The electrochemistry of porous lead dioxide

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THE ELECTROCHEMISTRY OF

POROUS LEAD DIOXIDE

by

Paul Casson

Supervisor: Dr. N.A. Hampson

Submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy of Loughborough University of Technology, June 1978.

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The work described in this thesis has not been submitted, in full or in part, to this or any other institution for a higher degree.
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SUMMARY

The reduction of electrodeposited $\beta$-lead dioxide to lead sulphate in 5M sulphuric acid has been studied at the stationary and RDE. Potential step and sweep experiments have been made and a model for the discharge process of lead dioxide has been proposed based on charge transfer and limited high field conduction. The potentiostatic oxidations of lead sulphate overlying lead and lead dioxide have been investigated.

The reduction behaviour of porous one-dimensional lead dioxide electrodes have been examined and shown to be independent of rotation speed in a large excess of 5M sulphuric acid. The reduction peak was broadened by the porosity. This broadening was interpreted in terms of the reaction being driven more deeply into the pore structure as the front of the electrode becomes progressively more resistive. The effect of different potential sweep rates on the current response and effects of progressive redox cycles can be fully explained on this model. The potentiostatic oxidation of porous electrodes of lead dioxide containing lead sulphate has also been investigated. The form of the current transient was found to depend on the balance of lead sulphate and lead dioxide.

Investigations have been carried out on the above electrodes using the techniques of scanning electron microscopy and alternating current. Possible interpretations of the results are discussed.
The influence of the solid/porous material interphase on the electrode behaviour has been investigated for a variety of alloy supports with special reference to the charge output on reduction, ease of reoxidation and electrode support/porous phase adhesion.

The progress made in the understanding of some of the problems associated with the lead acid cell has been discussed.
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LIST OF SYMBOLS

A  area, electrode area, time independant rate of nucleation
A_o  electrode area at time = 0
C_j  concentration of species j
C_L  double layer capacitance
C_o^b, C_R^b  bulk concentrations of O and R
C_o^s, C_R^s  surface concentrations of O and R
D_o, D_R, D_j, D_a  diffusion coefficients
E  electrode potential on a suitable reference scale
E^e  standard electrode potential
E_i  potential at time = 0
E_p  potential at current maximum of potentiodynamic curve
E_r  reversible electrode potential (potential at i = 0)
E_z  potential of zero charge
F  Faraday constant
h  height of a nucleus, thickness of lead sulphate deposit required to passivate the electrode (Appendix II)
i  current density
i_a, i_c  partial anodic and cathodic current densities
i_i  current density at time = 0
i_lim  limiting current density
i_m  maximum current density
i_ma  average maximum current density
i_o  exchange current density
maximum current of a potentiodynamic curve

growth rate constant, rate constant for the cathodic reduction of lead dioxide (Appendix II)

parallel growth rate constant

orthogonal growth rate constant

apparent standard rate constant

potential dependant rate constants for cathodic and anodic reactions.

molecular weight

symbol for chemical formula of species j.

number of nuclei

initial number of nuclei

charge

radius of a nucleus

gas constant

charge transfer resistance

electrolyte ohmic resistance

temperature

time at maximum current density

average time at maximum current density

function of \( x_n \) when equation (2.19) has been solved at each value of \( x_n \).

mobility of ionic species j.

Warburg impedance

distance from the electrode

A co-ordinate describing solvent or ligand geometry.

a number of electrons involved in electrode reaction

cathodic charge transfer coefficient

charge transfer coefficient in the anodic direction
\( \alpha_c \) charge transfer coefficient in the cathodic direction.

\( \gamma \) surface tension

\( \rho \) density

\( v \) sweep rate

\( \phi_\Delta \) change in potential at the electrode

\( \sigma \) coverage

\( \chi_e \) solution to wave equation for electrons

\( \chi_n \) solution to wave equation for nuclei

\( \psi \) solution to wave equation for reactant and surrounding solvent.

\( \omega \) angular velocity, angular frequency.
CHAPTER 1

INTRODUCTION

A considerable amount of work has been carried out on the system \( \text{PbO}_2/\text{PbSO}_4/\text{H}_2\text{SO}_4/\text{Pb} \) \(^{1-6}\). This arises from the central position occupied by this cell in the energy conversion field. Recent economic developments, however, have made a detailed re-examination of the limits of the energy storage capacity and performance of the lead-acid cell desirable.

Work of a fundamental nature on the \( \text{Pb}/\text{PbSO}_4/\text{H}_2\text{SO}_4 \) system (the so-called negative battery plate) has recently been reported \(^7,8\). Consequently, it seemed that a re-examination of the \( \text{PbO}_2/\text{PbSO}_4/\text{H}_2\text{SO}_4 \) electrode (the so-called positive battery plate) was timely.

An examination of the literature indicated a lack of systematic work on the fundamental redox processes involved in the interconversion of lead dioxide and lead sulphate since the classical papers of Fleischmann et al \(^9,10\). These authors described experiments in which grown lead sulphate was electro-oxidised to lead dioxide; the papers are of some importance to the development of electrocrystallisation theory.

There has been little impetus to enlarge the field of study of the porous lead dioxide electrode outside that of immediate use to the battery technologist. What has been done has been well reviewed by De Levie \(^11\) and Newman and Tiedemann \(^12\). The lead dioxide electrode has been modelled by Simonsson \(^13\), and appears to be comprehensive.
In the present studies the electrometric responses of massive and porous lead dioxide films on both platinum and lead bases, and one-dimensional porous lead dioxide electrodes with solid supports of either pure lead or various lead based alloys are investigated.
2.1. The Electrode-Electrolyte Interphase

An interphase may be considered as the region between two phases in which the properties have not yet reached the bulk of either phase. The structure of the electrode-electrolyte interphase is of fundamental importance as a knowledge of the distribution of ions and the variation of potential with distance near the electrode is required in understanding the electrode kinetics. The number of ions next to the electrode will determine the reaction rates and whilst these rates are sensitive to changes in potential, the only changes which affect the actual electrode processes are those of the solution-interface itself.

The simplest model for the distribution of ions at the interphase was proposed by Helmholtz in 1879. He regarded the interphase as consisting of two layers of equal and opposite charge, one layer situated on the electrode and the other on the solution side of the interphase, a fixed distance away from the electrode. This arrangement approximates to a parallel-plate condenser. The separation of charge is responsible for the term double layer. The following assumptions are inherent in this and other models of the double layer.

(a) the separated charges at the interphase are in electrostatic equilibrium.

(b) there is no transfer of charge in either direction across the interphase with changes in electrode potential.
(c) with changes in electrode potential the charge in solution near to the electrode interphase changes.

The above assumptions imply that the electrical double layer is purely capacitive and has no parallel resistive components. Electrodes which closely obey the above assumptions are termed "ideally polarisable". In practice only metal-solution interphases approximate to the ideal condition, an example being the mercury/KCl solution (1M) interphase. In this case, the high hydrogen overvoltage and relatively poor affinity for the mercury electrode of oxygen engenders the approximation to ideality.

Guoy\textsuperscript{15} and Chapman\textsuperscript{16} extended the Helmholtz model by assuming that excess ions are released from next to the electrode and as a result of thermal motions, roam in the region of the electrode. This gives a diffuse rather than compact layer. Chapman's mathematical theory\textsuperscript{16} was based on the assumption that the ions were point charges which could approach the electrode within any distance. More realistically, Stern\textsuperscript{17} proposed that ions have finite sizes, approach the electrode only to within a certain critical distance, and in some cases may be specifically adsorbed (i.e. undergo adsorption due to other than purely electrostatic interactions). Combining the ideas discussed, a model of the double layer divided into two regions is obtained. Next to the electrode, there is the region of high field and low dielectric constant with a row of firmly held ions; beyond that there is the diffuse layer extending from the plane of closest approach to the bulk of solution where the electrostatic forces are in balance with the random thermal motions. The difference of potential between the electrode and solution can therefore be divided into two parts:
\[ \phi_0 = (\phi_o - \phi_H) + \phi_H \]  

where \( \phi_0 \) is the potential difference between the electrode and solution (\( \phi_s \): the potential on the solution side of the double layer, is zero by convention) and \( \phi_H \) is the potential at the plane of closest approach. From (2.1) we obtain

\[ \frac{\partial \phi_o}{\partial \phi} = \frac{\partial (\phi_o - \phi_H)}{\partial \phi} + \frac{\partial \phi_H}{\partial \phi} \]  

which may be written as

\[ \frac{1}{C} = \frac{1}{C_H} + \frac{1}{C_{DL}} \]

where \( C \) is the overall double layer differential capacitance and \( C_H \) and \( C_{DL} \) are the differential capacitances corresponding to the compact and diffuse layers respectively. It is evident that the double layer can be regarded as two capacitances connected in series.

Grahame\textsuperscript{18} demonstrated a failure of the theory as described so far. He presented a series of \( \gamma/E \) curves for different 1:1 electrolytes which theoretically should behave identically. This is found to be the case when \( \phi_A \) is negative but not when \( \phi_A \) is positive. The reason for this is that the cations remain hydrated and hence for negative \( \phi_A \) line up correctly on what is termed the outer Helmholtz plane. For positive \( \phi_A \) the anions can become dehydrated and thus get closer to the electrode, lining up on what is termed the inner Helmholtz plane. Thus Grahame\textsuperscript{18} modified Søren's\textsuperscript{17} model by considering not a common
plane but two distinct planes of closest approach, the inner and outer Helmholtz planes.

A more recent theory (1963) of the distribution of ions and solvated dipoles in the double layer has been advanced by Devanathan, Bockris and Muller\textsuperscript{19}, in which adsorbed solvated cations are regarded as remaining outside a layer of strongly orientated solvent dipoles. Specifically adsorbed anions are regarded as being able to penetrate the inner solvent layer. Figure 2.1. shows a schematic representation of the solvent adsorption model of the electrode-electrolyte interphase according to Devanathan et al. Water molecules are regarded as being adsorbed with their negative ends pointing either towards or away from the metal surface, depending on the electrode charge or potential.

Equation (2.3) shows that the smaller of the two capacitances determines the overall capacitance. If $C_H$ and $C_{DL}$ are of very different size, then the term containing the larger one can be neglected. Grahame\textsuperscript{18} has shown, using the Guoy-Chapman theory, that $C_{DL}$ is related to potential and concentration of an aqueous symmetrical electrolyte ($C^5$) at $25^\circ C$ by the equation:

$$C_{DL} = 228.5 \ |z| \ (C^5)^{\frac{1}{2}} \cosh (19.46 \ |z| \varphi_H) \quad (2.4)$$

It is evident from equation (2.4) that as the electrolyte concentration is lowered, $C_{DL}$ is reduced. At low electrolyte concentrations (\textasciitilde 1mM) the observed capacity/potential curve for an ideally polarisable electrode in a symmetrical electrolyte which exhibits little specific adsorption (e.g. mercury in NaF solutions), shows a pronounced minimum centred around the potential of zero charge. As the electrolyte concentration
Fig 2.1 Possible structure of a metal-electrolyte interphase (Bockris et al., 1963)

Inner Helmholtz plane
Metal plane
Outer Helmholtz plane
Solvated cations
Specifically adsorbed anions
Normal water structure
Secondary water layer
Primary water layer
increases, this minimum becomes less and less pronounced and ultimately disappears. At high electrolyte concentrations (~ 1M) it follows from (2.4) that $C_{DL}$ is large. Hence the capacitance of the diffuse double layer does not contribute much to the observed capacitance and $C \approx C_{H}$. According to the simplest Helmholtz model $C_{H}$ should be constant, and is found to be a rough approximation. As the concentration decreases the contribution from $C_{DL}$ will increase. When $C_{DL} \approx C_{H}$, the contribution from $C_{DL}$ will decrease $C$ near the potential of zero charge where $\cosh \varphi_{H} = 1$, but will be negligible at larger values of $\varphi_{H}$. Thus the sharp minimum is caused by the $\cosh \varphi_{H}$ term. Grahame has modified the theory for unsymmetrical electrolytes.

The $C_{H}$ term of equation (2.3) is not accessible for experimental determination. However, Grahame calculated $C_{H}$ from experimental values of $C$ and from $C_{DL}$ values calculated from the Guoy-Chapman theory. The $C_{H}$ values were computed for concentrated electrolyte solutions since $C_{DL}$ is then much higher than $C_{H}$. Grahame's work shows that $C_{H}$ depends solely on the charge on the electrode and not on the electrolyte concentration, for the case of an electrolyte exhibiting little specific adsorption.

Many attempts have been made to improve the above model of the electrical double layer and the comprehensive review of Payne (1973) gives details of recent progress in this field.

Frumkin has discussed the influence of the potential of zero charge on the electrochemical behaviour of metals. The charge on the electrode plays an important role in determining which species are adsorbed at the electrode. The magnitude of the charge is determined
by the quantity \((E - E_z)\) which is referred to as a rational potential, 
\(E_R\). At positive \(E_R\)'s adsorption of negative ions is favoured and at negative \(E_R\)'s adsorption of positive ions is favoured. When \(E_R\) tends to \(E_z\) adsorption of neutral molecules competes favourably with ionic adsorption.

In conclusion, a study of the differential capacitance together with a knowledge of the p.z.c. is of fundamental importance in establishing conditions under which the exchange reaction at an electrode-electrolyte interphase may be studied in the absence of adsorption and film formation at the electrode surface.
2.2. The Charge Transfer Process

The charge transfer process may be represented by the overall equation:

\[ \text{O} + z\text{e} \xrightarrow{k_c} \text{R} \quad (2.5) \]

The Faradaic current, i.e. the current (per unit electrode area) which flows in (2.5) at a given potential, can be expressed as the difference between the forward and reverse rates

\[ i = zF(k_c C_o^S - k_a C_R^S) \quad (2.6) \]

The potential dependant rate constants \( k_a \) and \( k_c \) are given by:

\[ k_c = k_c^0 \exp \left( \frac{-\alpha zF \epsilon}{RT} \right) \quad (2.7) \]

\[ k_a = k_a^0 \exp \left( \frac{(1-\alpha) zF \epsilon}{RT} \right) \quad (2.8) \]

where \( k_c^0 \) and \( k_a^0 \) are the values of \( k_c \) and \( k_a \) at the reference potential.

Substituting for \( k_a \) and \( k_c \) in (2.3) gives:

\[ i = zF \left[ k_c^0 C_o^S \exp \left( \frac{-\alpha zF \epsilon}{RT} \right) - k_a^0 C_R^S \exp \left( \frac{(1-\alpha) zF \epsilon}{RT} \right) \right] \quad (2.9) \]

at \( E_r \quad i_c = i_a = i_o \quad (2.10) \]

hence it follows that:

\[ i_o = zFk_c^0 C_o^S \exp \left( \frac{-\alpha zF \epsilon}{RT} \right) = zFk_a^0 C_R^S \exp \left( \frac{(1-\alpha) zF \epsilon}{RT} \right) \quad (2.11) \]
substituting (2.11) in (2.9) we obtain:

\[ i = i_o \left[ \exp \left( \frac{-\alpha zF(E-E_R)}{RT} \right) - \exp \left( \frac{(1-\alpha)zF(E-E_R)}{RT} \right) \right] \]  \hspace{1cm} (2.12)

where \((E-E_R)\) is defined as the charge transfer overpotential\(^{24}(\eta_D)\). Equation (2.12) is known as the Erdey-Gruz and Volmer equation\(^{25}\).

At low overpotentials \(|\eta_D| \ll \frac{RT}{\alpha zF}\) or \(|\eta_D| \ll \frac{RT}{(1-\alpha)zF}\) the overpotential-current curve is linear. Differentiation of The Erdey-Gruz and Volmer equation (2.12) and putting \(\eta_D = 0\) gives

\[
\left( \frac{di}{d\eta_D} \right)_{\eta_D = 0} = \frac{zF}{RT} i_o = R_D^{-1} \]  \hspace{1cm} (2.13)

At high overpotentials \(|\eta_D| \gg \frac{RT}{\alpha zF}\) or \(|\eta_D| \gg \frac{RT}{(1-\alpha)zF}\)

The Tafel\(^{26}\) relationship at cathodic overpotentials is obtained:

\[ \eta_D = \frac{RT}{\alpha zF} \ln i_o - \frac{RT}{\alpha zF} \ln i \]  \hspace{1cm} (2.14)

and at anodic overpotentials

\[ \eta_D = \frac{RT}{(1-\alpha)zF} \ln i_o + \frac{RT}{(1-\alpha)zF} \]  \hspace{1cm} (2.15)

The concentration dependance of \(i_o\) is given by\(^{27}\)

\[ i_o = zFk_o(c_o)^{(1-\alpha)}(c_R)^\alpha \]  \hspace{1cm} (2.16)

The above theory is only applicable to reactions in which all electrons are transferred simultaneously.
The simplest process occurring at the electrode is the single electron transfer. The most recent developments of the theory have been the work of Levich\textsuperscript{23}, Marcus\textsuperscript{29} and Dogonadse\textsuperscript{30}.

The reaction does not occur in one smooth step over a single energy barrier but proceeds in stages. Initially the reactant diffuses to the electrode. Then there is the arrangement of the ionic atmosphere and the orientation of the solvent suitable for the transition state. Finally the electron is transferred. Only this final step has to be treated as a rate process, the first stages of the reaction are all in equilibrium and can be treated by thermodynamics. After the reactants have diffused together, on moving from reactant to product, the electron is transferred, the ligand bond distances are altered and the solvent dipoles and ion atmosphere are reorientated. When an electron is transferred there is no change in energy which is an important central feature of the Marcus and Levich theories. In quantum mechanical terms, the Schrodinger equation gives

\[ H \psi = U \psi \quad (2.17) \]

where this equation and \( \psi \) refer to the reactant and its surrounding solvent. Using the Born-Oppenheimer approximation, the description of the electrons is separated from the rest of the heavy particles.

\[ \psi = \psi_e(X_e) \psi_n(X_n) \quad (2.18) \]

For the electron \( X_n \) is fixed and we have as a function of \( X_e \)

\[ H_e \psi_e = U_e \psi_e \quad (2.19) \]
and for the slower movements of the nuclei
\[ H_n \psi_n = E_n \psi_n \]  \hspace{1cm} (2.20)

where \( E_n \) is the total energy. The electron transfers firstly with no change in \( E_n \) and secondly with no change in \( E_n \). These conditions are satisfied by the interaction of the ion with the solvent dipoles and with its ligands. Due to chance fluctuations around the reactant, the necessary conditions are fulfilled and the non-radiative electron transfer can occur.

Levich and Dogonadse\(^3\) have worked out a detailed theory for the process of solvent re-organisation. They assumed that in a polar solvent the main change that occurs along the solvent co-ordinate is the chance fluctuations of the solvent dipoles around the ions. The variation of potential energy with displacement along the solvent co-ordinate was shown to be parabolic, which is equivalent to assuming that the solvent undergoes simple harmonic oscillations. This is probably true for small perturbations. Levich and Dogonadse\(^3\) showed that the main process requiring activation is the movement of the system along the solvent co-ordinate to the iso-energetic point, where electron transfer can occur, the activation energy \( E^* \) being given by

\[ E^* = \frac{(E_\Delta + E_s)^2}{4E_s} \]  \hspace{1cm} (2.21)

where \( E_\Delta \) is the change in energy between reactant complex and product complex and \( E_s \) describes the change in solvation energy to alter the solvation of the reactant complex to that of the product complex without any electron transfer. These results were derived as a special case of their full quantum mechanical treatment. Marcus\(^3\) took a less specific
model of the solvent and obtained an expression in terms of free energy.

\[ G^*_t = \frac{G_\Delta + G_S}{G_S} \]  \hspace{1cm} (2.21)

This more general theory also took into account changes in the bond lengths attaching the ligands to the central ion.

For the observed rate constant the expression

\[ k = K_E V S K \exp \left( \frac{G^*_t}{RT} \right) \]  \hspace{1cm} (2.22)

was obtained where \( G^*_t \) is given by equation (2.21) and \( K_E \) is the equilibrium constant for locating the reactant near the electrode, \( V_S \) is the frequency of oscillation of solvent molecules and contains the transition probability. \( G_\Delta \), the difference in free energy between the reactant complex and product complex can be expressed in terms of the overall change of free energy \( \Delta G_{TD} \) by

\[ G_\Delta = \Delta G_{TD} - \Delta G_R^+ + \Delta G_P^+ \]  \hspace{1cm} (2.23)

where \( G_R \) is the standard free energy change for forming the reactant complex from the reactants and \( G_P \) is the standard free energy change for forming the product complex from the products.

The Tafel relation can be derived from equations (2.22) and (2.23) since \( G_{TD} \) depends on the potential. The charge transfer coefficient is given by

\[ \alpha = \frac{RT}{F} \frac{\partial \ln k}{\partial E} = - \frac{\partial G^*_t}{F \partial E} \]

\[ = - \left( \frac{1}{2F} \right) \left[ 1 + \frac{G_\Delta}{G_S} \right] \frac{\partial G_\Delta}{\partial E} \]
\[
\alpha = \left[ \frac{1}{2} \right] \left( 1 + \frac{G_A}{G_S} \right)
\] (2.24)

Hence when \( G_S \gg G_A \) implying that the kinetics are slow but the thermodynamics are in balance, \( \alpha = \frac{1}{2} \), which is found to be the case in many reactions. For fast reactions, where \( G_S \) is small, the theory predicted that \( \alpha \) would not be constant, but decrease continuously as the reaction is driven harder. This indeed has been found by Frumkin for the \( \text{Fe(CN)}_6^{3-} / \text{Fe(CN)}_6^{4-} \) system.

Simple electron transfer reactions take place by changes in the solvation and metal-ligand distances such that the radiationless iso-energetic electron transfer can take place.

Electrode reactions in which a number of electrons are transferred successively have been comprehensively reviewed by Losev from both theoretical and experimental viewpoints. He has considered processes with a single limiting step and processes with comparable rate constants for successive steps.
2.3. Mass Transfer Processes

The electrode process may be represented by the overall equation

$$0 + ze \rightarrow R$$ \hspace{1cm} (2.25)

This may be considered to be composed of the following individual parts:

$$O_{\text{bulk}} \rightarrow O_{\text{electrode}}$$ \hspace{1cm} (2.26)

$$O_{\text{electrode}} + ze \rightarrow R_{\text{electrode}}$$ \hspace{1cm} (2.27)

$$R_{\text{electrode}} \rightarrow R_{\text{bulk}}$$ \hspace{1cm} (2.28)

If (2.26) has a slower rate than (2.27), the process is limited by mass transfer of 0 to the electrode and termed mass transfer controlled. If (2.27) is the slower, the process is limited by the rate of electron transfer and termed charge transfer controlled. In some instances neither of the above processes are as slow as a chemical transformation involving the electroactive species, in which case the chemical transformation is the rate determining process.

Three modes of mass transfer are normally encountered: migration, convection and diffusion.

Mass transfer by migration is a result of the forces exerted on charged particles by an electric field. In the presence of a large excess of supporting electrolyte migration of electroactive material is minimised to an extent where it can be neglected.

