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ELECTROCHEMISTRY OF THE POROUS LEAD ELECTRODE

by

John Barry Lakeman

Supervisor: Dr. N.A. Hampson

A Doctoral Thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University of Technology

June 1980

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The electrochemistry of lead and porous lead electrodes has been examined using the techniques of linear sweep voltammetry, potential step and alternating current impedance at static and rotating disc electrodes. Investigations were made using sulphuric acid solutions at ambient and low temperatures. The behaviour of porous electrodes containing additives conventionally used to improve lead-acid battery redox processes were studied. Complementary data has been obtained by Scanning Electron Microscopy and galvanostatic cycling experiments.

The solution reaction at the porous electrode of typical commercial thickness, controlled by factors affecting the diffusion layer in a direction away from the porous face, was found to be insignificant in comparison with reactions occurring within the porous matrix. The thickness of PbSO₄ films developed on the electrode is potential-dependent, with thicker films at lower potentials.

The development of PbSO₄ on the solid lead electrode is controlled by nucleation and growth processes. At low overpotentials the process is three-dimensional but becomes two-dimensional at higher overpotentials. The behaviour of the porous electrode can be interpreted in terms of well-established porous electrode theory, assuming the same crystallisation processes are observed in the case of solid electrodes.

On reduction at both solid and porous lead sulphate electrodes, the electrode process has a finite depth of penetration into the electrode. The kinetics of the formation of metallic lead from lead
sulphate on both types of electrodes appear to be by instantaneous nucleation and two-dimensional growth, with subsequent current limitations owing to overlap of growing lead and PbSO₄ depletion. The current limitation processes are complex; the subsequent current decay rate varies with the porosity of the electrode.

Ambient temperature investigations of the additives used in the commercial lead electrode demonstrated that lignosulphonate facilitated the nucleation of lead on recharge, and effected a progressive increase in surface area/porosity of the electrode. These effects promoted an increased utilisation of the electrode active material on discharge. BaSO₄ was found to provide nucleation centres for PbSO₄ formation. The low-temperature electrochemistry of solid and porous lead has been investigated and the effects of additives are discussed.
ACKNOWLEDGEMENTS

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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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<tr>
<td>$a$</td>
<td>area, electrode area</td>
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<td>$a_x$</td>
<td>activity of species $x$</td>
<td></td>
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<tr>
<td>$A$</td>
<td>nucleation rate constant</td>
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<td>$C$</td>
<td>concentration, concentration at pore mouth</td>
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<td>$C_0$</td>
<td>equilibrium concentration of $O$, concentration of $O$ in equation 2.25.</td>
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<td>equilibrium concentration of $O$ at $E^0$</td>
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<td>$E^0$</td>
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<td>$E_p$</td>
<td>potential of peak current in LSV</td>
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<td>$E_{r}, E_{rev}$</td>
<td>reversible potential</td>
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<td>$F$</td>
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<td>$G$</td>
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h thickness of layer, height of nucleus
H degree of coverage
H<sub>E</sub> degree of coverage in absence of overlap
H<sub>p</sub> degree of coverage at peak current in LSV
i current density, current entering pore
i<sub>0</sub> exchange current density
i<sub=m</sub>, i(t=0) current density after elimination of mass transport effects
i<sub>m</sub> maximum current in i-t transient
i<sub>p</sub> peak current in LSV
I galvanostatic discharge current
J<sub>O</sub> flux of O
k constant in equation 5.5.
k<sub>a</sub>, k<sub>c</sub> anodic and cathodic rate constants
k<sub>E</sub>, k<sub>1</sub>, k<sub>2</sub> electrocrystallisation rate constants
k<sup>0</sup> standard rate constant
k<sub>n</sub> frequency factor
K constant in Peukert equation
l pore length
M molecular weight
N number of nuclei contributing to growth of deposit
N<sub>0</sub> total number of available nucleation sites
O oxidised species
p reciprocal of penetration depth
P porosity
Q charge
Q<sub>A</sub> charge in anodic LSV sweep
Q<sub>C</sub> charge in cathodic LSV sweep
Q<sub>m</sub> charge in i-t transient
charge in rising part of transient

radius

gas constant, reduced species

ohmic resistance of solution

ohmic resistance of deposit

electrolyte resistance in pores of deposit at $E_p$ and $i_p$

surface free energy

time

time to galvanostatic discharge

time to current maximum in $i$-$t$ transient

temperature

$\text{LSV sweep rate, viscosity}$

flow velocity normal to the electrode

volume

frequency

Warburg impedance

distance, constant in Peukert equation

mean distance of the net ion excess from the electrode

diffusion layer thickness

hydrodynamic layer thickness

number of electrons transferred

solution (or electrode) resistance

charge transfer resistance

cell impedance

cathodic charge transfer coefficient

overpotential
\( \Theta \) charge transfer resistance

\( \kappa \) solution conductivity

\( \rho \) density

\( \sigma \) Warburg coefficient

\( \phi \) phase angle, dimensionless quantity in equation (1.6).
1.1. Thermodynamics

At the negative electrode of the lead-acid battery, the reaction is

\[
Pb + SO_4^{2-} \xrightleftharpoons{\text{Discharge}} \xleftarrow{\text{Charge}} PbSO_4 + 2e^- \quad (1.1)
\]

The \( E^0 \) for the reaction has been measured at -0.357V\(^{\text{(1,2)}} \). Results based on thermodynamic calculations range from -0.353 to -0.359V\(^{\text{(1,3,4)}} \).

\( E^0 \) for the reaction

\[
Pb^{2+} + 2e \xrightleftharpoons{} Pb \quad (1.2)
\]
is 0.126V from cell measurement\(^{\text{(5)}} \) and confirms thermal data\(^{\text{(4)}} \).

The solubility of \( PbSO_4 \) in sulphuric acid is shown in Figure 1.1. Craig and Vinal\(^{\text{(6)}} \) suggest that the initial fall in solubility is caused by the common ion effect and depression of the \( Pb^{2+} \) ion concentration according to the solubility relation

\[
K_s = a_{Pb^{2+}} a_{SO_4^{2-}} \quad (1.3)
\]

The rise in solubility is attributed to possible complexes such as \( PbSO_4 \) and \( Pb(HSO_4)^+ \). The effect of temperature on the solubility of \( PbSO_4 \) is also illustrated in Figure 1.1, and temperature also has a significance for electrolyte conductivity (see Figure 1.2) and the \( H_2O/H_2SO_4 \) system (see Figure 1.3); both these factors have significance.
Figure 1.1. Solubility of PbSO₄ in H₂SO₄ at 25°C and 0°C as a function of acid concentration (mass fractions: 5M 0.385, 1M 0.093).
Figure 1.2. Specific conductivity of $\text{H}_2\text{SO}_4$ as a function of mass fraction at different temperatures; dotted line denotes the maximum of conductivity\(^{(35)}\). (mass fractions: 5M 38.5%, 1M 9.3%)
Figure 1.3. Relevant part of the phase diagram of the $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ system (6).
Figure 1.4. Potential-pH diagram of the Pb/H_2SO_4 system in the presence of sulphate ions of unit activity (7)
for the performance of the lead-acid battery.

Figure 1.4. shows the potential-pH diagram for lead in the presence of sulphate ions of unit activity\(^{(7)}\). The equilibria between solid phases are represented by solid lines, whereas those between the soluble lead species are given by broken lines. Diagrams of different sulphate activities\(^{(8)}\) have the same pattern, but the area of stability for the various phases are shifted with respect to the axes. The high stability of lead in sulphuric acid is due to the high hydrogen overvoltage\(^{(9)}\) and passivation\(^{(10, 11)}\).

In the normal operating regime of the negative electrode of the lead-acid cell, equation 1.1. shows that the reactions of interest are the oxidation of lead to lead sulphate (discharge), and the reduction of lead sulphate to lead (charge). The oxidation of \(\text{Pb}\) to \(\text{PbSO}_4\) in \(\text{H}_2\text{SO}_4\) can occur by two processes; a reversible solution-precipitation mechanism, and solid state nucleation and growth. The evidence for these processes at the planar lead electrode in deoxygenated \(\text{H}_2\text{SO}_4\) will be discussed.

1.2. The Solution Region

1.2.1. Linear sweep voltammetry

Linear sweep voltammetry (LSV) studies on solid \(\text{Pb}\) in \(1\text{M H}_2\text{SO}_4\) have demonstrated a reduction peak, following an anodic current, which disappeared on electrode rotation\(^{(12)}\). This demonstrated the formation of a solution species during the anodic process at low anodic potentials. As the anodic limit of the sweep was increased, and the sweep rate decreased, the reduction peak became rotation-speed-independent.
indicating the reduction of solid PbSO₄ at the electrode surface. Similar measurements on concentrated Pb(Hg) confirmed these observations (13) and showed that as the production of solid PbSO₄ increased, the amount of soluble Pb species decreased. This demonstrated that Pb dissolved between the PbSO₄ crystals and not through them. The dissolution reaction was found to have the characteristics of a reversible 2e process (14). These results have been confirmed by other workers (15) on solid Pb in 0.5 M H₂SO₄.

1.2.2. Potential step studies
Archdale and Harrison (12) investigated the transient response to potential steps of low anodic overpotentials. The pulses were found to be diffusion controlled, and the oxidation could be considered as a reversible 2e electrochemical process.

1.2.3. Rotating ring-disc
Current-time transients recorded at a polished ring-disc electrode in 1M H₂SO₄ demonstrated the existence of solution-soluble Pb species (16). When the disc current rose owing to solid PbSO₄ formation, the ring current fell as less soluble species were formed. Similar observations have been made using a galvanostatically discharging Pb rotating-disc-electrode, with a ring under potentiostatic control (17). The collection efficiency was found to decrease with increasing acid concentration, and decreasing temperature, indicating that solid state formation of PbSO₄ predominated as the acid concentration increased, and the temperature decreased.
1.2.4. Rotating disc

Using LSV at slow sweep rates at a rotating disc, Fleming and Harrison\(^\text{(16)}\) concluded that the dissolution reaction could be studied separately from solid state PbSO\(_4\) formation, provided the anodic excursion was not greater than \(-940\) mV in 1M H\(_2\)SO\(_4\). Tafel slopes of \(\sim 30\) mV were observed, which represented a reversible 2e process. The curves were found to depend on H\(_2\)SO\(_4\) concentration, suggesting that a complex species such as PbSO\(_4\) or PbHSO\(_4\)\(^+\), or even small particles of PbSO\(_4\), was diffusing away from the electrode. Rotation-speed-dependence studies on anodic pulses into the dissolution region showed current intercepts at infinite rotation speed, indicating that the dissolution process was not totally reversible\(^\text{(18)}\).

1.2.5. a.c. impedance

Lazarov et al\(^\text{(19)}\) studied the dependence of capacitance and resistance on potential. The capacitance increased as the potential was made more anodic, reached a peak which they concluded to be Pb\(^{2+}\) ions passing into solution, and then fell as a passive PbSO\(_4\) film was formed. The dissolution process has also been confirmed by other Russian workers\(^\text{(20-21)}\).

At potentials in the active dissolution region in 0.1M H\(_2\)SO\(_4\), Armstrong and Bladen\(^\text{(23)}\) obtained complex impedance plane plots which showed straight lines of unity slope. Only slight evidence of a charge transfer semicircle was observed at high frequency, and it was concluded that the dissolution process is both fast and reversible. In contrast, other workers\(^\text{(18,24,25)}\) showed evidence for high frequency semicircles on
Figure 1.5. Schematic diagram of the composition of the film formed on anodic oxidation of Pb in H₂SO₄ with potential (26)

H₂O₂ + 2H⁺ + 2e = 2H₂O
2H₂O₂ + PbO₂ + PbO₂ + 2H₂O + O₂

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

\[ \text{PbO}_2 \text{, stable above this potential, unstable below this potential} \]

\[ \text{O}_3 + 6e + 6 \text{H}^+ = 3 \text{H}_2 \text{O} \]

\[ \text{PbO}_2 + 2 \text{H}^+ + 2e = \text{PbO}_1 + \text{H}_2 \text{O} \]

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

\[ 20 + 4e + 4 \text{H}^+ = 2 \text{H}_2 \text{O} \]

\[ \text{SO}_4^{2-} + \text{PbO}_1 + 2 \text{H}^+ + 2e = \text{Pb} + \text{H}_2 \text{O} \]

\[ \text{Pb} + 10 \text{OH}^- + 2e = 2 \text{H}_2 \text{O} + \text{Pb} \cdot 2 \text{H}_2 \text{O} \]

\[ \text{PbO}_1 \cdot \text{PbSO}_4 \cdot 2 \text{H}^+ + 4e = 2 \text{Pb} + \text{H}_2 \text{O} + \text{SO}_4^{2-} \]

\[ 2 \text{H}^+ + 2e = \text{H}_2 \]

\[ \text{PbSO}_4 + \text{H}^+ + 2e = \text{Pb} + \text{HSO}_4^- \]
solid lead and Pb(Hg), indicating a charge transfer resistance, and a Warburg impedance, in parallel with a capacity. It was suggested (18) that a precipitation mechanism to form PbSO₄ occurred under some conditions prior to the solid state reaction.

1.3. The Solid Phase Region

At anodic potentials above a critical value, the solid-state nucleation and growth of PbSO₄ occurs. Fleming and Harrison (18) concluded that progressive nucleation probably occurred at structural defects in the substrate, and that nucleation could occur in the charging spike of potential step experiments. Fletcher and Matthews (15) used the potential step technique to show that solid-state formation of PbSO₄ occurred by progressive nucleation and 3-D growth in 0.5M H₂SO₄. The rate of crystallisation was found to be controlled by a "shape-preservation" model and not mass transfer in the electrolyte.

The composition of the film formed, on anodic oxidation of Pb, depends on potential (26), as shown in Figure 1.5. A laminar structure results because of free energy gradients in the film, so that different compounds that are stable in contact with the solution may be different from those that are in contact with the metal. It is thought that the PbSO₄ film is permeable to H⁺ and H₂O, but not to SO₄²⁻ (27-30). As the potential for film formation is increased, the number of nucleation centres increases, and the thickness of the film decreases (28).

1.4. The Effect of Oxygen

The presence of oxygen has a marked effect on the kinetics of Pb dissolution in H₂SO₄ (16). Armstrong and Bladen (23) found that diffusion-
controlled oxygen reduction occurred over a wide potential range, but was inhibited in the lead dissolution region by anion adsorption.

1.5. The Reduction of PbSO₄

The study of PbSO₄ reduction to Pb(charge) has received little attention. Brennan and Hampson (31) assumed that Pb electrocrystallisation occurred by an instantaneous nucleation and 2-D growth at a planar electrode. Fleming and Harrison (18) thought this unlikely as the i-t transient to a potential step had a long tail. These authors suggested that lead electrocrystallisation at a sulphated Pb electrode probably occurred by a progressive nucleation and 3-D growth process. Fletcher and Matthews (15) suggested that the reduction reaction was not a solid-state process, but PbSO₄ crystals dissolved at the Pb/PbSO₄/H₂SO₄ interface, and the Pb²⁺ ions diffused slowly to the electrode surface. Evidence for this mechanism was provided by Scanning Electron Microscopy (SEM), where Pb dendrites were observed as a result of the discharge of Pb²⁺ ions proceeding through localised diffusion zones.

1.6. The Electrochemistry of the Porous Lead Electrode

In 1971, Burbank et al (32) reviewed some aspects of research into the electrochemistry of the lead-acid battery. In 1977, Ruetschi (33) discussed the history, development and science of the system, and this was followed in 1979 (34) by a critical analysis of the future role of the cell in the context of other systems under development. An account of the technological aspects of the battery was published in 1977 (35), which complemented Vinal's classic, 'Storage Batteries' (36).
In the lead-acid battery, electrical energy is produced from the reaction:

$$\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O} \quad (1.4)$$

The reaction occurs at porous active masses supported on lead alloy grids; the grids act as current collectors and the cell contains sulphuric acid in excess of the requirements of reaction (1.4). The positive and negative electrodes are normally separated by microporous sheets which prevent short-circuiting, and shedding of active material from the electrodes.

The equation for the negative electrode is given by equation (1.1).

The charge/discharge cycle at the negative electrode involves a considerable redistribution of the active material during the dissolution, nucleation and growth of the solid phases. In the electrolyte, uncharged species may be transported by diffusion and convection, whereas ions can also move by migration in an electric field. The occurrence of one or all of these modes of transport depends on electrode properties such as geometry, porosity, conductivities of the solid and liquid phases, and the current/voltage characteristics of the electron transfer reaction. Modelling of the negative electrode is further complicated owing to the change in electrode volume that occurs on cycling; the lower density of $\text{PbSO}_4$ effects a decrease of cell porosity on discharge.

Because of the highly complex behaviour of the negative electrode, attempts to improve battery performance have taken a rather empirical
approach, which has proved costly and time-consuming. With so many factors interacting to determine the overall electrode behaviour, a highly detailed knowledge of the electrode is required to achieve an optimum combination of all the possible variables. Steps have been taken to achieve this through the developments of theories explaining the behaviour of porous electrodes.

1.6.1. Porous Electrode Theory

Industrial electrodes are normally porous because it is necessary to carry out electrode reactions at significantly high current densities. The specific surface area of porous lead electrodes has been determined as $0.3 - 0.46 \text{ m}^2 \text{ g}^{-1}$\(^{(37,38)}\) although the effective surface area is quoted as $0.04 - 0.05 \text{ m}^2 \text{ g}^{-1}$\(^{(39,40)}\). Because of the large surface area of the porous electrode, the driving force for the reaction, the overvoltage, is smaller. However, the current distribution in the practical porous electrode is non-uniform because of the mass-transfer and ohmic hindrances. The capacity/performance of the porous lead electrode is determined by the following factors\(^{(41)}\):

(a) the amount of active material in the electrode  
(b) the thickness of the electrode  
(c) the rate of discharge  
(d) the temperature  
(e) the quantity and concentration of the electrolyte  
(f) the porosity  
(g) the design of the electrode  
(h) the previous history of the electrode
The task of modelling the electrode to account realistically for all these factors is daunting, and porous electrode theory has to be developed in concert with experimental observations. The porous electrode model is at best a simplified mathematical expression for the transport and kinetic phenomena occurring at the electrode. Various assumptions have to be made, and each one involves its own limitations. The goal of porous electrode modelling is the provision of design criteria for the perfectly optimised electrode. The model has to be based on analyses of actual elementary processes occurring within the electrode matrix, such as transport and charge transfer kinetics. Theoretical aspects of electrode modelling have evolved considerably, from the simple picture of Daniel-Bek (42), using invariant reaction kinetics and fixed geometry, to the comprehensive models of today.

Work on mathematical modelling has been well reviewed by a number of authors (43-46). The majority of models use a one-dimensional representation, where the pore geometry is ignored. This approach is valid when the distances over which there is significant variation in concentration and potential are large compared with the characteristic dimensions of the pore system. The models of flooded porous electrodes may be divided into three categories (41): (a) The pore model: represented by parallel cylindrical pores of constant radius, perpendicular to the outer surface (47). (b) The analogue model: makes use of equivalent circuits, with the resistance of carrier materials and electrolytes in conjunction with polarisation resistance (48,49). (c) The macrohomogeneous model: views the electrode on a macroscopic scale and disregards the geometric detail of its structure. The whole electrode-electrolyte system is described as the superposition of
two continua: the electrode matrix, and the electrolyte which fills the voids within the matrix. Variables in the two phases, such as potential and current are regarded as continuous functions of time and space\(^{(50)}\). There are certain drawbacks to models (a) and (b). The pore model is difficult to apply to electrodes which must be considered as two-dimensional, because questions would arise concerning the direction of the pores. In the case of the analogue model, non-linear resistances must be used when the over-voltage does not vary linearly with the current density, and the influence of diffusion cannot be satisfactorily modelled.

These difficulties are eliminated in the case of the macrohomogeneous model, where variables such as matrix and electrolyte conductivities, physical structure and electrolyte conductivity, can be averaged into continuously varying functions in time and space. The model is, therefore, based on equations describing mass transfer, ionic and electronic currents, electrode kinetics, conservation equations for each dissolved species, and, more recently, structural changes of the electrode occurring during cycling. However, the pore model uses equations which are essentially identical\(^{(43)}\), yielding complementary results in some cases, and will be discussed in more detail.

1.6.1.1. The Pore Model

Work on the pore model up to 1966 has been well reviewed by de Levie\(^{(43)}\) and it is sufficient here to report some of the conclusions. The porous electrode is considered as a single pore of uniform cross-section, homogeneously filled with electrolyte, with a negligible matrix resistance. The curvature of the pore is considered
unimportant, and the pore is represented by an RC transmission line. Assuming mass transport is not rate-limiting, but the electrode is reaction-controlled, then the pore behaves like a resistance where

\[ \frac{h}{l} = \left(\frac{Z}{Z'}\right)^{\frac{1}{2}} \cotanh \left( \frac{p}{1} \right) \]

hence, the current in the porous electrode is inversely proportional to \((ZZ')^{\frac{1}{2}}\), and \(p = \left( \frac{Z}{Z'} \right)^{\frac{1}{2}}\). In contrast, the current at a flat electrode is inversely proportional to \(Z'\).

Austin\(^{(51)}\) also considered the case where the porous electrode might be controlled by solution resistance and/or diffusion. Considering a redox system with soluble reactants at inert electrodes, a dimensionless quantity was derived

\[ \phi = \frac{2F^2CD}{MRT} \]  (1.6)

Austin\(^{(51)}\) concluded that if \(\phi > 5\), electrode processes are resistance-controlled; if \(\phi < 0.5\), electrode processes are diffusion-controlled. Using equation (1.6) Bode\(^{(35)}\) calculated a value of \(\phi = 0.7\) for a charged lead-acid battery. This value decreases with discharge and indicates that the performance of the lead-acid battery may be influenced by the diffusion of acid in the porous matrix.

Another important concept to arise from porous electrode theory is the penetration depth, \(\frac{1}{p}\), which characterises the distance to which a reaction can penetrate a porous electrode\(^{(47,52)}\).
(see equation (1.5)). This length indicates the optimum thickness for a porous electrode and has, therefore, considerable significance, because electrodes much thinner than the penetration depth behave like planar electrodes of enhanced surface, while electrodes much thicker than the penetration depth are inefficient. If electrodes could be manufactured at a thickness corresponding to a calculated penetration depth, a battery of improved efficiency could be achieved; this has considerable importance for the lead-acid battery where weight is such an important criterion. Unfortunately, de Levie (43) has shown that this characteristic length varies with the mechanism of current control. For a reaction-controlled porous electrode (52)

$$1/p = \left(\frac{RT \cdot \rho H}{2\pi F \cdot i_0}\right)^{1/2}$$  \hspace{1cm} (1.7)

and for diffusion control, Bode (35) has derived

$$1/p = \frac{CDEF}{i(1-i)}$$  \hspace{1cm} (1.8)

From equation (1.7), Bode (35) calculated a value for the penetration depth of 1 mm for the lead-acid battery. From equation (1.8), the penetration depth varies with reactant concentration, and hence the rate of discharge. For low discharge rates, the penetration depth was 3–5 mm, and for high discharge rates was 0.12 mm. These values indicate the undesirability of high rate discharges of the lead-acid battery in diffusion-limiting situations, but are only applicable to steady-state regimes.
The measurement of the double-layer capacity of the porous electrode has considerable significance because it directly reflects the amount of surface area available for electrochemical reaction, and is, therefore, a valuable non-destructive method of electrode characterisation. Ksenzhek and Stender (53, 54) were the first to consider time-dependent response of a porous electrode to a current-step function. For a practical porous electrode, however, de Levie (43) has shown that constant-current conditions cannot be achieved because of the variations in pore size of the electrode. A potential-step technique is more readily applicable, and for a potential-step of amplitude $E$, the charging current is (55, 56)

$$i = E \left( \frac{C}{\pi Zt} \right)^{\frac{1}{2}}$$

(1.9)

Therefore, the double-layer charging response of a porous electrode to a potential-step is a current-time transient which decays as $1/\sqrt{t}$. In contrast, for a planar electrode, the current decays linearly with time.

