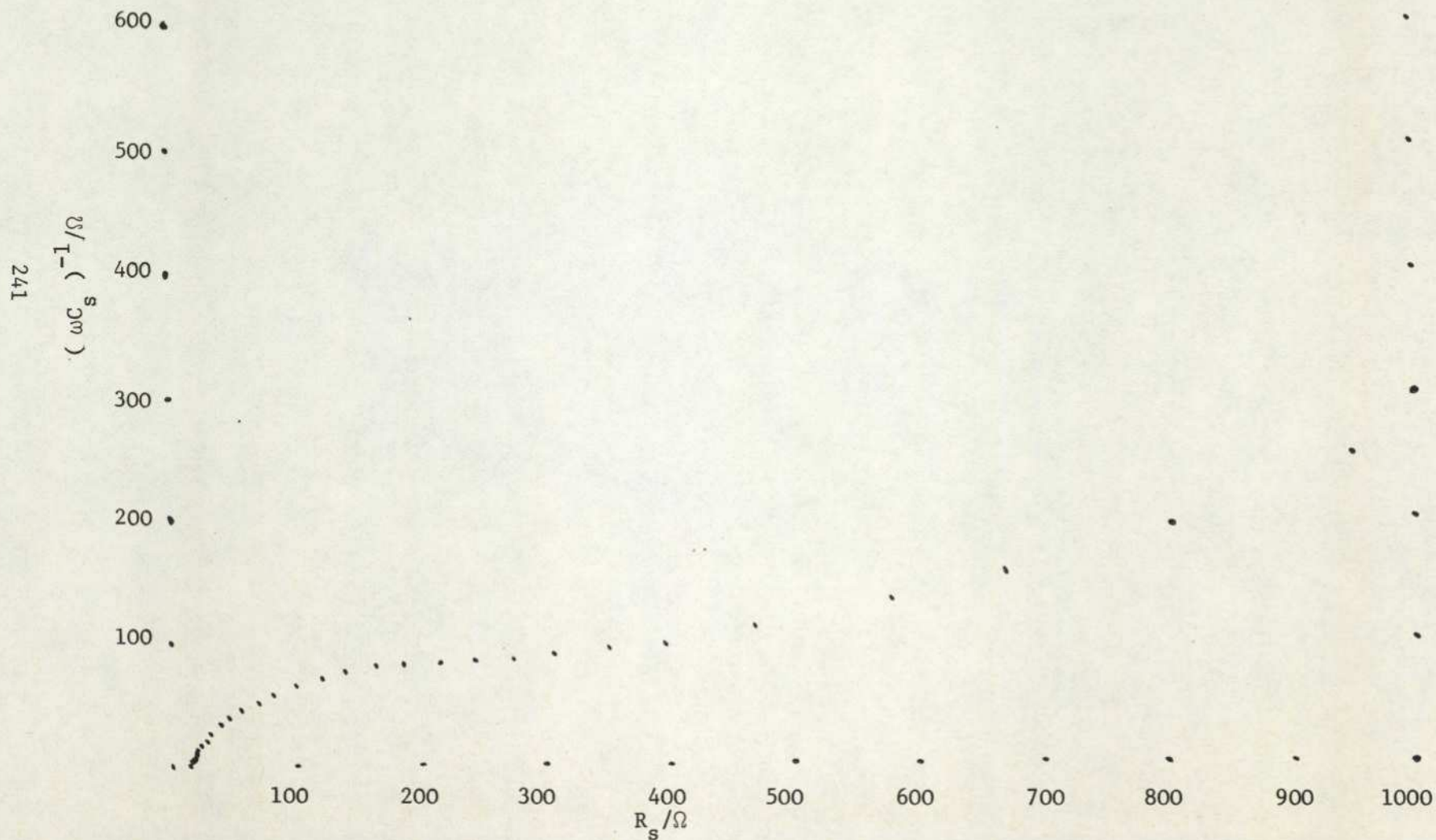


Figure 10.48 Complex Plane Impedance Diagram for Planar Cd Electrode in Deoxygenated
5M KOH + 5mls Saturated PVA, at a Potential of -1075 mV vs Calomel

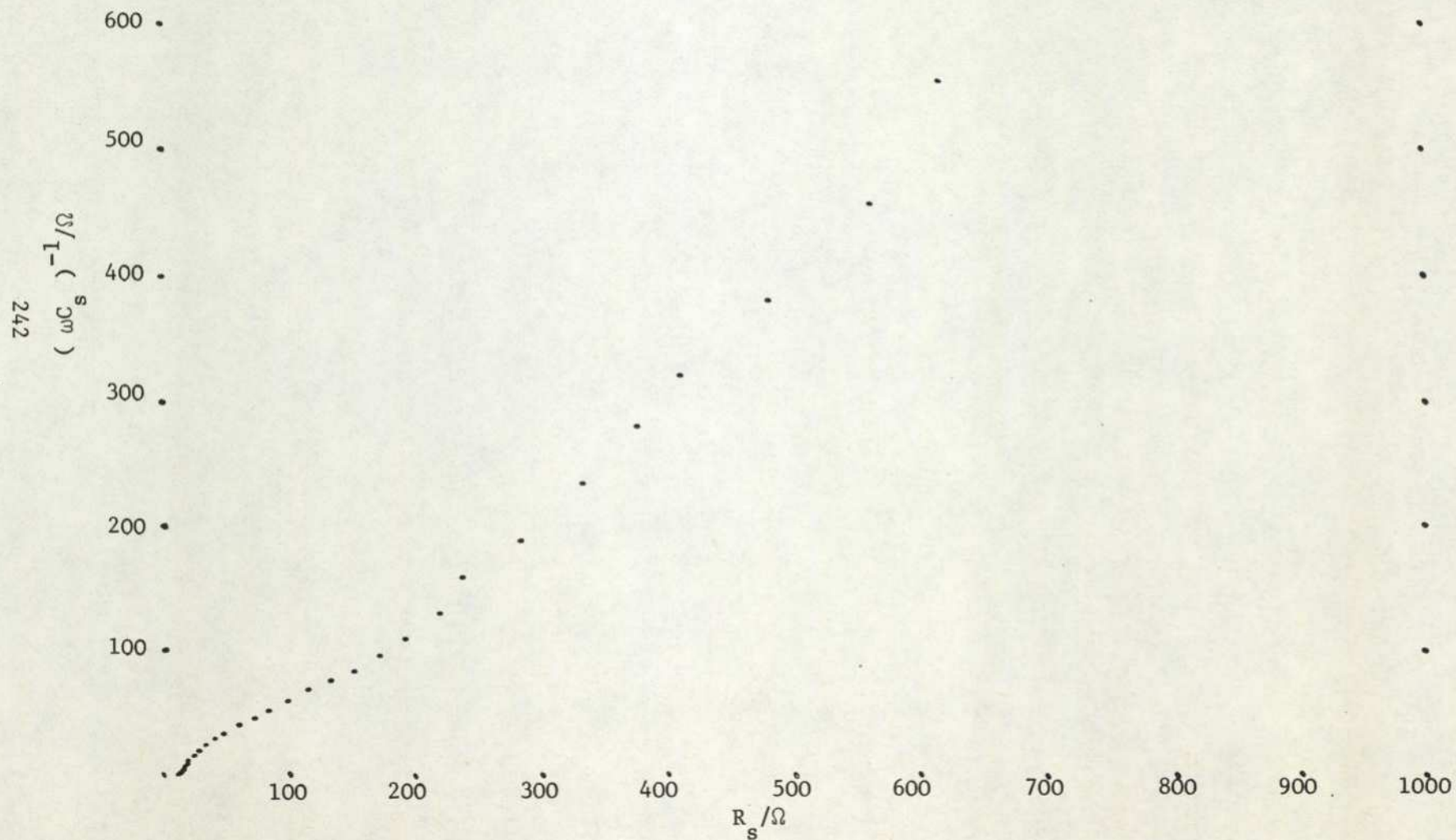
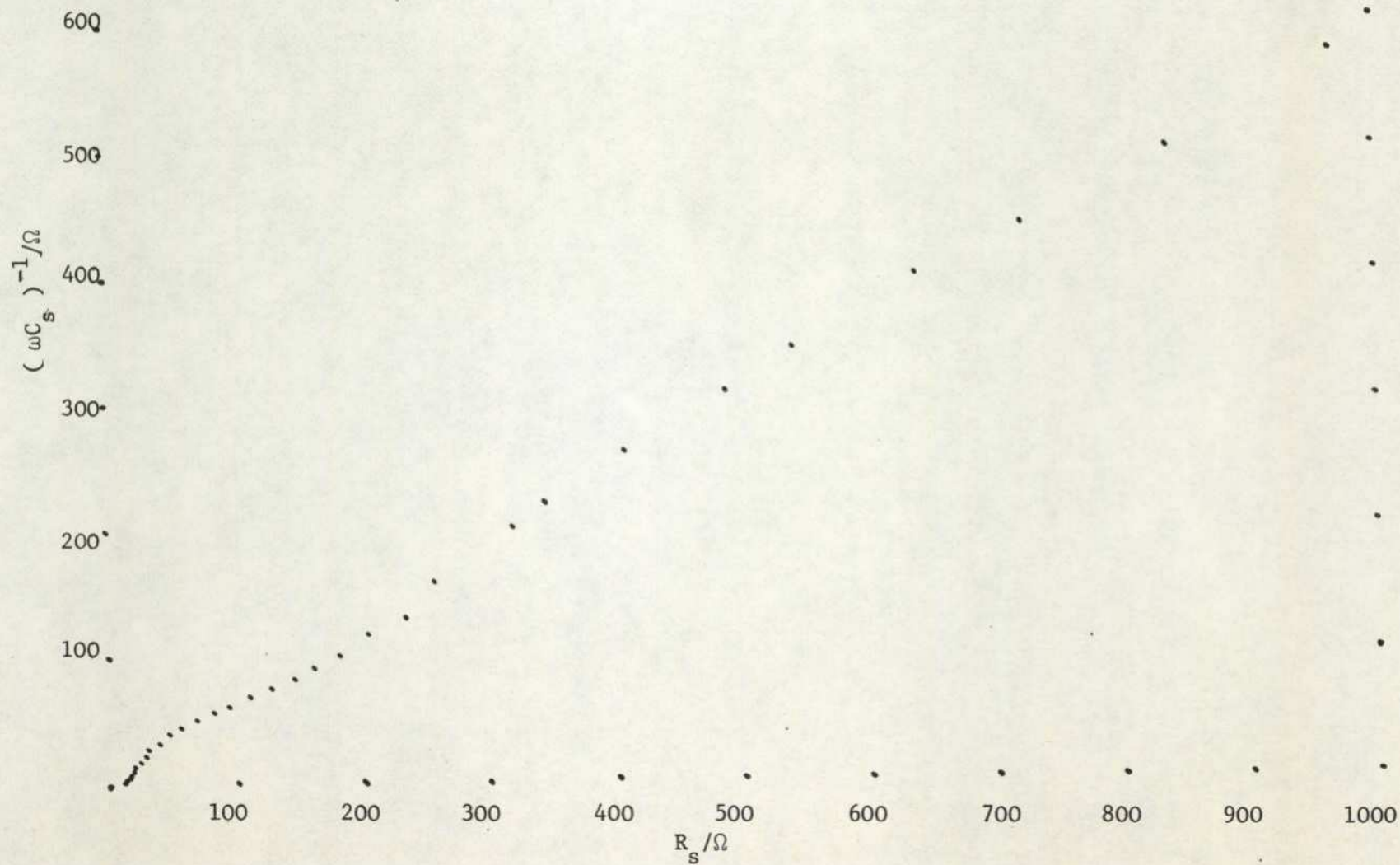


Figure 10.49 Complex Plane Impedance Diagram for Planar Cadmium Electrode in Deoxygenated 5M KOH + 10mls Saturated PVA, at a Potential of -1075 mV vs Calomel.



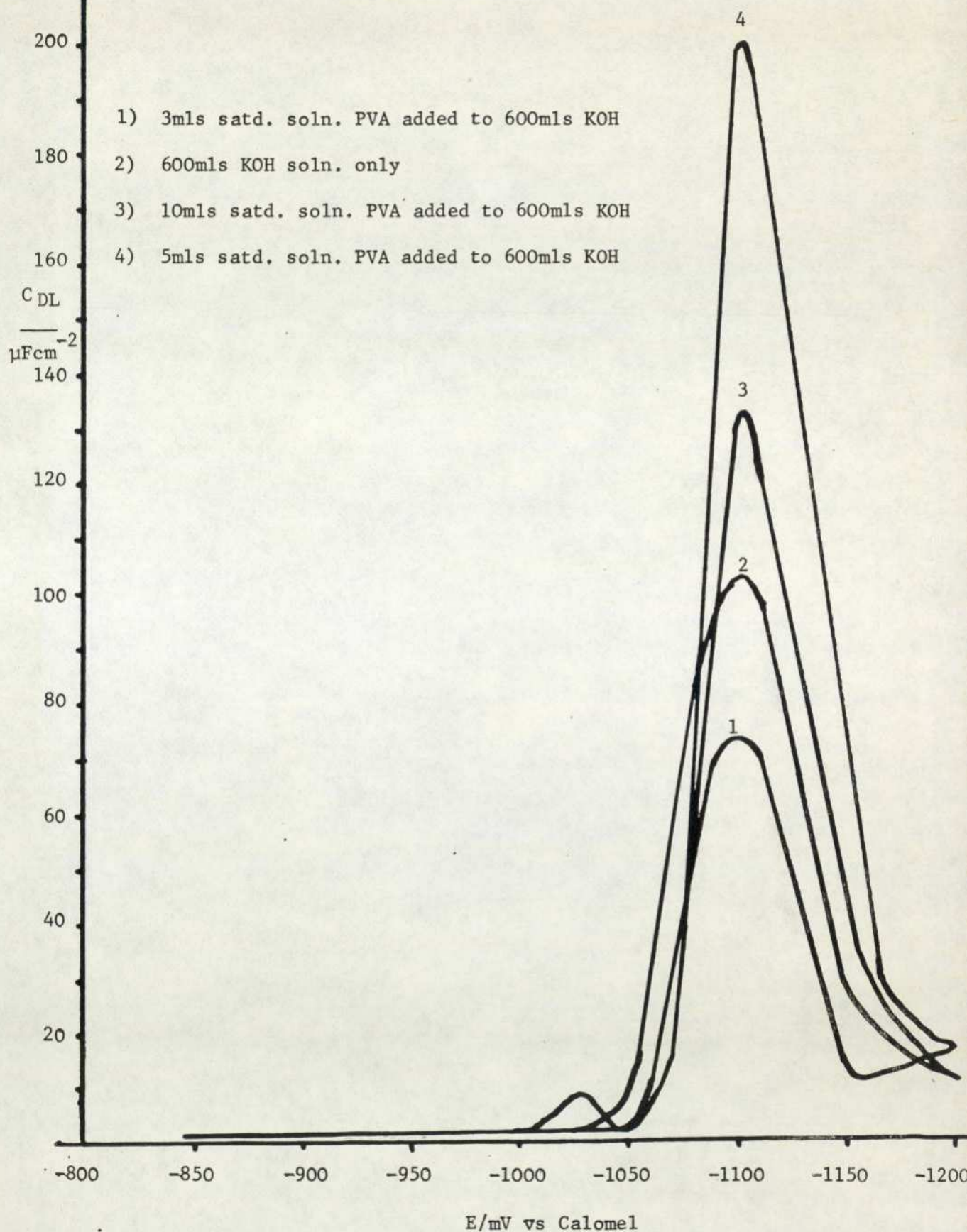
Thus, a concentration of 5 mls of a saturated solution of PVA in 600 mls of KOH electrolyte appears to give the optimum result in terms of adsorption phenomena. This is expected however since it is universally known that too much of an organic additive is detrimental to any electrochemical system and too little is insufficient for any effect to be observed.

The interface of cadmium in alkaline solution, in the presence of PVA can also be depicted as consisting of two regions. One the double layer of cadmium and the other of PVA. Both these regions may be considered as being a network of resistors and capacitors in parallel with each other. The values of these resistances and capacitances are likely to be greatly different between the two regions. Two separate and identifiable sets of impedance data are thus expected giving rise to two semicircles. In our experiment using 5 mls PVA, a second very large semicircle was apparent, due mainly to the PVA layer adsorbed on the cadmium surface.

The double layer capacities were computed from the impedance data and the potential dependence of the double layer capacity is shown in Fig. 10.50. It is seen that the increase in the double layer capacity with variable concentrations of PVA agree well with the results of the complex plane plots obtained above. The sharp increase in C_{DL} up to the potential where passivation occurs must be due to OH^- adsorption prior to film formation and in the presence of additives the increase in C_{DL} is primarily due to PVA adsorption.

Thus, the action of PVA is confirmed to be one of adsorption

Figure 10.50 Plot of C_{DL} against E in the Active and Passive Regions.



on the surface of the cadmium electrode at the potential where passivation takes place.

Hampson and Brennan¹²⁸ stated from their results of impedance on lead electrodes that the mechanism of tanning agents as potential expander materials appears to be the suppression of the solid-state reaction route to lead sulphate. Since their impedance spectrum in the electrolyte without any additive was not measured down to very low frequencies and the one with additive was, it is difficult to say if there would have been any difference except in the magnitude perhaps of the two complex plane plots.

It is equally difficult to say from our result whether or not the solid-state reaction route of cadmium to cadmium hydroxide is suppressed.

However, a much more reasonable mechanism appears to be the adsorption of PVA on the cadmium electrode to increase the negative charge surrounding the cadmium ions and facilitates their transfer to interstitial sites thus leading to a higher concentration of cadmium ions in the interstitial sites where under the effect of the concentration-potential gradient they move via defect or vacancies to the film/solution interface to form cadmium hydroxide. At the same time the ionic conductivity of the film increases together with the capacity current (Chapter 9).

It has also been shown in Chapter 7 that PVA produces smaller grain-like crystals in the battery plate than in its absence and hence the double layer capacity would be expected to be higher as confirmed by the impedance data.

CHAPTER 11

AN INVESTIGATION OF EXPANDER ACTION AT THE PLANAR Cd/Cd(OH)_2 ELECTRODE INTERFACE USING THE PULSE TECHNIQUE

CHAPTER 11

AN INVESTIGATION OF EXPANDER ACTION AT THE PLANAR

Cd/Cd(OH)₂ ELECTRODE INTERFACE USING

THE PULSE TECHNIQUE.

11.1 INTRODUCTION.

Although impedance measurements gave indication that the PVA organic is generally adsorbed on the cadmium electrode, it gives little information as regards to its full mechanism as an expander. To obtain this, it is necessary to carry out kinetic measurements using the pulse techniques. Galvanostatic and potentiostatic transient techniques have already been carried out by many researchers on the cadmium electrode but not in the presence of organics.

In this chapter, the mechanism of the solid Cd(OH)₂ formation at the planar electrode in the presence and absence of PVA is investigated using the potential step technique. The variation, if any, of the Tafel slopes obtained is particularly considered because it would enable us to distinguish whether or not PVA alters the mechanism of the cadmium/cadmium hydroxide oxidation mechanism.

11.2 Theoretical Principles.

11.2a Forms of Polarisation.

This section will deal briefly with the reaction which occur at the interface between a solid electrode and an aqueous electrolyte.

The ideal open-circuit potential of a cell or an electrode, E^0 , can be estimated for a given set of conditions using reversible thermodynamics. Useful work is obtained from the cell only when a reasonably large current is drawn, but the cell potential will then generally fall due to its irreversible effect in the cell reaction. The difference between the measured potential and that of ideal open-circuit potential, E^0 , is called polarisation. The observed total polarisation ζ_t is made up of individual polarisation terms such as activation, concentration, ohmic, and nucleation polarisation where,

$$\zeta_t = \zeta_a + \zeta_c + \zeta_o + \zeta_n$$

Activation polarisation, ζ_a , predominates when processes which determine the reaction activation energy such as adsorption, electron transfer, surface reaction etc. are rate determining. Ohmic polarisation, ζ_o , is due to resistance to ion flow through the electrolyte and electron flow through the electrode material respectively.

Since electrolyte and electrode materials generally behave according to Ohm's law, ohmic polarisation effects can easily be calculated for simple geometrics.

Concentration polarisation, ζ_c , is due to mass transfer limitations arising at the electrode under current flow. At high current densities, depletion of reactants (or build up of products) at the electrode interface may occur when their removal or supply by the electrode process exceeds their physical mass transfer rate at the reaction sites.

Hinderance of processes involving the formation of new phases on an electrode surface give rise to nucleation polarisation (ζ_n) effects.

11.2b Electrochemical Kinetics.

It is usually difficult to resolve total polarisation into its various constituent factors, because of the interrelation of the effects of activation, mass transfer, ohmic and nucleation processes. However, it is well known¹⁹⁴ that for a simple first order charge transfer process of the type:



the electrochemical rate equation written such that the net current i is in the forward (left to right) direction is:

$$i = i_0 \{ \exp(\alpha n F \zeta / RT) - \exp(-(1-\alpha) n F \zeta / RT) \} \quad 11.2$$

i is the measured current per unit geometric area of the electrode, ζ is the activation polarisation, α is the fraction of ζ which aids the reaction from left to right and generally has a value close to 0.5. Bockris¹⁹⁵ has related α to the geometry of the intersection of potential energy curves; $(1-\alpha)$ is the fraction of ζ that assists the reaction from right to left; n is the number of electrons transferred in the rate controlling step, F is the Faraday constant, T is the absolute temperature, R is the gas constant.

i_0 is called the exchange current per geometric area of the electrode and represents the equilibrium forward and reverse currents flowing at open circuit. Overall, no external current

flows at equilibrium. However, at the electrode-electrolyte interface, there occurs a constant exchange of charge carriers (ions and electrons) across phase boundaries. The magnitude of these mutually compensating anodic and cathodic current densities at equilibrium is the exchange current density. The values of i_0 are usually different for each electrode material and strongly influence the rate of reaction at a given voltage.

