Some aspects of the preparation and behaviour of Plante cell electrodes

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SOME ASPECTS OF THE PREPARATION
AND BEHAVIOUR OF PLANTÉ CELL ELECTRODES

BY

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Doctoral Thesis
Submitted in partial fulfilment of the requirements
for the award of

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of the
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SUMMARY

The anodic behaviour of lead in sulphuric acid was examined using the potentiodynamic method. Simultaneous diffusion-in-solution and solid state reactions were suggested to account for the observed behaviour. The contribution of each process being determined by the sweep rate.

The effects of different anions added to the sulphuric acid solutions on the anodic behaviour of lead were studied. The perchlorate ion was found to be most effective in promoting oxidation of the metal lattice and therefore this ion can be regarded as that most useful for the formation of Planté plates. Less effective than the perchlorate ion was the nitrate, followed in order by the acetate and the fluoroborate ions.

An attempt to use an a.c. ripple superimposed on the d.c. level was used for the formation process. This did not result in a marked increase in the electrode discharge capacity, certainly not exceeding the efficiency achieved in the original Planté technique.

Kinetic studies of lead using the faradaic impedance measurement method have led to the estimation of some parameters, viz, $\alpha$ the transfer coefficient, $K_{sh}$ the reaction rate constant, $C$ the double layer capacitance and $\Delta H$ the enthalpy of activation.
It was concluded that a charge transfer mechanism determines the rate process in nitrate solutions, while in fluoroborate solutions the reaction was complicated by possible adsorption of the additive ion on lead and/or complex formation between lead ions in solution and the fluoroborate ion and its hydrolysis products. Results were not sufficiently comprehensive to make it possible to draw a decision on the actual reason for the complications.

The electrodeposition of lead was studied from simple fluoroborate solutions and from complex solutions containing various organic compounds. The aim was to produce a larger surface area, and thus a greater discharge capacity by virtue of the formation of a dendritic form of lead. A considerable increase in capacity was achieved by this method.

Differential capacitance measurements were used for the detection of surface roughness during lead electrodeposition. This technique proved very informative regarding the shape of the deposit obtained, however, the technique itself was too complicated for use as a tool of detection of surface changes.
I would like to thank my supervisors, Professor R. F. Phillips and Dr. N. A. Hampson, for their help and encouragement they have given to me throughout this work.

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CHAPTER 1

INTRODUCTION
Introduction

1.1 Historical

The storage battery of today grew out of the investigations of many early experimenters. In 1859 Plante devised a battery for the storage of electrical energy, consisting of two sheets of lead separated by strips of rubber and rolled into the form of a spiral. The element thus formed was immersed in dilute 10% H₂SO₄. He studied the charge and discharge of this cell and described it as "storing the chemical work of the voltaic pile". Other experimenters entered the field, but it remained for Plante to develop a valuable form of cell. Plante's name has been perpetuated in connection with the storage battery by the so-called Plante plate.

1.2 Plante Cells

Two main kinds of plates are used nowadays, the Plante plates and the pasted and tubular plates. The latter consist of either a mesh or a set of spines of antimony-lead alloy to which the active material is applied as either a paste or powder of lead compounds. These compounds are then converted into lead dioxide at the positive and sponge lead at the
negative by a 'formation' process. In Plante plates the active material is derived from the body of the plate itself which is made from pure lead.

Due to its mechanical peculiarities, lead dioxide is gradually lost from the positive plate during its life. In forms other than Plante this loss is irretrievable, but in the Plante positive it is made good from the lead of the plate. It is this property which gives the Plante positive its long life. No such cycle of loss and replacement occurs at the negative. Consequently it is short lived and is far too heavy and costly for the service it has to perform. The Plante negative has been superseded, usually by the box negative described later.

Except for certain specialised applications for which a standard flat type of negative is advisable, the box negative is the standard type for use in Plante cells. This consists of a pair of antimony lead alloy frames each with an outer face of perforated sheet lead. The frames are riveted together after applying the active material which is thus enclosed in a number of boxes.

Where a battery is required to have a long life in circumstances where considerations of space and weight are not of paramount importance, the Plante cell has been for many years and still remains supreme. The cells are used on
stand-by applications. They are frequently used in power stations, telephone exchanges and by commercial firms for emergency lighting. Small numbers of cells were being used as stand-by for computers, micro-wave stations and even lighthouses.

1.3 Formation of Planté Plates

The original technique used by Planté for the formation of the plates was to apply a current with periodic reversals of its direction until the plates had acquired sufficient capacity. Sponge (finely divided) lead was formed on the plates and the effective surface was 6 to 10 times greater than the apparent surface. This process is discussed in detail in 4.2.4.

The demand for a more efficient process of formation led to the use of 'forming agents', which were added to the sulphuric acid solution to hasten the formation by chemically attacking the lead of the plate. These include the perchlorates, nitrates, acetates, fluoroborates and fluorosilicates. The whole process takes about a week as against at least six weeks for the old process and increases tremendously the efficiency of the plate.
1.4 Lead Dioxide

Since lead dioxide forms the main topic, its relevant chemistry will be briefly reviewed.

The naturally occurring lead dioxide is known as Plattnerite and it is used in the paste of lead acid grids.

Two main varieties of PbO₂ are known, the β (tetragonal) modification and the α (orthorhombic) modification. The former is the more stable one. Both modifications have been shown to contain hydroxyl groups replacing some oxygen atoms in the lattice structure and all attempts to produce stoichiometric PbO₂ have so far failed.

α- and β- lead dioxide may be distinguished from each other by means of x-ray analysis. This method has been used extensively to estimate the proportion of polymorphs in a mixture of the two by means of the standard diffraction patterns.

The existence of a pseudo tetragonal form (γ) has been suggested by a number of workers. Chemical and thermogravimetric analyses indicated a second polymorph other than the expected β-polymorph in their experiments.
Lead dioxide is highly conducting and has close similarities to metals. Ruetschi and Cahan have suggested that free electrons in lead dioxide may be due in part to OH⁻ groups substituting for oxygen in the lattice.

1.4.1 Standard Electrode Potentials

The potential of the Pb/PbO₂ electrode, which corresponds in acid solutions to

\[ \text{PbO}_2 + 4\text{H}^+ + 4\text{e} \rightleftharpoons \text{Pb} + 2\text{H}_2\text{O} \]

has been determined as 0.666V by Lander⁹.

The PbO₂/PbSO₄ reaction is of the most interest because of the commercial applications,

\[ \text{PbO}_2 + \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e} \rightleftharpoons \text{PbSO}_4 + 2\text{H}_2\text{O} \]

Vosburg and Craig¹⁰ have determined E₀ for the reaction as 1.681V.

Using a Pt/H₂ reference electrode, Hamer¹¹ determined the potential of the lead dioxide/lead sulphate as a function of temperature (0-60⁰C) and H₂SO₄ concentration (0.0005-7 mol l⁻¹) to be:

\[ E_0 = 1.67699 + 2.85 \times 10^{-4}T + 1.2467 \times 10^{-6}T^2 \]
Ruetschi and co-workers\textsuperscript{12,13} found a potential of 1.7085V for the $\alpha$ - lead dioxide/PbSO$_4$ electrode and 1.7015V for the $\beta$ - lead dioxide/PbSO$_4$ electrode with respect to a Pt/H$_2$ reference electrode at 25\textdegree{}C in 4.4 mol l$^{-1}$ H$_2$SO$_4$.

1.4.2 Electrode Reactions in Sulphate Solutions

The electrode reactions taking place on the +ve plate of the lead acid battery have been reviewed by Vinal\textsuperscript{14} and Burbank\textsuperscript{15}. Other articles on the Pb/sulphate systems are summarised in ref. 16 and 17. Generally, the discharge of the cell may be represented by the two oxidation-reduction couples:

\[
PbO_2 + SO_4^{2-} + 4H^+ + 2e \overset{\rightarrow}{=} PbSO_4 + 2H_2O\]
\[E_0 = 1.685V\]

\[
PbSO_4 + 2e \overset{\rightarrow}{=} Pb + SO_4^{2-}\]
\[E_0 = -0.356V\]

giving a cell reaction of

\[
PbO_2 + 2SO_4^{2-} + 4H^+ + Pb \overset{\rightarrow}{=} 2PbSO_4 + 2H_2O\]
\[E = 2.041V\]

and in more detail:
$\text{PbSO}_4$  \[\text{Pb}^{2+}\]  \[\text{SO}_4^{2-}\]  \[2\text{H}^+, \text{H}_2\text{O}^-, 2\text{H}^+\]

$\text{H}_2\text{SO}_4$  \[\text{Pb}^2+\]  \[\text{SO}_4^{2-}\]  \[-2\text{e}\]

$\text{PbO}_2$  $2\text{H}_2\text{O}^+$

negative plate  positive plate
1.4.3 The Nucleation of Lead Dioxide on PbSO$_4$:

For the formation of lead dioxide deposits on PbSO$_4$, it is necessary to form lead dioxide nuclei which act as active centres for the spreading of lead dioxide through the bulk of the material. Fleischmann, Thirsk and co-workers have considered the conversion of lead sulphate to lead dioxide in some detail$^{18,19}$. The current-time data was found to obey a cubic law of the form:

$$i = \frac{ABt^3}{3},$$

where $A$ is the nucleation constant, $B$ is a potential dependent constant and $t$ is time. The rate of the oxidation was found to reach a maximum and then exponentially decay. It was assumed that the growth of a lead dioxide centre was confined to discrete single lead sulphate crystals and that the decay was due to the completion of the reaction. The relationship connecting the number of nuclei and time was shown to be

$$N = N_0 (1 - \exp (-At)), $$

where $N$ is the number of nuclei on unit surface and $N_0$ the maximum number of nuclei on unit surface.
1.4.4 The Self Discharge of Lead Dioxide Electrodes

One disadvantage of the preparation of lead dioxide electrodes on a lead basis is that reaction between the lead dioxide and the underlying Pb lattice is able to proceed in the solid phase. Due to the high electronic conductivity of lead dioxide electron exchange facilitates the formation of Pb (II) ions able to react with O²⁻ ions to form a non-conducting PbO layer.
1.5 **Aim of the Work**

The purpose of the present study is to provide information concerning the oxidation of lead to lead dioxide (and the reverse process) in electrolytes based on sulphuric acid. This will enable the main features of the process by which positive Planté plates are produced to be described. Further investigation will extend the study to mixed electrolytes containing fluoro-borates, acetates and nitrates.

The possibility of the replacement of the attack process by direct superimposition of an a.c. component on the d.c. used for charging the plate will also be considered.

For this, a systematic investigation of the anodic oxidation of lead in \( \text{H}_2\text{SO}_4 \), then in perchlorate - containing \( \text{H}_2\text{SO}_4 \) solutions was the starting point of the work.
CHAPTER 2

THEORETICAL PRINCIPLES
CHAPTER 2

Theoretical Principles

2.1 The Electrode-Electrolyte Interphase

The system considered is that of a metal in contact with an aqueous electrolyte. Ions are the charge carriers in the electrolyte and electrons the charge carriers in the metal. Since ions have a finite size, it is impossible to build up a charge layer infinitesimally small and therefore immediately associated with the metal surface. Thus, for this initial layer of ions, a potential profile can be drawn commensurate with the size of the ions and their attendant charge. The potential profile continues to be modified normal to the electrode surface, by a diffuse concentration gradient of ions into the bulk of the electrolyte. In contrast, the charge to mass ratio of the electrons in the metal makes the introduction of concentration vectors for charge carriers in the metal unnecessary in the discussion of the overall energetics of the interphase. Thus, the charge on the metal can be regarded as in infinitesimally thin layer immediately associated with the metal surface. Disregarded in this discussion is the inhomogeneity of charge due to the exposure of different crystal planes in dimensions parallel to the surface of the electrode.
The overriding factor in the overall control of charge transfer across the interphase is the structure of the electrolyte in the interphase, and thus the potential profile in this region. Knowledge of this structure is therefore essential to the understanding of the mechanism of charge transfer. The earliest model of the electrical double layer at an electrode/electrolyte interphase was put forward by Helmholtz who stated that in order to maintain a potential across the boundary, one phase must carry a positive charge and the other a negative charge equal in magnitude, approximating to a parallel plate condenser. From thermodynamic considerations such a system is not stable and values of the differential capacitance calculated using this model did not agree with experimental results.

Gouy modified the above theory by regarding the charge distribution in the electrolyte as having a diffuse nature, brought about by the thermal motion of ions. Chapman developed the concept that the electrostatic force must be equal to the osmotic pressure of the ions. The theory however did not take into consideration the finite size of the ions although the basic concept proved to be substantially correct. Their calculation was very similar to the ionic atmosphere theory of Debye and Hückel, the solution side of the double layer effectively act as an ionic atmosphere of the electrode.
Stern\textsuperscript{24} was the first to suggest the concept of a plane of closest approach for ions and considered the electrical double layer to consist of two parts, a compact layer and a diffuse layer extending into the solution. Grahame\textsuperscript{25} improved the Stern model by considering specific adsorption of ions and represented the double layer as:

a) The inner Helmholtz plane which is governed by the plane of closest approach of the solvent dipoles and specifically adsorbed ions.

b) The outer Helmholtz plane which is determined by the plane of closest approach of the solvated cations.

Fig. 1 shows a model of the electrode-electrolyte interphase\textsuperscript{26}, and Fig. 2 illustrates the electrical analogue of the interphase.

Grahame\textsuperscript{25} showed that the total double layer capacitance is represented by:

\[
\frac{1}{C_L} = \frac{1}{C_{\text{diff.}}} + \frac{1}{C_{\text{comp.}}} \quad \text{............... 2.1}
\]

where \(C_L\) is the double layer capacitance, \(C_{\text{diff.}}\) the capacitance of the diffuse layer and \(C_{\text{comp.}}\) the capacitance of the compact layer. A relationship for the diffuse layer
Fig. 1. Possible structure of a metal electrolyte interface (Bockris et al., 1963)
(a) Charge transfer and diffusion control.

\[ R_E \] Ohmic resistance of electrolytic system.
\[ C_L \] Double layer capacitance.
\[ R_D \] Charge transfer resistance.
\[ R_d \] Diffusion resistance.
\[ C_d \] Diffusion capacitance.

(b) Charge transfer, diffusion and crystallisation control.

\[ R_K \] Lattice crystallisation resistance.
\[ C_K \] Lattice crystallisation capacitance.

Fig. 2. Electrical analogues of the electrode interphase.
capacitance is given by (at 25°C): 

\[ C_{\text{diff.}} = 228.5 \frac{Z}{(C^S)^{1/2}} \cosh \left( 19.46 \frac{Z}{q_n} \right) \]  

where \( Z \) is the charge of the ion concerned, \( C^S \) the bulk concentration of the electrolyte and \( q_n \) is the potential at the plane of closest approach.

This expression predicts that as \( q_n \) passes through zero, the diffuse layer capacitance goes through a characteristic minimum. Also, \( C_{\text{diff.}} \) decreases with decreasing bulk concentration of electrolyte near the potential of zero charge, \( E_Z \). Thus for electrolyte solutions of sufficiently low concentration, the measured capacitance vs potential curves approximate to the diffuse layer capacitance curves.

Further corrections to the above double layer theory have been introduced concerning the finite size of the ions in the diffuse layer, dielectric saturation, polarisation of the components of the system, the association effect, and the self atmosphere effect. Barlow and McDonald, and Levine and Bell have considered the discreteness of charge effect on the double layer but this has been only interpreted for the diffuse layer.

The value of the pzc that can be obtained from the differential capacitance - bias potential curves for low electrolyte
concentrations has been shown by Frumkin\textsuperscript{35} to be of major importance. It determines the charge on the electrode, hence the extent of adsorption at the surface. The charge is determined by the quantity $E - E_z$, which is termed the rational potential $E_{\text{rat}}$. At positive $E_{\text{rat}}$, adsorption of negative ions is favoured while at negative $E_{\text{rat}}$, positive ions are attracted to the electrode. When $E_{\text{rat}}$ is small, adsorption of neutral ions or molecules competes favourably with ionic adsorption.

Kabanov et al.\textsuperscript{35} came to the conclusion that the diffuse double layer theory could be applied to lead dioxide electrodes; they have estimated the pzc for this electrode from a minimum in the capacitance curve.
Charge and Mass Transfer Kinetics

Electrode processes are reactions which can be divided into 3 consecutive steps: electron transfer at the electrode, transfer of the species being electrolysed toward the electrode, and removal of the reaction products. The overall rate at which an electrode reaction proceeds generally depends on the kinetics of these 3 steps. An addition adsorption phenomena may have to be considered and there may be complications resulting from the coupling of the electron transfer process with purely chemical reactions.

Three modes of mass transfer should be considered, namely diffusion, convection and migration. Diffusion is observed whenever there exists a difference of concentration of solute. Convection results from stirring of the solution by a mechanical device and even in the absence of any external stirring - by differences in densities from one point of the solution to another as resulting from a gradient of concentration or temperature.

Migration is the motion of charged particles in an electric field. This is negligible in fairly concentrated solutions as the contribution of the reducible or oxidisable ion in 'carrying' the current is negligible in comparison to the supporting electrolyte.
2.2 Charge Transfer Kinetics

For the simple overall electrode reaction, \( 0 + z e = R \), the free energy barrier considerations have been discussed by Vetter\(^{37} \) and Delahay\(^{38} \). The transference of charge across the double layer gives rise to an overpotential \( \eta_D \). For such a process, the current overpotential relationship has been derived by Erdy-Gruz and Volmer\(^{39} \):

\[ i = i_0 \exp \left( -\alpha \frac{ZF \eta_D}{RT} \right) - \exp \left( (1-\alpha) \frac{ZF \eta_D}{RT} \right) \quad \text{2.3} \]

where \( i_0 \) is the exchange current and depends on the concentrations of the reactants and products as:

\[ i_0 = ZF k_o \left( C_0 \right)^{1-\alpha} \left( C_R \right)^{\alpha} \quad \text{2.4} \]

\( \alpha \) is the charge transfer coefficient, 
\( k_o \) the heterogeneous rate constant, 
\( C_0 \) and \( C_R \) the concentrations of \( 0 \) and \( R \) respectively, and \( Z, R, T, F \) have their usual meanings. Horiuti and Polanyi\(^{40} \) have also obtained this equation using a quantum mechanical treatment.

The charge transfer coefficient has been shown by Marcus\(^{41} \) to be a function of several terms which are dependent on potential. However, if the potential is not far removed from the equilibrium potential (\pm 250 \text{ mV}) and the double
layer effects are reduced by using an excess of the supporting electrolyte, \( \alpha \) becomes independent of potential.