Because the pore model is more restrictive than the macro-homogeneous model, analytical solutions can be found to non-steady-state situations. Even so, compared with the theoretical investigations on the steady state, information on the transient response of flooded porous electrodes is scarce. Early contributions were made by Ksenzhek (57-59), Guruvich and Bagotskii (60, 61) and Grens 11 and Tobias (62), and more latterly, by Rangarajan (63) and Kunimatsu (64). Winsel (47) looked at transient response under constant-potential and constant-current
conditions to model the discharge conditions in storage batteries. Dunning and Bennion (65) used a more sophisticated approach to examine the effects of varying solution properties on the discharge of porous electrodes with sparingly soluble reactants; this is analogous to the porous lead electrode, where PbSO₄ is the sparingly soluble reactant. These authors used a single pore model and a pseudo steady-state approach to examine the effect of varying solution conditions on the mass transfer between salt crystallites and the metal surface, and found pore blockage to be a significant cause of capacity limitation. Szpak et al. (66) also used the pore model to predict reaction profiles for the charging of porous Ag electrodes in 1N KCl, and compared the theoretical results with experimental observations on an idealized porous electrode. This work may or may not be relevant to the porous Pb electrode, as the model assumed a solution-diffusion step for the Ag/AgCl system. For the Ag/AgCl system this approach is valid, but for the porous Pb electrode this is still a controversial issue.

Winsel et al. (67) developed a simple pore model of the positive and negative electrodes to investigate the behaviour of the electrodes at high rate low temperature discharges. Based on the solution/precipitation model of Vetter (68), and assuming that pore plugging was the capacity limiting process, then the capacity of the negative electrode was found to be proportional to the square of the surface area. At -18°C, and low electrolyte concentration, calculations showed that pore plugging could be due to the formation of ice crystals as well as PbSO₄.
1.6.1.2. The Macrohomogeneous model

At a given time, there will be a large range of reaction rates within the pores, the distribution of which will be determined by physical structure, conductivities of electrode and electrolyte, and by parameters that characterise the rate of reaction. This rate distribution directly influences the net power available from a battery and changes during the course of charge or discharge. These microscopic variations are averaged over the dimensions of the porous electrode, into continuously varying functions. The parallel plate configuration, together with the high conductivity current collectors in most batteries, means that quantities such as potentials, current densities and concentrations vary only with depth into the electrode, and the problem becomes one-dimensional. These variables can be inter-related by several equations to describe the behaviour of the porous electrode. The structural changes occurring during discharge of porous electrodes (such as the lead electrode) need to be considered. One of the first contributions in this field was made by Alkire et al (69) who investigated flooded porous metal electrodes undergoing structural change by anodic dissolution. Alkire and Place (70) later used the steady-state approach again to examine the transient behaviour of porous electrodes during depletion of a limited quantity of solid reactant.

One of the most comprehensive models has been described by Bennion and co-workers (71,72) for porous electrodes with sparingly soluble reactants (as in the porous lead electrode). The model is based on the solution of a set of coupled partial differential equations representing the various applicable laws of transport and conservation. The authors allowed for non-uniform current distributions, and also
for significant changes in the relative distribution of reactants and products, but not the effect of pore-plugging. This model was further refined in 1976(73) to model specifically the Ag/AgCl electrode, and included allowances for electrode tortuosity. Gidaspow and Baker(74) characterised the structural changes that occur during discharge or charge of storage batteries and emphasised the significance of pore-plugging in capacity limitation.

Specific applications of the macrohomogeneous model to the lead-acid cell have been made by Micka and Rousar(75-77), Simonsson (41,78-81) and others(82-84), using the steady-state approach to predict current distributions, discharge profiles and acid depletion profiles.

Micka and Rousar followed the earlier work of Stein(85,86) in assuming reversible electrode kinetics but included allowances for the effects of volume changes on the porosity of the electrode. These authors examined the positive plate(76), the negative plate(75), and the complete lead-acid cell(77). For the positive plate, they obtained 22 ordinary differential equations, which were solved using a digital computer. Diffusion coefficients, activity coefficients and equilibrium potentials were allowed to vary with concentration, but the effect of activation polarisation was ignored. It was found that capacity limitation of the positive was largely due to acid depletion at the pore mouth(76). Modelling of the negative electrode was carried out in an identical manner(75), but in the later paper on the modelling of the whole cell(77), the effect of activation polarisation was considered. It was concluded that the theoretical capacity of the cell is normally limited by the positive plate, and that a certain optimum plate distance exists.
which gives maximum cell capacity. However, Micka and Rousar\textsuperscript{(77)} neglected the effect of electrolyte concentration gradients between the plates, assuming efficient mixing by convection. Turner\textsuperscript{(84)} considered this unlikely in view of the presence of separators between the plates, and investigated the effects of inter-plate concentration gradients. It was shown that inefficient mass transport limited the capacity of the cell at high discharge rates, and optimisation of plate areas and porosities could lead to an improvement in performance.

The comprehensive work of Simonsson\textsuperscript{(78-81)} concentrated on the discharge behaviour of the positive plate, and has been well summarised by the author\textsuperscript{(41)}. It was concluded that the capacity of the positive electrode is mainly determined by the combined effects of structural and mass transfer hindrances; this was confirmed by electron microprobe analysis of PbSO\textsubscript{4} in the positive plate\textsuperscript{(81)}. The confirmation of theoretical predictions by direct observations has developed into a necessary and fruitful area of research into porous electrode theory. This aspect deserves separate consideration from indirect observations on the porous lead electrode.

1.6.1.3. Experimental Verification of Porous Electrode Theory

Experimental verification of the predicted current and potential distributions in the porous electrode have progressed along two paths: those dealing with idealised single pores\textsuperscript{(87-91)} and those treating idealised porous electrodes\textsuperscript{(66,69,92-98)}. In single pore studies the pore is considered to represent a real electrode made up of multiple aggregates of this pore. However, this technique is rather unrealistic because practical porous electrodes often have smaller pores than can be made artificially, and in real porous electrodes, the pores
are interconnected and tortuous. Model electrodes having some resemblance to real electrodes have been studied with varying degrees of success in understanding the prevailing reaction modes and distributions. Generally, electrodes are sectioned after charging or discharging and the current distribution inferred from chemical changes. Electron microprobe analysis has proved particularly useful (78), but surface morphology investigations have also been used (94, 95).

Experimental verification of the modelling of porous electrodes using model or real electrodes, as opposed to single pores, is obviously more relevant to the industrial situation. The experimental studies or the developed mathematical representations can be used separately, but together they provide the most valuable means for optimising electrode performance. Experimental verification of porous electrode theory using the positive and negative plates of the lead-acid cell has tended to use standard industrial electrodes which were analysed for PbSO$_4$ after discharging to different levels at varying rates.

Formerly, this analysis was carried out by the autoradiographic technique using $^{35}$S-labelled H$_2$SO$_4$ (99-104), but this has been superseded by the improved resolution of the electron microprobe analyser (78, 105-107). Yantschenko and Selitsky (108) used a section electrode and measured the current in each section; this technique has been used for other electrodes (92, 93), but again suffers from poor resolution. Simonsson and his co-workers (81) used conductivity measurements to investigate the effect of structural changes on the conductivity of the pore electrolyte and found extensive pore plugging of the positive electrode at low discharge rates. These authors reproduced the classical forced-flow experiments of Liebnow (109) to demonstrate that the high rate discharge capacity
of the positive electrode suffered from mass transfer limitations; similar results were reported by Haebler et al. (107).

Studies on the porous electrodes of the lead-acid battery generally confirm the predictions of mathematical modelling; at high discharge rates, the reaction is largely confined to the front of the electrode, but at low discharge rates there is a more even distribution of the product PbSO₄. Major difficulties arise in attempting to transform the theoretically derived optimisations into real electrodes because of the intransigence of the present methods of electrode manufacture.

1.6.2. The Manufacture of the Porous Lead Electrode

The lead electrode most commonly associated with the lead-acid battery is the pasted plate configuration introduced by Faure in 1881 (110). This is manufactured by applying a paste, made of incompletely oxidised lead powder and sulphuric acid, to a cast lead-alloy grid structure. The electrode is then "cured", followed by reducing (charging) in dilute sulphuric acid, to form sponge lead. The manufacture of the porous lead electrode has been comprehensively treated (35,36) and the materials and mechanisms of the lead-acid battery have been recently reviewed (111). It is sufficient here to review briefly the pasting, curing and forming processes.

1.6.2.1. Pasting

The grid which forms the basis of the porous lead electrode acts as current collector to the active material, which is also held in place by the mesh of the grids. Numerous grid geometries have been
used, and alloying additions are made to improve the functioning of the grid, which has to withstand electrochemical corrosion and act as a load-bearer for the active material. Grids are normally cast, and to achieve optimal castability, corrosion performance and load-bearing characteristics, most grids are manufactured from Pb-Sb or Pb-Ca. Antimony is typically alloyed in amounts ranging from 4-18% Sb, and commercial Pb-Sb alloys typically include small amounts of As, Cu and Sn. Batteries manufactured using Pb-Sb alloys have self-discharge problems, and this is overcome by the use of Pb-Ca alloys in certain applications; these alloys typically contain 0.07% Ca and 1% Sn. For a detailed discussion of grid materials, the reader is referred to the review of Perkins.

The initial paste is manufactured by mixing Pb, sulphuric acid, water, and certain additives. The oxide is formed by air oxidation of lead dust and is normally < 50μm particle size. Three groups of additives are added to the negative paste, alone or in combination, to improve performance:

(a) Inorganic additives, mainly BaSO₄ - typically 0.1-0.3 wt %.
(b) Organic additives such as lignin or its derivatives - typically 0.1-0.3 wt %.
(c) Lampblack (soot) - typically 0.1-0.3 wt %.

These additives are designated as expanders and their influence on battery performance will be discussed in Section 1.6.4. Lignin-type compounds are obtained from purified and dried wood flour, and a typical lignin structure, suggested by Adler, is shown in Figure...
Figure 1.6. Schematic formula for a section of spruce lignin according to Adler (112)
1.6. Lignin molecules are formed from three primary precursors: E-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol\(^\text{[113]}\); the proportions of these precursors varies with the origin of the lignin\(^\text{[114,115]}\) and may have some significance for battery performance.

When the partially oxidised lead powder is mixed with water and \(\text{H}_2\text{SO}_4\), complex chemical reactions give rise to a paste composed of \(\text{Pb}, \text{PbO}, \text{PbSO}_4, \text{PbO}\cdot\text{PbSO}_4\) and \(3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}\)\(^\text{[111,116,117]}\). The exact composition depends on factors such as starting mixture, rate of mixing, and temperature. At equilibrium, the major compounds are \(\text{PbO}\) and \(3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}\)\(^\text{[116]}\). After mixing, the paste is applied to the electrode grid and cured.

1.6.2. Curing

The plates are generally cured over a period of days in a humid atmosphere. Three main effects are observed\(^\text{[116]}\):

(a) paste hardening
(b) a reduction of free lead content by conversion to \(\text{PbO}\).
(c) a corrosive attack on the metal grid, which promotes bonding of the active material.

The residual moisture content is important in determining the rate of oxidation of the remaining free lead\(^\text{[118]}\), probably because of the dissolved oxygen\(^\text{[119]}\). The type and proportion of the basic sulphates occurring in the cured paste depends on the curing conditions. At temperatures and humidities around ambient, a cured paste contains mainly \(\text{PbO}, \text{PbSO}_4\) and \(3\text{PbO} \cdot \text{PbSO}_4\), but at curing temperatures > 70\(^\circ\)C and higher humidities, tetrabasic lead sulphate \(4\text{PbO} \cdot \text{PbSO}_4\) predominates\(^\text{[36,120,121]}\). Schlotter and Fleischmann\(^\text{[122,123]}\) have demonstrated that the pore volume
of the cured paste varies linearly with dry paste density, and the 
gradient of the line varies with curing conditions. It was also 
demonstrated that pore volumes were highest in the pastes which contained 
the greater amounts of tetrabasic lead sulphate; this observation is 
significant for the optimisation of plate capacity.

1.6.2.3. Forming

Commercial battery plates are usually galvanostatically 
formed in dilute $\text{H}_2\text{SO}_4$, but during the early stages of formation the 
interior of the plate remains alkaline, allowing more efficient 
reduction$^{(116)}$. Earlier work demonstrated that the formation of sponge 
lead occurred by an electro-deposition process$^{(37,124)}$, and the nature 
of the deposit depended on the forming conditions$^{(125-127)}$. These 
observations have been confirmed in a comprehensive investigation of 
the formation process by Pavlov and his co-workers$^{(117,128)}$. Electron 
microprobe analysis, X-ray analysis and microscopy were used to look 
at the formation process$^{(117)}$ under normal galvanostatic conditions, 
and two stages were observed. During the first stage, some of the PbO 
(free or bound to $3\text{PbO}.\text{PbSO}_4.\text{H}_2\text{O}$) was reduced to Pb, while another 
part was transformed into $\text{PbSO}_4$. This initially formed Pb provides a 
network for the deposition of the lead subsequently formed in the 
second stage when $\text{PbSO}_4$ is reduced to Pb. During formation the pore 
radii and the active mass increase. The advance of these processes 
across the plate shows that the reaction is initiated at the grid 
bars$^{(117,124,128,130)}$. A zone consisting of Pb and $\text{PbSO}_4$ crystals 
is formed which advances along the plate surface, and then penetrates 
into the interior of the plate. The first stage ends when the paste 
is totally converted to Pb-$\text{PbSO}_4$, and the formation of the plate ends
when the PbSO₄ is reduced to Pb.

1.6.3. Physical characterisation of the Porous Lead Electrode

The morphology of the charged porous lead electrode approaches the ideal configuration for a porous electrode\(^{(32)}\). The structure of the formed electrode has been microscopically studied by a number of workers\(^{(124,128-132)}\), and lead crystals with rough porous surfaces have been observed. This structure gives a high surface area and an unimpeded circulation of electrolyte through the matrix. It also possesses good material strength and electronic conduction properties\(^{(32)}\).

Simon and Jones\(^{(124)}\) demonstrated that electrode morphology depended on forming conditions such as current density, temperature and electrolyte concentration. The major influence was found to be electrolyte concentration; as the concentration increased, the surface area/porosity of the electrode decreased. The major influences on electrode structure are generally considered to be the expander additions\(^{(32,35)}\) (these will be considered further in Section 1.6.4). In the presence of lignin, smaller, more uniform, rough-surfaced and porous particles of lead are observed in the charged lead electrode. Therefore, the presence of lignin effects a greater surface area/porosity\(^{(132-135)}\), and improved cycling capabilities\(^{(133,136-139)}\). At high cycle numbers, the specific surface area decreases with cycle number\(^{(39)}\) as the lead crystals agglomerate into large particles which are difficult to discharge\(^{(135)}\).

Values for the specific and effective surface area of the porous lead electrode have already been given in Section 1.6.1.
show an order of magnitude difference. This is probably reflected in the relatively low values of double layer capacitance of $10^{-11}$ F cm$^{-2}$, based on B.E.T. surface (38,140,141). Micka et al (142) have recently investigated the structural characteristics of the positive and negative electrodes. The formed active mass of the lead electrode was found to have a mean composition of 76.8% Pb; 3.3% PbSO$_4$; and 19.9% PbO (tetragonal). The mean porosity after formation was 0.55 and this value fell linearly with the charge passed during discharge. The apparent density (including voids) on formation was 4.70 g cm$^{-3}$, and comparison with the density of Pb (11.34 g cm$^{-3}$) indicates the effect of porosity. These authors also found that the negative electrode had a more regular structure than the positive, which gave better transport properties and a correspondingly lower value for the tortuosity factor. The mean pore radius was found to be an order of magnitude greater for the negative electrode, while the specific surface area was an order of magnitude lower. After charging, the tortuosity factor may be higher owing to entrapped hydrogen bubbles in the matrix (143), but this value decreases as the bubbles are removed by capillary action. This phenomenon also affects measurements of inter-electrode solution conductivity (141).

Bode (35) examined the variation of porosity during the formation process and in subsequent cycling. A volume decrease in the solid mass of the lead electrode was observed during formation, and this was accompanied by an increase in pore volume. The author quoted a mean pore diameter of 4.5 $\mu$m, with a narrow pore spectrum, for the formed negative. A pore volume of 0.25 cm$^3$ g$^{-1}$ was also quoted which is in close agreement with the 0.215 cm$^3$ g$^{-1}$ measured by Wünsel et al (67).
The specific surface area \(0.5 \times 10^4 \text{ cm}^2 \text{ g}^{-1}\) and pore diameter of the electrode were found to remain constant during subsequent cycling, but the porosity increased from 0.69 for the formed mass to 0.80 at the 50th cycle. These physical characteristics of the porous lead electrode: surface area, pore dimensions, and porosity, govern its response in electrochemical investigations.

1.6.4. The Electrochemistry of the Porous Lead Electrode in H\(_2\)SO\(_4\)

1.6.4.1. The Function of Expanders

In Section 1.6.2.1, the use of expanders in the active material of the porous lead electrodes was described, and their effect on morphology in Section 1.6.3. The high rate low temperature performance of the lead-acid battery is limited by the negative electrode\(^{(32)}\) (see below), and this is improved by expander additions \((133, 135, 136, 144)\). Many effects have been ascribed to lignin and its derivatives. These compounds have been found to adsorb to the surface of metallic lead\(^{(14, 135, 136, 144)}\) and Simon\(^{(14)}\) suggested that lignins had to be first oxidised in solution before adsorption could take place. Many authors have suggested that lignins beneficially affect the lead structure formed on charge, and hence the surface area\(^{(132-135, 148)}\), presumably because lignin adsorption lowers the surface energy of the lead, making the formation of smaller and more loosely packed lead crystals more favourable\(^{(35)}\). Lignins are also claimed to influence the formation of PbSO\(_4\), making the crystals smaller, the film more porous, and easier to reduce \((133, 135, 149-151)\). The onset of passivation is also said to be delayed by lignins \((14, 135, 152)\), while Le Mehaute observed the effect of lignins before and after
passivation\(^{(153)}\). Mahato\(^{(135)}\) also investigated the influence of different lignosulphonate salt cations on the charge and discharge processes and found that the sodium salt gave the best performance.

The function of the other two expander additions in the negative electrode are more easily defined. Lampblack has no electrochemical effect on battery performance and is added to increase electrode conductivity during formation. \(\text{BaSO}_4\) acts synergistically with lignin to give an even greater effective surface area/porosity and hence capacity\(^{(134,136)}\). This is because \(\text{BaSO}_4\) provides nucleation centres for \(\text{PbSO}_4\), with which it is isomorphous\(^{(136)}\). Hence, \(\text{BaSO}_4\) influences the size of \(\text{PbSO}_4\) crystals\(^{(137)}\), and probably makes discharge more efficient, and the resultant \(\text{PbSO}_4\) film easier to reduce. The formation of \(\text{PbSO}_4\) from \(\text{Pb}\) - the oxidation or discharge process, is the critical capacity - determining process at the porous lead electrode.

1.6.4.2. The Discharge of the Porous Lead Electrode

In the battery industry, the performance of the lead electrode is generally assessed galvanostatically. The electrode is discharged at constant-current, and the resultant potential-time behaviour of the electrode is recorded. Features of this E-t plot include: (a) resistance of solution and materials, (b) double layer capacity, (c) supersaturation, nucleation and crystallisation phenomena, (d) the discharge of \(\text{Pb}\) to \(\text{PbSO}_4\), and (e) rapid polarisation owing to acid depletion and pore plugging\(^{(33)}\). The performance (capacity) of the electrode is assessed by the time taken, \(t_d\), to reach phase (e) at different discharge currents.
The performance characteristics of the lead-acid battery are complex and numerous, and battery developers have been content to assess performance in terms of empirical relationships such as the Peukert equation

\[ I^x t = K \]  

(1.10)

where \( x \) and \( K \) are constants determined from discharge data. For intermediate currents, \( x \approx 1.3-1.4 \), but tends to 2 at high current and 1 at low current, and the equation is therefore only valid at intermediate currents (35).

Equation (1.10) simply expresses experimental observations that capacity decreases with increasing load (discharge rate) (155, 156), where discharge is limited by the formation of PbSO₄, and concentration changes at the electrode surface (40, 131, 156). PbSO₄ crystal size is found to decrease with increasing discharge rate (131, 157), and this makes the passivation of the lead active surface more effective.

A number of workers have suggested that the discharge (and charge) processes at the negative electrode involve a dissolution-precipitation mechanism (33, 68, 155, 158). The discharge and charge of lead electrodes may then be considered as anodic dissolution, and cathodic electroplating, of a soluble lead species. S.E.M. evidence has been used to support this hypothesis (159, 160), and a soluble lead species has been detected using a flat lead electrode at small overpotentials (12, 13, 17, 18, 23).
As the temperature is decreased below 0°C, the capacity of the porous lead electrode decreases (155), as does the size of the PbSO₄ crystals formed (157). Berndt (155) showed that at 40°C, 35-60% of the theoretical capacity could be discharged, depending on discharge rate, but at -30°C this fell to 10-30%. The author also observed variations in the constants, x and K, of the Peukert equation (1.10). As the temperature decreased, x increased and K decreased, and the author concluded that these constants simplified the complex nature of the interactions involved. Winsel et al (67) examined the high rate discharge of the porous lead electrode at -18°C and found that the capacity varied linearly with the square of the surface area. Mahato (135) observed a linear relationship between capacity and surface area under similar conditions, but the results showed a lot of scatter. Winsel et al (67) predicted, and observed, ice passivation of the porous lead electrode at -18°C.

The introduction of mark/space motor controllers in electric vehicles has necessitated the investigation of the lead-acid battery under pulsed current discharge. Jayne (161) has investigated the behaviour of lead-acid cells under continuous discharge, interrupted discharge and pulsed discharge conditions. The constant-current discharge behaviour of the cell was found to provide a conservative estimate of the available capacity from pulsed and interrupted discharge, provided a mean value of discharge current was used. The improvement in performance was attributed to a recovery phenomenon which occurs during current interruption. Turner (162) explained this phenomenon in terms of the relaxation of concentration depletion. Alternatively the pulse time durations are so short compared with the total discharge time, that the...
average current and electrolyte depletions will look the same as in the continuous case. Berndt's work on the porous lead electrode\textsuperscript{(127)} confirms these observations somewhat, where electrodes fully discharged at various rates and temperatures could be further discharged at 25\degree C.