Equation (11.2) can be simplified for situations in which the polarisation is small ($\zeta \leq 20\text{mV}$, room temperature) or large ($\zeta \geq 50\text{mV}$, room temperature). When it is small, the exponential may be expanded and the current is given by the linear expression,

$$i = i_0 \frac{nF\zeta}{RT} \quad 11.3$$

At high polarisation, when the reverse reaction (second exponential) can be neglected, equation (11.2) reduces to the well known Tafel equation,

$$i = i_0 \exp(\alpha nF\zeta/RT) \quad 11.4$$

$$\text{or } \log i = \log i_0 + \frac{\alpha nF\zeta}{RT} \quad 11.4a$$

A plot of ζ versus $\log i$ will give a straight line of slope b which is called the Tafel slope and yields important kinetic information; b is a function of temperature and is given by the expression

$$b = 2.3RT/\alpha nF \quad 11.5$$

The derivation of the simple rate equations assumes that the activities of the reactants and products remain constant as current is drawn. At high current densities, the reactants cannot reach the surface rapidly enough to maintain a constant concentration,

Therefore the basic rate equation must be modified¹⁹⁶ to correct for changes in reactant and product concentration, then

$$i = i_o \left\{ (R'/R'_b) \exp(\alpha n F \zeta / RT) - (P'/P'_b) \exp(-(1-\alpha) n F \zeta / RT) \right\} \quad 11.6$$

where R' and P' represents the activities of the reactant and product at the electrode/electrolyte interface; R'_b and P'_b represent the activities in the bulk of the electrolyte. Precise treatments, however, of the effect of mass transfer are often difficult, but a number of approximations can be made. Diffusional mass transport can be described approximately by Fick's first law of diffusion (steady-state flux).

$$J_o = -D_o \left(\delta C_o / \delta x \right) \quad 11.7$$

Fick's second law describing the non-steady change of local concentration in terms of the differential diffusion coefficient gives

$$\delta C_o / \delta t = D_o (\delta^2 C_o / \delta x^2) \quad 11.8$$

where x is the positive perpendicular distance from a planar electrode interface; the electrode being immersed in electrolyte solution containing P , which is reduced according to equation (11.1).

Equation (11.8) is readily solved for straight initial and boundary conditions to give the time dependant flux or current density to the electrode surface. The simplest case is when k_c from equation (11.1) is so fast that all of the impedance occurs in the concentration polarisation resulting from diffusive mass transport, and the reverse process may be neglected. This

situation arises for a reversible reaction when the potential is stepped to a region that is far removed from the equilibrium value. The boundary conditions are:--

$$t = 0, \quad x \geq 0: \quad C_O^s = C_O^b \quad 11.9$$

$$t \geq 0, \quad x \rightarrow \infty: \quad C_O^s \rightarrow C_O^b \quad 11.10$$

$$t \geq 0, \quad x = 0 \quad C_O^s = 0, \quad i = nFD_O(\delta C_O/\delta x) \quad 11.11$$

The appropriate solution of equation (11.8) is

$$C(x,t) = C_O^b \operatorname{erfc}(x/2D^{1/2}t^{1/2}) \quad 11.12$$

Differentiation of equation (11.12) at $x = 0$ then leads to the Cottrell equation:

$$i = nFD_O(\delta C_O/\delta x)_{0,t} = nFC_O^b(D/\pi t)^{1/2} \quad 11.13$$

Hence equation (11.13) is useful for the determination of diffusion coefficients and concentrations. Greater interest attaches to the determination of chemical rate constants which describe aspects of the faradaic process and the mechanisms involved in it. Not surprisingly, therefore, considerable effort has been given to the description of voltametric transients controlled, at least in part, by the rate of the charge-transfer process. Except in the case of slow chemical kinetics, the current will be eventually controlled solely by mass transfer, but in the early stages at least it is often possible to deconvolute the contribution to the overpotential associated with the charge transfer step. The involvement of this additional consideration invariably leads to expressions of a much higher degree of complexity and, in consequence, to the imposition

of approximations or its restriction to limiting cases.

The starting point of all derivations is the equation of continuity.

$$nFD(\delta C/\delta x)_{x=0} = nFC^b_k \exp(-\alpha nF\zeta/RT) \quad 11.14$$

The development of concentration profiles and the evaluation of the mass transfer flux follow as before from particular solutions of Fick's second law. Again, only the potentiostatic case will be considered here. Several exact analytical formulations of the potentiostatic current transients have been published. The best known is that relating linear diffusion to a planar electrode and takes the form²⁰⁹,

$$i = i(t=0) \exp(\lambda^2 t) \operatorname{erfc}(\lambda t^{1/2}) \quad 11.15$$

$$\text{where } \lambda = k_a/D_p^{1/2} + k_b/D_R^{1/2} \quad 11.16$$

and $i(t=0)$ is given by

$$i(t=0) = nF(k_c C_p^b - k_a C_R^b) \quad 11.17$$

At short times, equation (11.15) approximates to

$$i = nFk_c C_p^b (1 - 2(k_c + k_a)(t/D_p)^{1/2}) \quad 11.18$$

A plot of i versus $t^{1/2}$ is a straight line and a plot of ζ versus $\log(di/dt^{1/2})$ has a slope of $2.3RT/2\alpha nF$. At $t=0$, the extrapolated $i(t=0)$ is dependant on k_c indicating that diffusion has no control over the initial current and a plot of ζ versus $\log i(t=0)$ has a slope of $2.3RT/\alpha nF$ i.e., b .

At $t > 0$ mixed control applies, but as long times equation

(11.15) simplifies to

$$i = nFC_p^b (D_p/\pi t)^{\frac{1}{2}} \quad 11.19$$

which corresponds to equation (11.13) and indicates that diffusion is the rate-limiting process. A plot of ζ versus $\log(di/dt^{-\frac{1}{2}})$ gives a slope of $2.3RT/nF$.

11.3 Previous Work on the Kinetics of Passivation of Cd.

In an early investigation of the growth of the passivating layer on cadmium under potentiostatic conditions¹², it was found that, except for short times, the growth of the layer followed a simple parabolic law. Croft concluded that growth of the hydroxide layer was due to transport of charge and mass through the film¹³. He explained the steps observed in his calculated $i^{1/2}$ vs t curves on the basis of local cracking of the passivating layer, exposing fresh cadmium metal to the electrolyte solution.

Devanathan and Lakshmanan¹¹ in a galvanostatic study of the kinetics of passivation of both cadmium metal and amalgams, suggested that their results were consistent with the formation of the passivating layer via a dissolution-precipitation mechanism in which the first step was the formation of a conducting monolayer of CdO. Behr and Taraszewska¹⁸⁵ have pointed out an error in the derivations used by these authors, which must make the validity of their conclusions open to question. It should also be noted that Armstrong¹⁹⁷ has demonstrated that the galvanostatic method cannot unambiguously distinguish between the dissolution-precipitation or solid-state mechanisms of passivation.

Kang⁷¹ in a study of the passivation of cadmium under galvanostatic conditions over a range of temperatures from +25 to -60°C showed that the passivation time was strongly dependant on temperature and current density, in agreement with the earlier work of Lake and Casey⁷ and Farr and Hampson¹⁸⁷. The data he obtained fitted reasonably well the work of Reddy et al¹⁸⁶ and erroneous equations of Devanathan and Lakshmanan based on a dissolution-precipitation mechanism involving a competing reaction. This mechanism was characterised by a linear dependence of $i\tau^{\frac{1}{2}}$ on i at low current densities, where τ is the passivation time at a constant current density. The observed values of $i\tau^{\frac{1}{2}}$ agreed reasonably well with the calculated ones, but the conclusions were invalid^{185,187}.

In a potentiostatic investigations of cadmium amalgams, Armstrong et al.²⁸ obtained current-time transients which showed that passivation occurred by successive deposition of unimolecular layers, a mechanism which was inconsistent with dissolution-precipitation^{11,185,197,71,7,187,186}. These authors supported the earlier work of Fleischmann et al.⁵⁷, who proposed a two-dimensional nucleation mechanism, although no detailed analysis of the pathways of the reaction was possible.

The most recent work on the mechanism of cadmium passivation has been carried out by Azim and El-Sobki⁴⁹ using potentiostatic and galvanostatic measurements. Their conclusions were based on insufficient experimental evidence.

Okinaka²⁹ considered that the presence of dissolved Cd¹¹ species (identified by the ring-disc technique) at the electrode

surface, super-saturated with respect to $\text{Cd}(\text{OH})_2$, can only be understood in terms of the dissolution-precipitation mechanism in which the cadmium metal first dissolves anodically and the dissolved species subsequently forms a precipitate of $\text{Cd}(\text{OH})_2$ on the metal surface. However, he failed to consider any possibility other than a dissolution-precipitation mechanism.

Armstrong and West⁴⁷ considered that since there is only one discontinuity in the i - E curve (see figure 21) slightly positive to the reversible $\text{Cd}-\beta\text{-Cd}(\text{OH})_2$ potential, where it is thermodynamically impossible for CdO to be present on the electrode surface, it must be the formation of a layer of $\beta\text{-Cd}(\text{OH})_2$ which is responsible for the inhibition of metal dissolution. Using a linear sweep on the ring-disc system, into the region of film formation they found, in agreement with Okinaka²⁹, that a small fraction of the disc current was consumed in the formation of a solution-soluble cadmium species. Linear sweeps at different rotation speeds showed that a change in the rotation speed did not change the i - E characteristics within experimental error, indicating that the solid-state mechanism is operative, in disagreement with Okinaka. They considered that Okinaka's reason for the dissolution-precipitation mechanism could be equally well explained by a nucleation overvoltage due to a solid-state mechanism together with parallel metal dissolution.

Transient measurements showed that film thickening follows approximately a parabolic law at short times, whereas at longer times a steady state condition is reached, with dissolution of the film at the outer surface balanced by its rate of formation,

The kinetics of passivation of cadmium in the presence of organic additives appears to have eluded many electrochemists. Although it has been common practice for many years to use organic additives in the manufacture of negative plates for nickel-cadmium batteries, a full and detailed explanation of the way in which these materials exert a beneficial effect has not been available. Previous work in this field has centred mainly around seeking to explain how organic materials present in the interior of the plate might modify the structure of cadmium hydroxide formed upon discharge.

The present report describes the results of potentiostatic pulse measurements carried out in order to investigate the effects of the organic expander, PVA, on a planar cadmium electrode

11.4 Experimental.

The cadmium used in this investigation was a disc electrode, area 0.283 cm^2 cut from a rod supplied by BDH (99.9% pure). It was set in an araldite holder. Measurements were made in a conventional enclosed 3-electrode cell using a Hg/HgO reference electrode and a large Ni-foil counter electrode as shown schematically in figure 9.1. The solution used throughout was 5M KOH prepared from Aristar potassium hydroxide pellets and distilled-dionised water. All solutions were deoxygenated with N_2 before use and the experiment conducted at room temperature ($25 \pm 2^\circ\text{C}$).

Prior to experiment the electrode was polished mechanically with 4/0 emery paper wetted with methanol, cleaned with methanol

and water and then polished with diamond paste. Subsequent polishing was carried out on a buff (particle size 1-3 μ m) and then by rinsing with methanol and deionised water before final immersion in the working solution

The potentiostat was a Wenking type, 10V-3A used in conjunction with a waveform generator (Chemical Electronics, type 01), a transient recorder (Data Lab, DL 901) and an X-Y-t recorder (Bryans, 29000). (Fig. 11.1),

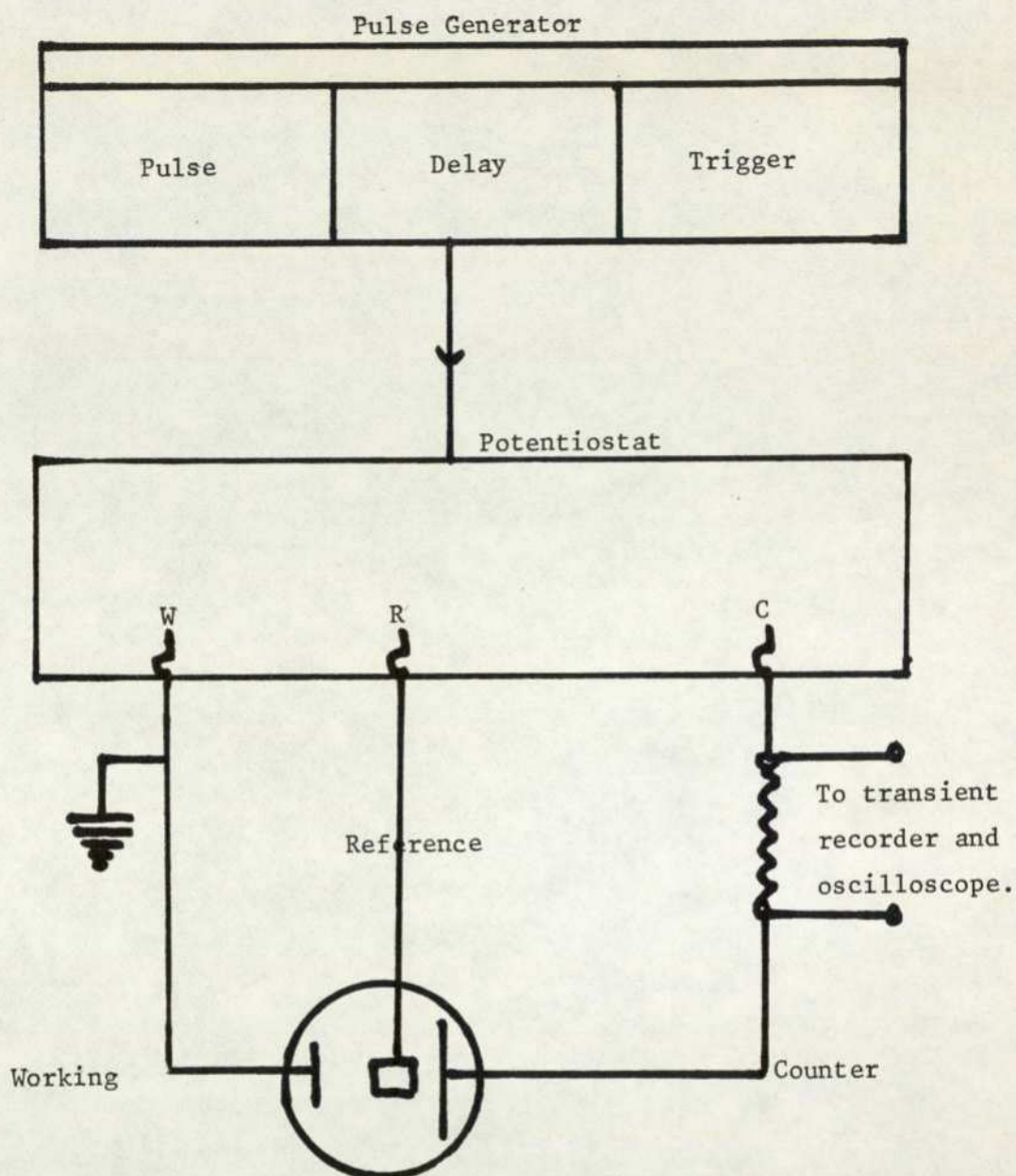
The electrode was allowed to equilibrate in the alkaline solution for about 15-30 minutes until a steady open circuit potential was reached (-0.925V vs Hg/HgO reference electrode). The cathode voltage was set at this value potentiostatically and a small voltage pulse (+15mV, 3mS, 100mS duration was applied to the electrode.

PVA is only sparingly soluble in KOH solution and once the experiment using the straight KOH solution had terminated, a 5ml portion of a saturated solution of PVA was added to 600mls of 5M KOH to study the effect of the organic expander on the cadmium electrode. This concentration was chosen because it gave the most optimum performance from cyclic voltametry measurement (Chapter 9).

11.5 Results and Discussion from Potentiostatic Pulse Technique.

This technique has been discussed in detail by Hobbs, Vassie and Tseung¹⁹⁸ and used for the study of hydrogen evolution on Teflon bonded Pt black¹⁹⁹.

Figure 11.1 Schematic Circuit Diagram for Potentiostatic Pulsing.



Since the voltage is applied on the electrode for a very short time interval (e.g., 5mS), the consumption of reactant is very little and so mass transfer effects are negligible and therefore the i - τ 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 and after an infinite time, steady state values 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 the double layer charging effects. This time depends on the capacity of the electrode double layer and consequently, on the electrode surface area.

In order to avoid mass transfer effects, it was important to determine the time interval at which current readings were taken. Ideally, the current should be measured immediately after the double layer charging of the electrode is complete. Unfortunately, in the case of cadmium, the double layer charging time could not be measured as the electrode is active at all potentials i.e., no non-faradaic region

The experimental current has to be measured after the double layer charging time and a simple calculation¹⁹⁵ allows a reasonable value to be worked out for this time.

Now in general the capacity of a planar electrode is about $20\mu\text{F}/\text{cm}^2$ for most metals (not allowing for surface roughness).

When surface roughness is taken into account the capacity C can then be calculated,

Since,

$$C = \frac{q_s}{V} \quad 11.20$$

where q_s is the charge on the electrode surface and V is the magnitude of the voltage pulse, the charge can be calculated once V is known,

Also, from

$$q_s = i \cdot t, \quad 11.21$$

i is the magnitude of the current maximum, and therefore, t, the double layer charging time, can be found,

In our case, assuming a surface roughness of 3 for cadmium, the capacity obtained is $3 \times 20 \times 0.283 \mu F$

Voltage pulses of 15mV was applied, Therefore,

$$q_s = 3 \times 20 \times 0.283 \times 0.015 \text{ Coulombs},$$

Because the maximum current obtained was approximately 0.5mA, therefore from equation 11.21 the double layer charging time was calculated to be,

$$3 \times 20 \times 0.283 \times 0.015 / 0.5 = 0.509 \text{ms}$$

So that the current should be measured after this time,

Jasem²⁰⁰ measured the double layer charging time on nickel-cobalt oxide porous electrode and found that it was approximately 0.2ms. Therefore the currents in our study were measured after 1ms.

In order to confirm the adsorption phenomenon from the impedance measurements, potentiostatic pulse measurements were made by stepping from a potential in the o.c.v. to one in the "dissolution region" and observing the transient current. The theoretical equations for a potential step experiment, where the electrode reaction is controlled by charge and mass transfer, is given by equations (11.7) to (11.19),

In the limit of very small time, the current density is proportional to $t^{\frac{1}{2}}$ as given by equation (11.18).

$$i = nFk_c C_o^b (1 - 2(k_c + k_a)(t/D\pi)^{\frac{1}{2}})$$

Thus a plot of i versus $t^{\frac{1}{2}}$ should give a straight line with an intercept of i_c ($t = 0$), the charge transfer current.

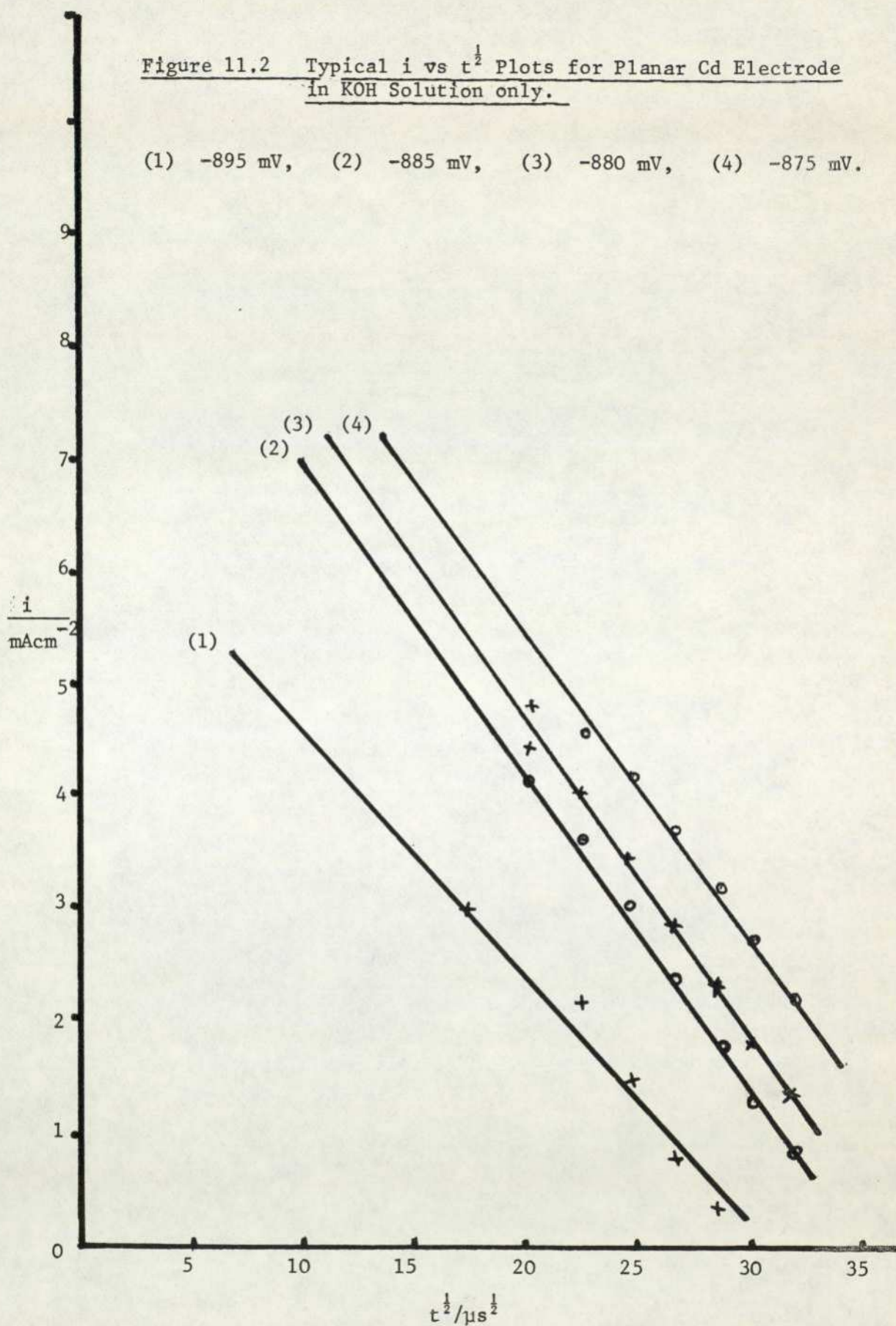
Figure 11.2 shows typical i versus $t^{\frac{1}{2}}$ plots taken from pulses into the anodic region from an o.c.v. of -0.925V in the absence of PVA and figure 11.3 (A) shows the corresponding plot of $\log i$ ($t = 0$) versus E .

Figure 11.4 is a typical i versus $t^{\frac{1}{2}}$ plot in which a saturated solution of PVA had been added to 600mls of the KOH electrolyte and figure 11.3B is the corresponding plot of $i(t = 0)$ versus E plot.

It is seen from figures 11.3A and 11.3B that Tafel slope of 120mV per decade occurs for both solutions indicating that the reaction path mechanism from cadmium to cadmium hydroxide is the same in both cases. The fact that the overvoltage on cadmium is lower in KOH solution containing PVA than in KOH solution, provides further evidence of adsorption by the PVA

Figure 11.2 Typical i vs $t^{\frac{1}{2}}$ Plots for Planar Cd Electrode
in KOH Solution only.

(1) -895 mV, (2) -885 mV, (3) -880 mV, (4) -875 mV.