Natural or free convection develops spontaneously in any solution undergoing electrolysis. This is a result of density differences which develop near the electrode and may also arise from thermal or mechanical disturbances. Forced convection may be effected
by stirring the solution, rotating the electrode, bubbling gas near to the electrode and so forth.

Diffusion exists whenever concentration differences are established. Since a concentration gradient develops as soon as electrolysis is initiated, diffusion occurs to some extent in every practical electrode reaction. If we consider a plane electrode immersed in an electrolyte solution containing \( O \) which is reduced typically according to equation (2.25) then the number of moles of \( O \) which diffuse past a given cross-section, area \( A/cm^2 \) in a time \( dt \), is proportional to the concentration gradient of diffusing species.

\[
\frac{dN}{Adt} = D_o \frac{\partial C_o}{\partial x}
\]

(2.29)

This is Fick's first law. The left hand side is called the flux \( (q) \) and is the number of moles diffusing per unit time through unit area. \( D_o \) is the diffusion coefficient, defined as the number of molecules per second crossing unit area under unit concentration gradient. If one now considers the electrolysis over a period of time, it is evident that \( C_o \) and hence \( \frac{\partial C_o}{\partial x} \) must decrease with time since \( O \) is being consumed at the electrode. Fick's second law describes the variation of \( C_o \) with time and may be summarised as

\[
\frac{\partial C_o}{\partial t} = D_o \frac{\partial^2 C_o}{\partial x^2}
\]

(2.30)

The solution of (2.30) in terms of \( C_o(x,t) \) is

\[
C_o(x,t) = C_o^b \frac{2}{\pi^{1/2}} \int_0^{x/2} D_o \frac{1}{t^{1/2}} e^{-y^2} dy
\]

(2.31)
The conditions for the solution of (2.30) are

\[
\begin{align*}
\text{at } t &= 0 & C_o^s &= C_o^b \\
\text{at } t > 0 & & C_o^s &= 0
\end{align*}
\]
also \( C_o \rightarrow C_o^b \) as \( x \rightarrow \infty \)

The instantaneous current, \( i_t \), is proportional to the flux at \( x = 0 \), thus

\[
i_t = xFAD \left( 0, t \right) = x \frac{FAD}{x} \frac{\partial C_o}{\partial x} \left( 0, t \right) \tag{2.32}
\]

The value of \( \frac{\partial C_o}{\partial x} \) is obtained by differentiating equation (2.31) and evaluating at \( x = 0, t \). The final expression for the instantaneous current at a plane electrode under diffusion control becomes

\[
i_t = \frac{xFAD}{\pi \tau} \frac{1}{t^2} C_o^b \tag{2.33}
\]

Since the instantaneous current is purely diffusion controlled it is often denoted by \( i_d \). The term \( i_t \) is preferable as it emphasises the transient nature of the instantaneous current.
2.4. **The Rotating Disc Electrode (RDE)**

Levich\textsuperscript{35} has shown that

\[ \delta = 1.62 \, D^{\frac{3}{2}} \, V^{1/6} \, \omega^{-\frac{1}{6}} \]  

(2.34)

where \( \delta \) is the diffusion boundary layer thickness, \( V \) the kinematic viscosity of the electrolyte and \( \omega \) the angular velocity of the electrode. In principle each electroactive species has its own value of

Consider the general anodic reaction:

\[
\frac{k_a}{k_c} \underset{R}{\text{Ra}_0^+ ze} \]  

(2.35)

The overall current (per unit electrode area) flowing in (2.35) at a given potential can be written as

\[
i = zF(k_c c_b^R - k_c c_o^R) \]  

(2.36)

with an anodic current considered to be positive for convenience.

Introducing Fick's first law into (2.36) gives:

\[
i = zF \frac{D_R}{\delta_R} (c_b^R - c_o^R) = \frac{D_o}{\delta_o} (c_o^R - c_o^R) \]  

(2.37)

Solving (2.37) for \( c_c^R \) and \( c_o^R \) gives:

\[
c_c^R = c_b^R - \frac{i \, \delta_R}{zF D_R} \]  

(2.38)

\[
c_o^R = c_o^R - \frac{i \delta_o}{zF D_o} \]  

(2.39)

substituting for \( c_c^R \) and \( c_o^R \) in equation (2.36) we obtain:

\[
i \left[ 1 + k_a \frac{\delta_R}{D_R} + k_c \frac{\delta_o}{D_o} \right] = zF(k_a c_b^R - k_c c_o^R) \]  

(2.40)
by definition

\[ i(\infty) = zF(k_a C_R^b - k_c C_0^b) \tag{2.41} \]

Hence (2.40) can be rewritten to obtain:

\[ \frac{1}{i(\infty)} + \frac{1}{i(\infty)} k_a \frac{\delta}{D_R} + k_c \frac{\delta}{D_0} = \frac{1}{i} \tag{2.42} \]

Introducing the Levich equation (2.34) into (2.42) we obtain:

\[ \frac{1}{i(\infty)} + \frac{k_c}{i(\infty)} k_a \frac{\delta}{D_R} + k_c \frac{\delta}{D_0} = \frac{1}{i} \tag{2.43} \]

where \( K = \frac{k_c}{i(\infty)} \)

Equation (2.43) predicts that a plot of \( i^{-1} \) vs \( \omega^{-0.5} \) should be linear with a slope of value \( K \) and an intercept \( i(\infty)^{-1} \) which gives a measure of the true kinetic currents in absence of diffusion effects.

If we substitute for \( i \) in (2.44) we obtain:

\[ \frac{\delta}{D_R} \frac{\omega^{0.5}}{k_a} + \frac{k_c}{k_a} \frac{\delta}{D_0} \frac{\omega^{0.5}}{} \tag{2.45} \]

\[ K = \frac{zF}{k_c} \left[ \frac{C_R^b}{k_a} - \frac{C_0^b}{k_a} \right] \]

From equations (2.7) and (2.8) we obtain:

\[ \frac{k_c}{k_a} = \frac{k_c^0}{k_a^0} \exp \frac{zFE}{RT} \tag{2.46} \]
which may be written as:

\[
\frac{k_c}{k_a} = k' \exp \frac{zF(E-E_R)}{RT} \tag{2.47}
\]

Introducing (2.47) into (2.45) gives:

\[
K = \frac{\frac{\delta R (\omega)^{\frac{1}{2}}}{D_R} + \frac{k' \delta \omega^{\frac{1}{2}}}{D_o} \exp \frac{zF(E-E_R)}{RT}}{zF(c_R^b - k' c_o^b \exp \frac{zF(E-E_R)}{RT}} \tag{2.48}
\]

When \( R \) is a solid and \( c_o^b \) is very small then \( \frac{\delta R (\omega)^{\frac{1}{2}}}{D_R} = 0 \)

and \( c_R^b \gg k' c_o^b \exp \frac{zF(E-E_R)}{RT} \) so that (2.48) reduces to:

\[
K = \frac{k' \exp \frac{zF(E-E_R)}{RT}}{zF(c_R^b)} \cdot \frac{\delta_o \omega^{\frac{1}{2}}}{D_o} \tag{2.49}
\]

Hence a plot of \( \log [\frac{\partial \chi^{-1}}{\partial \omega^{-2}}] \) vs \( (E-E_R) \) will be linear with a slope proportional to \( z \).
Various methods have been proposed for the determination of $\Theta$ and $\sigma$ from impedance measurements. Vector methods were used by Randles\textsuperscript{36} and Delahay\textsuperscript{39} et al. Gerischer\textsuperscript{40} determined $\sigma$ and $\Theta$, however he neglected the imaginary part of the Warburg impedance. Vetter\textsuperscript{41} corrected the cell impedance for the double layer capacitance and solution ohmic resistance. In the present studies the complex plane impedance technique devised by Sluyters\textsuperscript{42} was used. This method entails plotting the real component ($Z'$) and the imaginary component ($Z''$) of the cell impedance against each other as a function of some varied parameter (frequency, concentration or d.c. voltage). It is possible to calculate $C_L$, $\Theta$ and $\sigma$ using the complex plane impedance method.

From figure 2.2a the cell impedance is given by

$$Z = R_{sol} + \frac{1}{j \omega C_L + \frac{1}{\Theta + \sigma \omega^{-\frac{1}{2}} - j \omega \sigma \omega^{-\frac{3}{2}}}}$$

(2.53)

After separation of the real and imaginary parts of $z$ we obtain

$$z = z' - jz''$$

(2.54)

where $z'$ and $z''$ are given by

$$z' = R_{sol} + \frac{\Theta + \sigma \omega^{-\frac{1}{2}}}{(\sigma \omega^{\frac{3}{2}} C_L + 1)^2 + \omega^2 C_L (\Theta + \sigma \omega^{-\frac{3}{2}})}$$

(2.55)

and

$$z'' = \frac{\omega C_L (\Theta + \sigma \omega^{-\frac{1}{2}}) + \sigma \omega^{-\frac{3}{2}} (\sigma \omega^{\frac{3}{2}} C_L + 1)}{(\sigma \omega^{\frac{3}{2}} C_L + 1)^2 + \omega^2 C_L (\Theta + \sigma \omega^{-\frac{3}{2}})^2}$$

(2.56)
Fig. 2.2a. Equivalent circuit of electrode impedance

Fig. 2.2b. $Z'-Z''$ plot at low frequencies
Although equation (2.54) is very complex, its two limiting cases, at low and high frequencies, give important results. At low frequencies (2.54) reduces to

$$Z = R_{sol} + \Theta + \sigma \omega^{-\frac{1}{2}} - j(\sigma \omega^{-\frac{1}{2}} - 2 \Theta^2 \omega^2 C_L)$$  \hspace{1cm} (2.57)

This equation predicts that a plot of $Z'$ vs $Z''$ gives a straight line of $45^\circ$ slope (Figure 2.2b). At high frequencies for a fairly irreversible reaction, concentration polarisation ($W$) can be neglected and (2.54) reduces to

$$Z = R_{sol} + \frac{\Theta}{1 + \omega^2 C_L^2 \Theta^2} - j \frac{\omega C_L \Theta^2}{1 + \omega^2 C_L^2 \Theta^2}$$  \hspace{1cm} (2.58)

In this case, if the real and imaginary parts of the impedance are plotted against each other, a semicircle is obtained. Values of $R_{sol}$, $\Theta$ and $C_L$ can be computed from such plots as is shown in Figure 2.3a. At lower frequencies diffusion polarisation will give rise to a distortion of the semicircle, as illustrated in Figure 2-3b., culminating in the attainment of a line of $45^\circ$ slope. The extent of this distortion is dependant upon the relative values of $\Theta$, $\sigma$ and $C_L$. 


Fig. 2.3a $Z'$-$Z''$ plot for irreversible reaction in the absence of concentration polarisation

Fig. 2.3b $Z'$-$Z''$ plot over whole frequency range
2.6. Electrocrystallisation

This section is restricted solely to the potentiostatic response of the nucleation and growth model (without edge effects).

2.6.1. Two Dimensional Nucleation and Growth

(a) Without Diffusion

When a pulse is started nuclei form as discrete centres, either instantaneously or progressively with time, and grow. On growing they can interact with themselves but not with the boundary. The calculation of the characteristic current-time curves in the early stages before the nuclei overlap, based on simple geometric arguments is for one nucleus:

\[ i = zFkS \]

(2.59)

\[ = \frac{zF}{\pi} \cdot \frac{\partial v}{\partial r} \cdot \frac{\partial r}{\partial t} \]

(2.60)

where \( S \) is the area on which material is deposited and \( V \) is the volume. Equation (2.60) gives \( r \) as a function of \( t \), (as \( \frac{\partial v}{\partial r} \) and \( S \) are known functions of the geometry) and consequently gives \( i(t) \). Multiplication by \( N_0 \), the nuclei formed initially, gives \( i(t) \) for instantaneous nucleation. The expression for progressive nucleation can be calculated given that the number of nuclei at any time is given by:

\[ N = N_0 (1 - \exp(-At)) \]

(2.61)

The processes of nucleation and growth occur simultaneously and the resulting current is given by:

\[ i = \int_{0}^{t} i(U) \left[ \frac{\partial N}{\partial t} \right]_{t=t-U} dU \]

(2.62)
where \( i(U) \) is given by equation (2.60) and \( \frac{d\dot{N}}{dt} \) by (2.61). A summary of the expressions for an unbound electrode, calculated on this basis, have been given previously \(^{44}\). The dependencies are all of the form \( i \propto t^\beta \) and are rising transients with \( \beta \) depending primarily on the geometry and type of nucleation.

When nuclei overlap the form of the current-time curve can still be calculated provided that the overlapping is random, the growth outwards is uniform and the boundaries of the electrode do not interfere. Avrami \(^{45}\) has shown how the calculation is effected. For random overlap

\[
S_1 = 1 - \exp(-S_{1ex}) \quad (2.63)
\]

\( S_{1ex} \) is the top area of an isolated nucleus, and \( S_1 \) is the actual area. Combining this with equation (2.60) allows \( i(t) \) to be determined.

The results for the growth of cylinders are:

\[
i = \frac{2F \pi M}{\rho} A k^2 t^2 \exp \left( - \frac{\pi k^2 A k^2 t^3}{3 \rho^2} \right) \quad (2.64)
\]

for progressive and

\[
i = \frac{2F \pi M}{\rho} N_0 k^2 t \exp \left( - \frac{\pi k^2 N_0 k^2 t^2}{\rho^2} \right) \quad (2.65)
\]

for instantaneous nucleation.

Equations (2.64) and (2.65) have the characteristic shape shown in Figure 2.4 when plotted in the nondimensional form. The experimental \( i-t \) plots have a similar shape. The maximum current \( i_m \) and time \( t_m \) are given by differentiating (2.64) and (2.65). The theoretical value of \( i_m t_m /Q_m \) is independent of potential and is 1.0 for progressive and 0.6 for
Fig 2.4 Theoretical current time curves according to
(a) equation (2.64)

(b) equation (2.65)

(c) Total current transient for layer by layer growth showing contribution from individual layers
instantaneous nucleation.

The arguments used to derive equations (2.64) and (2.65) can be extended to layer by layer growth. Figure 2.4(c) displays the i-t transient.

(b) With Diffusion.

The i-t relationship can be estimated when the nuclei are surrounded by a fixed diffusion zone. A simulation shows that the \( \frac{i_m}{Q_m} \) value is no longer a fixed constant but is less than the values for progressive nucleation, and for instantaneous nucleation. The chemistry and electrochemistry of the system will determine how the apparent fixed diffusion zone arises.

The problem when the diffusion zone increases with time without overlap has been considered by Frank for the growth of one two-dimensional nucleus expanding at a rate determined by the flux. The diffusion zone is concentric to the nucleus. The radius at time \( t \) is considered to obey:

\[
r(t) = \Theta (Dt)^{\frac{1}{2}}
\]

where \( \Theta \) is controlled by the potential, \( M \) and \( \rho \). For instantaneous nucleation the Avrami treatment gives:

\[
i = a_m \Pi \Theta^2 D \exp - \Pi \Theta^2 D \Omega t \quad (2.67)
\]

and for progressive nucleation gives:

\[
i = a_m \Pi \Theta^2 D \Delta t \exp - \frac{\Pi \Theta^2 D \Delta t^2}{2} \quad (2.68)
\]
An alternative model to that for equation (2.51) arises when a large number of very small nuclei are formed initially and the diffusion zones around each have overlapped very soon after the potentiostatic pulse is started. As a limiting situation it can be assumed that planar diffusion operates from \( t=0 \) parallel to the electrode surface. The predicted \( i/t^{-\frac{3}{2}} \) plot for this case is given by Astley et al.

2.6.2. Three Dimensional Nucleation and Growth

The problem can be attacked in the manner of Figure 2.5 where the rates of advance \( V_1, V_2 \) and \( V_3 \) are defined. A slice \( x \) from the surface and height \( dx \) will grow out horizontally. It is assumed that the nuclei are distributed at random on the surface and the interaction of slices at a height \( x \) can be described by the Avrami equation. A number of models are shown in Figure 2.5 and the corresponding \( i-t \) curves in Figure 2.6. Three dimensional nucleation and growth is considered more fully in a later chapter.
Fig 2.5 Three dimensional models

(a) growth of circular cones on an inert substrate (metal deposition)

(b) growth of circular cones on a substrate of the same material, the base plane moves with velocity $V_3$ (metal deposition)

(c) current only flows into the uncovered area (passivation)
Fig 2.6 The form of current time transients for the models of Figure 2.5

(a)

(b)

(c)
2.7. Porous Electrodes.

Various theoretical models have been used to describe the processes in flooded porous electrodes mathematically. Winsel suggested a model consisting of circular cylindrical pores with constant radius, parallel to each other and perpendicular to the outer face. Other authors have used a model represented by electrical equivalent circuits. In this way the behaviour of the electrode can be simulated with a network of ohmic and charge transfer resistances.

These two models both have their disadvantages. The first model cannot be used with electrodes of cylindrical shape or with electrodes which must be considered two dimensional, since in these cases complications arise concerning direction of the pores. The second model has been applied by Euler to some practical electrodes, among them the lead dioxide electrode. However, this model makes use of a linearised polarisation equation and is thus realistic only for small current densities since it becomes unrealistic for high current densities when the polarisation equation is of the exponential type. Furthermore it is difficult to include the influence of concentration in the electrical model.

Newman and Tobias proposed a macroscopic treatment of porous electrodes in which the actual geometric detail of the pores was neglected. A potential in the solid matrix material $\phi_1$ and another in the pore filling electrolyte $\phi_2$ were defined. Similarly, two current densities may be correspondingly defined, $i_1$ for the matrix phase and $i_2$ for the electrolyte. In this model, current densities were referred to the projected area of the electrode, rather than to the areas of individual phases and the equations are written in vector notation for generality and brevity. Applying ohm's law to the matrix
\[ \vec{i}_1 = -\sigma \nabla \phi \]  

(2.69)

where \( \sigma \) is the effective conductivity of the solid matrix in mho/cm.

The flux of a mobile ionic species is due to migration, diffusion, dispersion and convection.

\[ \frac{N_j}{\mathcal{E}} = -(D_j + D_a) \nabla c_j - z_j U_j F c_j \nabla \phi + \frac{v c_j}{\mathcal{E}} \]  

(2.70)

Since \( N_j \) is the superficial flux based on the area of both matrix and pore and \( \mathcal{E} \) is the void volume fraction within the element, \( N_j / \mathcal{E} \) can be considered as the flux of the solution phase. Similarly, \( v / \mathcal{E} \) will be roughly the velocity in the solution phase if \( v \) is taken to be a superficial bulk fluid velocity, for example, the volumetric flow rate entering the electrode divided by its superficial area. The molar-average velocity \( v^* \) would thus be given by

\[ c_{T^*} = \sum_j N_j \]  

(2.71)

where

\[ c_T = \sum_j c_j \]  

(2.72)

is the total solution concentration. (The solvent is to be included in both these sums).

The ionic diffusion coefficient and mobility of a free solution require a correction for the tortuosity of the pores in order to yield \( D_j \) and \( U_j \). \( D_a \) represents the effect, axial dispersion - the attenuation of concentration gradients as the fluid flows through a porous medium and \( c_j \) is the concentration of species \( j \) per unit volume of solution.
The superficial current density \( i_2 \) in the pore phase is due to the movement of charged solutes:

\[
i_2 = F \sum_j z_j N_j \quad (2.73)
\]

From equation (2.70) we obtain

\[
i_2 = -K_1 \nabla \phi_2 - \varepsilon F \sum_j z_j d_j \nabla c_j \quad (2.74)
\]

where

\[
K_1 = \varepsilon F^2 \sum_j z_j^2 u_j c_j \quad (2.75)
\]

is the effective conductivity of the solution phase. The second term on the right in equation (2.74) represents the diffusion potential. Convection and dispersion have made no contribution to this equation since the solution is electrically neutral. If the ionic diffusion coefficients are all equal, the diffusion-potential term will disappear as well.

There are two limiting cases which are likely to receive treatment, for the reaction of a minor component from a solution with excess supporting electrolyte in which case migration is neglected, and for the case of the binary electrolyte.

A volume element within the porous electrode will be, in essence electrically neutral because it requires a large electric force to create an appreciable separation of charge over an appreciable distance. Each phase is also taken separately to be electrically neutral. For the solution phase, this takes the form

\[
\sum_j z_j c_j = 0 \quad (2.76)
\]
This assumption means that the interfacial region which comprises the electric double layer (where departures from electroneutrality are significant) constitutes only a small volume compared to any of the phases or the electrode itself. This will not be true for finely porous media and very dilute solutions, where the diffuse layer may be more than 100 angstroms thick. It is a consequence of the assumption of electroneutrality that the divergence of the total current density is zero. For the macroscopic model this is expressed as

\[ \nabla \cdot \mathbf{i}_1 + \nabla \cdot \mathbf{i}_2 = 0 \quad (2.77) \]

Within a pore, in the absence of homogeneous chemical reactions, a differential material balance can be written for the species \( j \). This equation can be integrated over the volume of the pores in an element of the electrode, and surface integrals can be introduced by means of the divergence theorem. Careful use of the definitions of average quantities yields the material balance for species \( j \):

\[ \frac{\partial \bar{c}_j}{\partial t} = \bar{1}_{jn} - \nabla \cdot \bar{n}_j \quad (2.78) \]

This result applies to the solvent as well as the solutes.

Three different averages are represented in equation (2.78). \( \bar{c}_j \) is an average over the volume of the solution in the pores. \( \bar{1}_{jn} \) the pore-wall flux of species \( j \) is an average over the interfacial area between the matrix and the pore solution, and \( \bar{n}_j \) is an average over a cross section through the electrode, cutting matrix and pore. It should be borne in mind that the averages include a volume which is large compared to the pore
structure and small compared to the regions over which considerable macroscopic variations occur.

Equation 2.78 states that the concentration can change at a point within the porous electrode because the species moves away from the point (divergence of the flux \( N_j \)) or because the species is involved in electrode processes (faradaic electrochemical reactions or double-layer charging) or simple dissolution of a solid material. In the macroscopic model, the transfer or creation from the matrix phases appears to occur throughout the bulk of the electrode because of the averaging process.

For a single electrode reaction represented as

\[
\sum_j S_j M_j Z_j \rightarrow n e^-
\]  

(2.79)

Faraday's law is expressed as

\[
al_{jn} = - \frac{a S_j}{nF} i_n = \frac{S_j}{nF} \nabla i_2
\]  

(2.80)

where \( S_j \) may be called the stoichiometric coefficient of species \( j \) and \( i_n \) is the transfer current per unit of interfacial area, if the electrode is operating in a steady state or a pseudo steady state where double-layer charging can be ignored. Equation (2.78) becomes

\[
\frac{\partial \xi C_j}{\partial t} = - \nabla N_j - \frac{S_j}{nF} \nabla i_2
\]  

(2.81)

The polarization equation is necessary to express the dependence of the local rate of reaction on the various concentrations and on the potential jump at the matrix-solution interface. Electrode kinetics do not follow fundamental laws which can be written down as reliably as the law of conservation of matter. The situation is the same here as in chemical...
kinetics or heterogeneous catalysis. The polarisation equation is the principal point where the macroscopic theory of porous electrodes will be subject to further refinement as attempts are made to account not only for the mechanism of the charge-transfer process but also for the morphology of the electrode, the formation of covering layers or of crystallites of sparingly soluble species, and the transport from such sparingly soluble phases to the site of the charge-transfer process.