1.6.4.3. The Charge of the Porous Lead Electrode

Data on the reduction (charge) of the porous lead electrode is scarce. Peters et al\textsuperscript{(163)} showed that the high-rate charging efficiency of 91\% at 40\degree C was reduced to 70\% at 0\degree C. Willihnganz\textsuperscript{(157)} observed that porous lead electrodes tested at -40\degree C accepted charge at a rate proportional to the degree of previous discharge. Bode\textsuperscript{(35)} found that the charge rate was significantly reduced below 0\degree C, and, at -50\degree C became impossible. Willihnganz\textsuperscript{(157)} observed that the charge rate increased as the size of PbSO\textsubscript{4} crystals formed on discharge decreased, and crystal size decreased with decreasing discharge temperature and increasing discharge rate.

The reduction of sulphated solid lead electrodes has been studied in this laboratory to examine the effect of organics on the electrocrystallisation of Pb from PbSO\textsubscript{4}\textsuperscript{(31)}. It was concluded that the process conformed to an instantaneous nucleation and two-dimensional growth process at a flat electrode.
CHAPTER 2

THEORETICAL PRINCIPLES

2.1. The Electrode-Electrolyte Interphase

An interphase may be regarded as the region between two phases in which the properties have not yet reached those of the bulk of either phase. In the simplest case the interphase is an interface. The interface between a metal and a solution could be visualised as a line of excess electrons at the surface of the metal, and an equal number of positive charges in the solution in contact with the metal. Hence, although each phase has an excess charge, the interface as a whole is electrically neutral. The separation of charge at a metal/solution interface results in a strong electric field in the space between the charged layers, and a potential difference across the extremities. Although the potential difference is small (typically <1V), the small distance of separation (Angstroms) of the charged layers results in a very high field strength (potential difference/distance). This high field strength is responsible for the facility with which electrons cross the interface during electrode reactions, and a very small change in excess charge at the interface can have a profound effect on the potential difference and the velocity of the electrode process.

The simplest model for the distribution of ions at the interphase was first suggested by Helmholtz (164): a plane layer of charges (excess adsorbed ions) confronts a plane layer of opposite charges in the electrode. The interphase is, therefore, equivalent to a parallel-plate...
capacitor, and electrodes which behave in this way are termed "ideally polarisable". The concept of a strict and rigid distribution of ions on a simple plane was oversimplistic because thermal agitation of ions in solution would effect their distribution over an appreciable distance into bulk solution.

Gouy (165) and Chapman (166) accounted for the interplay of thermal and electrical forces in solution. The interphase was still simulated by a parallel-plate capacitor, but, whereas in the Helmholtz model potential varied linearly with distance, potential now varied exponentially with distance across the interphase. This model is only applicable to ions whose thermal energy is of the same order as their energy of interaction with the electrode field, and is not applicable to those ions that are adsorbed in the Helmholtz double layer.

The ideas of Helmholtz, Gouy, and Chapman were improved and combined in the model of Stern (167). Whereas the Gouy-Chapman model assumes that all ions are point charges, Stern pointed out that ions of a finite size cannot approach more closely to the surface than their effective radius. He also recognised that at short distances from the surface there may exist a specific interaction between the ions and the surface. Stern proposed two distinct regions of charge separation:

(a) The interface region from the electrode to the locus of the centres of ions in contact with the electrode, across which the potential varies linearly (Helmholtz or compact layer).

(b) The region from the Helmholtz plane into the solution, across which the potential varies exponentially (Gouy-Chapman layer).
The Stern model predicts that the interphase can be modelled by two capacitors in series. When the concentration of electrolyte is large, most of the charge is confined in or near the Helmholtz (compact) layer, and the interphase approximates to the Helmholtz model. In dilute solution, the converse situation applies and the interphase approximates to the Gouy-Chapman model.

Grahame (168) attempted to modify the Stern theory by postulating the existence of two types of ion, one of which is specifically adsorbed on the electrode, the other being merely a normal hydrated ion at its distance of closest approach to the surface. In Grahame's model, the specifically adsorbed ion is assumed to lose some of its water of hydration and be closer to the surface than the other ion. The model consists of two parallel planes at different potentials, one associated with each type of ion. These two layers are usually called the inner and outer Helmholtz planes. The ions in the compact layer are assumed to adsorb on to lattice points which are empty prior to the arrival of the ion. The electrical work involved in the adsorption is therefore determined by the potential at the lattice point and not by the average potential in the compact layer.

Grahame also suggested that, in the case of negligible specific adsorption, the capacity of the compact layer was solely dependent on the charge on the electrode. This capacity was unaffected by electrolyte concentration, whereas the capacity of the Gouy-Chapman layer is directly proportional to electrolyte concentration. Using an ideally polarisable electrode, with negligible specific adsorption
Model of the electrical double layer.
and a symmetrical electrolyte (e.g. Hg in NaF), Grahame was able to demonstrate the validity of his model under ideal conditions (168-170). He obtained capacitance-potential curves which showed a pronounced minimum at the potential of zero charge (p.z.c.), which lessened in intensity, and ultimately disappeared with increasing concentration. The minimum corresponds to a predominant influence of the capacitance of the Gouy-Chapman layer. The capacitance maximum on the cathodic side of the p.z.c. is virtually independent of cations present, and is thought to show the effect of water molecules in the Helmholtz layer. The anodic side exhibits a larger capacitance peak reflecting two opposing effects, the specific adsorption of anions and dielectric saturation.

The fact that water molecules in contact with the electrode will no longer have the same structure as water in the bulk of the solution, but will be oriented as dipoles on to the electrode (thus contributing to the potential difference across it), was realised by Bockris et al (171). Their model is illustrated in Figure 2.1, and is divided into three regions. The innermost region contains specifically adsorbed anions (and water dipoles) such that the inner Helmholtz plane (IHP) passes through their centres. Outside this layer, there exists an additional layer of nonadsorbed hydrated ions whose centres define the outer Helmholtz plane (OHP). Beyond the OHP the population of ions of given charge at any point from the surface is determined by the opposing effects of the electric field and thermal agitation. This region is referred to as the diffuse layer. The difference between ions in the inner and outer Helmholtz planes is of great importance because chemical work must be done to remove the
hydration shell around the ion of the IHP, and one or more water molecules from the electrode surface. The final state is stabilised by the specific interactions between the ion and the surface; this effect is absent for the ions in the OHP where the interactions are mainly electrostatic.

The water layer in the IHP is stressed by the force exerted on it by the electrode field. Hence, the dielectric constant, with fully oriented water dipoles, is only 6. Outside the IHP, water dipoles are only partially oriented by the electrode field, and the dielectric constant of the secondary water layer increases with distance from the electrode to the bulk value of 78.5 (at room temperature).

To a first approximation the potential drop is linear with distance across the metal-IHP and IHP-OHP regions, but decays exponentially with distance in the Gouy-Chapman diffuse region. The total potential drop across the interphase is, therefore, the summation of the potential drops across the three regions. By differentiation of this summation with respect to the charge (Q) on the metal and using the definition of differential capacitance

\[ C' = \frac{dQ}{d\varepsilon} \]  

the following expression for the overall double-layer capacitance of the interphase is:

\[ \frac{1}{C_I} = \frac{1}{C_{\text{IHP}}} + \frac{1}{C_{\text{OHP}}} + \frac{1}{C_{\text{G-C}}} \]  

(2.2)
Equation (2.2) suggests that an electrical analogue of the interphase is the series combination of three capacitors, where the overall capacitance is determined by the smallest of the three capacitances on the right hand side of equation (2.2). However, the capacitance of the interphase is generally found to be dependent on the potential drop across it, but the analogy is still useful for the analysis of electrode response to ac perturbations.

Recent studies on the structure of the interphase have been mainly concerned with the orientation of the water dipoles in the compact layer (e.g. 172-174). Cooper and Harrison (175-179) have reappraised the conceptualisation of the interphase. The structure of the interphase is considered to arise specifically from the known differences between anions and cations in aqueous solution, and the net distributed charge acts at a mean distance, $\bar{x}$, from the electrode. The effective dielectric constant of the interphase will vary directly with $\bar{x}$, and $\bar{x}$ varies inversely as the surface charge density and the electrolyte concentration. The distance, $\bar{x}$, is also determined by the different effective sizes of anions and cations in aqueous solution. It is envisaged that the development of detailed statistical theories for the distribution of ions in the interphase will lead to a clearer understanding of experimental data which is not totally explained by equations such as (2.2).

The description of the interphase above assumes that the capacitance minimum of the interphase occurs at the p.z.c. Frumkin (180,181) has shown that for anion adsorption, the p.z.c. moves to more negative potentials; for cation adsorption the converse applies. Where anion and cation adsorption occur, the direction of shift of the
p.z.c. may be reversed by concentration changes.

Capacity-potential curves for most uncharged substances and some bulky organic ions exhibit two peaks\(^{(182-184)}\). The region between these peaks corresponds to the maximum in the surface coverage-potential curves\(^{(171,184,185)}\), where coverage varies rapidly with potential. The capacity is the same as that of the electrolyte alone at sufficiently positive or negative potentials when desorption has occurred. Damaskin\(^{(184)}\) described organic adsorption in terms of the Frumkin isotherm\(^{(186)}\), and stressed the strong electrical effect of organic-electrode interaction, and the change of shape of the interface connected with it. The influence of water molecules was not considered, but has been stressed by Bockris et al\(^{(171)}\) in the water-competition theory. The assumptions are made:

(a) The organic is undissociated
(b) Only electrostatic forces apply
(c) The forces in (b) mainly affect the water molecules.

When these assumptions apply, the adsorption of the organic molecules will largely be determined by the electrical behaviour of the water molecules. When the excess charge on the electrode is highly positive, the water molecules will be more strongly adsorbed than when the charge is near zero (because the molecule is assumed to have a much stronger moment than that of the organic molecule). Therefore, the maximum adsorption of the organic molecules is expected around the p.z.c. for the metal concerned, and the adsorption-charge density relation will tend to be parabolic.
This simple model rarely applies, and there are often other interactions which become important. The electrical effect of Damaskin (184) (described above) could be more significant than the water effect in certain situations. When an organic molecule dissociates in the same step in which it is being adsorbed, water competition will become insignificant.

2.2. Charge Transfer

Electrochemical reactions that involve the transfer of charge at an electrode/solution interphase are examples of heterogeneous processes. Consider the cathodic reduction of an ion, which passes through the energy barrier between the OHP and the electrode, and discharges at the electrode surface. This could be represented by a simple one-step reaction

\[
O + ze \xrightarrow{k_c} R \quad \xleftarrow{k_a} \quad (2.3)
\]
The observed current (per unit area) flowing through an external circuit is the difference between the partial currents for the forward and reverse processes, \( i = i_c - i_a \):

\[
i = zF \left( k_c^S C_0^S - k_a^S C_R^S \right)
\]  

(2.4)

where \( k_c \) and \( k_a \) are constants at fixed potential. The convention adopted here is that the overall current for a reaction that proceeds from left to right as written is positive.

In the potentiostatic technique, the current is dependent on the potential of the working electrode (which is dependent on the reference electrode employed) so that:

\[
k_c = k_c^0 \exp \left( \frac{-\alpha zFE}{RT} \right) \quad (2.5)
\]

\[
k_a = k_a^0 \exp \left( \frac{(1-\alpha) zFE}{RT} \right)
\]

(2.6)

where \( \alpha \) is the transfer coefficient. The constants \( k_c^0 \) and \( k_a^0 \) do not depend upon \( E \) directly, but are functions of the standard Gibbs energies of activation and the electrical potentials at the initial states (assumed to reside at the IHP).

Substitution of equations (2.5) and (2.6) in (2.4) gives

\[
i = zF \left[ k_c^0 C_0^S \exp \left( \frac{-\alpha zFE}{RT} \right) - k_a^0 C_R^S \exp \left( \frac{(1-\alpha) zFE}{RT} \right) \right]
\]

(2.7)

At equilibrium \((E=E_r)\) the total current is zero, and hence no concentration gradients exist at the surface. Therefore,
\[ i_0 = zFk_c^0 C_0^S \exp \left( \frac{-\alpha zF (1-\alpha)}{RT} \right) \]
\[ = zFk_a^0 C_R^S \exp \left( \frac{(1-\alpha) zF E_r}{RT} \right) \]  
(2.8)

where \( i_0 \) is the exchange current density. Elimination of \( k_c^0 \) and \( k_a^0 \) from (2.7) using (2.8) gives

\[ i = i_0 \left[ \frac{C_0^S}{C_R^b} \exp \left( -\alpha zF \frac{\eta}{RT} \right) - \frac{C_R^S}{C_R^b} \exp \left( (1-\alpha) zF \frac{\eta}{RT} \right) \right] \]  
(2.9)

where \( \eta \) is the overpotential

\[ \eta = E - E_r \]  
(2.10)

Equation (2.9) relates the current to both the surface concentration, and the overpotential and is therefore useful in the prediction of \( i - t \) transient response to potential perturbations.

The forms of equations (2.5) and (2.6) demonstrate that at the standard potential \( E^0 \)

\[ k_c = k_a = k^0 \]  
(2.11)

and,

\[ k_c^0 \exp \left( -\alpha zF E^0 / RT \right) = k_a^0 \exp \left( (1-\alpha) zF E^0 / RT \right) = k^0 \]  
(2.12)

\[ E^0 = \frac{RT}{zF} \ln \left( \frac{k_c^0}{k_a^0} \right) \]  
(2.13)

Similarly, rearrangement of (2.8) gives

\[ E_r = \frac{RT}{zF} \ln \left( \frac{k_c^0}{k_a^0} \right) + \frac{RT}{zF} \ln \left( \frac{C_0^b}{C_R^b} \right) \]  
(2.14)
which upon substitution of equation (2.13) yields

\[ E_r = E^0 + \frac{RT}{zF} \ln \left( \frac{C_o^b}{C_R^b} \right) \]  \hspace{1cm} (2.15)

Equation (2.15) is the Nernst equation with the assumption of unit activity coefficients. Thus, \( E_r = E^0 \) when \( C_o^b = C_R^b \), or strictly when \( a_o = a_R \). At low concentrations, the activity coefficients approach unity and \( E_r \longrightarrow E^0 \).

By substitution of (2.14) into (2.8) (187):

\[ i_o = nFk^0 \frac{C_o^b}{C_R^b} (1 - \alpha) \]  \hspace{1cm} (2.16)

It is apparent that \( i_o \) depends upon the bulk concentrations and is not a unique function of reaction rate.

If the rate constant \( k^0 \) is sufficiently small that no appreciable concentration gradients exist at the surface, then \( C_o^S \approx C_o^b \) and \( C_R^S \approx C_R^b \). The current for a completely activation-controlled process is obtained from (2.9):

\[ i = i_o \left[ \exp \left( - \frac{zF\eta}{RT} \right) - \exp \left( 1 - \frac{zF\eta}{RT} \right) \right] \]  \hspace{1cm} (2.17)

and was first derived by Erdey-Gruz and Volmer (188). The tacit assumption in this expression is that the potential varies linearly with distance across the interphasial region. This is only true in the region from the metal surface to the OHP (see Section 2.1), where the real kinetics of charge transfer are determined (189).

For overpotentials \( \eta < 0.010 \text{V} \), the exponentials in equation (2.17) can be expanded, and taking the first term only in \( e^x \approx 1 + x + \ldots \).
valid for small values of $x$, gives the following relationship:

$$i = (i_0 Fz/RT)\eta$$  \hspace{1cm} (2.18)

Hence, $\eta$ against $i$ is linear with a slope of $RT/i_0 Fz$, which is defined as the charge transfer resistance, and the interphase behaves like an ohmic resistor.

At high overpotentials, one of the exponentials in (2.17) becomes negligible and the well-known Tafel law is derived, for negative overpotentials:

$$\eta = \frac{2.3RT}{Fz} \log i_0 - \frac{2.3RT}{Fz} \log i$$  \hspace{1cm} (2.19)

The exchange current density can be obtained from the values of charge transfer resistance at low $\eta$ (see equation (2.18)), and from $\eta$-log $i$ extrapolations to $E_p$ at high $\eta$ (see equation (2.19)).

The charge transfer process as outlined above applies only to the simple electrode reaction for which all the electrons are transferred simultaneously. If two electrons are transferred in separate transfers and the second is rate-determining we have:

$$0 + e \rightarrow R_1$$  \hspace{1cm} (2.20)

$$R_1 + e \rightarrow R_2$$  \hspace{1cm} (2.21)

For a Nernst diffusion layer the flux due to equation (2.20)

$$i = (i_m) / (c^b_0 - c^c_0)$$  \hspace{1cm} (2.22)
is equal to the flux due to equation (2.21)

\[ i_1 = F k_0 C_0^{i_0} \exp \left( -\frac{\alpha F (E - E_0)}{RT} \right) \tag{2.23} \]

Elimination of \( C_0 \) and use of \( i = 2i_1 \), allows \( i \) to be calculated.

\[ \ln \left( \frac{i}{2i_1} \right) = \ln \left( \frac{F k_0 C_0^{i_0}}{(i_1)_1} \right) - \left( 1 + \alpha \right) \frac{F (E - E_0)}{RT} \tag{2.24} \]

When \( i < (i_1)_1 \), a plot of \( E \) versus \( \log i \) has a Tafel slope of \( \frac{2.3RT}{(1+\alpha)F} \), or 40mV.

Multistep electron transfers have been well reviewed by Losev (192).

Quantum mechanical concepts have indicated that even for the simple case of equation (2.3), charge transfer does not occur in one smooth step over a single energy barrier, but proceeds in various stages. The reactant must first diffuse to the electrode and then the ionic atmosphere arrange and solvent orientate to form a transition state. Finally the electron is transferred, and only this step has to be treated kinetically. The first stages of the reaction are all in equilibrium and can be treated by thermodynamics. Following electron transfer, the ligand bond distances are altered and the solvent dipoles and ion atmosphere reorientated. When an electron is transferred there is no change in energy; radiationless iso-energetic electron transfer is a central feature of the theories of Marcus (193) and Levich (194).

2.3. **Mass Transport**

The simple electrochemical reaction of equation (2.3) is comprised of at least five separate steps:

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(a) Transport of $O$ from bulk solution to the interface
(b) Adsorption of $O$ to the surface
(c) Charge transfer at the electrode to form $R$
(d) Desorption of $R$ from the surface
(e) Transport of $R$ from the interface into the bulk of solution

Steps (b)-(c) are commonly referred to as the activation process, whereas steps (a) and (d) are mass transport processes.

Three main mass transport processes are responsible for the movement of ions in solution: migration, diffusion and convection. Migration is the result of forces exerted by an electric field on a charged particle, which causes ions to move. In the presence of a large excess of supporting electrolyte, migration of electroactive material is minimised and can be neglected.

Natural or free convection develops spontaneously in any solution undergoing electrolysis, as a result of density differences which develop near the electrode. It may also arise from thermal or mechanical disturbances. Forced convection may be effected by stirring the solution, rotating the electrode (see section 2.4), bubbling gas near the electrode etc.

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. It is an irreversible process linearly proportional to the gradient of potential energy, in this case the gradient of concentration. Fick’s first and second laws describe
respectively the steady-state flux and the non-steady change of local concentration in terms of the differential diffusion coefficient. For a planar electrode immersed in electrolyte solution containing $O$, which is reduced according to equation (2.3), Fick's first law gives:

$$J_0 = -D_0 \left( \frac{\delta C_0}{\delta x} \right)$$  \hspace{1cm} (2.25)

Fick's second law gives:

$$\frac{\delta C_0}{\delta t} = D_0 \left( \frac{\delta^2 C_0}{\delta x^2} \right)$$ \hspace{1cm} (2.26)

where $x$ is the positive vertical distance from the planar electrode interface.

Equation (2.26) is readily solved for straightforward initial and boundary conditions to give the time dependent flux or current density to the electrode surface. The simplest case is when $k_c$ from equation (2.3) is so fast that all of the impedance occurs in the concentration polarisation resulting from diffusive mass transport, and the reverse process may be neglected. This situation arises for a reversible reaction when the potential is stepped to a region that is far removed from the equilibrium value. The boundary conditions are:

$$t = 0, \ x > 0: C^b_0 = C^b_0$$  \hspace{1cm} (2.27)

$$t > 0, \ x \to \infty: C^b_0 = C^b_0$$  \hspace{1cm} (2.28)

$$t > 0, \ x = 0: C^b_0 = 0, i = zFD_0 \left( \frac{\delta C_0}{\delta x} \right)$$  \hspace{1cm} (2.29)
The appropriate solution of equation (2.26) is

$$C(x,t) = C^b_o \text{erf} \left( \frac{x}{2D^{\frac{1}{2}}t^{\frac{3}{2}}} \right)$$  \hspace{1cm} (2.30)

Differentiation of equation (2.30) at \(x = 0\) then leads to the Cottrell equation:

$$i = zF D^o \left( \frac{\delta C^o}{\delta x} \right)_{t=0} = zF C^b_o \left( \frac{D}{\pi t} \right)^{\frac{1}{2}}$$  \hspace{1cm} (2.31)

Hence equation (2.31) is useful for the determination of diffusion coefficients and concentrations. Greater interest attaches to the determination of chemical rate constants which describe aspects of the faradaic process and the mechanisms involved in it. Not surprisingly, therefore, considerable effort has been given to the description of voltammetric transients controlled, at least in part, by the rate of the charge-transfer process. Except in the case of slow chemical kinetics, the current will be eventually controlled solely by mass transfer but in the early stages at least it is often possible to deconvolute the contribution to the overpotential associated with the charge transfer step. The involvement of this additional consideration invariably leads to expressions of a much higher degree of complexity and, in consequence, to the imposition of approximations or its restriction to limiting cases.

The starting point of all derivations is the equation of continuity

$$zF D \left( \frac{\delta C}{\delta x} \right)_{x=0} = zF C^b_o k_c \exp \left(-zF \frac{\omega}{RT} \right)$$  \hspace{1cm} (2.32)
The development of concentration profiles and the evaluation of the mass transfer flux follow as before from particular solutions of Fick's second law. Again, only the potentiostatic case will be considered here. Several exact analytical formulations of the potentiostatic current transients have been published. The best known is that relating linear diffusion to a planar electrode and takes the form

\[ i = i(t = 0) \exp(\lambda^2 t) \text{erfc}(\lambda t^{\frac{1}{2}}) \]  

where \( \lambda = k_a / D_o^{\frac{1}{2}} + k_b / D_R^{\frac{1}{2}} \)  

and \( i(t=0) \) is given by

\[ i(t=0) = zF (k_c c_o^b - k_c c_R^b) \]  

At short times, equation (2.33) approximates to

\[ i = zF k_c c_o (1 - 2(k_c + k_a)(t/D_o)^{\frac{1}{2}}) \]

A plot of \( i \) vs \( t^{\frac{1}{2}} \) is a straight line and a plot of \( \ln|\text{vs log} (\text{di/dt})^{\frac{1}{2}} | \) has a slope of \( 2.3 \text{RT}/2zeF \). At \( t=0 \), the extrapolated current \( i(t=0) \) is dependent only on \( k_c \) indicating that diffusion has no control of the initial current, and a plot of \( \ln|\text{vs log} i(t=0) \) has a slope of \( 2.3\text{RT}/z \text{mF} \). At \( t>0 \), mixed control applies, but at long times equation (2.33) simplifies to

\[ i = zF c_o^b (D_o^{\frac{1}{2}})^{\frac{1}{2}} \]
which corresponds to equation (2.31) and indicates that diffusion is the rate-limiting process. A plot of \( \eta \text{ vs } \log (d_i/d_t^{-1}) \) gives a slope of \( 2.3RT/zF \).