Equation 2.3 reduces to a linear relationship for low overpotentials \((\eta_D < 7 \text{ mV})\), and on differentiation it gives

\[
-\left( \frac{d(i)}{d\eta_D} \right) \eta_D \rightarrow 0 = \frac{ZF}{RT} i_0 \quad \text{............... 2.5}
\]

\( -\frac{d(i)}{d\eta_D} \) is constant and the reciprocal of which is analogous to a simple resistance termed the charge-transfer resistance as is given by

\[
R_D = \frac{RT}{ZF} \cdot \frac{1}{i_0} \quad \text{............... 2.6}
\]

At higher overpotentials \((\eta_D > 50 \text{ mV})\), the rate of the reaction opposed by the overpotential is reduced, hence for cathodic overpotentials:

\[
i = i_0 \exp \left( -\frac{ZF}{RT} \right) \eta_D \quad \text{............... 2.7}
\]

and

\[
\ln i = \ln i_0 - \frac{ZF}{RT} \eta_D \quad \text{............... 2.8}
\]

\[
\eta_D = \frac{RT}{\alpha ZF} \ln i_0 - \frac{RT}{\alpha ZF} \ln i \quad \text{............... 2.9}
\]

which is the Tafel equation \( \eta = a - b \log i \).
\[ a = 2.303 \frac{RT}{\alpha ZF} \log i_0, \]

\[ b = 2.303 \frac{RT}{\alpha ZF} \]

For an anodic process:

\[ \eta_D = \frac{RT}{(1-\alpha)ZF} \ln i_0 + \frac{RT}{(1-\alpha)ZF} \ln i \quad \ldots \ldots \quad 2.10 \]

Hence the magnitude of the exchange current density may be obtained from high overpotential measurements extrapolated back to the equilibrium potential.

From equation 2.4, maintaining one of the components \( R \) or \( \alpha \) constant whilst varying the other it follows that,

\[ \left( \frac{\partial \ln i_0}{\partial \ln C_R} \right)_{\alpha, \theta, T} = \alpha \]

\[ \left( \frac{\partial \ln i_0}{\partial \ln C_0} \right)_{\alpha, \theta, T} = (1-\alpha) \]

Hence the value of \( \alpha \) may be deduced from the slope of the linear plot of \( \log i_0 \) versus \( \log C \).
2.3 **Mass Transfer Kinetics**

The case considered is that of a plane electrode immersed in a solution of a substance $0$ that is reduced to $R$ at the electrode surface. The current flowing depends on the kinetics of the electrochemical reaction and on the rate of mass transfer of the substances involved in the electrode process. When the electrochemical reaction is reversible, mass transfer with diffusion control in unstirred, fairly concentrated solutions will control the current totally.

The rate of diffusion of substance $0$ per unit area, according to Fick's first law, termed the flux, $q$ at a distance $x$ perpendicular to the electrode is given by

$$q(x,t) = D_0 \frac{\partial C_0(x,t)}{\partial x} \quad \cdots \cdots \cdots \cdots \cdots 2.11$$

The proportionality factor $D_0$ is the diffusion coefficient, $t$ is the time elapsed since the beginning of the electrolysis. The rate of change of concentration $C_0(x,t)$ at distances $x$ and $x + dx$ is

$$\frac{\partial C_0(x,t)}{\partial t} = \frac{\partial}{\partial x} \left[ D_0 \left( \frac{\partial C_0(x,t)}{\partial x} \right) \right] \quad \cdots \cdots \cdots \cdots \cdots 2.12$$

$D_0$ is a function of the concentration $C_0(x,t)$ and consequently a function of the variable $x$. However, in presence of a
large excess of supporting electrolyte the ionic strength is virtually independent of the concentration of substance 0, one can assume that $D_0$ is independent of $x$.

Equation 2.12 can be written

$$\frac{\partial C_0(x,t)}{\partial t} = D_0 \frac{\partial^2 C_0(x,t)}{\partial x^2} \quad \ldots \quad 2.13$$

This is the fundamental equation for linear diffusion 'Fick's second law'.

**Initial and Boundary Conditions:**

(1) When substance 0 is reduced at a very high rate it may be assumed that

$$C_0(o,t) = 0 \quad \text{for } t > 0$$

(2) The concentration of $C_0$ before the electrolysis is equal to the bulk concentration $C^0$, thus

$$C_0(x,0) = C^0$$

(3) Also $C_0(x,t)$ approaches $C^0$ when $x$ tends to infinity.

The solution of equation 2.13 under these conditions is given by:

$$C_0(x,t) = C^0 \text{erf} \left( \frac{x}{2D_0 \frac{1}{2} \frac{1}{2}} \right) \quad \ldots \quad 2.14$$
The notation \( \text{erf}(\lambda) \) represents the error integral defined by the formula

\[
\text{erf}(\lambda) = \frac{2}{\sqrt{\pi}} \int_{0}^{\lambda} \exp(-z^2) \, dz
\]

where \( z \) is an auxiliary variable.

The most important properties of the error function are: the error function is equal to zero when its argument is equal to zero, and the function approaches unity when \( \lambda \) becomes sufficiently large (larger than 2). From equation 2.14 it is seen that for a given electrolysis time, the argument of the error function increases as \( x \) increases. Thus, for a given value of \( t \), the concentration \( C_0(x,t) \) increases with \( x \). Conversely, for a given distance from the electrode, the concentration \( C_0(x,t) \) decreases during electrolysis.

The current is equal to the product of the charge involved in the reduction of one mole of substance 0 by the flux of this substance at the electrode surface. Thus, for a plane electrode of area \( A \) the current is

\[
i = nFAq(o,t) \quad \text{.......................... 2.15}\]

\( n \) is the number of electrons involved in the reduction of 0, \( F \) is the faraday and \( q(o,t) \) is the flux of substance 0 for \( x = 0 \).
The flux is readily obtained by differentiating equation 2.14 with respect to \( x \) and introducing the value \( x = \sigma \) in the resulting formula. The value of \( q \) obtained in this manner is introduced in equation 2.3.5, thus the value of current is given by:

\[
i = nF \frac{D_0^{1/2} C_0}{\pi^{1/2} t^{3/2}} \quad \text{............... 2.16}
\]

\( i \), in amperes, \( F \) in coulombs, \( A \) in cm\(^2\), \( D_0 \) in cm\(^2\). sec\(^{-1}\), \( C_0 \) in moles per cubic centimeter and \( t \) in seconds.

Two important properties of \( i \) can be deduced from the above equation:

1. the current at any time is proportional to the concentration of the substance being reduced at the electrode,
2. the current is inversely proportional to the square root of time.

Equation 2.16 is also valid in the case of an anodic process. This equation has been verified experimentally by Laitinen and Kolthoff\textsuperscript{[14]}, and by Laitinen\textsuperscript{[15]}. Good agreement between theoretical and experimental results was obtained by these authors.
CHAPTER 3

POTENTIODYNAMIC STUDIES
CHAPTER 3

Potentiodynamic Studies

3.1 Theory of Potentiodynamic (L.S.V.) Method:

In the potentiodynamic method a potential, varying linearly with time is applied to the electrode. This potential $E$, of the electrode at which the substance $O$ is reduced (or $R$ is oxidised) is a linear function of time according to,

$$E = E_i - vt$$

where $v$ is the rate of potential change in volt sec$^{-1}$ and $E_i$ the initial potential. $E_i$ is adjusted to a value at which substance $O$ is virtually not reduced. As the potential increases in the proper direction, the rate of electron transfer at the electrode increases and the current increases accordingly. The substances reacting at the electrode are progressively removed from the solution in the immediate vicinity of the electrode causing a current limitation. As this limitation becomes more severe, the current-potential curve develops a maximum. The magnitude of the maximum current is proportional to the concentration at the electrode of the species which controls the current flow.
For the reversible formation of an insoluble substance by a cathodic reaction, Berzins and Delahay\(^{16}\) assuming linear diffusion, applied the general theory of Randles\(^{47}\) and Sevcik\(^{18}\) and obtained the relationship:

\[
I = -\frac{2}{\pi} \frac{Z^\frac{3}{2}}{R^\frac{3}{2}} \frac{F}{T^\frac{3}{2}} AD^\frac{1}{2} CV^\frac{1}{2} \Phi(\lambda) \quad 3.1
\]

where

\[
\Phi = \exp\left(-\lambda^2\right) \int_{-\infty}^{\lambda} \exp\left(p^2\right) dp
\]

and

\[
\lambda = \left(\frac{ZFv}{RT}\right)^\frac{1}{2} = -\left[\frac{ZF\left(E-E_i\right)}{RT}\right]^\frac{1}{2}
\]

\(I\) is the current density, \(D\) is the diffusion coefficient of the electroactive substance \(s\), \(C\) (mol.l\(^{-1}\)) is the bulk concentration of \(s\), \(v\) (vs\(^{-1}\)) is the rate of potential change, \(p\) is an ancillary variable, \(E\) is the potential of the system at a particular point in time and \(E_i\) is the initial potential of the sweep.

When \(\Phi(\lambda)\) passes through a maximum, the current density \(I\) shows a maximum value \(I_m\), which at \(25^\circ\)C is given by\(^{46,49}\):

\[
I_m = -3.67 \times 10^5 Z^\frac{3}{2} D^\frac{1}{2} CV^\frac{1}{2} \quad 3.2
\]

where \(I_m\) is the current density in mA/cm\(^2\), \(D\) in cm\(^2\) sec\(^{-1}\).
Similar equations can be deduced for an anodic reaction. The theory of Berzins and Delahay\textsuperscript{46} assumes reversibility of the system and that the activity of the deposit is equal to unity, equation 3.1 only strictly holds for solid-metal ion electrodes where only pure diffusion overpotential is present.
3.2 Experimental Techniques

3.2.1 The Cell:

A pyrex glass cell of ~ 200 ml capacity with grease-free ground glass openings a, b and c for the working, counter and reference electrodes respectively was used (Fig. 3). The reference electrode compartment was connected to the main compartment via a luggin capillary opening directly beneath the electrode surface. The luggin capillary ideally should not shield any part of the electrode surface, and not increase the ohmic resistance between the working electrode and the tip of the luggin/reference electrode. The best compromise is to make the distance between the luggin capillary and the electrode surface about 0.5 mm. In the present experiments where the ohmic resistance could be assessed it was found to be insignificant.

The counter electrode was surrounded by a glass tube ending with a glass frit as shown in Fig.

3.2.2 The Electrolyte:

Analar H₂SO₄ was used, water, doubly or triply distilled from deionised stock was used for the preparation and dilution of solutions. Other chemicals used were of the Analar grade.
Fig. 3. Cell for potentiodynamic studies
3.2.3 The Electrodes:

Polycrystalline lead electrodes were prepared by introducing a lead wire (99.999% purity, Johnson and Matthey) of 3 mm diameter, into a glass tube. A polythene sheath was then formed around the end of the wire as shown in Fig. 4. The electrode is fitted in the cell by means of a 'quickfit' adaptor with a teflon sleeve for easy adjustment of height. The electrode was cut perpendicular to the long axis, exposing a surface area of 0.0706 cm$^2$.

The counter electrode was a Pb rod of the same purity, 7 mm diameter and 3.5 cm length thus exposing a large surface area. It was fitted into a glass support with polythene as described above.

A Hg/Hg$_2$SO$_4$/M Na$_2$SO$_4$ electrode (654 mv vs N.H.E.) was used as a potential reference. All potentials given throughout this chapter will be relative to this electrode unless otherwise stated.

3.2.4 Treatment of the Electrode:

Before each experiment the electrode was immersed in a saturated ammonium acetate solution to dissolve off any surface oxide layer, washed repeatedly with water, mechanically polished on roughened glass using water as a lubricant.
Fig. 4. The electrode
and finally wiped gently with filter paper. For the high concentration perchlorate containing solutions, a freshly cut surface of the electrode was prepared before each experiment. For this operation a sharp scalpel was quite adequate.
3.3 Sulphuric Acid Solutions: Results

3.3.1 Potentiodynamic Measurements in 3 M H₂SO₄:

Anodic potentiodynamic sweeps of lead were made using different sweep speeds ranging between 1.33 and 33.3 mv/sec⁻¹. The electrode was held at a negative potential for 2 min before the experiment was commenced. Hydrogen was evolved at this stage which ensured that the electrode was completely freed from any oxide film. This is similar to the cleaning process conventionally used in the production of Plante' plates.

Fig. 5 shows a typical linear sweep voltammogram in 3 M H₂SO₄. A rapid decrease of current is observed when the potential is changed positively from the potential of the h.e.r. Only one sharp anodic peak (a) appears on the curve; it occurs at about -0.95V. At the positive limit of the sweep (about 1.4V) O₂ evolution commences.

The relation between the peak current i_max and the sweep rate s.r. is shown in Fig. 6, in which a curve was obtained by plotting i_max against \( \sqrt{s.r.} \). The plot tended to the origin at very low sweep rates.
Fig. 5. Anodic potential sweep for lead in 3M H₂SO₄

s.n. = 6.67 mv/sec
A = 0.0706 cm²
Fig. 6. Anodic peak current-√sweep rate for PbSO₄ formation on lead in 3 M H₂SO₄.

A = 0.0705 cm²
3.3.2 Potentiodynamic Measurements in M and 0.5 M H$_2$SO$_4$:

In these two solutions the main anodic peak (a) is followed by a flat plateau (b) at about -0.5V as represented in Fig. 7a,b. The $i_{\text{max}} - \sqrt{s.r.}$ relationship shows the same general shape (Figs. 8,9) as that shown in Fig. 6. The lower slope region of the curve, however, extended over a somewhat larger range sweep speeds than in the more concentrated solution.

3.3.3 Potentiodynamic Measurements in 0.1 M H$_2$SO$_4$:

The same features of the anodic curve as observed in the case of the 3M, 1M and 0.5M H$_2$SO$_4$ solutions are observed in this solution as represented in Fig. 10. There is a main difference, however, in the effect of the sweep speed on $i_{\text{max}}$. Fig. 11 shows a straight line relationship passing through the origin for this solution.
Fig. 7a. Anodic potential sweep for lead in $\text{M H}_2\text{SO}_4$.
Fig. 7b. Anodic potential sweep for lead in 0.5M H₂SO₄.
Fig. 8. Anodic peak current vs sweep rate for PbSO₄ formation on lead in M H₂SO₄
Fig. 9. Anodic peak current—sweep rate for PbSO$_4$ formation on lead in 0.5M H$_2$SO$_4$. 

\[ A = 0.0706 \text{ cm}^2 \]
Fig. 10. Anodic potential sweep for lead in 0.1 M H₂SO₄
Fig. 11. Anodic peak current-$\sqrt{\text{sweep rate}}$ for PbSO$_4$ formation on lead in 0.1 M H$_2$SO$_4$. 

A = 0.0706 cm$^2$
3.3.4 Discussion

The position of the sharp peak (a) at about -300 mV (NHE) agrees well with the potential of the system Pb/PbSO₄, \( E_0 = -318 \text{ mV (NHE)} \). 

The plateau observed around +150 mV (NHE) has been attributed\(^8,12,52,53\) to the formation of another compound under the PbSO₄ layer where alkaline conditions may well prevail. This could possibly be tetragonal PbO, basic lead sulphates or Pb(OH)\(_2\). Burbank\(^52\) has suggested that the formation of tetragonal PbO or Pb(OH)\(_2\) and the consequent build up of a sandwich structure\(^54,55\) such as Pb.PbO.PbSO₄, rather than Pb • oxy lead salt • PbSO₄\(^56\) at the electrode occurs.

No discrete peak corresponding to the formation of PbO\(_2\) was observed. This agrees with earlier observations that PbO\(_2\) is always masked by O\(_2\) evolution in the potential range of 2000 mV (NHE) and higher. A well known high overpotential of PbO\(_2\) formation is reported\(^57\) in the literature. Many authors\(^8,12,52,58\) have suggested that \( \alpha \) and \( \beta \) modifications of PbO\(_2\) were formed on the electrode surface, the \( \alpha \) modification being formed next to the electrode surface as a result of the oxidation of PbO\(_2\) and \( \beta \) PbO\(_2\) adjacent to the electrolyte being formed from PbSO₄ when oxidised.
On the whole, however, our observations are in agreement with the generally accepted behaviour\textsuperscript{59-62} of lead under potentiodynamic and potentiostatic conditions.

**Effect of Sweep Speed**

In the anodic oxidation of lead in sulphuric acid solutions the rate of passivation may be controlled by either:

1. diffusion of $\text{SO}_4^{2-}$ and $\text{HSO}_4^-$ in solution,
2. transport of charge and mass through an insoluble layer at the electrode,
3. charge transfer between lead atoms in the lattice and lead ions either in solution or adsorbed at the electrode.

It is of interest to investigate which of these processes is rate controlling. The charge transfer step (3) is unlikely since the standard rate constant for the Pb (II)/Pb reaction is very large.

In case of the very dilute $\text{H}_2\text{SO}_4$ solution a linear relationship between $i_{\text{max}}$ and the sweep speed is observed. If we assume that equation 3.2 applies, we can calculate $D$, the diffusion coefficient of the rate controlling ion in
solution. This gives a value of $3.64 \times 10^{-7}$ cm$^2$ sec$^{-1}$ for 0.1 M H$_2$SO$_4$, which is considerably lower than the $D$ value generally accepted for the sulphate ion $1.08 \times 10^{-5}$. This suggests that the rate controlling process is not purely diffusional in solution, but a certain contribution of solid phase diffusion across the sulphate film exists (i.e. a parallel solid phase and solution phase process).

For higher sulphuric acid concentrations, the correlation between the peak currents and the sweep rates did not show linearity. That the lines of Figs. 6, 8 and 9 were curves might possibly be due to experimental error. This, however, was not very likely because of the reproducibility of the data. Moreover, straight lines over the whole of the experimental region were observed in the case of 0.1 M H$_2$SO$_4$ and there is no reason to expect the absence of any error in this case which was apparent in the others. In fact, the ohmic error due to luggin position might be expected to be greater in the dilute solution.

These curves may be interpreted in terms of a change in the nature of the sulphate film formed on the electrode surface. At the lower sweep speeds the PbSO$_4$ film is expected to be formed of fine crystals firmly attached to the surface, thus the 'solid phase diffusion' contribution to the rate controlling process is larger and since this would have the lower diffusion coefficient result in a lower slope of
Using higher sweep speeds the film will probably form via a solution-precipitation mechanism, i.e., PbSO₄ crystals being formed in solution then depositing on the electrode surface, thus being less adherent. Consequently a higher contribution of diffusion in solution to the rate control holds.