It is common to begin with a polarisation equation of the form

$$\nabla \cdot i_2 = ai_0 \left[ \exp \left( \frac{\alpha e F}{RT} \eta_s \right) - \exp \left( - \frac{\alpha c F}{RT} \eta_s \right) \right]$$  \hspace{1cm} (2.82)

where $i_0$ is the exchange current density and $\eta_s$ is the local value of the surface overpotential.

Consider a redox reaction such as the oxidation of ferrous ions to ferric ions, thereby leaving the electrode structure unchanged. It is frequently assumed that the composition dependance of the exchange current density and the composition dependance of the equilibrium potential cancel in such a way that the polarization equation can be written

$$\nabla \cdot i_2 = ai_o \left[ \frac{c_1}{c_1^o} \exp \left( \frac{\alpha e F}{RT} (\phi_1 - \phi_2) \right) - \frac{c_2}{c_2^o} \exp \left( - \frac{\alpha c F}{RT} (\phi_1 - \phi_2) \right) \right]$$  \hspace{1cm} (2.83)

where $i_o$ is a constant representing the exchange current density at the composition $c_1^o, c_2^o$, which might conveniently be taken to be the initial concentrations of the reactants or the concentrations prevailing external to the electrode.

Simonsson\textsuperscript{56} has shown that the initial current distribution in the porous lead dioxide electrode can be satisfactorily predicted by application
of the macrohomogeneous model. He also proposed a theoretical model for the porous lead dioxide electrode\textsuperscript{13} based on the macrohomogeneous model, in which the structural changes during discharge, due to precipitation of lead sulphate, were considered. This model is presented in Appendix 1.
3.1. Electrolytic Systems

3.1.1. Electrolyte Solutions

Electrolyte solutions were prepared from AnaLaR grade chemicals and water bidistilled from dionised stock.

For differential capacitance measurements the electrolytes were purified by constant pumping over specially prepared activated charcoal. White spot nitrogen, deoxygenated by passing over copper at 400°C and prehumidified, was used to circulate the electrolytes over the charcoal. In general electrolytes were circulated for at least 14 days before measurements were made.

3.1.2. Electrolytic Cells

All cells were made from borosilicate glass and cell fittings were lubrication free ground glass joints (Figures 3.1 to 3.4). These cells together with all glassware were cleaned by steeping in a 50:50 mixture of nitric and sulphuric acids for 7 days. The acid was removed by thoroughly washing with bidistilled water and finally by soaking in bidistilled water for 24 hours.

3.1.3. Planar electrodes

The rotating disc electrode is shown in Figure 3.5. The shape and dimensions of the electrode were in accordance with hydrodynamic requirements. A mercury pool provided the electrical contact between the rotating and the external circuit.
Fig 3.1 Double layer cell

A, test electrode compartment
B, reference electrode compartment
C, counter electrode compartment
D, water trap
E, purification limb containing activated charcoal
FGH frits

N₂
Fig 3.2 Rotating disc, L.S.V and pulse cell

Fig 3.3 Impedance cell
A working electrode
B reference electrode
C counter electrode
Fig 3.5 Rotating disc electrode

Fig 3.6 Porous electrode construction
$\beta$-PbO$_2$ electrodes were prepared by electrodeposition (0.7 m cm$^{-2}$) onto platinum (polished to a mirror-like finish using four grades of Emery paper and finally 6, 1 and 0.25 $\mu$m diamond paste, and then etched with HNO$_3$:H$_2$SO$_4$ (50:50 by volume)) from acid lead perchlorate solution (4.6%ClO$_4^-$, 0.1M$^+$).

Lead electrodes were prepared by electrodepositing lead (5 m cm$^{-2}$) on to polished lead (roughened glass and finally tissue paper) from acid lead perchlorate solution.

For Scanning Electron Microscope studies, experiments were made on specially constructed stubs. These consisted of a Teflon shrouded electrode (Pt or Pb) which screwed into the end of a rotating disc electrode assembly with liquid tight sealing.

3.1.4. Porous Electrodes

The electrode is shown in Figure 3.6, and is basically a RDE with a solid support (pure lead or various lead, calcium, tin, aluminium and lead, antimony based alloys) lying beneath the level of the Teflon shrouding so that pasting the electrode flush with the Teflon produced a porous layer of leady-oxide (0.762 mm in depth; 3 mm diameter). This porous matrix was converted to lead dioxide by galvanostatic polarisation (0.3 M H$_2$SO$_4$; ~25 mA cm$^{-2}$) which was continued until the potential was steady (1.250 V vs Hg/Hg$^+$SO$_4$; 0.3 M H$_2$SO$_4$) and oxygen was freely evolved from the lead dioxide (final porosity 56.6%). It should be noted that it was necessary to convert the electrode to lead dioxide in the upward facing position otherwise oxygen gas saturating the matrix interfered with the oxidation.

For examination in the SEM, the solid support plus porous matrix was removed from the Teflon shroud.
3.1.5. Counter and Reference Electrodes

The counter electrode used for all experiments (except for electrodeposition and galvanostatic oxidation experiments when the counter electrode was a pure lead (99.9999%) wire coil) was a large area platinum gauze.

The reference electrode used for all experiments was a mercury, mercurous sulphate, sulphuric acid (at the concentration of the cell electrolyte) electrode.

3.2. Electrical Circuits

3.2.1. Faradaic Impedance and Double Layer Measurements

Two techniques were employed:

(1) A Schering bridge, shown in Figure 3.7, was used to match the interphase as a series combination of resistance $R_{xs}$ and capacitance $C_{xs}$. The A.C. generator and detector were a phase sensitive lock-in amplifier (Brookdeal, model 401A) in conjunction with a signal source and reference unit (Brookdeal, Model 472).

The output from the A.C. signal source was applied to the bridge via an isolated 65:1 step down transformer. The bridge components used were all Muirhead 0.1% grade. The A.C. and D.C. circuits were separated by a 40H choke. The amplitude of the A.C. was adjusted to 7mV peak to peak.

The polarising circuit consisted of a simple battery/resistance combination. Potentials were measured using a Hewlett Packard Multimeter (type 3490A) which has a large input impedance ($>10^{10}$Ω).
Fig 3.7 Electrical circuit for faradaic impedance studies

\[ C_{\text{XS}} = \frac{C_4 R_2}{R_1} \quad \text{and} \quad R_{\text{XS}} = \frac{R_1 C_2}{C_4} \]
The experimental arrangement is shown schematically in Figure 3.8 and is based on the Solartron 1172 Frequency Response Analyser. Essentially this consists of a programmable generator that provides the perturbing sinusoidal signal, a correlator to analyse the response of the system, and a display to present the results. The fundamental response of a system to a sinusoidal perturbation of the form, $\Delta E \sin (\omega t)$, will be of the form $A \sin (\omega t + \theta)$. This instrument analyses the response of the system by a correlation process to determine $A$ and $\theta$ which has the advantages of rejecting all harmonics present in the output of the system and minimising the effects of random noise. A single measurement at a particular frequency can be made by programming the generator with the required frequency and signal amplitude. More usually, however, the generator is programmed to sweep through a large frequency range by choosing suitable values of the maximum frequency, limited at present to 10kHz, the minimum frequency, down to 0.1mHz, and the number of points per decade at which measurements are to be taken. The instrument will take measurements sequentially in either direction at equally spaced intervals (either on a logarithmic or a linear scale) over a required range. The response is given once a measurement has been completed and can be displayed in one of three possible notations: amplitude($A$) and phase angle($\theta$) relative to the output signal, log($A$) and $\theta$, or the real and imaginary parts of the impedance. The results were plotted onto a XY recorder (Bryans 26000 A3) to give the impedance spectrum directly.

3.2.2. Rotating Disc Studies

A block diagram of the apparatus is shown in Figure 3.9. Currents were measured using a Scalamp galvanometer (Pye, cat.no. 7892/S) in conjunction with a potentiostat (Chemical Electronics, type TR70-2A) at fixed potentials measured with a digital multimeter (Hewlett Packard,
Fig 3.8 Circuit for automated impedance measurements
Fig 3.9 Rotating disc electrode circuit

Fig 3.10 L.S.V and potentiostatic pulse circuit
The rotation speed was controlled (60-3400 r.p.m.) by a control unit (designed by O.R. Brown, Newcastle upon Tyne) and calibrated using a stroboscope (Dawe, type 1200E).

3.2.3. Linear Sweep Voltammetry (L.S.V.) and Potentiostatic Pulse

Potentiostatic control was obtained using a Chemical Electronics potentiostat type TR70-2A and monitored by the use of a digital multimeter (Hewlett Packard, type 3490 A). A function generator (designed by O.R. Brown, Newcastle upon Tyne) was used in conjunction with an X-Y recorder (Bryans 26000 A4) or oscilloscope (Hewlett Packard 130C). Figure 3.10 shows the experimental set up.

3.2.4. Galvanostatic Experiments

A Chemical Electronics potentiostat, type TR70-2A was set up for operation as a galvonostat. Figure 3.11 shows the experimental set up.

3.3. Scanning Electron Microscopy (SEM)

The microscope used for all examinations was a JEOL JSM 35R (beam accelerating voltage 20kV, filament current 100 A). Prior to examination, the specimens were gold shadowed (film thickness 100-200Å) using a diode sputtering technique.
Fig. 3.11 Circuit for galvanostatic experiments

[Diagram of a circuit with labels: Ammeter, Load resistance, Multimeter]
CHAPTER 4

POROUS LEAD DIOXIDE - A REVIEW

The lead-acid system has been established commercially for over one hundred years and the historical details have been adequately treated by Vinal\textsuperscript{2}. An extensive review of the lead-acid cell was compiled in 1966 by Burbank, Simon and Willingham\textsuperscript{6}. Sharpe\textsuperscript{59} and more recently Ruetschi\textsuperscript{60} have presented limited reviews of the lead-acid cell, the latter being the most recent. Whilst these reviews deal with the lead-acid cell as a whole, this thesis is concerned with the lead dioxide (positive) electrode.

The reaction at the positive plate may be written

\begin{equation}
\text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{2-} + 2e^- \rightleftharpoons \text{PbSO}_4 + 2\text{H}_2\text{O} \quad (4.1)
\end{equation}

Beck, Lind, and Wynne-Jones\textsuperscript{61} have very succinctly described the restrictions of this reaction.

From a practical viewpoint the reaction equation (4.1) implies that every gram of lead dioxide should yield 0.224 A hr of electricity. However, the discharge capacity is usually 10-50% of this value\textsuperscript{2}. Capacity limitations have been related to such factors as crystallite size and surface area of lead dioxide\textsuperscript{62,63}, modification of lead dioxide (\(\alpha\) or \(\beta\))\textsuperscript{62,64,65}, acid starvation effects\textsuperscript{2,62}, pore size distribution\textsuperscript{62}, grid alloy\textsuperscript{2,66}, and passivation by lead sulphate\textsuperscript{62,67}. With repeated cycling the positive plate may fail from a combination of grid corrosion and shedding (loss) of active material.

The behaviour of the porous lead dioxide electrode is to a large extent governed by current distribution and reactant depletion. Optimizations
of porous electrodes must therefore be based upon some model able to predict how these phenomena influence the discharge behaviour. Over the last few years various mathematical models have been proposed for the theoretical analysis of electrode reactions in porous media. While the theoretical work in this field has been extensive comparatively few applications of these models have however been made to practical electrodes. Prior to the work of both Simonsson and Micka and Rousar, in the case of the practically important lead dioxide electrode, theoretical and experimental investigations of current distribution gave contradictory results. Simonsson's model for the porous lead dioxide electrode is given in appendix 1. The Micka model followed Stein in assuming reversible electrode kinetics. This led to the conclusion that the potential in the pore electrolyte is a unique function of the concentration and this obscures the formulation of boundary conditions. In the two models, the figures of concentration versus position within the electrode, with time as a parameter, provide an interesting contrast. Simonsson assumed a constant concentration at the pore mouth; Micka and Rousar show a concentration which eventually goes to zero at the pore mouth.

A recent review of porous electrode theory with battery applications has been published by Newman and Tiedemann. They concluded that the theory of the operation and behaviour of porous electrodes has been developed to the point where almost any system can be treated. In particular, equations were developed to provide the bases for examining the behaviour of specific systems such as primary and secondary batteries, adsorption and double layer charging, and flow-through electrochemical reactors.
Experiments have verified the predictions of non-uniform current distribution in several types of porous electrodes, but experimental information on the transient behaviour of porous electrodes is scarce. The polarisation expression applicable to a given system is subject to refinement to account for the morphology of the electrode, the formation of covering layers or of crystallites of sparingly soluble species, and the transport from such sparingly soluble phases to the site of the charge-transfer process.

There are several areas which remain to be examined in greater detail. These include the complete analysis of an entire electrochemical cell, the prediction of the centre polarisation curve for a given battery, the dynamic behaviour of flow-through electrochemical reactors and the complete optimisation of a given electrochemical system.
5.1. Introduction

Examination of the literature showed that since the work of Fleischmann et al, a systematic examination of the fundamental redox processes involved in the interconversion of lead dioxide and lead sulphate was lacking.

The \( \text{PbO}_2/\text{PbSO}_4/\text{H}_2\text{SO}_4 \) electrode has a high \( E^{\circ} \) value and consequently requires a suitably inert base for the construction of a satisfactory working electrode.

Fleischmann and Thirsk in their experiments preferred to start with lead electrodeposited onto a copper-plated platinum basis and prepare their lead sulphate from this by electro-oxidation in sulphuric acid; the subsequent oxidation to lead dioxide was studied. A study of the relevant literature revealed that some objection might now be raised to this procedure because of the possibility of further reaction of lead metal from beneath a surface supposedly passivated by a blocking film of lead sulphate. In addition to this, it was clear that the electro-oxidation of lead sulphate might produce both \( \alpha \) and \( \beta \) lead dioxide at different formation sites on the electrode. It was clearly desirable to select the basis metal so that parasitic side reactions were eliminated. The inert metals conventionally chosen as bases are platinum, gold and tantalum. Of these, platinum has been the most widely used and appears to be satisfactory. Furthermore it is well established that lead dioxide can be electrodeposited exclusively in \( \beta \)-form onto a platinum basis from acid solutions of lead perchlorate at small current densities. The choice
of $\text{Pt}/\text{PbO}_2$, therefore, gives a well-defined starting material which enables the elimination of side reactions.

In the investigations of Fleischmann et al, little attention was paid to the electrocrystallisation reactions involved in the reduction of lead dioxide to lead sulphate. This present work commences with a study of aspects of this reaction. Potential step and linear sweep experiments have been made at the stationary and the RDE. Some impedance measurements are also described. The electrolyte concentration was fixed at $5\text{M}$ by commercial usage.
5.2. Experimental

5.2.1. Rotating Disc Studies

All measurements were made on a disc electrode as described in 3.1.3. The electrical circuit is given in 3.2.2. and the electrolytic cell shown in Figure 3.2. Potential step and sweep experiments were conducted using the experimental set up of 3.2.3. and the cell of Figure 3.2.

The electrolyte was deoxygenated with nitrogen. All measurements were made at 23 ± 1°C.

5.2.2. Impedance measurements

Impedance measurements were made over the frequency range 9000 - 1 Hz. The electrical circuit is described in 3.2.1. (2) and the electrolytic cell is shown in Figure 3.3. The electrolyte was deoxygenated with nitrogen. All measurements were made at 23 ± 1°C.

5.2.3. SEM studies

Experiments were made on stubs especially made to fit into the examination chamber of the Scanning Electron Microscope as described in 3.1.3. The microscope operating conditions are given in 3.3.
5.3. Results and Discussions

5.3.1. Rotating Disc Studies

Figures 5.1 and 5.2 show the results of potential sweep experiments between 1550mV and 750mV and also between 1200mV and 750mV. These curves show that of the two peaks (1060mV and 880mV) apparent when sweeping over the wider potential range, the peak at 1060mV is due to oxygen whilst that at 880mV is due to the reduction of lead dioxide. This conclusion follows from the fact that with the narrower potential range no excursion into the oxygen region is made so that only the lead dioxide peak (880mV) can be identified. There was no effect of rotation speed on these curves so that it can be concluded that the reduction of lead dioxide in sulphuric acid is not rate determined by solution reactions under the present experimental conditions. Presumably, even at a stationary electrode the diffusion layer was sufficiently thin for control of the current by mass transfer in solution to be absent.

It was found that both the potential $E_p$ and the current density $i_p$ at the maximum in the potentiodynamic reduction of lead dioxide were dependant upon the sweep rate $V$ in the range $3.2\text{mVs}^{-1}$ to $1.0\text{Vs}^{-1}$. Figure 5.3 shows the correlation between $E_p$ and $V$ in the form $E_p$ versus log $V$ and Figure 5.4 shows data connecting $i_p$ and $V$ in the form $\ln(i_p/V)$ against $1/V$. Table 5.1 shows the results of calculating the passivating charge for the reaction:

$$\text{PbO}_2 + 4\text{H}^+ + 4\text{SO}_4^{2-} + 2e \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O} \quad (5.1)$$

by integration of the areas under the reduction peaks and division by $V$.

Footnote: All potentials are referred to the $\text{Hg}_2\text{SO}_4/\text{Hg}$ electrode in 5M $\text{H}_2\text{SO}_4$ at the temperature of the experiment, $E_h = 0.60925\text{V}$.

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Fig. 5.1 Potential sweep experiment between 1550 mV and 750 mV
Fig. 5.2 Potential sweep experiment between 1200 mV and 750 mV

A, initial sweep
B, repeat
Fig. 53 $E_p$ vs. $\log_{10} V$ for linear sweep experiments
Fig. 5.4 $\ln(i_p/V)$ vs $V^{-1}$ for linear sweep experiments
The passivating charge is seen to be independent of sweep rate which indicates that the passivating layer is of constant thickness for a wide variety of sweep rates and suggests that the lead sulphate growth mechanism is relatively simple and controlled by charge transfer kinetics at the lead dioxide electrode. (This system is treated mathematically in Appendix 11). It has been shown that if a model is considered for which the current through the electrode is controlled by charge transfer at an electrode of ever diminishing area (as passivation proceeds) then the following requirements must be met.

### TABLE 5.1

Passivating charge obtained at various sweep rates for electrodeposited PbO$_2$ in 5M H$_2$SO$_4$

<table>
<thead>
<tr>
<th>$\text{mVs}^{-1}$</th>
<th>Charge, mC cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>68</td>
</tr>
<tr>
<td>320</td>
<td>60</td>
</tr>
<tr>
<td>100</td>
<td>68</td>
</tr>
<tr>
<td>32</td>
<td>57</td>
</tr>
<tr>
<td>10</td>
<td>77</td>
</tr>
<tr>
<td>3.2</td>
<td>101</td>
</tr>
</tbody>
</table>
(a) The charge required to reach passivation must be constant
(b) The current response in a potentiostatic pulse experiment stepping into the passivation region to form a stable phase must follow the equation:

$$\log i = A - Bt \quad (5.2)$$

(c) The potential of the peak maximum in a potentiodynamic passivation experiment follows the equation

$$E_p = C - D \log V \quad (5.3)$$

(d) The current at the peak maximum in a potentiodynamic experiment follows the equation:

$$\log (i_p/V) = G + H/V \quad (5.4)$$

(e) For the whole potential sweep the current and potential relationship is:

$$\log \left( \frac{i}{i_p} \right) = J + L(E - E_p) - M \exp \left( E - E_p \right) \quad (5.5)$$

A, B, C, D, G, H, J, L and M are constants, the values of which are given in Appendix 11.

Table 5.1 and Figures 5.3 and 5.4 shows that requirements (a), (c) and (d) are obeyed. That the requirement (e) is met is shown by plotting:

$$\ln\left( \frac{i}{i_p} \right) + \exp \left( \frac{QZF}{RT}\right)(E_p - E) \text{ against } (E_p - E) \quad (5.6)$$

in Figure 5.5 when a satisfactory straight line is obtained. Any deviation from linearity occurs at the more negative values of E when the passivating
Fig. 5.5 Test of equation (5.3) for linear sweep experiments

- 0.1 \text{ Vs}^{-1}
- 0.032 \text{ Vs}^{-1}
- 0.01 \text{ Vs}^{-1}
- 0.0032 \text{ Vs}^{-1}

\[ \alpha = 0.5 \]
layer of lead sulphate is relatively thick and other roughness and geometrical factors might be of great importance e.g. if porosity is present. For an assumed value of 0.5 for $\alpha$, the theoretical slope of Figure 5.5 should be $(39.2\text{mV})^{-1}$; the experimental value is $(45\text{mV})^{-1}$. Figure 5.3 requires a theoretical slope of $-59\text{mV}$, in fair agreement with the experimental value $-38\text{mV}$.

The general correctness of the model has been confirmed by potentiostatically stepping into the reduction region from positive potentials. A falling transient only is obtained (no nucleation process detectable) which is shown in the form of equation (5.2) in Figure 5.6. A straight line is clearly evident as required by the theory. The discrepancy in the passivating charge constancy (Table 5.1) apparent at slow sweep speed, is not altogether unexpected since difficulties in controlling deposit morphology and surface preparation introduce large errors. The tabulated results may be regarded as quite satisfactory.

Attempts to calculate electrode coverages at passivation indicate that either the blocking layer is considerably thicker than one monolayer if the nominal electrode area is introduced into the calculation or a roughness factor of approximately 50 must be assumed if a monolayer coverage is sufficient to isolate the electrode. Since the maximum roughness factor ever recorded for electrodeposited $\beta$-PbO$_2$ is 10-20, it seems likely that some thickening of a lead sulphate monolayer is required before passivation results. This is in agreement with the early work of Kabanov et al., who estimated the thickness of the passivating lead sulphate layer as $10^8$. 
Fig. 5.6 $\ln(i) vs. t$ for a potential sweep experiment stepping into the reduction region (870mV)
5.3.2. Impedance Studies

The $\beta$-lead dioxide electrode in 5M sulphuric acid exhibits a marked time dependancy of differential capacitance (Figure 5.7). The values of capacitance tend to increase with time after immersion in the electrolyte. At lower frequencies the effect is more pronounced as can also be seen in Figure 5.7. Kabanov et al.\textsuperscript{77} attributed this behaviour to a modification of the lead dioxide surface by specific adsorption of sulphuric acid molecules at positive surface charges. Since adsorption occurs at positive sites, the extent of adsorption is dependant on the electrode potential. Associated with the rise in capacitance is a slight fall in resistance, although over the experimental time period (typically 130 seconds for a frequency scan from 9.0 KHz to 1Hz) this can be neglected. A knowledge of this time dependance is essential if impedance measurements are to be normalised to values equivalent at $t = 0$s. Valid comparisons can only be made if the finite scanning time is allowed for and adjustments made in the described manner. The impedance measurements have all been corrected in this way. Previous workers\textsuperscript{78} encountering this problem have allowed prolonged contact between the electrode and the electrolyte (approx 26 hours) in order to achieve an equilibrium. Some objection may now be raised against this procedure since immersion over long periods of time is found in some cases to seriously affect the adhesion between the lead dioxide film and the platinum base.