2.4. The Rotating Disc Electrode

The kinetic equations derived in the previous section can be experimentally demonstrated only under particular conditions which restrict the range of mass transfer to that of diffusion. In unstirred solutions this restricts the experiments to short times and limits the analysis to that of transients. The subsequent evaluation of the kinetic parameters is seldom straightforward. It often involves approximations and is invariably lacking in precision.

One of the ways out of this is to carry out the experiments over longer periods of time and to overwhelm the effects of the onset of accidental convection by forced mass transfer induced by forced convection; in brief, by stirring the solution or rotating the electrode.

The rotating disc electrode (RDE) was developed following the mathematical solution given by Levich for the hydrodynamic equations describing the rate of transfer of a substance in solution to a rotating disc surface, in terms of angular velocity of rotation \( \omega \), the diffusion coefficient \( D \), the concentration \( C \) of the substance and the kinematic viscosity \( v \) of the solution. The detailed
mathematical treatment is given in Levich's book(195), but in principle the technique involves solving equations relating to a fluid moving past a solid surface. Assuming axial symmetry to the disc, the differential equation describing mass transport to the surface of the disc involves Fick's second law with a term added to account for convective transport:

\[
\frac{\delta C}{\delta t} + v \times \frac{\delta C}{\delta x} = D \frac{\delta^2 C}{\delta x^2}
\]  

(2.38)

This leads to the concept of a thin diffusion boundary layer \( x_D \) close to the electrode surface. The greatest fall in concentration occurs within this layer and is given by

\[ x_D = 1.61 D^{1/6} v^{1/6} w^{-1/2} \]

(2.39)

In principle each electroactive species has its own value of \( x_D \), and \( x_D \) is much thinner than the hydrodynamic boundary layer given by

\[ x_H = 3.6 \left( \frac{v}{w} \right)^{1/2} \]

(2.40)

If the reaction is relatively fast (e.g. at high over-potentials), the surface concentration will be zero, and the current is determined by mass transport. This condition defines the limiting current density at the RDE which is independent of potential over a wide range and is given by

\[ i_L = 0.62 z F D^{1/4} v^{1/4} w^{1/2} \]

(2.40a)
If the reaction of the electrode has a higher activation energy, its rate is correspondingly lower and the current is controlled both by mass transport and by activation:

\[ \frac{1}{i} = \frac{1}{i_\infty} + \frac{1}{B w^\frac{1}{2}} \]  

(2.41)

where \( i_\infty \) is the activation-controlled current density at infinite rotation speed given by equation (2.35) and \( B \) is given by

\[ B = \frac{i}{w^\frac{1}{2}} \]  

(2.42)

The activation-controlled current density \( i_\infty \) can be evaluated by plotting \( 1/i \) vs. \( 1/w^\frac{1}{2} \) and extrapolating to zero, i.e. to infinite rotation speed. A plot of \( A vs \log i_\infty \) has a slope of 2.3RT/ \( \alpha F \), whereas a plot of \( A vs \log (di^{-1}/dw^\frac{1}{2}) \) has a slope of 2.3RT/ \( \alpha F \).

The above treatment is only valid for certain conditions, namely (a) laminar flow, (b) the thickness of \( x_D \) is much smaller than the disc radius, (c) uniform accessibility to the disc surface, and (d) steady-state conditions apply. These conditions are sensitive to factors such as surface roughness and edge effects.

2.5. Impedance

In the a.c. impedance technique, a small-amplitude sinusoidal potential signal is imposed on the electrode. The interphasial response to this signal is compared to the components of an equivalent
FIG. 2-2a Electrical analogue of the electrode interphase

\[ R_d + C_d = W \]

FIG. 2-2b Complex plane display - diffusion control
circuit containing a resistance and a capacitance connected in series. However, experimentally measured resistance and capacitance values will also include the charge transfer resistance $\Theta$, the double layer capacitance $C_{dl}$ and the solution resistance $R_{sol}$.

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

2.5.1. The Randle's method

This technique uses vector analysis based on an equivalent circuit for the cell impedance shown in figure 2.2a. The Warburg impedance ($W$) is a complex frequency-dependent quantity and is the impedance associated with the diffusional movement of charged species.

Randles derived the following expressions for $\Theta$ and $W$

$$\Theta = \frac{RT}{2F^{2}}k_0^{\alpha}(C_{o}^{s})^{\alpha}(C_{R}^{s})^{1-\alpha}$$

and

$$W = \sigma \omega^{-1} (1-j)$$

where $\sigma$ is the Warburg coefficient, $\omega$ is the angular frequency of the sinusoid and $j = (-1)^{\frac{1}{2}}$. The Warburg coefficient can be expressed as

$$\sigma = \frac{RT}{2F^{2}}k_0^{\alpha}(1/C_{o}^{s} D_{o}^{\frac{1}{2}} + 1/C_{R}^{s} D_{R}^{\frac{1}{2}})$$

In (2.43) and (2.45), $C_{o}^{s}$ and $C_{R}^{s}$ can be replaced by $C_{o}^{b}$ and $C_{R}^{b}$ if
measurements are made at the equilibrium potential. At potentials away from this value, \( \sigma \) and \( \Theta \) can be expressed in terms of bulk concentrations, provided that (2.43) and (2.45) are suitably modified. A disadvantage of this method is that if \( C_{dl} \) is influenced by the concentration of one of the electroactive species the results may become erroneous.

2.5.2. The Shuytera Method (198)

The Shuytera method uses the same equivalent circuit as figure 2.2a but the impedance is displayed as a vector in a Cartesian co-ordinate system – the so-called complex impedance plane. The components of the impedance vector are related to the absolute value \( |Z_s| \) and the phase angle \( \phi \) of the impedance by:

\[
Z_s' = |Z_s| \cos \phi \quad \text{real component} \quad (2.46)
\]

\[
Z_s'' = |Z_s| \sin \phi \quad \text{imaginary component} \quad (2.47)
\]

\[
Z_s = Z_s' - jZ_s'' \quad (2.48)
\]

where \( Z_s' \) and \( Z_s'' \) are given by

\[
Z_s' = R_{so1} + \frac{\Theta + \omega^{-1/2}}{(\omega^{1/2} C_{dl} + 1)^2 + \omega^2 C_{dl}^2 (\Theta + \omega^{-1/2})^2} \quad (2.49)
\]

\[
Z_s'' = \omega C_{dl} (\Theta + \omega^{-1/2})^2 + \omega^{-1/2} (\omega^{1/2} C_{dl} + 1) \quad (2.50)
\]
FIG. 2-3a Complex plane display - charge transfer control

\[
\omega = \frac{1}{\theta C_{dl}}
\]

FIG. 2-3b Complex plane display - mixed control
Two limiting situations arise from equation (2.48):

(a) If the activation polarisation term is neglected (i.e., $Q$ is small compared to $W$ - usually at low frequencies) then (2.48) reduces to

$$Z_s = R_{\text{sol}} + \theta + j\omega W'^{1/2} - j\left(\omega W'^{1/2} + 2\sigma^2 C_{dl,1}\right)$$

(2.51)

When the real and imaginary parts are plotted against each other we obtain a straight line of unit slope as shown in figure 2.2b.

(b) At high frequencies, the concentration polarisation ($W$) can be neglected for a fairly irreversible reaction, and (2.48) reduces to

$$Z_s = R_{\text{sol}} + \frac{\Theta}{1 + \omega^2 C_{dl}^2 \sigma^2} - \frac{j\omega C_{dl} \sigma^2}{1 + \omega^2 C_{dl}^2 \sigma^2}$$

(2.52)

In this case, if the real and imaginary parts are plotted against each other, a semi-circle is obtained. Values of $R_{\text{sol}}$, $\Theta$ and $C_{dl}$ may be computed from these plots as shown in figure 2.3a. At lower frequencies diffusion polarisation will give rise to a distortion of the semi-circle, as illustrated in figure 2.3b, leading to a line of unit slope eventually. The extent of this distortion is dependent upon the relative values of $\Theta$, $\sigma$ and $C_{dl}$. 
2.6. **Electrocrystallisation**

In crystal growth, the primary process is the incorporation of a atomic species into the crystal lattice. This can only occur where interaction can take place with several other species already in the lattice, such as a step line or kink site. In any other position on the surface, the species would simply be adsorbed. Therefore, before crystal growth can proceed, an edge has to be formed. This requires the formation of nuclei so that growth can occur at their peripheries.

The theoretical expression for electrochemical nucleation is based on two models - thermodynamic and atomistic. The atomistic model\(^{(199,200)}\) considers the interaction among atoms of clusters, using computed potential energies of the clusters to characterise a critical nucleus. The atomistic theory is valid for the system of high supersaturation, when small critical nuclei are formed.

The thermodynamic model uses the macroscopic surface energy to calculate the free energy for defining the critical nucleus. However, this value is not usually known, and application of the theory is restricted to the system of low supersaturation, when large clusters are formed. The thermodynamic model for nucleation and growth has been studied in great detail at Newcastle\(^{(201)}\). This group has studied the deposition of a new phase onto a surface under potentiostatic conditions. As a consequence, the theoretical interpretation of potentiostatic transients for electrocrystallisation is well established, and will be briefly considered.
2.6.1. Nucleation

The rate of nucleation is determined by the free energy necessary to form a critical size of nucleus.

Nuclei smaller than the critical size will dissolve and those of greater size will grow. For a two-dimensional cylindrical nucleus, growing on a flat electrode of the same material, the free energy of formation of the nucleus is

\[ \Delta G_n = \pi r^2 h p z F n / M + s \cdot 2 \pi r h \]  \hspace{1cm} (2.53)

where \( h \) is the height of the nucleus and \( s \) is the surface energy of the nucleus/solution interface; other symbols have their usual significance. Differentiation gives the critical nuclear radius, \( r_{\text{crit}} \), which must be reached for growth to take place:

\[ r_{\text{crit}} = \frac{s M / z F n p}{2} \]  \hspace{1cm} (2.54)

This occurs at a free energy given by

\[ \Delta G_{\text{crit}} = \pi M h s / z F n p \]  \hspace{1cm} (2.55)

To a first approximation, nucleation can be considered to be an activation process with a free energy of activation, \( \Delta G_{\text{crit}} \). Assuming a stationary distribution of nuclei, the nucleation rate \( A \) is given by

\[ A = k_n \exp \left( -\Delta G_{\text{crit}} / RT \right) \]  \hspace{1cm} (2.56)

where \( k_n \) is a frequency factor. Substitution of (2.55) in (2.56)
gives

\[ A = k_n \exp \left( -\pi M hs^2 N/zFRT \right) \]  

(2.57)

where \( N \) is the number of nuclei contributing to the growth of the deposit. Strictly speaking (2.57) is inexact because \( s \) is also a function of potential. Taking account of the potential dependence of \( s \) when differentiating equation (2.53) gives

\[ r_{crit} = \left( \frac{M_s}{2zFnp} \right) + \left( \frac{M/\rho zF}{n} \right) \frac{ds}{dn} \]  

(2.58)

which corresponds to (2.54).

The total number of nuclei contributing to the growth of a deposit will depend upon the time dependence of the nucleation process. Assuming that:

(a) nuclei usually form randomly on preferred sites, which may be surface imperfections, and (b) there is a uniform probability of conversion of growth centres into nuclei with time, the first order nucleation rate law is expressed by

\[ N = N_o \left( 1 - \exp \left( -At \right) \right) \]  

(2.59)

where \( N_o \) is the total number of available nucleation sites. Two limiting forms are encountered in the initial time range.

(a) When \( A \) is large, \( At \gg 1 \) for much of the period of growth and

\[ N \approx N_o \]  

(2.60)

so that the \( N \) nuclei are immediately nucleated onto almost all the initial available sites - instantaneous nucleation, and the probability
of nucleus formation is uniform with time.

(b) If $A$ is small, $A t \ll 1$ and

$$N = A N_0 t,$$  \hspace{1cm} (2.61)

which describes progressive nucleation. This applies when $A$ is small at preferred sites, or when there are no preferred sites for nucleation so that the total number of nuclei increases linearly with time whatever the magnitude of $A$. A solid electrode will often provide preferred sites for nucleation, e.g. dislocations at which the adsorption energy is large so that the surface energy at the nucleus/electrode interface is small.

2.6.2. The Growth of Isolated Centres

If the transport of material to a growing centre is not rate determining, then its rate of growth depends upon geometric factors. In the simplest case it is assumed that after imposition of the potential step, two-dimensional cylindrical nuclei form at discrete centres and grow laterally across the surface. It is also assumed that the rate of growth (current) is proportional to the area onto which deposition occurs, and that the growth area may be modified by overlap with adjacent nuclei. The above assumptions therefore permit the current to be written as

$$i = zF k_g S$$  \hspace{1cm} (2.62)

where $k_g$ is the electrochemical rate constant for the growth process at the growing surface of area $S$. Now the current is also equal to the rate of change of accumulated charge (phase) with time on the
surface. Therefore application of Faraday's law yields

$$i = zFp \frac{(dV/dt)}{M}$$

(2.63).

where $\rho$ and $V$ are the density and volume, respectively, of the deposited phase of molecular weight $M$. The derivative $dV/dt$ may be expanded using the chain rule with respect to the radius $r$. Equating (2.62) and (2.63) gives

$$\frac{dr}{dt} = \frac{Mk_E S}{\rho} \frac{(dV/dr)}{}$$

(2.64)

which upon substitution for $S$ and $V$ for a cylinder

$$a = 2\pi rh$$

(2.65)

$$V = \pi r^2 h$$

(2.66)

gives

$$\frac{dr}{dt} = \frac{Mk_E}{\rho}$$

(2.67)

Integrating (2.67) with respect to time gives

$$r = \frac{Mk_E t}{\rho}$$

(2.68)

(assuming $r = 0$ at $t = 0$). Substitution for $r$ in equation (2.65) followed by insertion of $S$ into (2.62) therefore gives the current for the growth of a single centre as a function of time:

$$i = 2 zFk_E^2 \frac{hM}{\rho} t$$

(2.69)

Equation (2.69) is readily combined with the nucleation laws (2.60) and (2.61) to allow for the contributions from all of the centres and to give the total growth rate. The results are
for two dimensional growth and instantaneous nucleation and

\[ i = (2zF^2MN^2 k^2_e / \rho) t \quad (2.70) \]

for progressive nucleation.

\[ i = (2zF^2MN^2 k^2_e / \rho) t^2 \quad (2.71) \]

2.6.3. The Overlap of Growth Centres

Equations (2.70) and (2.71) hold only at short times before the growing centres begin to coalesce. The form of the expression describing the complete growth process can be obtained by allowing for the effects of this overlap. This can be evaluated by making use of the Avrami theorem (202),

\[ \frac{dH}{dH_E} = 1 - H \quad (2.72) \]

where \( H \) is the fraction of the surface covered and \( H_E \) is the fraction that would be covered if the centres were all separated and there was no overlap. This equation holds if the probability of finding a centre is uniform over the surface and there is no interaction of growing centres with the boundaries of the electrode surface. For instantaneous nucleation

\[ H_E = N_0 \pi r^2 \quad (2.73) \]

and for progressive nucleation

\[ H_E = \int_0^t r(u)^2 (dN/dt)_{t-u} \; du \quad (2.74) \]
Substitution for \( r \) in terms of \( t \) using (2.68) gives

\[
\Pi_E = \pi N_o M^2 k_E^2 t^2/\rho^2 \quad \text{(instantaneous)}
\]

\[
\Pi_E = \pi N_o AM^2 k_E^2 t^3/3\rho^2 \quad \text{(progressive)}
\]

Integration of (2.72) to yield \( \Pi \) in terms of \( H_E \), and hence in terms of time, by substitution of equations (2.75) and (2.76), yields

\[
\Pi = 1 - \exp\left(-\pi N_o M^2 k_E^2 t^2/\rho^2\right) \quad \text{(instantaneous)}
\]

\[
\Pi = 1 - \exp\left(-\pi N_o A M^2 k_E^2 t^3/3\rho^2\right) \quad \text{(progressive)}
\]

Finally, the volume per unit of area of total surface is \( V = \Pi h \), which upon substitution into (2.63) yields the desired expression for the transients. For instantaneous nucleation and two dimensional growth:

\[
i = (2zF M N_o k_E^2 h^2/\rho) \exp\left(-\pi^2 N_o k_E^2 t^2/\rho^2\right)
\]

and for the progressive case:

\[
i = (zF M N_o A k_E^2 h^2/\rho) \exp\left(-\pi^2 N_o A k_E^2 t^3/3\rho^2\right)
\]

Comparison of equations (2.79) and (2.80) with equations (2.70) and (2.71), respectively, shows that the effect of overlap is accounted for by the exponential terms in time. As \( t \) approaches zero, equation (2.79) reduces to (2.70) and equation (2.80) reduces to (2.71). The potentiostatic transients according to (2.80) and
Fig 2.4 Theoretical current time curves according to
(a) equation (2.80)

(b) equation (2.79)

(c) Total current transient for layer by layer growth showing contribution from individual layers
are plotted in Figures (2.4a) and (2.4b) respectively, where $i = 0$ at $t = 0$ and $t = \infty$. Figures (2.4a) and (2.4b) are reduced variable plots using $i/i_m$ and $t/t_m$, where $i_m$ and $t_m$ are the parameters of the maximum which are readily found by differentiation. For instantaneous nucleation

$$t_m = \frac{p}{(2\pi N_0)^{\frac{1}{2}}} M k_E$$  \hspace{1cm} (2.81)

$$i_m = (2\pi N_0)^{\frac{1}{2}} \frac{zF k_e}{T} e^{-\frac{Z}{2}}$$  \hspace{1cm} (2.82)

and for progressive nucleation

$$t_m = \frac{2\rho^2/\pi M^2 N_0 \Delta k_E^2}{2}$$  \hspace{1cm} (2.83)

$$i_m = zF(4\pi N_0 \Delta k_E^2 \rho/\mu)^{\frac{1}{2}} e^{-\frac{Z}{2}}$$  \hspace{1cm} (2.84)

In both cases, the time at which the maximum occurs decreases with increasing growth rate constant $k_E$, the dependence being greatest for instantaneous nucleation. Also the size of the maximum increases with $k_E$, and the dependence is again greater for instantaneous nucleation.

The analysis given above for the instantaneous and progressive nucleation of two-dimensional phases can be extended to other geometries by using appropriate expressions for $S$ and $V$ instead of equations (2.65) and (2.66). Similar expressions for other growth models, including cases where diffusion in solution is assumed to be rate determining, are summarised by Harrison and Thirsk (201).
The effect of overlap on the transient for instantaneous nucleation and three-dimensional growth (right circular cones) has been considered by Armstrong et al. \(^{(203)}\). The following expression was obtained:

\[
i = zFk_2(1 - \exp(-\frac{\pi k_2 n^2 t^2}{f^2}))
\]

where \(k_1\) and \(k_2\) are the rate constants for growth parallel and perpendicular to the plane respectively. At long times the current attains a constant maximum, rather than approaching zero as predicted for the two-dimensional case. Only in very few instances (e.g. deposition on amalgams) is true monolayer formation apparently found. In the great majority of cases, the formation of successive layers of deposit is observed. This gives rise to significantly different transients than those given by equations (2.79) and (2.80), especially at times greater than \(t_m\). Using equation (2.80), Armstrong and Harrison \(^{(204)}\) have achieved a solution by numerical integration.

The contributions from the first five monolayers are plotted schematically in figure (2.4c), together with the total current, which is obtained by summation. The steady state, which is constant, is reached after the oscillations have died away. Armstrong and Metcalfe \(^{(205)}\) have refined this approach and have shown that the limiting value is reached after four or five monolayers.

2.7. The Linear Potential Sweep

The advantage of linear sweep voltammetry (LSV) is that it shows up all electrochemical phenomena (double-layer and Faradaic) in the system over a wide potential range in the course of recording
a few scans at differing sweep rates. Combined with the use of a rotating-disc electrode it provides a powerful tool to locate phenomena and also to identify those which involve mass transfer control. Although usually other techniques (rotating disc electrode, potential step, impedance) are preferred for the identification of processes and the acquisition of precise electrode kinetic data, theoretical treatments for "stationary electrode polarography" have been developed for a number of model systems, together with reversible and irreversible multiple-step electrode processes (with diffusion being taken into account) on plane electrodes (206-210).
CHAPTER 3

EXPERIMENTAL TECHNIQUES

3.1. Cells

Electrolytic cells were made from borosilicate glass and conformed to one of four patterns.

3.1.1. Rotating-disc-cell

A cell was devised for incubation in a liquid medium for low temperature studies, but which could also be used for studies at ambient temperature. Figure 3.1. shows a schematic diagram of the three compartment cell used, which is free of joints and taps. Normally, the reference electrode is connected to the working electrode solution via a Luggin capillary and a closed liquid-seal tap. In this case, the liquid-seal tap was replaced by forming a ground glass seat between the reference electrode and the reference electrode compartment. The cell is also fitted with facilities for gassing the working electrode solution via a porous glass frit (not shown). For a.c. impedance experiments on planar Pb electrodes, the counter electrode was placed in the bottom of the working electrode compartment and not in the counter electrode compartment.

3.1.2. Cell for a.c. impedance experiments on porous Pb rotating electrodes

Because of the requirements for a large surface area counter electrode parallel to the working electrode, a large volume, one compartment, cell was manufactured as shown in figure 3.2. This cell has facilities for gassing and electrode rotation, and has the normal Luggin capillary arrangement for the reference electrode.
Figure 3.1. Schematic drawing of cell used for potentiostatic studies at 23°C and -30°C, and a.c. impedance studies on the planar Pb electrode at 23°C.
Figure 3.2. Photograph of cell used for a.c. impedance studies of porous Pb electrodes at 23°C. Picture shows Luggin probe, reference electrode, working electrode, gas bubbles and counter electrode.
Fig 3.3 Galvanostatic polarisation cell

A working electrode
B reference electrode
C counter electrode
3.1.3. **Cell for galvanostatic discharge of battery plates**

For cycling experiments, a battery negative plate was tested between two counter electrodes of lead sheet of the same nominal area. The cell was simply a tank with no facilities for solution gassing. The potential of the negative electrode was measured with a reference electrode via a Luggin capillary.

3.1.4. **Cell for galvanostatic charging of porous rotating Pb electrodes**

Galvanostatic charging was carried out in the upward facing position to prevent hydrogen gas retention in the porous matrix. This was achieved using the cell depicted in figure 3.3.

3.1.5. **Cell cleaning**

Cells were prepared by soaking in a 50:50 mixture of nitric acid and sulphuric acids for a minimum of 3 days. This was followed by a minimum of 5 washes in tridistilled water and a final soaking in tridistilled water for 24 hours before use.