A further test of this postulation was made by measuring the limiting slopes of each curve at both ends. The limiting slope near the origin, $S_1$, is that corresponding to a solid state diffusion dominated mechanism, while the limiting slope at the other end of the curve, $S_2$, corresponds to a relatively higher contribution of diffusion in solution. It is emphasized, however, that the solution diffusion process is not the dominating rate control. When $S_1$ and $S_2$ values were plotted as a function of concentration, the curves I and II shown in Fig. 12 respectively were obtained. Curve I shows a more or less constant value, but curve II has a clear maximum at the concentration of 1 M H₂SO₄ which agrees approximately with the concentration of highest solubility of PbSO₄ in sulphuric acid (compare Fig. 13 from Vinal¹⁴).

Carr and Hampson⁶¹ have suggested that both diffusion in solution and diffusion through the solid phase influence
Fig. 12. Relation between concentration of sulphuric acid and slopes of $i_{\text{max}} - (\text{s.r.})^{1/2}$.
Fig. 13: Solubility of lead sulphate in solutions of sulphuric acid
the rate controlling process during potential sweep measurements. Archdale and Harrison\textsuperscript{63-64} have investigated the problem of PbSO$_4$ formation on solid lead under potentiostatic conditions. They concluded that at low anodic potentials Pb$^{2+}$ dissolves predominantly, whereas at more anodic potentials PbSO$_4$ crystals are formed via a solid state reaction or a solution - precipitation mechanism. Mathematical models for both the solid state reaction mechanism\textsuperscript{65,66} and the dissolution - precipitation mechanism\textsuperscript{64,67} are given in the literature.
3.4 Sulphate - Perchlorate Mixtures

Results

3.4.1 Potentiodynamic Measurements in M \( \text{H}_2\text{SO}_4 \) + 0.05 M \( \text{KClO}_4 \):

In presence of the perchlorate ion in solution, the anodic peak (a) was not much influenced either in shape or in magnitude. However, the plateau appearing at \(-0.5\) \( \text{V} \) was more clearly apparent (Fig. 14). This plateau is replaced by a small peak at about \(-0.7\) \( \text{V} \) (c) at the higher sweep speeds as illustrated in Fig. 15 corresponding to a speed of 13.3 mV/sec.

The sweep speed – peak current relationship shown in Fig. 16 is similar to that obtained in M \( \text{H}_2\text{SO}_4 \) (Fig. 8).

3.4.2 Potentiodynamic Measurements in 0.5 M \( \text{H}_2\text{SO}_4 \) + 0.02 M \( \text{KClO}_4 \):

No effect on the sulphate peak was observed in this mixed electrolyte solution as illustrated by the \( \text{i}_{\text{max}} - \sqrt{s.r.} \) curve (Fig. 17). Both the small peak at \(-0.7\) \( \text{V} \) and the plateau at \(-0.5\) \( \text{V} \) appeared; the peak manifesting itself more as the sweep is increased as seen in Fig. 18a,b.
Fig. 14. Anodic potential sweep for lead in $\text{MH}_2\text{SO}_4 + 0.05 \text{M KClO}_4$. 

$s.r. = 3.33 \text{ mV/sec}$

$A = 0.0706 \text{ cm}^2$
Fig. 15. Anodic potential sweep for lead in \( \text{M}_2\text{H}_2\text{SO}_4 + 0.05 \text{M} \text{KClO}_4 \)
Figure 16. Anodic peak current vs. sweep rate for PbSO₄ formation on lead in MH₂SO₄ + 0.05 M KClO₄.
A = 0.0706 cm²

Fig. 17: Anodic peak current - sweep rate for PbSO₄ formation on lead in 0.5M H₂SO₄ + 0.02MKClO₄
Fig. 18. A Anodic potential sweep for lead in 0.5 M H₂SO₄ + 0.02 M KClO₄
Fig. 18.8 Anodic potential sweep for lead in 0.5 M H₂SO₄ + 0.02 M KClO₄

s.r. = 6.67 mV/sec
A = 0.0706 cm²
3.1.3 Potentiodynamic Measurements in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.05 M KClO<sub>4</sub>:

The features revealed in this solution were particularly interesting. In Fig. 19 where a slow sweep speed of 3.33 mV/sec was used, the hump at -0.5V is preceded by another (c) at -0.7V. Meanwhile, a region of steady increase in current beginning at about 0.2V is observed directly preceding O<sub>2</sub> evolution that starts at ≈ 1.25V. When a higher sweep speed was used (Fig. 20), the hump at -0.7V develops into a small peak at -0.65V, while the hump at -0.5V and the region of increased anodic current are still clearly observed. The $i_{\text{max}} - \sqrt{s.r.}$ relationship no longer shows linearity at the higher sweep speeds but a continuous curve is obtained as shown in Fig. 21.
Fig. 19. Anodic potential sweep for lead in $0.5 \text{ M} \text{H}_2\text{SO}_4 + 0.05 \text{M KClO}_4$
Fig. 20. Anodic potential sweep for lead in 0.5M H$_2$SO$_4$ + 0.05M KClO$_4$. 

s.r. = 13.33 mv/sec 

A = 0.0706 cm$^2$
Fig. 21. Anodic peak current- \( \sqrt{\text{sweep rate}} \) for PbSO\(_4\) formation on lead in 0.5M H\(_2\)SO\(_4\) + 0.05MKClO\(_4\)
3.4.4 Discussion:

The effectiveness of the perchlorate forming agent added to sulphuric acid in the process of "electrolytic forming" of Plante plates depends on its concentration in solution. It has been shown previously that lead suffers from pitting corrosion if it is anodically polarised in $H_2SO_4 - HClO_4$ mixtures, provided that the acid ratio is maintained within a certain range. Abdul-aziz and Afifi have estimated the ratio of $\frac{ClO_4^-}{SO_4^{2-}}$ enough to engender an enhanced pitting effect to be 0.02, using both galvanostatic and potentiostatic techniques. The criterion for the establishment of pitting corrosion is the formation of an electronically conducting oxide film on the electrode surface.

Our results using the potentiodynamic method agrees well with the previously reported observations. Thus, in presence of the lower ratios of perchlorate/sulphate namely 0.05:1 and 0.02:0.5 a small peak at -0.05V (NHE) was observed. This potential is directly comparable with the Pb/Pb$^{2+}$ system, $E_0$ for which is -0.126V (NHE). Hence, it could be postulated that a further dissolution of Pb takes place after the formation of the sulphate layer due to the presence of adsorbed perchlorate ions in the intercrystalline spaces where the metal surface remains active. The fact that as
the sweep speed increases this peak becomes more distinct, is in support of the previous assumption that the sulphate film is less compact when formed under higher sweep rates of potential. However, using the slow sweep speeds the plateau corresponding to the PbO formation becomes clearer. This contradicts the fact that as the film becomes less protective, the approach of $SO_4^{2-}$ is easier and the migration of $H^+$ is less, hence the alkaline conditions favouring the formation of PbO are less likely to occur. The increased value of current in this region would thus be more probably attributed to the overlapping of two humps at potentials corresponding respectively to soluble $PbClO_4$ and PbO formation, rather than an increased quantity of PbO. However, clear resolution of the two processes was observed when higher sweep speeds or higher ratios of $ClO_4^- / SO_4^{2-}$ were used. This agrees with previously reported data of Abdul-Azim et al. where it was shown that under galvanostatic conditions, progressive increments in $HClO_4$ added to $H_2SO_4$ give rise to the appearance of a small anodic step at more positive potentials than that of sulphate formation. In addition, they bring about a shift of the step corresponding to the reduction of basic sulphate toward more negative potentials, i.e. in the direction of lower basisity.
As the perchlorate/sulphate ratio is increased (0.05:0.5) an additional transpassive dissolution sets in at about 0.85V (NHE), as revealed by the steady increase in current as the potential is changed to more positive values. At the positive end of the sweep the current is seen to increase at a slightly less positive potential of 1.9V (NHE). This might reveal the onset of pitting corrosion enhanced at the potential of PbO₂ formation, thus adding a further attacking action of the perchlorate ion on the lead metal resulting in an increased quantity of the 'active material' on the electrode surface. The alternative explanation of a reduced overpotential of O₂ evolution does not seem very likely.

The values of the peak currents are slightly increased in this solution especially at the higher sweep speeds denoting an increased quantity of sulphate formed on the electrode surface.
3.5 Sulphate - Acetate Mixtures:

Results

3.5.1 Potentiodynamic Measurements in 0.5 M H_2SO_4 + 0.02 M or 0.05 M CH_3COOK

The sulphate anodic peak was not markedly influenced by the presence of the acetate ion. Fig. 22 shows the peak currents correlated with \( \sqrt{\text{s.r.}} \), which is similar to that obtained in 0.5M H_2SO_4 (Fig. 9). However, the peak currents are slightly lower in presence of 0.05 M CH_3COOK compared to those in acetate-free sulphuric acid as illustrated in Fig. 23. The plateau at \(-0.5\text{V}\) and the region of increasing anodic current starting at \(\approx0\text{V}\), preceding the o.e.r are clearly apparent in Figs. 24, 25.
Fig. 22. Anodic peak current–Vsweep rate for PbSO₄ formation on lead in 0.5M H₂SO₄ + 0.02M CH₃COOK

$$A = 0.0706 \text{ cm}^2$$
Fig. 23. Anodic peak current-sweep rate for PbSO₄ formation on lead in 0.5M H₂SO₄ + 0.05 M CH₃COOK
Fig. 24. Anodic potential sweep for lead in 0.5 M $\text{H}_2\text{SO}_4 + 0.02\text{MCH}_3\text{COOK}$
Fig. 25. Anodic potential sweep for lead in 0.5M H$_2$SO$_4$ + 0.05M CH$_3$COOK
3.5.2 Discussion:

The presence of acetate ions in the sulphuric acid solution did increase the dissolution of the lead electrode in the region positive of the PbSO₄ peak. This is seen in the increased value of current at the region between the main anodic peak and the plateau corresponding to PbO formation. The previous discussion of this increased current in case of the perchlorate ion applies generally well in this case. A region of transpassive dissolution starting at 0.65V (NHE) was always observed.

The fact that the lead sulphate peak is slightly diminished in presence of the acetate ion can be attributed to the organic anion being adsorbed on the surface of the electrode and partially blocking the passage of Pb²⁺ into solution. Nevertheless the transpassive dissolution was clear in both concentrations used.
3.6 Sulphate-Fluoroborate Mixtures:

Results

3.6.1 Potentiodynamic Measurements in $0.5 \text{M H}_2\text{SO}_4 + 0.02 \text{ or } 0.05 \text{M KBF}_4$.

The anodic LSV curves obtained in these solutions are typified in Figs. 26, 27. A small peak was observed between $-0.7$ to $-0.65\text{V}$. In addition, the current after passing through a minimum started to increase again at $-0.1\text{V}$. This increase continued until the o.e.r. region was attained at $1.5\text{V}$.

The peak current values are slightly lower in the presence of the fluoroborate ion (Figs. 28, 29) compared with those in $0.5\text{M}$ sulphuric acid alone shown in Fig. 9. However, the same general shape of curve is obtained.
Fig. 26. Anodic potential sweep for lead in $0.5 \text{M} \text{H}_2\text{SO}_4 + 0.02 \text{KBF}_4$
Fig. 27. Anodic potential sweep for lead in $0.5 \text{M H}_2\text{SO}_4 + 0.05\text{M KBF}_4$.
Fig. 28. Anodic peak current vs. sweep rate for PbSO$_4$ formation on lead in 0.5M H$_2$SO$_4$ + 0.02MKBF$_4$
Fig. 29. Anodic peak current-$\sqrt{\text{sweep rate}}$ for PbSO$_4$ formation on lead in 0.5M H$_2$SO$_4$+0.05MKBF$_4$
3.6.2 Discussion:

The fluoroborate ion hydrolyses in a stepwise manner to the hydroxy-fluoroborate ions BF$_3$OH$^-$, BF$_2$(OH)$_2^-$, BF(OH)$_3^-$ and H$_3$BO$_3^-$ and the coproduct of each step is HF. Wamser$^{72}$ found that the monohydroxy-fluoroborate ion is the major product of hydrolysis, approximately 5.5% in 5.4 M solution. The degree of hydrolysis of this monohydroxy-fluoroboric acid is quite small. The presence of the highly ionised fluoroboric acids apparently completely suppresses the ionisation of the HF that is present. These hydrolysis products could probably be the cause of the slightly decreased values of the sulphate peak currents due to their adsorption on the electrode surface forcing the solution to occur through an adsorbed layer.

Other features showing an increased dissolution of the lead are maintained in these solution mixtures, i.e. the small peak at -0.05 to 0 V (NHE) and the transpassive dissolution that starts at a potential of 0.75V.
3.7 Sulphate-Nitrate Mixtures:

Results

3.7.1 Potentiodynamic Measurements in $0.5 \text{ M } \text{H}_2\text{SO}_4 + 0.02 \text{ M } \text{KNO}_3$

The behaviour of the lead electrode in this solution, using an s.r. of $1.33 \text{ mV/sec}$ is illustrated in Fig. 30. The cathodic current in the h.e.r. region is considerably increased in presence of the nitrate ion. Directly following the sulphate peak, a region where the current is again cathodic is observed.

An anodic hump around $-0.7\text{V}$ is developed followed by another broad hump (d) around $0.0\text{V}$. A gradual increase in current as the potential is changed to more positive values then follows, whereupon sudden oscillations of current occur and finally the o.e.r. commences at $1.3\text{V}$.

As the speed of the potential variation increases, hump (d) is gradually shifted to more positive potentials and greatly increased in magnitude forming a clear, very broad peak having a maximum at $0.5\text{V}$ using a sweep speed of $13.33 \text{ mV/sec}$ (Fig. 31). The oscillations become severe before the o.e.r. sets in. Some pits are observed on the electrode surface.

The peak current - s.r. relationship shows a curve as seen in Fig. 32, with the $i_{\text{max}}$ values being higher than the corresponding ones in nitrate-free sulphuric acid.
Fig. 30. Anodic potential sweep for lead in 0.5M H₂SO₄ + 0.02M KNO₃.
Fig. 31. Anodic potential sweep for lead in $0.5\text{M} \text{H}_2\text{SO}_4 + 0.02\text{M} \text{KNO}_3$.
Fig. 32: Anodic peak current vs. sweep rate for PbSO₄ formation on lead in 0.5M H₂SO₄ + 0.02M KNO₃.
3.7.2 Potentiodynamic Measurements in 0.5 M H₂SO₄ + 0.05 M KNO₃

In presence of the higher concentration of nitrate ion, the increments in the cathodic current in the h.e.r. region, the sulphate peak-current, the post-peak cathodic current and the broad hump (d) are clearly observed. Hump (d) has its maximum around 0V, as illustrated in Fig. 33.

Comparing the curve obtained at the sweep speed of 13.33 mV/sec (Fig. 34) with the corresponding one in presence of 0.02 M KNO₃ (Fig. 31), it can be observed that the same features are generally maintained except that hump (d) is shifted to slightly more positive potentials (around 0.1V). A general increase in all currents between the -ve and +ve extremities of potential is also observed at this high sweep speed.

The $i_{\text{max}} - \sqrt{s.r.}$ correlation is a curve as presented in Fig. 35; the curvature is greater than in presence of 0.02 M nitrate ion in solution.

An interesting observation was the appearance of large well-defined pits on the electrode surface at the end of each experiment, the number being larger as the sweep speed is increased.
Fig. 33. Anodic potential sweep for lead in $0.5 \text{M} \text{H}_2\text{SO}_4 + 0.05 \text{MKNO}_3$.
Fig. 34. Anodic potential sweep for lead in 0.5M $\text{H}_2\text{SO}_4$ + 0.05M $\text{KNO}_3$
Fig. 35. Anodic peak current-sweep rate for PbSO₄ formation on lead in 0.05M H₂SO₄ + 0.05M KNO₃
3.7.3 Discussion:

In aqueous solution, the nitrate ion participates in the equilibrium.

\[
\text{NO}_2^+ + H_2O \rightleftharpoons \text{H}_2\text{NO}_3^+ \rightleftharpoons \text{HNO}_3 + H^+ + \text{NO}_3^- + 2H^+ \ldots \ldots \ldots 1
\]

yielding the nitronium ion \( \text{NO}_2^+ \) with the possible intermediate formation of nitric acidium ion \( \text{H}_2\text{NO}_3^+ \) \(^{73-75} \), according to the acidity of the medium. The left hand equilibrium leading to the formation of \( \text{NO}_2^+ \) is established in strongly acidic media (almost 100% in 87.5% \( \text{H}_2\text{SO}_4 \))\(^{76,77} \).

The similarity of polarographic waves obtained by Mašek\(^{77} \) for nitrate and nitrite ions in sulphuric acid solutions of strengths \( 10^{-1} \) to \( 18 \text{M} \), have suggested that the nitrate ion undergoes a further reaction yielding the nitrosonium ion \( \text{NO}^+ \), which is the product of dissociation of nitrous acid according to:

\[
\text{NO}^+ + H_2O \rightleftharpoons \text{H}_2\text{NO}_2^+ \rightleftharpoons \text{HNO}_2 + H^+ + \text{NO}_2^- + 2H^+ \ldots \ldots \ldots 2
\]

Consequently, Mašek has put forward the following reaction mechanism at high acidities (higher than \( 15 \text{M} \text{H}_2\text{SO}_4 \)): 
At lower acidities the mechanism proposed is:

\[ (\text{HNO}_3 + 2\text{NO} + \text{H}_2\text{O} \rightarrow 3\text{HNO}_2) \] ......................... 10

\[ (\text{HNO}_2 + \text{H}^+ \rightarrow \text{H}_2\text{NO}_2^+) \] .............................. 11

\[ (\text{H}_2\text{NO}_2^+ \rightarrow \text{NO}^+ + \text{H}_2\text{O}) \] ........................... 12

\[ (\text{NO}^+ + \text{e} \rightarrow \text{NO}) \] ........................................ 13

\[ (\text{HNO}_3 + 3\text{e} + 3\text{H}^+ \rightarrow \text{NO} + 2\text{H}_2\text{O}) \] ............... 14
Equation (10) expresses another way of yielding the particle NO$^+$ from the product of the electrode reaction NO and the nitric acid which at lower acidities represents the prevailing species in the solution. The set of equations 10-14 (mechanism II) leads to the same overall reaction as mechanism I (equations 3-9) which is seen from comparison of equations (9) and (14).