A complex plane diagram for the test electrode held at a potential of 1100mV is shown in Figure 5.8. There is no reduction reaction at this potential, shown by the absence of any cathodic current and confirmed by the impedance plot of Figure 5.8. The graph forms part of a very large radius semi-circle indicating that the charge transfer resistance is also very great.
Fig. 5.7 Capacitance vs. time for PbO$_2$ ($\beta$) in 5M H$_2$SO$_4$
Fig 5.8 Complex plane impedance plot; $\beta$ PbO$_2$ in 5M H$_2$SO$_4$

measurements made at 1100 mV

frequencies (Hz) in parentheses

$z''/\Omega \cdot \text{cm}^2$

$z'/\Omega \cdot \text{cm}^2$
At 1044mV a semicircular complex plane diagram (Figure 5-9) is observed indicating the presence of a charge transfer controlled regime. This is typical for electrode potentials in the range 1050 - 1035mV. The measurements were found to be independent of rotation speed confirming that the reaction is not controlled by any diffusion process in solution. The cathodic currents in this range are typically 1mA cm\(^{-2}\). Excursions to potentials more negative than 1030mV leads to a rate of passivation too fast to follow using this technique. Table 5.2 gives values of the charge transfer resistance in the potential range 1035 - 1050mV.

### Table 5.2

<table>
<thead>
<tr>
<th>E/mV</th>
<th>(\Theta / \Omega_{cm^2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1048</td>
<td>113.7</td>
</tr>
<tr>
<td>1044</td>
<td>98.5</td>
</tr>
<tr>
<td>1040</td>
<td>86.9</td>
</tr>
<tr>
<td>1037</td>
<td>81.8</td>
</tr>
<tr>
<td>1035</td>
<td>75.8</td>
</tr>
</tbody>
</table>

It is shown in the following section that for electrodeposited \(\beta\)-PbO\(_2\) the true electrochemical surface area is considerably greater than the nominal value. Surface heterogeneity leads to the centre of the semi-circle in the complex plane diagrams falling below the abscissa.

Figure 5.10 shows a graph of \(\log_{10} \Theta\) vs E and yields a slope of 64 mV/decade. This indicates that the charge transfer coefficient is 0.47. The exchange current density \(i_o\) derived from the expression

\[
i_o = \frac{1}{\Theta} \cdot \frac{RT}{nF}
\]  

(5.7)
Fig. 5.9 Typical complex plane impedance plot: $\beta$PbO$_2$ in 5M H$_2$SO$_4$ in the reduction region

Measurements made at 1044 mV; frequencies (Hz) in parentheses.
Fig. 5.10 $\log_{10} \Theta$ vs $E$ for impedance experiments
has a value of $1.1 \times 10^{-4}$ A cm$^{-2}$. Aguf$^{79}$ calculated $i_0$ for a mixture of $\alpha$- and $\beta$- lead dioxide to be $3.2 \times 10^{-4}$ A cm$^{-2}$. The discrepancy in $i_0$ values would be expected since $\alpha$- lead dioxide is more reactive i.e. has a lower charge transfer resistance and hence a higher $i_0$.

If $\ln R_9$ is plotted against time at 1044mV, a straight line is obtained (Figure 5.11). Thus at a fixed potential the charge transfer resistance can be seen to increase as the passivation process continues until a layer of lead sulphate completely covers the electrode.

Figure 5.12 shows a complex plane diagram for a passivated electrode ($E = 800$ mV) and once more it can be seen that very little reaction is occurring at the electrode. We conclude that a relatively thick layer of lead sulphate is completely covering the lead dioxide and that this effectively seals off the electrode from further reaction.

5.3.3. SEM Studies

Figure 5.13 shows a $\beta$-PbO$_2$ surface at two magnifications after prolonged contact with 5M sulphuric acid at 1200mV. The surface consists of small condensed particles of even size ($\sim 5 \times 10^2$ nm); no evidence of PbSO$_4$ crystallites is visible. The true surface area is considerably greater than the apparent value in agreement with differential capacitance measurements$^{28}$. Figure 5.14 shows the effect on the surface of a potential sweep to 700mV at 10mVs$^{-1}$ followed by a 10min. period in the electrolyte at 700mV; the surface is shown tilted in Figure 5.14c. Clusters of PbSO$_4$ crystals are observed to have grown orthogonally from the surface. It is evident that the surface is not completely blocked by PbSO$_4$; some access of the sulphuric acid to underlying PbO$_2$ is possible. This confirms electrometric observations that after one sweep to 700mV the surface is
Fig 5.11 $\log_{10} \Theta$ vs $t$ for impedance experiments at 1044 mV.

\[
\log_{10}(\Theta/\Omega \text{cm}^2) \quad \text{vs} \quad t/\text{min}
\]
Fig. 5.12 Complex plane impedance plot for a PbSO$_4$ film on PbO$_2$ ($\beta$) in 5M H$_2$SO$_4$

measurements made at 800mV
frequencies (Hz) in parentheses
Fig. 5.13 $\beta \text{PbO}_2$ after immersion in 5M $\text{H}_2\text{SO}_4$ at 1200 mV
Fig. 5.14 PbSO crystal clusters grown from the PbO by a potential sweep at 10 mVs⁻¹ from 1200 mV to 700 mV.
not completely passive. A repeat sweep on the electrode results in a small amount of charging.
5.4. **Conclusions**

(1) Electrodeposited $\beta$-PbO$_2$ is reduced at approximately 900mV in 5M H$_2$SO$_4$.

(2) The process of reduction is controlled by charge transfer and terminated by a blocking film of lead sulphate which conducts only by a high field process.

(3) A mathematical model can be set-up which satisfactorily describes the electrometric results.

(4) No evidence was found for diffusion control via the electrolyte.

(5) No evidence was found for a nucleation process.

(6) The exchange current density obtained from impedance data was found to be $1.1 \times 10^{-4}$ A cm$^{-2}$. 
CHAPTER 6

STUDIES OF THE OXIDATION OF LEAD SULPHATE

6.1. Introduction

In the previous chapter the reduction of $\beta$-lead dioxide electro-deposited onto a platinum base was discussed. The conversion of lead sulphate to lead dioxide under potentiostatic control has been studied by Fleischmann and Thirsk\textsuperscript{9}. In their work the working electrode consisted of a layer of lead sulphate formed potentiostatically on an underlying lead base. This system is different from the one which occurs in general battery operation, where lead dioxide cuts off access to the underlying lead; the lead sulphate that is subsequently oxidised rests on a lead dioxide base. This chapter commences with an examination of the oxidation of the sulphate layer produced by the reduction of the $\beta$-lead dioxide. This system differs from the industrial system in that the basis was platinum and the lead dioxide non-porous, whereas, the commercial "positive" is porous lead dioxide based on lead passivated by a coherent dioxide layer.

Under the conditions used by Fleischmann and Thirsk\textsuperscript{9} the response to a potential step was a transient that rose and fell; this behaviour is similar to the well known rising and falling transients observed during the oxidation of lead monoxide in alkaline solution\textsuperscript{81}. It is interesting to note, however, that such rising and falling outputs are not often observed in battery practice.

In this chapter, details of an investigation at a stationary and a RDE are recorded in which a lead disc electrode was oxidised to lead sulphate and finally cycled. The kinetics of the nucleation and growth
processes have been studied for the first and subsequent cycles.

6.2. Experimental

Experimental details of the rotating disc and SEM techniques are outlined in section 5.2.

All electrolytes were deoxygenated by thoroughly purging with oxygen-free nitrogen prior to making measurements. All measurements were made at 23 ± 1°C in 5M H₂SO₄.
6.3. Results and Discussions

6.3.1. Rotating Disc Studies

6.3.1(a) Lead Sulphate on a lead dioxide base.

Figure 6.1 shows a reductive sweep on electrodeposited \( \beta \text{PbO}_2 \) from 1055mV to 700mV which was typically employed to produce a sufficient layer of lead sulphate at the electrode to study the reformation of lead dioxide.

Figure 6.2 shows a series of potentiostatic transients obtained by stepping a reduced and equilibrated electrode to a series of overpotentials in the range from 200mV to 400mV from the equilibrium potential; the results are independent of the speed of rotation of the working electrode.

It is clear that no well-defined rising transient is formed: this rules out a rate-determining (current controlling) nucleation process. This behaviour is observed presumably because the underlying lead dioxide provides adequate centres for growth and development of the new lead dioxide. Consequently, the rise and fall in current characteristic of the generation and growth of such centres is not observed in these experiments although it is observed during the oxidation of lead sulphate on lead.

The current time decay at constant potential follows the equation

\[
\frac{i}{i_{\text{lim}}} = t^{-0.2}
\]  

(6.1)

as is apparent from Figure 6.3 which shows plots of ln(i) versus ln(t).

At low overpotentials the agreement is very good. At long times and high

Footnote: All potentials are referred to the \( \text{Hg/Hg}_2\text{SO}_4 \) electrode at the temperature of the experiment.
Fig 6.1 Potential sweep experiment between 1065 mV and 700 mV.

- Anodic:
- Cathodic:

10 mA cm$^{-2}$

$E$ (mV) at 10 mVs$^{-1}$

Range:
- 1050 to 950 mV
- 950 to 850 mV

Graph showing the potential sweep experiment.
Fig 6.2 Potentiostatic pulse experiments from 1030 mV to various overpotentials ($\eta$)
Fig 6.3 $\ln i$ vs $\ln t$ for potentiostatic pulse experiments to various overpotentials ($\eta$) into the oxidation region.

- $\eta = 400$ mV
- $\eta = 365$ mV
- $\eta = 300$ mV
- $\eta = 250$ mV
- $\eta = 200$ mV
overpotentials, oxygen evolution makes a significant contribution to the current as indicated by the upward curvature of the lines.

The independence of the current flowing through the electrode on the rotation speed indicates that the current controlling process is not dependent upon mass transfer in solution. The concentrations of the reactants water and sulphuric acid are both considerable and the observed currents are considerably less than the limiting currents due to these species. It follows then that solution soluble lead reaction intermediates do not leave the electrode and the reaction involves only lead species on the electrode.

After short periods of time an exponential relationship was observed between current and potential. The Tafel curves of Figure 6.4 indicate a very high slope of approx. 200mV per decade. This value is a marked departure from the 60mV per decade expected for the oxidation of lead sulphate under charge transfer control. The high Tafel slope and the form of equation 6.1 for the current-time dependence (which cannot be satisfactorily interpreted quantitatively) indicate the complexity of the process. The migration of electrons through the poorly conducting sulphate layer presumably accounts for the major part of the high overpotential and the apparent high Tafel slope.

Figures 6.5 - 6.7 show repeat reductive sweeps on electrodes reoxidised at overpotentials in the range 200-400mV. (The reoxidation process was judged complete when the rate of current decay was negligible). Figures 6.6 and 6.7 show the progressive development of a second peak due to oxygen (930mV Pb3O4, 1060 mV O2); this peak becomes more important as the overpotential is increased and illustrates the significance of the
Fig 6.4 Ln i vs \( \eta \) from Fig. 6.3

- \( t = 4s \)
- \( t = 8s \)
Fig. 6.5 Potential sweep experiment between 1230 mV and 700 mV
Fig. 6.6 Potential sweep experiment between 1330mV and 700 mV

E / mV at 10 mVs$^{-1}$

5 mA cm$^{-2}$

anodic

cathodic

0
Fig 6.7 Potential sweep experiment between 1430 mV and 700 mV

E/mV at 10 mV s⁻¹

10 mA cm⁻²

anodic

cathodic
oxygen evolution reaction as a side reaction in the initial stages of the operation of the lead dioxide electrode. Comparison of Figures 6.1 and 6.5 shows a change in form with a shift of peak potential to more positive values as the result of the reduction/oxidation cycle.

The form of Figure 6.1 was discussed in the previous chapter. The process which gave rise to this response was interpreted as two-dimensional passivation. The theory presented in Chapter 5 predicts a straight line for the plot shown in Figure 6.8. This Figure contains data for both freshly prepared and cycled lead dioxide electrodes; it is clear that the simple two-dimensional model is incorrect for the cycled surface. Rotating disc experiments show that currents are independant of rotation speed therefore; processes involving diffusion of species in solution are not rate-determining.

It is suggested that the change in mechanism is due to morphological differences in the lattice. The original lead dioxide surface, relatively smooth and dense, becomes microporous as the result of the oxidation of a relatively less dense lead sulphate lattice \((\text{PbSO}_4, \text{PbO}_2 \text{ densities } 6.2, 9.4 \text{ g cm}^{-3})\). The reduction becomes essentially three-dimensional in character with the loss of the simpler two-dimensional characteristics. The reduction of a porous lead dioxide electrode is discussed in greater detail in a later chapter.

Figures 6.6 and 6.7 correspond to potential steps large enough for oxygen to be evolved as a side reaction. The evolution of oxygen at these relatively high overpotentials shows up in the fact that the potentiostatic transients do not decay to zero. When sufficient lead dioxide is exposed to the solution the oxygen reaction becomes significant.
Fig. 6.8 Comparison of data from first reduction and repeat reduction

1st reduction:
- expt 1
- expt 2
- expt 3
- expt 4

2nd reduction:
- x expt 1
- Δ expt 2
- • expt 3
- ▽ expt 4
During the later stages of the oxidation, however, there is a depletion of \( \text{OH}^- \) ions in those parts of the electrode to which access of the electrolyte solution is restricted. This is due to the process

\[
PbSO_4 + 2H_2O \rightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \quad (6.2)
\]

Most of the oxygen is therefore evolved at the lead dioxide surface directly in contact with the bulk solution; the interior of the lead dioxide electrode contributes little to the oxygen evolution reaction.

6.3.1. (b) Lead sulphate on a lead base.

Figure 6.9 shows the typical current-time characteristics of the sulphate covered electrode when stepped from 700mV to a potential in the range 1325 - 1400mV. The main features are the initial rising and subsequent falling portions indicative of nucleation and growth behaviour. These observations are in good agreement with those of Fleischmann and Thirsk who found that the initial rising portion corresponded to a \( t^3 \) relationship (for a 3-dimensional nucleation process) and the subsequent portion to an exponential decay as centres overlapped. It was not possible to compare the rate of exponential decay with the earlier work, however, the value approx. -0.2, for the exponent, compares very well with work discussed earlier in the chapter with a lead sulphate layer on lead dioxide. In this system there were adequate growth centres at all times and the rising portion of the curve was not observed.

Some variation was found to occur in replicate experiments, the extent of which appeared to be too large to be due only to random variation. It was considered that two factors might contribute to the scatter, oxygen evolution (especially at higher overpotentials) and area variation. In order to discount the area factors \( i/i_m \) was plotted
Fig. 6.9 Current-time response of a potential step experiment on an uncycled electrode from 700mV to 1350mV
Fig 6.10 $(i/i_m)$ vs $(t/t_m)^3$ for the rising part of the transient (uncycled electrode) for replicate experiments from 700 mV
against \((t/t_m^3)\) where \(i_m\) and \(t_m\) refer to the current density and time at the maximum of the transient. This plot is shown in Figure 6.10. In the range 1325 – 1350mV, where the oxygen evolution reaction was insignificant, reasonable agreement was obtained, however, at 1375 and 1400mV where the oxygen evolution reaction was more significant, the agreement was rather less good.

In order to establish a characteristic behaviour over the whole potential range, a number of experiments (>20) were performed at each potential and the mean behaviour established. This was done at fixed potentials in the range 1325 – 1400mV, and \(i_a\), the average current, was calculated after set times. Figure 6.11 shows that good straight lines were obtained by plotting \(i_a\) against \(t^3\). This plot confirms early work\(^9\) and indicates that a progressive three-dimensional nucleation and growth process is occurring. Ultimately, as the growing centres overlap a limitation of the current density is expected, the maximum value \((i_m, t_m)\) being predicted by an equation obtained, for example, by an Avrami\(^45\) type treatment for random overlap. Armstrong et al\(^50\) have considered one situation, the growth of right circular cones for which an analytical solution can be obtained as

\[
i = zFk_2\left(1-\exp(-9k_1^2At^3)/(3\rho^2) \exp (-9k_1^2At^3)/(3\rho^2)\right) (6.3)
\]

That equation (6.3) represents the current response to a potential step into the lead dioxide region is indicated by Figure 6.12, the reduced plot \(i/i_m\) against \(t/t_m\) for which the theoretical curve has been drawn. At short times the fit is very reasonable, bearing in mind that solid electrodes are involved, however, at longer times the divergence from the theoretical curve is significant. Efforts to force the experimental data to fit the theory more closely were made by correcting for the parasitic current. This procedure had an insignificant effect on the fit.
Fig 6.11 $i_d$ vs $t^3$ for the rising part of the transient (uncycled electrode) for experiments from 700 mV to: (□) 1350 mV, (●) 1375 mV, (○) 1400 mV
of the experimental points. It is interesting to note that the divergence at long times is more serious at high potentials and suggests that oxygen evolution intrudes increasingly into the oxidation reaction as the lead sulphate becomes progressively converted to lead dioxide. The abstraction of a constant current would not, therefore, be expected to be an effective correction. That oxygen was evolved during the later stages of the reaction was confirmed by observations.

The position of the transient was dependant upon the potential to which the electrode was stepped. It can readily be shown that both \( i_m \) and \( t_m \) depend on the rate constants, however, it turns out that \( k_2 \) is related only to \( i_m \) and \( k_1 \) is related to \( t_m \), viz

\[
\frac{zFk_2}{l_4} = i_m \quad (6.4)
\]

and

\[
t_m = \left(3D^2n2/\Pi M^2k_1^2A\right)^{\frac{1}{2}} \quad (6.5)
\]

Figure 6.13 shows the Tafel line from which the potential dependence of \( i_{ma} \) is found to be 90mV/decade. Figure 6.14 shows corresponding \( t_{ma} \) data over the same potential range and indicates a potential dependence of \( t_{ma} \) of -220mV per decade and this implies a potential dependence of 330mV per decade for \( k_1 \). These two Tafel slopes can be interpreted in terms of the potential dependence of the rates of orthogonal growth (outward) and parallel growth (overlap of growing centres). The former \( (k_2) \) is much more sensitive to changes of potential than the latter \( (k_1) \). The maximum current dependence may be compared with data given in the Fleischmann and Thirsk\(^9\) paper when an approximate 75mV per decade is reported. The potential dependance of the rate constants reported here is considerably higher than that reported by Armstrong et al\(^{50} \), for the growth of oxide films on mercury. It must be concluded that the need to
Fig 6.12 \( (i/i_m) \) vs \( (t/t_m) \) for potential step experiments on an uncycled electrode from 700 mV to: (square)1350 mV, (circle)1400 mV
Fig 6.13 Log $i_{ma}$ vs $E$ for potential step experiments on an uncycled electrode.
Fig 6.14 Log $t_m$ vs $E$ for potential step experiments on an uncycled electrode
transport charge to the growing lead dioxide centres on the lead sulphate phase by a high field conduction mechanism is responsible for the marked difference from the mercury system. This expansion of the growing centre laterally across the lead sulphate surface for parallel growth might also be expected to be less potential sensitive than the conversion of lead sulphate at the electrolyte side of the growing lead dioxide layer (where access of water molecules and electrons would be relatively easier).

For the falling portion of the transient, Figure 6.15 shows $i/i_m$ plotted against $(t-t_m)$. This curve is composed of two parts. At the start, the effects of the unrestricted nucleation and growth processes are still important and a curve results. At longer times, the form of the decay is

$$i/i_m = (t - t_m)^{-0.2}$$  \hfill (6.6)

which have been found experimentally to correspond to the simple falling transient which is obtained when sufficient lead dioxide growth centres are available. It is concluded circumstantially, therefore, that the overlapping process for both systems which leads to a current density restriction is similar.

Figure 6.16 shows reductive sweeps on electrodes oxidised potentiostatically in the range 1350 - 1450 mV. At 1350mV when sweeping the potential at -1mVs$^{-1}$, one peak was observed at 1050mV and corresponded to the reduction of lead dioxide to lead sulphate. The observed peak reduction potential is more positive than that observed for freshly deposited lead dioxide after one cycle at this
Fig. 6.15 \( \ln(i/i_m) \) vs \( \ln(t-t_m) \) for the falling part of the transient (uncycled electrode) for experiments from 700 mV to (D) 1375 mV, (o) 1350 mV, (e) 1400 mV.
Fig 6.16 Potential sweep experiments from the oxidation region, (a) 1450 mV, (b) 1400 mV, (c) 1350 mV, to 700 mV for PbO₂ formed from a lead disc electrode.
sweep rate, for which a peak potential of 990mV would be expected. The potential shift suggests that for the electrooxidation from lead sulphate a more reactive electrode surface is formed than from the oxidation of soluble Pb(II) species. This is possibly due to the presence at the electrode of adsorbed oxygen produced at the potential used to convert lead sulphate to lead dioxide. Another possible answer is that a mixture of α and β lead dioxide as produced by the electrooxidation of the lead sulphate would be expected to be more reactive than pure β lead dioxide. As in previous sweep experiments, the peak potential was observed to shift with sweep rate confirming that the processes controlling the current are irreversible.

For the reduction of lead dioxide prepared potentiostatically at higher potentials two peaks are clearly visible in the l.s.v. curves. The second peak at 1090mV is due to oxygen. The intrusion of the oxygen evolution reaction into the oxidation of lead sulphate is a function of time, however, and the oxygen peak was observed with electrodes oxidised at the lower overpotentials if the oxidation time was sufficiently long. For example, at 1350mV no visible oxygen peak was observed after 15 min. oxidation; after 30 min. a subsidiary peak due to oxygen was just visible; ultimately visual observations confirmed the evolution of gaseous products. The reoxidation of reduced electrodes was accomplished with electrodes which had been maintained for a sufficient time at 700mV for the current to fall below 3μA. It was considered that such electrodes were fully reduced. Figure 6.17 shows the potentiostatic response of such electrodes when stepped from 700mV to 1350mV. A comparison with Figure 6.9 shows a marked difference between the two responses, indicating two different
Fig 6.17 Current-time response for a potential step experiment from 700mV to 1300mV on an electrode after one cycle
growth mechanisms. Analysis of the initial rising portion ($t_m = 7.5s$) showed a linear relationship between $i$ and $t$ suggesting the instantaneous nucleation and growth of a two dimensional layer. This was tested by comparing the experimental data with the theoretical equation:

$$i = \left(\frac{2\pi \rho \mu}{\rho N_0 k^2}\right) \exp\left[-\frac{2\pi^2 N_0 k^2 t^2}{\rho^3}\right]$$

(6.7)

in the form of the dimensionless plot of $i/i_m$ versus $t/t_m$ shown in Figure 6.18. The fit provides a satisfactory proof that the first section of the transient represents an instantaneous nucleation and growth of a two dimensional layer of lead dioxide. Calculation of the charge corresponding to a potential of 1350mV in the rising part of this first section (~50mC cm$^{-2}$) and comparison with corresponding data for the rising part of the transient of Figure 6.9 (~500 mC cm$^{-2}$) shows this conclusion to be reasonable. It is also important that the charge under the first section of the reoxidation was reasonably independant of potential (charges ranged between 40 and 50 mC cm$^{-2}$). The magnitude of the charge in this single layer (~100 mC cm$^{-2}$) is surprisingly large and emphasises the porous nature of the surface on which these experiments are being carried out. The falling portion of the first section of Figure 6.18 has an exponential decay:

$$\frac{i}{i_m} = (t - t_m)^{-0.5}$$

(6.8)

which is sufficiently different from that of the first oxidation to confirm again that the processes differ in some respects.