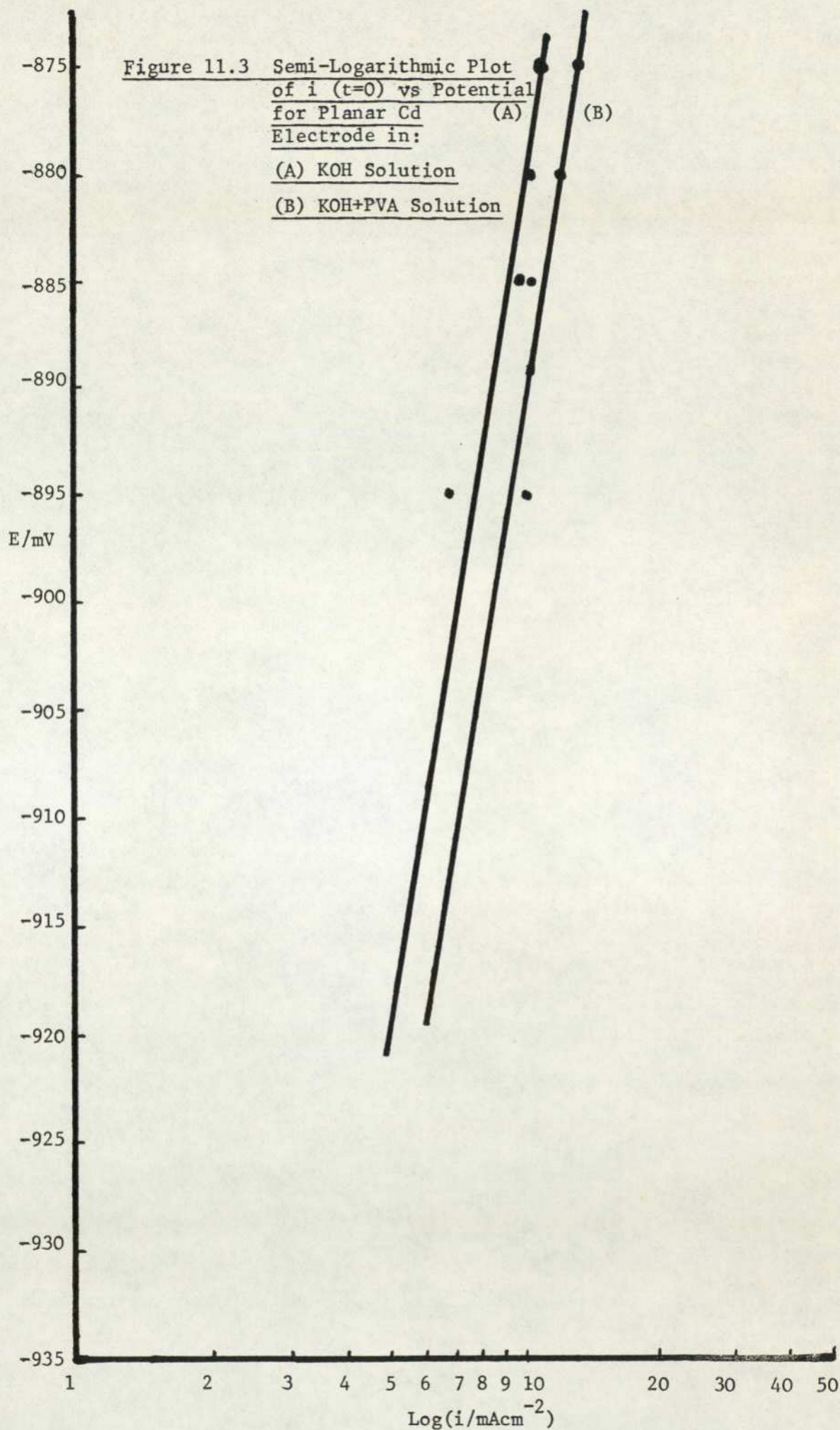
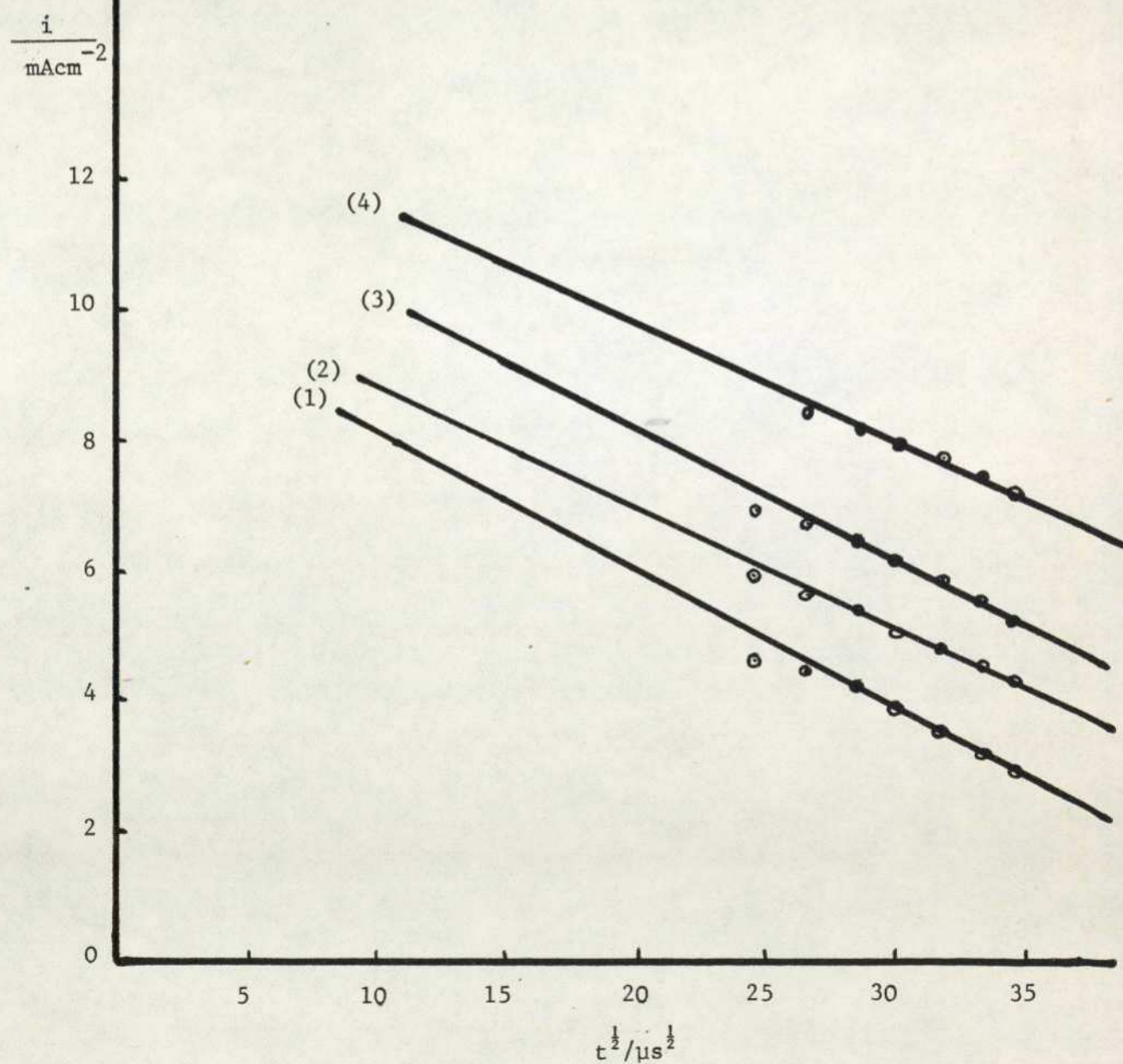


Figure 11.4 Typical i vs $t^{\frac{1}{2}}$ Plots for Planar Cd Electrode
in KOH + PVA Solution.

(1) -895 mV, (2) -885 mV, (3) -880 mV, (4) -875 mV.



on the cadmium electrode,

It has been shown¹⁹⁶ that anion specific adsorption lowers the overvoltage on a metal and cation specific adsorption increases the overvoltage and the above results confirm this theory.

Impedance measurements have shown that the differential double layer capacitance of cadmium is much greater in the presence of PVA than in its absence and this is due to the strong adsorption of PVA.

Integration of the i - t transients gave the charges under the curve and this showed that these were higher by a factor of approximately 3.5 in the presence of PVA.

Furthermore, it is evident from figure 11.3A and 11.3B that a higher apparent exchange current density is obtained when PVA was added to the electrolyte, indicating that a higher available surface area of cadmium-cadmium hydroxide is probably created.

This is due to the increased porosity of the cadmium-cadmium hydroxide matrix resulting from the adsorption of PVA on the metal lattice sites. This in turn increases the anionic concentration surrounding the cadmium ions and facilitates their transfer to interstitial sites leading to a higher ionic conductivity of the cadmium-cadmium hydroxide interface and eventually easy access of discharge of the cadmium ions to cadmium hydroxide.

Similar results were obtained when the pulsing time was increased to 100mS except the anodic film formed was considerably thicker.

11.6 Conclusion.

The above observations confirm the results of the a.c. impedance, limiting current and cyclic voltametry measurements in that the PVA increases the capacity of the cadmium electrode by helping to maintain a fine porous structure of the cadmium-cadmium hydroxide matrix. This is brought about by a complex mechanism involving the process of adsorption on the cadmium by the PVA resulting in a higher ionic conductivity of the film and also increasing the charge in the i - t curve and higher current in the i - E curve.

CHAPTER 12

ELECTROCRYSTALLISATION

Chapter 12

ELECTROCRYSTALLISATION

INTRODUCTION

12.1

The electrochemical oxidation of cadmium in potassium is a complicated process. The mechanism is of considerable interest in relation to the operation of the commercial Nickel-Cadmium battery. In spite of previous studies there are still uncertainties concerning some aspects of this mechanism.

Most mechanistic studies have been performed using either flat cadmium electrodes or amalgams. The thickness of the passivating cadmium hydroxide film which is formed on the electrode surface is of considerable interest, for this dimension determines the extent of the cadmium oxidation reaction (the capacity).

To gain a fuller understanding of the mechanism of the electrocrystallisation process, work is necessary on long term pulse experiment.

Thus the present investigation was undertaken in an attempt to obtain the variation of cadmium hydroxide film thickness with potential as well as to elucidate the undergoing nucleation reaction in the presence and absence of PVA in the oxidation of cadmium to cadmium hydroxide.

The first part of this chapter deals with the early work on electrocrystallisation followed by the theoretical expressions obtained by Thirsk and Harrison²⁰⁹.

Faraday's laws were enunciated in 1834 and because they were experimentally established²⁰¹ by means of the electro-deposition of Sn, Pb and Sb onto Pt, it is probable that the study of electrocrystallisation is one of the oldest parts of experimental electrochemistry. Correspondingly, early concepts of the nucleation were mentioned by Gibbs²⁰² in 1878 and the "discharge" process was discussed by LeBlanc²⁰³ in 1896. The first observations of the form of electrodeposits under a microscope were recorded in 1905 by Huntington²⁰⁴ and the first X-ray examinations were made by Glocker and Kaupp²⁰⁵ in 1924 .

The problem of the kinetics of electrocrystallisation reactions has had a long history. In the case of metal deposition Erdey-Gruz and Volmer²⁰⁶ in 1931 suggested that two dimensional nucleation and growth would be the rate determining step. However, no evidence could be obtained for this mechanism. It was then assumed until fairly recently, without any convincing evidence, that growth was similar to the gas phase. Here it was thought that the large number of screw dislocations would control the growth by a surface diffusion mechanism. Recently it has been found experimentally that a two-dimensional nucleation and growth mechanism applied when the number of dislocations is drastically reduced. This leads to the possibility for the first time of investigating the formation of metal or non-metal deposits in an exact way.

The overall process of electrodeposition i.e. the process commencing with the deposition of metal ions in solution to a stable lattice built-up of metal atoms is complex and involves several steps. Eventually, however, once a small new phase has been nucleated, its subsequent growth can proceed. The morphology of crystal growth may be one-dimensional, two-dimensional or three-dimensional.

The primary process in crystal growth, i.e. the incorporation of an atomic species into the crystal lattice only occurs where interaction can take place with several other species already in the lattice, such as a step formed by the edge of a crystal plane or at a kink site in the edge. In any other position on the surface, the species would simply be adsorbed. For crystal growth to take place, therefore, the generation of an edge is essential. This requires the formation of nuclei so that growth can occur at their peripheries.

The theoretical expression for electrochemical nucleation is based principally on two models, namely the thermodynamic and atomistic models.

The thermodynamic model uses the macroscopic surface energy to calculate the free energy for defining the critical nucleus. This is a major shortcoming because the exact value of this quantity is usually not known. The application of this theory is thus restricted to the system of low supersaturation, i.e. when the surface tension concept does not lack physical sense which is the case when large clusters are formed.

The atomistic model^{207,208} involves no macroscopic physical quantity. Instead, the interaction among the atoms of the clusters is considered, i.e. the computed potential energies of the clusters are used to characterize the critical nucleus. Although, these quantities have clear physical meaning their values are usually unknown. The atomistic theory is valid for the system of high supersaturation, when small critical nuclei are formed. At the present time, neither theory has been proved to be more adequate. Nevertheless, the thermodynamic theory for nucleation and growth has been studied in great detail by Thirsk and Harrison²⁰⁹. These researchers have studied the deposition of a new phase on to a surface under potentiostatic conditions. Hence the theoretical interpretation of potentiostatic transient for electrocrystallisation has been well established and will, therefore, be briefly considered.

12.2 The Thermodynamic Theory of Nucleation

The formation of a nucleus is an inherently improbable event and usually requires a high supersaturation for it to occur. The rate of nucleation is determined by the free energy necessary to form a critical size of nucleus.

Nuclei smaller than the critical size will dissolve and those of greater size will grow. For a two-dimensional cylindrical nucleus, growing on a flat electrode of the same material, the free energy of formation of the nucleus is²⁰⁹

$$\Delta G_n = -\pi r^2 \ell \rho z F \eta / M + 2\pi r \ell \sigma \quad 12.1$$

where ℓ is the height of the nucleus, σ is the surface energy

of the nucleus/solution interface, ρ is the density of the nucleus, M the molecular weight, and $zF\eta$ the bulk energy per mole involved in forming the nucleus at an overpotential η .

Differentiation gives the critical nuclear radius, r_{crit} , which must be reached for growth to take place

$$r_{crit} = \sigma M / zF\eta\rho \quad 12.2$$

This occurs at a free energy given by,

$$\Delta G_{crit} = \pi M \sigma / zF\eta\rho \quad 12.3$$

To a first approximation, nucleation can be considered to be an activation process with free energy of activation, ΔG_{crit} . Therefore, assuming a stationary distribution of nuclei, the nucleation rate, A , may be written as

$$A = k_n \exp(-\Delta G_{crit}/RT) \quad 12.4$$

where k_n is a frequency factor. Substitution of 12.3 into 12.4 gives

$$A = k_n \exp(-\pi M \sigma N / zFRT\rho\eta) \quad 12.5$$

where N is the number of nuclei contributing to the growth of the deposit. Strictly speaking, 12.5 is inexact since σ is also a function of potential. Taking into account the potential dependence of σ when differentiating equation 12.1 gives

$$r_{crit} = (M\sigma / 2zF\eta\rho) + (M/\rho zF) (d\sigma/d\eta) \quad 12.6$$

which corresponds to 12.2

The total number of nuclei contributing to the growth of a deposit will depend upon the time dependence of the nucleation process. Fleischman and Thirsk²¹⁰ have derived a complete equation for charge-transfer controlled nucleation under potential-current-time transients for processes in which the growth of a new phase i.e. lattice incorporation, is slow. They assumed that the nuclei usually form randomly on preferred sites which may be imperfections on the surface of the substrate. Assuming a uniform probability of conversion of growth centres into nuclei with time, the first order nucleation rate law is expressed by:

$$N_t = N_0 (1 - \exp(-At)) \quad 12.7$$

where N_t is the total number of nuclei growing at a time t , and N_0 is the total number of available nucleation sites.

Two limiting forms are encountered in the initial time range.

- (a) When A is large, $At \gg 1$ for much of the period of growth and thus

$$N_t \approx N_0 \quad 12.8$$

so that the number of nuclei immediately nucleated onto almost all the initial available sites, i.e. to instantaneous nucleation.

- (b) If A is small, $At \ll 1$ and thus

$$N_t = AN_0 t \quad 12.9$$

which describes progressive nucleation. This applies when A is small at preferred sites, or when there are no preferred sites for nucleation so that the total number of nuclei increases

linearly with time whatever the magnitude of A. A solid electrode will often provide preferred sites for nucleation, e.g. dislocations at which the adsorption energy is large so that the surface energy at the nucleus/electrode interface is small.

12.3 The Growth of Discrete Centres.

If the transport of material to a growing centre is not rate determining, then its rate of growth depends upon geometric factors. Discrete centres can grow on electrodes in a number of ways²¹¹⁻²¹⁵. In the simplest case, it is assumed that after imposition of the potential step, two dimensional cylindrical nuclei form at discrete centres and grow laterally across the surface. It is also assumed that the rate of growth (current) is proportional to the area on to which deposition occurs and that the growth area may be modified by overlap with adjacent nuclei. The above assumptions therefore permit the current to be written as:

$$i = zFk_E S \quad 12.10$$

where k_E is the electrochemical rate constant controlling the growth round the periphery and S is the area on which material is deposited.

Now the current is also equal to the rate of change of accumulated charge (phase) with time on the surface. Therefore application of Faraday's law yields

$$i = \frac{zFQ}{M} \frac{(dV)}{dt} \quad 12.11$$

where ρ and V are the density and volume respectively of the deposited phase of molecular weight M . The derivative dV/dt may be expanded using the chain rule with respect to the radius r .

Equating equations 12.10 and 12.11 gives:

$$k_E S = \frac{\rho}{M} \frac{(dV)}{(dr)} \frac{(dr)}{(dt)} \quad 12.12$$

Once S and $\frac{dV}{dr}$ are known by taking a particular geometry, then integration of equation 12.12 gives r as a function of t . The resulting value of S as a function of time in equation 12.10 gives the result.

For deposition round the edge

$$S = 2\pi r \ell \quad 12.13$$

and

$$V = \pi r^2 \ell \quad 12.14$$

hence,

$$\frac{dr}{dt} = Mk_E / \rho \quad 12.15$$

Integrating 12.15 with respect to time gives:

$$r = Mk_E t / \rho \quad 12.16$$

(assuming $r = 0$ at $t = 0$)

Substitution for r in equation 12.13 followed by insertion of S into 12.10 therefore gives the current for the growth of a single centre as a function of time.

$$i = zF2\pi \ell k_E^2 \frac{M}{\rho} \cdot t \quad 12.17$$

Equation 12.17 is readily combined with the nucleation laws 12.8 and 12.9 to allow for the contributions from all of the centres and to give the total growth rate. For the examples discussed, the results are:

$$i = (2zF\pi M\ell N_0 k_E^2 / \rho) \cdot t \quad 12.18$$

for two dimensional growth and instantaneous nucleation, and

$$i = (zF\pi M\ell A N_0 k_E^2 / \rho) \cdot t^2 \quad 12.19$$

for two dimensional growth and progressive nucleation. Similar equations for other geometries have also been formulated²⁰⁹

12.4 The Overlap Problem of Growth Centres.

In the later stages of crystal growth the centres overlap, and the area available for electrodeposition becomes restricted.

Equations 12.18 and 12.19 therefore hold only at shorter times before the growing centres begin to coalesce. Reaction must finally stop either when the electrode surface is "blocked" or when the parent phase has been completely converted into the new phase. The current must therefore pass through a maximum. The form of the expression describing the complete growth process can be obtained by allowing for the effects of this overlap. This can be evaluated exactly for a number of simple cases by making use of the Avrami²¹⁶ Theorem.

$$\frac{d\theta}{1-\theta} = d\theta_{\text{ext}} \quad 12.20$$

where θ is the fraction of surface covered and θ_{ext} is the

fraction that would be covered if the centres were all separated and there was no overlap. This equation holds if the possibility of finding a centre is uniform over the surface and there is no interaction of growing centres with the boundaries of the electrode surface.

For instantaneous nucleation

$$\Theta_{\text{ext}} = N_0 \pi r^2 \quad 12.21$$

and for progressive nucleation

$$\Theta_{\text{ext}} = \int_0^t r(u)^2 (dN/dt)_{t-u} du \quad 12.22$$

Substitution for r in terms of t using equation 12.16 gives

$$\Theta_{\text{ext}} = \pi N_0 M^2 k_E^2 t^2 / \rho^2 \text{ (instantaneous)} \quad 12.23$$

and

$$\Theta_{\text{ext}} = \pi N_0 A M^2 k_E^2 t^3 / 3 \rho^2 \text{ (progressive)} \quad 12.24$$

Integration of 12.20 to yield Θ in terms of Θ_{ext} and hence in terms of time, by substitution of equation 12.23 and 12.24 yields.

$$\Theta = 1 - \exp(-\pi N_0 M^2 k_E^2 t^2 / \rho^2) \text{ (instantaneous)} \quad 12.25$$

and

$$\Theta = 1 - \exp(-\pi N_0 M^2 A k_E^2 t^3 / 3 \rho^2) \text{ (progressive)} \quad 12.26$$

Finally, the volume per unit area of total surface is $V = \Theta \ell$, which upon substitution into 12.11 gives the desired expression for the transients.

For cylindrical centres growing in two dimensions with instantaneous and progressive nucleation laws respectively, the complete growth expressions are:

$$i = (2zFMNok_E^2 \ell t / \rho) \cdot \exp (-M^2 N o k_E^2 t^2 / \rho^2) \quad 12.27$$

and

$$i = (zFMNoAk_E^2 \ell t^2 / \rho) \cdot \exp (-M^2 NoAk_E^2 t^3 / 3\rho^2) \quad 12.28$$

These describe peaked transients with $i = 0$ at $t = 0$ and $t = \infty$. Comparison of equations 12.27 and 12.28 with equations 12.18 and 12.19 respectively shows that the effect of overlap is accounted for by the exponential terms in time. As t approaches zero, equation 12.27 reduces to 12.18 and 12.28 reduces to 12.19.

Figs. 12.1a and 12.1b are reduced variable plots of 12.27 and 12.28 respectively using i/i_m and t/t_m where i_m and t_m are the parameters of the maximum which are readily found by differentiation. Experimental transients can be compared with such plots to show which growth law is being followed.