Topol et al.$^{78}$ and Calandra et al.$^{79}$ agree that the concentrated H$_2$SO$_4$ solutions of NO$_3^-$ are reduced electrochemically at metal electrodes according to the scheme:

\[
\text{NO}_3^- + 3\text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + 3\text{HSO}_4^- + \text{H}_3\text{O}^+ \quad \text{(chemical reaction)}
\]

\[
\text{NO}_2^+ + 2e^{-} \rightarrow \text{NO}_2^- \quad \text{(chemical reaction)}
\]

\[
\text{NO}_2^- + 3\text{H}_2\text{SO}_4 \rightarrow \text{NO}_3^- + 3\text{HSO}_4^- + \text{H}_3\text{O}^+ \quad \text{(chemical reaction)}
\]

\[
\text{NO}^+ + e^{-} \rightarrow \text{NO} \quad \text{(chemical reaction)}
\]

The NO oxidation (anodic) peak observed was around 0V w.r.t. the Hg/Hg$_2$SO$_4$ reference electrode, the anodic peak for the reformation of NO$_2^+$ was not observed indicating an irreversible reduction reaction. The detailed mechanism includes catalytic reactions involving the base gold electrode.$^{79}$ The nitryl ion is also reported to attack the electrode chemically.
In dilute sulphuric acid solutions, the presence of the nitronium ion is not excluded according to the equilibrium 1.

Vaidyanathan and co-workers 80, have published recently the anodic curve of lead in dilute nitric acid, showing the formation of PbO and PbO$_2$ at about 0.65\(\text{V}\) and 1.35\(\text{V}\) (NHE) respectively using a sweep speed of 9\(\text{mV/sec}\).

The features revealing the behaviour of lead in nitrate solutions are superimposed on the anodic curve of lead in sulphuric acid in addition to a dissolution and pitting effects of the nitrate ion as is shown in the anodic curves obtained in these solutions. Nevertheless there is some uncertainty in the discussion of the results. Thus, the h.e.r. is increased and takes place even at potentials around the sulphate peak either due to the generation of H$_3$O$^+$ as a result of the chemical equilibrium (17), or to an enhanced h.e.r. reaction because the adsorbed nitrate ions keeps the electrode surface more active compared to complete layer of adsorbed sulphate ions.

The peak around 0.65\(\text{V}\) (NHE) is even more difficult to interpret. This could be due to the formation of PbO at the sites occupied by the nitrate ions on the electrode surface, as shown by Vaidyanathan 80, or due to the NO oxidation, the potential of which coincides closely with the former. Although the acid concentration may affect the NO oxidation potential, it might
be expected that it takes place at approximately the same potential in presence of dilute sulphuric acid. However, the evidence for the formation of PbO and even PbO₂ is not lacking since the peak at 0.65V (NHE) is shifted under some circumstances of higher sweep rates, the more positive potentials \( \approx 1.2 \text{ V (NHE)} \) and it is broad, covering a higher range of potential. This is also substantiated by the earlier formation and development of pits on the electrode as revealed by the current oscillations encountered at potentials less positive than the h.e.r. potential.

That the pits are relatively few in number is due to the incomplete formation of an oxide film covering the whole surface before pitting starts. The number of pits increases with the increased sweep speed as the sulphate film formed is less adherent under these circumstances as illustrated in section 3.3.4, i.e. there are more sites available for the adsorption of nitrate ions with the consequent formation of oxide and pits at these sites.

An increased curvature of the \( i_{\text{max}} - \sqrt{s.r.} \) line as the nitrate ion concentration is increased, shows an increased attacking action even in the region of sulphate formation.
3.8 Comparison of Different Behaviours of the Various Systems:

The previous study was aiming to throw more light upon the action of different anions with soluble lead salts in the process of anodic 'formation' of lead in sulphuric acid to which these salts are added, particularly in comparison with the usually-used perchlorate ion. The four anions investigated (the perchlorate, the acetate, the fluoroborate and the nitrate) could be divided into two groups.

(1) The acetate and the fluoroborate produce an enhanced dissolution of lead. This is revealed by the appearance of the small peak directly following the sulphate peak, and by the transpassive dissolution region at more elevated potentials extending into the o.e.r. region.

The transpassive dissolution sets in at less positive potentials especially in the case of the acetate ion. This could be attributed to a mixed transpassive and chemical reaction of the type$^{31}$.

\[ \text{PbO} + 2\text{CH}_3\text{COOH} \rightarrow \text{Pb} \text{(CH}_3\text{COO)}_2 + \text{H}_2\text{O} \]

\[ 2\text{PbO} + \text{Pb} \text{(CH}_3\text{COO)}_2 \rightarrow \text{Pb} \text{(CH}_3\text{COO)}_2 \cdot 2\text{PbO} \]

Nevertheless, there was no sign of an increased anodic solubility at the PbSO$_4$ formation potential, but rather
slightly decreased values of peak currents due to the probable adsorption of the anions on the electrode.

(2) The nitrate and the perchlorate ions which induce all the previous mentioned effects and in addition an increased dissolvability in the sulphate formation region as revealed by the higher values of $i_{\max}$. Another feature of the perchlorate and the nitrate ions is their pitting corrosion effect on lead. Pitting corrosion increases to a considerable extent the quantity of soluble lead as illustrated by the weight loss measurements of Abdul-azim. Pitting is reported to occur at elevated anodic potentials where the formation of the electronically conducting PbO$_2$ film enhances the process of pit growth and the Pb$^{2+}$ passing into solution are deposited as PbSO$_4$, thus increasing the 'active material' eventually formed on the electrode.

Pitting corrosion is generally industrially deleterious because of the localised nature of the attack that leads in severe cases to the complete perforation of the metal. Moreover the pits are more likely to form in certain areas, e.g. edges, stressed areas of the surface and the line of contact between the solution and air. Thus, the concentration of a 'pitting' agent should be carefully chosen to avoid the possible disadvantages. As far as the perchlorate ion is concerned, the
ratio of \( \frac{\text{ClO}_4^-}{\text{SO}_4^2-} \) used in industry is just enough to produce a relatively small degree of pitting during the first formation process. The perchlorate is then washed out thoroughly to avoid further attack on the lead electrode plate.

The nitrate ion engenders a more pronounced pitting action, but has certain draw-backs in practical use. These may be summarised in the light of our own results in the following:

(a) An increased 'gassing' in the h.e.r. region.

(b) An irreversible reduction reaction of the nitryl ion (see section 3.7.3) which means a continuously decreasing quantity of the forming agent through the several reversals of current for the formation of subsequent plates. This may in fact be a hidden advantage in that it may enable the forming agent to be more frequently renewed.

It can then be concluded that the ClO\(_4^-\) is the most suitable for the formation process of Plante plates, followed by the nitrate, but none of the other ions approach the efficiency of the perchlorate as an attacking agent.
CHAPTER 4

FORMATION OF A PLANTÉ TYPE POSITIVE PLATE
4.1 The Industrial Process of Formation:

The basic processes used industrially to produce the Plante type positive plates of a lead-acid battery are:

1. Cathodic cleaning of the electrode.

2. Anodic etching using potassium perchlorate - sulphuric acid electrolyte; this is known as the 'Attack' or 'First formation' process.

3. Reduction of the attacked plate, washing free of electrolyte followed by drying.

4. Sulphuric acid formation of the reduced plate known as 'Second formation' or 'Peroxidation'.

5. Testing the capacity of the plate. These processes were all reproduced in this work in detail and the potential variations on the plate during processes (2), (3), (4) and (5) were followed, to get a clear picture of the reactions taking place during these processes.
4.1.1 Experimental Techniques:

The Cell

Fig. 36 shows the transparent plastic box used as an electrolyte cell. A cooling spiral, a thermometer and a hydrometer dip into the electrolyte; in addition to the two negative plates and the positive plate under investigation.

The Electrolytes

1.075 ± 0.005 s.g. H₂SO₄ at 16°C (1.29M) containing 8g/l of KClO₄ (≈ 0.058M) was prepared for the attack process. This solution is almost saturated with KClO₄. Another H₂SO₄ concentration of s.g. 1.2 - 1.215 at 16°C (≈ 3.578M) was used for the 'second formation' process.

The Electrodes

Lead electrodes known as 'blanks' of dimensions 7.5 x 12 x 0.5 cm, supplied by "Electric Power Storage Limited" were used. An Hg/Hg₂SO₄/M Na₂SO₄ electrode (654 mv NHE) was the potential reference.

The Circuit

The circuit used (Fig. 37) included a variable d.c. supply,
A Working electrode.
B The negatives.
C Reference electrode.
D Thermometer.
E Hydrometer.
F Cooling spiral.
G Separators.

Fig. 36: The electrolytic cell.
Fig. 37. The D.C. circuit.
ammeter, reversing switch of the current and a recording
potentiometer (Type B D 8, Kipp and Zonen).
4.1.2 Results

(1) Cathodic Cleaning

The electrode was polarised negatively using a current of 1.56A/electrode, when hydrogen evolved freely, and held under these conditions for 15 minutes to ensure the removal of all traces of oxides and other impurities from the surface.

(2) The Attack Process

The anodic potential profile of lead in the sulphuric acid-perchlorate solution was as shown in Fig. 38. There was a tendency for a rise in temperature to occur during this process, but the system was always kept at a temperature within 12 - 20°C. The anodising current was 1.56A/electrode. The process was continued for 21 hours. It is seen from Fig. 38 that a well defined sulphate step, followed by the familiar quick rise of potential forming a sharp peak, then a continuous gradual decrease of potential and even a step were observed. A final value of potential of 670 mV was achieved.
Fig. 38. Potential vs time curve for lead in H_2SO_4-KClO_4 mixture. Attack process.
(3) **Reduction of the Attacked Plate**

Fig. 39 shows the cathodic curve of the attacked plate. It was observed that the potential did not change appreciably when the current was reversed, attaining a value of +500 mV where an arrest is formed, lasting for less than 2 hours. Nevertheless when the potential changed to the negative value corresponding to the system Pb/PbSO₄, the time elapsed amounted to 17 hours before the h.e.r. potential was finally achieved. The electrode was rinsed several times with hot water (90°C) until ultimately free from the acid (methyl orange was used to test for the acidity of the washings); and dried in an oven at 80°C until dry.

(4) **Second Formation Process**

The attacked plate was charged in sulphuric acid and the temperature always kept below 37°C, at a current of 1.36A/electrode. The current is passed for 36 hours with occasional rests for some hours according to the manufacturers' scheme.

Fig. 40 illustrates the potential behaviour obtained during this process. An irregular increase of potential was observed on which two potential arrests could be distinguished at -620 mV and at +200 mV. Finally the potential rests at a value of 1.1V whereupon it increases very slowly during the subsequent 22 hours reaching a value of 1.34V.
Reversal of current

Fig. 39. Potential vs time curve for lead in $\text{H}_2\text{SO}_4-\text{KClO}_4$ mixture. Reduction process.
Fig. 40. Potential vs time curve for lead in $\text{H}_2\text{SO}_4$—Second formation.
Controlled Test Discharge

To test the discharge capacity of the plate it is washed and dried first as described in (3). A controlled discharge at the 10 hr rate, namely 0.75A is carried out. The potential of the +ve plate (750 mV after 2 minutes discharge) decreases gradually to a final value of 250 mV before the "knee" denoting nearly complete discharge is reached.

The plate is recharged for 24 hours and a final controlled discharge is carried out. In this second discharge test, the potential remains nearly constant at ≈ 0.43V all the way through. A discharge capacity of more than 12 hours was achieved in our results.
4.1.3 Discussion

In the light of the previous discussion of section 3.4.4, the present results could be interpreted as follows: In the attack process, the high current applied resulted first in a very rapid increase of potential, formation of the sulphate and the peak of potential before PbO₂ nucleation and O₂ evolution take place. A subsequent decline of potential was then observed indicating the increasing attacking action of the perchlorate ion in this region, hence increasing areas suffering the destruction of the PbO₂ film via pitting corrosion of lead. The ratio of S^{2-}_4⁻/ClO₄⁻ present in the solution lies in the region of 'pitting attack' of the perchlorate, as could be deduced from a study by Abdul-azim. The final potential attained after more than 20 hours of attack, 1.32V (NHE) is lower than that of the lead/PbO₂ formation in sulphuric acid, 1.68V. Presumably a mixed potential of PbO₂ formation and the dissolution process taking place at the sites of pitting corrosion is established.

The same argument applies in the case of the reduction process where the potential did not change appreciably after the reversal of current. The PbO₂/PbSO₄ step did not last long as would be expected, since the quantity of PbO₂ remaining on the surface is decreased during the long attack process. Meanwhile, at the negative potential of Pb/PbSO₄, the
discharge time was quite long, all the soluble Pb\textsuperscript{2+} is now deposited as PbSO\textsubscript{4} on the electrode surface and discharged to sponge lead.

**Second Formation Process**

In perchlorate-free sulphuric acid, the features revealing continued attack of the electrode were well-defined. A small step at -30 mV (NHE) characteristic in presence of HClO\textsubscript{4} has appeared. The complete disappearance of the subsequent peaking could probably be due to the inhibited formation of a protective sulphate layer and consequently the poorly conducting lower oxides of lead (causing the appearing of the potential peak as discussed by Ikari\textsuperscript{82}) does not take place. A slow increase of potential is observed as the PbO\textsubscript{2} formation process takes place.

**The Controlled Discharge Tests**

Also reveals the same characteristically lower potential than that of PbO\textsubscript{2} on lead in perchlorate-free sulphuric acid. The capacity of the attacked plate amounted, under the discharge conditions mentioned, to about 12 hours, compared to 8 minutes in the unattacked plate (see section 4.2.3).

The high capacity of the plate is attributed to the continuous process of adsorbed perchlorate ions attacking lead and making for the lost active material of the plate.
4.2. Superposed a.c. on d.c. Formation Process

In this part, attempts were made aiming at the replacement of the attack process by direct application of an a.c. component on the d.c. charging current. The effect of variation of frequency and amplitude of the a.c. were studied.

The same sulphuric acid solution (1.2 - 1.215 s.g.), cell and electrodes as those described in section 4.1.1 were used.

4.2.1 The Circuit

A 50A Potentiostat (Chemical Electronics) was used as a d.c. supply. The a.c. was fed as an external input through the potentiostat using a signal source (Type 471, Brookdeal). The circuit (Fig. 41) contained in addition an oscilloscope, an ammeter and a recording potentiometer (type 27000, Bryans).

4.2.2 The Experimental Technique

A d.c. of 1A was cathodically applied to the electrode for 15 minutes for cleaning and removal of oxides. The a.c. component was then switched on and the polarity was reversed immediately after adjusting the value of the d.c. and the amplitude of the a.c. applied. The passage of current was
Fig. 41. The electrical circuit of superimposed a.c. on d.c.
continued under these conditions for 24 hours. The a.c. was then discontinued, the d.c. reduced to the 10 hour capacity discharge-rate (0.75A) and a controlled discharge test was then performed in the same solution.

4.2.3 Results

A reference experiment in which the electrode was charged at the usual charging current of 1.36A for 24 hours then discharged at 0.75A was carried out. The duration of the discharge step PbO$_2$/PbSO$_4$ was taken as a measure of the capacity of the plate; this is shown in Fig. 42.

The charging current (1.36A) was first chosen as a d.c. level on which the a.c. ripple was superimposed. An applied a.c. of different frequencies ranging from 1000 Hz, including 100, 50, 1 and down to 0.01 Hz did not result in any change of the capacity. A representative experiment is shown in Fig. 43. However, using the lower frequencies 50, 1 and 0.01 Hz, the applied a.c. resulted in a potential change around the potential-time profile which was absent at higher frequencies. Nevertheless, this, too, did not affect the discharge capacity of the plate as exemplified in Fig. 44.
Fig. 42. Potential vs time curve for lead in \( \text{H}_2\text{SO}_4 \) - reference experiment.
Fig. 43: Potential vs time curve for lead in H$_2$SO$_4$.

After 24 hours, anodic polarisation at 136 Amp/electrode and cathodic reduction at 0.75 Amp/electrode.

Impedance f = 1000 Hz, amplitude = 0.5 Amp.
Fig. 44. Potential vs time curve for lead in H$_2$SO$_4$.

(Imposed ac. f = 0.01 Hz, amplitude = 0.5 Amp.)

Anodic polarisation at 136 Amp./electrode.
Cathodic reduction at 0.75 Amp./electrode.

after 24 hrs.
Fig. 45: Potential vs time curve for lead in $\text{H}_2\text{SO}_4$.

(Imposed ac: $f = 0.001$ Hz, amplitude = 1 Amp.)
Improvements in the capacity were ultimately achieved when lower d.c. levels were chosen accompanied by a very low frequency of the a.c. applied. Thus with 0.5A d.c., 0.001 Hz a.c. of amplitude ±1A, a discharge step lasting for 46 minutes was obtained (Fig. 45), compared to 8 minutes discharge step of the plate in the reference experiment (Fig. 42).

When the d.c. level was reduced to 0.22A, keeping the a.c. frequency and amplitude the same, a nearly similar result was obtained. The duration of the discharge step was 39 minutes. Lower d.c. levels affected the amplitude of the superposed a.c. A negative d.c. level was tried, namely - 0.2A, but the discharge step lasted for 3 minutes only in this case. Table 1 shows the results obtained.
### TABLE 1

Capacity of Plates Charged with Coupled a.c. and d.c.

<table>
<thead>
<tr>
<th>d.c. amplitude (A)</th>
<th>a.c. frequency (HZ)</th>
<th>a.c. amplitude (A)</th>
<th>Length of discharge step (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.36</td>
<td>1000</td>
<td>±0.5</td>
<td>8</td>
</tr>
<tr>
<td>1.36</td>
<td>100</td>
<td>±0.5</td>
<td>9</td>
</tr>
<tr>
<td>1.36</td>
<td>50</td>
<td>±0.5</td>
<td>8.5</td>
</tr>
<tr>
<td>1.36</td>
<td>1</td>
<td>±0.5</td>
<td>8.5</td>
</tr>
<tr>
<td>1.36</td>
<td>0.01</td>
<td>±0.5</td>
<td>8</td>
</tr>
<tr>
<td>0.22</td>
<td>0.001</td>
<td>±1</td>
<td>39</td>
</tr>
<tr>
<td>0.5</td>
<td>0.001</td>
<td>±1</td>
<td>46</td>
</tr>
<tr>
<td>-0.2</td>
<td>0.001</td>
<td>±1</td>
<td>3</td>
</tr>
</tbody>
</table>
A final experiment in which an applied sine potential wave (±2V, 0.001 Hz) was applied to the electrode for 24 hours. The discharge capacity obtained did not exceed 35 minutes.
4.2.4 Discussion

The results of the present investigation could be interpreted in the light of an understanding of the original technique of 'Planté' for the formation of high capacity plates. This was mainly charging and discharging the electrode successively in a cyclic manner under d.c. During the first charging half cycle (oxidation), a compact layer of PbO$_2$ is formed on the surface of the electrode. When the current is reversed during the next half cycle, this is reduced to PbSO$_4$. The PbSO$_4$ crystals are known to have a smaller specific volume than that of PbO$_2$, hence a less protective film of sulphate will be produced. More Pb$^{2+}$ issue through the cracks between PbSO$_4$ crystals, forming more PbSO$_4$ on the surface. Further reduction will result in the formation of finely divided lead on the surface. This process is repeated in the subsequent cycles resulting in the formation of a progressively increasing layer of 'sponge' lead hence larger surface area and capacity of the plate. The discharge capacity obtained using this technique did not exceed 6-10 times the capacity of a plate that is charged only once.