The remainder of the oxidation charge for the second cycle is contained in the more drawn-out humped section of Figure 6.17. The nature of the growth process operative here was tested in Figure 6.19 by plotting the reduced $i/i_m$ versus $t/t_m$ data. The points
Fig 6.18 ($i/i_m$) vs ($t/t_m$) for the first rising and falling portion for potential step experiments on an electrode after one cycle from 700mV to (o) 1350mV, (o) 1400mV.
Fig 6.19: $i_t/i_m$ vs $(t/t_m)$ for the second rising and falling portion with varying allowances for parasitic current.
are shown for the unadjusted values and also for cases where allowance was made for the parasitic current. It is clear that again the growth of an instantaneously nucleated layer is being dealt with for although the match of the data to equation (6.7) is not particularly good, the form of the curve rules out progressive nucleation and the initial linear i-t relationship points to a two-dimensional process. The abstraction of further information from these transients is rendered difficult by the presence of the parasitic current which is made up from the oxygen evolution reaction and the "tail" of the first nucleation and growth process. The charge in the first (rising) part of the second section was computed and the parasitic current correction made by choosing this at the level required for the best fit in Figure 11. The charge was found to be \( \sim 300 \, \text{mC cm}^{-2} \), that is of the order of that required for the oxidation of the first cycle.

6.3.2. SEM Studies

6.3.2.1. Massive \( \beta \)-lead dioxide on platinum

6.3.2.1(a) The oxidation of lead sulphate on \( \beta \)-lead dioxide.

Figure 6.20 shows the results of a potentiostatic experiment on a grown lead sulphate layer (Figure 5.14) in which the potential is stepped from 800mV to 1300mV and has been maintained at the higher potential for 30s. It is evident that the formation of lead dioxide from the lead sulphate crystals has commenced at selected spots and this is seen to be further developed in Figure 6.21 which corresponds to a potentiostatic polarisation time of 2min. Here the quantity of large block-type crystals has decreased significantly and the structure has become much finer-grained. Figures 6.22 and 6.23, for reaction times of 5 and 15 min, show little
Fig. 6.20 Growth of PbO$_2$ from the grown PbSO$_4$ layer after 30s at 1300mV
Fig 6.21 Growth of PbO$_2$ from the grown PbSO$_4$ layer after 2 min at 1300 mV.
Electrode tilted in (d) to show topography
Fig. 6.22 Growth of $\text{PbO}_2$ from the grown $\text{PbSO}_4$ layer after 5 min at 1300 mV
Fig 6.23 Growth of PbO$_2$ from the grown PbSO$_4$ layer after 15 min at 1300 mV
difference in the quantity of fine-grained lead dioxide crystallites present. This is in agreement with electrometric measurements in which the \( \text{Pb}(II) \rightarrow \text{Pb}(IV) \) oxidation current in a potentiostatic experiment (\( 500 \rightarrow 1300 \text{mV} \)) is negligible after 8 min.

The results of the incomplete cleaning on an electrode during the preparation of the lead dioxide surface was evident from Figure 6.24. The effect appeared during the reoxidation of the lead sulphate surface rather than in the first reduction of the lead dioxide. This is shown in Figure 6.24 where the results of a potential step on a reduced 'contaminated' electrode was to leave unconverted a significant area (20%) of the sulphate. The nature of the contamination was a layer (possibly oxide or intruding organic) on the platinum upon which the lead dioxide was originally electrodeposited caused by an insufficient cleaning period in the sulphuric acid/nitric acid mixture prior to the electrodeposition. This observation is of considerable interest and indicates that the effect of contaminants on the positive plate in a lead acid battery is on the nucleation step in the recharging process. Confirmation of this explanation was provided by making experiments on insufficiently etched platinum electrodes, reduced to give coherent complete layers of sulphate. The worst cases of contamination were observed to have almost intact layers of lead sulphate after several minutes potentiostatic polarization at 1400mV. With adequate preparation, satisfactory oxidation was always observed.

6.3.2.1(b) The reduction of \( \text{PbO}_2 \) grown from \( \text{PbSO}_4 \) (2nd reduction cycle)

Following the reduction of the electrodeposited \( \beta \)-lead dioxide surface the electrode was pulsed back to 1300mV (from 700mV) and held at that potential until the electrode was effectively
Fig 6.24 Evidence of a contamination effect by the presence of PbSO₄ crystal structures on an electrode oxidised at 1300 mV for 15 min.
reconverted to lead dioxide. Figure 6.25 shows the effect on the surface of returning to 700mV by a potential sweep. The most important feature is the surface closely packed with lead sulphate which effectively blocks and thus passivates the surface of the underlying lead dioxide. A comparison with the micrographs of Figure 5.14 shows that there is an important difference between lead sulphate surfaces produced from electrodeposited lead dioxide and those from lead dioxide formed via lead sulphate. This lies in the form of the lead sulphate which is very fine-grained. Isolated large columnar crystals of lead sulphate are however observed randomly; it appears that these remain from the first reduction.

It can be concluded from the work on massive β-lead dioxide that there is a difference in morphology in the lead sulphate formed in the initial and subsequent reactions. This agrees with earlier observations. The effect of impurity in lead dioxide electrodes occurs in the nucleation step of the oxidation process (PbSO₄ → PbO₂)

6.3.2.2. Massive Lead electrodes.

6.3.2.2(a) The formation of lead sulphate.

Previously in the chapter electrometric work has shown that at a potential of 700mV reaction times of the order of 1 h are required for the development of a completely blocking film of lead sulphate on lead. Figure 6.26 shows such a film where it is apparent that there are large lead sulphate crystals in the 'valleys' of the electrode surface and smaller crystals on the tops of the 'hills'. This is in agreement with a solution-precipitation process as envisaged by Harrison and Archdale, restricted diffusion in the hollows giving rise to larger crystals. This observation may account for
Fig 6.25 Reduction of the grown PbO$_2$ to PbSO$_4$ by a potential sweep at 10mVs$^{-1}$ from 1300mV to 700mV
Fig 6.26 PbSO\textsubscript{4} grown on electrodeposited Pb at 700mV for 1h
differences in the response of lead electrodes to electro-oxidation in sulphuric acid observed as a result of different surface treatments. Surfaces with large roughness factors would be expected to engender a large proportion of large lead sulphate crystals. When the reaction time at 700mV is restricted to 15min (Figure 6.27), the gradual covering of the lead base with lead sulphate is observed. Here the surface topography of the lead appears to be followed by nucleation of the small crystallites occurring within the deep hollows of the surface. Such crystals once nucleated grow orthogonally to the surface, possibly in extreme cases developing to quite large sizes. This is actually seen in Figure 6.27d which suggests that the point of crystallite development lies below the general surface level. It is clear that the explanation advanced here gives an adequate explanation of variability due to surface treatment factors. This possibly explains why electrodeposited lead on lead surfaces give the most reproducible electrodes, for with these types of electrode the number of gross surface defects would be expected to be constant for constant electrodeposition parameters.

6.3.2.2(b) The oxidation of lead sulphate on lead to lead dioxide

Stepped from 700 to 1350mV, the lead sulphate electrode is converted to lead dioxide, exhibiting the well known rising transients for phase growth. As soon as potential control is removed, the reaction:

$$\text{PbO}_2 + \text{Pb} + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$$

(6.9)

occurs between the underlying lead, lead dioxide and any sulphuric acid available at the boundary between these two solid phases. Figure 6.28 shows an electrode on which this reaction was allowed to
Fig 6.27 PbSO₄ grown on electrodeposited Pb at 700 mV for 15 min
proceed, the potential falling to that characteristic of lead sulphate rather than lead dioxide. The large crystals of lead sulphate observed have never been transformed to lead dioxide (if sufficient conversion to lead dioxide occurs the surface is 'passivated' inasmuch as sulphuric acid cannot penetrate the lead dioxide layer and the reaction given by equation (6.9) cannot take place). The highly porous lead sulphate structure observed between the isolated large crystals is the developed surface due to the reaction given by equation (6.9). This emphasizes the beneficial effects of rests in positive battery plate formation; an increase in porosity improves the ultimate discharge behaviour.

6.3.2.2(c) The reduction of lead dioxide on lead to lead sulphate in 5M sulphuric acid.

A coherent complete film of lead dioxide was prepared by completely converting the lead sulphate layer to lead dioxide at 1350mV and then sweeping down to 700mV at 1mVs⁻¹. Figure 6.29 shows that results differ markedly from those shown in Figure 6.28. In the swept electrode, the product lead sulphate is very ordered and composed of quite large crystals, the porous deposit of the self-discharged electrode being absent. It can be concluded that the self-discharge of the reaction in which lead is consumed is much more effective in surface area development than the single electrochemical conversion of a lead sulphate surface.

6.3.2.2(d) The second oxidation of lead sulphate to lead dioxide (2nd cycle)

Following the reduction corresponding to Figure 6.29, a subsequent potentiostatic oxidation at 1350mV produced the surfaces shown in Figure 6.30. Here rod-like crystals of lead dioxide were
Fig 6.29 Reduction of the grown PbO$_2$ to PbSO$_4$ by a potential sweep from 1350mV to 700mV at 1mV s$^{-1}$
Fig 6.30 Effect of oxidation of the PbSO$_4$ layer shown in Figure 6.29 at 1350mV
observed to be growing across the deposit. It is clear that morphological changes between subsequent cycles occur and these are the reasons for differences in the responses of lead dioxide electrodes in charge/discharge cycling.
6.4. Conclusions

The potentiostatic oxidation of lead sulphate overlying lead dioxide is not rate-determined by a nucleation process. The underlying lead dioxide provides adequate centres for the growth and development of the new lead dioxide. In contrast, the oxidation of lead sulphate to lead dioxide on a lead base is a three-dimensional growth process with progressive nucleation and current limitation due to overlap of growing centres. The kinetics fit the theory for the growth of cones. The potential dependence of the growth constant orthogonal to the electrode is considerably greater than that parallel to the electrode. At higher positive potentials and long times the oxygen evolution reaction intrudes progressively into the oxidation of lead sulphate to lead dioxide. The appearance of an oxygen peak in the subsequent reconversion of lead dioxide to lead sulphate depends on the potential and time of the formation of the lead dioxide. The reoxidation of lead sulphate (2nd cycle) is more complicated than the original conversion. A two-dimensional growth process with instantaneous nucleation is first observed in which about 10% of the available lead sulphate is converted. This is followed by a further growth process in which the remaining lead sulphate is converted. The second process most closely conforms to an instantaneous nucleation and two-dimensional growth, however, analysis of the kinetic features of this process is complicated by the tail of the first growth process and the intruding oxygen evolution reaction. The unique porous character of the surface obtained by a self-corrosion process is of considerable importance in the surface development process.
CHAPTER 7

THE REDUCTION OF POROUS LEAD DIOXIDE ELECTRODES IN SULPHURIC ACID

7.1. Introduction

Over the last century the kinetics of the lead/sulphuric acid battery reactions have been actively investigated. It is only since the classical work of Fleischmann et al\textsuperscript{9,10} that the true nature of the phase formation reactions occurring at the positive (PbO\textsubscript{2}) electrode have been recognised. In view of a renewed scientific interest in the PbO\textsubscript{2}/PbSO\textsubscript{4}/H\textsubscript{2}SO\textsubscript{4} system it was thought timely to embark upon a re-examination of certain aspects of the kinetic behaviour of this system. Earlier chapters have dealt with the discharge behaviour of electrodeposited \(\beta\)-lead dioxide in sulphuric acid, the oxidation of lead sulphate on a \(\beta\)-lead dioxide base and the oxidation of porous lead sulphate on electrodeposited lead.

There has been little impetus to enlarge the field of study of the porous lead dioxide electrode outside that of immediate use to the battery technologist. What has been done has been well reviewed by de Levie\textsuperscript{11} and Newman and Tiedemann\textsuperscript{12}. Simonsson,\textsuperscript{13} using a computer technique satisfactorily calculated the discharge profile of a battery being discharged at a relatively quick rate. The modelling of porous electrodes has generally been done on the basis of a straight pore simplification leading to a one-dimensional approximation. De Levie\textsuperscript{11} has emphasised that mathematical equations for planar and porous electrodes are similar although some of the parameters have slightly different interpretations. The relative
conductance of the solution and solid phases of the porous matrix gives rise to a non-uniform reaction rate at the electrode as far as electrode depth is concerned. For a highly conducting solid and poorly conducting solution phase it is clear that the reaction will take place preferentially at the mouth of the pores. It has been shown, initially by Frumkin \(^{83}\) that the electrode has a characteristic "penetration depth", electrodes much thicker than this are not fully utilised. If, as in the case of the lead dioxide electrode being reduced in sulphuric acid, poorly conducting solid phase is produced, then it follows that the reaction is driven more deeply into the porous electrode structure as the reaction proceeds. The lead dioxide system can be simplified by the provision of a large excess of electrolyte and forced convective transport (RDE) and by using a truly "one-dimensional" electrode. This chapter describes some experiments with such a system.
7.2. Experimental

7.2.1. Rotating Disc Studies

All measurements were made on an electrode as described in 3.1.4. The electrical circuit is given in 3.2.2. and the electrolytic cell shown in Figure 3.2. Potential step and sweep experiments were conducted using the experimental set up of 3.2.3. and the cell of Figure 3.2.

The electrolyte was deoxygenated with nitrogen. All measurements were made at 23 ± 1°C in 5M H₂SO₄.

7.2.2. Impedance Measurements

Impedance measurements were made over the frequency 9000 - 0.1 Hz on electrodes as described in 3.1.4. (For impedance measurements the thickness of the porous layer was 0.3mm c.f. 0.762mm for rotating disc studies). The electrical circuit is given in 3.2.1(2) and the electrolytic cell is shown in Figure 3.3. The electrolyte was purged with nitrogen. All measurements were made at 23 ± 1°C in 5M H₂SO₄.

7.2.3. SEM Studies

The construction of a "one-dimensional" porous lead dioxide electrode of similar thickness to a conventional lead-acid battery positive plate is described in 3.1.4.

After the electrochemistry had been performed at the porous electrode, the electrodes were very quickly washed by rapid rotation in tri-distilled water to ensure the complete removal of electrolyte. Drying was accomplished very rapidly in a powerful
vacuum oven at 40°C. The washing and drying procedure is extremely important and it is crucial that the electrodes do not remain in the sulphuric acid electrolyte at an uncontrolled potential otherwise chemical changes occur which vitiate further structural study. The dried electrodes were removed from the Teflon shroud. The porous part of the electrode was detached from the pure lead support and fractured axially (sectioning destroys the topography).

SEM observations were carried out along the axial fracture and at the front of the electrode (porous lead dioxide/electrolyte interphase). The microscope operating conditions are described in 3.3
7.3. Results and Discussions

7.3.1. Rotating Disc Studies

Experiments at all potentials showed that in the present system the current passing through the electrode was independent of the rotation speed. To some extent this observation was rather surprising since it seemed that diffusion inside the pore would be a current limiting process. It must be concluded that either the change in the equivalent diffusion layer geometry does not alter the diffusional processes within the porous matrix or that diffusion within the pore is not important under the present conditions.

An important feature of the present experiments is the large excess of electrolyte solution so that "acid starvation" cannot be a current limiting factor as it often is in the operation of commercial lead dioxide electrodes; were "acid starvation" possible in the immediate vicinity of the electrode it is likely the current would be rotation speed dependant.

7.3.1.1. Cycles of galvanostatic oxidation and potentiodynamic reduction

Figure 7.1. shows l.s.v. reduction curves corresponding to typical electrodes oxidized galvanostatically to full capacity following varying numbers of cycles of galvanostatic oxidation and potentiodynamic reduction. Differences between the massive and porous lead dioxide are immediately clear. In the case of the porous material the reduction peak (co-ordinates of maximum $E_p, i_p$) is noticeably broader with a charge density in considerable excess of that reported in Chapter 5 for the electrodeposited (massive) lead dioxide electrode. It was shown that this peak can be represented by
Fig 7.1 Potential sweep experiments at 0.1 mVs\(^{-1}\) between 1250 mV and 700 mV on electrodes oxidised galvanostatically: (a) previously unreduced, (b) following 2 cycles, (c) following 4 cycles, (d) following 10 cycles
a relatively simple model in the case of the massive lead dioxide in which the current is controlled by charge transfer kinetics and available surface area. Figure 7.2 shows that this model does not hold in the porous case for the whole of the discharge. Only the first part (up to the current maximum) conforms to the simple model, thereafter the current obtained is considerably greater than the predicted value. The behaviour can be explained using the penetration depth concept. Initially the electrode behaves as a planar electrode of much enhanced area (of the order of $10^2$ that of the massive electrode). When the electrode is covered significantly with lead sulphate so that the resistance is increased substantially, the reaction is driven deeper into the electrode. Enhanced currents are obtained vis-a-vis the expected value in accordance with increase in available specific surface. This penetration of the electrochemical reaction into the porous electrode is shown by the "long tail" of the L.S.V. peak. (This tailing complicates the calculation of the reduction charge). The effects on the reduction charge recovered when cycling with a galvanostatic oxidation (until oxygen was freely evolved and the potential of the electrode was constant), followed by potentiodynamic reduction were most readily demonstrated by calculating the charge in the first part of the current peak (up to $i_p$). These data are related to the charge in the penetration volume of the electrode and are shown in Figure 7.3. Figure 7.4 shows the effect of cycle number on peak current. Both discharge responses were observed to increase up to a maximum which occurred after 15 cycles; thereafter the recoverable capacity on reduction remained constant. The increase is due to an increase of the porosity of the deposit arising from the development of the surface through successive
Fig. 7.2 Comparison of data from potentiodynamic reductions

(Δ) Previously unreduced electrode, reduced at 0.1 mVs$^{-1}$

(□) " "  "  " 1 mVs$^{-1}$

(●) Cycled electrode  "  "  0.1 mVs$^{-1}$

(○) " "  "  "  1 mVs$^{-1}$
Fig 7.3 Charge under the curve up to the peak maximum of a potential sweep experiment vs cycle number.
Fig 7.4 $i_p$ vs cycle number (as Figure 7.3)
density changes (from the less dense lead sulphate to lead dioxide). When cycling the lead dioxide electrode in the lead acid battery, Simon et al. observed the growth of voids in the porous active material giving increased surface area.

### 7.3.1.2. Effect of sweep rate

The magnitude of the peak current increased with sweep rate as might be expected, however the \( i_p \propto \sqrt{v} \) relationship characteristic of a process rate controlled by diffusion in solution does not hold. It was demonstrated in Chapter 5 with "smooth" electrodes of electrodeposited β-lead dioxide that the charge under the current peak was constant within the limits expected for a solid oxide electrode. Table 7.1 shows that in the present experiments there is a monotonic increase of charge up to \( i_p \) with decreasing sweep rate. (The data provided are for electrodes on the first cycle of galvanostatic oxidation and potentiodynamic reduction although the phenomenon was observed throughout the cycle life).

#### TABLE 7.1

<table>
<thead>
<tr>
<th>Sweep rate/mVs(^{-1})</th>
<th>Charge/C cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>9.59</td>
</tr>
<tr>
<td>0.32</td>
<td>8.66</td>
</tr>
<tr>
<td>1</td>
<td>7.72</td>
</tr>
<tr>
<td>3.2</td>
<td>7.09</td>
</tr>
<tr>
<td>10</td>
<td>5.94</td>
</tr>
</tbody>
</table>

*Footnote: In the case of "smooth" electrodes, the charge in the whole peak was considered, there being no complication due to porosity effects.*
This is in agreement with the accepted theory of porous electrodes, the rate of discharge of the electrode (sweep rate), to some extent, influencing the "available area" of the electrode. At low rates of reduction, the reaction trends to penetrate to deeper areas of the electrode.

7.3.1.3. Cycles of potentiostatic and potentiodynamic reduction

Figure 7.5 shows the effects when the reduction sweeps are made at 1 mVs\(^{-1}\); the quantity of charge gradually decreases for all purposes to a limit. At low sweep rates of the order of 0.1mVs\(^{-1}\) a large decrease in charge was observed between the first and second cycle, thereafter the capacity only diminished very slightly, being reasonably constant for the successive cycles. The initial high charge in a reduction cycle could be recovered at any time by a galvanostatic oxidation in the oxygen region. This behaviour indicates the development of a difficultly oxidisable layer of lead sulphate. It is only when a considerable overpotential is applied as is present under galvanostatic conditions that the complete transformation of the lead sulphate in the porous electrode occurs. The process which gives rise to the intractable lead sulphate may be the production of very large lead sulphate crystals or the complete removal of nucleation centres from areas of the electrode. One could well imagine a situation where under potentiostatic conditions at 1.2V\(^+\) areas of the electrode exist where the resistance of the lead sulphate grown in the reduction cycle decrease the current flow to such a low value that the rate of oxidation to lead dioxide was ostensibly zero. It follows from this argument that whereas the front of the electrode is the first area (i.e. that at less than the penetration depth) to

*Footnote: All potentials are referred to the Hg\(_2\)SO\(_4\)/Hg electrode in 2H\(_2\)SO\(_4\), \(E^\circ = 0.60925\) V.
Fig 7.5: Potential sweep experiments between 1200 mV and 600 mV at 1 mV s\(^{-1}\) of a cycled electrode. (a) 1st reduction, (b, c, d, e,) subsequent reductions. The potential is returned in each case to 1200 mV at the end of the sweep by a potential step experiment lasting 10 min.
suffer reduction, the inner regions may be the first areas to be oxidised.