For instantaneous nucleation

$$t_m = \rho / 2\pi No)^{\frac{1}{2}} M k_E \quad 12.29$$

$$i_m = (2\pi No)^{\frac{1}{2}} z F k_E \ell e^{-\frac{1}{2}} \quad 12.30$$

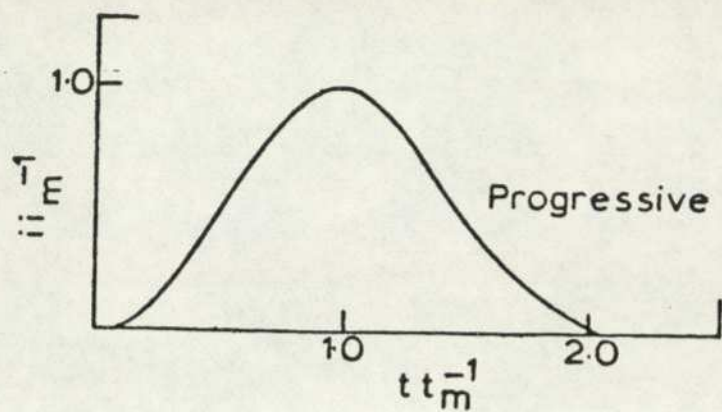
and for progressive nucleation

$$t_m = (2\rho^2 / \pi M^2 NoAk_E^2)^{\frac{1}{3}} \quad 12.31$$

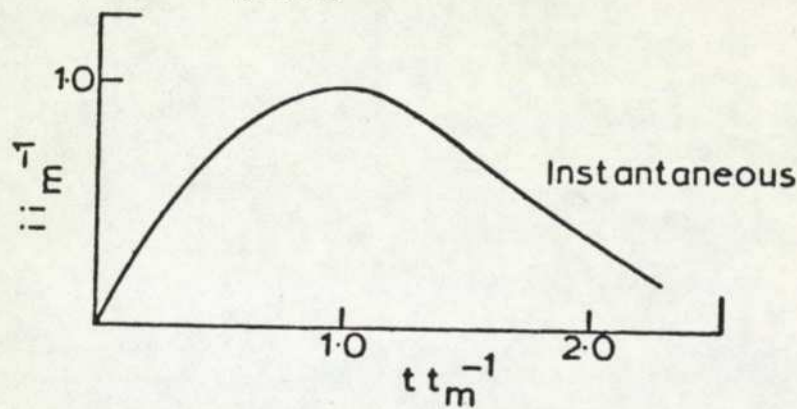
$$i_m = z F (4\pi NoAk_E^2 \rho / M)^{\frac{1}{3}} \ell e^{-\frac{2}{3}} \quad 12.32$$

In both cases, the time at which the maximum occurs decreases with

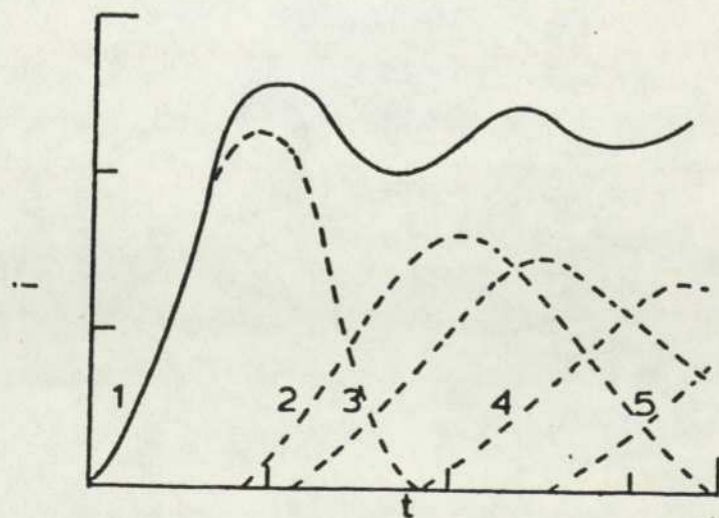
Figure 12.1a Theoretical Current - Time Curves According to (a) Equation 12.27



(b) equation (12.28)



(c) Total current transient for layer by layer growth showing contribution from individual layers



increasing growth rate constant k_E , the dependence being greatest for instantaneous nucleation. Also the size of the maximum increases with k_E and the dependence is again greater for instantaneous nucleation. Theoretical value of $i_m t_m / Q_m$ is independent of the potential dependence of k_E and is 1.0 for progressive and 0.6 for instantaneous nucleation. The constancy of $i_m t_m / Q_m$ with potential is a useful experimental test.

The above analysis can be extended to other geometrics by using appropriate expressions for S and V , including cases where diffusion in solution is assumed to be the rate determining, and are summarised by Thirsk and Harrison ²⁰⁹.

Armstrong et al. ²¹⁷ have described the instantaneous nucleation and growth of a three-dimensional deposit leading to the passivation of an electrode. In order to simplify the mathematics, the nuclei are considered to be right circular cones. However, the geometry of the deposit does not appear to be a major consideration in determining the shape of the growth transient. This was shown by Armstrong et al., who also considered the growth of hemi-spherical centres. The final equation describing the current as a function of time after the application of a potential step is given as

$$i = ZFk_2(1 - \exp(-\pi N_0 k_1^2 M^2 t^2 / \rho^2)) \quad 12.33$$

where k_1 is the rate constant describing crystal growth parallel to the plane surface of the electrode, and k_2 is the rate constant perpendicular to the surface. At long times the current attains a constant maximum, rather than approaching zero as predicted for the two-dimensional case. Only in very few instances (e.g. deposition on amalgams) is true monolayer formation apparently found. In the

great majority of cases, the formation of successive layers of deposit is observed. This gives rise to significantly different transients than those given by equations 12.27 and 12.28, especially at times greater than t_m .

Using equations 12.28, Armstrong and Harrison²¹⁸ have achieved a solution by numerical integration. The arguments used to derive equations 12.27 and 12.28 can be extended to layer by layer growth and Fig. 12.1c displays the potentiostatic current-time transient for the first five monolayers, together with the total current which is obtained by summation. The steady-state which is constant is reached after the oscillations have died away.

Armstrong and Metcalfe²¹⁹ have refined this approach and have shown that the limiting value is reached after four or five monolayers.

12.5 Background Work

For many years expanders (usually organic acids or alcohols) have been added to the negative plates of nickel-cadmium batteries. The well-known result of this process is to inhibit crystal growth of the cadmium hydroxide which would thus lead to a lowering in the surface area available for electrochemical processes to take place. However, little information is available concerning the use of organic additives to control the morphology of the cadmium electrode.

Recently, Udupa et al.¹¹¹ have found that the discharge efficiency of the sintered-plate cadmium electrode is improved when quaternary ammonium compounds such as cetyltrimethylammonium

halides are incorporated in the active material at the time of impregnation.

In earlier studies, Gossenberger¹¹² made an evaluation of the behaviour of various cellulose and starch derivatives on the capacity of the cadmium electrode. It was tentatively suggested that growth of Cd metal was inhibited by the additives. Fleischer¹¹³ subsequently patented the use of cellulose ethers and derivatives such as CMC for reducing the fall in capacity of the cadmium electrode on cycling.

Unfortunately, however, there appears to be no clear consensus as to the mode of action of expander materials. As a result, this work has been undertaken to investigate the influence of one type of expander, PVA, used in industry, upon the formation of thick films of cadmium hydroxide on a planar cadmium electrode.

An earlier investigation⁵⁷ of anodic film formation on cadmium amalgam in alkaline solutions showed that the film was one degree oriented β -Cd(OH)₂ with the basal plane parallel to the electrode surface. Examination of potentiostatic *i-t* transients led to the conclusion that the Cd(OH)₂ was formed by the successive deposition of monomolecular layers. The concentrations of cadmium species²⁷ in equilibrium with Cd(OH)₂ indicate that it should be possible to measure the kinetics of dissolution of Cd at potentials which include the potentials of stability of the anodic film.

The thickness of the passivating Cd(OH)₂ film which is formed on the electrode surface is of considerable interest, for this dimension determines the extent of the Cd oxidation reaction

(the capacity).

In this chapter the mechanism of thick films of cadmium hydroxide formation at the planar Cd electrode in the presence and absence of PVA is investigated using the potential step technique. The variation of $\text{Cd}(\text{OH})_2$ film thickness with potential is particularly considered because of its implications for battery performance.

12.6 Experimental

The cadmium used in this investigation was a disc electrode, area 0.283 cm^2 cut from a rod supplied by BDH (99.9% pure). It was set in an Araldite holder. Measurements were made in a conventional 3-electrode cell using a Hg/HgO reference electrode and a large Ni counter electrode. The solution used throughout was 5M KOH prepared from Aristar potassium hydroxide pellets and distilled-deionised water. All solutions were deoxygenated with N_2 before use and the experiment conducted at room temperature ($25 \pm 2^\circ\text{C}$).

Prior to experiment, the electrode was polished mechanically with 4/0 emery paper wetted with methanol, cleaned with methanol and water and then polished with diamond paste. Subsequent polishing was carried out on a buff (particle size $1\text{--}3\mu\text{m}$) and then by rinsing with methanol and deionised water before final immersion in the working solution.

The potentiostat was a Chemical Electronic, type 40V-3A used in conjunction with a waveform generator (also Chemical Electronic, type 01) and a PL4 JJ x-y-t recorder.

The electrode was allowed to equilibrate in the alkaline solution for about half-hour at -1.100V until the current drain was negligible. The cathode voltage was set at this value potentiostatically and voltage pulses of varying magnitudes and long duration were applied to the electrode.

PVA is only sparingly soluble in KOH solution and once the experiment using the straight KOH solution had terminated, a 5ml portion of a saturated solution of PVA was added to 600 mls of 5M KOH to study the effect of the organic expander on the cadmium electrode.

12.7 Results and Discussion

Potentiostatic oxidation steps were carried out from -1.100V to potentials ranging from -0.950V to $-.700\text{V}$ and four quite distinct forms of the i - t transients were obtained as shown in Figs. 12.2-12.5.

Integration of the area under the curves provided the charge, which in turn gave the number of $\text{Cd}(\text{OH})_2$ monolayers on the assumption that the calculated charge for the basal plane of $\beta\text{-Cd}(\text{OH})_2$ is $302.5\mu\text{C cm}^{-2}$. The data are shown in Table 13 together with the dimensionless quantity $i_m t_m / Q_m$, where i_m and t_m are the co-ordinates of the current maximum. A change in the value of this quotient indicates a transformation in the mechanism for nucleation and growth. It is clear from the data that the thickness of the deposit varies with the formation potential, the more positive potential giving rise to a thinner layer. This confirms the suggestions of Fleischmann and Thirsk²¹⁴ that the deposit thickness decreased with overpotential. The

Figure 12.2 Transients Obtained on Solid Cd Electrodes in
5M KOH After Stepping From -1.100V to -0.930V

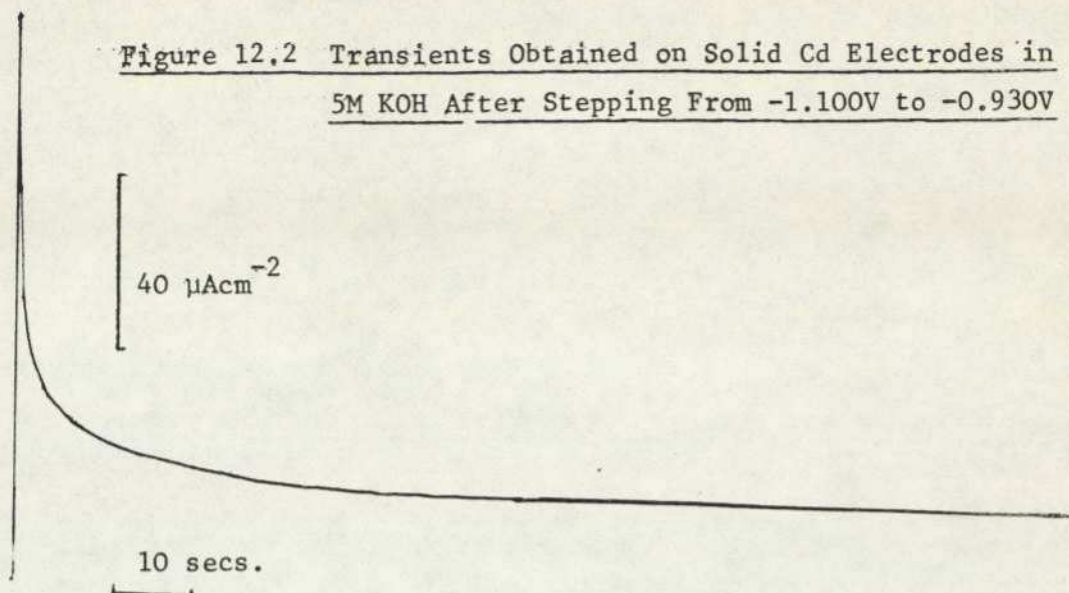


Figure 12.3 Transients Obtained on Solid Cd Electrodes in
5M KOH After Stepping From -1.100V to -0.892V

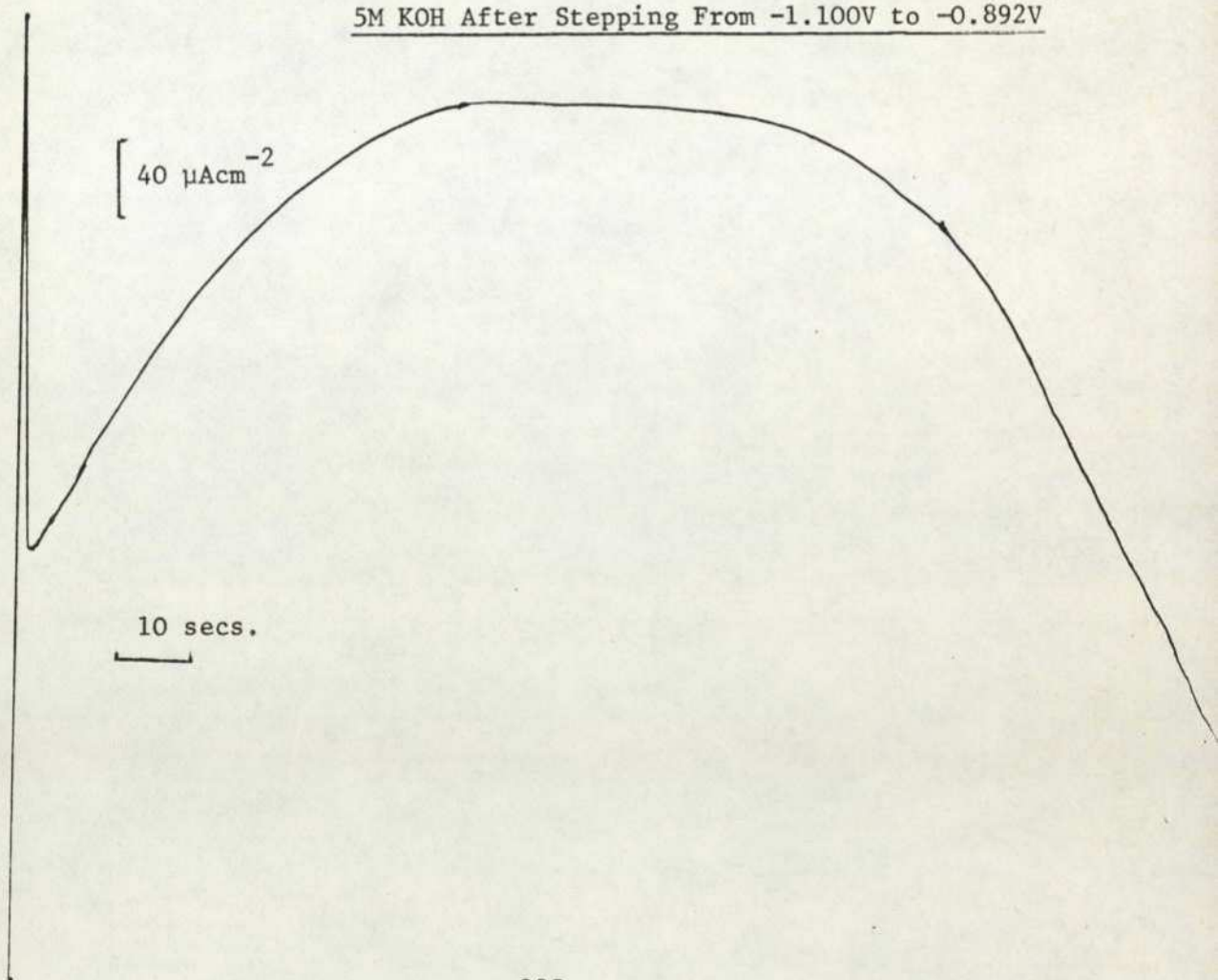


Figure 12.4 Transients Obtained on Solid Cd Electrode in 5M
KOH After Stepping From -1.100V to -0.882V

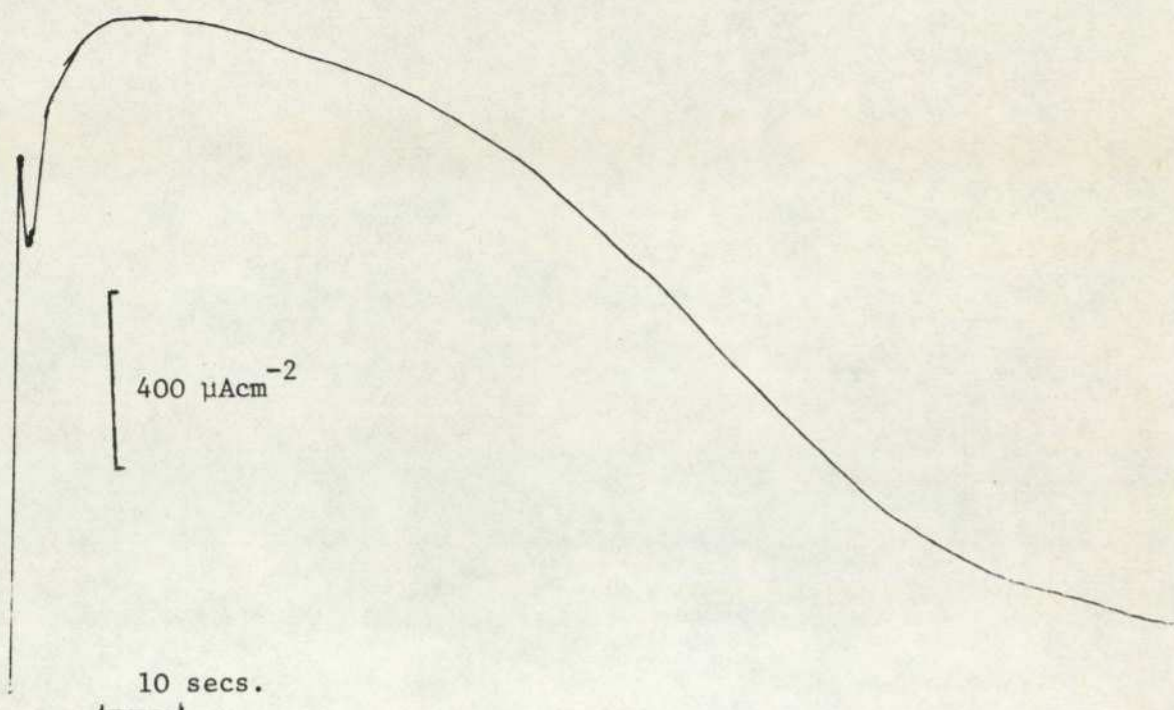
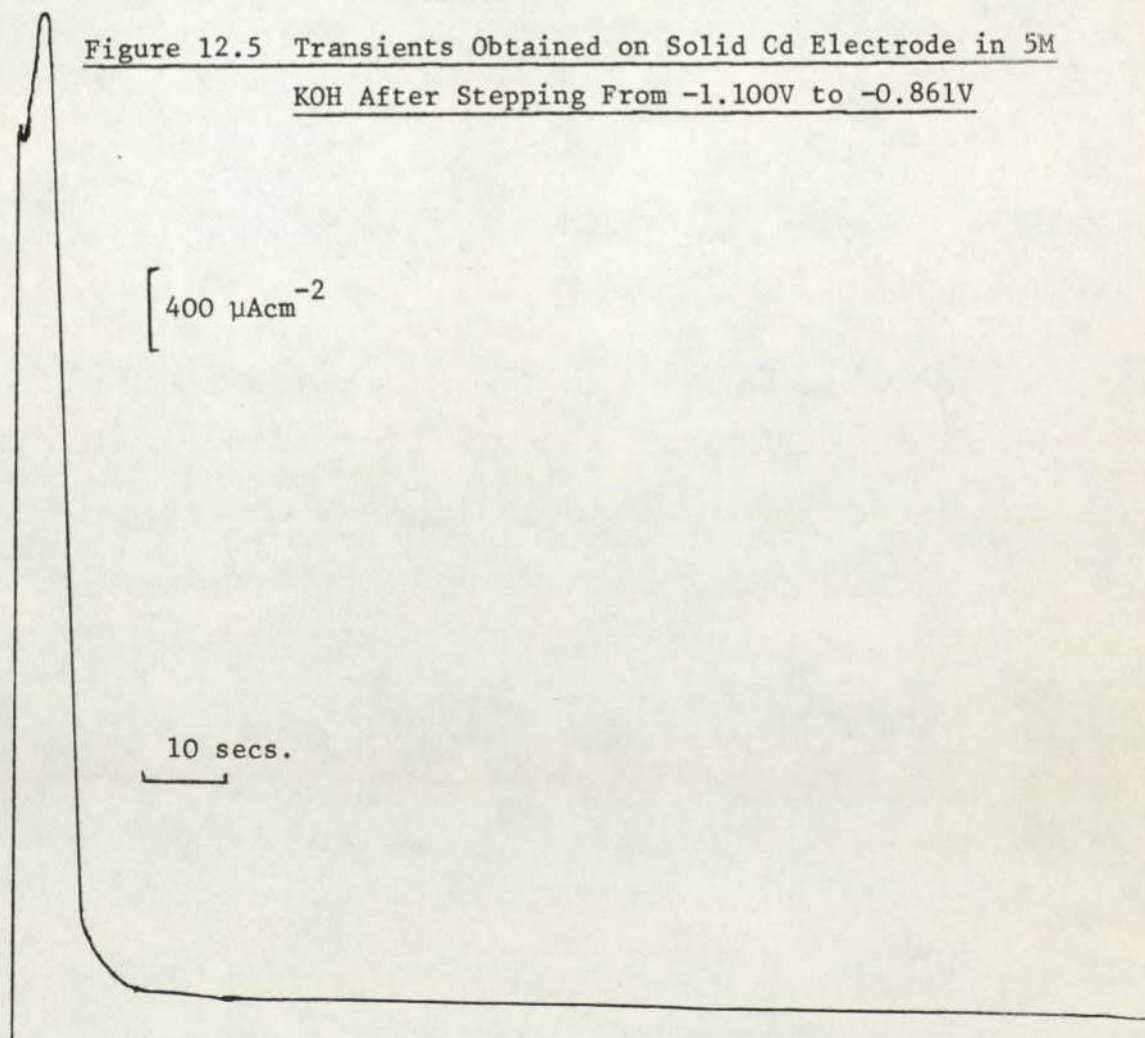


Figure 12.5 Transients Obtained on Solid Cd Electrode in 5M
KOH After Stepping From -1.100V to -0.861V



values of the quotient $i_m t_m / Q_m$ are interesting in that they decrease with increasing overpotential. This indicates that with increasing overpotential, changes occur in the current control by the crystallisation process.