3.2. **Electrodes**

3.2.1. **Counter electrodes**

For potentiostatic experiments on porous and planar Pb electrodes, a glassy carbon rod (Morganite) was used. For a.c. impedance experiments on planar Pb electrodes, Pb sheet (Koch-Light 5N purity) of large surface area was placed parallel to the working electrode. Because of the large surface area required for a.c. experiments on porous Pb rotating electrodes ($\approx 14000 \text{cm}^2$), a battery plate was used. This negative plate (Code MNA; Chloride) had a Pb plated Pb-alloy grid and was galvanostatically charged before...
Figure 3.4. Schematic diagram of the wick-type Hg/Hg$_2$SO$_4$ electrode
Figure 3.5. Schematic drawing of Pb rotating disc electrode

Figure 3.6. Schematic diagram of equipment for rotating-disc experiments at low temperatures.
use against Pb sheet (as above). Porous Pb rotating electrodes were charged in the cell of figure 3.3 against a Pb rod (Koch-Light 5N purity). Galvanostatic cycling experiments of battery plates were carried out against two sheet Pb electrodes (as above) of the same nominal area.

3.2.2. **Reference electrode**

Potentials were always measured with reference to a $\text{Hg/Hg}_2\text{SO}_4$ electrode in $\text{H}_2\text{SO}_4$ of the same concentration as the working solution. The construction of the wick-type reference electrode is shown in figure 3.4.

3.2.3. **Planar Pb electrodes**

Test electrodes were always manufactured as rotating-disc-electrodes, as shown in figure 3.5. Pb electrodes of $0.071\text{cm}^2$ were manufactured by machining rod (Koch-Light 5N purity) and setting in a Teflon shroud. The electrode shroud was threaded to fit a Teflon electrode holder, and a brass retaining mount specially manufactured for the Scanning Electron Microscope (SEM). The rotating-disc-electrode assembly was clamped to a rotating stainless-steel shaft by a stainless-steel grub screw, and electrical contact between the electrode and shaft was effected using a stout steel spring (soldered at the electrode end). A mercury pool provided the electrical contact between the rotating electrode and the external circuit.
3.2.3.1. **Planar Pb electrode preparation**

Electrodes were pretreated by lightly polishing on different grades of roughened glass using tridistilled water as lubricant in order to remove any embedded material. Immediately prior to an experiment the electrode was etched (60s; HNO₃ 1.58M) in order to produce a surface free from oxides. It was then rinsed several times with tridistilled water and immersed in the electrolyte solution while still wet from the final rinse water. As soon as the rest potential had been attained the electrode was held at a cathodic potential close to the onset of hydrogen evolution for two hours.

3.2.4. **Porous Pb electrodes**

3.2.4.1. **Porous Pb rotating electrodes**

These were manufactured in a similar manner to figure 3.5, except that the Pb rod was recessed by 0.76mm below the front of the electrode shroud. This recess was flush pasted with a paste of one of four constitutions as shown in Table 3.1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Paste</th>
<th>Paste</th>
<th>Paste</th>
<th>Paste</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grey leady oxide, remainder</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>BaSO₄, 0.2%</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Carbon black, 0.2%</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Indulin C, 0.2% (a lignosulphonate)</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Dry ingredients were mixed with a 50:50 mixture of tridistilled water and 1400 s.g. sulphuric acid, using a mortar and pestle. The paste
was applied to the electrode and allowed to set in a 100% humid atmosphere for 24 hours and then dried at 20°C. Electrodes were then placed in 0.1M H₂SO₄ and reduced at 0.02Ag⁻¹ in the charging cell of figure 3.3 until hydrogen was freely evolved, and a charge of at least four times the theoretical capacity (16.85C) had been passed. In this way a porous deposit was produced similar to that associated with a conventional automotive negative (1.52mm thick but both sides utilised). After formation, the electrode was washed in tridistilled water, fitted into the electrolytic cell, and cycled until a constant response was observed. The ambient temperature cycling regime involved charging at -1050mV until a negligible, constant, current was measured, and then galvanostatically discharging to 7.9% conversion at 0.01Ag⁻¹. The degree of discharge was expressed as a percentage of the theoretical capacity of the electrode, which was calculated at 16.85 C for the total conversion of the active material.

3.2.4.2. Porous Pb battery plates

Negative electrodes were manufactured using pastes of the following constitution:

<table>
<thead>
<tr>
<th>Material</th>
<th>Paste</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grey leady oxide, remainder</td>
<td>+</td>
</tr>
<tr>
<td>BaSO₄, 0.41%</td>
<td>-</td>
</tr>
<tr>
<td>Carbon black, 0.29%</td>
<td>+</td>
</tr>
<tr>
<td>Indulin C, 0.2% (a lignosulphonate)</td>
<td>-</td>
</tr>
</tbody>
</table>
Dry ingredients were mixed as above and then applied to Pb-6% Sb battery grids (70x50mm) and allowed to set as above. Formation conditions were also as above.

3.3. Electrolyte

Solutions were normally prepared using AnalaR grade reagents and tridistilled water. For a.c. impedance experiments, the electrolyte was prepared from Aristar grade H$_2$SO$_4$.

Experiments were normally carried out under an atmosphere of nitrogen (B.O.C. white spot), which had been deoxygenated by passing over copper turnings at 400°C. The gas was then passed through water and introduced to the cell through a porous glass frit. For experiments using aerated solutions, washed air was introduced into the cell using a rotary pump.

3.4. Temperature

Experiments were generally carried out at an ambient temperature of approximately 23°C. For rotating-disc experiments at -30°C, temperature control apparatus is schematically shown in figure 3.6. The incubation system for the test cell was a lightweight, polystyrene insulated, polypropylene bath filled with methanol. The bath was fitted with a double-glazed observation window and could be raised and lowered by a standard laboratory jack. Using a combination heater (300W)/thermistor/thermostat temperature control system with the Townson-Mercer refrigerator unit, temperatures down to -70°C can be controlled to ± 1°C.
Fig. 3.7a L.S.V and potentiostatic pulse circuit

Fig. 3.7b Circuit for galvanostatic experiments

\[ R_L, \text{ Load resistor} \]
3.5. **Potentiostatic Experiments**

Potentiostatic experiments were carried out at stationary and rotating discs. The circuit used for L.S.V. and potentiostatic pulse experiments is shown in figure 3.7a. For ambient temperature experiments a normal potentiostat (Chemical Electronics, Type TR 70/2A) was used, but for low temperature experiments an IR compensating model (Thompson, Ministat 251 I.R.) was used. The function generator was manufactured by J. Dawson (Newcastle upon Tyne) and the electrode response was monitored with an XY recorder (Bryans, series 26700) and/or a digital storage oscilloscope (Gould series O$4000). The potential of the working electrode was measured using a multimeter (Hewlett Packard, 3490A).

For steady-state and rotating-disc experiments, the function generator was not used and the cell current was monitored by measuring the voltage drop across a counting resistor in the counter electrode circuit with a multimeter (Hewlett Packard, 3490A).

3.6. **Galvanostatic Experiments**

A generalised circuit for galvanostatic experiments is shown in Figure 3.7b.

3.6.1. **Solution IR drop measurement**

The solution resistance between the tip of the Luggin capillary and the working electrode was measured by galvanostatic pulse. Here, the current step was supplied at P by a Hewlett Packard pulse generator (214A), and the E-t response was measured at R with a digital storage oscilloscope (Gould, series O$4000).
At a normal Luggin-working electrode gap of approximately 1mm, the resistance using 5M H₂SO₄, was found to be ~0.03Ω at ambient temperature and ~0.3Ω at -30°C. These values are in good agreement with the conductivity values of figure 1.2.

3.6.2. **Galvanostatic cycling of battery plates**

For cycling of battery plates the current source, P, was a Chemical Electronics TR20/50A used in the galvanostatic mode, and the E-t response was measured with a Yt recorder (Bryans). Current could be monitored by using an ammeter (AVO) in circuit.

3.6.3. **Galvanostatic charge and discharge of porous microelectrodes**

For low rate charges and discharges, a constant current power pack (Thurlby) was used at P and the current was monitored by using an ammeter (AVO) in series. The potential of the electrodes was measured at R using a multimeter (Gould, Beta).

3.7. **Impedance Measurements**

Impedance measurements on porous and planar Pb electrodes were carried out by using a frequency response analyser (Solartron 1172). It essentially consists of a programmable generator that provides the perturbing sinusoidal signal, a correlator to analyse the response of the system, and a display of the results. The fundamental response of a system to a sinusoidal perturbation of the form, ΔE sin wt, will be of the form A sin (wt + θ). The FRA has the advantage of rejecting all harmonics present in the output of the system and minimises the effect of random noise. The generator was programmed to sweep through a large frequency range from 9.9kHz.
Fig 3.8 Circuit for automated impedance measurements

Potentiostat

SOLARTRON 1172

Generator

ΔE
Δi

Analyser

XY Recorder

Data Transfer Unit

Teletype

Tape Punch
to 1mHz, and sampled at ten points per frequency decade. The response was recorded as the real and imaginary parts of the impedance simultaneously on a tele-type printer, a tape-punch and an XYt recorder (Bryans, series 26000).

The time required for the FRA to make a single measurement is equal to the period of the signal (i.e. 1 second at 1 Hz) and this becomes a major contribution to the total experimental time at low frequencies. Automated impedance measurements were carried out under potentiostatic conditions using a Kemitron potentiostat and the circuit is shown in figure 3.8.

3.8. **Scanning Electron Microscope (SEM)**

The SEM was used to examine the surfaces of porous and planar Pb electrodes, and cross-sections of cycled battery negative plates.

Before examination, electrodes were removed from the electrolyte and thoroughly rinsed in tridistilled water. Rotating electrode assemblies (planar and porous) were then disassembled and the threaded Teflon electrode shroud and electrode were rinsed in acetone. Pieces were broken from charged battery plates, followed by further water rinses and a final rinse in acetone. For examination, rotating electrodes were mounted in the specially made brass holder. Using this holder and recording the coordinates of the SEM mounting stage, the same area of electrode could be re-examined after each cycle. The dried pieces of battery plate were mounted on Al stubs with conducting adhesive so that the cross-section of the electrode could be examined. Examinations were carried out at the same distance from the surface of the plate for all electrodes tested. The instrument used was a Stereoscan Mark 2 (Cambridge Instruments).
4.1. Introduction

In spite of its long history, it is clear from the large volume of work recently published that interest in the electrochemical science and technology of the lead-acid battery is increasing. The basic electrochemistry of the negative electrode has only been satisfactorily studied relatively recently (see Chapter 1). This was partly due to the slow progress in the development of suitable instrumentation, and partly because of the difficulties involved in investigating the kinetics of an electrode at which a solid phase is being formed.

Investigations by the Newcastle group on the electrochemical oxidation of solid Pb in H₂SO₄ have been reviewed in Chapter 1. At potentials slightly positive to the Pb/PbSO₄ potential, the active dissolution of lead has been shown to occur by a fast reversible dissolution controlled reaction, to produce Pb(II) species which diffuse away from the electrode surface. However, there are considerable difficulties in investigating the Pb(II)/Pb reaction in the limited "solution region". Not the least of these is the preparation of electrodes to obtain reproducible results. Indeed, this uncertainty results in enough scatter in all the experimental data on this system to throw some doubt on the assessment that the reaction is completely free from any charge transfer control. A further difficulty in tackling the kinetics is the inaccessibility of the reduction reaction in the "solution region". This arises from the intrusion
of the h.e.r. which obscures the precise measurement of the small currents involved. Also, work in other laboratories has indicated that the demonstration of a "solution region" depends on $\text{H}_2\text{SO}_4$ concentration and temperature. In 1M $\text{H}_2\text{SO}_4$, the solubility of $\text{PbSO}_4$ is high (see Figure 1.1), and the "solution" reaction is more easily demonstrated. In 5M $\text{H}_2\text{SO}_4$, when the solubility of $\text{PbSO}_4$ is low, the solid-state formation of $\text{PbSO}_4$ predominates (5M $\text{H}_2\text{SO}_4$ is the normal electrolyte concentration of the charged lead-acid cell).

Other published work suggests that for other $\text{Pb(II)/Pb}$ exchanges at both solid and amalgam electrodes kinetic data can be measured. Thus, Haruyama (211) finds that for 50mM $\text{Pb}^{2+}$ supported in 1M $\text{HClO}_4$, the standard exchange current is 0.3 Acm$^{-2}$. For the amalgam exchange the value of $k^0$ in various electrolytes varies in the range 0.2 - 5 cm s$^{-1}$ corresponding to an exchange current density in the range 40 to 10$^3$ Acm$^{-2}$ (212). The charge transfer coefficient (212) is variously reported as 0.5 for the simple amalgam exchange in $\text{HClO}_4$ solution to 1.0 for the amalgam exchange in 1$^{-}$ solution. The value of the charge transfer coefficient on the solid electrode has been determined as 0.8 in nitrate supported electrolyte (213, 214) and 0.6 in the $\text{SO}_4^{2-}/\text{ClO}_4^-$ mixture (211).

The study of porous lead electrodes has received relatively little attention, although this aspect of the electrochemistry of lead is highly relevant to the modern lead-acid industry. This Chapter describes experiments made with solid and porous electrodes to investigate the "solution" reaction of the porous electrode.
4.2. Experimental

The manufacture and pretreatment of solid and porous rotating Pb electrodes has been described in Chapter 3. Paste A of Table 3.1 was used to manufacture the porous electrode and other experimental details have been given. Working solutions were either 1 or 5 M H$_2$SO$_4$ and all measurements were made at ambient temperature.

4.3. Results and Discussion of Potentiostatic Experiments

4.3.1. Solid Electrodes

The results of a number of experiments made with 5 M H$_2$SO$_4$ indicated that the potential range in which only a solution reaction could be observed was much smaller than with 1 M H$_2$SO$_4$. This is in agreement with a lower solubility of PbSO$_4$ at the higher concentration (see Figure 1.1) and confirms the observations of other workers (17, 153).

In the higher concentration, the driving force for the development of solid PbSO$_4$ at the electrode is increased considerably, and true steady-state dissolution currents could not be observed at the rotating disc. The results of experiments conducted in 1 M H$_2$SO$_4$ are discussed below.

4.3.1.1. Linear Sweep voltammetry

If the positive limit of the potential sweep was limited to -930 mV (corresponding to an overpotential of 40 mV) then for the sweep speeds employed (~135 mV s$^{-1}$) the charge in the positive and negative going sweeps on either side of the equilibrium potential were equal. This indicates that the anodic electrode products were able to leave the electrode as required by the production of solution soluble Pb$^{2+}$ only.
At more positive potential limits, charge not recovered in the positive excursion was recorded at potentials negative of $E_r$. This indicates the development of a solid phase, PbSO$_4$, at the electrode at potentials more positive than $-930$ mV. Figure 4.1 shows that this limit depends on the sweep speed, at the higher sweep speed the positive limit is increased as indicated in Table 4.1. The limit was quite reproducible and could be detected to a precision of 1 mV with the experimental set-up. It seems likely that solid lead sulphate is developed on the electrode by a dissolution-precipitation mechanism and that at the slower sweep speeds time is available for PbSO$_4$ deposition at a smaller overpotential.

**TABLE 4.1**

Maximum anodic potential limit before the onset of solid phase deposition at different sweep rates

<table>
<thead>
<tr>
<th>Sweep Speed, mV s$^{-1}$</th>
<th>Maximum anodic potential, mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25</td>
<td>-926</td>
</tr>
<tr>
<td>13.10</td>
<td>-922</td>
</tr>
<tr>
<td>42.50</td>
<td>-913</td>
</tr>
</tbody>
</table>

Plots of $E$ vs log $i$ from the foot of the oxidation wave gave Tafel slopes of 36 mV, in good agreement with the work of Le Mehaute (153). The significance of this Tafel slope will be further discussed below.
Figure 4.1. LSV curves for a solid lead electrode between -1200mV and -916mV in 1M H$_2$SO$_4$ at varying sweep rates
(a) 1.25 mV s$^{-1}$, (b) 4.05 mV s$^{-1}$, (c) 13.1 mV s$^{-1}$, (d) 42.5 mV s$^{-1}$ and (e) 135 mV s$^{-1}$.

Figure 4.2. Typical $i^{-1}$ vs $w^{-2}$ plots for a solid lead rotating disc electrode in deoxygenated 1M H$_2$SO$_4$ (23°C) at various potentials.
(A) -955mV, ( ) -952mV, ( ) -951mV, ( ) -947mV
4.3.1.2. Rotating disc experiments

In order to further investigate the kinetics of the dissolution process within the "dissolution region" the effect of rotation speed on the steady-state current was investigated in the limited potential range -947 mV to -957 mV. The rotation speed dependence of the current at constant potential for a metal disc electrode freely dissolving at a rate controlled by charge transfer and mass transport in solution has been discussed in Chapter 2 using equations (2.38) to (2.42). For a Pb dissolution current, \( i \), which is much less than the limiting current owing to \( \text{H}^+ \) and \( \text{HSO}_4^- \) diffusion, and a first order removal of \( \text{Pb}^{2+} \) from the lattice, the modified equations of Armstrong and Bulman (215) can be used. Hence

\[
\frac{1}{i} = \frac{1}{i_\infty} + \frac{k_c 1.61 D_0 \frac{q}{1.6} \frac{v}{w}}{i_\infty}
\]

At infinite rotation speed, the current passing is controlled only by the process of charge transfer, and this current depends on potential according to

\[
\frac{i}{i_{\text{Fk}}} = C_o \frac{e^{E-E^0}}{E_{\text{F}}/RT} \]

Therefore plots of \( i^{-1} \) versus \( w^{-\frac{1}{2}} \) should have an intercept of \( i_\infty^{-1} \) and a slope showing a 30mV/decade Nernstian dependence on potential. Also, plots of \( \log i_\infty \) versus potential are Tafel curves corresponding to the charge transfer reaction. Figure 4.2 shows typical \( i^{-1} \) versus \( w^{-\frac{1}{2}} \) plots for a solid lead electrode in deoxygenated 1M \( \text{H}_2\text{SO}_4 \). These plots were extrapolated to give \( i_\infty \) and \( \log i_\infty \) versus potential is plotted in Figure 4.3.
The slope of the Tafel curve in Figure 4.3. was approximately 36mV/decade. This is somewhat surprising for a two electron charge transfer reaction, Pb(0)→Pb(II), and indicates a value of the cathodic charge transfer coefficient of ≈ 0.84. This seems rather a low value for this reaction, particularly remembering that potentials are negative of the standard potential. A better explanation for the observed Tafel slope is that the exchange is two 1 - e steps, as discussed in section 2.2 (see equations 2.20 -2.24):

\[ \text{Pb} \rightleftharpoons \text{Pb}^+ + e \quad \text{lattice} \]  \hspace{1cm} (4.3)

\[ \text{Pb}^+ \rightarrow \text{Pb}^{2+} + e \quad \text{rate determining} \]  \hspace{1cm} (4.4)

with a transfer coefficient for equation (4.4) of ≈ 0.7. The observed Tafel slope results if the reaction (4.3) remains in equilibrium in the Nernstian sense. This seems to be not unattractive in view of the probable small energy of hydration of a Pb\(^+\) species, compared with the solvent reorganisation energy required for the Pb\(^+\)→Pb\(^{2+}\) change. Extrapolation of the Tafel curve of Fig. 4.3. to the standard(E\(^0\)) potential (-0.788 V on the present scale) gives a value for the standard exchange current of 1.5 Acm\(^{-2}\) which compares quite well with other values\(^{(211)}\) from impedance measurements in sulphate electrolytes. This extrapolation is over a long interval of potential and gives rise to a great deal of uncertainty due to the possible curvature of the E-E relationship. It is, however, unlikely that a larger potential range will be available for the extrapolation due to the positive limit imposed by the sulphate precipitation reaction and the negative limit imposed by the hydrogen
Figure 4.3. Semilogarithmic plot of $\log i_\infty$ vs. potential from the data of Fig. 4.2. Line drawn at 36 mV/decade.

Figure 4.4. Semilogarithmic plot of $\log \sigma = \frac{d_i}{d\omega^{-1}}$ vs. potential from the data of Fig. 4.2. Line drawn at 30 mV/decade.
evolution reaction.

Figure 4.4. shows a plot of the log slopes of the $i^{-1}$ versus $w^{-1/2}$ lines against E. This plot had a 30mV/decade dependence, confirming that the Pb dissolution reaction involves two electrons.

The above conclusions are in apparent contradiction with the Newcastle group, who concluded that Pb dissolution was a fast reversible 2e process. The impedance measurements of Armstrong and Bladen showed virtually no evidence for charge transfer control. However, Fleming and Harrison always observed high frequency semi-circles in the solution region but concluded that this phenomenon was due to a precipitated film of PbSO$_4$ on the electrode surface. Also, positive current intercepts at infinite rotation speed were observed by Fleming and Harrison for Pb dissolving in 1M H$_2$SO$_4$. The Tafel slopes of 36mV obtained by LSV in section 4.3.1.1., and confirmed elsewhere, also support the conclusion that the charge transfer reaction proceeds via two single electron transfers (see equations 4.3 and 4.4).

4.3.1.3. Potential step experiments

In order to confirm the rotating disc measurements, potential step experiments were made by stepping from a potential in the polarizable region to one in the "dissolution region" and observing the transient current.
Figure 4.5. Typical $i$ vs $t$ plots for a solid lead electrode in 1M $\text{H}_2\text{SO}_4$.

(•) -949 mV, (■) -951.5 mV, (▲) -953 mV, (▲) -958 mV.

Figure 4.6. Semilogarithmic plot of $\log_i$ at $t = 0$ vs potential for a solid lead electrode in 1M $\text{H}_2\text{SO}_4$. The broken line indicates a slope of 40 mV/decade.
The theoretical equations for a potential step experiment, where the electrode reaction is controlled by charge and mass transfer, is given by equations 2.25 to 2.37 of Chapter 2. In the limit of very small time, the current density is proportional to $t^\frac{1}{2}$ as given by equation 2.36

$$i = zF k_c \frac{c_0}{b} \left(1 - 2 \left(k_c + k_a\right) \left(t/D_0 \eta\right)^{\frac{1}{2}}\right)$$

Thus, a plot of $i$ versus $t^\frac{1}{2}$ should give a straight line with an intercept of $i(\infty)$, the charge transfer current.

Figure 4.5 shows typical $i$ versus $t^\frac{1}{2}$ plots taken from pulses into the lead dissolution region from a potential of $-1300\text{mV}$, and figure 4.6 shows the plot of log $i$ (t=0) versus $E$. It should be noted that $i(t=0)$ is equivalent to the $i(\infty)$ of the rotating disc experiments, and comparison of figures 4.3 and 4.6 demonstrates a reasonable agreement for the measured currents. Unfortunately, the data of figure 4.6 conforms to a lower Tafel slope of 22mV/decade. However, analysis of these transients by the usual extrapolation method is only valid provided that a relatively small amount of lead is dissolved from the electrode during the double layer charging period. Assuming the equivalence of the present experiments to the $\text{Pb}^{2+}/\text{Pb(Hg)}$ electrode, with a value of $k^0$ in the region of 1 cm s$^{-1}$, it would be required to charge the double layer in the sub-$\mu$s range, which is not possible.
Figure 4.7. Steady-state current-voltage curves for rotating electrodes in 1M H₂SO₄ at 16.7 Hz with a sampling time of 45s. Upper figure is for the porous lead rotating electrode, and the lower figure is for a solid lead rotating disc electrode.
with a single potentiostatic step, using a conventional
pulse generator/potentiostatic circuit. Also, transients
were recorded using an XYt recorder, with a rise time of
approximately 100ms. At long times, the current in the
transient decayed as $t^{-\frac{1}{2}}$ (see equation 2.37) and plots
of $E$ versus $\log(\frac{dE}{dt}t^{-\frac{1}{2}})$ gave a slope of $\sim 33\text{mV/decade}$,
confirming that Pb dissolution is a 2e process$^{(12)}$.