7.3.1.4. **Effect of prolonged oxygen evolution during galvanostatic oxidation.**

The effect of oxygen is to distort the peak (Figure 7.6). A subsidiary peak (1060mV) is observed on the positive slope of the peak with electrodes which have been galvanostatically polarised in the oxygen region for a considerable time. It was surprising to observe that on cycling such electrodes to a series of potentiostatic oxidations limited to 1.2V followed by a negative going sweep down to 0.6V, the shoulder persisted for a number of cycles. The potential 1.2V is barely in the oxygen region and certainly unless the electrode is maintained at this potential for a considerable time (3h) the reduction peaks characteristic of oxygen are not observed on massive lead dioxide electrodes. It is therefore concluded that the evolution of oxygen from the surface of the porous lead dioxide produces a rather more reactive lattice species.

7.3.2. **Impedance measurements**

The frequency response of a porous lead dioxide electrode is shown in Figure 7.7. A linear relationship is observed between the in-phase($\Re$) and out-of-phase components in the electrode impedance provided that the potential is on the positive side of 1150mV. The slope of the line is 72°. A feature of the curve is an inductive shape at high frequencies.

This shape is unobserved in the response of the massive lead dioxide electrode and must be a concomitant of the porous morphology. Gutmann\(^{85}\) has discussed the experimental observations of
Fig 7.6 Potential sweep experiment between 1200 mV and 600 mV with prolonged oxygen evolution following oxidation.
Fig 7.7 Complex plane impedance plot: porous PbO$_2$ in 5M H$_2$SO$_4$

Measurements made at 1150 mV; frequencies in parentheses (Hz)

- 0.142
- 0.179
- 0.225
- 0.357
- 0.45
- 0.567
- 0.714
- 0.898
- 1.13
- 1.42
- 1.79
- 2.25
- 4.5
- 9000
himself and others that inductive effects are frequently encountered in the frequency response of batteries. He concludes that an inductive component of the electrode impedance results whenever the electrode system is able to behave as a negative resistance and furnish energy to the measuring device. He also instances the case where desorption occurs with increasing potential so that $d\theta/dE$ is negative. These behaviours would be expected to be most significant at low frequency rather than high and sufficient evidence exists to show that this is so. The work of Epelboin and co-workers\textsuperscript{86} for example provide experimental evidence and theoretical justification for this. Gutmann\textsuperscript{85} in his treatment points out that the time relationship of the current $i = I_0 \sin \omega t$ at the electrode solution interphase may not hold particularly if the electrolyte is viscous. This leads to a lag in the electrode response and a corresponding inductive region at high frequency due to this energy storage and in the limit a phase angle of $-45^\circ$ (lagging) should be observed at all frequencies. Darby\textsuperscript{87} has shown that inductive reactances arise naturally from mass transport and electrochemical reaction which can occur simultaneously over a distributed region of the electrode. The problem which Darby considers is one in which a gas reacts at a three phase interphase, one phase being porous. Essentially his treatment shows that at sufficiently high frequencies the phase angle of the faradaic impedance is negative. This arises because of a change in reactant concentration with depth inside the porous electrode which is unapplicable to a solid electrode. Darby neglects the double layer, capacity effects and ohmic resistance effects. These are both important in the present context, however both effects will be minimal at high frequencies and it is concluded that these effects should not
effect the qualitative picture. Confirmation of the presence of the high frequency inductive region of the complex plane diagram is provided by Keddam et al\textsuperscript{88} who studied the impedance of a lead acid battery in various stages during a discharge. Well defined inductive regions were observed at frequencies in excess of 1kHz, the differences between the behaviours at different states being sufficiently sensitive to provide a basis for a "state of charge" battery test.

As the potential is moved negative of the equilibrium potential the line bends at the lower frequency end, eventually resulting in a straight line at 22.5°. Complex plane diagrams at various potentials are shown in Figure 7.8. In no case is a semi-circular response observed (c.f. Figure 5.9 for a massive electrode). In the porous case an impedance due to electrocrystallisation is considered to be a significant contributor. It was shown previously that the current-time response to a potential step of a lead sulphate film on a massive lead dioxide electrode yields a purely falling transient. This may be compared with the porous case given in the following chapter where a complex response involving a series of rising and falling transients is obtained. An important series of papers by Fleischmann, Rangerajan and Thirsk\textsuperscript{89} considered in a formal mathematical treatment the diffusion of an ion in solution, charge transfer, followed by diffusion of adatoms on the electrode surface. This treatment differed from the earlier ones of Lorenz\textsuperscript{90}, Gerischer\textsuperscript{91}, and Mehl and Bockris\textsuperscript{92} in that the diffusion processes on the surface and in solution are linked. Equations were proposed for faradaic impedance experiments and these were extended to the case of finite rates of lattice formation. The original model of Gerischer and of Mehl
Fig 7.8 Typical complex plane plots on porous PbO$_2$ in 5M H$_2$SO$_4$ in the reduction region, measurements made at

- (●) 1138 mV
- (○) 1130 mV
- (□) 1100 mV

frequencies (Hz) in parentheses

\[ \text{frequencies (Hz)} \quad \text{in parentheses} \]

\[ (0.142) \]

\[ (0.179) \]

\[ (0.225) \]

\[ (0.284) \]

\[ (0.357) \]

\[ (0.45) \]

\[ (0.566) \]

\[ (0.714) \]

\[ (0.898) \]

\[ (1.13) \]

\[ (1.42) \]

\[ (2.25) \]

\[ (2.84) \]

\[ (4.5) \]

\[ (7.14) \]

\[ (9.000) \]
and Bockris still gives useful interpretations although the formulation of kinetically hindered steps may not always be precisely specified. Rangarajan's papers are helpful in reinterpreting constants characteristic of the electrode exchange reactions. The distinction between the two cases and the original model proposed by Randles is shown in Figure 7.9. It is clear that at high frequency (when $\omega^{-\frac{1}{2}}$ shrinks to 0) the faradaic impedance tends to $R_D$, the charge transfer resistance. At low frequency, if $W$ (the Warburg impedance) is eliminated, the faradaic impedance is $R_D + R_K$ (where $R_K$ is the electrocrystallisation resistance) from II but rather more complex from III; II and III become identical if $Z_8$ is very small, that is if lattice formation is the slow step in the surface diffusion incorporation process.

Present in the porous electrode but absent in the planar is diffusion within the pore. Winsel assumed that radial diffusion in a pore can be described by the laws of semi-infinite plane (Warburg) diffusion. Since the corresponding Warburg impedance is proportional to $\omega^{-\frac{1}{2}}$ and has a phase angle of $-45^0$, a semi-infinite pore should exhibit an impedance $Z_o$ proportional to $\omega^{-\frac{1}{2}}$ and with a phase angle of $-22.5^0$.

Figure 7.10 shows how a theoretical frequency response can be obtained qualitatively using a Gerischer model taking into account inductance, charge transfer, electrocrystallisation and diffusion within the pore. This proposed response agrees well with the experimental data given in Figure 7.8. Due to the complexity of the process it was not possible to isolate the various contributors to the frequency response. The equivalent circuit for the electrode is given in Figure 7.11.
Fig 7.9 Distinction between the models of Randles, Gerischer and Rangarajan et al.

I Randles
II Gerischer
III Rangarajan et al.
A...B Faradaic impedance
Fig 7.10 Components of the frequency response of the porous lead dioxide electrode

I charge transfer
II electrocrystallisation
III diffusion within the pore
IV inductive reactance (porous morphology)
V response
Fig. 7.11 Equivalent circuit for the porous lead dioxide electrode
7.3.3. SEM Studies

Figure 7.12 shows the front of the porous layer of dried and set leady oxide (paste) immediately prior to conversion to lead dioxide. Chemically the material consists of lead oxide and basic sulphates of lead. The structure of the electrode is clearly complex. The mixed crystal types evident are arranged in a quite random manner to give a very porous structure (40-50% porosity).

This morphology is to be compared and contrasted with that of Figure 7.13 which corresponds to lead dioxide produced by the electrooxidation of the paste. (The conversion to lead dioxide is sensibly complete and the porosity of the electrode is 57%). The porous matrix consists of small particles of fairly even size ($\sim 5 \times 10^2$ nm). It is interesting to note that this crystallite size is of the same order as that of $\beta$-lead dioxide crystallites when electrodeposited from lead perchlorate onto a platinum surface (although this latter surface contains no gross porosity). Figure 7.14 shows the inside of the porous lead dioxide 0.075cm below the surface. Here the crystallites are less well-developed than those at the surface as might be expected because of spatial restrictions within the matrix. The well-developed porous structure is quite evident and the average crystallite size is similar to that at the front of the electrode.

Figure 7.15 typifies the surface of a porous electrode after a reductive sweep from $1250$ mV to $700$ mV in 5M sulphuric acid. The surface is covered with well-defined lead sulphate crystals of widely varying sizes. It can be seen that only very small regions of
Fig 7.12 Front of pasted (leady oxide) and dried electrode prior to oxidation to PbO$_2$. 
Fig 7.13 As Figure 7.12 following galvanostatic oxidation to \( \text{PbO}_2 \)
Fig 7.4 Structure of the inner regions of porous PbO$_2$
Fig. 7.15 As Figure 7.13 following a potential sweep to 700 mV at 0.1 mVs$^{-1}$ in 5M $\text{H}_2\text{SO}_4$. 
the electrode remain uncovered by lead sulphate. This almost complete surface coverage would support the argument that the front of the electrode becomes very highly resistive and the current must come increasingly from the inner regions. The structure inside the porous matrix is rather more compact than that at the electrode front. Fig. 7.16 shows the SEM images at various depths from the front. At 0.005 cm below the surface some compacting is evident. Presumably this is due to the difference in densities between the product lead sulphate and the reactant lead dioxide (PbSO₄ 6.2; PbO₂ 9.4 g cm⁻³). On the surface the unrestricted development of lead sulphate can occur outward into the solution phase. Within the porous structure this freedom is denied and a more compacted structure is obtained as observed. On examination of the material at greater distances from the electrode front, the same tendency for compacted structure is observed, however, at the greatest depth the extent of compacting is less than just below the surface. This again provides good evidence for the argument that the reaction takes place initially at depths below the penetration distance and that the reaction is progressively driven further into the electrode. This point is confirmed by the photographs of Figure 7.17 which show the structure of the front of the electrode when the reduction is limited to 1000mV which is just less than the current maximum at 1070mV. Here an almost identical surface structure is obtained than was observed for the more extensive reduction. However, within the porous matrix itself Figure 7.18 shows quite clearly that the material is much less compact than at similar depths for the more extensive reduction to 700mV. It can be concluded therefore that the front surface of the porous electrode is almost fully utilised quite early on in the reductive sweep.
Fig 7.16 Structure of the inside of the porous electrode following a potential sweep to 700mV at 0.1mVs⁻¹ in 5M H₂SO₄

(i) Schematic diagram of fractured porous electrode
(ii) A, corresponding to position a
B corresponding to position b
C corresponding to position c
Fig 7.17 As Figure 7.15 but potential sweep limited to 1000 mV
Fig 7.18 As Figure 7.16 but potential sweep limited to 1000mV
A corresponding to position a
B corresponding to position b
C corresponding to position c
The examination revealed that following the reduction of a fully oxidised porous lead dioxide electrode cycled to a constant response (>10 cycles) using a sweeping technique to 700mV at 0.1 mVs⁻¹, the porous surfaces were identical to those observed with the "newly formed" electrodes which are typified by the Figures 7.15 and 7.17.
7.4. Conclusions

(i) The reduction behaviour of porous lead dioxide electrodes is independent of rotation speed in a large excess of 5 M H₂SO₄.

(ii) The reduction peak is broadened by the porosity. This is due to the reaction being driven more deeply into the pore structure as the front of the electrode becomes progressively more resistive.

(iii) The frequency response of a porous lead dioxide electrode in the reduction region is complex. Charge transfer, electrocrystallisation, diffusion within the pore and a concomitant of the porous morphology yielding an inductance all contribute to the observed spectrum.
CHAPTER 8

STUDIES OF THE OXIDATION OF POROUS LEAD SULPHATE

8.1. Introduction

In previous chapters experiments on massive lead dioxide prepared by electrodeposition on platinum, lead dioxide prepared from base lead by electrooxidation (the Plante process) and porous lead dioxide prepared from conventional leady oxide pastes by electrooxidation (modern positive plate process) have been reported. In this chapter the previous work on lead dioxide is extended to the reoxidation of lead sulphate to lead dioxide in a matrix of porous material.
8.2. Experimental

Experimental details of the rotating disc and SEM techniques are described in Chapter 7.

All electrolytes were deoxygenated by thoroughly purging with oxygen-free nitrogen prior to making measurements. All measurements were made at 23 $\pm$ 1°C in 5M $\text{H}_2\text{SO}_4$. 
8.3. Results and Discussions

8.3.1. Preliminary Experiments

Preliminary experiments on the reduction/oxidation behaviour of "one-dimensional" porous lead dioxide disc electrodes indicated that a bewildering range of electrode responses could be obtained representing the reoxidation of a partially reduced lead dioxide porous electrode. The crucial factor determining the particular electrode behaviour obtained was the history of the reduction immediately preceding the oxidation. A further, though less important factor, was the more remote cycling pattern. This is in broad agreement with battery experience where it is well-known that the immediate electrochemical history of the battery affects subsequent behaviour. This aspect of the porous lead dioxide electrode is a significant feature of the continuing development of the investigation of the lead acid battery and ultimately comprehensive theories will have to be developed to explain the historical aspect of the behaviour.

In the presently reported series of experiments the field of study was restricted to two representative porous matrices. Firstly the behaviour of a well-cycled (equilibrated) electrode is described. Secondly the behaviour of a newly formed electrode is described. With these two extreme types of porous structure, the most readily reproduced experimental conditions which can be obtained have been selected. It is emphasised, however, that by varying the historical treatment conditions it is possible to vary the behaviour of the electrode by quite large amounts. Two main series of experiments were performed. In the first, electrodes were studied which had been cycled to a constant electrical response. This required ten cycles of reductive sweep from 1250mV to 700mV followed by

Footnote: All measurements were made against the \( \text{Hg/Hg}_2\text{SO}_4\cdot5\text{M}\text{H}_2\text{SO}_4 \) electrode at the temperature of the experiment.
galvanostatic reoxidation (12mAm⁻²). In the second series of experiments, the electrochemical behaviour during an initial few cycles of potentiodynamic reduction and potentiostatic reoxidation was examined.

8.3.2. Rotating Disc Studies

8.3.2.1. Stabilised Electrodes (>10 Cycles)

Figure 8.1 shows the effects of stepping electrodes to 1200mV following a reductive sweep at a rate of 0.1mAcm⁻². The terminal potential of the reduction was found to govern the behaviour of the subsequent reoxidation current.

Figure 8.1A shows that a clearly defined rising current transient is not observed until the terminal potential of the reduction is less than about 800mV. Only a current falling with time is observed if the terminal potential is greater than 800mV.

When the final reduction potential is more negative than 800mV, rising parts of the reoxidation current transient become clearly defined indicating the occurrence of a layered growth process. At a final potential of 700mV a great deal of complexity is observed in the form of the reoxidation transient as shown in Figure 8.1B due to the removal of growth centres (lead dioxide) at the more negative potential.

In the previous chapter it was suggested that the well-established "penetration depth" conception can be usefully used to explain the behaviour of porous lead dioxide electrodes. It was supposed that initially on reduction the front of the electrode (at the electrode/electrolyte interface) is preferentially converted to lead sulphate, the reaction being driven more deeply into the
Fig 8.1A Potentiostatic pulse experiments on electrodes cycled to a constant response between varying terminal sweep potentials and 1200mV
Fig 8.1B Potentiostatic pulse experiments from 700mV to 
(a) 1200 mV, (b) 1300 mV
porous structure as the potential is made progressively more negative. On stepping the potential back to the lead dioxide potential, simultaneously all regions composing the porous electrode will commence to oxidise, the resulting transient being the superposition of currents from all the electrode regions. For electrodes swept to final potentials greater than 800mV and consequently reduced to only a small extent ( > 800mV) the reaction will be predominantly at the front of the electrode. Under these conditions the behaviour corresponds to that of the planar electrode of large surface area. A simple falling transient is to be expected provided that the reduction does not annihilate enough of the growth centres to curtail the current. This is in agreement with the observations. Figure 8.1B is a typical oxidation transient for a deeply reduced electrode stepped from 700mV to 1300mV. Two well-defined current peaks and a shoulder suggest the nucleation and subsequent growth of three fairly distinct layers of lead dioxide.

It is very difficult to draw precise boundaries around three physically different regions of the electrode. However, in general three broad regions can be identified which would be expected to react somewhat differently. First there is the material which exists at depths less than the penetration depth, secondly there is that in the inner regions of the electrode, thirdly there is that lead dioxide produced from the massive lead bounding the porous lead dioxide which has been produced by the self corrosion reaction:

\[ \text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 \rightarrow 2\text{PbO}_2 \]  

(8.1)

On reducing these triplex electrodes, the regions react in order of reactivity, however, on reoxidation all the three regions will
reoxidise starting at the same time. The current response of the electrode is made up of three components. It is suggested that the data conforms well to this model, three distinct peaks being apparent in the case of deeply reduced electrodes typified by Figure 8.1B. In order to explore further the form of the transients typified by Figure 8.1B, the curves were deconvoluted*. Figures 8.2A and 8.2B show the deconvolution process carried out on transients corresponding to reoxidations from 700mV.

The actual current-time curves can be considered to be composed of three separate rising and falling transients (a), (b), and (c). The broken lines of Figure 8.2A represent the results of the completed deconvolution process. $(b_1^1)$ and $(b_2^2)$ are the limits of the tail for the second peak and $(c_1)$ and $(c_2)$ are the limits of the rising part of the third transient peak (see Appendix III). The most reasonable decomposition of the current-time curve is into two instantaneous two dimensional nucleation and growth processes followed by a final progressive three dimensional nucleation and growth process. This is confirmed by the dimensionless tests of the separated transients carried out in Figure 8.2B. The agreement of the data points with the theoretical line is quite good when the difficulties of the process and the heterogeneous nature of the electrode are considered. The identification of the current peaks with the specific areas of the electrode is also a problem. The most sensible solution to this is that the first peak corresponds

*Footnote: The deconvolution was carried out using the computer technique shown in Appendix III.
Fig 8.2A Figure 8.1Bb deconvoluted into three distinct transients (see Appendix III).
Fig 8.2B $i/|m$ vs $t/t_m$ for the deconvoluted transients from Figure 8.2A

- o a
- o b
- o b₁
- o b₂
- △ c₁
- ■ c₂
to the inner regions of the electrode (the self corrosion layer),
the second, to those areas beneath the outer electrode surface at
distances greater than the penetration depth and the final peak
corresponds to the front layer of the electrode.

This agreement is based on considerations of the final
conductance of the reduced electrode when it seems likely that the
current path between the lead base and lead sulphate/lead dioxide
will be the lowest resistance nearest the lead base at the back of
the electrode. Clearly all regions will begin to oxidise simultaneously,
however the back region will complete the conversion to lead dioxide
in the shortest time.

In support of this contention are the magnitudes of
the charges corresponding to these processes. The largest charge
being contained in the third peak which corresponds to the front
of the electrode which on recharge would seem to be the last region
converted to lead dioxide.

8.3.2.2. Newly formed porous lead dioxide electrodes

Figure 8.3 shows the current-time response resulting
from a step back to 1300mV after a swept discharge down to 700mV
on a newly formed electrode. The response can be interpreted in
terms of two superimposed peaks and these can be deconvoluted as
shown in Figure 8.4. Figure 8.4A shows the reduced plots corresponding
to the deconvoluted data. It is confirmed by these that the best
interpretation of the data is that the first peak is a two dimensional
instantaneous nucleation and growth process and the second represents
a three dimensional progressive nucleation process. The fit of the
Fig 8.3 Potentiostatic pulse experiment between 700 and 1300 mV
Figure 8.4 Figure 8.3 deconvoluted

Figure 8.4A, $a_1$, $a_2$, $b_1$, $b_2$
abstracted data to the theoretical reduced plots is not particularly good. This is to be expected since the electrode would be expected to be very heterogeneous particularly during its early history and consequently much experimental scatter is to be expected.

If the electrode is progressively cycled with no resting periods it is observed that the first peak becomes a three dimensional growth process as shown by the response curves and reduced plots of Figures 5A and 5B. The interesting point here is that by comparison with "well cycled" electrode responses which exhibited three peaks, the first peak seems to be the one missing in these experiments. It is concluded from these experiments that large crystals of lead sulphate have, with recycling, developed inside the front of the porous electrode/electrolyte interface.

In order to confirm the identity of the "regions" responsible for each individual peak in the multipeaked response (electron microscope evidence that such regions can be identified is given later in the chapter) a number of experiments were made on newly formed electrodes in which the extent of the self-corrosion region of the porous electrode was enhanced. The enhancement was achieved by prolonged contact at the end of the first formation in 5M H₂SO₄ when the self corrosion reaction readily occurs. The effect of a prolonged open circuit period on completion of the initial formation of the porous electrode is shown on the reoxidation behaviour after the swept discharge. As shown in Figure 8.6A an initial falling transient is observed followed by two rising transients, the latter respectively representing two dimensional growth and three dimensional growth processes as shown by the reduced plots of Figure 8.6B.
Fig 8.5A Potentiostatic pulse experiment between 700mV and 1300mV on an electrode cycled twice without removal of potential control.
Fig 8.5B Figure 8.5A deconvoluted

$i/i_{m}$ vs $t/t_m$ for the first peak
Fig 8.6A Potentiostatic pulse experiment from 700mV to 1300mV ('rest' period was incorporated in the formation to develop a layer of self discharges material.)
Fig 8.6B $i/i_m$ vs $t/t_m$ for the transients from Figure 8.6A
The incorporation of a resting period immediately before the reoxidation process in the cycling pattern ultimately results in the more normal current response to potentiostatic reoxidation. The initially enhanced first peak being gradually lost at the expense of longer time responses. Figure 8.7 show the development of the long drawn out (third) peak at prolonged times with the elimination of the early rising transient responses, thus after four cycles the first peak is reduced to a shoulder. This is in accord with the transformation with continued cycling of very reactive inner (corrosion layer) regions of the electrode to the more normal porous structure. A plausible explanation can be given in terms of the particle size of the lead sulphate produced, during reduction the initially produced fine-grained material being gradually transformed into large block-type crystals. These morphological changes are recorded in the following section.

It is concluded therefore that the enhancement of the first peak in the initial stage of this cyclic experiment corresponds to the development of fine grained material in the self-corrosion layer. With cycling, transformation to a larger-grained less reactive material occurs.

8.3.3. SEM Studies

8.3.3.1. Newly formed porous lead dioxide electrodes

Figure 8.8 shows the result of a potentiostatic experiment on the reduced lead dioxide electrode surface (Figure 7.15) in which the potential has been stepped from 700mV to 1300mV and maintained at the higher potential for 15 min. Comparison with Figure 7.15 shows that the quantity of large block type lead sulphate
Fig 8.7 Potentiostic pulse experiment between 700 mV and 1300 mV
Fig 8.8 Electrode of type in Figure 7.15 reoxidised potentiostatically at 1300mV for 15 min.
crystals has been significantly decreased and the structure has become finer grained. Lead dioxide can be observed growing amongst the lead sulphate. The compact nature of the electrode material tends to obscure any structural change which may occur. It is clear from Figure 8.8 that even at 1300mV for 15 min, numbers of large lead sulphate crystals remain unoxidised. This confirms the observation that the complete oxidation of such electrodes potentiostatically at low overpotentials is relatively slow and the most convenient way of reestablishing the fully oxidised state is by a galvanostatic process. A possible reason for this follows from a study of Figure 8.8 in which the small area of contact between the lead dioxide and the highly resistive lead sulphate would be expected to result in a low oxidation current.