Table 13

The variation of $i_m t_m / Q_m$ and deposit thickness (P monolayers equivalent) with potential.

<u>E, mV</u>	<u>$i_m t_m / Q_m$</u>	<u>P (No. of monolayers)</u>
-892	0.383	714
-882	0.138	555
-861	0.111	213
-798	0.109	452

The shapes of the transient response were similar to that predicted for two dimensional nucleation and growth. Two models for nucleation and growth possibly describe this relationship²⁰⁹. However, one of them (for progressive nucleation and two-dimensional growth) is unlikely in view of the thickness of the deposit (200-750 monolayers). Moreover, this process would require $\log(i/t^2) \propto t^3$ at long times, but this is not observed. The other possibility is that of instantaneous nucleation two-dimensional growth from cylindrical nuclei.

Equation 12.27 describes the current due to the growth of a two-dimensional layer from instantaneously formed cylindrical

centres.

The usual diagnostic test for two-dimensional nucleation and growth is to check that the transient, when plotted in the non-dimensional form ii_m^{-1} versus tt_m^{-1} conforms to a theoretical plot derived from equation 12.27. This is demonstrated in Fig. 12.6a where the transient of Fig.12.3 is plotted in dimensionless form against equation 12.27 derivative. The correlation is quite good, especially when it is remembered that we are quite near the potential region for cadmium dissolution.

The form of the transients does not change drastically with the addition of PVA (Fig. 12.7-12.10). The data for the monolayer equivalent derived from the charges under the curve together with the dimensionless quantity $i_m t_m / Q_m$ are shown in Table 14

Table 14

The variation of $i_m t_m / Q_m$ and deposit thickness (P monolayers equivalent) with potential in the presence of PVA.

<u>E, mV</u>	<u>$i_m t_m / Q_m$</u>	<u>P (no. of monolayers)</u>
-894	0.627	763
-879	0.788	441
-858	0.821	438
-787	0.483	537

Fig. 12.6b shows a typical transient plotted in the non-dimensional form; the solid line giving the theoretical curve. It can be seen that although the experimental curve has the same overall shape, the quantitative fit is not very good.

Figure 12.6a The Transient of Figure 12.3 Plotted in Dimensionless Form and Compared with the Curve of Equation 12.27 Derivative

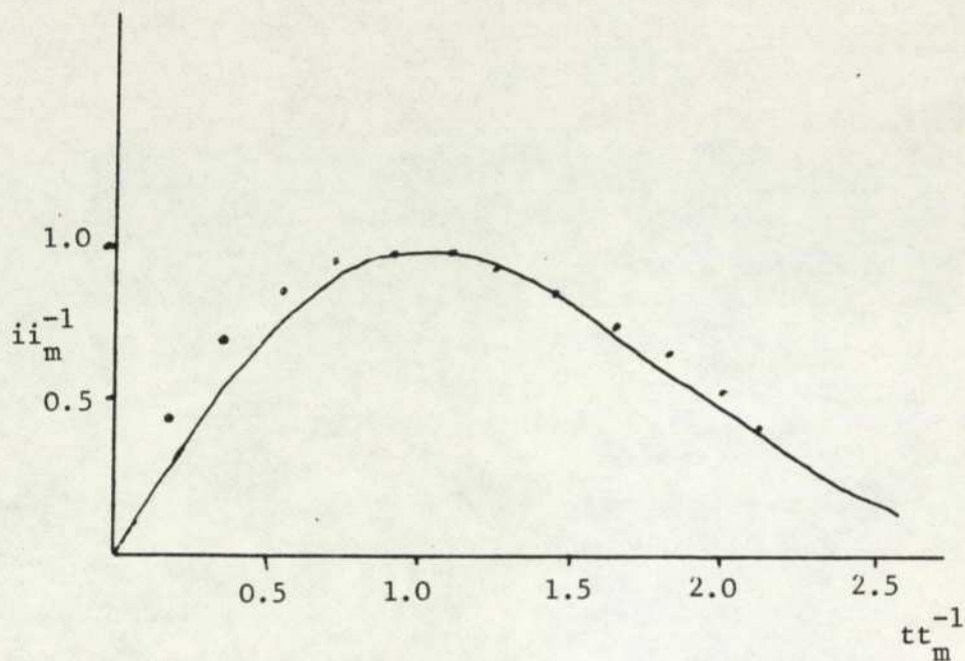


Figure 12.6b The Transient of Figure 12.8 Plotted in Dimensionless Form and Compared with the Curve of Equation 12.28 Derivative.

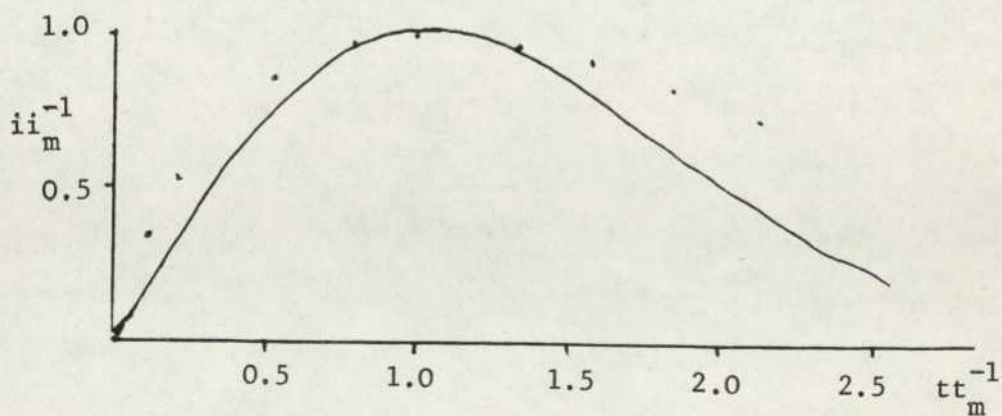


Figure 12.7 Transients Obtained on Solid Cd Electrodes in
5M KOH After Stepping From -1.100V to -0.930V
in the Presence of PVA

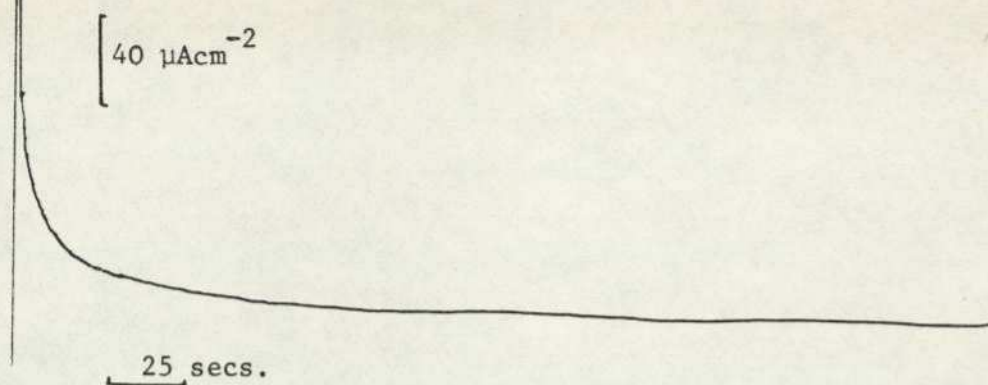


Figure 12.8 Transient Obtained on Solid Cd Electrodes in
5M KOH After Stepping From -1.100V to -0.894V
in the Presence of PVA

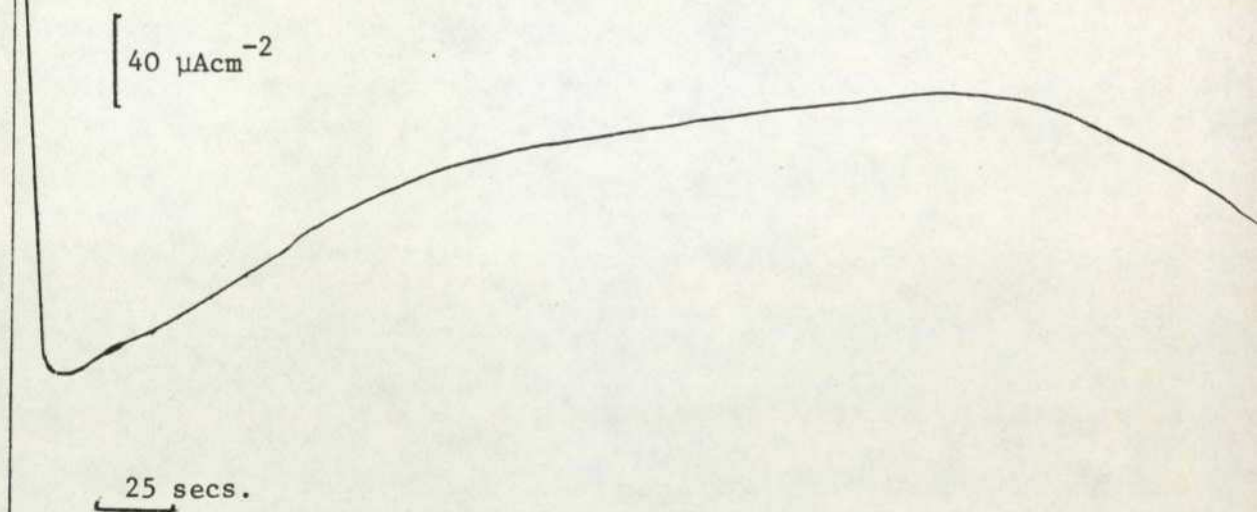


Figure 12.9 Transients Obtained on Solid Cd Electrodes in
5M KOH After Stepping From -1.100V to -0.879V
in the Presence of PVA

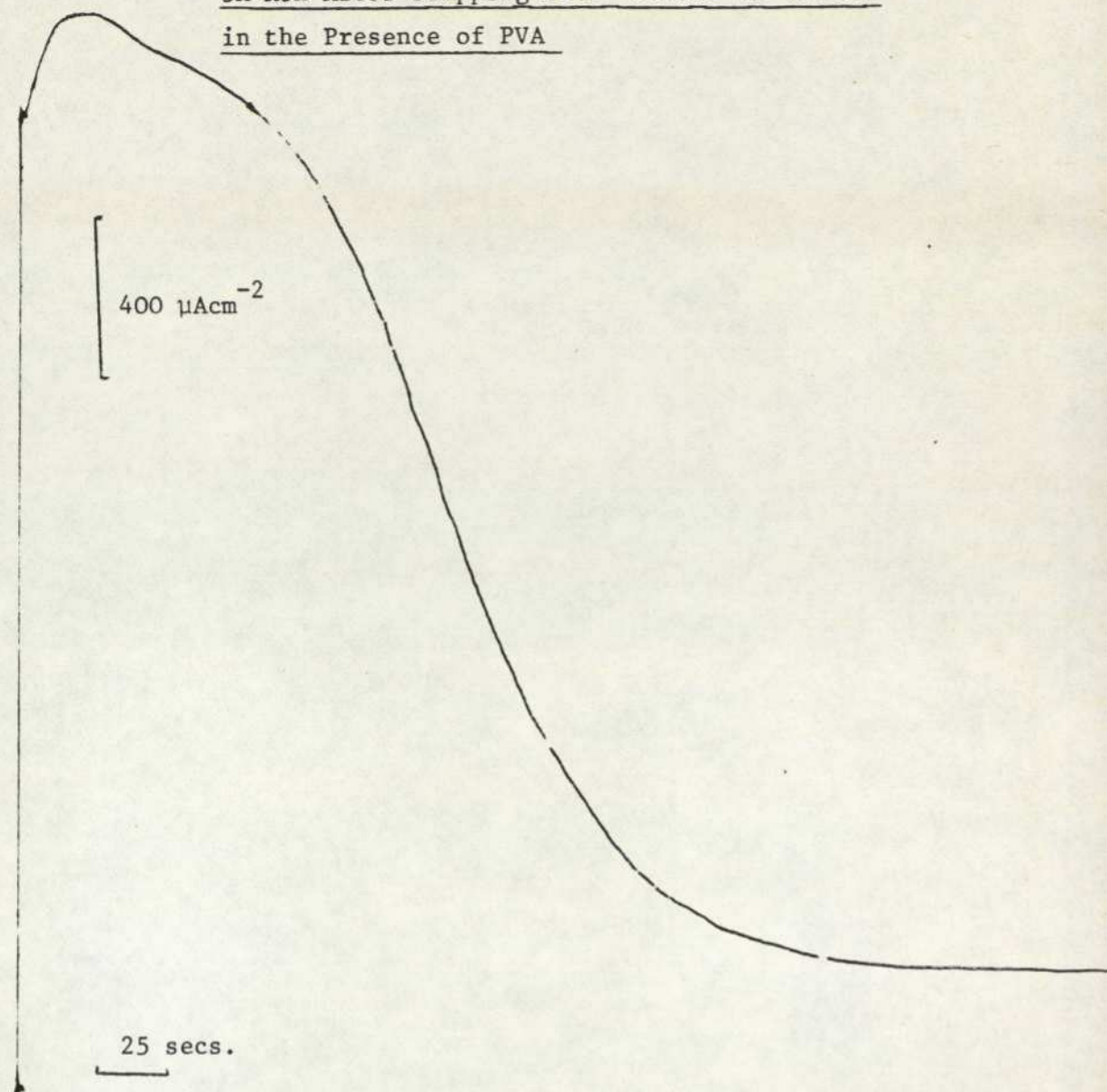
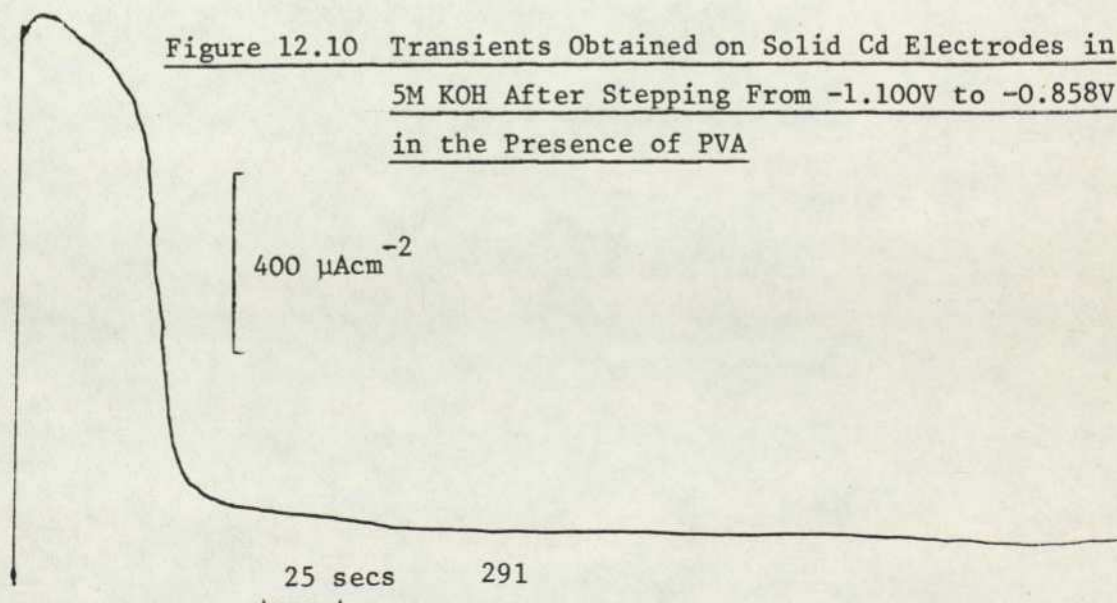


Figure 12.10 Transients Obtained on Solid Cd Electrodes in
5M KOH After Stepping From -1.100V to -0.858V
in the Presence of PVA



Although the monolayer equivalent indicates instantaneous nucleation and two-dimensional growth, the fact that the quantity $i_m t_m / Q_m$ suggests progressive is further shown by the not too good-a-fit of the experimental curve with the theoretical curve for instantaneous nucleation.

The effect of the PVA expander material on the formation of thick layers of cadmium hydroxide thus appear to modify the two-dimensional nucleation process.

Perhaps the adsorption effect which has been shown in the previous chapter distorts the general procedure for two dimensional instantaneous nucleation. If progressive nucleation does occur then this explains the uniform crystallite size of cadmium hydroxide crystals on discharge.

It is not possible on the basis of the present results to state unequivocally which parameter in the growth equation k or N_0 is affected by expanders. Comparison of the number of monolayers in the presence and absence of PVA clearly shows, that in general, the overall process is inhibited.

Since the rate constant k is probably diffusion-controlled, it might be concluded that this would be unchanged by expander presence and the main effect is a reduction in N_0 by adsorptive blocking of latent nuclei.

CHAPTER 13

FINAL DISCUSSION, CONCLUSION AND RECOMMENDATION

FOR FUTURE WORK

Chapter 13

FINAL DISCUSSION, CONCLUSIONS AND RECOMMENDATION FOR FUTURE WORK.

13.1 The Cadmium Electrode of the Nickel-Cadmium Battery.

The Nickel-Cadmium battery has been in use for about seventy years on a commercial scale. If it is to remain viable in an age of new energy storage systems, then its performance has to be improved. The increasing cost of fossil fuels has recently stimulated renewed interests in energy storage. Efforts to develop batteries with enhanced performance and low cost usually focus on the active materials which participate in the electrochemical reactions. The choice is limited and the more important generalised criteria for selection are low cost, high reactivity and low equivalent weight. The nickel-cadmium battery needs to be improved in performance because the battery has a low energy density.

The present work has considered the negative electrode, where there is obvious scope for improvement because at present only about 75% of the active material is utilized on discharge (energy production). Therefore, energy density could be substantially increased by greater utilisation of the active material. At present in Chloride Alcad's nickel-cadmium pocket plate flooded batteries this improvement has been carried out by the incorporation into the negative active material of certain additives or expanders which would enhance the performance of the negative plate. The additives in question are α -iron-oxide and polyvinylalcohol(PVA). Unfortunately the iron oxide has a tendency to migrate to the positive electrode

where it has a detrimental effect.

This thesis is concerned with an initial investigation into possible replacement expander materials for ferric oxide in current use in the negative pocket plates of nickel-cadmium batteries.

It is necessary to remove all iron from the Alcad cell due to iron poisoning of the positive plate resulting in low capacity and premature failure of the cell.

The relevance of the porous pocket-type electrode to the actual behaviour of the battery plates had already been established experimentally, and the input parameters investigated in this thesis will be briefly reviewed in terms of alternative expanders, and expander function in present use in the cadmium electrode.

13.2 Alternative Expanders.

Chapter 3 on Surface Energy Consideration showed that surface-free energy values of inorganic oxide materials could have important bearings on whether a material is a good expander or not. Although the experiment was not as successful as was originally thought and the data obtained were inadequate there were signs of some trend. For instance cadmium on graphite and barium hexaferrate (low energy substrates) did not wet the solids as expected, (The surface free energy of cadmium is about 600 dyne cm^{-1} at 450°C whereas the surface free energy value for a graphite single crystal is only 119 dyne cm^{-1} at room temperature). Cadmium on TiO_2 (higher surface energy substrate) wets the solid but Fe_2O_3 and $\alpha\text{-Al}_2\text{O}_3$ showed inconclusive results due to surface

chemical reactions.

Additives investigated during this project using cycling techniques included α -iron oxide, precipitated iron oxide calcined iron oxide, titanium dioxide, magnesium hydroxide, calcium oxide, boron nitride, barium hexaferrate and PVA (Chapter 7). The materials were evaluated by means of an experimental accelerated crystal grow test used in Chapter 6, SEM and X-ray crystallographic analysis. The accelerated crystal growth test used within this project proved a quick and efficient method of promoting crystal growth of the active materials.

Certain additives appeared to beneficially affect the crystal growth, namely the iron-oxides, titanium dioxide, magnesium hydroxide and PVA. Cycling test data (illustrated in Table 8 and 10 of Chapter 7) indicated that the standard new negative mixture had greater capacity than PVA or α -Fe₂O₃ mixture on their own. The general trend was as follows:

Std. New Negative > PVA > iron-oxide = magnesium hydroxide
> TiO₂ > straight Cd(OH)₂ > Ba_{0.6}Fe₂O₃ > CaO.

The high surface energy substrates TiO₂, gave promising results in the negative electrode. The capacities that were obtained at various cycles were just as good as the iron-oxides even though the amount of TiO₂ added to the negative plate was only 1/3rd of that of the α -Fe₂O₃. The presence of PVA changed the growth behaviour of the cadmium hydroxide crystals that were formed during the discharge process. The nature of the change was such that the extensive growth of large rhombic-like crystals

associated with a low surface area from a straight $\text{Cd}(\text{OH})_2$ electrode (Figs. 7.1-7.3) was transformed to one of plate-like crystals of relatively high surface area in the presence of PVA (Figs. 7.4-7.7). All the iron oxides provided granier deposits with a high surface area although the shape of the crystals were of a three dimensional kind, (Figs. 7.8-7.10 and 7.17-7.22). Barium hexaferrate, boron nitride and calcium oxide, all low surface energy substrates gave poor cycling results and their microstructure were of a very low surface area.

Magnesium hydroxide gave very encouraging results. The capacities were almost as good as the iron-oxides but the point in its favour was that only about 1% or less was necessary to give good results compared to 16% $\alpha\text{-Fe}_2\text{O}_3$ that is normally added to the negative plate. Besides, the magnesium hydroxide mixture was made in the laboratory whereas the others were made on a much larger scale at Chloride Alcad and also pocket-size electrodes were used in the case of magnesium hydroxide. Therefore it is possible that with efficient mixing and plate type cell used, the capacity can be further enhanced. PVA produced greater capacity in the negative plate than any of the solid inorganic expanders. This immediately gives rise to the question as to whether or not the inorganic materials are actually expanders. One might ask is it the PVA or the iron-oxide that controls the crystal growth of the cadmium hydroxide or is it a combination of both. Attempts were made to answer these questions from further screening works of $\alpha\text{-Fe}_2\text{O}_3$ and PVA.

13.3 Expander Function.

In Chapter 8 it was demonstrated that the α -Fe₂O₃, incorporated in the negative plate, undergoes dissolution to a small extent, This explains its change in structure from the α -form to the γ -form and also when the active material is examined after a few cycles, the reddish colour of the iron-oxide disappears and the whole mass is greyish black. We believe that one of the criteria for a good inorganic expander is that it must not be completely inert but at the same time must not take part in any electrochemical reaction so as to cause a detrimental effect. If the expander dissolves to a minute extent then it is an indication that it is also being mixed within the matrix of the cadmium electrode, randomly. If the expander is completely inert, then the chances of it being collected together in the negative electrode increases. The fact that iron-oxide dissolves to a certain extent gives rise to much granier deposit of cadmium hydroxide in the negative electrode (Fig.7.8-7.10).

The use of a planar micro-electrode in conjunction with linear sweep voltammetry, limiting current measurements, a.c. impedance, and potential step techniques was found to be a cheap and efficient means of organic expander assessment. In this way organic additives can be screened to assess their potential and optimal concentrations can be established.