Costa and Hoar$^{83}$ stated that the application of an a.c. frequency 50 Hz of differing amplitudes on lead anodes oxidized at 25-150 mA/cm$^2$ produces a small increase in the fraction of PbO$_2$ formed that is adherent, and a very small decrease in the total attack on the metal. Ghosh$^{84}$ has prepared $\alpha$ and $\beta$ PbO$_2$ by
superimposing a.c. on d.c. In the case of PbO\textsubscript{2} the percentage a.c. superimposed increased the formation of PbO\textsubscript{2}.

The present results obtained show that when the frequency of applied a.c. was 1000-50 Hz no significant variation of potential occurred around the PbO\textsubscript{2} potential, and obviously no increase in the capacity of electrode was observed. Even when potential variations were recorded (using lower frequencies) the capacity remained unaltered. This means that the reduction process did not take place considerably to produce the less protective PbSO\textsubscript{4} layer.

When the potential variations took place and the PbSO\textsubscript{4}/Pb potential was reached (the H\textsubscript{2} evolution potential in some cases) a considerable increase in capacity was observed. A "limiting" value of about 5-fold increase in capacity was achieved, approaching the figure using the original "Plante" technique, but far below the increase due to the use of chemical agents. Adding KClO\textsubscript{4} to the forming solution resulting in a vast increase of capacity from e.g. a few minutes to more than 10 hours under the previously mentioned conditions.

One is forced to conclude from these experiments that the superposition of a.c. on d.c. fails to give an increase of discharge capacity greater than that obtained by deep cycling.
according to the original Plante' technique. The maximum increase in capacity was 5-6 fold whereas that engendered by the perchlorate process is not less than 75 fold.
CHAPTER 5

FARADAIC IMPEDANCE MEASUREMENTS
CHAPTER 5

Faradaic Impedance Measurements

5.1 Theoretical Principles

5.1.1 Impedance Measurements:

A.C. methods for studying electrode processes, particularly those involving impedance bridges, have as their immediate objective the evaluation of the components of the equivalent circuit of an electrode-electrolyte system as a step in the elucidation of electrode mechanisms and evaluation of kinetic parameters.

The use of equivalent circuits to represent the dynamic characteristics of electrode - solution interface dates back to the turn of the century. Warburg\textsuperscript{85} (1899) derived an equation for the faradaic impedance for diffusion controlled processes (the Warburg impedance). The influence of the double-layer capacity was considered in 1903 by Kruger\textsuperscript{86}. The first application to electrode kinetic studies and the development of appropriate equations for the faradaic impedance were carried out by Dolin and Ershler\textsuperscript{87}, Ershler\textsuperscript{88,89}, Randles\textsuperscript{90} and Rozental and Ershler\textsuperscript{91}. Proposed electrical analogues are shown in Fig. 2 (Chapter 1).
Since then, a.c. impedance has become an important tool for the study of electrode kinetics for:

(a) the charge-transfer step (e.g. Randles\textsuperscript{90}, Grahame\textsuperscript{92} Delahay\textsuperscript{93}, Baticle and Perdu\textsuperscript{94} and Sluyters-Rehbach and Sluyters\textsuperscript{95})

(b) Coupled homogeneous and heterogeneous chemical processes (e.g. Gerischer\textsuperscript{96} and Baker\textsuperscript{97})

(c) adsorption (Laitinin and Randles\textsuperscript{98}, Ilopis et al\textsuperscript{99} Senda and Delahay\textsuperscript{100}, Sluyters-Rehbach et al\textsuperscript{101}, Timmer et al\textsuperscript{102}, Baker\textsuperscript{97}, Holub et al\textsuperscript{103}).

Double layer effects associated with ion transport in the diffuse layer have been considered in conjunction with faradaic impedance by Matsuda\textsuperscript{104} and re-examined by Senda and Delahay\textsuperscript{100}.

5.1.2 The Complex Plane Analysis

Sluyters and his co-workers (Sluyters\textsuperscript{105}; Sluyters-Rehbach and Sluyters\textsuperscript{95}; Sluyters et al\textsuperscript{106-109}) have used a particularly convenient approach, the complex plane method of analysis involving plots of the capacitive components vs the resistive component. This method will be considered in detail.
According to Sluyters\textsuperscript{105}, the impedance of an electrolytic cell is represented by the network\textsuperscript{88,90,95} shown in Fig. 46 where $R_n$ is the ohmic resistance of the electrolyte and the outer connections to the electrodes, $C$ the double layer capacitance, $\theta$ is the resistance representing the activation polarisation of the electrode reaction, and $W$ impedance of diffusion polarisation, Warburg impedance.

Solution of Fick's second law of diffusion, taking into account the appropriate boundary conditions affords for the Warburg impedance written as a complex quantity:

$$W = \sigma' \omega^{-\frac{3}{2}} - j\sigma' \omega^{-\frac{3}{2}}$$ \hspace{1cm} \text{.......................... 5.1}$$

in which $\sigma' = \frac{RT}{n^2 F^2 \sqrt{2}} \left[ \frac{1}{C_{ox} D_{ox} \omega^\frac{3}{2}} + \frac{1}{C_{red} D_{red} \omega^\frac{3}{2}} \right]$ \hspace{1cm} \text{.......................... 5.2}$$

The activation polarisation resistance $\theta$ is related to the concentrations $C_{ox}$ and $C_{red}$ and the reaction rate constant $k_{sh}$ by:

$$\theta = \frac{RT}{n^2 F^2 k_{sh} C_{ox}^{\alpha} C_{red}^{1-\alpha}} \hspace{1cm} \text{.......................... 5.3}$$

Various methods have been proposed for the determination of $\theta$ and $\sigma'$ from impedance measurements. Vector methods were
Fig. 46. Equivalent circuit of electrode impedance.
used by Randles and Delahay. Neglecting the imaginary part of the Warburg impedance, Gerischer determined $\theta$ and $\sigma$.

The cell impedance was corrected for the double-layer capacity and the ohmic resistance by Vetter.

The following procedure is that introduced by Sluyters:

From Fig. 46 it follows that the cell impedance is

$$Z = R_n + \frac{1}{j\omega C + \frac{1}{\theta + \sigma \omega^{-\frac{1}{2}} - j\sigma \omega^{-\frac{1}{2}}} .}$$

or, after separation of the real and imaginary parts of $Z$:

$$Z = Z' - jZ'' = R_n + \frac{\theta + \sigma \omega^{-\frac{1}{2}}}{(c_\sigma \omega^{-\frac{1}{2}} + 1)^2 + \omega^2 c^2 (\theta + \sigma \omega^{-\frac{1}{2}})^2} - \frac{j \omega c (\theta + \sigma \omega^{-\frac{1}{2}})^2 + \sigma \omega^{-\frac{1}{2}} (\omega^2 c \sigma + 1)}{(\omega^2 c \sigma + 1)^2 + \omega^2 c^2 (\theta + \sigma \omega^{-\frac{1}{2}})^2}$$

The two border cases of this formula are:

(I) at low frequencies, the impedance reduces to:

$$Z = R_n + \theta + \sigma \omega^{-\frac{1}{2}} - j (\sigma \omega^{-\frac{1}{2}} + 2 \sigma^2 c)$$

When plotting $Z'$ (the imaginary part of $Z$) against $Z'$ (the real part of $Z$), a straight line is obtained of $45^\circ$ slope (Fig. 47).
Fig. 47. Electrode impedance at low frequency.
(II) If concentration polarisation \( W \) can be neglected (i.e. at higher frequencies and a considerably irreversible electrode reaction) reduces to:

\[
Z = R_n + \frac{\theta}{1 + \omega^2 C^2 \theta^2} - j \frac{\omega C \theta^2}{1 + \omega^2 C^2 \theta^2} \quad \cdots \quad 5.6
\]

If in this case, the imaginary and real parts are plotted against each other, a semicircle is obtained (Fig. 48); this can be demonstrated by elimination of \( \omega \) between \( Z' \) and \( Z'' \), leading to:

\[
(Z' - R_n - \frac{\theta}{2})^2 + Z''^2 = (\frac{\theta}{2})^2 \quad \cdots \cdots \cdots \cdots 5.7
\]

This is entirely analogous to a method used in the theory of dielectric constant (Cole and Cole-plot)\(^{114}\). Semicircles as given in Fig. 48 have been measured and discussed for some technical batteries by Euler and Dehmelt\(^{115}\).

The activation polarisation resistance \( \theta \) can be obtained directly from such a diagram, being equal to the diameter of the semicircle. The value of the double layer capacity \( C \) in the presence of the redox system can be computed from the frequency at the top point of the semicircle: \( \omega = \frac{1}{\theta C} \)

At lower frequencies, i.e. at the right hand part of semicircle, diffusion polarisation will give rise to a distortion of the circle as shown in Fig. 49. At low frequencies a straight line of \( 45^\circ \) slope will be obtained. How far this distortion influences the accuracy of determination of \( \theta \) depends on the relative values of \( \theta, \sigma' \) and \( C \) as illustrated in Fig. 49.
Fig. 48. Impedance of the electrode with irreversible electrode reaction in the absence of concentration polarisation.
Fig. 49. Impedance of the electrode over the whole frequency range.

---- Values of $Z'$ at higher double layer capacity ($C$).
5.1.3 The Linearised Plot

Another method for the determination of $\theta$, also in use in the field of dielectrics$^{116}$, is a plot of $Z'$ against $\omega Z''$ (Fig. 50). A straight line is obtained, the slope of which is $\theta C$. The reciprocal value of this gives $\omega = \frac{1}{\theta C}$. As this frequency corresponds to a point equidistant from $\omega = 0$ and $\omega = \infty$, the point $\omega = \infty$ can be found. Projection of $\omega = \infty$ on the vertical axis gives $\theta$. In this diagram too, distortion will be found at low frequencies; diffusion polarisation causing an upward deflection (Fig. 50).

The complex plane analysis yields the values of the impedance parameters $\theta$ (transfer resistance) and $\sigma'$ (Warburg Coefficient) and $C$ (double layer capacity). Once these are known, an attempt can be made to calculate the values of $k_{sh}$, $\alpha$ and $D$ from the parameters obtained.

The above theoretical principles have been experimentally verified by many workers. Sluyters and his co-workers$^{102}$ have considered this method of analysis of impedance data for electrode systems both with and without specific adsorption, and concluded that the non-faradaic capacitance is essentially frequency-independent for systems with weak or no specific adsorption of reactants (e.g. Cd (Hg)/Cd$^{++}$ and Zn (Hg)/Zn$^{2+}$ in KCl$^{95}$ and Tl(Hg)/Tl$^+$ in KN0$^3_{310}$) with strongly adsorbed reactants (e.g. In (Hg)/In$^{3+}$ in KCNS and Pb (Hg)/Pb$^{2+}$ in KCl$^{102}$,
Fig. 50. Graphical determination of $\theta$ from impedance measurement.
(The linearised plot).
the analysis of impedance measurements must be carried out with the more complicated approach of Holub et al\textsuperscript{103}.

Armstrong\textsuperscript{117}, using the method of Frumkin and Melik-Gaikazyan\textsuperscript{118} for the adsorption of organic molecules under heterogeneous control, presented a theory to account for the impedance - frequency spectrum of an electrode undergoing an active to passive transition, where an oxygen species is present on the electrode surface. This theory is applied for the kinetic study of dissolution of Titanium\textsuperscript{119} and Chromium\textsuperscript{120}. 
5.2 Experimental Techniques:

5.2.1 The Electrodes:

The lead electrode was similar to that described in 3.2.3 Chapter 3. A platinum gauze served as the counter electrode. Saturated calomel electrode was used as a reference electrode throughout these measurements.

5.2.2 The Electrolytic Cell:

An all pyrex glass cell (Fig. 51) was used. The electrolyte was pumped through a column of charcoal by means of a stream of nitrogen gas passed through opening (D).

5.2.3 The Circuit:

The electrical circuit used in the impedance studies is shown in Fig. 52. A modified Schering bridge \(^{121,122}\) was used to match the interphase as a series combination of resistance and capacitance. For zero out of balance current:

\[
\frac{Z_1}{Z_{\text{cell}}} = \frac{Z_2}{Z_4}, \quad \text{hence} \quad C_{xs} = \frac{Q_1 R_2}{R_1} \quad \text{and} \quad R_{xs} = \frac{R_1 C_2}{C_4}
\]
Fig. 51 Cell for faradaic impedance studies

A - Reference electrode compartment
B - Test electrode compartment
C - Counter electrode compartment
D - Purification limb
E - Glass frits
\[ C_{xs} = \frac{C_4 R_2}{R_1} \quad R_{xs} = \frac{R_1 C_2}{C_4} \]

Fig. 52 Electrical circuit for impedance measurements
The a.c. was applied to the bridge by an audio frequency generator (Brockdeal, type 9741) via a screened 65:1 isolating transformer. The amplitude of the a.c. was \( \approx 5 \text{ mV} \) peak to peak. The out of balance signal was passed via a filter (muirhead, type D-925-B), set to reject 50 Hz, to a tuned amplifier (General Radio type 1232A). The amplifier was continuously tunable in the frequency range 20 - 20,000 Hz; higher values of 50,000 and 100,000 Hz were also tunable. The dial accuracy was 3\% and the meter sensitivity 1V F.S.D.

The bridge was polarised symmetrically and during all experiments the test electrode was connected to earth in order to avoid screening difficulties. a.c. and d.c. were separated by a 40 Hz Choke. Potential measurements were made using an electrometer (Vibron Model 33B), the input impedance of which was effectively infinite \((7 \times 10^2)\).

Before any measurements were made the frequency response of the bridge was tested by measuring the impedance of a high stability resistance and a standard capacitance in series over a range of frequencies. The discrepancies between bridge readings and known values are shown in table 5:1.
TABLE 5.1

Response of Impedance Bridge

<table>
<thead>
<tr>
<th>Frequency Range</th>
<th>30-500 Hz</th>
<th>500-1000 Hz</th>
<th>1 - 5 KHz</th>
<th>5 - 10 KHz</th>
<th>10 - 20 KHz</th>
<th>20 KHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Error %</td>
<td>±1</td>
<td>±1</td>
<td>±2</td>
<td>±5</td>
<td>±9</td>
<td>±10</td>
</tr>
</tbody>
</table>

The bridge has a satisfactory response over the frequency range 30 Hz - 10 KHz.

5.2.4 Pretreatment of the Electrode:

Prior to the experimental measurements, the electrode was electrolytically polished in either of 10% perchloric acid or Na acetate/acetic acid bath. The constitution of the latter was

Anhydrous Na acetate 60 g
Glacial acetic acid 315 cc
Water 80 cc
Although a highly polished, bright surface was obtained in this electropolishing solution, the reproducibility of results was better when electropolishing was carried out in 10% perchloric acid. This was used for all subsequent pretreatments.

All impedance measurements were performed at $E_{i=0}$, the potential of zero net flow of Faradaic current across the electrode surface. This was checked for about 20 minutes before measurements were started, unless otherwise stated.
5.3 Results:

5.3.1 Impedance Measurements in MKNO₃ Solutions:

The E - i curve for lead in MKNO₃ is shown in Fig. 53. It could be said that the electrode is nearly ideally polarisable. The region of the 'experimental polarisability' was between -0.6 and -1.2V (SCE), bound by lattice dissolution at the less negative potential and H₂ evolution at the more negative.

The frequency dependence of cell impedance was investigated by measuring and plotting $Z'$, the real part of impedance against $Z''$, the imaginary part at different frequencies of a.c. The real part varies very little with the variation of frequency confirming the polarisability of lead electrode in this solution. This is illustrated in Fig. 54 corresponding to an experiment carried out at -0.9 V.

5.3.2 Impedance Measurements in Nitrate Solutions in Presence of the Pb²⁺/Pb System

The necessary weight of Pb(NO₃)₂ was dissolved in MKNO₃ and added to the cell-electrolyte to make up the required concentration. The solution was allowed to circulate for two days to ensure homogeneous distribution of Pb²⁺ in solution. The
Fig. 53. Faradaic current vs Potential curve for lead in MKNO₃.

\[ A = 0.0706 \ cm^2 \]
Fig. 54: Dependence of cell capacitance on frequency.
tap separating the reference electrode compartment was subsequently closed and the measurements started.

The complex plane plots of cell impedance have shown the predicted semicircles, but instrumental limitations made it difficult in this medium to obtain many points on the semicircles.

A sample of the solution was checked analysed directly after the completion of measurements to determine the exact concentration of Pb\(^{2+}\). The complexometric titration of Pb\(^{2+}\) with EDTA method using xylenol orange indicator (appendix 1) was used throughout these determinations.

The curves obtained in presence of 12.4 x 10\(^{-3}\), 9.3 x 10\(^{-3}\), 6 x 10\(^{-3}\), 4.2 x 10\(^{-3}\), 2.3 x 10\(^{-3}\) M/lit. Pb\(^{2+}\) are shown in Figs. 55-59 respectively. At lower frequencies, a straight line of slope = 1 was always obtained.

5.3.3 Calculation of the Reaction Parameters:

1. Determination of the Charge Transfer Coefficient:

Despite the experimental difficulties, an attempt was made for the determination of \(\alpha\) (the transfer coefficient of the redox reaction Pb\(^{2+}\)/Pb in nitrate solutions), by
Fig. 55. Complex plane display of electrode impedance as a function of frequency.
Fig. 56. Complex plane display of electrode impedance as a function of frequency.
Complex plane display of electrode impedance as a function of frequency.

Pb/M KN03 + 6.00 x 10⁻³ M Pb²⁺
Fig. 5.8. Complex plane display of electrode impedance as a function of frequency.

Pb/M KNO₃⁺ 4.26×10⁻³ M Pb²⁺
Fig. 59. Complex plane display of electrode impedance as a function of frequency.
plotting \( \log \theta \), the diameter of the semicircle, as a function of \( \log C \), the \( \text{Pb}^{2+} \) concentration in solution. Fig. 60 shows the straight line obtained, the slope of which gives the value of \( \alpha \) according to equation 5.3. The value obtained for \( \alpha \) is 0.59.