In Figure 8.9 the interphase between the porous lead dioxide electrode and the pure lead support is examined. (This corresponds to the grid/paste interphase in a lead acid positive plate). Lead dioxide is observed growing in between gaps in the lead sulphate layer which appears to have cracked and peeled back. Careful examination of the higher magnification picture indicates that lead dioxide is growing on the lead sulphate layer which confirms that even though the lead sulphate is highly resistive penetration by the current can occur at preferred points.

8.3.3.2. Porous lead dioxide electrodes cycled to a constant response (>10 cycles)

The electron micrographs of Figure 8.10 correspond to the reoxidation (step from 700 to 1300mV) of a reduced (to 700mV at 0.1 mVs⁻¹) porous electrode for 15 min. Areas were chosen which corresponded to those previously examined (Figures 7.15 and 7.16).
Fig 8.9 The self corrosion layer corresponding to Figure 8.8
Fig 8.10 As Figure 7.16 but cycled (potential sweep to 700 mV, step back to 1300 mV) to a constant electrode response A corresponding to positions a and b.
B corresponding to position c
The same broad pattern is observed, the porous material becoming progressively more compact as the front of the electrode is approached.

The structure of the "corrosion layer" at the lead/porous lead dioxide interphase is shown in Figure 8.11. Here the lead dioxide is very fine grained and there is no evidence of lead sulphate crystals as was obtained at this interphase during the early cycling history (Figure 8.9). This is an important observation since a region of the porous electrode has been identified which is fundamentally modified with cycling. It is known that the early part of a reduction transient depends markedly on the number of cycles during the early history, the charge obtained during the initial stages increasing with cycle number. 'It can be concluded by the more ready conversion of the material in the lead/porous lead dioxide region that this layer has become more reactive electrochemically.

In a previous part of the chapter it was shown that the current-time response for the potentiostatic reoxidation of a porous electrode could be understood if the electrode was considered to consist of three regions. These regions each contributed a peak to the response transient. It is now suggested that these regions are the three shown in Figures 8.10 and 8.11. The first peak in the time sense corresponds to oxidation of the lead/porous electrode interphase, the second to the less compact material beneath the surface and the third peak to the compacted material at the front and somewhat below the surface of the electrode. This third layer is to be pictured as the extent of the penetration depth for a reduction reaction before the increasing ohmic resistance drives the reaction further inwards.
Fig 8.11 The self-corrosion layer corresponding to Figure 8.10
8.4. Conclusions

For the reoxidation of porous electrodes of lead dioxide containing lead sulphate, the form of the current transient depends on the balance of lead sulphate and lead dioxide. For relatively small amounts of lead sulphate a simple falling transient is obtained. For larger amounts the transient becomes more complicated and may be deconvoluted using a computer technique. For a porous lead dioxide electrode cycled to a constant response three well-defined regions exist within the electrode.
CHAPTER 9
THE INFLUENCE OF THE SOLID/POROUS ELECTRODE INTERPHASE ON THE BEHAVIOUR OF POROUS LEAD DIOXIDE ELECTRODES

9.1. Introduction

It has been shown in Chapter 7 how the reduction of porous lead dioxide electrodes using a potential sweep from 1250mV* to 700mV gives a curve which indicates that the porous inner structure contributes significantly to the overall charge output on reduction. Moreover, the final potential of the sweep can be used as a method of obtaining a measure of the ease of reoxidation of the electrode.

Specifically, on stepping back a reduced electrode to the lead dioxide region, the development of an initially rising transient in the current-time response indicates a slow process in the crystallisation of lead dioxide on sulphate. In practice this is observed as a "coup de fouet" in the recharge. The limiting potential to which the electrode may be driven before a step back generates a rising transient is a measure of the rechargability. The number of cycles taken without deterioration in the magnitude of the area under the reductive sweep curve is a measure of the cycle life of the electrode. The magnitude of the peak and the area under the curve of the reductive sweep are measures of the electrode output. A technique has been devised in which all these criteria are incorporated in a single repetitive experiment.

*Footnote: All measurements were made against the Hg/Hg₂SO₄/SMH₂SO₄ electrode at the temperature of the experiment.
The development of low loss batteries and the alternator for recharging has made the use of antimony free grids (electrode supports) desirable. Over the last few years alloys of lead with calcium, tin and aluminium have been used to replace antimonial lead alloys. However, it has been reported that low cycle lives appear when the alloy contains less than 3% antimony, and moreover the lead, calcium, tin, aluminium alloys show unsatisfactory recharging characteristics. Experiments using the above technique have been made on a number of alloys selected in order to pick out likely enhancing ingredients for lead, calcium, tin, aluminium alloys. This chapter records the results.
9.2. Experimental

Experimental details of the rotating disc technique are described in Chapter 7. Porous electrodes were constructed as described in 3.1.4, however, the solid supports for the porous electrode material were either pure lead or various lead, calcium, tin, aluminium or lead, antimony based alloys.

Experiments were made by sweeping the electrode potential negatively to 700mV, followed by a potential step back to 1300mV. The electrode was completely reconverted to lead dioxide by a galvanostatic charge (25mA cm\(^{-2}\)) and the cycle of operations repeated. These cycles were repeated until a constant response was obtained.

On a stabilised electrode the terminal potential to which the reductive sweep could be taken without the development of an initial rising transient on stepping back to 1300mV was determined. If the electrode failed prior to stabilisation, the number of cycles prior to failure was recorded.
9.3. Results

Figure 9.1 shows the reduction by a potential sweep of porous lead dioxide with an antimonial alloy solid support. The long tail is characteristic of all newly produced porous lead dioxide electrodes and indicates that the discharge is being driven into the porous matrix.

Figure 9.2. shows the reduction curve for the lithium alloy after three cycles. The long tail has disappeared indicating that the inner structure of the electrode contributes but little to the reduction. This appears to be a prelude to the complete collapse of the electrode. In later stages adhesion between the porous matrix and electrode support is lost. The co-ordinates of the maxima in Figures 9.1 and 9.2 reflect the initial potential of discharge of a battery.

Figure 9.3 shows two curves for the reoxidation (step back) of reduced porous lead dioxide electrodes. The potential step is initiated from different final sweep potentials. In one the final potential is insufficient to cause the rising transient observed in the other. The terminating potential prior to the occurrence of a rising transient is a measure of the ease of recharge.

Table 9.1. shows the constitution of the alloys.

Table 9.2. shows the results of the experiments.
Fig 9.1 Negative going sweep on porous PbO$_2$ on 6\% Sb/94\% Pb support
Fig 9.2 Negative going sweep on porous PbO on 0.74% Sn/Pb/0.051% Ca/0.004% Al/0.003% Li support
Fig 9.3 Potential step experiments to 1300 mV on porous PbO$_2$ following negative going sweeps at 0.1 mVs$^{-1}$
<table>
<thead>
<tr>
<th>ALLOY</th>
<th>X(%)</th>
<th>Sb(%)</th>
<th>Ca(%)</th>
<th>Sn(%)</th>
<th>Al(%)</th>
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Alloy 1 contains 0.02% Se
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<th>$E_{MS}$ (mV)</th>
<th>C.L</th>
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where  
- **CL** - life in cycle number  
- **CRT** - Number of cycles before the development of a rising transient on stepping back from 700mV  
- **$E_{M_1}$** - Potential co-ordinate of maximum in the first negative going sweep  
- **$E_{MS}$** - Potential co-ordinate of maximum in the "stabilised" negative going sweep.  
- **$E_T$** - Minimum potential of sweep for the development of a rising transient on step back to the lead dioxide region.  
- **$i_{MS}$** - Current co-ordinate of maximum in the "stabilised" negative going sweep.
9.4. Discussion

The antimony alloys occupy a position of their own vis-a-vis the other alloys. Cycling could be carried out extensively (20 cycles) with no disastrous loss in charge output in the reduction. It has been reported\textsuperscript{63,93} that the small particle size, large specific surface area, and prismatic morphology of the lead dioxide crystals were preserved when antimony was present in the plates. During the course of charge and discharge cycles\textsuperscript{63}, the particle size of the lead dioxide increased, and the end of life was associated with this increase, as well as the anhedralization of the grains. Freshly prepared active material had about the same morphology and particle size characteristics, whether formed on pure lead or antimonial lead\textsuperscript{63,94}. Kordes\textsuperscript{63} found that, in active materials on pure lead grids, the increase in particle size with cycling was more rapid than on antimonial grids, reaching a maximum after only 8-10 cycles. The same paste on antimonial grids increased in particle size at a markedly slower rate and reached a maximum after twenty cycles. It has been reported\textsuperscript{93} that the presence of antimony in the grid metal gives rise to an increased content of $\alpha$ PbO$_2$ in the formed active material.

Of the other alloys, bismuth is observed to give the best performance. Comparison with the basic lead, calcium, tin, aluminium, alloy(alloy 4) shows that bismuth is the only additive to enhance the electrode behaviour. It appears that barium addition is not particularly detrimental but it is observed that in this experiment the amount of barium present in the alloy is much lower than the other alloys (due to difficulties encountered when making the alloys).
The remaining additives all have marked detrimental effects on the electrode behaviour. It was evident that following the alloy preparation, the alloys containing magnesium strontium and lithium corroded when left exposed to the atmosphere. This phenomena would greatly affect the alloy/porous interphase in terms of adhesion of the two phases due to the presence of a passivating oxide film and also an increase in the rate of the self-discharge reaction. The most destructive effect of the antimonial alloys is the increased rate of self discharge induced at both the positive and negative plates. Hence an increased rate of self discharge in alloys missing the enhancing effects of antimony would give the dramatically short cycle lives observed for the majority of the alloys. Thus it is proposed that bismuth acts in a similar vein to antimony, which is not unexpected due to the close proximity of the two metals in the periodic table.

The theoretical background of these results is not understood and an exhaustive study of the literature has not revealed any satisfactory theory on which to base any argument. The most attractive idea appeared to be invoking semiconductor behaviour which might give enhanced electrochemical responses due to band bending and electron tunnelling. This does not appear to be a factor in the present studies since metals expected to show this effect are valueless as doping agents.
9.5. Conclusions

Antimony at 6% is far superior to the other electrodes investigated. Bismuth appears to be an enhancing ingredient. The remaining additions accelerate porous electrode failure to a marked degree.
CHAPTER 10

FINAL DISCUSSIONS

There are a number of challenging problems connected with the lead-acid cell which need to be solved in order to perfect the performance.

The lead-acid battery that uses a lead-calcium alloy for the grids, the so-called "maintenance free battery" is a recent development. The lead calcium alloy reduces the float current, hydrogen evolution and water consumption by a factor of about ten over the more common lead-antimony alloy and when properly made and operated, these cells can be made maintenance free for a period of 5 years. Unfortunately, should the cell undergo a particularly deep discharge, recharging is difficult.

The importance of antimony is not fully understood. The mechanism by which antimony in the grid alloy delays the onset of positive plate failure is unknown. Possible substitutes for antimony have been discussed, but other enhancing agents may have similar detrimental side effects.

Corrosion of the positive grid metal and the nature of the bond between the grid and the active mass of lead dioxide present complex and interrelated problems.

Only fifty per cent of active material which makes up half the plate weight is utilised. Thus only 25% of the lead present is used at low rates of discharge. At high rates the figure is much lower,
typically 5%. The basic response of the porous pastes is not fully understood. The effect on capacity of the immediate cycle history is another area requiring further research.

It has been shown in this thesis that the basic kinetics of electrodeposited lead dioxide are fairly well understood. The exchange current and electrocrystallisation kinetics are well documented.

With porous electrodes some progress towards a better understanding of the lead acid battery problems has been made. This progress is discussed under the appropriate headings.
10.1. The appearance of rising transients

The oxidation of porous lead sulphate has been discussed in Chapter 8, the form of the current-time transient depending on the relative amounts of lead sulphate and lead dioxide present in the matrix. The practical situation is somewhat different, the electrode being effectively three not simplified to one dimensional. Hence the total response observed is the sum of reactions occurring on many different component areas within the electrode. It is unlikely therefore that the type of response obtained for the "one-dimensional" case, where in some well-defined experimental conditions three separate rising and falling outputs have been observed, would be found for the three-dimensional case. Under the most practical conditions of lead cell operation, rising and falling outputs are not usually encountered. Only a simple falling transient is normally observed because the underlying lead dioxide at some region in the plate is able to provide adequate centres for the growth and development of new lead dioxide. The appearance of the "coup de fouet" (rising transient) in the charge behaviour of batteries is however well known. The early part of the recharge of a negative plate is quite efficient (the Pb(II)/Pb reaction is fast) and there are no crystallisation effects to take into account. The main factor which will cause changes in the current passing through the battery is the positive plate, and this will be due to possible nucleation and growth effects. The "coup de fouet" is normally observed on the charge behaviour of a very considerably discharged battery particularly when the plates are lead calcium based alloys rather than lead antimony based alloys. A relatively new 12V 40 A - hr battery was investigated using a constant potential charger to recharge from the
fully discharge condition. Figure 10.1 shows the current response to a charge. A distinct "coup de fouet" is observed immediately the fall from the double layer charging peak os obtained. The current then falls away in the expected manner.

Following a deep discharge, batteries with lead calcium based alloy plates are particularly difficult to recharge under normal operating conditions, recharging in some cases proving impossible in a potentiostatic mode. It has been shown in Chapter 8 that the depth of discharge prior to the appearance of a rising transient is a measure of the rechargability. Thus a "coup de fouet" in the charge cycle is undesirable, its presence showing that during the discharge growth centres have been annihilated up to the point when there are insufficient to support the growth and development of new lead dioxide. It has been shown that by the application of the kinetic equations for the current-time curve assuming instantaneous nucleation and two dimensional growth that a typical "coup de fouet" fits exactly the expected curve confirming that current limitation is due to lack of growth centres.
Fig 10.1 Typical “COUP DE FOUET” observed in a constant potential recharge of a 12V 40Ah lead acid battery
10.2. The penetration depth

The kinetics of the discharge of lead dioxide are now well understood. The discharge of porous lead dioxide electrodes has been discussed in terms of the Frumkin penetration depth in Chapter 7.

The shape of the potentiodynamic reduction curve has been considered as a measure of imminent electrode failure in Chapter 9. The "tail" characteristic of the porous electrode is due to current from the inner areas of the electrode. Disappearance of this tail indicates the passivation of these inner regions. This change of shape is particularly interesting in terms of the effect of the grid alloy on battery performance. One of the observed beneficial effects of antimony in the grid is the conservation of the tail over an extensive cycle life. In comparison lead calcium based alloys lose the "tail" after only a few cycles. This indicates that lead calcium based alloys have a greater tendency for passivation of the inner regions, which effectively insulates the active material with a blocking layer of lead sulphate. The resulting removal of centres for the growth of new lead dioxide leads to the "coup de fouet" discussed previously. In practical terms more care must be taken with the lead calcium based alloy grid battery than the lead antimony based alloy grid battery during discharge as deep discharges have a far more destructive effect on the former than the latter.
10.3. The self-discharge reaction

It is well known that the immediate electrochemical history of the battery affects subsequent behaviour. Allowing a battery "rest periods" (amounts of time on open circuit) during the charging cycle gives an enhanced output capacity. This is due to the self discharge reaction.

\[
Pb + PbSO_4 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O \quad (10.1)
\]

that occurs at the grid-active material interphase. This reaction has been discussed at length in Chapter 8. Since morphological studies have shown the resulting material to be extremely porous, when the cell is fully charged this layer of lead dioxide will contribute significantly to the output.

The form of the current-time response for the oxidation of porous lead sulphate has been thoroughly examined on an electrode simplified to be effectively one dimensional in Chapter 8. It was shown that of the three rising and falling outputs the porous material produced by the self discharge reaction was responsible for the first, that is the reaction that reaches the current maximum in the shortest time. Thus the nature of the material produced in the grid-active material has an important effect on the initial charge behaviour. It is evident from previous discussion that the porous material produced from the antimonial alloy would be easier to recharge than that from lead calcium alloys. Indeed it is possible that the rising transient (the "coup de fouet") often observed with lead calcium alloys is largely due to the reaction occurring in this self-corrosion layer.
10.4. Electrode utilisation

The reaction at the positive plate of a lead-acid cell may be written

\[ \text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{2-} + 2e^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O} \] (10.2)

Practically the reaction of equation (10.2) implies that every gram of lead dioxide should yield 0.224 of A-hr electricity. Actually only 25-50% of this is normally available. The improvement of this efficiency is an aim of many studies of the system. The Frumkin penetration depth model has been discussed and is essentially correct for the discharge of a porous lead dioxide electrode. Electrodes much thicker than the penetration depth are not fully utilised.

It has been shown in Chapter 7 that for the discharge the charge output increases as the rate of discharge of the electrode is decreased. This decrease of discharge rate increases the "available area" of the electrode due to the reaction being able to penetrate further into the porous matrix.

Unfortunately many other factors must be considered when attempting a battery optimisation. For example, although it may be desirable to reduce the thickness of the porous layer to obtain a more satisfactory porous material utilisation, the resulting size of the new plate in order to obtain the same amount of electricity may be prohibitive. A certain amount of work has been done on grid design and the size of the basic pellet which is continuing.
10.5. The limitations of porous electrode theory

The most comprehensive treatment of the porous lead dioxide electrode presented thus far is that of Simonsson\textsuperscript{13}. He proposed a theoretical model on the basis of the macrohomogeneous model for porous electrodes in which the structural changes during discharge due to the precipitation of lead sulphate were considered. The two main structural effects, plugging of the pores and gradual insulation of the active electrode surface by the reaction product lead sulphate were both considered by relating them to the local degree of discharge. At high current densities it was shown that the discharge capacity is limited by both structural and transport restrictions. At the end of discharge a layer of lead sulphate blocked the electrode surface in the outer layers of the electrode. The current could then neither be transferred across this insulated surface nor reach remaining active material in the inner parts of the electrode because of acid depletion, which is furthermore accelerated by the decreasing porosity.

This theoretical model presented by Simonsson\textsuperscript{13} rested upon rough approximations concerning the rather complicated discharge behaviour of the porous lead dioxide electrode. As a result the model gave a qualitative analysis rather than exact detailed description. An exact treatment would require more knowledge about electrolytic data and about the details of the discharge mechanisms and the structural effects in the porous electrode.

The study of the electrochemical kinetics of the porous lead dioxide electrode involving potentiodynamic and potentiostatic techniques have been discussed in Chapters 7 and 8. The measurements
are relatively simple to make and interesting electrometric results have received confirmation from morphological studies.

Equipment has been developed\(^9\text{6}\) for the determination of the faradaic impedance of porous lead dioxide electrodes with accurate control in time and potential. It was shown that the results obtained could only be discussed qualitatively due to the complexity of the response and the lack of a detailed theory. The inductance observed at high frequency has been observed by many workers\(^8\text{5}, 8\text{8}, 9\text{7}, 9\text{8}\) but merely considered as a concomitant of the porous morphology. Darby\(^8\text{7}\) has shown that inductive reactances arise naturally from mass transport and electrochemical reaction which can occur simultaneously over a distributed region of the electrode. Darby\(^8\text{7}\) however neglected the double layer capacity and ohmic resistance effects, both of which are important in the present context.

Electrocryrstallisation has been shown in Chapter 8 to play an important part in the behaviour of the porous lead dioxide electrode. Equations have been proposed\(^8\text{9}-9\text{2}\) for the faradaic impedance including the effects of electrocryrstallisation. Application of these equations to experimental systems, even solid electrodes, has not yet been made, due to the complexity of the problem of matching the experimental data to a model containing a relatively large number of kinetic terms. Porosity complicates the picture still further.

A further complication is the effect of diffusion within the pore, important at low frequencies.
It is considered that a more accurate model of the porous lead dioxide electrode must be found before any serious quantitative interpretation of the above data can be attempted. The porous lead dioxide electrodes described in this thesis are much simplified from the commercial battery positive plate yet the situation remains complex.
10.6. Further Work

The practical importance of the lead acid cell and the ever increasing need for isolated power supplies ensures that the porous lead dioxide electrode will continue to receive intensive study. The following are topics highlighted by the present work where further research may prove profitable.

1. A more thorough investigation of the frequency response of the porous lead dioxide electrode to alternating current should prove interesting, more intensive study at the high frequency end should yield more information about the inductive reactance. Stricter definition of the experimental conditions may yield a response that can be analysed quantitatively.

2. A further more exhaustive study of the influence of the solid-porous material interphase on the behaviour of porous lead dioxide electrodes may yield information on the nature of the bond between the porous material paste and the grid alloy. Possible enhancing agents e.g. bismuth, should be thoroughly studied to discover the extent of both beneficial and detrimental effects.

3. The effect of varying the size of the grid pellet of the positive plate should be studied with respect to the charge output. A more efficient grid design may be obtained.

4. The effect of the cycle history on the electrode behaviour is still not fully understood. Further investigation should be made into this aspect.
A mathematical model for the porous lead dioxide electrode

1. The model.

The mathematical model presented below is based upon a porous lead dioxide electrode, in which the accessible pores are completely filled with the electrolyte, a solution of sulphuric acid.

The porous body is regarded as macrohomogeneous. When the electrode is discharged, a cathodic current will cross the matrix-electrolyte interface through the electrode reaction:

\[
PbO_2 + 4H^+ + SO_4^{2-} + 2e \rightleftharpoons PbSO_4 + 2H_2O \tag{1}
\]

This stoichiometric reaction formula indicates two major changes during discharge. The sulphuric acid in the pores is consumed, whereby an acid concentration gradient is established. Simultaneously lead sulphate will precipitate on the shrinking lead dioxide matrix giving to a decrease in porosity due to the lower density of lead sulphate, compared to lead dioxide.

In order to facilitate analysis a number of simplifying assumptions are introduced.

a. When the discharge is not too deep, the conductivity of the lead dioxide matrix is much higher than the pore electrolyte. This also means that the electrode can be regarded as one-dimensional.
b. The time constant of the charging of the electrical double layer is small compared to the discharge time.

c. The transport processes in the electrolytic solution can be adequately described by the equations of dilute solution theory.

d. Electrolyte flow in the pores is due only to the decreasing porosity.

e. Bivalent lead ions are transported only over very short distances with respect to the electrode thickness before they precipitate with sulphate ions to form lead sulphate.

f. At the outer surface of the electrode the concentration of sulphuric acid is equal to its value in the bulk of the electrolyte.

g. The system is isothermal.

h. The sulphuric acid can be regarded as a binary electrolyte, completely dissociated into $\text{H}^+$ and $\text{HSO}_4^-$ ions only.