Experimental data on the oxidation of the cadmium electrode in which the overpotential was the independent and the current the dependent variable showed that the ionic conductivity of

the oxidised product increased with the addition of PVA in the alkaline solution (Fig. 9.3). Impedance measurements provided the answer that adsorption of PVA occurs on the cadmium electrode. The impedance was made over the active and passive potential regions and in the active region the impedance was consistent with a simple Randle's circuit whereas in the passive region it was necessary to include an additional Warburg diffusion impedance to account for diffusion of species in the film present on the electrode surface.

Transients measurements showed that the reaction path of the cadmium oxidation mechanism is the same in the presence of PVA (Figs. 11.3a, 11.3b), but perhaps the nucleation of the cadmium hydroxide formation alters, (Chapter 12).

In each of the above experiments there were signs that the capacity of the planar electrode increased by many folds when PVA was included in the electrolyte. Thus the major function of PVA appears to be to increase the surface area/porosity of the electrode by acting in a complex way and may be a means of improving the active material utilisation. PVA acts by promoting cadmium nucleation and possibly inhibiting cadmium hydroxide formation; adsorption plays a major part in this. The $\alpha\text{-Fe}_2\text{O}_3$ cannot adsorb on to the cadmium-cadmium hydroxide electrode or vice-versa and it is postulated that the only way its function is best served in the negative electrode is by providing nucleation centres or spacers for the cadmium hydroxide and therefore acts synergistically with the organic PVA in increasing the surface area for cadmium hydroxide formation. This

in turn would also make the cadmium hydroxide layer thinner and therefore easier to reduce. This explains why a combination of iron-oxide and PVA in the negative electrode gives the most optimum result whereas any of the material used separately gives a lower performance.

The microscopic structure of the PVA doped porous electrode after cycling can be closely compared with the pulse and impedance result obtained on a planar electrode. The microstructure (Fig. 7.5) shows the crystals to be plate-like, growing almost in a two dimensional path to create a high surface area.

A.c. impedance demonstrated that adsorption by PVA was occurring on the planar Cd electrode and this could have been in such a way that growth of cadmium hydroxide was inhibited in one of the directions. Also cyclic voltammetry showed that the charge under the $i-v/t$ curve (Fig. 9.5) was much greater in the presence of PVA than in its absence. This immediately suggests that there is either a greater surface area or greater porosity or both in the presence of PVA.

Pulse work (Chapter 12) indicated that there was a possible progressive nucleation of the cadmium hydroxide in the presence of PVA rather than an instantaneous one in its absence. This is clearly differentiated when microstructures of electrodes containing only cycled cadmium hydroxide (Figs.7.1-7.3) are compared with those containing PVA additive (Figs.7.4-7.7).

Thus the results of all the above techniques on a planar cadmium electrode in the presence of PVA could be compared well with those results obtained from a porous cycled electrode containing

PVA and at the same time this also justifies the use of a planar electrode.

To conclude then, any sparingly soluble organic material such as PVA and an inorganic material of a high surface area which is also sparingly soluble but does not dissolve away from the electrode nor take part in any electrochemical reaction in any way should be able to suffice as good expanders and hence increase the performance of a negative nickel-cadmium battery plate.

13.4 Suggestions for Further Work.

Further work is required to fully evaluate the effects of the recommended additives in the negative plate. The required work can be envisaged in the following areas:

- a) Further plate testing of the additives shown to exhibit beneficial effects from this project, such as TiO_2 and Mg(OH)_2 . The work being planned to optimise fully the concentration levels of the additives, to determine any detrimental effects of the additives on the positive plate and to analyse any cost benefits.
- b) Further screening on possible additives extracted from the literature using the above techniques are valuable.
- c) The use of a pore model is recommended for the confirmation and further investigation of processes already established. Although it is extremely difficult, porous electrode theory needs to be further investigated to explain the behaviour of experimental electrodes undergoing progressive phase change.
- d) Better and more refined techniques to measure surface free energy should be closely looked into since it is felt that this is still one of the major factors involved in choosing good inorganic expanders.

- e) Any methods currently available to measure porosity and surface area in situ should be attempted to elucidate the physical properties of a porous cadmium electrode.
- f) For an efficient energy density, the utilisation of the active material must be improved and this can be done if the methods of manufacture of the active material can be modified to be commercially viable and also to develop mathematical concept of penetration depth to define optimal electrode thickness.

APPENDIX 1

Patent Survey

This appendix contains a brief abstract of the patents relating to cadmium electrodes and additives thereto which are relevant to this project. The patent survey was carried out by Kilburn & Strode, Patent Agents.

1) Patent No. 7338 Patentee: Jungner, Sweden

Addition of iron to cadmium electrodes which it states, reduces the tendency of cadmium to "cake or clod".

2) 239,603 John Ferreol Monnot, U.S.A.

Addition of 2% asbestos wool to active material. It states that this addition reduces the loss of capacity of the cadmium electrode on cycling.

3) 242,290 Carl Hilding Ossian, Sweden

Use of cadmium-iron mixture as active material. Addition of graphite to improve conductivity.

4) 328,096 I.G. Farbenindustrie Aktiengesellschaft, Germany

Outlines an extrusion process for filling pockets of alkaline plates. Negative active material consist of cadmium oxide, Fe_3O_4 and 10% glycerine. The glycerine being added to aid extrusion and briquetting and it is stated that the addition has no detrimental effect on capacity.

5) 685,341 Bureau Technique Gautrat, France

Addition to the negative plate of a sealed Ni-Cd cell of "another body, preferably a metallic one, this body chosen in such a manner that its potential" is lower than the potential of the active material but that preferably, its overvoltage with hydrogen in alkaline solutions is at least equal to and preferably higher than the overvoltage of the main metals of the electrode. The use of copper in a powder form or in amalgam with mercury is advised. Oxygen evolved on collapse of the negative would oxidise this addition of an auxillary metal.

6) 711,947 E.S.B. Co., U.S.A.

Relates to additions to zinc negatives of silver-zinc cells

to arrest crystal growth. States that these additions should be effective for other couples including nickel-cadmium. Additive materials stated include gum arabic, gum tragacanth, gum karaya, starch, licorice, lignin and glues of animal origin in amounts up to 2% by weight.

7) 763,452 V.E.B. Grubenlampenwerke, Germany

Addition of nickel sulphate to the cadmium electrode. This addition is supposed to "regenerate the electrode and reduce capacity loss". The addition may be made to pure cadmium electrode or cadmium with up to 1.5% iron, graphite and nickel flakes added.

8) 784,851 Accumulatoren-Fabrik Aktiengesellschaft, Germany

Addition to sealed cells of nickel hydroxide, cobalt hydroxide or copper powder to cadmium electrodes as anti-polar masses. Graphite and/or nickel flakes added to enhance the effects of the anti-polar mass. These additives undergo, it states, an electrochemical reaction and thereby suppress the evolution of gas after the reversal of cells.

9) 819,780 McGraw Edison, U.S.A.

States that polyvinylpyrrolidone is a "very effective and economical addition agent". Used with cadmium electrodes with or without iron addition the additive is said to have caused a 5% reduction in capacity over first 8-20 cycles, but after 300 cycles performance was 60-70% higher.

10) 862,092 V.E.B. Grubenlampenwerke, E. Germany

Concerns sealed nickel-cadmium cells. Addition to both nickel and cadmium electrodes are outlined. Addition to the cadmium electrode:-

1) up to 5% by weight of a nickel salt preferably as nickel sulphate as an anti-polar mass;

2) up to 5% of an electrolyte absorbing substance, e.g. gelatine, silica gel, sodium carboxymethyl cellulose, regenerated cellulose and polyvinyl alcohol.

These substances are supposed to aid in the reconversion of cadmium hydroxide to cadmium by absorbing more electrolyte into the plate.

3) up to 3% of a finely distributed synthetic substance, e.g. polyamide or polystyrene to "prevent the active material of the electrode from being sintered".

Appendix 1 (continued)

11) 865,894 Secretary of the Army, U.S.A.

Use of polyethylene glycol in the impregnation solution for sintered cadmium electrodes to reduce the amount of nickel dissolved from the plaques which concentrates in the cadmium nitrate solution and is precipitated with the cadmium and decreases the capacity of the cadmium electrode on cycling. 1g/l of polyethylene glycol is used, the polyethylene glycol having a MW of approximately 6000.

12) 886,463 E.S.B. Corp., U.S.A.

Relates to use of a cellulosic filler material to alter surface growth. The cellulosic material (e.g. cellulose or cellulose nitrate) is precipitated into the active material from cellulose xanthate solutions.

13) 910,516 Accumulatoren-Fabrik Aktiengesellschaft, Germany

Relates to sealed nickel cadmium cells. Addition to negative plates to prevent "ageing" and falling off in capacity. Examples stated include one or more of the metals indium, mercury, iron or one or more of their oxides or hydroxides, or high polymer organic substances, e.g. cellulose, cellulose esters or polyvinyl acetate.

14) 1,093,828 Alkaline Batteries Limited, Redditch

Addition of dissolved silicate, e.g. potassium metasilicate is stated to improve cycle life. Addition levels 0.5-5g/l of electrolyte calculated as SiO_2 .

15) 1,357,504 E.S.B. Incorporated, U.S.A.

Method of producing metallic powder for the cadmium electrode by adding aluminium, zinc, magnesium or calcium to an acidic solution of cadmium and nickel salts and then drying the precipitated cadmium and nickel powder and pressing into plates. Binding agents such as rubber, latex or polyvinyl pyrrolidone can be used. The active material powder contains 0.1-10% nickel and contains amounts of an intermetallic compound Cd_4Ni which is harder than cadmium and thus resists compression and gives a strong, highly porous matrix having low electrical resistance.

Appendix 1 (continued)

16) 1,375,462 Gates Rubber Co., U.S.A.

A method of making electrodes of the powder type substantially free of polymeric binder by:-

- a) coating active material with an electrolyte porous layer of conductive material
- b) blending with a conductive material having an abhorescent structure
- c) apply mixture to conductive substrate by pressing

Abhorescent materials mentioned include carbonyl iron powder, carbonyl nickel powder, tantalum, tungsten, graphite fibres, electrolytic iron and electrolytic nickel. The electrodes also contain anti-polar masses.

17) 1,398,080 International Nickel Ltd., London

Outlines a method of electrodepositing cadmium active material containing 1-10% nickel hydroxide. It states the nickel hydroxide action is "by assisting nucleation and growth in the course of redeposition reduces or eliminates the loss of surface area".

18) 1,406,007 Compagnie Generale D'Electricite, France

Process for making plates overcoming disadvantages due to growth of the active materials by having an addition of a partially crosslinked polymer. Example used is PVA crosslinked by the addition of dimethyl urea, ammonium chloride, and sodium sulphate which crosslinks PVA by the formation of polyvinyl acetal.

U.S.A. Patents

1) 2,771,499 Nickel Cadmium Battery Corporation

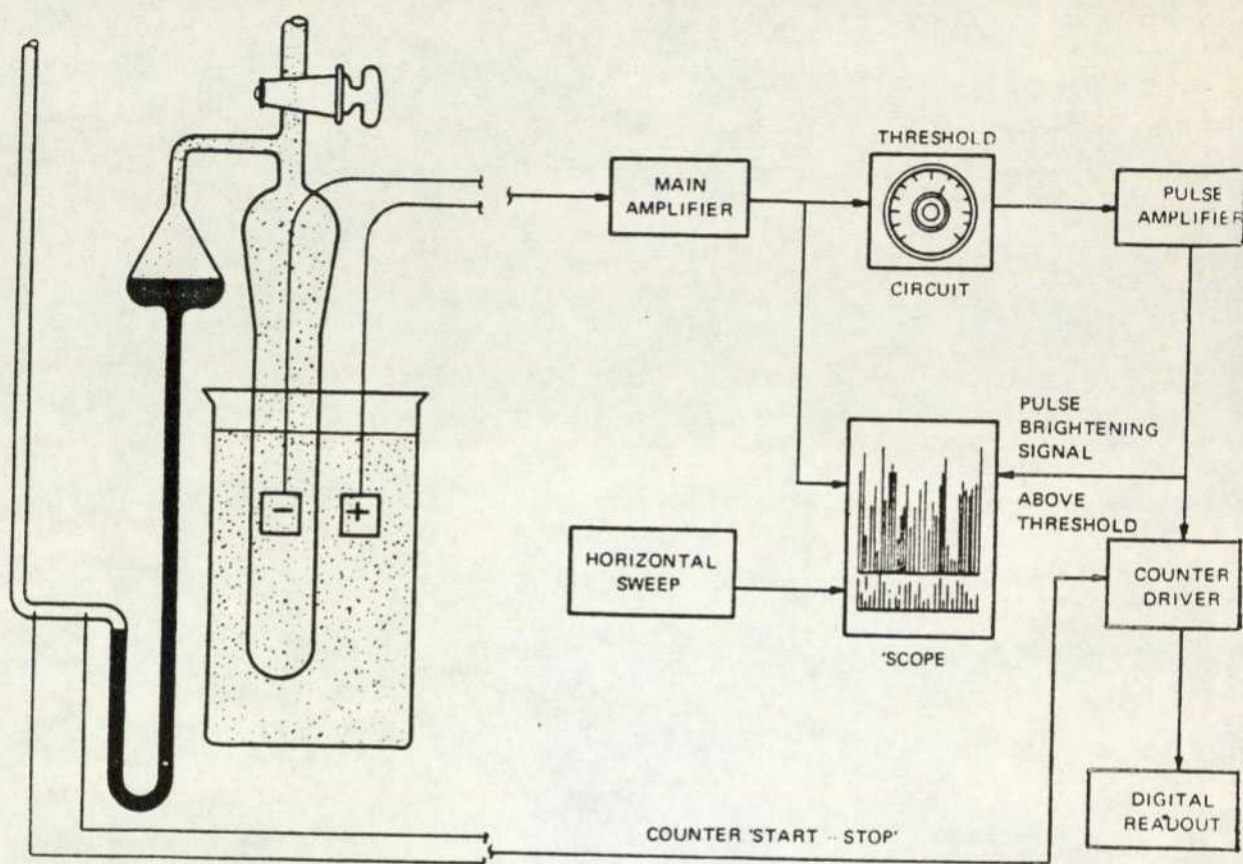
Describes the use of indium (0.5-5%) in sintered cadmium negative plates to improve performance on cycle life. Also describes a method of producing electrodes by impregnation techniques.

2) 2,802,043 Nickel Cadmium Battery Corporation

Relates to the use of a cellulose substance in the concentration range of 1-10g/l added to the electrolyte to improve cell life. Cellulose additives used:- beta cellulose, carboxymethyl cellulose, carboxymethyl hydroxyethyl cellulose (CMHEC) and Natrosol.

APPENDIX THEORY OF THE COULTER COUNTER®

(Bulletin T-1, Coulter Electronics Inc., 1957.)



The Coulter Counter® determines the number and size of particles suspended in an electrically conductive liquid. This is done by forcing the suspension to flow through a small aperture having an immersed electrode on either side.

As a particle passes through the aperture, it changes the resistance between the electrodes. This produces a voltage pulse of short duration having a magnitude proportional to particle size. The series of pulses is then electronically scaled and counted.

When the stopcock is opened, a controlled external vacuum initiates flow from the beaker through the aperture and unbalances the mercury siphon. Closing the stopcock then isolates the system from the external vacuum and the siphoning action of the mercury continues the sample flow.

The advancing mercury column contacts start and stop probes to activate the electronic counter. The probes are placed precisely 0.5ml apart, providing a constant sample volume for all counts.

Appendix 2

The voltage pulses are amplified and fed to a threshold circuit having an adjustable threshold level. If this level is reached or exceeded by a pulse, the pulse is counted. The threshold level is indicated on an oscilloscope screen by a brightening of the pulse segments above the threshold, facilitating the selection of appropriate counting levels.

By taking a series of counts at selected threshold levels, data is directly obtained for plotting cumulative frequency (larger than stated size) versus particle size. Integration of all or part of the resultant curve provides a measure of the particle content of the suspension.

Before plotting, the counts are first corrected for coincident particle passages (doublets, triplets, etc.). These corrections are quite precise and if kept to a moderate level (say, 15%), an overall accuracy of measurement of better than 1% is readily achieved. This is due in part to the large numbers of particles counted (tens of thousands), which provide low statistical deviations.

The pulse height and instrument response are essentially proportional to particle volume and to fluid resistivity. The particle resistivity has very little effect on the response, unless it is quite close to the resistivity of the fluid. If particle conductivity changes from one millionth to one hundredth that of the electrolyte, there is less than 1% change in the response. Either the fluid or the particle may be the better conductor, as only a simple signal polarity reversal is needed to switch from one case to the other. Colloidal charges on the particles are too minute to have detectable effect on the count.

The principle does not permit significant discernment of particle shape and results are expressed in spherical equivalents. This proves to be valid, as sufficiently high numbers of particles are counted to assure an averaging of orientations of particles traversing the aperture. There is evidence that particle porosity may be measured, if the Coulter method is used in conjunction with some other means such as sieving.

The combination of both liquid and electrical current flow through the aperture does not lend itself to simple analysis. However, certain approximations prove quite useful, as developed on the following pages. In the main, the theoretical bases of the Coulter Counter[®] are quite simple and 'side effects' are notably few in number and small in their influence on the results. The accuracy of the measurements is not limited by the instrument, but is simply a matter of the degree of care exercised in its use.

The instrument is inherently simple to calibrate, requiring only a laboratory balance and a pipette.

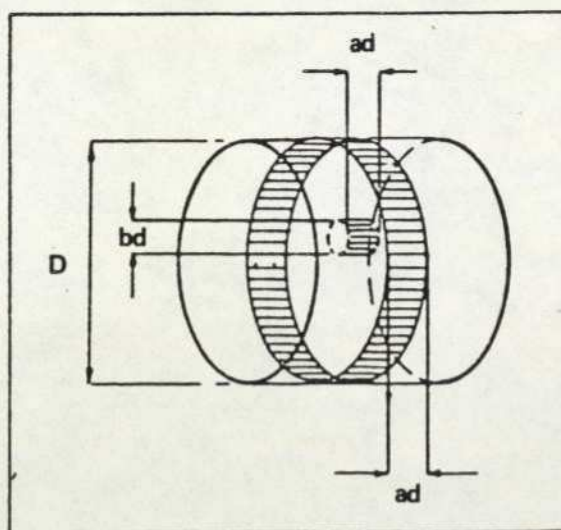
Accumulated evidence indicates that most materials respond in the Coulter Counter[®] sensing zone as if they were insulators (this includes copper, aluminum and silver).

DERIVATION OF ELECTRICAL RESPONSE FROM PARTICLE SIZE

Let us assume that:

- (1) The aperture contents form a cylindrical resistor in which current density is uniform.
- (2) Multiplying the aperture length by an appropriate factor covers the electrically effective zones outside the aperture.
- (3) The passages of individual particles occur at random and are evenly distributed through the aperture cross-section.
- (4) The electrically effective volume of a particle in the aperture may be expressed as a cylinder having the same resistivity as the particle.

Let this cylinder be ad in length and bd in diameter, where d is the diameter of a sphere having the same volume as the cylinder. This d is thus the particle dimension as measured electrically (not necessarily the same as the physical dimension).



Now consider the aperture as having a disc segment containing a given particle, having a diameter D equal to that of the aperture and a thickness ad equal to the length of the particle-cylinder (see diagram). Let ρ_0 and ρ be the resistivities of the liquid and the particle respectively.

Then, the disc segment resistance without the particle is:

Appendix 2

$$R_o = \rho_o \frac{ad}{(\pi/4)D^2}$$

and the resistance with the particle is that of two resistors in parallel, or:

$$R = \frac{1}{\frac{1}{\rho_o \frac{ad}{(\pi/4)(D^2 - b^2d^2)}} + \frac{1}{\rho \frac{ad}{(\pi/4)b^2d^2}}}$$

Thus, the resistance change caused by the particle is:

$$\Delta R = R - R_o = \frac{1}{\frac{(\pi/4)(D^2 - b^2d^2)}{\rho ad} + \frac{(\pi/4)b^2d\rho_o}{\rho a\rho_o}} - \frac{\rho_o ad}{(\pi/4)D^2}$$

simplified:

$$= \frac{\rho_o a}{(\pi/4)D^4} \frac{d^3(1 - \rho_o/\rho)}{\frac{1}{b^2} - \frac{d^2}{D^2}(1 - \rho_o/\rho)}$$

But, for an equivalent sphere and cylinder of equal volume:

$$(\pi/6)d^3 = (\pi/4)b^2d^2ad, \text{ and } (1/b^2) = 1.5a$$

Thus,

$$\Delta R = \frac{4\rho_o}{\pi D^4} \frac{d^3}{\frac{1.5}{1 - \rho_o/\rho} - \frac{d^2}{aD^2}}$$

This equation is confirmed by several intuitive checks; i.e.: $\Delta R = 0$ when $d = 0$ or $D = \infty$ or $\rho_o = \rho$. Also, when the particle-cylinder completely fills the aperture, $bd = D$ and $d = \sqrt{1.5aD}$. By substitution in the equation or by direct calculation, this results in:

$$\Delta R = \frac{4a\sqrt{1.5a}}{D} (\rho - \rho_o)$$

Response is thus directly proportional to particle volume, except as modified by the last term in the denominator. This effect is limited because, to adequately prevent aperture jamming, d/D should not exceed a maximum of about 0.5. In practice, deviation from volumetric response has proven to be negligible for aqueous electrolytes and relatively insulating particles, due to these probable compensating factors:

- (1) A larger particle makes a greater increase in the current density and hence electrical heating in the rest of the aperture, thus momentarily lowering the resistivity of the electrolyte and the response to particle passage.

- (2) The factor a is probably somewhat greater than unity (elongated interruption pattern in electric flow to 'dodge' the particle), especially for larger particles which are the more likely to have irregular shapes and thus become 'feathered' to align with the flow stream.

Thus, ignoring the last term in the denominator, the response equation becomes:

$$\Delta R = \frac{4d^3}{1.5\pi D^4} \rho_0(1 - \rho_0/\rho) = A\rho_0(1 - \rho_0/\rho).$$

Differentiating and setting equal to zero for maximum response:

$$\frac{d(\Delta R)}{d\rho_0} = A - 2A\rho_0/\rho = 0, \text{ and } \rho_0 = \rho/2.$$

Usually, it will be impractical to achieve this 'best' resistivity ratio of 2 : 1, as the required fluid resistivity for many particulate materials will be too high to permit the required current in the aperture without excessive resistive noise, heating of the aperture contents, or both. Adequate pulse height is readily achieved, however, so this is of little concern.

CORRECTION FOR COINCIDENT PASSAGES

Although ideally, perfect data would result if the particles traversed the aperture singly, there are inevitable probabilities of multiple passages. Though these probabilities can be closely computed, particle concentrations should be such that coincidence corrections are moderate.