2. Determination of the Diffusion Coefficient:

It follows from equation 5.5 that in the region of the straight line with slope 1, if \( Z \approx \omega^{\frac{1}{2}} \) is calculated, the product will be constant and equal to \( \sigma \) if \( 2 \sigma^2 C \) is small. Indeed \( Z \approx \omega^{\frac{1}{2}} \) was found to be independent of frequency in this region within 3\% at each \( \text{Pb}^{2+} \) concentration (except in one case). The diffusion coefficient of the oxidised species could be found using equation 5.2 as the term \( \frac{1}{C_{\text{red}} D_{\text{red}}^2} \) is equal to zero in case of a pure metal with the same metal ion, hence,

\[
\sigma' = \frac{RT}{n^2 F^2 \sqrt{2}} \times \frac{1}{C_{\text{ox}} D_{\text{ox}}^2}
\]

from which \( D \) could be calculated. Table 5.2 shows the results:
Fig. 60. Logarithmic plot of 'activation polarisation resistance' dependence on concentration of Pb$^{2+}$ in Mnitrate solutions.
### Table 5.2

<table>
<thead>
<tr>
<th>C x 10^6 mol/cm³</th>
<th>α'</th>
<th>% error</th>
<th>D cm² sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.4</td>
<td>6.1376</td>
<td>1.0</td>
<td>3.74 x 10⁷</td>
</tr>
<tr>
<td>9.3</td>
<td>6.371</td>
<td>2.1</td>
<td>6.18 x 10⁷</td>
</tr>
<tr>
<td>6.0</td>
<td>14.190</td>
<td>2.0</td>
<td>2.99 x 10⁷</td>
</tr>
<tr>
<td>4.0</td>
<td>15.757</td>
<td>6.0</td>
<td>5.46 x 10⁷</td>
</tr>
<tr>
<td>2.3</td>
<td>146.780</td>
<td>3.6</td>
<td>2.0 x 10⁸</td>
</tr>
</tbody>
</table>

3. **Determination of the Reaction Rate Constant:**

Considering equation 5.3,

\[
k_{sh} = \frac{RT}{n^{-2}F_{ox}^{2}C_{ox}^{0}} \cdot \theta
\]

The value of \( \theta \) could be directly obtained from the plot. Table 5.3 shows the values of \( \theta \), \( C_{ox}^{0} \) and the product \( C_{ox}^{0} \cdot \theta \) for each concentration of \( \text{Pb}^{2+} \). A mean value of \( C_{ox}^{0} \cdot \theta \) was calculated, excluding the value of \( 6 \times 10^{-6} \) mol/cm³ which is rather high, the value obtained is \( 1.9125 \times 10^{-1} \).
the percent error is 4%
from which $k_{sh}$ was calculated to be $3.456 \times 10^{-4}$ cm/sec

<table>
<thead>
<tr>
<th>$c \times 10^6$ mol/cm$^3$</th>
<th>$\theta$ m·cm$^2$</th>
<th>$c^{\infty}$</th>
<th>$c^{\infty} \cdot \theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.4</td>
<td>0.144</td>
<td>$1.274 \times 10^{-3}$</td>
<td>$1.834 \times 10^{-4}$</td>
</tr>
<tr>
<td>9.3</td>
<td>0.179</td>
<td>$1.075 \times 10^{-3}$</td>
<td>$1.92 \times 10^{-4}$</td>
</tr>
<tr>
<td>6</td>
<td>0.284</td>
<td>$8.30 \times 10^{-4}$</td>
<td>$2.35 \times 10^{-4}$</td>
</tr>
<tr>
<td>4.26</td>
<td>0.282</td>
<td>$6.782 \times 10^{-4}$</td>
<td>$1.912 \times 10^{-4}$</td>
</tr>
<tr>
<td>2.3</td>
<td>0.42</td>
<td>$4.714 \times 10^{-4}$</td>
<td>$1.98 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
5.3.4 Impedance Measurements in Fluoroboric Acid Solutions:

The E - i curve shown in Fig. 61 reveals that the lead electrode is nearly ideally polarisable in the potential region -0.45 to -0.7V (SCE).

At -0.6V, the impedance of the cell was measured as a function of frequency. It is clear from Figs. 62,63 that the cell impedance is very little affected by variation of frequency denoting the polarisability of Pb in both M and 0.51 M HBF₄.

5.3.5 Impedance Measurements in Presence of the Pb²⁺/Pb System:

Better results were generally obtained in these solutions. The Pb²⁺ concentration ranged between 0.94 x 10⁻³ and 6.6 x 10⁻³ M/lit. The relevant plots of Z' and Z'' are shown in Figs. 64-68.

A general consideration of these curves reveals that:

(a) the slope of the straight line obtained at lower frequencies is not unity as predicted and as was found in the case of nitrate solutions.

(b) the points between the semicircular region and the straight line, are seen to form a flat 'plateau' that is more pronounced as the concentration of Pb²⁺ increases.
Fig. 61. Faradaic current vs Potential curve for lead in MHBF₄.
Fig. 62: Dependence of cell capacitance on frequency.
Fig. 63. Dependence of cell capacitance on frequency.
Fig. 64. Complex plane display of electrode impedance as a function of frequency.
Fig. 65. Complex plane display of electrode impedance as a function of frequency.
Fig. 66. Complex plane display of electrode impedance as a function of frequency.

Pb/M HBF$_4 \times 1.7 \times 10^{-3}$ M Pb$^{2+}$
Complex plane display of electrode impedance as a function of frequency.

Figure 67 - Complex plane display of electrode impedance as a function of frequency.
Fig. 68: Complex plane display of electrode impedance as a function of frequency.
5.3.6 Effect of Potential Variation:

Experiments were made at $E = E_{10} - 10 \text{ mV}$. The resulting curves showed more points on the semicircle and a straight line directly following it, with a very high slope. This effect is shown in 3.7 m mol $\cdot l^{-1}$ Pb$^{2+}$ and 6.6 m mol $\cdot l^{-1}$ Pb$^{2+}$ – M fluoboric acid solutions, in Figs. 69,70.

5.3.7 Determination of Reaction Parameters:

1. Determination of the Charge-Transfer Coefficient:

The transfer coefficient $\alpha$ for the redox reaction of Pb in this solution was determined from a plot of log $C$ vs. log $\theta$, the slope of which was found to be 0.56 (Fig. 71). This gives directly the value of $\alpha$.

2. Enthalpy of Activation:

A few experiments were performed in M HBF$_4$ containing $4 \times 10^{-3}$ M/l Pb$^{2+}$, in order to determine the enthalpy $\Delta H$, of the reaction. Temperature variation was shown to affect markedly the value of $\Theta$, the diameter of the semicircle as shown in Fig. 72.

$\log \frac{1}{\Theta}$ was plotted as a function of $\frac{1}{T\text{abs}}$. The slope of the line obtained would be equal to $-\frac{\Delta H}{2.303 R}$, from
Fig. 69. Complex plane display of electrode impedance as a function of frequency.
Effect of potential variation

$$E = E_{i=0} - 10 \text{ mv}$$

$Pb/M \text{ HBF}_4 + 6.6 \times 10^{-3} M \text{ Pb}^{2+}$

Fig. 70. Complex plane display of electrode impedance as a function of frequency.
Fig. 71. Logarithmic plot of activation polarisation resistance dependence on concentration of Pb\(^{2+}\) in M fluoroboric acid.
**Fig. 72.** Complex plane display of electrode impedance as a function of frequency: Effect of temperature.
which (Fig. 73), the value of $\Delta H$ was calculated as $23^{\pm2} \text{kJ mol}^{-1} \text{deg. k.}$

3. Determination of the Reaction Rate Constant:

Following the same procedure used in case of the nitrate
Table 5.4 shows the values of $a$, $C^\infty$ and the product $C^\infty \cdot a$ for each concentration of $\text{Pb}^{2+}$. The mean value of $C^\infty \cdot a$ is $2.218 \times 10^{-4}$, excluding the first figure
% error $= 3\%$.

<table>
<thead>
<tr>
<th>$C \times 10^6$ mol/cm$^3$</th>
<th>$\theta$ cm$^2$</th>
<th>$C^\infty \times 10^{-3}$</th>
<th>$C^\infty \cdot a$ cm$^2$/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.60</td>
<td>0.202</td>
<td>1.256 $\times 10^{-3}$</td>
<td>2.537 $\times 10^{-4}$</td>
</tr>
<tr>
<td>3.70</td>
<td>0.250</td>
<td>0.908 $\times 10^{-3}$</td>
<td>2.270 $\times 10^{-4}$</td>
</tr>
<tr>
<td>2.30</td>
<td>0.323</td>
<td>0.696 $\times 10^{-3}$</td>
<td>2.248 $\times 10^{-4}$</td>
</tr>
<tr>
<td>1.70</td>
<td>0.360</td>
<td>0.588 $\times 10^{-3}$</td>
<td>2.115 $\times 10^{-4}$</td>
</tr>
<tr>
<td>1.40</td>
<td>0.430</td>
<td>0.527 $\times 10^{-3}$</td>
<td>2.266 $\times 10^{-4}$</td>
</tr>
<tr>
<td>0.94</td>
<td>0.520</td>
<td>0.422 $\times 10^{-3}$</td>
<td>2.192 $\times 10^{-4}$</td>
</tr>
</tbody>
</table>

$K_{sh}$ was calculated in this case to be $2.9687 \times 10^{-4}$
$\pm 3\% \text{ cm/sec.}$
Fig. 73. Logarithmic plot of activation polarisation resistance variation with temperature.
5.3.8 The Linearised Plot (Section 5.1.3):

This method was tried for comparison in one case only (Fig. 74), in which $\omega Z''$ is plotted against $Z'$. A typical straight line was obtained. The slope gives $\theta \, C$ and the reciprocal gives a value of $\omega$ in the middle between $\omega_o$ and $\omega_{oo}$, from which the point corresponding to $\omega_{oo}$ was determined. The projection of this gives the value of $R$ on the $Z'$ axis, hence $\theta$ is directly read on the graph. This graph also gives the value of $C$, the double layer capacity, determined in this case as $4.464 \times 10^{-5}$ farad/cm$^2$.

A value of $K_{sh}$ using this method was determined to be $2.76 \times 10^{-4}$ cm/sec, in good agreement with the mean value.

\[
\frac{1}{\text{slope}} = \frac{7.65}{0.084} \times 10^3 = 91.071 \times 10^3 = \omega_{\text{half}}
\]

\[
\theta = 0.248 \, \mu
\]

\[
R = 2.612 \, \mu
\]

\[
\frac{1}{C} = 22.4 \times 10^3
\]

\[
C = 4.464 \times 10^{-5} \, \text{farad/cm}^2
\]
Fig. 74. The linearised plot: dependence of cell capacitance on frequency.
5.4 Discussion:

5.4.1 Pb in Nitrate Solutions:

The very high frequencies that had to be used to obtain a few points in the semicircular region indicate a very small value of double layer capacitance in these solutions, e.g. as

\[ \omega_{\text{top}} = \frac{1}{\theta C} \]

hence, for Pb/0.006M Pb\(^{2+}\) in M nitrate (Fig. 57), the point corresponding to a frequency of 50 KHz is approximately the top point on the semicircle. Substituting for \( \omega = 314 \times 10^3 \) and \( \theta = 0.285 \)

\[ C = \frac{1}{0.285 \times 314 \times 10^3} = 1.117 \times 10^{-5} \text{ farad/cm}^2 \]

As predicted in theory, the distortion of the semicircles obtained in this solution is little as the double layer capacity is small.

The determination of D, the diffusion coefficient of Pb\(^{2+}\) has given different values, and considerably lower figures than those published in literature (8.02 \( \times 10^{-6} \))\(^{123} \). However, the straight line obtained at 45° slope, indicates a diffusion in solution controlled reaction. The determination of D for Hg/Hg\(^{2+}\) reported in the
literature was carried out from plots where $g$ was negligible (which is not the case in our results) and at an ideally smooth surface of mercury, so it could be stated that this method of calculating $D$ is not suitable for solid metal surfaces.

5.4.2 Lead in Fluoborate Solution:

A calculation of $C$, the double layer capacitance, has given a value of the same order of magnitude as that in nitrate solutions. The deformation of semicircles could not be attributed then to a high value of double layer capacitance. Alternatively it may be postulated that an adsorption process of the fluoborate or its various hydrolysis products or rather a complex of fluoborate and $\text{Pb}^{2+}$ on the electrode surface causes that deformation.

The straight line following the semicircular region came at slopes much higher than 1. Armstrong et al.\textsuperscript{119,120} have shown different models of impedance plots in the case of adsorption of reaction products. Similar deformation of the semicircles have been shown in their results. The higher slopes of the lines obtained at lower frequencies is also shown by them in the case of active dissolution of $\text{Cr}$ and $\text{Ti}$.

The reaction rate constant calculated ($2.968 \times 10^{-4}$ cm/sec) is lower than those reported for $\text{Pb}$ in perchlorate solutions viz. ($5 \times 10^{-3}$)\textsuperscript{125}. This is to be expected because of the complexing action of the fluoroborate ions.
It could be suggested as well that at the more negative potentials the complexes and the adsorption is less likely to happen as the deformation of semicircles is less.
CHAPTER 6

ELECTRODEPOSITION OF LEAD
6.1 Theoretical Principles

Metal deposition and dissolution usually involve more than a simple discharge or formation of hydrated metal ions. In most practical cases, reactions of complex dissociation or formation occur simultaneously as well as deposition and incorporation of foreign substances (impurities or additives) etc. They all affect the structure and appearance of the deposit obtained. In particular, the shape of the deposit, the surface roughness and surface coarseness (see 6.1.1) are found to depend strongly on the path of the flow of electric current and the path and rate of flow of the species involved, directly or indirectly in the electrolytic process. Thus, this last factor has a profound effect on the morphology of the deposit and may be a cause of seemingly unrelated phenomena. According to Despić and Popov\textsuperscript{126} these phenomena are:

a) Amplification of surface irregularities has been known to appear in electrode processes of high specific rate when deposition is carried out at low concentration of simple ions in solution.
Surface roughness is defined as the ratio between the true and apparent surface area; in the case when the surface is made up of elevations with triangular cross-section, it is equal to the inverse cosine of the elevation angle. This is seen to undergo a considerable increase during plating.

b) **Dendritic growth** represents the extreme case of the above phenomenon, when at some points of the surface protrusions occur, penetrating deeply into the solution. Needlike, spadelike or pinetree like deposits of well-defined crystalline nature are obtained. A large number of phenomenological studies\textsuperscript{127,128} have been reported.

c) **Growth of whiskers**, i.e. threadlike deposits, is known to occur when deposition is carried out from baths containing substances which exhibit a tendency for preferential adsorption on certain crystal planes\textsuperscript{129,130}.

d) **Powdery deposits** are formed in many metal depositions in a current density range in which sufficient difficulties in the transport of depositing species are encountered\textsuperscript{131}.

e) **Leveling** is the phenomenon opposite to the ones described above, when surface irregularities are "ironed out" at prolonged deposition. The effect is obtained when plating is carried out from concentrated metal salt baths containing
strongly adsorbing organic substances as additives in small concentrations\textsuperscript{132}.

f) \textbf{Electropolishing} has been known since the work of Jacquet\textsuperscript{133}, to occur when a metal surface is subjected to anodic dissolution in special baths containing small concentrations of agent with strong complexing affinity for the metal ions, in an electrolyte forming insoluble products with the same ions. A great number of practical applications of this phenomenon have been described in the electroplating literature\textsuperscript{134}.

g) Prevention of dendritic growth by application of pulsating current (i.e. half rectified a.c.) for deposition, has recently been reported in several cases as being a process with great practical potential\textsuperscript{135-137}.

A common feature in all of the preceding phenomena is the difficulty in transporting some species involved in the process. The first two of these phenomena will be dealt with in more detail.

6.1.1 \textbf{Amplification of Surface Irregularities:}

\textbf{Coarseness and roughness:}

Any solid metal surface, which represents a substrate for metal deposition, possesses a certain roughness; it may appear coarse
or smooth and this is not necessarily related to the roughness. Surfaces may have equal roughness and profoundly different coarseness and vice versa. It is the level of coarseness which determines the appearance of metal deposits, while even with considerable roughness, if below the visual level the surface may appear smooth.

It is convenient to define the surface coarseness as the difference in thickness of the metal at the highest and lowest points above an arbitrary reference plane facing the solution. Roughness is defined (in 6.1) as the ratio between the real and the apparent surface area of the electrode.

Historically, it was realised that under certain conditions of dissolution, the surface coarseness tends to decrease\textsuperscript{138}. Krichmar\textsuperscript{139} was the first to point out that in some cases of deposition, under conditions in a way analogous to the previous ones, an inverse effect should take place, i.e. in prolonged cathodic reduction at conditions of diffusion controlled processes, the amplification of both the surface roughness and the surface coarseness arises.

In this respect one should distinguish between linear and spherical diffusion. The limiting current for linear diffusion is
\[ i_{\text{lim}} = \frac{nFDC_b}{\delta} \] 

\[ i_{\text{lim}} = \frac{nFDC_b}{r} \]

n and F have their usual meaning; 

\( D, \) diffusion coeff. of the rate determining species; 

\( C_b, \) bulk concentration; 

\( \delta, \) the thickness of diffusion layer

whereas for spherical diffusion, the limiting current is given by:

\[ i_{\text{lim}} = \frac{nFDC_b}{r} \]

where \( r \) is the radius of curvature of the sphere. Hence, for surface elevations with spherical tips, the rate of growth of the tip will be much higher than that of the rest of the surface, provided that \( r \) is smaller than \( \delta \), otherwise, the linear diffusion equation (1) should be applied, even if the surface is not ideally plane.

This should result in a change in shape of the elevation from a triangular to a paraboloidal one.\(^{1}^{4}^{0}\).

Mathematical models for the variation of amplification factor with the radius of curvature of the surface irregularity are given by Despić and Popov.\(^{12}^{6}\). They tested the validity of these models, and found reasonable experimental evidence.
6.1.2 Time Dependence of the Overall Current at Constant Overpotential:

A direct consequence of the increase in roughness and coarseness of a surface should be an increase in the deposition current at a constant electrode potential. This is due to the increase of the true surface area of the electrode and the increase in limiting current density at the tips of elevations with time as they penetrate into the diffusion layer.

6.1.3 Appearance and Growth of Dendritic Deposits:

Systematic investigation of the problem of dendritic growth in electrocrystallisation is of relatively recent origin. The first extensive accumulation of data on a number of systems (Pb, Ag, Sn, Cd in a variety of electrolytes) is due to Wranglen. He systematised the results both according to the conditions of appearance of dendrites in terms of the current density range and according to structural characteristics of the outgrowth. He found that the minimum current density at which dendrites appear is related to the specific rate of the deposition process.