The last assumption is justified by the fact that a concentration of $5\text{M}$ sulphuric acid dissociates by about $85\%$ into $\text{HSO}_4^-$ ions and by $5\%$ into $\text{SO}_4^{2-}$ ions, whilst about $10\%$ of the molecules remain undissociated.

2. Development of the basic equations.

The basic transport equations for the one-dimensional, porous lead dioxide electrode can now be derived by application of porous electrode theory.

The $\text{H}^+$ ions are denoted by the index 1 and the $\text{HSO}_4^-$ ions by the index 2.
The fluxes of $H^+$ and $\text{HSO}_4^-$ ions may be expressed as a sum of three terms describing diffusion, migration and convection respectively.

$$N_i = -D_i \frac{\partial c_i}{\partial x} - c_i l_i \frac{z_i}{l_i} \frac{\partial \varphi}{\partial x} + c_i v \quad (i = 1, 2) \quad (ii)$$

where

- $N_i = \text{flux of species } i \ (\text{kmole m}^{-2}\text{s}^{-1})$
- $D_i = \text{effective diffusion coefficient of species } i \ (m^2\text{s}^{-1})$
- $c_i = \text{concentration of species } i \ (\text{kmole m}^{-3} \text{ of electrolyte})$
- $l_i = \text{ionic mobility of species } i \ (m^2\text{s}^{-1}\text{v}^{-1})$
- $z_i = \text{charge of species } i$
- $2 = \text{potential of pore electrolyte (V)}$
- $v = \text{electrolyte velocity (ms}^{-1})$

From the condition of electroneutrality it follows that,

$$C_1 = C_2 = C \quad (iii)$$

where $C = \text{concentration of sulphuric acid (kmole m}^{-3})$

The current density in the electrolyte, $i_2$, is determined by the flux of ions:

$$i_2 = F \sum z_i N_i = F(N_1 - N_2) \quad (iv)$$

where

$$i_2 = (Am^{-2})$$

$F = \text{Faraday's constant, } 96.5 \times 10^6 \text{ As (kg equiv)}^{-1}$. With the use of equations (ii) and (iii); equation (iv) can be transformed into

$$i_2 = -K \frac{\partial \varphi_2}{\partial x} - F(D_1 - D_2) \frac{\partial c}{\partial x} \quad (v)$$
where

\[ K = F \sum_i z_i \frac{c_{i1}}{l_i} \]

\( l_i \) the effective conductivity of the pore electrolyte \((\Omega^{-1} \cdot m^{-1})\)

The electrode potential is defined as \( E = \phi_1 - \phi_2 \) \((\phi_1 = \) potential of matrix phase \((V))\). Since the matrix phase can be regarded as equipotential

\[
\left[ \frac{\partial \phi_1}{\partial x} = 0 \right]
\]

\[
\frac{\partial \phi_2}{\partial x} = -\frac{\partial E}{\partial x}
\]  

Equations (v) and (vi) lead to the final expression for the current density in the pore electrolyte.

\[
i_2 = K \frac{\partial E}{\partial x} - F(D_1 - D_2) \frac{\partial c}{\partial x}
\]  

(vii)

The local concentration change may be expressed in a differential material balance for species 1:

\[
\frac{\partial (Ec_{11})}{\partial t} = -\frac{\partial N_{11}}{\partial x} + R_1
\]  

(viii)

where

\( E \) = porosity

\( t = \) time(s)

\( R_1 = \) source term for species 1 (kmol m^{-3}s^{-1})
A suitable expression for $N_1$ can be obtained from equation (ii) after elimination of $c_1$ and $\phi_2$ by application of equations (iii) and (v) respectively. Together with the Nernst-Einstein relation:

$$D_1 = \frac{RT}{|z_i|F l_i}$$  \hfill (ix)

where

$R = $ universal gas constant, joule (k mole deg)$^{-1}$

$T = $ temperature, °K

this leads to

$$N_1 = \frac{t_1}{F} - D \frac{\partial c}{\partial x} + cv$$  \hfill (x)

where

$$t_1 = \frac{c_1 |z_1| l_i}{c_i |z_i| l_i}$$

the transference number of the hydrogen ion and

$$D = \frac{2D_1 D_2}{D_1 + D_2}$$

the binary diffusion coefficient (m$^2$s$^{-1}$).

In accordance with the bisulphate electrolyte model, the stoichiometry of the electrode reaction (i) may now be described in the equivalent form:

$$\text{PbO}_2 + 3\text{H}^+ + \text{HSO}_4^- + 2e = \text{PbSO}_4 + 2\text{H}_2\text{O}$$  \hfill (xi)
From this stoichiometric formula it follows that the source term in equation (viii) can be related to the local discharge rate per unit volume, \( \frac{\partial i_2}{\partial x} \) according to Faraday's law:

\[
R_1 = \frac{3}{2F} \frac{\partial i_2}{\partial x}
\]

(xii)

The transference number of the \( H^+ \) ion, \( t_1 \), is fairly constant in the concentration interval which is of interest, and equations (iii), (x) and (xii) may thus be inserted into equation (viii) to give

\[
\frac{\partial (E_c)}{\partial t} = \frac{3 - 2t_1}{2F} \frac{\partial i_2}{\partial x} + \frac{\partial}{\partial x} (D \frac{\partial c}{\partial x}) - \frac{\partial}{\partial x} (cv)
\]

(xiii)

3. The kinetics of the electrode reaction

It has been reported\(^{13}\) that in the region -30 to -100mV, the current overvoltage relation for the electrode reaction in 5M \( \text{H}_2\text{SO}_4 \) can be expressed by a Tafel equation in which the prelogarithmic coefficient has a value of about 30mV per decade. When these experiments were repeated for successively lower concentrations down to 1.0M it was found that, within the experimental limits of error, the same relation holds for the whole concentration range of interest, 1-5M \( \text{H}_2\text{SO}_4 \).

The overvoltage, \( V \), is here defined as the difference between the maximum, rather constant electrode potential, \( E \), obtained after the initial drop of voltage at the beginning of discharge and the equilibrium, open circuit potential at the actual concentration, \( E_c(V) \).
In this specific case, it is thus possible, as an approximation, to express the local electrode potential as the sum of two additive terms

\[ E = E_c + \eta \]  

(xiv)

where \( \eta \) is independent of the concentration of sulphuric acid. The potential gradient \( \partial E/\partial x \) appearing in equation (vii) may consequently be written

\[ \frac{\partial E}{\partial x} = \frac{\partial E_c}{\partial c} \frac{\partial c}{\partial x} + \frac{\partial \eta}{\partial x} \]  

(xv)

The kinetic expression for the reaction rate per unit volume is then, approximately

\[ \frac{\partial i}{\partial x} = -Sj_0 \exp\left(-\frac{2F\eta}{RT}\right) \]  

(xvi)

where

- \( S \) = specific active surface (m\(^{-1}\))
- \( j_0 \) = exchange current density (Am\(^{-2}\))

4. Consideration of the structural effects.

The effective transport coefficients in equations (vii) and (xiii) will decrease during the discharge process, which leads to a continuous plugging of the pores, since lead dioxide is converted into lead sulphate with a larger molar volume. In addition the free active surface, available to the charge transfer process, \( S \), which appears in equation (xvi), depends on the fraction of the surface not yet
covered by insulating lead sulphate crystals. It is thus necessary
to introduce equations describing the structural changes in the
electrode. A simple way to do this is to relate these structural
changes to the local degree of discharge, $X$, which may be defined
as proportional to the amount of charge which has been consumed to the
actual time, $t$:

$$X = - \frac{1}{\frac{q_o}{\sigma_0}} \int_0^t \frac{\partial i}{\partial x} \, dt$$  \hspace{1cm} (xvii)$$

where

$q_o = \text{initially available quantity of charge per unit volume (As m}^{-3})$.

A relation between the local porosity, $\varepsilon$, and the local degree
of discharge, $X$, can now be easily derived:

$$\varepsilon = \varepsilon_o - k(1 - \varepsilon_o)X$$  \hspace{1cm} (xviii)$$

where

$\varepsilon_o = \text{initial porosity, prior to any discharge, } k = 0.917, \text{ a constant}
determined by the difference in specific volume between lead dioxide
and lead sulphate.$

The simplest way to take into account how the structural changes
affect the transport coefficients is to assume that they vary in
proportion to the porosity. Thus, as an example, the diffusion
coefficient, $D$, can be expressed as

$$D = \frac{\varepsilon}{\varepsilon_o} D_c$$  \hspace{1cm} (xix)$$

where the index $C$ denotes pure concentration dependance.
In the absence of detailed knowledge, the free active surface is assumed to be linearly related to the quantity $X$.

$$S = S_o \left( 1 - \frac{X}{X_{\text{max}}} \right)$$  \hspace{1cm} (xx)

$S_o \, (\text{m}^{-1})$ is the initially available active surface in the fully charged electrode, while $X_{\text{max}}$ is the maximum fraction of the electrode material which can be utilized at the actual current density. It may be expected from previous results$^{13}$ that this quantity depends on the applied current density. This seems reasonable also in view of the decreasing capacity of flat lead dioxide electrodes with increasing current density.

The convective term in equation (xiii) will, for simplicity, be related only to the decreasing porosity during discharge, which leads to a net flow of electrolyte out of the volume element.

Thus, neglecting the density changes:

$$\frac{\partial E}{\partial x} = - \frac{\partial E}{\partial t}$$  \hspace{1cm} (xxi)

However, the rate of change of porosity is also proportional to the rate of conversion of lead dioxide to lead sulphate and to the difference in molar volume between products and reactants:

$$\frac{\partial E}{\partial t} = \frac{1}{2F} \frac{\partial i_2}{\partial x} (V_p - V_r)$$  \hspace{1cm} (xxii)

$V_p = \text{molar volume of lead sulphate, } 48.9 \times 10^{-3} \, \text{m}^3 \, \text{kmole}^{-1}$
$V_r = \text{molar volume of lead dioxide, } 25.5 \times 10^{-3} \, \text{m}^3 \, \text{kmole}^{-1}$
Thus, after elimination of \( \frac{\partial E}{\partial t} \) in equation (xxi)

\[
\frac{\partial v}{\partial x} = -\frac{1}{2F} \frac{\partial i_2}{\partial x} (v_p - v_r)
\]  

(xxiii)

Since at \( x = 0, v = i_2 = 0 \) (because of symmetry reasons) equation (xxiii) can easily be integrated:

\[
v = -\frac{i_2}{2F} (v_p - v_r)
\]  

(xxiv)

When the structural equations above together with equation (xv) are inserted into the basic equations (vii), (xiii) and (xvi), the following equations are obtained, which describe the dynamic behaviour of the electrode.

\[
i_2 = \frac{E}{E_0 K_c} \frac{\partial E}{\partial c} \frac{\partial c}{\partial x} + \frac{\partial \eta}{\partial x} - F \frac{E}{E_0} (D_1 - D_2) c \frac{\partial c}{\partial x} \]  

(xxv)

\[
\frac{\partial c}{\partial t} = \frac{3-2t_1}{2FE} \frac{\partial i_2}{\partial x} + \frac{1}{c} \frac{\partial}{\partial x} \left( \frac{E}{E_0} \frac{D_c}{\partial x} \right) + \frac{i_2}{2FE} (v_p - v_r) \frac{\partial c}{\partial x}
\]  

(xxvi)

\[
\frac{\partial i_2}{\partial x} = -S_0 j_0 \left[ 1 - \frac{X}{X_{max}} \right] \exp \left( -\frac{2F \eta}{RT} \right)
\]  

(xxvii)

where \( E \) is defined by equation (xviii) and \( X \) by equation (xvii)

The equations can be transformed into the more convenient dimensionless form through the following transformations:

\[
z = \frac{x}{L} = \frac{c}{c_o} ; \quad t = \frac{D_c t}{L^2}
\]
\[ \eta' = \frac{F(\eta - \eta_{x=0})}{RT} \quad ; \quad E' = \frac{FE_c}{RT} \quad ; \quad i = \frac{i_0}{I} \]

where

- \( L \) = the thickness of one symmetric half of the porous electrode (m)
- \( C_o \) = the initial concentration of sulphuric acid (k mole m\(^{-3}\))
- \( D_o \) = the diffusion coefficient at the initial conditions (m\(^2\)s\(^{-1}\))
- \( \eta_{x=0} \) = activation overvoltage at \( x = 0(V) \) (time dependant)

The equations representing the electrode model then become

\[ i = a \frac{E}{E_o} \frac{K_c}{K_o} \left[ \frac{\partial E'}{\partial c} \cdot \frac{\partial c}{\partial z} + \frac{\partial \eta}{\partial z} \right] - b \frac{E}{E_o} \frac{\partial c}{\partial z} \tag{xxviii} \]

\[ \frac{\partial c}{\partial t} = (3-2t) \frac{f}{\varepsilon} \frac{\partial i}{\partial z} + \frac{1}{\varepsilon} \frac{\partial}{\partial z} \left[ \frac{E}{E_o} \frac{D_c}{D_o} \frac{\partial c}{\partial z} \right] + \frac{f}{\varepsilon} c_o (V_p - V_r). \tag{xxix} \]

\[ \frac{\partial i}{\partial z} = g(1 - \frac{\chi}{\chi_{\text{max}}}) \exp(-2\eta') \tag{xxx} \]

\[ \chi = - \frac{IL}{D_o c_o} \int_0^\tau \frac{\partial i}{\partial z} \, d\tau \tag{xxxi} \]

where \( k_o \) is the initial conductivity and where the new dimensionless parameters have the following definitions:

\[ a = \frac{k_o \cdot RT}{ILF} \]

\[ b = \frac{F(D_1-D_2)c_o}{IL} \]
\[ f = \frac{IL}{2FD_o c_o} \]

\[ g = - \frac{S_o j_o L}{I} \exp \left(-\frac{2F \eta}{RT} \right) \]

Before any discharge of the electrode the acid concentration in the pores is uniform and equal to the concentration in the bulk. The electrode is assumed to be fully charged. Thus the initial conditions are:

at \( t = 0 \), \( c(X) = c_o \), or equivalently, \( C = 1 \).

\[ X(x) = 0 \]

Since mass transfer resistances exterior to the porous electrode are assumed to be negligible, the following boundary condition exists:

at \( z = 1 \), \( c = c_o \) or \( C = 1 \)

Also, at this surface the current density in the electrolyte must be the total current density applied.

At \( z = 1 \), \( i_2 = I \) or \( i = 1 \)

At the plane of symmetry of the electrode, symmetry conditions may be expressed as:

At \( z = 0 \) \[ \frac{\partial c}{\partial z} = \frac{\partial \eta'}{\partial z} = \frac{\partial E}{\partial z} = 0, \ i = 0 \]
Also, by the choice of reference voltage $\eta' = 0$ at $z = 0$.

The equations above represent a rather complicated non-linear problem of the boundary value type. Solution of these equations requires the application of suitable numerical methods.

5. Numerical procedure

The partial differential equation system was first solved by an implicit finite difference method and the quasi-linearisation technique.

Only equation (xxix) was linearised. It was decoupled from equations (xxviii) and (xxx) by solving for the concentration in the $(k + 1)$ iteration for other dependant variables. However, this application of the implicit method requires a very large number of arithmetic operations. For the most interesting case as regards transient behaviour, the high rate discharge, the explicit difference-method actually proved to be more advantageous in spite of its restrictive stability conditions. For very rapid discharges the larger number of time steps required with this method was more than compensated by the smaller number of arithmetic operations required at each time step. Therefore the explicit method was preferred in the calculations for very rapid discharges, while the implicit method was used only to check the results from the explicit method. The calculations were tested for convergence and stability by successively decreasing the length and time steps until the results did not change appreciably.
The current-voltage-time relationship in potentiostatic and sweep experiments.

It is assumed that passivation is brought about by the formation of a monolayer of lead sulphate. The current through the lead sulphate is due to high field ion conduction and is small compared with the current at the uncovered areas of the electrode. The current through the uncovered areas of the surface is charge-transfer controlled and follows the equation

\[ i = zFkA \exp(-\alpha zFE/RT) \]  \hspace{1cm} (i)

The area decreases with time according to the equation.

\[ -dA = iMdt/zF \rho \ h \]  \hspace{1cm} (ii)

For the potential step experiment we have

\[ -dA/A = (kM/\rho h) \exp(-\alpha zFE/RT)dt \]  \hspace{1cm} (iii)

whence

\[ -\ln(A/A_0) = \left[(kM/\rho h) \exp(-\alpha zFE/RT)\right]t \]  \hspace{1cm} (iv)

\[ -\ln(i/i_1) = \left[(kM/\rho h) \exp(-\alpha zFE/RT)\right]t \]  \hspace{1cm} (v)

For the linear sweep experiment we have

\[ E = E_i - \nu t \]  \hspace{1cm} (vi)

Equation (iii) becomes

\[ -dA/A = \left[(kM/\rho h) \exp(-\alpha zFE/RT)(E_i - \nu t)\right]dt \]  \hspace{1cm} (vii)
Equation (vii) gives on integration

\[-\ln \frac{A}{A_0} = \frac{kM}{\rho h} \cdot \frac{RT}{\alpha zFV} \left[ \exp - \frac{\alpha zFE_i}{RT} \right] \left[ \exp \frac{zFVt}{RT} - 1 \right] \] (viii)

Substitution in equation (i) gives

\[\ln i = \ln(zFk) + \ln A_0 - \frac{\alpha zFE}{RT} - \left( \frac{kM}{\rho h} \right) \left( \frac{RT}{\alpha zF} \right).\]

\[\exp \left[ (-\alpha zF/RT)E_i \right] \left[ \exp(zFVt/RT-1) \right] \] (ix)

According to equation (ix) \(i\) goes through a maximum \((E_p, i_p)\).

\(E_p\) is given by

\[E_p = -RT/\alpha zF \left[ \ln \left( \frac{\rho h/kM}{\alpha zF/RT} \right) + \ln V \right] \] (x)

and \(i_p\) is given by

\[\ln\left( \frac{i_p}{V} \right) = \ln \left[ \left( \frac{zF^2/\rho h}{kM} \right) A_0 \alpha \rho h \right] + \left( \frac{kM}{\rho h V} \right) \left( \frac{RT}{\alpha zF} \right) \exp \left( -\frac{\alpha zFE_i}{RT} - 1 \right) \] (xi)

The relation between \(i\) and \(E\) is given by

\[\ln \frac{i}{i_p} = -\frac{\alpha zF}{E-E_p} \cdot \frac{1}{RT} - \left( \exp \left[ -\frac{\alpha zF(E-E_p)}{RT} \right] - 1 \right) \] (xii)
APPENDIX III

The deconvolution of current response time transients

This technique was developed for the deconvolution of current response time transients from potentiostatic step experiments. The experimental technique was to sweep the potential of a "porous lead dioxide" 5M sulphuric acid electrode from 1250 mV to a lower limit of 700mV (lead sulphate region) and then step the potential back to a potential in the lead dioxide region. The resulting transient contained up to three peaks.

From work described in the previous chapters it was known that the transformation lead sulphate to lead dioxide corresponded either of two crystal growth processes. These were either an instantaneous two dimensional nucleation and growth or a progressive three dimensional nucleation and growth. Both these processes have been discussed in detail. The equations for these processes are

\[ i = \frac{\pi F M \rho}{\rho} N_0 k^2 t \exp \left( -\frac{\pi M^2 N_0 k^2 t^2}{\rho^2} \right) \]  \hspace{1cm} (i)

for the instantaneous case and

\[ i = \frac{\pi F M h}{\rho} A k^2 t^2 \exp \left( \frac{\pi M^2 A k^2 t^3}{3 \rho^2} \right) \]  \hspace{1cm} (ii)

for the progressive case.

The present procedure was to assume that the initial rise of the experimental current (current response) curve was determined solely by the first process i.e. that responsible for the first peak. This
is justified by the sharpness of the first maximum (Figure 8.1). The falling portion of the first curve (dotted curve (a) in Figure 8.2A) was calculated from this rising transient. In a similar manner by considering the final falling portion of the experimental response curve the initial rise of the third transient (c2 of Figure 8.2A) can be computed. The second component transient response can be obtained by simple subtraction.

An alternative approach can be made since it is possible to identify the maxima of the first and final transient.

Equations (i) and (ii) can be written

\[ i = \alpha_1 t \exp(-\beta_1 t^2) \quad \text{(iii)} \]

\[ i = \alpha_2 t^2 \exp(-\beta_2 t^3) \quad \text{(iv)} \]

These have single maxima given by \( \frac{di}{dt} = 0 \) \((i_m, t_m)\) from whence

\[ \alpha_1 = \frac{i_m}{t_m} e^{0.5} \quad \text{(v)} \]

\[ \beta_1 = \frac{1}{2t_m^2} \quad \text{(vi)} \]

\[ \alpha_2 = \frac{i_m}{t_m^2} e^{0.67} \quad \text{(vii)} \]

\[ \beta_2 = \frac{2}{3t_m^3} \quad \text{(viii)} \]
The mathematical technique employed for this approach was to calculate complete theoretical response curves for the first and third peak using the co-ordinates of the respective maxima (\(a\) and \(c_2\) respectively of Figure 8.2A). Subtraction of the sum of these from the actual response in order to isolate the second peak leads to two limiting cases for the second peak (\(b_1\) or \(b_2\)) due to the broadness of the third peak. Recalculation of the rising part of the final transient now gives an alternative (\(c_1\)) for (\(c_2\)).

In the computer program the co-ordinates of the maximum for the third peak were varied over the limits of uncertainty until the best self consistent fit was obtained as estimated from a reduced (\(i/i_m, t/t_m\)) plot.
INTEGER J, L;

A1 := (48/13) * EXP(0.5);
B1 := 1/338;
A := (71/240100) * EXP(1176490/1764735);
B := 1/176473500;

FOR J = 0 STEP 2 UNTIL 2000 DO
    BEGIN
        T = J;
        I1 := A1 * T * EXP(-B1 * T * T);
        I3 := A * T * T * EXP(-B * T * T3);
        NEWLINE(1);
        PRINT(T, 2, 3);
        SPACE(3);
        PRINT(I1, 3, 10);
        SPACE(3);
        PRINT(I3, 3, 10);
    END

END
REFERENCES


2. G.W. Vinal, Storage Batteries, Wiley, New York, 1965


4. C.K. Morehouse, R. Glicksman and G.S. Lozier,

5. J.P. Hoare, The Electrochemistry of Oxygen, Interscience,
New York, 1969, Ch. 7B.


19. M.A.V. Devanathan, J. O'M Bockris and K. Muller,


60. P. Ruetschi, J.Power Sources 2 (1977/78) 3.


71. W. S. Yantschenko and I. A. Selitsky, Electrotekhnika 37 (1966) 34.


79. I.A. Aguf, Elektrokhim. 4 (1968) 1130.


96. N.A. Hampson and M.J. Willars, Surface Technology - in press.