4.3.2. Porous electrodes

Figure 4.7. shows that there is a considerable
difference in current obtained from the same nominal
diameter electrode, and it is clear that the difference
between the magnitudes of the currents is due to the
porous structure on the "inside" of the electrode.
Attempts were made with both 1M and 5M $\text{H}_2\text{SO}_4$ to obtain
a rotation speed dependence for the porous electrode,
however, it was found that with these two electrolytes
none could be detected. The observation of no rotation
speed dependence of current follows from a recognition that
the electrode/electrolyte situation within the pores is
unaffected by rotating the electrode, since the majority
of the current comes from "inside" the electrode, and
rotation modifies only the diffusion layer thickness.

This hypothesis was tested by investigating the
rotation speed dependence of a thin layer of porous Pb,
obtained by the reduction of a layer of lead sulphate
formed on solid lead. Linear relationships were obtained
by plotting $i^{-1}$ against $\omega^{-\frac{1}{2}}$ indicating that the diffusion layer geometry was affected as predicted by Levich (195). Table 4.2 shows the characteristics of these plots over a range of potential which indicate that in this case $i_\infty$ is larger, and the slope $di^{-1}/d\omega^{-\frac{1}{2}}$ less than with solid electrodes. These data confirm that the effect of the porosity is to reduce the relative rotation speed dependence of the current due to the extra current contribution from the porous structure beneath the surface, which is unaffected by the hydrodynamic flow. The layer of porous material was thickened by cycling and it was observed that this resulted in an increase in $i_\infty$ and a decrease in the slope $\sigma$. Thus the rotation speed dependence is reduced as the layer is thickened.

**TABLE 4.2.**

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$E$, mV</th>
<th>$\sigma (di^{-1}/d\omega^{-\frac{1}{2}})$</th>
<th>$i_\infty$, $\mu$Acm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thin porous</td>
<td>-945</td>
<td>0.0034</td>
<td>127.5</td>
</tr>
<tr>
<td></td>
<td>-950</td>
<td>0.0070</td>
<td>67.0</td>
</tr>
<tr>
<td>Solid</td>
<td>-945</td>
<td>0.0282</td>
<td>76.5</td>
</tr>
<tr>
<td></td>
<td>-950</td>
<td>0.0354</td>
<td>36.0</td>
</tr>
</tbody>
</table>

That a porous electrode behaved in a similar manner to a solid one as far as the existence of a well defined diffusion layer is concerned was tested using the well-known oxygen reduction reaction (16) at a lead surface.
Fig. 4.8. The rotation speed dependence of the lead electrode for the oxygen reduction reaction. Figure 9a shows steady-state current-voltage curves at cathodic potentials for 45s sampling time. (■) solid lead electrode at 8.3 Hz. (●) porous electrode at 16.7 Hz, (▲) solid electrode at 50 Hz.

Figure 9b shows $i^{-1}$ vs $w^{-1/2}$ plots at -1100 mV. (■) porous electrode, (●) solid electrode.
Oxygen is reduced at the lead electrode at a sufficiently negative potential at a fast rate, controlled only by mass transport in solution, as a four electron process. Figure 4.8 demonstrates the rotation speed dependence of reduction current for air saturated 1M H$_2$SO$_4$ on porous and solid electrodes. Since the reaction is very fast, oxygen must be supplied to the electrodes only via the solution and a similar effect of rotation on the hydrodynamic layers of both electrodes is expected. A similar potential dependence for the solution reaction is observed with both electrodes as shown in Figure 4.8a, which shows steady-state current-voltage curves for porous and solid lead electrodes at potentials cathodic to E_r in oxygenated 1M H$_2$SO$_4$. One curve is shown for the porous electrode at a rotation speed of 16.7Hz. Figure 4.8b shows plots of $i^{-1}$ vs $w^{-1/2}$ for porous and solid electrodes in oxygenated 1M H$_2$SO$_4$ at a potential of -1100mV and a rotation speed of 16.7Hz. The mechanism (4e reversible reduction) is clearly the same on both electrodes.

4.4. Conclusions from Potentiostatic Experiments

1. The existence of a potential region in which lead dissolves freely in 1M and 5M H$_2$SO$_4$ is confirmed. The positive limit of this region is lower in 5M H$_2$SO$_4$.

2. The rotation speed dependence of steady-state currents suggests that the charge transfer reaction is two single electron transfers, the second (Pb(I)$\rightarrow$Pb(II)) being the rate determining step.
3. A porous electrode in the form of a shrouded RDE does not show a rotation speed dependence. This is interpreted in terms of the major current source being the porous structure beneath the face of the electrode.

4.5. Results and Discussion of Impedance Studies

Automated impedance measurements were carried out in deoxygenated 1M or 5M H$_2$SO$_4$ on solid and porous Pb electrodes. Experiments were carried out in the region up to 20mV positive of the Pb/PbSO$_4$ potential at zero rotation speed. The Pb/PbSO$_4$ potential is approximately -970mV with the reference electrode system used.

4.5.1. Solid electrodes

Figure 4.9 shows typical impedance measurements recorded in the solution region in 1M H$_2$SO$_4$. The experimental data are shown in the complex plane and can be fitted at high frequencies to a semicircle, and at low frequencies to a straight line of approximately unit slope. Thus, from the shapes generated in the complex plane, the experimental data are consistent with the equivalent circuit of figure 2.2a. At high frequencies, the equivalent circuit for the electrode impedance reduces to a charge-transfer resistance in parallel with a double-layer capacitance. Values of the charge transfer resistance for the relevant potentials were calculated from extrapolations of figure 4.3, using equation 2.18. Semicircles are drawn in figure 4.9.
Figure 4.9a Complex plane impedance diagram for a solid lead electrode (area = 0.071 cm$^2$) in deoxygenated 1M H$_2$SO$_4$ at zero rotation speed, at a potential of -960mV. Frequencies in Hz from right to left are: 393; 197; 78.5; 38.3; 24.8; 12.4; 7.8; 3.9; 2; 0.5; and 0.1 Superimposed semicircle is drawn from a calculated charge transfer resistance of 540$\mu$cm$^2$ using a roughness factor of 2.3.
Figure 4.9b. Complex plane impedance diagram for a solid lead electrode (area = 0.071 cm$^2$) in deoxygenated 1M H$_2$SO$_4$, at zero rotation speed, at a potential of -950 mV. Frequencies in Hz from left to right are: 495; 156; 62.4; 31.2; 12.4; 6.2; 3.1; 2; 1.6; 1.2; 1.0; 0.6; and 0.4. Semicircle is drawn from a calculated charge transfer resistance of 350 $\Omega$ cm$^2$ using a roughness factor of 1.7.
Figure 4.10a Complex plane impedance diagram for a solid lead electrode (nominal area = 0.071 cm\(^2\)) in deoxygenated 5 M H\(_2\)SO\(_4\), at zero rotation speed, at a potential of -960 mV. Superimposed semicircle is drawn from the calculated value of charge transfer resistance of 540 \(\Omega\) cm\(^2\) using a roughness factor of 2.4. Frequencies in Hz from left to right are:

1241; 988; 624; 312; 156; 124; 78.5; 62.4; 49.5; 31.2; 24.8; 19.7; 15.6; 9.9; 6.2; 3.1; and 2.0
Figure 4.10b  Complex plane impedance diagram for a solid lead electrode (area = 0.071cm$^2$) in deoxygenated 5M H$_2$SO$_4$, at zero rotation speed, at a potential of -950mV. Frequencies from right to left are: 785; 312; 156; 78.5; 31.2; 12.4; 4.9; 2.5; 1.2; 0.8; and 0.5. Semicircle is drawn from a calculated charge transfer resistance of 540$\mu$cm$^2$ using a roughness factor of 3.8.
using these values which show reasonable agreement with
the impedance data (allowing for electrode roughness),
and charge transfer resistance was found to decrease
with increasing anodic potential. The centres of the
semicircles all lie below the $R_s$ axis to a greater or
lesser degree. This depression of the centres has been
observed in many systems where the surface is rough\(^{(216)}\).
At low frequencies, the Warburg impedance becomes the most
important element of the equivalent circuit. The line of
approximately unit slope generated at low frequencies is
characteristic of diffusion control.

Figure 4.10 shows that similar behaviour was
observed for the Pb electrode in 5M$\text{H}_2\text{SO}_4$ at potentials
up to 20mV positive of the Pb/PbSO$_4$ potential. As the
potential is increased anodically, the diameter of the
semicircle decreases. Semicircles are again superimposed on
the diagrams using the calculated values of charge transfer
resistance. At lower frequencies, the Warburg impedance
does not show ideal behaviour. This is probably due to
the progressive passivation of the electrode during the
course of the experiment\(^{(217)}\), and confirms the rotating-
disc experiments of section 4.3.2.

The above observations confirm the previous work
of Fleming and Harrison\(^{(18,24)}\) although the conclusions
reached are different. Fleming and Harrison\(^{(18,24)}\)
concluded that any high frequency semicircle behaviour was
due to a precipitated PbSO₄ film. Armstrong and Bladen(23) found little evidence for semicircles when using 0.1M H₂SO₄. It was concluded in both cases that Pb dissolution was a fast, reversible 2e process.

The present work, and the work of Le Mehaute(153), contradict this view. The a.c. impedance data of figures 4.9 and 4.10 confirm conclusions made from the rotating-disc experiments of section 4.3.2. that Pb dissolution occurs in two one electron transfers. A similar mechanism has been observed by Armstrong and Bell for the dissolution of Zn(218).

4.5.2. Porous electrodes

Results of corresponding experiments on porous electrodes are summarised in figures 4.11 to 4.14. Figures 4.11 and 4.12 show results obtained on the porous lead electrode in 1M H₂SO₄ at overpotentials of 10mV and 20mV respectively. Figures 4.13 and 4.14 summarise the corresponding data obtained in 5MH₂SO₄.

The shapes generated in the complex impedance plane are consistent with data obtained for the solid electrode. At high frequencies, part of a semicircle, characteristic of a charge transfer resistance in a parallel with a double layer capacitance, is observed. At lower frequencies, Warburg impedance-type behaviour is observed, consistent with a reaction under diffusion control. This Warburg slope bends over twoards the real axis at progressively lower frequency because of the
Figure 4.11 Complex plane impedance diagram for a porous lead electrode (nominal area = 0.071 cm$^2$) in deoxygenated 1M H$_2$SO$_4$, at zero rotation speed, at a potential of -960 mV. Frequencies in Hz from left to right are: 9900; 3120; 1563; 495; 197; 62.4; 31.2; 19.7; 9.9; 4.9; 3.1; 2.0; 1.2; 0.8; 0.5; 0.3; 0.2; 0.08; 0.05.

Figure 4.12 Complex plane impedance diagram for a porous lead electrode (nominal area = 0.071 cm$^2$) in deoxygenated 1M H$_2$SO$_4$, at zero rotation speed, at a potential of -950 mV. Frequencies in Hz from left to right are: 9900, 3120, 785, 393, 124, 39.3, 15.6, 6.2, 3.9, 2.5, 1.6, 1.0, 0.4, 0.2, and 0.08.
Figure 4.13. Complex plane impedance diagram for a porous lead electrode (nominal area = 0.071 cm$^2$) in deoxygenated 5M H$_2$SO$_4$, at zero rotation speed, at a potential of -960mV. Frequencies in Hz from left to right are: (a) 3120; 312; 99; 39.3; 12.4; 3.9; 1.5; 1.0; 0.6; 0.4; 0.2; 0.1; 0.06; 0.04; and 0.02.

Figure 4.14. Complex plane impedance diagram for a porous lead electrode (nominal area = 0.071 cm$^2$) in deoxygenated 5M H$_2$SO$_4$, at zero rotation speed, at a potential of -950mV. Frequencies in Hz from left to right are: (a) 9900; 4949; 3120; 1563; 495; 248; 156; 78.5; 31.2; 19.7; 12.4; 7.8; 4.9; 3.1; 2.0; and 1.2.
interaction of the a.c. and d.c. diffusion layers.

The shapes illustrated in figures 4.11 to 4.14 for the porous electrode are different in certain significant respects from the idealised behaviour of the planar electrode shown in figure 4.9. In figures 4.11 and 4.13, a Warburg slope of approximately $45^0$ is observed, indicating planar electrode-type behaviour at lower overpotentials. At the higher overpotentials, depicted in figures 4.12 and 4.14, the Warburg slope tends to half the value observed at the planar electrode. This indicates that at higher overpotential, the porous lead electrode is behaving as an ideal semi-infinite porous electrode as described by de Levie$^{(43)}$. The theory of the semi-infinite porous electrode has already been discussed in section 1.6.1.1. Whereas for a planar electrode the current lines are normal to the electrode surface, in the porous electrode the lines are effectively parallel to the surface. The impedance of a planar electrode is the sum of the component impedances, but the impedance of the porous electrode is the geometric mean of these components (see equation 1.5). This causes the impedance representing the diffusional mass transport in porous electrodes to be dependent in terms in $\omega^{-1}$ instead of those containing $\omega^{-\frac{1}{2}}$ given in equation (2.51) for a planar electrode. Hence, for an ideal semi-infinite porous electrode, the slope of $45^0$ expected for a Warburg impedance at a flat
The electrode is halved to 22.5°. Therefore, at low over-potentials in the solution region, the porous electrode behaves as a planar electrode, but as the overpotential increases the electrode tends to ideal semi-infinite porous behaviour. Whether a porous electrode behaves as a planar electrode or a porous electrode depends on the penetration depth (1/p) concept discussed in section 1.6.1.1. When 1/p is small, the electrode behaves as a porous electrode, and when 1/p is large, the electrode behaves as a planar electrode. In Chapter 1, the penetration depth was shown to vary inversely with solution resistance and current density, and directly with concentration. Hence, as the overpotential increases, the penetration depth will decrease, and the electrode will tend to ideal porous electrode behaviour. This confirms the observations made in figures 4.11 and 4.13, and figures 4.12 and 4.14.

The complex impedance plane shapes of the present work confirm previous observations made by French workers (219). These authors examined the impedance of a fully charged negative electrode in a lead-acid battery at equilibrium. Indian workers (220) have also examined the impedance of the lead-acid battery over a limited frequency range. These authors explained the kinetic processes in terms of diffusion of ions within porous electrodes and reactions at the pore wall-active material. These authors also demonstrated that the lead-acid cell could be modelled
by the de Levie porous electrode theory(43).

At very low frequencies a new feature is apparent in the complex plane diagrams of figures 4.11 and 4.12. Here, an inductive region is observed, which was also observed in 5M H$_2$SO$_4$ at zero overpotential. Inductive regions were never observed on the planar Pb electrode, and must, therefore, relate to some peculiarity of the porous Pb electrode in the solution region. Inductive regions have also been observed by French workers, who investigated the corrosion of iron in the presence of organic inhibitors(221). These authors demonstrated that at low frequencies coverage is potential-dependent, and relaxation of inhibiting coverage gives rise to an inductance.

In the porous lead electrode used for the present experiments, the active material was formulated with Indulin C, which is a derivative of lignin (see figure 1.6). The action of lignin has already been discussed in section 1.6.4.1, and different workers have observed the adsorption of this organic molecule on the electrode surface(14,135,145,146). It seems clear, therefore, that the inductive component observed in the present experiments represents an adsorption phenomenon owing to the organic expander. Gutman(222) has observed that, whenever the electrode system behaves as a negative resistance and furnishes energy to the measuring device, an inductance is observed.
4.6. Conclusions from Impedance Measurements

1. The mechanism for the dissolution of Pb by two single electron transfers is confirmed.

2. Charge transfer resistances, calculated from rotating disc data, fit observed impedance data for the solid electrode.

3. At higher dissolution rates, the porous Pb electrode behaves as an ideal semi-infinite porous electrode, and obeys the de Levie theory (43).

4. At very low frequency, an adsorption phenomenon, owing to the organic lignin derivative, is observed as an inductive component in the complex plane plots for the porous Pb electrode.
CHAPTER 5

PHASE FORMATION AT LEAD ELECTRODES

5.1. Introduction

The electrochemical oxidation of lead in sulphuric acid is a complicated process. Since the first classical study of Fleischmann and Thirsk (223) a number of kinetic studies have appeared in the literature (12-24). The difficulties associated with this particular system are threefold. First, the solubility of lead sulphate gives rise to a potential region where the reaction occurs purely as a simple exchange reaction between the metal lattice and ions in solution. Second, the structure of lead sulphate has led a number of authors (27-30) to suggest that at certain positive potentials the inner regions of the lead sulphate layer act as a membrane. This supposedly blocks the access of sulphate ion to the metal interfacial region. Thirdly, the electrode tends to become porous as the lead sulphate deposit thickens and grows.

The thickness of the passivating PbSO₄ film which is formed on the electrode surface is of considerable interest, for this dimension determines the extent of the lead oxidation reaction (the capacity) and the quantity of PbO₂ which may be produced in the event of continued oxidation.
In this Chapter, the mechanism of solid PbSO₄ formation at porous and solid Pb electrodes is investigated using the potential step technique. The variation of PbSO₄ film thickness with potential is particularly considered because of its implications for battery performance.

5.2. Experimental

Solid Pb electrodes were manufactured and pretreated as described in Chapter 3, and then reduced at -1050 mV for 2h until the current drain was small and constant, at which point it was assumed that the electrode was wholly metallic. Potentiostatic oxidation pulses were then carried out to various potentials. For porous lead electrodes, polishing was not used and the reduction was carried out potentiostatically at -1050 mV for at least 16 hr. until the current drain was very small and constant. (Paste A of Table 3.1 was used as the paste formulation). Analar grade reagents were used and all experiments were carried out in deoxygenated 5M H₂SO₄ at approximately 23°C.

5.3. Results and Discussion

5.3.1. The solid lead electrode

Potentiostatic oxidation steps were carried out from -1050 mV to potentials ranging from -930 mV to -600 mV and three quite distinct forms of the i-t transient were obtained as shown in figure 5.1.
Figure 5.1. Transients obtained on solid lead electrodes in 5M H$_2$SO$_4$ after stepping from -1050 mV to (A) -920mV, (B) -900mV, and (C) -600mV.

Figure 5.2. The relation between the monolayer equivalent M of the passivating layer and the potential.
Figure 5.2a  Scanning electron micrographs of deposits of PbSO₄ formed in 5 M H₂SO₄ at potentials of (A) -600mV (TOP) (b) -930mV (BOTTOM)

Magnification: 1 cm = 1 μm
It can be seen that at more negative potentials in the experimental range considerably more charge is involved in the process of phase lead sulphate formation than at the higher potentials. A determination of the number of PbSO₄ monolayers equivalent to the charge passed during the potentiostatic experiment was made by integration of the i-t curves and assuming that a charge, of $325 \mu$C cm$^{-2}$ is required to form a monolayer of orthorhombic PbSO₄. The data are shown in Table 5.1 and figure 5.2, together with the dimensionless quantity $i_m t_m / Q_m$, where $i_m$ and $t_m$ are the co-ordinates of the current maximum. A change in the value of this quotient indicates a transformation in the mechanism for nucleation and growth. It is clear from the data that the thickness of the deposit varies with the formation potential, the more positive potential giving rise to a thinner layer. This confirms the suggestions of Fleischmann and Thirsk (223) that the deposit thickness decreased with overpotential. Scanning electron microscopy gives convincing evidence for this: in Figure 5.2a, PbSO₄ crystals obviously vary with potential. Also, the size of the crystals are approximately the same, suggesting instantaneous nucleation. The values of the quotient $i_m t_m / Q_m$ are interesting in that they decrease with increasing overpotential, This indicates that with increasing overpotential, changes occur in the current control by the crystallisation process.
### TABLE 5.1

The variation of $i_m t_m/Q_m$ and deposit thickness (p monolayers equivalent) with potential

<table>
<thead>
<tr>
<th>$E$, mV</th>
<th>$i_m t_m/Q_m$</th>
<th>p (number of monolayers)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-920</td>
<td>0.504</td>
<td>320</td>
</tr>
<tr>
<td>-910</td>
<td>0.51</td>
<td>230</td>
</tr>
<tr>
<td>-900</td>
<td>0.47</td>
<td>160</td>
</tr>
<tr>
<td>-875</td>
<td>0.45</td>
<td>150</td>
</tr>
<tr>
<td>-850</td>
<td>0.3</td>
<td>90</td>
</tr>
<tr>
<td>-830</td>
<td>0.3</td>
<td>70</td>
</tr>
<tr>
<td>-700</td>
<td>0.13</td>
<td>40</td>
</tr>
<tr>
<td>-600</td>
<td>0.1</td>
<td>30</td>
</tr>
</tbody>
</table>

At low overpotentials ($E \sim -930$ to $-920\text{mV}$), the current at short times in the resultant transient obeyed an $i \propto t^2$ relationship (see figure 5.1A). Two models for nucleation and growth possibly describe this relationship\(^{(201)}\). However, one of them (for progressive nucleation and two-dimensional growth) is unlikely in view of the thickness of the deposit (300-400 monolayers). Moreover, this process would require $\ln(i/t^2) \propto t^3$ at long times, but this is not observed. The other possibility is that of instantaneous nucleation followed by three-dimensional growth for which the current-time relationship is given in Chapter 2 by equation (2.85).
This equation can be extended to incorporate the effect of the isolation of the electrode due to a passivating film by considering the velocity of advance of the deposit perpendicular to the surface as being proportional to the area of the electrode not passivated by lead sulphate. Equation (2.85) then becomes

\[ i = zFk_2 \left(1 - \exp\left(-\frac{\pi N_0 k_1 m^2 t^2}{p^2}\right) \right) \exp\left(-\frac{\pi N_0 k_1 m^2 t^2}{p^2}\right) \] (5.1)

Equation (5.1) can be expressed in non-dimensional form by the equation

\[ \frac{i}{i_m} = 4\left(1 - (0.5)(t/t_m)^2\right)(0.5)(t/t_m)^2 \] (5.2)

where

\[ \frac{i}{i_m} = zFk_2/4 \text{ and } t_m = \left(\frac{p^2 \ln 2}{\pi N_0 k_1 m^2}\right)^{1/2} \] (5.3)

The most convenient way of testing experimental data against a theoretical nucleation and growth model is to plot the experimental data against theory in the dimensionless form. This is demonstrated in figure 5.3, where the transient of figure 5.1A is plotted in dimensionless form against equation (5.2). The correlation is quite good, especially when it is remembered that we are quite near the potential region for lead dissolution. At short times the current is larger than predicted because of direct dissolution of the electrode; at long times the current is higher because of the need to maintain the dissolution of lead sulphate into the electrolyte solution and because of the necessity of film repair.
Figure 5.3. The transient of Figure 1A plotted in dimensionless form and compared with the curve of equation (5.2).