Thorough investigation of the growth of silver dendrites showed that (a) a certain critical overvoltage must be exceeded in order to provoke dendritic growth, (b) the growth exhibited a certain induction period before it became visible, (c) a critical c.d. for the dendritic growth is directly
proportional to the concentration of the depositing ions. These observations were confirmed by the work of Despic et al.\textsuperscript{142,143.}

Dendrites grow in the same manner as surface irregularities. It seems that there is a critical overvoltage below which general amplification of irregularities occur, and above which the dendritic growth is enhanced. The rate of growth $v_n$ is similarly governed by:

$$v_n = \frac{v_D (C_e^{\text{MZ}^+} - C_i^{\text{MZ}^+})}{r} = \frac{v_D \cdot A \cdot C}{r}$$

where $r$ is the linear growth rate,

- $C_e^{\text{Z}^+}$ is the bulk concentration,
- $C_i^{\text{Z}^+}$, concentration at the tip,
- $r$, radius of curvature of the tip.

Detailed equations are illustrated by Despic and Popov\textsuperscript{126.}

6.1.4 The Effect of Crystal Structure of the Depositing Metal on the Direction of Growth and Shape of Dendrites:

It is clear that there should be a preferential way of building the discharged adatoms into the crystal lattice which should result in favouring a certain direction for the growth of the structure;
two types of sites are particularly favourable: (a) the screw-dislocation sites and (b) the separation planes in twining.

The first are favourable because they can provide for continuous growth without the necessity for nucleation. If the direction of spiral growth is inclined with respect to the direction of the diffusion field, the rate of growth would be less and given by:

$$v_n = v \cos \theta = \left( \frac{VDC^0}{\delta} \right) \left( \frac{h}{r} \right) \cos \theta$$

$v_n$ = rate of growth concerned
$v$ = max. rate of growth
$\theta$ = angle of inclination
$h$ = height of the dendrite
$r$ = radius of curvature at the tip
$\delta$ = thickness of diffusion layer

The regularities in the appearance of side branches and the well defined angle between them and the main stem found in most dendrites seem to have their origin in the phenomenon of twining. The separation plane provides a particularly suitable location for incorporation of atoms into a crystal lattice.
6.2 Experimental:

6.2.1 The Electrodes:

The previously described electrode (3.2, Fig. 4) was used throughout these measurements and a lead strip served as the anode in a 250 ml. beaker.

6.2.2 The Electroplating Solutions:

The basic fluoroborate solution used was prepared as follows (according to Chloride Industrial Batteries Ltd): 362.83g of litharge added to 1 l. of 40% fluoroboric acid. The mixture is stirred for 72 hours. Water added to bring the specific gr. to 1.170-1.175 at $\approx 16^\circ$C. The solution should contain 37-50 g/l free fluoroboric acid (soln. A). It was found necessary to filter the solution through a 04 sintered glass crucible. Gelatine was added in the proportion of 0.276 g/l to prepare soln. B. It was dissolved first in a small quantity of water at $\approx 38^\circ$C then added to the main soln.

6.2.3 The Circuit

D.C. current was driven from a d.c. supply (type pp3 Advance) through a variable resistance. Current densities were obtained
by dividing the current through the cell by the initial area of the cathode because the area of the total growing tips of the dendrites is not known.

Galvanostatic charging and discharging was followed by an x-y recorder (type BD8, Kipp and Zonen).

6.3 Results:

6.3.1 Lead Deposition from Fluoroborate Solutions:

An introductory investigation of the deposition of lead was carried out. The electrodeposit obtained from soln. A (lead fluoroborate + fluoroboric acid soln.) under various electro-deposition conditions was investigated under the microscope. Deposits from soln. B (soln. A + gelatine) under the same conditions of electroplating were compared with the former ones.

Keeping the quantity of electricity constant and using different current densities (for different periods of time), the appearance of the deposit was examined and compared to that from soln. B. A different quantity of electricity is passed using various current densities for deposition and the comparison is made and so on.
Table 6.1 summarizes the appearance under the microscope (magnification of 100x) of the electrodeposit.

**TABLE 6.1**

<table>
<thead>
<tr>
<th>c.d. (i/mA.cm^{-2})</th>
<th>I/(mA) current passing</th>
<th>(t/\text{min})</th>
<th>(Q/\text{mA.min})</th>
<th>SOLUTION A</th>
<th>SOLUTION B</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.54</td>
<td>0.25</td>
<td>80</td>
<td>20</td>
<td>spongy deposit, homogeneous</td>
<td>spongy deposit homogeneous</td>
</tr>
<tr>
<td>7.08</td>
<td>0.5</td>
<td>40</td>
<td>20</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>14.16</td>
<td>1</td>
<td>20</td>
<td>20</td>
<td>slightly thicker deposit around the edge</td>
<td>normal plating conditions</td>
</tr>
<tr>
<td>35.41</td>
<td>2.5</td>
<td>8</td>
<td>20</td>
<td>&quot;</td>
<td>spongy deposit, slightly thicker around the edges</td>
</tr>
<tr>
<td>70.82</td>
<td>5</td>
<td>4</td>
<td>20</td>
<td>&quot;</td>
<td>crystallites around the edges</td>
</tr>
<tr>
<td>70.82</td>
<td>5</td>
<td>20</td>
<td>100</td>
<td>crystalline growth around the edge</td>
<td>round edged crystals on the edge</td>
</tr>
<tr>
<td>41.64</td>
<td>10</td>
<td>10</td>
<td>100</td>
<td>long crystals esp. around the edge</td>
<td>Treeing all over, denser on the edge</td>
</tr>
<tr>
<td>354.1</td>
<td>25</td>
<td>4</td>
<td>100</td>
<td>long crystals, much longer on the edge, easily separated</td>
<td>Treeing, branching at the top, round edges, easily separated</td>
</tr>
</tbody>
</table>
It is clear that both current density and the quantity of electricity 'Q' used for electroplating affect the appearance of the deposit, e.g. when Q was 20 mA.min/electrode and the current densities ranged between 3.54 and 14.16 mA/cm², the deposits were all similar being smooth and homogenous on the whole area of the electrode surface. The usual practical plating conditions of lead lie in this region. If higher current density is used (70.82 mA/cm²), developed crystals began to appear around the edge of the surface, and even "treeing" was encountered.

At higher Q and i values the crystalline growth became more and more pronounced. At very high current density, namely 354 mA/cm², the crystals had the elongated prismatic shapes.

Some difference in the appearance of growths in solutions A and B was observed. The crystals were sharp and long (in soln. A), while they were round edged in soln. B. At the very high current density, branching of the deposits was particularly clear in solution B. A common feature when using this high current density is the ease with which the crystals electro-deposited from both solutions could be separated from the surface.
6.3.2 Lead Deposition from Fluoroborate Solutions Containing Some Organic Additives:

The second step in this investigation was to choose some organic compounds to be added to the plating solution in order to try to modify the deposit. Lead was electrodeposited from these complex solutions and the oxidation-reduction properties of the deposit studied.

A survey of the literature has shown that the organic surfactants most used in combination with the fluoroborate solution include: gelatine, hydroquinone, 1-naphthol-4-sulphonic acid and a sodium salt of lignin (Mordex powder), see e.g. ref. 141, 145. These were chosen to study their effect on the lead deposit.

Procedure:

Electrodeposition was carried out using different current densities and passing different quantities of electricity. The electrode was then washed carefully in tridistilled water, and transferred immediately to the polarisation cell (3.2.3. Fig. 3), whereupon it was anodically polarised at constant current till oxygen evolution in \( \text{H}_2\text{SO}_4 \). The electrode was maintained under \( \text{O}_2 \) evolution conditions for 10 minutes. The current was then reversed and the discharge \( E - t \) curve recorded. The reduction
process was allowed to take place until the potential of PbSO$_4$/Pb system was achieved. The current used for both charge and discharge was 50 $\mu$A/electrode.

From these curves, the discharge capacity was determined from the duration of the PbO$_2$/PbSO$_4$ potential step. This was compared to the corresponding step in case of unplated lead electrode, charged and discharged under the same conditions.

The results are summarised in Table 6.2. The plating conditions are illustrated in the first three columns, the discharge characteristics in the following two. $Q_2/Q_1$ is the ratio between the quantities of electricity derived from and consumed for the formation of the electrodeposit respectively. The last column shows the quantity of electricity obtained at the discharge of electroplated lead compared to this obtained from unplated charged and discharged lead electrode (same area and same conditions of charging).

Consideration of table 6.2. shows the following: When the quantity of electricity passed for electrodeposition $Q_1$ was 20mA.min., the discharge capacity obtained from electrodes plated in different solutions ranged between 3.3 and 8 times the capacity of the unplated electrode. But when $Q_1$ was 100 mA.min, the increase in capacity was either around 6 fold (especially using a current of 5 mA for electroplating, or increased to 20
to 30 fold. In some experiments a capacity as high as 50 times that of unplated lead was obtained, but these were not readily reproducible because of the noncoherency of the deposited crystals.
TABLE 6.2
Deposition of Lead in Presence of Organic Additives and Discharge Capacity in M H₂SO₄.

Surface area of the electrode = 0.0706 cm²
Discharge current = 50 μA/electrode

<table>
<thead>
<tr>
<th>SOLUTION</th>
<th>i/mA</th>
<th>t/min</th>
<th>Q₁/mA.min</th>
<th>t₂/min discharge step</th>
<th>Q₂/0.05x t₂ mA.min</th>
<th>(Q₂/Q₁) x 10³</th>
<th>(Q₂/Q₂ in H₂SO₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) H₂SO₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2) Pb(BF₄)₂ +HBF₄</td>
<td>1</td>
<td>20</td>
<td>20</td>
<td>1.9</td>
<td>0.095</td>
<td>4.75</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>20</td>
<td>100</td>
<td>2.7, 8</td>
<td>0.135, 4</td>
<td>1.35, 4</td>
<td>6.7, 20</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>10</td>
<td>100</td>
<td>8.1, 11.4</td>
<td>0.405, 5.7</td>
<td>4.05, 5.7</td>
<td>20.2, 22</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>20</td>
<td>200</td>
<td>16</td>
<td>0.8</td>
<td>4</td>
<td>40</td>
</tr>
<tr>
<td>(3) Pb(BF₄)₂ +HBF₄ + Gelatine</td>
<td>1</td>
<td>20</td>
<td>20</td>
<td>3</td>
<td>0.15</td>
<td>7.5</td>
<td>7.5</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>20</td>
<td>100</td>
<td>4.8, 8.3</td>
<td>0.24, 4.15</td>
<td>2.4, 4.15</td>
<td>12, 20.7</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>10</td>
<td>100</td>
<td>8.3</td>
<td>0.368</td>
<td>4.15</td>
<td>20.7</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>20</td>
<td>200</td>
<td>7.35</td>
<td></td>
<td>1.84</td>
<td>18.4</td>
</tr>
<tr>
<td>(4) Soln (2) + hydroquinone</td>
<td>1</td>
<td>20</td>
<td>20</td>
<td>1.35</td>
<td>0.067</td>
<td>3.35</td>
<td>3.35</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>20</td>
<td>100</td>
<td>2.7</td>
<td>0.135</td>
<td>1.35</td>
<td>6.75</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>10</td>
<td>100</td>
<td>5.1, 12.2</td>
<td>0.255, 6.1</td>
<td>2.55, 6.1</td>
<td>12.7, 30</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>4</td>
<td>100</td>
<td>11.3</td>
<td>0.565</td>
<td>5.65</td>
<td>28</td>
</tr>
<tr>
<td>(5) Soln (2) + 1-naphthol 4-sulphonic acid</td>
<td>1</td>
<td>20</td>
<td>20</td>
<td>1.25</td>
<td>0.062</td>
<td>3.1</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>20</td>
<td>100</td>
<td>4.1, 9.9</td>
<td>0.22, 4.95</td>
<td>2.2, 4.95</td>
<td>11, 25</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>10</td>
<td>100</td>
<td>11.4</td>
<td>0.57</td>
<td>5.7</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>4</td>
<td>100</td>
<td>21</td>
<td>0.61, 7.35</td>
<td>6, 7.35</td>
<td>30, 36.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.05</td>
<td>10.5</td>
<td>50.2</td>
</tr>
<tr>
<td>(6) Soln (2) + soluble salt of lignin (Mordex)</td>
<td>1</td>
<td>20</td>
<td>20</td>
<td>3.2, 3.4</td>
<td>0.16, 0.17</td>
<td>8, 8.5</td>
<td>8, 8.5</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>20</td>
<td>100</td>
<td>6.2, 7</td>
<td>0.31, 0.39</td>
<td>3.1, 3.9</td>
<td>15.5, 19.5</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>10</td>
<td>100</td>
<td>8.8</td>
<td>0.4</td>
<td>4</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>4</td>
<td>100</td>
<td>10.5, 10.2</td>
<td>0.52, 0.51</td>
<td>5.2, 5.1</td>
<td>26, 25.5</td>
</tr>
</tbody>
</table>
The capacities of electrodes plated in the fluoborate solution without any organic additive, were generally lower than those plated in presence of the organic compounds.

Moreover, a further increase in $Q_1$ (to 200 mA.min or i, did not affect much the capacity of the obtained electroplate.
6.3.3 Discussion:

The fluoroborate bath is widely used for the electroplating of lead in practical purposes. Wranglen\textsuperscript{127} has shown excellent microphotographs of lead dendritic growths from different depositing solutions including the fluoborate used throughout this investigation. The effect of organic compounds added to the plating electrolyte was studied\textsuperscript{144,145} for a large number of compounds. It is stated that the effect of these, being adsorbed on the metal surface, is to produce better homogeneity of deposits and decrease the degree of onset of dendrite formation. These observations are confirmed by our findings except for the fact that once dendrites were formed, treeing was more pronounced in case of the additive-containing solution.

As regards the capacity of deposited lead some conclusions could be drawn:

The marked increase in the capacity of electrodes obtained by just electroplating at a higher current density, while the same quantity of electricity is passed, may indicate the onset of dendrite formation, hence a big increase in surface area of the electrode. This leads to the higher capacity of the plate. One could not say that higher capacities are obtained when electrogrowths were achieved in presence of any organic compound compared to those from the free fluoborate solution.
Once more, it is just a question of these crystalline growths being formed on the surface or not.
6.4 Detection of Changes in the Surface Area of the Electrode by Capacitance Measurements

6.4.1 Experimental Techniques

1. Throughout these measurements, the electrode used was similar to that described in Chapter 3, section 3.2 and the circuit was that shown in Fig. 52, Chapter 5.

The electrolyte studied first was $\text{M NaF}$, then a $0.01\text{M}$ solution was used for the subsequent measurements. The fluoroborate solution used for electrodeposition was described in Chapter 6 section 6.2.2. All potentials were referred to the SCE.

2. Pretreatment of the electrode

After a large number of preliminary experiments the best procedure was found to be as follows:

The electrode was first mechanically polished. In some cases it was necessary to cut off a layer of the electrode surface if it was very rough.

The electrode was then electropolished using 10% perchloric acid and a current of $100 \mu\text{A/electrode}$ for 3 min. The electrode was then rinsed thoroughly in tridistilled water followed by cell electrolyte and transferred to the cell in a wet condition. The capacitance was then measured and the
cycle of operations repeated until a constant value of electrode capacitance was obtained. The electrode was finally rinsed in tridistilled water and observed under the optical binocular microscope before electrodeposition was commenced.*

6.4.2 Differential Capacitance Measurements in Sodium Fluoride Solutions

Reproducible capacitance-bias potential curves of lead in M sodium fluoride solutions were very difficult to obtain even after 4-5 weeks of circulation of the solution over purified activated charcoal (appendix 2).

Fig. 75 is representative of the most satisfactorily reproducible results that were obtained. These results agree well with those of Rybalka et al.\textsuperscript{116} and Ivanov et al.\textsuperscript{117}. The capacitance data in M NaF solution were not much affected by changes of frequency in the range used, but lower frequencies generally gave better reproducibility. However, the independency of results from frequency indicates the absence of any appreciable contribution of faradaic component to the impedance measurements\textsuperscript{117}.

* In this section, the roughness coefficient of the polished surface was taken as unity and the current density is calculated for a unit of the apparent surface area.
Fig. 75. Capacitance-bias potential curve of lead in M NaF.
Measurements in 0.01 M NaF were carried out at very low frequencies, since at higher frequencies the bridge was difficult to balance due to the high resistance of the system. The frequency found to be most satisfactory was 20 Hz, this gave good reproducible results as shown in Fig. 76. The diffuse layer minimum observed on the differential capacitance curve occurred at -0.9V, which is slightly different from the value published by Ivanov. However, it has been stated \(^{147}\) that the determination of the potential of zero charge in the fluoride solutions is not very accurate, although it is difficult to see why this should be so. A possible reason for the discrepancy between the present work and that of the Russians may be the very low frequency used in our work compared to the frequencies used in Ivanov's experiments (210-1000 Hz). In any event the difference between the observed potentials at the capacitance measurements is small and consequently it was considered that this dilute fluoride solution would be suitable as a test solution with which to explore the quality of electrodeposited lead surfaces by capacitance measurements.
Fig. 76. Capacitance-bias potential curve of lead in 0.01 M NaF.
6.4.3 Polarisability of Lead in Sodium Fluoride Solutions:

The region of 'experimental' polarisability of lead in M NaF solutions was determined by measuring the faradaic current curve (E-i curve) shown in Fig. 77. This region lies approximately between -0.6V (SCE) and -1.1V (SCE) bounded by lattice dissolution at -0.6V and hydrogen evolution at potentials more negative than 1.1V.

Since it was intended to monitor the quality of lead surfaces using capacitance measurements, it was considered necessary to check that faradaic effects were absent at the particular potential chosen for surface examination, vis -0.9V (PZC). This was demonstrated by the plot of the real part of the cell impedance against the imaginary part, which showed very little effect of variation of frequency on the cell impedance as shown in Fig. 78.
Fig. 77. Faradaic current vs Potential curve for lead in M NaF.
Fig. 78. Dependence of cell capacitance on frequency.
6.4.4 Electrodeposition and Measurement of Capacitance

1. The technique used:
The electrode was pretreated as previously described (6.4.1), then a lead layer was electrodeposited. It was subsequently carefully rinsed with tridistilled water and cell electrolyte, transferred wet to the capacitance measurement cell and its capacitance is determined. The electrode was rinsed again and the process is repeated with occasional observation of the electrode surface under the microscope.