The primary effect of coincident passages is that of loss in count. The following is taken from 'Determination of Number and Size of Particles by Electrical Gating' by Mattern, Brackett, and Olson (National Institute of Health) published in Journal of Applied Physiology, Vol. 10, No. 1, January 1957, p.56-70.

The aperture may be thought of as having a critical volume within which two or more cells cannot be resolved as individual impedance pulses. The size of the critical volume can be determined by selecting the best fit of theoretical data (calculated by equation developed below) to empirical data. Using an aperture of 100 μ diameter and 75 μ depth, the critical volume appears to be three times the aperture volume. This is visualized in Figure A. Figures B and C show schematically the relative height and width of the pulse from a single cell and for two coincident cells separated by different distances in transit through the critical volume. It may be seen that coincidences of moderate number will not produce pulses in a staircase effect (all doublets of nearly constant height), but rather will result in a continuum of heights of pulses.

Appendix 2

The coincidence loss due to doublets, triplets, etc., can be expected to follow the Poisson distribution. Thus for m = the average number of particles per unit critical volume of suspension,

$e^m = P_0$, the probability of no cells in the critical volume.

$me^m = P_1$, the probability of 1 cell in the critical volume.

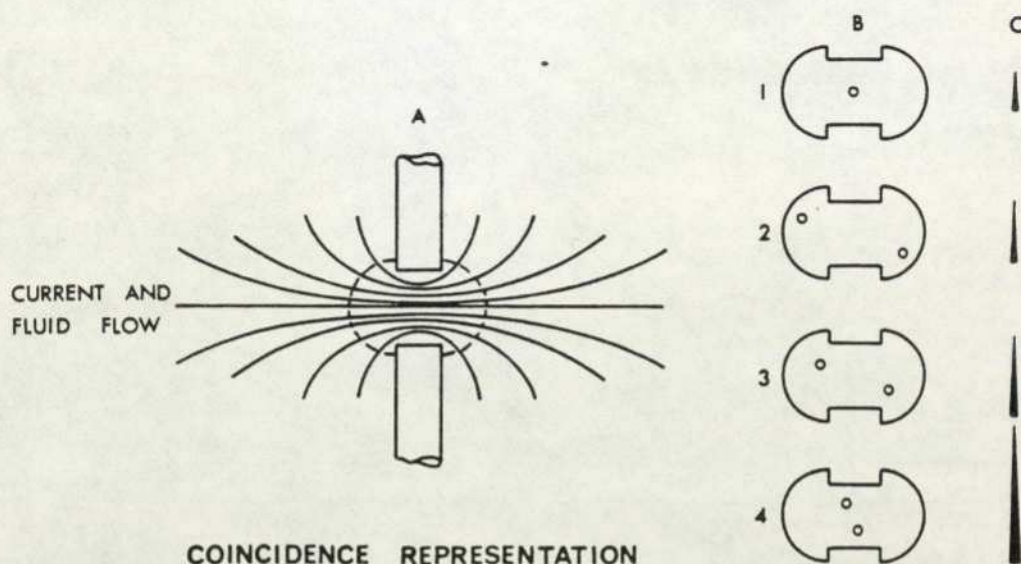
$\frac{m^n}{n!} e^m = P_n$, the probability of n cells in the critical volume.

Since $1 = P_0 + P_1 + P_2 + \dots + P_n + \dots$, the theoretical ratio of instrument count to actual number of cells passing through the aperture is

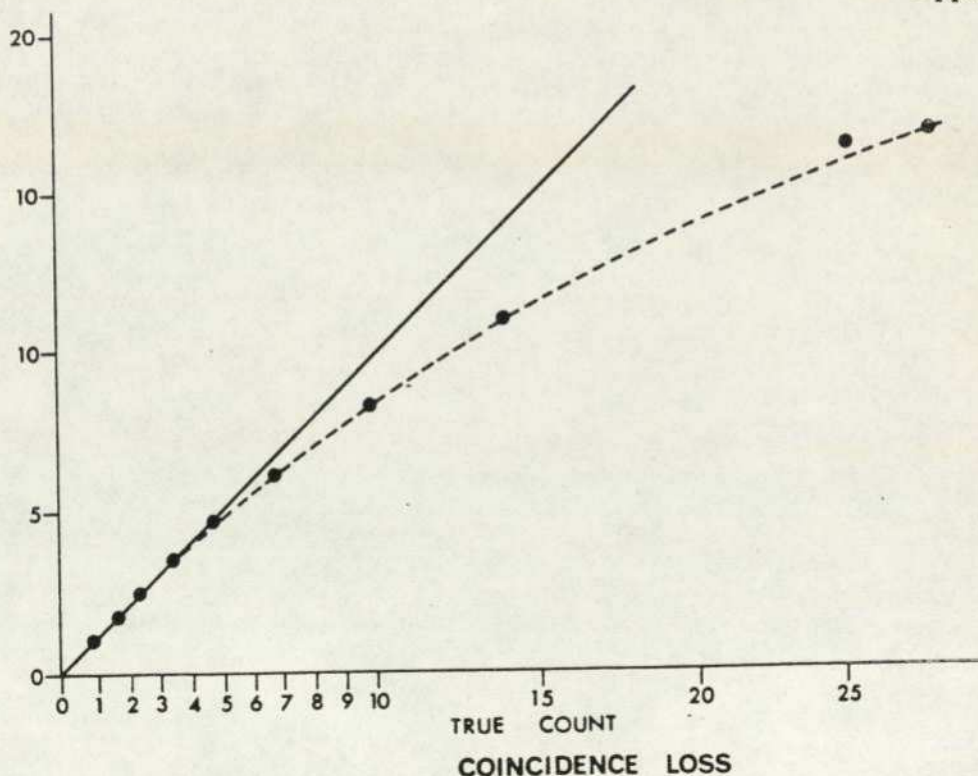
$$\frac{P_1 + P_2 + P_3 + \dots + P_n + \dots}{P_1 + 2P_2 + 3P_3 + \dots + nP_n + \dots} = \frac{1 - P_0}{1 - P_0 + (P_2 + 2P_3 + \dots + (n-1)P_n + \dots)}$$

This ratio deviates from unity only to the extent that doublets, triplets, etc. are encountered within the critical volume and register as $\frac{1}{2}$, $\frac{1}{3}$, etc. of their actual number.

A secondary coincidence effect exists which may tend to displace a distribution curve slightly. That is, there will be some pulses which are above a given threshold setting, yet are caused by multiple passages of particles smaller than the threshold setting. For example, at a threshold equivalent to 10 microns, doublets having both particles larger than 8 microns, with very close particle proximity (Figure B4), may cause a counted pulse.



- A. Schematic representation of aperture (heavy lines), current density lines (light lines) and critical volume (broken lines).
- B. Schematic drawing of several different aperture events within the critical volume.
- C. Resulting pulses.



Instrument count plotted against true count. True count calculated under the assumption that there is no count loss from coincidence at the greatest dilution. Triangles, empirical; circles, theoretical, explained in text; straight line, hypothetical, assuming no coincidence loss at any dilution. Counts expressed in millions/mm³ whole blood.

Note, however, that two very confining specifications must be met: (1) narrow size range for both particles (above 80% of threshold diameter) and (2) close proximity. The probabilities of such doublets, etc. will depend on the distribution curve of a given population and the point on the curve being considered. In general, these probabilities will be quite small, especially when coincidence corrections are kept at moderate values. In these circumstances, no detectable effect on size distribution curves has been found experimentally.

In practice, to retain an overall accuracy of better than 1%, it has been desirable to limit coincidence corrections to about 10%, while taking maximum counts in the tens of thousands to keep the standard deviations below $\frac{1}{2}\%$. For convenience in estimating requirements of a sample, the following is useful:

As aperture size is varied to accommodate population size range, the critical volume will be roughly proportional to aperture volume (assume aperture length proportional to aperture diameter).

Thus, to stay within a given coincidence correction limit, the volume per cent of particles in suspension should be nearly proportional to aperture volume, or $\%_v \propto D^3$.

Appendix 2

Also, to maintain a given high total count level and low deviation, the sample volume per count should be nearly proportional to aperture volume, or: $v_s \propto D^3$

Since the flow rate through the aperture is proportional to area, the time per count, assuming above conditions have been met, is nearly proportional to sample volume divided by aperture area, or: $T_c \propto D$.

For an aperture with $D = 100$ microns, the values are approximately:

$$\%v_s = 0.01\% \quad V_s = \frac{1}{2} \text{ cc} \quad T = 15 \text{ sec.}$$

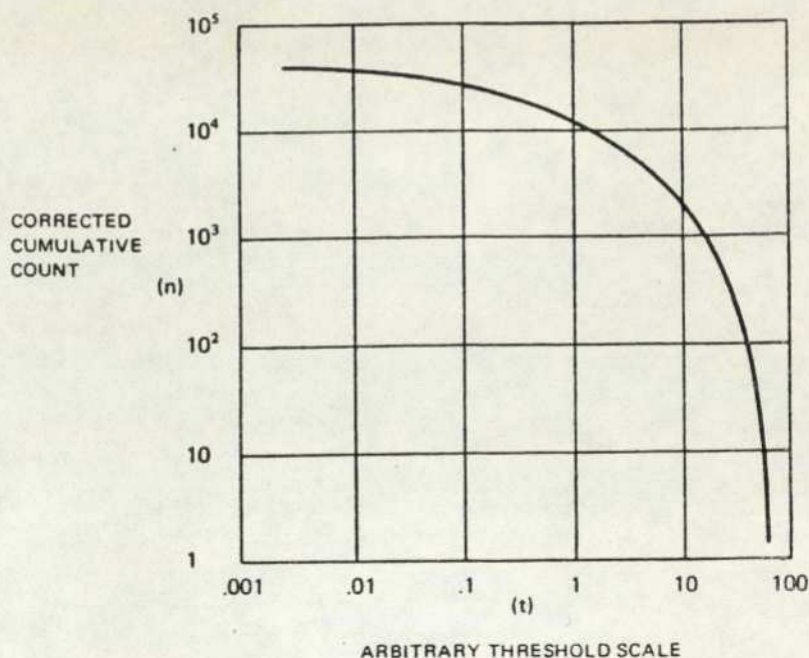
These apply for a typical distribution from $2\frac{1}{2}$ to 50 microns and for fluid flow properties equivalent to water. At a count of 60,000, coincidence correction is 14% and Standard Deviation is about 0.4%.

CALIBRATION OF THE THRESHOLD SCALE

It has been shown that, for a given suspension, the response of the Coulter Counter is essentially proportional to particle volume. The threshold scale, being linear with pulse height, thus provides a relative scale of individual particle volume. The counter is readily calibrated in terms of physical dimensions, given the following conditions:

- (1) The volume per cent of particles in the calibration suspension is known (or the weight per cent and particle density).
- (2) The particle size range of the calibration suspension is such that substantially all of the particulate mass is accounted for by the largest count taken and the largest particles (near $\frac{1}{2}$ aperture diameter) are relatively few.

The repeated counts taken at various threshold levels, after coincidence correction, may be plotted as a curve of cumulative frequency vs. relative particle volume, as shown on Page 57. Log-log co-ordinates are chosen to facilitate accurate integration and to indicate by asymptotes the satisfaction of condition (2) above. (Probability grids might also be used.) Integration of this curve to the ordinate produces a relative measure of total volume of particles in the suspension counting volume (e.g. $\frac{1}{2}$ cc). Thus:



$V_p = f \cdot \Sigma (\Delta n) \bar{t}$, where:

V_p - is total particle volume in the suspension counting volume (cc),

f - is the proportionality factor,

Δn - are the count increments read from the curve for integration,

$\bar{t}$ - are the average values of the threshold t for corresponding count increments.

But, V may be independently computed from the known volume percentage composition of the suspension, as measured by laboratory balance and pipette, so that:

$$V_p = \frac{v_s}{V_s} \cdot \frac{W_p}{\rho_p}$$

where: v_s is suspension counting volume (cc),

V_s is total suspension volume (cc)*,

W_p is total particulate mass (gm),

ρ_p is particle density (gm/cc).

*NOTE: For all practical purposes, V_s is equal to the volume of liquid, as particles are generally well below 0.1%.

Appendix 2

The proportionality factor f , which is the scale factor for the threshold scale, is then simply:

$$f = \frac{1}{\Sigma(\Delta n)t} \cdot \frac{v_i W_p}{V_i \rho_p}$$

($\times 10^{12}$ to give readings in microns³).

and $f(t) = (\pi/6)d^3$, or particle volume.

From the response equation, it is apparent that a single calibration of the Counter will provide a basis for estimating the factor for any other aperture size, fluid conductivity, or particle conductivity. However, calibration is comparatively easy and it is advisable to calibrate for each aperture size and each electrolyte.

Where the conductivity ratio, ρ_0/ρ , is very small, as is often the case, a single calibration factor will serve for many materials (e.g. the factor for 1% saline with silica applies to 1% saline with a host of other relatively poor conductors).

Needless to say, there may be occasions when it is desirable or necessary to calibrate the Counter indirectly by fitting the Counter data to that obtained by microscope or other means.

APPENDIX 3

Transfer Function Analysers

Transfer function analysers, or more correctly frequency response analysers (TFA or FRA) have been available for a number of years and although originally intended for electrical engineering applications they have recently been applied to measurements in many other fields. Designs are at present commercially available from several sources, e.g. from Solartron-Schlumberger Ltd. or from SE Labs (EMI) Ltd.

The former was used in the course of the present work, namely the Solartron 1172. Details of circuitry were available only for the SE SM 2001 model but it is not unreasonable to assume that the 1172 operates on a similar principle.

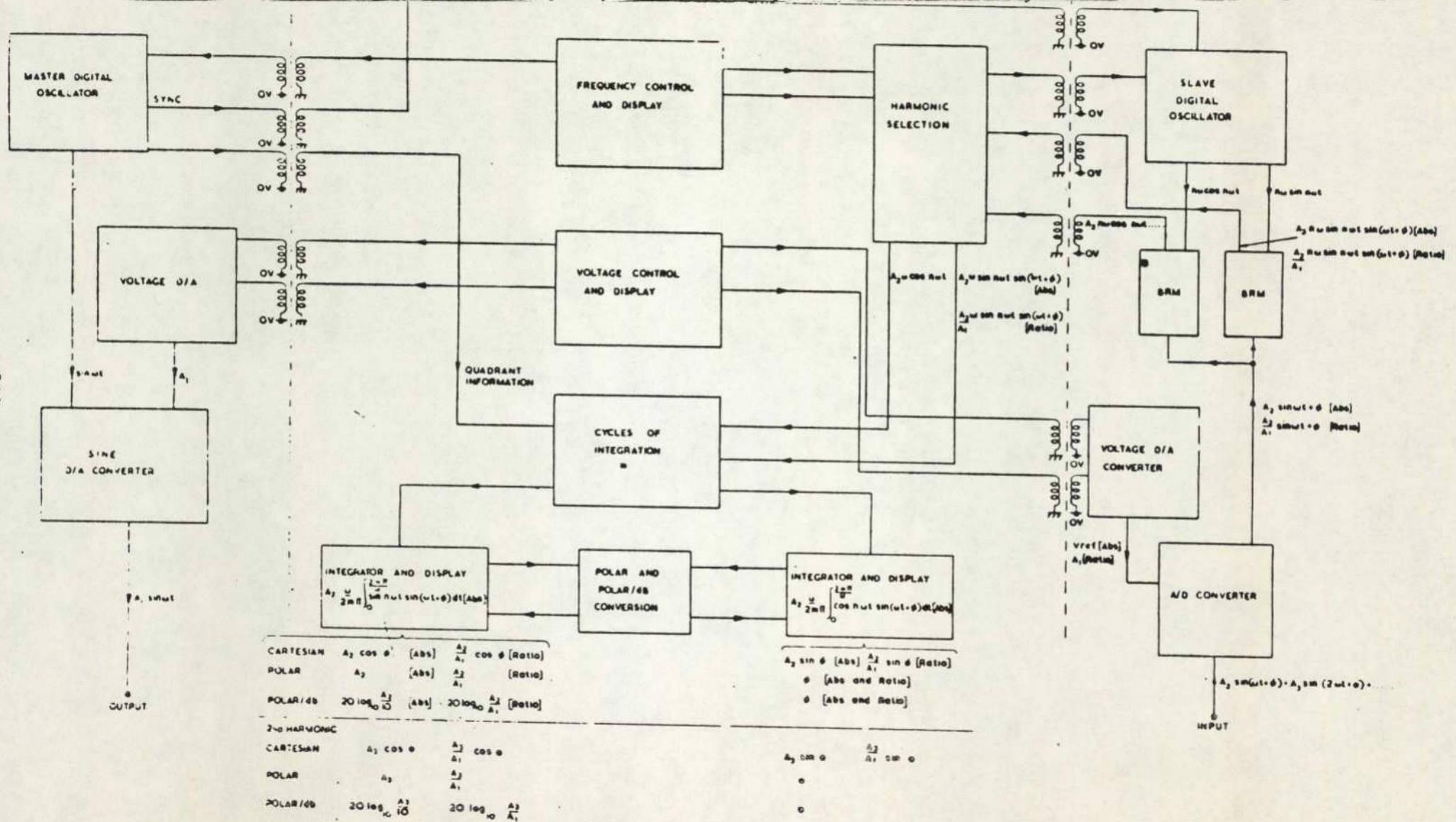
The analyser can be considered to comprise two interconnected sections, a precision digitally controlled sine wave generator and a digital correlator. Digital techniques make it possible to generate and correlate very low frequency waveforms to a high degree of accuracy. The upper limit of the frequency range is determined chiefly by the switching speed of the logic elements used. Frequency multiplication techniques can extend this limit to 1MHz and beyond.

The operating principle of the SM 2001 is best explained with reference to Figure A.3.1, a block diagram of this particular analyser. A master digital oscillator controlled by the frequency control circuitry generates ' $\sin \omega t$ ' waveform. This is fed to the D/A converter which sets the peak amplitude. The waveform is generated in four segments, for each cycle, polarity switching ensures a continuous $A_1 \sin \omega t$ waveform appearing at the generator output.

The input to the correlator will have the general form of $A_2 \sin(\omega t + \phi) + A_3 \sin(2\omega t + \phi) + \dots$, i.e. it will in general contain the fundamental of the output as well as the higher harmonics. The correlator A/D converter changes this to the form of either $A_2 \sin(\omega t + \phi) + \dots$ or $A_2/A_1 \sin(\omega t + \phi) + \dots$ depending on the selected mode. This waveform is multiplied by the $\cos n\omega t$ and $\sin n\omega t$ outputs of a slave digital oscillator using a pair of binary rate multipliers (BRM), n being the selected harmonics. After passing the harmonic selector (set n) and cycles of integration selector (set m) the two waveforms reach a pair

Figure A.3.1 Frequency Response Analyser SM 2001 - Block System.

318



Appendix 3 (continued)

multipliers (BRM), n being the selected harmonic. After passing the ha the harmonic selector (set n) and cycles of integration selector (set m) the two waveforms reach a pair of integrators. These give outputs of

$$A_2 \frac{w}{2m\pi} \int_0^{\frac{2m\pi}{w}} \sin nwt \cdot \sin(wt+\phi) dt = A_2 \cos\phi$$

$$A_2 \frac{w}{2m\pi} \int_0^{\frac{2m\pi}{w}} \cos nwt \cdot \sin(wt+\phi) dt = A_2 \sin\phi$$

i.e. the in-phase and the out-phase components of the input signal at frequency w . The output of the integrator is then converted to polar or polar/dB coordinates if required.

Correlation inherently results in an improvement of the signal to noise ratio, at the expense of bandwidth. This means that instruments of this type are capable of analysing signals containing high levels of noise at frequencies other than that under analysis.

The present generation of TFA's uses TTL logic or MSI type IC's. The next generation is likely to be microprocessor oriented giving a considerable reduction in circuit complexity and possibly cost.

REFERENCES

1. S. Falk and A.J. Salkind—Alkaline Storage Batteries, 54.
2. A. Estelle — British Patent 9,964, (1910).
3. The Modern Ni-Cd Battery, Alkaline Batteries Ltd.
4. S.A. Rozentveig, B.V. Ershler, E.L. Strum and M.M. Ostania, Trudy Soveshehaniya Elektrokhim. Akad. Nauk, SSSR, Otdel. Khim, Nauk, 1950, 571, (1953).
5. K. Huber, J. Electrochem. Soc., 100, 376, (1953).
6. K. Huber and S. Stucki, Helv. Chim. Acta, 51, 1343, (1968).
7. P.E. Lake and E.J. Casey, J. Electrochem. Soc., 105, 52, (1958).
8. P.E. Lake and E.J. Casey, J. Electrochem. Soc., 106, 918, (1959).
9. I. Sanghi, S. Visvanathan and S. Ananthanarayanan, Electrochim. Acta, 3, 65, (1960).
10. S. Yoshizawa and Z. Takehara, *ibid.*, 5, 240, (1961).
11. M.A.V. Devanathan and S. Lakshmanan, *ibid.*, 13, 667, (1968).
12. G.T. Croft, J. Electrochem. Soc., 106, 278, (1959).
13. G.T. Croft and D. Tuomi, *ibid.*, 108, 915, (1961).
14. J.P.G. Farr and N.A. Hampson, Electrochem. Technol., 6, 10, (1969).
15. A.J. Bard, "Encyclopedia of Electrochemistry of the Elements", Marcel Dekker, New York, (1973).
16. L. May, "The Effect of the Electrolyte on the Open-Circuit Potentials in the Nickel-Cadmium Cells", Goddard Space Flight Centre Report X- 711 - 75 - 271, Oct. 1975.
17. P.C. Milner and U.B. Thomas, "The Nickel-Cadmium Cell", Advances in Electrochemistry and Electrochemical Engineering" Vol. 5, N.Y. 1, (1967).
18. N.A. Hampson and R.J. Latham, J. Electroanal. Chem. and Interfacial Electrochem., 32, (3), 337-344, (Oct. 1971).
19. P.E. Lake and J.M. Goodings, Can. J. of Chem., 36, 1089-1096, (1958).
20. J. Harivel, B. Morignat, J. Migeon and J. Laurent, Advances in Battery Technology Symposium, Electrochem. Soc., 219-240, (Dec. 1965).