Figure 5.4. Transients obtained after stepping to (●) -900mV and ( ) -890mV from -1050mV plotted in dimensionless form. Full curve is the dimensionless form of equation (2.79).
As the overpotential is increased, the parabolic form of the rising part of the curve changes to linear (see figure 5.18), and remains so throughout the potential region -920 mV to -880 mV. This indicates that in this region nucleation and growth conforms to an instantaneous nucleation and two-dimensional growth process. The change in growth law fits in well with the observed change in deposit thickness shown in Table 5.1 and figure 5.2. The current for the two-dimensional process has been discussed in Chapter 2 and is given by equation (2.79). A reduced variable plot is shown in figure 5.4 and is compared with the reduced form of equation (2.79). It can be seen that agreement between experiment and theory is excellent. However, as emphasised in Table 5.1, the charge under the transient is much greater than that expected for a monolayer of orthorhombic PbSO₄ and indicates the development of a relatively thick passivating PbSO₄ layer.

At potentials more positive than ~ -850 mV the transients have a distorted appearance with a negligible rising portion (see figure 5.1C). Fleischmann et al (224) have discussed the distortion of transients at high overpotentials and have demonstrated that this type of transient distortion may arise if the process involved adspecies adsorption and this became rate determining at higher overpotentials. These authors used equation (2.79) and studied the variation of $\frac{i_m t_m}{Q_m}$ with potential. The
value of this quotient from equation (2.79) should be 0.607. The variation observed in the present work is
shown in figure 5.5 and it is clear that the theoretical
value is not observed. The reason for this may indeed
be the intrusion of rate-control by adsorbed species into
the current flow. However, it is not clear that this
can be the case here in view of the complications due to
the solubility of PbSO₄ and the possible development of
porosity at long times. It is interesting to note, however,
that in the potential range for the undistorted transient
(-920 mV to -880 mV) the rising part of the experimental
transients conforms exactly with theory. This is
demonstrated by measuring the charge under the rising part
of the transient and comparing this with the theoretical
value of the quotient \( \frac{i_{m}t_{m}}{Q'} \) (where \( Q' \) is the charge in
the rising portion of equation (2.79)) which should be 1.54.
This confirms the data of Figure 5.4 where the experimental
results at short times fit the theory, but at long times
there is more current than predicted. This high current
could be due to the repair of the passivating film, or the
slow growth of a porous structure.

It is interesting to observe the discrepancy between
the theoretical model predicted by equation (2.79) and
the monolayer equivalents tabulated in Table 5.1. The
dependence of the number of monolayers with potential is
greater at relatively low overpotentials and two
Figure 5.5. $i_{m}t/Q_{m}$ plotted against potential for the solid lead electrode in 5M H$_2$SO$_4$

![Graph showing $i_{m}t/Q_{m}$ plotted against potential](image.png)

Figure 5.6. A typical transient obtained after stepping the porous lead electrode from -1050 mV to -870 mV

![Typical transient graph](image.png)
explanations can be suggested for this. At low overpotentials the resultant transient shows some $i \propto t^2$ behaviour at very short times, which changes to an $i \propto t$ dependence. There is a possibility of an instantaneous nucleation and 3D growth process, as described by equation (5.1), at very short times which rapidly transforms into an instantaneous nucleation and 2D growth process. Nucleation centres equivalent to many monolayers in height could be formed and then lateral growth would occur to passivate the surface. As overpotential increases, there is a concomitant reduction in the degree of intrusion of the three-dimensional growth process, and the passivating film becomes relatively thin.

An alternative explanation is that growth could be mainly 2D with a relatively slow growth perpendicular to the metal surface. Thus, as the overpotential increases, the passivation rate increases and the film becomes relatively thin and approaches the theoretical monolayer expected for a 2D growth process. Fleming and Harrison\(^{(18)}\) suggested that the double layer charging current may be sufficient to nucleate solid state PbSO$_4$ and completely change the kinetics of growth. Here, the basal potential is made more positive, to reduce the effects of double layer charging, and the rising transients do extrapolate to approximately zero current at $t = 0$ as would be required if the solution reaction had been suppressed.
At all times, and at all oxidation potentials investigated the current in the i-t transients was always rotation-speed-independent. This indicates that the current is controlled by the electrocrystallisation process, and confirms the work of Fletcher and Matthews (15). Soluble species may exist in the potential region of solid phase PbSO$_4$ electrocrystallisation, but only in very small proportions (17). The solution-precipitation model of Vetter, therefore, appears unlikely (68).

5.3.2. The porous lead electrode

Potential steps were carried out to various potentials from -1050mV and a typical transient is shown in figure 5.6. (N.B. Current densities in figures 5.7 to 5.11 assume the nominal surface area of the solid electrode = 0.071 cm$^2$). The response consists of a rapidly rising and falling current which reaches a minimum (after $\sim$100ms) and then rises and eventually falls. This behaviour although qualitatively similar to that of the planar electrode differs quantitatively in several important respects. The initial rise and fall is considerably more significant in the porous case than the planar. This conforms to the considerably greater surface area of the porous electrode requiring a commensurably greater double layer charge when the potential is stepped. The surface area of the electrode can be estimated from this charge by assuming a value of $\sim$50$\mu$F cm$^{-2}$ for the average double
layer capacitance for polycrystalline lead in the potential region including the potential of lattice oxidation in 5M $\text{H}_2\text{SO}_4$ \textsuperscript{(225)}. The value of the specific surface area was estimated to be $25 \times 10^3 \text{cm}^2 \text{cm}^{-3}$, which compares well with the B.E.T. data reported by Tiedmann and Newman\textsuperscript{(141)}. It should be noted, however, that these authors estimated the true double layer capacity of lead at potentials near that of lattice dissolution to be $10^{-2} \text{F cm}^{-2}$; this value seems to be too small.

Figure 5.7 shows that the double layer charging transient decays as $i \propto t^{-\frac{1}{2}}$, as predicted by porous electrode theory\textsuperscript{(43)} (c.f. eqn.1.9). The intercept of the $i-t^{-\frac{1}{2}}$ plot is not at infinite time, because the ohmic electrode resistance prevents an infinite current density at zero time\textsuperscript{(226)}.

When double layer effects have died away, the current again rises characteristically indicating an electrocrystallisation process. We can be sure that in the initial stages the mechanism for the development of lead sulphate would be identical with that observed on the planar electrode. The actual electrometric response, however, will be modified by the porous structure.

Relatively little work has been done on the transient response of a porous electrode to a potential step. The expectation of porous electrode behaviour is best determined in terms of the penetration depth discussed in sections 1.6.1.1. and 4.5.2, and given in equations
Figure 5.7. The double layer charging transient for the porous lead electrode at -930mV, with $i$ versus $t^{-1/2}$ as inset.

Figure 5.8. Typical $i$ versus $t^{3/2}$ plots after stepping the porous lead electrode to various potentials.
1.7 and 1.8. These equations apply to the steady state and do not allow for the crystallisation kinetic parameters, so that the penetration depth for the solid phase reaction will be much smaller than the values calculated by Bode(35). Therefore, the porous lead electrode is expected to exhibit gross effects owing to porosity, and explains the change in shape of transients shown in figures 5.1 and 5.7.

In the initial stages before the pore structure contains significant lead sulphate, the transient behaviour of the porous electrode will be modified by the process of "square rooting" as described by de Levie(43). In principle, this arises from the fact that whereas in the planar electrode the current lines are orthogonal to the electrode, in the porous electrode they are parallel to and the effective impedance becomes the geometric mean of the impedance (resistance) of the solution and the interfacial impedance of the electrode (see equation 1.5). This has the effect of halving the exponent of time dependence. With this in mind we can expect to see the observed results of figure 5.8 for the initial rise in current where the linear relationship between i and t observed for the planar electrode becomes one in which i varies as $t^{1/2}$. A convincing confirmation of this is observed occasionally at low overpotentials when the current is proportional to t, conforming to the $t^2$ behaviour of the planar electrode at low overpotentials. Figure 5.8 also demonstrates the potential-dependent nature of the
Figure 5.9. Typical $i$ versus $t^{-1/2}$ plots after stepping the porous lead electrode to (Δ) -920mV, (Θ) -890mV, (O) -880mV, and (□) -860mV.

Figure 5.10. Plots of $\ln i$ versus $t$ for transients at long times obtained after stepping to different potentials (indicated).
transients at short time and a semilogarithmic plot of log slope against potential gave a $50\text{mV/decade}$ dependence. Similarly, a plot of log $i$ at $t = 0$ against potential gave a $50 \text{mV/decade}$ dependence. The current at zero time may represent the intrusion of the solution reaction and/or the pre-existence of lead sulphate nucleation centres of a finite size.

After the attainment of the maximum, the current in the transient falls. It might be expected by analogy to the previous discussion that "halving" the time dependence characteristic of the solid electrode would yield the observed porous electrode behaviour. This is not the case and the system behaves phenomenologically as a $t^{-1/2}$ fall at times greater than the maximum ($\sim 4t_m$ to $150t_m$) and at long times a fall as log $t$. These dependences are shown in the figures 5.9 and 5.10.

Figure 5.9 shows that as the potential is stepped to progressively lower potentials, the extrapolated intercept occurs at increasingly longer times and so stepping to $-930 \text{mV}$ gives an extrapolated intercept of zero current at infinite time.

Whether or not the porous electrode concept can be applied to this system depends on the reaction time, that is, the extent of the development of the lead sulphate phase within the pores. The crucial point is that the developed porous electrode theory demands a surface inside
the pore which is relatively uniform, however, in the present situation the nature of the reacting surface within the pore is continuously changing as lead sulphate develops on the pore wall. At the front of the electrode, the current going into the formation of lead sulphate will be considerably greater than that inside the electrode. However, once the front parts of the electrode pores are blocked the reaction is driven deeper inside. Also the interfacial potential between the electrolyte and the electrode must change as distance from the electrode front increases. This will result not only in a thicker blocking deposit inside the pore than at the front (Table 5.1) but also a different current-time relationship (Figure 5.1). Under these conditions the conformation of the current to a $t^{-\frac{1}{2}}$ decay at intermediate times must be fortuitous.

At long times ($>150 \ t_m$) when large amounts of lead sulphate are blocking the porous structure, we can assume that pore plugging is the final current-limiting process. This is equivalent to the growth of a thick deposit at the front of the pores.

The equation for the incremental change in current, assuming ohmic control, is

$$\frac{di}{dt} = -\frac{C}{R^2_D} (dR_D/dt)$$ (5.4)
With $\frac{dR_0}{dt}$ for the thickening layer proportional to the current, we get

$$\ln i = (-k \frac{E}{R_0^2}) t + \text{constant} \quad (5.5)$$

Figure 5.10 shows plots of $\ln i$ versus $t$ and we conclude that at long times the current is controlled by pore plugging.

Therefore, at long times two competing processes occur during the oxidation of a porous lead electrode - passivation and pore blocking. Passivation is a process which occurs on both the solid and porous lead electrodes but in the former it is essentially a two-dimensional process, whilst in the latter it can be considered to be essentially three-dimensional. Pore blocking is a phenomenon which can be considered to be peculiar to the porous electrode and to be in direct competition with the conventional passivation process. At low overpotentials (or discharge rates), passivation will predominate and the effective capacity of the electrode will be high. At high overpotentials (or discharge rates), the reaction will be concentrated mainly on the surface of the electrode and pore blocking will become a significant means of current control and effect a concomitant decrease in the capacity of the electrode. The increasing influence of pore plugging with increasing potential is evidenced in the concomitant decrease of the extrapolated time intercepts of Figure 5.9, and the decrease in charge required to passivate the electrode shown in Table 5.2. Comparison of the charge
values in Table 5.1 and 5.2, illustrate that the porous electrode is less affected by discharge rate than the solid electrode, presumably because of the large pore size and high surface area.

5.4. Conclusions

1. The current in i-t transients conforms to control by nucleation and growth processes.

2. The development of $\text{PbSO}_4$ on solid Pb is potential-dependent and becomes two-dimensional at more positive potentials. This 2D process is equivalent to a normal passivation process where instantaneous nucleation occurs, followed by lateral growth and insulation of the surface.

3. The thickness of the $\text{PbSO}_4$ film decreases as the passivating potential increases.

4. Deposit thickness is determined by crystallite size and hence the number of nucleation centres.
The processes occurring at the porous Pb electrode can be explained in terms of the theory for the semi-infinite porous electrode, by extrapolation from solid electrode data.

The capacity of the porous electrode decreases with increasing discharge rate.

The solution-precipitation model for negative plate discharge proposed by Vetter (68) is unlikely.
6.1. **Introduction**

The regeneration of Pb from PbSO\textsubscript{4} is a most important reaction in the lead-acid battery, because this reaction limits the energy input to the cell.

The reduction of lead sulphate, in spite of this important aspect, has received considerably less scientific attention than the discharge reaction. In battery technology the solution-precipitation model of Vetter\textsuperscript{(68)} for charge and discharge of the negative electrode is widely accepted \((33,67,155)\), although evidence for it is still only circumstantial. Fletcher and Matthews\textsuperscript{(15)} also postulated a solution stage in the regeneration of Pb from PbSO\textsubscript{4} on SEM evidence. Electrocrystallisation studies on the sulphated Pb electrode are expected to be complex because even a planar electrode becomes effectively porous after sulphation. The profound influence of porosity on transient behaviour has already been discussed in Chapter 5 for the discharge reaction. This Chapter presents data from potential step studies on the conversion of PbSO\textsubscript{4} to Pb on porous and solid electrodes.

6.2. **Experimental**

The manufacture and pretreatment of porous and solid Pb electrodes has been discussed in Chapter 3.
For solid lead, electrodes were held in the reduction region at \(-1050 \text{ mV}\) until the current drain was negligibly small and constant, at which point it was assumed that the electrode was wholly metallic. Oxidation was then carried out potentiostatically until the steady state current in the lead sulphate region was negligible. Oxidation was generally carried out at \(-850 \text{ mV}\) for two hours, but times and potentials were varied with no significant difference in the results.

For porous electrodes (using Paste A, Table 3.1), oxidation was generally carried out galvanostatically at a rate of 2.5 mA cm\(^{-2}\) until the required degree of conversion was obtained. Electrodes were then potentiostatted at the potential of zero current and stepped into the region of lead sulphate reduction. Porous electrodes were also potentiostatically discharged with similar results, but galvanostatic oxidation was preferred because of the greater control of the charge taken out of the electrode. The porous electrode had an electrometric equivalent charge of 16.85C and the degree of discharge was expressed as a percentage of this value.

Potentiostatic reduction of the product lead sulphate could be carried out at both stationary and rotating electrodes. Analytical grade reagents were used and all experiments were carried out in deoxygenated SMH\(_2\)SO\(_4\) at approximately 23\(^0\)C.
6.3. Results

6.3.1. Solid electrode

Figure 6.1. shows a typical reduction transient corresponding to a potentiostatic step from the lead sulphate region to the lead region. This figure, obtained with portions alternately representing a static and rotating electrode (10 Hz), also demonstrates that the current in the transient is rotation-speed-independent.

At short times, the current in the rising transient was found to obey a $i \propto t^{\frac{1}{2}}$ law (see figure 6.2). Extrapolation of these $i - t^{\frac{1}{2}}$ plots to $t = 0$ indicates that there was a significant current intercept which was also potential-dependent. A plot of $\log{t=0}$ versus potential gave a 50 mV decade$^{-1}$ dependence and $\log(\text{d}i/\text{d}t^{\frac{1}{2}})$ versus potential had a 30 mV decade$^{-1}$ dependence.

Figure 6.3. shows that at intermediate times the current in the transient fell as $i \propto t^{-\frac{3}{2}}$. The slopes of these plots were also found to be potential-dependent and $\log(\text{d}i/\text{d}t^{-\frac{1}{2}})$ versus potential was found to have a 60 mV decade$^{-1}$ dependence. At long times the current decay rate accelerated, however, the $i - t$ relationship was complex and could not be quantified with any degree of certainty.
Figure 6.1. $i-t$ transient for potentiostatically discharged solid Pb electrode stepped from -850 mV to -980 mV demonstrating the rotation speed independence of the reaction by stepping alternately between 0 and 10 Hz.

$AB = 10 \text{Hz}; \quad BC = 0 \text{ Hz}; \quad CD = 10 \text{ Hz}; \quad DE = 0 \text{ Hz}; \\
EF = 10 \text{ Hz}$. 

[Diagram of the transient showing the steps.]
Figure 6.2. Plots of $i$ versus $t^{1/2}$ for rising transients of potentiostatically discharged solid Pb electrodes after stepping to various cathodic potentials from $-850$ mV.
Figure 6.3. Plots of $i$ versus $t^{-1/2}$ for falling part of transients of potentiostatically discharged solid Pb electrodes after stepping to various cathodic potentials from -850mV.
6.3.2. Porous electrode

Figure 6.4. shows a typical reduction transient recorded after stepping a sulphated porous lead electrode from -968 mV (E<sub>rev</sub>) to -1020 mV in the lead region. The transient is shown on two time scales to demonstrate the rising and falling parts more clearly. (N.B. Current densities assume nominal surface area).

The rising transient was also found to obey a \( i \propto t^{1/2} \) law and figure 6.5. again demonstrates that the slope of the rising transient is again potential-dependent. Extrapolation of the \( i - t^{1/2} \) plots to \( t = 0 \) showed that a positive current intercept was again observed but this current did not bear a definite relationship to potential. \( \log (\text{di/dt}^{1/2}) \) versus potential was again found to have a 30 mV decade\(^{-1} \) dependence.

At intermediate times, the current was found to fall as \( i \propto t^{-0.3} \), as shown in figure 6.6. This current-time decay rate was observed for electrodes galvanostatically oxidised to levels ranging from 7.5% to 30% of their theoretical oxidisable capacity. For a fully oxidised porous electrode, the current decay rate was found to obey a \( i \propto t^{-0.2} \) relationship. A plot of \( \log (\text{di/dt}^{0.3}) \) versus potential had a 140 mV decade\(^{-1} \) dependence for an electrode discharged to 15% of its capacity. At long times the current decay rate accelerated, as it did on the solid electrode, and again the \( i - t \) relationship was obscure.
Figure 6.4. Transient response of a galvanostatically discharged (7.5%) porous Pb electrode to a potential step from $E_{rev}$ (-968 mV) to -1020 mV.
Figure 6.5. Plots of $i$ versus $t^{1/2}$ for rising transients of galvanostatically discharged (7.5%) porous Pb electrodes after stepping the various cathodic potentials from $E_{rev}$ (-968 mV).
Figure 6.6. Plots of $i$ versus $t^{-0.3}$ for falling parts of transients galvanostatically discharged (15\%) porous Pb electrode after stepping to various cathodic potentials from $E_{rev}$. 
6.4. Discussion

The \( i-t \) transient depicted in figure 6.1, is qualitatively similar to results previously obtained in this laboratory\(^{(31)} \). The initial abrupt rise in current contains elements of the reaction current and the double layer charging current. The reaction current may be complex and in general will include any reduction of solution species, in addition to the solid phase reaction. The largest component of the charge in this experiment is clearly the solid phase transformation, since the rising and falling transient is characteristic of a crystallisation and growth mechanism.

The current intercepts of the \( i-t \) plots of figure 6.2, at \( t=0 \) could represent reductive processes occurring in the solution phase, or the pre-existence of growth centres of a finite size. The potential-dependent nature of these currents would lend support to the former explanation, unless there is some nucleation during the double layer charging region. Attempts to further resolve this problem are hindered by the fact that the current in the transient was found to be rotation-speed-independent at all times. It is well known that the form of the lead sulphate deposit on lead is disordered, and in this case is \( \sim 1000 \) Å thick, and therefore changes in the superficial diffusion layer geometry would be unable to affect diffusion within the pores (where the reaction at the lead surface must occur from conductivity considerations). This is confirmed by the fact that rotation-speed-dependence
could not be observed for the oxidation of a porous lead electrode in the solution region (see Chapter 4).

The $i \propto t^{1/2}$ relationship, observed at short times for the reduction of lead sulphate on solid lead, was also observed for the reduction of sulphated porous lead electrodes (see figures 6.4 and 6.5), and the oxidation of porous lead electrodes (see Chapter 5). However, for the oxidation of solid lead electrodes, the current was generally found to rise in direct proportion to $t$. This discrepancy in the behaviour of solid and porous lead electrodes is explained in the light of contemporary porous electrode theory. This predicts that the time dependency expected for the porous electrode will be obtained by halving the exponent of time dependence on the solid electrode. It seems reasonable to treat the sulphated solid lead electrode as a porous electrode because the oxidation of solid lead to lead sulphate involves the dissolution of the basal lead, with the concomitant formation of etch pits. Figure 5.1. shows that at long times in the recorded transients for lead sulphate formation at solid lead electrodes, there is more current than predicted by the theoretical model for nucleation and growth. This current was concluded to represent the dissolution of lead at pores in the lead sulphate film so that a quasi-porous electrode surface ($\text{Pb/PbSO}_4$) is formed. This has also been demonstrated by the B.E.T.
method (227) and other workers have discussed the dissolution of lead at points in the lead sulphate film (28-30), which would give rise to semiporosity. On oxidation, therefore, the originally planar lead electrode becomes roughened owing to metal dissolution at sites not covered by lead sulphate crystals. Eventually, these sites are also covered by lead sulphate but the electrode is never completely passivated owing to mechanical breakdown of the lead sulphate film. The basal lead surface therefore becomes three-dimensional, and, because of the small penetration depth, the electrode can be considered porous. This is confirmed by the fact that at short times, the current also rises in proportion to $t^{\frac{1}{2}}$ for the sulphated porous lead electrode, and log (di/dt$^{\frac{1}{2}}$) versus potential gave the same 30 mV decade$^{-1}$ dependence for the porous and solid lead electrodes. Therefore, it may be concluded that the i $\propto t^{\frac{1}{2}}$ behaviour observed at short times for the sulphated porous and solid electrodes is equivalent to the i $\propto t$ behaviour of a flat electrode. The conversion of lead sulphate to lead could, therefore, occur by the same mechanism as that used to describe lead oxidation in Chapter 5. This involved an instantaneous nucleation and 2D growth process. Modification of equation 2.79 for a porous electrode gives:

$$i = N_0 k_1 C_1 t^{\frac{1}{2}} \exp \left(-\frac{C_2 k_1}{t}\right)$$  \hspace{1cm} (6.1)

where $k_1$ is the growth rate, $N_0$ is the number of nucleation centres, and $C_1$ and $C_2$ are constants containing density.
the Faraday, molecular weight, and number of electrons. Differentiation of equation 6.1 demonstrates the potential-dependent factors involved at short times. The $30 \text{ mV decade}^{-1}$ dependence of the $i \propto t^{1/3}$ slopes on the sulphated porous and solid lead electrodes is due to the variation of the number of growth centres, $N_0$, with potential. Also, $i_m$ and $t_m$ (the co-ordinates of the current maximum) were found to be potential-dependent, and log $i_m$ and log $t_m$ yielded slopes of approximately $40 \text{ mV decade}^{-1}$ for both electrodes. This indicates a variation of the number of growth centres, and the growth rate, with potential.