In some of the experiments the Planté type capacity of the plate was determined after a certain period of electrodeposition using the cell shown in Fig. 3, Chapter 3, and the circuit shown in Fig. 37, Chapter 4, but the same electrode was not used again for further electrodeposition. Another electrode was used for the subsequent whole period of lead deposition, the capacitance was measured, then the discharge capacity and so on.

2. Results:
Capacitance Measurements at Low Current Density
Fig. 79 shows the variation of capacitance of the electrode as a function of time of electrodeposition at a rate of 3.5 mA/cm². The initial constant capacitance of the polished electrode (see section 6.4.1) was around 12 μF/cm² in all cases.
Fig. 79. Differential capacitance-time curve for lead in 0.01M NaF.

Electrodeposition at 3.54 mA/cm².
Lead electrodeposition was conducted for 10 min. after which the surface of the electrode was observed under the microscope. An imperfect patchy layer of deposit was observed on the surface. The electrodeposition process was resumed for a further 20 min. and the microscopic examination repeated. A perfect layer of coarse pyramidal deposit was developed on the surface (the linear region of the plot in Fig. 79).

Observation of the electrode after 50 min. revealed a slightly smoother surface; this was the region corresponding to a nearly constant value of surface capacitance. A slight increase in capacitance was observed after 1 hr and the experiment was consequently terminated at this stage.

Capacitance Measurements at the Higher Current Densities

Figs. 80-83 show the capacitance-time relationships for the lead electrode surfaces formed by electrodeposition at 10, 15, 20 and 25 mA/cm² respectively. The same behaviour was observed in all four cases; a region of rapid increase in capacitance taking the form of a slightly curved line and extending for nearly 5 min (except in the case of fig. 83, the highest c.d., where the increase occurred over a shorter time interval). This increase is followed by a straight line region. The microscopic examination of the
Electrodeposition at 10 mA/cm²

Fig. 80: Differential capacitance-time curve for lead in 0.01M NaF.
Fig. 81. Differential capacitance-time curve for lead in 0.01M NaF.
Electrodeposition at 20 mA/cm²

Fig. 82. Differential capacitance-time curve for lead in 0.01 M NaF.
Electrodeposition at 25 mA/cm$^2$.

Fig. 83: Differential capacitance-time curve for lead in 0.01M NaF.
electrode surface showed an imperfect layer of deposit in the first region and pyramidal growths (cone shaped deposits) in the straight line region. The 'pyramids' were observed under the microscope after 45 min (Fig. 80), 30 min (Fig. 81) and 20 min (Fig. 82).

**Capacitance Measurement at the Highest Current Densities**

When very high c.d. of 35 and 50 mA/cm² were used, the features of the differential capacitance time curves (Figs. 84, 85) differed from those obtained at lower c.d. Thus they consisted of a region of rapid increase in capacitance, followed by a short linear part extending for not more than 10 min, followed by a curving portion. At the highest c.d. (50 mA/cm²) an inflection on the curve was also observed after the elapse of a longer electro-deposition time.

When the electrode was inspected microscopically these regions corresponded respectively to: surface coverage of the electrode, pyramidal growth, and crystalline (dendritic) growth in the curved region especially around the edges of the electrode surface.

The Plante discharge capacity of these plates - with dendritic growths - was determined after oxidation to PbO₂. Figs. 86 and 88 show the curves for non electrolytic (unplated)
Fig. 84. Differential capacitance – time curve for lead in 0.01 M NaF.
Fig. 85. Differential capacitance-time curve for lead in 0.01 M NaF.

Electrodeposition at 50 mA/cm².
Fig. 86. Potential-time curve for lead in $\text{MH}_2\text{SO}_4$ reference experiment.
Fig. 87 Potential-time curve for lead in M H₂SO₄ after electrodeposition at 35 mA/cm² for 70 min.
Discharge at 2.3 mA/cm²

Fig. 88. Potential-time curve for lead in 0.5 M H₂SO₄ reference experiment.
lead in sulphuric acid. Fig. 87 reveals the increase in discharge capacity of the electrode after electrodeposition at 35 mA/cm\(^2\) for 70 min\(^*\). Figs. 89 and 90 reveal the gradual increase in discharge capacity of the electrode after electroplating at 50 mA/cm\(^2\) for 20 and 40 min respectively.

\* The Pb\(^{2+}\)/Pb\(^{4+}\) discharge step duration is taken as the means of comparison (see Chapter 4).
Fig. 89. Potential-time curve for lead in 0.5M H₂SO₄ after electrodeposition at 50 mA/cm² for 20 min.
Fig. 90. Potential-time curve for lead in 0.5 M H$_2$SO$_4$ after electrodeposition at 50 mA/cm$^2$ for 40 min.
6.5 Discussion

Numerous publications exist on the electrodeposition of metals and alloys. These are concerned with the smooth deposition desired by electroplaters. Only rarely the dendritic or some other unwanted growth form are mentioned or discussed. Relatively recent publications have appeared on dendritic growth in electrodeposition. Dendrites of several metals grown in aqueous electrolytes were reported by Wrangel\textsuperscript{127,151}. Detection of surface area variations due to dendritic growth above and below the critical overpotential required for zinc dendrite initiation - by the measurement of the electrical double layer (edl) capacitance - was carried out by Diggle et al\textsuperscript{148}. A preliminary potentiostatic investigation on lead deposition on a smooth platinum ball-shaped electrode showed an extremely low $\eta_{\text{crit}}$ (the critical deposition overpotential); using the technique of Diggle et al\textsuperscript{149} in a previous publication. Obviously $\eta_{\text{crit}}$ on a lead base would be even less than that on platinum. Hence, current density measurements alone are conducted in this investigation.

Diggle, Despić and Bockris\textsuperscript{149} have concluded that dendrite initiation is the result of pyramidal growth under bulk diffusion control until the required radius of curvature to give spherical flux to the propagating tip is attained.
Our results show that the deposition of the initial layer of deposit seems to initially reproduce the primary substrate roughness and increases the surface roughness by a ratio of nearly $\frac{22}{12} = 1.8$ times as deduced from the increase in surface edl capacitance (Figs. 80-85). The subsequent development of pyramids (cone shaped growths) during the following period of deposition increases the surface roughness by $\frac{33}{15} = 2.2$ (Fig. 79), and over an unlimited range (exceeding 2 as predicted from Figs. 80-83). This is probably the region where the current density is not high enough for the development of dendrites - at least within the period of time of the experiment. These pyramids are regarded as the dendrite precursors.

When the current density is increased, however, the growth rate also increases and the probability of initiation of twin boundaries in the nuclei becomes high. Once the twin planes are formed, the twin grooves in the nuclei are lower energy sites for further nucleation and growth than on the faces. The crystals will then grow as dendrites (branched) by the twin plane re-entrant edge (TPRE) mechanism.

In a recent publication by Liaw and Faust\textsuperscript{150}, the morphology and habit of growth from Pb(NO\textsubscript{3})\textsubscript{2} - NH\textsubscript{4}NO\textsubscript{3} solutions of electro-deposited lead dendrites was examined at different current densities and lead ion concentrations. Using x-ray diffraction
and the scanning microscope they concluded that all electrodeposited dendrites were found to contain twin planes.

The growth of dendrites follow an exponential law as shown by Despic et al. until they become comparable to the diffusion layer thickness. After this initial process, the protrusion forms its own diffusion layer, the conditions of spherical diffusion to the tip are established and growth becomes governed by a law of the type derived by Barton and Bockris.

These common rules apply clearly in our results, thus, as the dendritic growth starts the t-C curve is no longer linear but is a curve with an upward inflection (see figs. 83, 84).

The reason of the reverse inflection seen on fig. 85 might lie in the fact that as the surface area grows tremendously the current density is much lower, hence the rate of growth might be affected and slowed down.

The charge and discharge of these electroplated electrodes with dendritic growths reveals the increase in discharge capacity induced by the large increase in surface area. Further deposition is restricted by the extreme fragility of the deposit at higher current densities or after the elapse of longer periods of time.
CHAPTER 7

GENERAL DISCUSSION AND CONCLUSIONS
CHAPTER 7

General Discussion and Conclusions

7.1.1 Behaviour of Lead in Sulphuric Acid Solutions

The potentiodynamic curves of lead in sulphuric acid have been discussed in the light of the well known behaviour of lead in this medium.

The formation of lead sulphate on lead has been studied thoroughly using the L.S.V. technique and correlating the sweep rate with the sulphate peak-current. It was concluded from these curves that a parallel solid state and solution phase processes occur simultaneously. The sweep speed determined which of the two is contributing more to the sulphate film formation. The limiting slopes of the 'peak current - \( \sqrt{s.r.} \) curves both at the lower and higher sweep speeds were compared with the solubility curve of PbSO\(_4\) in H\(_2\)SO\(_4\). A close resemblance was observed between the maxima of the latter and the limiting slope curve at the higher sweep speed. Thus, it was concluded that the solid state reaction mechanism predominates when using slower sweep speeds, while at the higher s.r., the solution precipitation or the diffusion in solution dominates in the sulphate formation process.
7.1.2 Effect of Different Anions on the Anodic Behaviour of Lead in Solution Mixtures:

The effect of industrially used perchlorate ion for the formation process of Planté plates was studied and compared to other anions having soluble lead salts. The results showed the following:

1. The addition of acetate and fluoroborate ions to sulphuric acid resulted in an increased solubilisation of lead in the region anodic to the sulphate formation potential. This was particularly clear in the case of the acetate ion where a chemical reaction was assumed to take place between the acetate ion and PbO. Nevertheless, rather decreased peak currents corresponding to lead sulphate formation were observed, probably due to the adsorption of the acetate and the various hydrolysis products of the fluoroborate on the electrode surface.

2. In the case of the perchlorate and nitrate ions, the effects were many and complicated. Both these ionic species increase the sulphate peak current denoting an increased quantity of lead dissolution in this region. Both increase the trans-passive dissolution especially the nitrate which was shown to enhance the formation of PbO and even PbO$_2$ at less positive potentials.
A very important effect of both ions was the 'pitting' corrosion they engender after the formation of the oxide layer. Pits are formed at lower potentials in the case of the nitrate. However, they are few in number and are dependent on the nature of the oxide film formed, while in the case of the perchlorate they are formed simultaneously with oxygen evolution.

The use of these ions leads to the formation of more soluble lead which is subsequently deposited as lead sulphate and finally transformed into lead dioxide, the active material on the Planté plate. These ions are known consequently as the 'forming agents' and they serve increase the capacity of the plate and decrease the time taken to form the plate according to the original Planté technique. It can be concluded that the perchlorate ion is the most suitable for the formation process, followed by the nitrate and finally the acetate and fluoroborate.

7.2 Formation of Planté Plates Using Superimposed a.c. on d.c.

The industrial technique of formation was first reproduced and interpreted as follows:

The perchlorate/sulphate ratio used lies well in the region of pitting attack of the perchlorate. Hence, a continuous process of dissolution and pitting of lead takes place and was clearly
revealed in the final potential of the attack process which lies below that of the PbO$_2$/PbSO$_4$ potential. The perchlorate ions are assumed to be adsorbed and held in the pits even after washing the electrode, the potential being below that required for PbO$_2$/PbSO$_4$ reduction. This is presumably a mixed potential between PbO$_2$ formation and the dissolution process taking place at the pit sites.

Secondly, an applied ripple of a.c. was superimposed on the d.c. of formation in perchlorate-free sulphuric acid. The higher frequencies of applied a.c. did not result in any increase in the discharge capacity of the plate. However, very low frequencies of 0.01 Hz and lower, resulted in an increase in the electrode discharge capacity, but only because they produce the same effect of 'deep cycling' of the electrode which is similar to the original Plante technique. Moreover, a limiting value of 5 fold increase in capacity or so was obtained using this technique. This could not be in any way compared to 70 fold or more brought about in the discharge capacity of the electrode by chemical attack.

7.3.1 Formation of Lead by Electrodeposition:

1. The first group of experiments revealed the effects of both current density and quantity of electricity on the growth of lead electrodeposits from fluoroborate solutions. The
current density was found to be more critical in determining the crystal growth on the electrode surface.

In presence of gelatine, the crystal shape was different - due to the adsorption of this substance - from those grown in the additive-free fluoroborate solution. They were round edged, and 'branching' was more often encountered than with the previous case.

2. Secondly, the electrodeposition was carried out from simple and complex fluoroborate solutions containing organic compounds. The electrodeposited lead was oxidised to PbO₂ and reduction capacity was determined. As the dendrites were observed on the electrode, the discharge capacity increased markedly.

7.3.2 Differential Capacitance Measurements of Electrodeposited Lead:

The electrodeposition of lead was studied using the differential capacitance measurements as a tool for the detection of increases in surface roughness (hence crystalline growth). Differential capacitance measurements were made in NaF solutions. Despite the various difficulties encountered in the case of the concentrated solution, the electrode was polarisable in the electrolyte and reproducibility of measurements was achieved at very low frequency in a 0.01 M solution.
The microscopic examination and differential capacitance-time of electrodeposition correlation curves both showed the following:

1. A region of rapid increase of roughness (nearly doubled) of the electrode corresponding to the surface coverage and magnification of surface irregularities of the electrode surface.

2. The cone shaped (pyramidal) growth of electrodeposit was always accompanied by a region of straight line relationship in the differential capacitance-time curves. Regions 1 and 2 were observed over the whole period of the experiment when current densities $< 25 \text{ mA/cm}^2$ were used.

3. At higher current densities of electrodeposition, well-developed crystals (dendrites) appeared on the electrode surface after the elapse of a short time of electrodeposition. The growth of these crystals is assumed to follow an exponential rate law. Indeed, the capacitance-time correlations showed curved regions in this case. It was assumed that at these higher current densities, dendrite formation is facilitated and that they are formed via the twin plane re-entrant mechanism.

The charge-discharge capacity of the electrodes with crystalline growths was determined and an increase of capacity was always observed.
over and above that observed with the smooth electrode.

It could be concluded that the differential capacitance measurement provides information about the surface changes, but is far too complicated to be used as a quick method for the detection of the onset of dendritic growth during electroplating. It is also noteworthy that often in the experiments showing an increase in the discharge capacity of electrodeposited lead in presence or absence of organic additives from fluoroborate solutions were limited by the incoherency of the deposit after a certain period of deposition. If this limitation could be prevented, the electrodeposition/oxidation process might provide an alternative to the present industrial method for positive Plante production.

7.4 Kinetic Studies of Lead Using the Impedance Measurements

Kinetic studies were made on lead using the technique developed by Sluyters and co-workers. Impedance measurements were performed in both the fluoroborate and the nitrate solutions. Some kinetic parameters were thus deduced. The results could be summarised in the following:

1. The polarisability range of lead is much wider in KNO₃ being -0.6 to -1.2V (SCE) than in the fluoroborate solution (-0.45 to -0.7 (SCE)).
2. The transfer coefficient \( \alpha \) was determined to be 0.59 and 0.56 for the nitrate and fluoroborate solutions respectively indicating a similar mechanism of charge transfer in both solutions.

3. The double layer capacity was approximately \( 1.117 \times 10^{-5} \) F/cm\(^2\) in the nitrate and \( 4.464 \times 10^{-5} \) in the fluoroborate solutions. A higher value of the double layer capacity is to be expected in the case of the fluoroborate due to its tendency of ionisation and adsorption on the electrode surface.

4. The reaction rate constant was determined in the nitrate solution to be \( 3.456 \times 10^{-4} \) cm.sec\(^{-1}\). For the fluoroborate solution it was determined in two ways, both gave very good confirmatory results, viz: \( 2.97 \times 10^{-4} \) cm.sec\(^{-1}\) and \( 2.76 \times 10^{-4} \) cm.sec\(^{-1}\) and it is interesting that there is not much difference from those obtained in the nitrate solution.

5. The most interesting observation was the behaviour shown by the plots of real and imaginary parts of cell impedance. The straight lines on the low frequency side of the semi-circular region go off exactly at a slope of unity for the nitrate solutions. Nevertheless, the deduced diffusion coefficient value was much lower than that published in the literature. It could be concluded that this method is not suitable for calculating \( D \) for solid metal electrodes,
however, these lines indicate a diffusion in solution controlled process.

In the case of the fluoroborate solutions, the lines following the semicircles did not come at 45°, especially at lower potentials than $E_{\text{i}=0}$ and at lower temperatures. This behaviour was interpreted in terms of either adsorption or complex formation between lead and the different hydrolysis products of the fluoroborate ion.

Further Work

1. The behaviour of lead in sulphate - nitrate mixtures was particularly interesting and further study of the reactions taking place in this medium both on lead and on lead dioxide would be of importance since nitrates are actually used in industry in place of the perchlorates in the process of formation of Plante plates.

2. It would be of interest to study the nature of possible complexes between lead and fluoroborate ions or their various dissociation products.

3. Further work could be done to solve the problem of incoherency of electrodeposited lead at high current densities of after a long period of electrodeposition. Thus, the Plante type capacity of electrodeposited lead could possibly be increased.
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APPENDIX 1

Determination of Lead Using Xylenol Orange as Indicator

Reagents:  EDTA solution, 0.02M, standardised against 0.05M Pb(NO₃)₂
Xylenol orange indicator, 5%
Hexamine 'Solid'

Procedure: Pipette 10 ml of the lead-ion solution into a 250 ml conical flask, dilute with ≈ 10 ml of distilled water and add 3 drops of the indicator solution. Add very dilute nitric acid, stir. The solution will acquire a yellow colour. Add powdered hexamine (hexamethylenetetramine) until the colour is intensely violet - this step ensures that the solution has the correct pH (about 6) for the subsequent titration. Titrate with standard EDTA until the colour changes to lemon yellow.
Granular gas adsorption charcoal was extracted in a soxhlet apparatus with constant boiling hydrochloric acid. The acid was changed weekly and the extraction was continued until the acid remained colourless. Generally this procedure took about 3 months. The charcoal was then washed with water (also replaced weekly) until the washings showed no positive test for chloride ion.
**APPENDIX 3**

**Cleaning of Glassware**

All Electrolytic cells and glassware were cleaned by steeping for 10 days in a 50/50 mixture of concentrated nitric and sulphuric acids. The acid was removed by numerous washings with deionised water, after which the cell was allowed to stand in bidistilled water for a day, and a final rinse with tri-distilled water was given.
APPENDIX 4

Purification of Electrolytes

Electrolytes were made up from A.R. grade chemicals using tri-distilled water from deionised stock.

The electrolytes used for impedance measurements were purified by constantly pumping over charcoal, the preparation of which is described in Appendix 2. Nitrogen, deoxygenated by passing over copper at 400°C and prehumidified, was used to circulate the electrolytes in the cell. The electrolyte purity was judged by the reproducibility of the a.c. impedance of the lead electrode. In general, about four weeks circulation was considered necessary to achieve a satisfactory level of cleanliness.