21. E.M. Jost, Electrochem. Soc. Fall Meeting, Battery Div., Phil., Pa. (Oct 9-14, 1966), Abstract No. 49, pp 130-131.
22. J.A. Keralla and J.J. Lander, Proc. of 17th Annual Power Sources Conference, (May 21-3, 1963).
23. R.D. Armstrong, K. Edmondson and G.D. West, Electrochemistry, Vol. 4, 18-32, (1974), London.
24. K.H. Gayer and L. Woontner, J. Phys. Chem., Vol. 61, 364-365, (1957).
25. R. Visco and R. Sonner, Electrochem. Soc. Fall Meeting, Abstract No. 7, (Oct. 1969).
26. E.J. Casey and C.L. Gardner, J. Electrochem. Soc., Vol. 122, No. 7, (July 1975).
27. D.E. Ryans, J.R. Dean and R.M. Cassidy, Can. J. of Chem., 999, Vol. 13, (1965).
28. R.D. Armstrong, J.D. Milewski, W.P. Race and H.R. Thirsk, J. Electroanal. Chem., Vol. 21, (1969), pp 517-524, (England).
29. Y. Okinaka, J. Electrochem. Soc., 117, pp 289-295, (1970).
30. S. Gilman and L. Sangermano, J. Electrochem. Soc., 118, pp 1953-1957, (1971).
31. R.D. Armstrong, A.D. Sperrin, F.L. Tye and G.D. West, J. Applied Electrochem., Vol. 2, No. 4, pp 265-273, (1972).
32. D.M. MacArthur, "The Anodic Dissolution of Cadmium, Zinc and Silver", Abst. No. 240, 1968 Spring Meeting of the Electrochem. Soc.
33. W.M. Latimer, "Oxidation Potentials", 2nd edn., Prentice Hall, N.Y. (1953).
34. D. Dryssen and P. Lumme, Acta. Chem. Scand., 16, 1785, (1962).
35. Y. Marcus, Acta. Chem. Scand., 11, 690, (1957).
36. J.T. Crennel and F.M. Lea, "Alkaline Accumulators", Lon., (1928), 94.
37. N.F. Budgen, "Cadmium, Its Metallurgy, Properties and Uses", C. Griffin and Co., London, (1924).
38. J.W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. 4, pp 454-473, London, (1952).
39. S.U. Falk, J. Electrochem. Soc., 107, (8), 661-667, (Aug. 1960).
40. S. Yoshizawa and Z. Takehara, "Studies on the Cd Elect., III. An Intermediate Product at the Discharge of the Cd Electrode", Denki-Kagaku, 32, 203, (1964). (See J. Electrochem. Soc., Japan, 32, 59, (1964)).

41. S. Yoshizawa and Z. Takehara, "Studies on the Cd Elect., IV. Overpotential During the Discharge of the Cd Electrode", *Denki-Kagaku* 32, 266, 1964. (See *J. Electrochem. Soc.*, Japan, 1964, 32, 107).
42. A. Fleischer, Quarterly Progress Report, (Dec. 31, 1947), Contract W - 36 - 039 - SC - 32271).
43. R.D. Armstrong, E.H. Boulton, D.F. Porter and H.R. Thirsk, *Electrochim. Acta*. Vol.12, 1967, pp 1245-1248, (England).
44. M.W. Breiter and W. Vedder, *Faraday Soc. Trans.* 63, (1957), 1042.
45. R.W. Ohse, *Z. Elektrochem.*, 64, (1960), 1171.
46. F.G. Will and H.J. Hess, *J. Electrochem. Soc.*, 120(1), (Jan. 1973), 1.
47. R.D. Armstrong and G.D. West, *J. Electroanal. Chem. and Interfacial Electrochem.*, 30(3), 385-393, (May 1971).
48. E.J. Casey, Private Communication.
49. A.A. Abdul Azim and K.M. El-Sobki, "On the Mechanism of the Cd Electrode in Alkaline Solns", Cairo, U.A.R., *Electrochim Acta.*, 17, (1972), 601-608.
50. M.W. Breiter and J.L. Weininger, *J. Electrochem. Soc.*, 113, (1969), 651.
51. O. Glemser, U. Hanschild and H. Richert, *Z. Anorg. Chem.*, 290, (1957), 58.
52. R.S. McEwen, *J. Phys. Chem.* 75, (1971), 1782.
53. K. Appelt, "Batteries", Vol. 2, (Ed. D.H. Collins) Pergamon Press, Oxford, (1965), pp 93-105.
54. Idem. *Electrochim. Acta.* 13, (1968), 1727.
55. P.M. de Wolff, *Acta. Crystallogr.* 21, (1966), 432.
56. G. Bianchi, *Metallurg. Acta.* 46, (1954), 49.
57. M. Fleischmann, K.S. Rajagopalan and H.R. Thirsk, *Trans. Faraday Soc.*, 59, (1963), 741.
58. Y. Okinaka and C.M. Whitehurst, *J. Electrochem. Soc.*, 117, (1970), 583.
59. V.P. Galushko, E.F. Zavgorodnyaya, N.V. Podolskaya and O.K. Tikhaya, *Ukr. Khim. Z.* 38, (1972), 432.
60. V.P. Galushko, E.F. Zavgorodnyaya, N.V. Podolskaya and Yu. P. Rodak, *Elektrokhim.* 8, (1972), 1216.

61. K. Huber, Z. Electrochem., 62, (1958), 675.
62. H. Winkler, Deut. Electrotech., 11, (1957), 223.
63. F. Lange and R. Ohse, Naturwiss, 45, (1958), 437.
64. J.L. Weininger and M.W. Breiter, Power Sources 1966, Symposium Publications Div., N.Y. 1967, pp 269-285.
65. E. Luksha, G.L. Juvinall and C.J. Menard, 9th Intersoc. Energy Conversion Engineering Conf., (1973), pp 881-87, (Paper No 749 125).
66. F. Przybyla and G.R. Ramsay and T.L. O'Nan, Power Sources 4 D.H.Collins, Ed., Sep. 1972, Oriel Press, Newcastle-Upon-Tyne, (Proc. 8th Int. Power Sources Symp), p401.
67. E.J. Casey and J.B. Vergette, Electrochim. Acta., 14(9), 897-907, (Sep. 1969).
68. E.A. Grens and C.W. Tobias, Berichte der Bunsengellschaff, 68(3), pp 236-249, (1964).
69. P. Selanger, J. Appl. Electrochem., 4, 249-57, (1974).
70. P. Selanger, J. Appl. Electrochem., 5, 255-62, (1975).
71. H.Y. Kang, J. Electrochem. Soc., 118, 462-64, (Mar. 1971).
72. P. Bro and H.Y. Kang, J. Electrochem. Soc., Electrochem. Sci., 118(4), 519-524, (April 1971).
73. K. Henson, Chloride Tech. Ltd. internal report, No. 2453, (1976).
74. R.W. Bramham, R.J. Doran, S.E.A. Pomroy and J. Thompson, Power Sources 6, (Proc. 10th Int. Power Sources Symp.) (Ed. D.H.Collins), Acad. Press, London, (1977), p129.
75. E.I. Papazova, V.A. Nikol'sky and N.G. Krivoplyas, Sh. Rab. Khim. 1st Toka 9, (1974), 145.
76. Idem, ibid., 11, (1976), 123.
77. D. Yamashita and Y. Yamamoto, Nippon Kagaku Kaishi 1, (1972), 309.
78. N.V. Kadnikova, L.A. L'vova and I.A. Kazarinov, Z. Prikl. Khim. 51, (1978), 1950.
79. J.P. Harivel, B. Morignat and J. Migeon, "Batteries 2" (Proc. 4th Int. Power Sources Symp.), Pergamon Press, Oxford, (Ed. D.H. Collins), (1964), p107.
80. A.J. Salkind, H.J. Canning and M.L. Block, J. Electrochem. Soc., 2, (1964), 254.
81. E. Lifshin and J.L. Weininger, Electrochem. Tech., 5, (1967), 5.

82. A.H. Reed and J. McCallum, Tech. Report AFAPL - TR - 72 - 20, AD743017, Batelle (1972).
83. A.H. Reed, P.W. Cover and J. McCallum, Tech. Report AFAPL - TR - 69 - 74, Batelle, (1969).
84. R. Barnard, J.A. Lee, A.H. Rafinski and F.L. Tye, Power Sources 5, (Proc. 9th Int. Power Sources Symp.) (Ed. D.H. Collins), Academic Press, London, (1975), p 183.
85. R. Barnard, K. Edmondson, J.A. Lee and F.L. Tye, J. Appl. Electrochem., 6, (1976), 107.
86. E. Luksha, D.J. Gordy and G.J. Menard, J. Electrochem. Soc., 120, (1973), 1447.
87. R. Barnard, G.S. Edwards, J.A. Lee and F.L. Tye, J. Appl. Electrochem. 6, (1976), 431.
88. R. Barnard and G.S. Edwards, unpublished work.
89. J. Marek, J. Mohyla and M. Stompfe, 28th Meeting of ISE, Varna, Extended Abstracts (1977), 397.
90. J. Marek, J. Mohyla, J. Kos and M. Krcek, J. Appl. Electrochem., 9, (1979), 89.
91. E.I. Papazova, G.P. Andreeva and V.A. Nikolskii, Z. Prikl. Khim. 46, (1973), 1693.
92. J.S. Dunning, D.N. Bennion and J. Newman, J. Electrochem. Soc., 118, (1971), 1251.
93. Idem. *ibid.* (1973), 906.
94. H. Gu, D.N. Bennion and J. Newman, *ibid.*, 123, (1976), 1364.
95. H. Gu, T. Katan and D.N. Bennion, *ibid.*, 123, (1976), 1370.
96. R.D. Armstrong, A.D. Sperrin, F.L. Tye and G.D. West, J. Appl. Electrochem. 2, (1972), 251.
97. F.G. Will and H.J. Hess, Final Report, NASA CR - 72777 (Mar. 1971).
98. M.H. Gottlieb, Electrochemical Technology, 5, (1-2), 12-17, (Jan-Feb. 1967).
99. S. Yoshizawa, Z. Takehara and M. Matsui, J. Electrochem. Soc., Japan, (Denki-Kagaku, overseas supplied Ed.), 28, No 1-3, E9-E14 (1960).
100. G. Halpert, Goddard Space Flight Centre Report X-711-75-135, (May 1975).
101. E.J. Rubin, Electrochem. Soc. Fall Meeting, Chic., 111, (Oct. 15-20, 1967), Abstract No. 51, pp134-135.

102. A. Fleischer, "Ni-Cd Batteries", 10th Annual Battery Research and Development Conference, (May 23, 1956), pp 37-41.
103. A. Fleischer, "Electric Battery Plate and Method of Producing the Same", U.S. Patent 2,771,499 (Nov.20, 1956).
104. A. Fleischer, Proc. of the 11th Annual Battery Research and Development Conference (May 22-23, 1957), pp83-86.
105. Per Kofstad, "Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides", Wiley and Sons, N.Y. 1972.
106. A. Fleischer, Private communication.
107. K. Beccu, Private communication.
108. Bureau Technique Gautrat, France, Patent No.685,341.
109. Grubenlampenwerke, Germany, Patent No. 763,452.
110. Accumulatoren-Fabrik Aktiengesellschaft, Germany, Patent No. 784,851.
111. P.V. Vasueva-Rao, T. Vasanthi and H.V.K. Udupa, J. Power Sources, 1, (1976-77), 81.
112. H.F. Gossenberger, PhD Thesis, Polytechnic Institute of Brooklyn, (1959).
113. A. Fleischer, U.S. Patent No. 2,802,043 (1957).
114. K.M. Solo'eva and E.M. Ryzhok, Sb. Rab. Khim. 1st Toka, 9, (1974), 121.
115. E. Kantner, R. Tarantino, P. Ritterman and R.C. Shzir, Technical Report AF/AFL-TR-66-77, (Sep. 1966).
116. G. Rampel, U.S. Patent No. 3,630,781 (Dec. 28, 1971).
117. A.J. Hartner, M.A. Vertes, V.E. Medina and H.G. Oswin, "Fuel Cell Systems" by G. Yong and H. Linden, American Chem. Soc., Washington D.C. (1965).
118. M. Cenek, O. Kouril, J. Sandera, A. Touskova and M. Calabek, "Power Sources 6" (Proc. 10th Int. Power Sources Symp.) (Ed. D.H. Collins), Academic Press, London (1977), p 215.
119. M. Cenek, J. Sandera, A. Touskova, M. Calabek, J. Mrha and J. Jindra, "Power Sources 7" (Proc. 11th Int. Power Sources Symp.) (Ed. J. Thompson) Acad. Press, London, (1979), p 239.
120. O.C. Wagner, J. Electrochem. Soc., 116(5), (1969), 693.
- 120a. O.C. Wagner, "State of the Art Alkaline Cadmium Anodes", Tech. Report ECOM- 3047, (Nov. 1968).
121. E. Willihnganz, Trans. Electrochem. Soc., 92, (1947), 281.

122. E.J. Ritchie, Trans. Electrochem. Soc., 92, (1947), 227.
123. E.J. Ritchie, Trans. Electrochem. Soc., 100, (1953), 53.
124. A.C. Zachlin, J. Electrochem. Soc., 98, (1951), 325.
125. H. Nicklas and H. Jakobljovich, J. Appl. Electrochem. 2, (1972), 165.
126. M.P.J. Brennan and N.A. Hampson, J. Electroanal. Chem. 48, (1973), 465.
127. M.P.J. Brennan and N.A. Hampson, J. Electroanal. Chem. 52, (1974), 1.
128. M.P.J. Brennan and N.A. Hampson, J. Electroanal. Chem. 54, (1974), 263.
129. A.C.C. Tseung and S.C. Dhara, Electrochim. Acta. 20, (1975), 1668.
130. J.J. Bikerman, Physica Status Solidi, 10, (1965), 3.
131. I.G. Bazhal, V.A. Mikhailik, E.N. Shirokikh and L.I. Trebin, Russian J. Phys. Chem. 52(4), (1978), 527.
132. M.C. Inman and H.R. Tipler, Met. Rev., 8, (1963), 105.
133. E.D. Hondros, Proc. Roy. Soc., 286, (1965), 479.
134. G.A. Chadwick and R.M. Meyer, Metals and Metallur. Rev. (May, 1968) 158.
135. H.H. Wawra, Aluminium, 46, (1970), 805.
136. E.D. Hondros, Acta. Met. 16, (1968), 1380.
137. D. McLean and L. Northcott, J. Inst. Metals, 72, (1946), 583.
138. D. McLean, J. Inst. Metals, 85, (1956-57), 468.
139. R.J. Good, Nature, 212, (1966), 276.
140. R.J. Good and L.A. Girifalco, J. Phys. Chem., 64, (1960), 561.
141. A.R. Miedema, Z. Metallkde, Bd 69, (1978) H.S. 287.
142. H. Jones, Metal Sci. Jour., 5, (1971), 15.
143. M.T. Lilburne, J. Mat. Sci., 5, (1970), 351.
144. P.S. Maiya and J.M. Blakely, J. Appl. Phys. 38(2), (1967), 698.
145. C.J. Smithells, "Metals Reference Book", Butterworths (1967).
146. L.F. Bryant, R. Speiser and J.P. Hirth, Trans. of the Met. Soc. of AIME 242, (1968), 1145.

147. D.W.G. White, *Met. Trans.*, 3, (1972), 1933.
148. A.C.C. Tseung, *J. Appl. Electrochem.*, 2, (1972), 137.
149. A.W. Adamson, "Physical Chem. of Surfaces", 2nd Ed. p352, (1967).
150. T. Young, *Miscellaneous Works*, Murray, London, 1, (1855), 418.
151. P.S. de Laplace, *Mechanique Celeste*, Supplement to Book 10 (1806).
152. W.C. Bigelow, D.L. Pickett and W.A. Zisman, *J. Colloid Sci.*, 1, (1946), 513.
153. J.J. Bikerman, *Ind. Eng. Chem., Anal. Ed.*, 13, (1941), 433.
154. Ya. O. Bikerman, "Surface Energy of Solids", Abstracts of papers presented to the 20th Int. Cong. on Theor. and Appl. Chem., Moscow, (1965), 103.
155. G.M. Bulman, Tech. Div. Report No. PP71 (Dec 1976), Chloride Alcad, Redditch.
156. G.M. Bulman, Memo on Iron-Rich Deposits: (Feb. 1977), Chloride Alcad, Redditch.
157. S.W. Mayer, *J. Electrochem. Soc.*, 123(2), (1976), 159.
158. J.L. Dawson, K. Henson and G.M. Bulman, Tech. Div. Report No. SP51, (1975), Chloride Alcad, Redditch.
159. O.C. Wagner, U.S. ECOM. Report 3047, State-of-the-Art Alkaline Cadmium Anodes, 1, (1968).
160. K. Henson, Chloride Technical Report, Project No. 2453, (Mar. 1976), Swinton, Manchester.
161. M.L. Green, private communication.
162. G. Troilius and G. Alfelt, *Power Sources*, (1966), 377, Ed. Collins.
163. G.M. Bulman and M.L. Green, private communication.
164. M. Pourbaix, "Atlas of Electrochemical Equilibria in Aq. Soln.", (1966), Pergamon Press.
165. A.J. Salkind, S.U. Falk and G.J. Venutu, *J. Electrochem. Soc.*, 111, (1964), 493.
166. L. Ojefors, *J. Electrochem. Soc.*, 123(8), (1976), 1139.
167. R.L. Tichenor, *Ind. Eng. Chem.*, 44, (1952), 973.
168. D. Tuomi, *J. Electrochem. Soc.*, 112, (1965), 1.
169. J. Parker, private communication.

170. J.C. Jarrousseau, J. Labat and J.F. Laurent, Power Sources 3, (1970), Brighton.
171. H.G. Silver and E. Lekas, J. Electrochem. Soc., 117, (1970), 5.
172. A.J. Salkind and G.W. Bodomer, "Batteries 2", (Proc. 4th Int. Power Sources Symp.), (Ed. D.H. Collins), Pergamon Press, (1964) 55.
173. R.D. Armstrong, K. Edmondson and J.A. Lee, J. Electroanal. Chem., 63, (1975), 287.
174. A.C. Simon, S.M. Caulder, J.R. Pierson and P. Gurlusky, J. Electrochem. Soc., 117(12), (1970), 1463.
175. A.C. Simon, S.M. Caulder, J.R. Pierson and P. Gurlusky, J. Electrochem. Soc., 121(4), (1974), 463.
176. A.C. Simon, S.M. Caulder, J.R. Pierson and P. Gurlusky, Electrochim. Acta., (1974), 739.
177. M.A.V. Devanathan, J. O'M. Bockris and K. Muller, Proc. Roy. Soc., London, A274 (1963), 55.
178. V.G. Levich, "Physicochemical Hydrodynamics", Prentice-Hall, Englewood, Cliff., N.J. (1962).
179. J.E.B. Randles, Disc. Faraday Soc., 1, (1947), 11.
180. P. Delahay and J.J. Adams, J. Am. Chem. Soc., 74, (1952), 5740.
181. H. Gerischer, Z. Physik. Chem., 202, (1953), 302.
182. K.J. Vetter, Z. Physik. Chem., 199, (1952), 285.
183. J.H. Sluyters, Rec. Trav. Chim., 79, (1960), 1092.
184. Ya. D. Zytner, E.A. Maksinyak, V.A. Nikotskii, N.I. Alekseeva and E.A. Berkman, Elektrokimiya, 7, (1971), 1581.
185. B. Behr and J. Taraszewska, J. Electroanal. Chem., 19, (1968), 373.
186. A.K.N. Reddy, J. Electrochem. Soc., 28, (1970), 217.
187. J.P.G. Farr and N.A. Hampson, Electrochem. Tech., 6, (1968), 10.
188. L.A. L'vova, D.K. Grachev and V.A. Panin, Elektrokimiya, 5, (1969), 627.
189. L.A. L'vova, D.K. Grachev and G.M. Pokatova, Issled. Ott. Khim. Istochnikova Toka., (1970), 10.
190. L.A. L'vova and D.K. Grachev, Elektrokimiya, 7, (1971), 230.
191. R.D. Armstrong and K. Edmondson, J. Electroanal. Chem., 53, (1974), 371.

192. L.E. Rybalka, D.I. Leikis and B.B. Damaskin, *Elektrokimiya*, 9, (1973), 62.
193. L.E. Rybalka, D.I. Leikis and B.B. Damaskin, *Elektrokhimiya*, 9, (1973), 414.
194. L.G. Austin, "Handbook of Fuel Cell Technol.", Ed. C. Berger, Prentice- Hall.
195. J.O'M. Bockris, "Modern Aspects of Electrochemistry", Ed. J.O'M. Bockris, Butterworths Scientific Publications, Lon.(1954).
196. P. Delahay, "Double Layer and Electrode Kinetics", Interscience Publishers, a Div. of J. Wiley and Sons., Inc. N.Y. (1960).
197. R.D. Armstrong, *Corrosion Sci.*, 11, (1971), 693.
198. B.S. Hobbs, P.R. Vassie and A.C.C. Tseung, "Electrochemical Engineering Symposium", Inst. of Chem. Eng. Ed. J.D. Thornton, 1, (1971), 123.
199. A.C.C. Tseung and P.R. Vassie, *Electrochim.Acta.*, 21, (1976), 315.
200. M.S. Jasem, PhD Thesis, (1978), The City University, London.
201. Faraday, *Phil. Trans. Roy. Soc., London*, 124, (1834), 77.
202. Gibbs, *Collected Works*, Vol I, footnote p 325, Longmans, No 1, (1928).
203. LeBlanc, "The Elements of Electrochemistry", p 250, Macmillan London, (1896).
204. Huntington, *Trans. Faraday Soc.*, 1, (1905), 324.
205. Glocker and Kaupp, *Z. Physik*, 24, (1924), 121.
206. J. Erdey-Gruz and M. Volmer, *Z. Physik. Chem.*, 157, (1931), 165.
207. D. Walton, *J. Chem. Phys.*, 37, (1962), 2182.
208. A. Milchev, S. Stoyanov and R. Kaishev, *Thin Solid Films*, 22, (1974), 255, 267.
209. J.A. Harrison and H.R. Thirsk, in A.J. Bard(Ed.), "Electroanal. Chemistry", Vol. 5, Marcel Dekker, N.Y. (1971), p 67.
210. M. Fleischmann and H.R. Thirsk, *J. Electrochem. Soc.*, 110(6), (1963), 688.
211. M. Fleischmann and H.R. Thirsk, *Electrochim. Acta.*, 2(1959), 146.
212. M. Fleischmann and H.R. Thirsk, *ibid.*, 2, (1960), 22.
213. M. Fleischmann and H.R. Thirsk, in "Advances in Electrochemistry", P. Delahay, Ed., Interscience, N.Y. to be published.

- 214. M. Fleischmann and H.R. Thirsk, *Trans. Far. Soc.*, 51(1955), 71.
- 215. I. Dugdale, M. Fleischmann and W.F.K. Wynne-Jones, *Electrochim. Acta.*, 5, (1961), 229.
- 216. M. Avrami, *J. Chem. Phys.*, 9, (1941), 177.
- 217. R.D. Armstrong, M. Fleischmann and H.R. Thirsk, *J. Electroanal. Chem.*, 11, (1966), 208.
- 218. R.D. Armstrong and J.A. Harrison, *J. Electrochem. Soc.*, 116, (1969), 328.
- 219. R.D. Armstrong and A.A. Metcalfe, *J. Electroanal. Chem.*, 63, (1975), 190.