After the attainment of the maximum, the current in the transient falls but the relationship is not the expected $\ln i/t^{1/3}$ versus $t$ (from equation 6.1). For the solid electrode, the current decays as $t^{-0.5}$ (see figure 6.3), whereas for the porous electrode the decay rate is generally $t^{-0.3}$ (see figure 6.3). The current decay rates cannot be quantitatively explained because the electrode characteristics are continuously changing. An important feature is that the charge in the transients is always greater than the charge in the preparative oxidation; this must reflect the fact that hydrogen is being produced in parallel with lead sulphate reduction. A $t^{-0.5}$ current decay rate was also observed for the oxidation of porous lead electrodes in sulphuric acid (see figure 5.10). The $t^{-0.3}$ behaviour observed for the sulphated porous lead
electrode probably reflects the greater degree of porosity associated with this electrode compared with the sulphated solid lead electrode and the porous lead electrode. In the case of the oxidation of porous lead, the degree of discharge is never greater than 40% of the theoretical capacity (see Table 5.2). Therefore, the oxidation reaction is restricted to the outer 40% of the electrode under potentiostatic conditions. Slow galvanostatic discharge, as used in the preparative oxidation of porous lead, causes the reaction to be driven deeper into the porous matrix so that on the subsequent reduction the electrode is being worked to a greater depth. This is confirmed by the current decay rate of $t^{-0.2}$ observed for the fully discharged electrode. Qualitatively, the fall-off in current at long times reflects the variation of the growth rate with potential, although the hydrogen evolution reaction must complicate this.

At long times, when the surface area of lead is large, and the amount of lead sulphate is small, the concentration of lead sulphate will be limiting. At long times, the current decay rate increases on the solid and porous electrodes so that the apparent limiting currents at infinite times from the $i - t^{-0.5}$ plots of figure 6.3, and the $i - t^{-0.3}$ plots of figure 6.6, are not achieved in practice. It can be concluded, however, that the $i - t$ behaviour at long times describes current limitation due to a rapidly decreasing area of small lead sulphate crystallites.
within a large area of growing lead.

A feature of the oxidation of solid lead (see Chapter 5) was the three-dimensional growth at low overpotentials and the two-dimensional growth at higher overpotentials. The reduction of grown sulphate layers is here shown to be two-dimensional over the potential range tested; this could indicate the growth orthogonal to the electrode is much slower than growth in a direction parallel to the electrode surface. Certainly, two-dimensional growth characteristics were observed for the oxidation of solid lead even though the lead sulphate film formed was approximately 2000 Å thick. It is also interesting to note that planar electrode two-dimensional growth kinetics were never observed for the reduction of oxidised planar electrodes over a wide range of lead sulphate thicknesses (18).

Comparison of the $i-t^2$ plots of figures 6.2 and 6.5 with those for the oxidation of porous lead in figure 5.8, indicates that the nucleation and growth of Pb from PbSO$_4$ is a significantly faster process than the formation of PbSO$_4$. Also, the SEM observations of figure 7.15, and those of Burbank et al (32) and Fletcher and Matthews (15), would suggest that Pb grows in the form of dendrites on regeneration from PbSO$_4$. Harrison and Thirsk (201) describe the model for the progressive nucleation and growth of dendrites in terms of a transient in which the current rises linearly with time, so that the above arguments are still applicable. Both of the nucleation
and growth models discussed describe current control in terms of the electrocrystallisation process. Therefore, if the solution-precipitation model of Vetter is applicable, then diffusion is not a rate-limiting process. This is partly confirmed by the fact that the current in the transient of figure 6.1 is always rotation-speed-independent, whereas a microporous Pb electrode did show some rotation-speed-dependence in the solution region (see Table 4.2).

6.5. Conclusions

1. Both "planar" and porous electrodes behave in a similar manner and indicate that the electrode reaction has a finite depth of penetration into the electrode.

2. The kinetics of the formation of metallic lead on both electrodes appear to be instantaneous nucleation and 2D growth processes with subsequent limitations owing to overlap and lead sulphate depletion.

3. The effect of porosity, and the depth of previous discharge, has a profound effect on the current decay rate observed on a porous electrode.

4. If the solution-precipitation model of Vetter is valid, then diffusion is not a significant form of current control in the reduction transient.
CHAPTER 7

THE EFFECT OF EXPANDERS AT AMBIENT TEMPERATURE

7.1. Introduction

The use, and mode of action, of expanders have already been discussed in Section 1.6. In Chapters 5 and 6, the oxidation and reduction of porous lead electrodes were discussed. In this chapter, the effects of BaSO₄ and lignosulphonate on the charge and discharge processes are investigated by the potential step technique, and by galvanostatic cycling.

7.2. Experimental

The mixing, constitution, and preparation of the electrodes have already been discussed in Chapter 3. Pastes were used in four formulations for potentiostatic and galvanostatic experiments (see Tables 3.1 and 3.2 respectively).

7.2.1. Potentiostatic experiments

To investigate the discharge (oxidation) reaction, electrodes were potentiostatted at \(-1050\) mV until a negligible, constant, current was measured. The electrode was then stepped to various potentials in the lead sulphate region and the resultant current-time transient recorded. To investigate the charge (reduction) reaction, electrodes were potentiostatically charged, as described above, and then discharged to 7.5% conversion at 0.01 A g\(^{-1}\). The
degree of discharge was expressed as a percentage of the theoretical capacity of the electrode which was calculated at 16.85°C for the total conversion of the active material. After discharge, electrodes were potentiostatted at the potential of zero current and then stepped to various potentials in the lead region; the resultant current-time transient was recorded.

Potentiostatic reduction, or oxidation, could be carried out at stationary or rotating electrodes. AnalaR grade reagents were used and all experiments were carried out in deoxygenated 5M \( \text{H}_2\text{SO}_4 \) at approximately 23°C.

7.2.2. Galvanostatic experiments

Galvanostatic cycling experiments were carried out on formed battery negative plates in 5M \( \text{H}_2\text{SO}_4 \), which was not deoxygenated to simulate normal battery operation. Electrodes were cycled by discharging and charging at 0.16 \( \text{Ag}^{-1} \) active material and electrode potential was recorded. The capacity of the electrode on discharge was measured by recording the time taken for the potential to drop 0.3V below the initial, on-load voltage.

7.3. Potentiostatic Experiments

7.3.1. Results

7.3.1.1. Oxidation

Figure 7.1. shows a typical current-time transient recorded after stepping a porous lead electrode, manufactured with paste C, from the lead region to the lead sulphate
Figure 7.1. A typical oxidation transient recorded on a porous lead electrode, containing BaSO\textsubscript{4} as additive, after stepping from -1050 mV to -900 mV.
Figure 7.2. Typical short-time $i - t^\frac{1}{2}$ plots obtained from the oxidation transients of a porous lead electrode using BaSO$_4$ as additive.
Figure 7.3. Typical short-time $i - t^{1/2}$ plots obtained from the oxidation transients of a porous lead electrode using lignosulphonate as additive.
Figure 7.4. Typical short-time \( i \cdot t^{1/2} \) plots obtained from the oxidation transients of a porous lead electrode containing no additives.
Figure 7.2 demonstrates that at short times, after double-layer charging, the current rises as the square root of time. In the case of paste C, significant current intercepts are observed at \( t=0 \) which have a 50 mV decade\(^{-1} \) dependence. A similar dependence is also observed for the slope (\( \sigma \)) of the short-time \( i - t^{\frac{1}{2}} \) plots of figure 7.2.

Figure 7.3 demonstrates that for paste B, there is no current intercept at \( t = 0 \), but there is a potential-dependent time intercept at zero current. This time intercept has a 12 mV decade\(^{-1} \) dependence, whereas the slope dependence of the \( i - t^{\frac{1}{2}} \) plots is 18 mV decade\(^{-1} \). This time intercept is illustrated by Figure 7.5, which shows a typical oxidation transient recorded on an electrode containing paste B. The dotted line at short time indicates the \( i - t^{\frac{1}{2}} \) line projected to zero current.

For the electrode using paste D, Figure 7.4 illustrates that at more positive potentials there is a current intercept at \( t = 0 \), and at more negative potentials there is a time lag. The current intercept has a 20 mV decade\(^{-1} \) dependence and the slope dependence was also 20 mV decade\(^{-1} \).

At long time, Figure 7.1 shows that the current in the transient falls in a complex manner. At intermediate times, the current falls as the inverse of \( t^{\frac{1}{2}} \), as illustrated in Figure 7.6 for the electrode utilising paste C. The more
Figure 7.5. A typical oxidation transient at short times recorded from a porous lead electrode, containing lignosulphonate as additive, showing the projection of $i - t^k$ plot to the time axis (dotted line).
Figure 7.6. Typical $i - t^{-rac{1}{2}}$ plots obtained from the falling part of oxidation transients recorded on a porous lead electrode containing $\text{BaSO}_4$. 
negative the potential, the longer the time to achieve zero current. At long times, the current falls in a complex manner which cannot be determined. The effect of potential on the total utilisable capacity is well illustrated by Table 7.1, where the three paste formulations (Pastes B, C and D) are compared with the standard battery negative paste (Paste A) results of Chapter 5.

**TABLE 7.1**

The utilisable capacities obtained at various potentials for porous lead electrodes using Pastes A–D. The total capacity of the electrode is 16.85C, assuming full conversion of the lead.

<table>
<thead>
<tr>
<th>$E$/mV</th>
<th>Paste A</th>
<th>Paste B</th>
<th>Paste C</th>
<th>Paste D</th>
</tr>
</thead>
<tbody>
<tr>
<td>-930</td>
<td>7.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-910</td>
<td></td>
<td>6.5</td>
<td></td>
<td>2.7</td>
</tr>
<tr>
<td>-900</td>
<td>6.8</td>
<td></td>
<td></td>
<td>2.4</td>
</tr>
<tr>
<td>-890</td>
<td></td>
<td>5.9</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>-880</td>
<td></td>
<td></td>
<td></td>
<td>1.7</td>
</tr>
<tr>
<td>-850</td>
<td>6.5</td>
<td></td>
<td></td>
<td>1.3</td>
</tr>
</tbody>
</table>

Capacity is determined by integration of the i–t curves and in all cases the theoretical capacity of the electrodes is 16.85C, assuming total conversion of the active material. Oxidation transient analysis is summarised in Table 7.2, where $i_m$, $t_m$, are the co-ordinates of the current
maximum in the i-t transient.

### TABLE 7.2

A summary of oxidation transient analysis for Pastes A - D

<table>
<thead>
<tr>
<th>Electrode</th>
<th>RISE</th>
<th>FALL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mV decade⁻¹</td>
<td></td>
</tr>
<tr>
<td></td>
<td>tₓ iₜ=0 or iₜ=0⁰</td>
<td>σ</td>
</tr>
<tr>
<td>Paste A</td>
<td>0.5 iₜ=0⁵⁰</td>
<td></td>
</tr>
<tr>
<td>Paste B</td>
<td>0.5 iₜ=0¹²</td>
<td></td>
</tr>
<tr>
<td>Paste C</td>
<td>0.5 iₜ=0⁶⁰</td>
<td></td>
</tr>
<tr>
<td>Paste D</td>
<td>varies 20 with E</td>
<td></td>
</tr>
</tbody>
</table>

7.3 Reduction

On reduction, after double layer charging, the current again rises as the square root of time, after a potential step from the lead sulphate region to the lead region. For Paste C, Figure 7.7, shows that a potential-dependent time lag is evident before the iₜ¹/₂ behaviour is observed. This is well illustrated in Figure 7.8, where the dotted lines represent the separated double layer charging and iₜ¹/₂ lines. The potential-dependency of the time lag was found to be 90mV decade⁻¹ whilst that of the slopes of the iₜ¹/₂ plots was 110mV decade⁻¹. Paste D shows similar behaviour (see Figure 7.9) with a slope dependency of 90mV decade⁻¹ and a lag dependency of 90mV decade⁻¹.
Figure 7.7. Typical short-time $i - t^{1/2}$ plots obtained from the reduction transients of a porous lead electrode, using BaSO$_4$ as additive, after stepping from the reversible potential (-968 mV).
Figure 7.8. A typical reduction transient at short times recorded from a porous lead electrode, containing BaSO\textsubscript{4} as additive, after stepping from -968 mV to -1010 mV.
Figure 7.9. Typical short-time $i - t^{1/2}$ plots obtained from the reduction transients of a porous lead electrode, containing no additives, after stepping from the reversible potential (-968 mV).
Figure 7.10. Typical short-time $i - t^{\frac{1}{2}}$ plots obtained from the reduction transients of a porous lead electrode, containing lignosulphonate as additive, after stepping from the reversible potential (-968 mV).
Figure 7.11 Typical $i - t^{-0.44}$ plots obtained from the falling part of reduction transients recorded on a porous lead electrode containing BaSO$_4$ as additive.
Figure 7.12 Typical $i - t^{-0.36}$ plots obtained from the falling part of reduction transients recorded on a porous lead electrode containing lignosulphonate as additive.
Figure 7.13 Typical $i - t^{-\frac{3}{2}}$ plots obtained from the falling part of reduction transients recorded on a porous lead electrode containing no additives.
Figure 7.10 shows that with Paste B there is no significant lag period but the i-t$^{1/2}$ plots extrapolate approximately to zero current at t=0. The potential dependence of the slopes was found to be 70 mV decade$^{-1}$.

At long times, the current in the transient decays as $i \propto t^{-x}$ (where $x \leq 0.5$). For Paste C, Figure 7.11 shows that the current decays as $i \propto t^{-0.44}$. At long times the current decays more rapidly, but at a rate which shows no simple relationship. For Paste B, Figure 7.12 shows that the current decays as $i \propto t^{-0.36}$, except at long times where the current decay rate accelerates as above. Figure 7.13 shows that Paste D behaves in a similar manner, except that the current decay rate at intermediate times is $i \propto t^{-3}$. Reduction transient analysis is summarised in Table 7.3, together with results obtained from Paste A in Chapter 6.

**Table 7.3**

A summary of reduction transient analysis for Pastes A - D.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>RISE</th>
<th>FALL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$t^x$</td>
<td>$t=0$ or $t=0$</td>
</tr>
<tr>
<td>Paste A</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>Paste B</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>Paste C</td>
<td>0.5</td>
<td>$t=90$</td>
</tr>
<tr>
<td>Paste D</td>
<td>0.5</td>
<td>$t=90$</td>
</tr>
</tbody>
</table>
7.3.2. **Discussion**

After double-layer charging, the current in the oxidation, and reduction, transients rises as $i \propto t^{\frac{1}{2}}$ (see figures 7.2, 7.3, 7.4, 7.7, 7.9 and 7.10). This time dependence has already been observed for porous electrodes manufactured from a standard battery negative paste in Chapters 5 and 6, and has been interpreted as the instantaneous nucleation and two-dimensional growth of a phase at a porous electrode.

For the oxidation transients obtained from the electrode using Paste C (BaSO$_4$ only), the $i-t^{\frac{1}{2}}$ plots of figure 7.2, extrapolate to positive current intercepts. These intercepts indicate the pre-existence of nucleation centres of a finite size. The potential-dependent nature of these intercepts (see Table 7.2) could indicate that the nucleation centres are formed during the double-layer charging process. The slope ($\alpha$) of the $i-t^{\frac{1}{2}}$ plots is also potential-dependent; this probably indicates that the number of nucleation centres formed after $t=0$ is overpotential dependent, because the slopes and intercepts have similar potential dependencies (see Table 7.2). In contrast, for the oxidation of Paste C (lignosulphonate only), the $i-t^{\frac{1}{2}}$ plots have potential dependent intercepts on the time axis. This intercept can be explained in terms of an "induction period" necessary before nucleation can proceed. The short-time oxidation transient behaviour of Paste D (no additives) is a composite of the behaviours of Pastes B
and C; at higher overpotentials there are positive current intercepts, whilst at lower overpotentials the intercepts occur on the time axis. This implies that there is a distribution of nucleation sites of different energies which nucleate at different overpotentials.

Table 7.2 also contains summarised results of oxidation experiments carried out on the standard battery negative paste used in Chapter 5. At short times, positive current intercepts are again observed, indicating the pre-existence of nucleation centres of a finite size. It is interesting to note the strong similarity in short-time behaviour of Pastes A and C. The potential-dependence of the slopes is lower for B and D and indicates that it is easier to nucleate PbSO$_4$ on these electrodes, but a large number of nucleation centres already pre-exist the nucleation process in the case of Pastes A and C.

The strong similarity in short-time behaviours of Pastes A and C, and of B and D, indicates that BaSO$_4$ has the major influence on the electrochemical oxidation process and does provide nucleation centres for lead sulphate. At long times, the presence of lignosulphonate has a major effect, as indicated by the utilisable capacities shown in Table 7.1. The presence of lignosulphonate effects a considerable increase in the utilisable capacity of the porous electrode, but is never greater than ~50%. The effect of the omission of lignosulphonates on the utilisable capacity can be seen in figure 7.1, where the current decay
has a complex behaviour. At intermediate times, the current decays as $t^{-\frac{1}{2}}$ (see figure 7.6), but for pastes A and D the periods of linearity are short and the $i-t^{-\frac{1}{2}}$ plots intercept the time axis at relatively short times. In contrast, the $i-t^{-\frac{1}{2}}$ plots of Paste A were rectilinear over long periods and extrapolated through the time axis at long times (see figure 5.10).

At long times, after the $i \propto t^{-\frac{1}{2}}$ behaviour, the current decays more rapidly. For Paste A, a $\ln i \propto t$ behaviour was observed (see figure 5.10), but for Pastes C and D the decay rate did not have a simple relationship. Final current limitations in the oxidation of porous lead electrodes are due to the effect of two competing processes; pore plugging, and the conversion of all the available active material. If pores are narrow, or non-existent, then zero current in the $i-t$ transient will occur after shorter times and give a lower capacity (as Pastes C and D). Therefore, lignosulphonate appears to increase the available active surface area/porosity of the porous lead electrode (35); this effect will be discussed further below. Table 7.1. also shows that increasing the overpotential decreases the utilisable capacity; that is, increasing the rate of discharge effects a decrease in the utilisable capacity. This is probably due to the fact that pore blocking has a significant effect after shorter periods of time.
On recharge (reduction) of a discharged porous electrode using Pastes C and D, an "induction period" is necessary before lead nucleation can proceed (see figures 7.7 to 7.9). The slopes and intercepts of the i-t^1/2 plots have similar potential-dependencies (see Table 7.3), which indicates that the nucleation process alone is potential-dependent, and not the growth rate. For Pastes A and B, no "induction period" is observed and the intercepts are not significantly potential-dependent (see figure 7.10).

Examination of the potential-dependency of the slope of the rising part of the reduction transient (as shown in Table 7.3) again demonstrates that lead nucleation is easier in the presence of lignosulphonate. Lead is most easily nucleated when the standard battery paste (Paste A) is used. This phenomenon could be a secondary effect due to a greater surface area in the presence of lignosulphonate effecting a thinner layer of discharged lead sulphate, which is easier to reduce. The presence of BaSO_4, as in Paste A, would cause even greater dispersal of the lead sulphate, and hence make the lead sulphate even easier to reduce.

Figures 7.11 to 7.13, and Table 7.3, demonstrate that the decay rate of the falling transient depends on paste constitution. The slowest decay rate is found for Paste A, which was also found to have the greatest utilisable capacity (see Table 7.1). This suggests that the varying decay rates reflect the effect of surface area/porosity; the
Figure 7.14 A plot of relative peak current (a measure of the number of nucleation centres) against cycle number for a porous lead electrode using a standard battery negative paste (containing $\text{BaSO}_4$ and lignosulphonate) Data obtained from reduction transients after stepping to $-1020 \text{ mV}$.
Fig. 7.15 continued

TOP
4 cycles

BOTTOM
8 cycles
greater the porosity/surface area, the slower the current decay. Integration of the reduction transients from electrodes not using lignosulphonate indicates that the charge taken out of the electrode on discharge (oxidation) cannot be totally recovered on recharge (reduction). In contrast, integration of the transients from Paste A in Chapter 6 indicated that there was more charge in the reduction transient than was actually discharged. This was interpreted as being due to the intrusion of the hydrogen evolution reaction in the charging process. In the absence of lignosulphonate, not all the lead sulphate formed on discharge can be removed on subsequent recharge.

The greater porosity/surface area of pastes containing lignosulphonate develops with cycling, as demonstrated by figure 14. Here, relative peak current, a measure of the number of nucleation centres, is obtained by normalising the current maximum \( i_m \) of the transient against the maximum value observed in all experiments. This increase in the number of nucleation centres with cycling reflects the development of a greater surface area/porosity. These observations are confirmed by the SEM pictures of figure 7.15. Here the same area of surface of a charged porous microelectrode (using Paste A) is shown at different cycle number. There is an obvious morphological change in the electrode surface, with some indication that Pb formed from the regeneration of PbSO\(_4\).
was dendritic in nature.

The greater porosity of lignosulphonate-containing electrodes has also been demonstrated by other workers using end-of-charge voltage measurements and B.E.T. surface measurement (35). Bode (35) and Skalozubov (39) also observed a significant increase in porosity of lignosulphonate-containing electrodes with cycling, which confirms the observations of figure 7.14. Without additives, Bode observed no change in total volume, but a decrease in capacity was observed which was ascribed to the development of large lead crystals which are difficult to discharge. In the presence of lignosulphonate, the surface energy of the porous lead was said to be reduced, making the formation of smaller and more loosely packed lead crystals more favourable. Winsel et al. (67) have also established a definite relationship between porosity/surface area and utilisable capacity for a standard battery negative paste.

7.4. Results and Discussion of Galvanostatic Cycling Experiments

Figure 7.16 shows a typical potential time curve recorded on discharge of Paste 2. In the absence of BaSO₄, an initial sharp drop and recovery of potential is observed at the beginning of discharge; this behaviour was also observed with Paste 1, but not Pastes 3 and 4. Kasparov et al. (149) also observed this behaviour, which it has been suggested (40, 131) is a result of supersaturation of lead.
Figure 7.16. A typical potential-time curve recorded from the discharge of a battery plate containing no BaSO₄.
Figure 7.17  Regression lines obtained for Pastes 1-4 for the variation of capacity (time to discharge, \( t_d \)) with cycle number.
sulphate in the absence of nucleation centres. It has been suggested (35, 136) that BaSO₄ provides nucleation centres for PbSO₄ and the presence of BaSO₄ would, therefore, minimise solution supersaturation by lead sulphate. Willhnganz (40, 131) observed this effect at the positive electrode only, but our results confirm the observations of the Russian workers (149) that a small voltage minimum is observed at the negative electrode in the absence of BaSO₄.

The effect of paste constitution on cycling behaviour is illustrated in figure 7.17, where it can be seen that paste constitution also influences the initial capacity on formation. The best performance was achieved using Paste 4 (containing BaSO₄ and Indulin C), giving a high initial capacity and a relatively slow deterioration in capacity with cycling. In the absence of additives, a significantly lower initial capacity is observed with a more rapid deterioration on cycling. The presence of Indulin C only (Paste 2) is more advantageous than the presence of BaSO₄ only (Paste 3), but significantly better performance is observed when BaSO₄ and Indulin C are used in combination (Paste 4). These observations confirm the results from potentiostatic experiments in section 7.3, except that figure 7.14 indicates a developing surface area/porosity. This would indicate that a concomitant rise in capacity should be observed. The previous observations were made on a microelectrode, which was only partially discharged.
Figure 7.18 Regression lines obtained for Pastes 1-4 for the variation of end-of-charge voltage with cycle number.
at the much slower rate of $0.01 \text{Ag}^{-1}$ and then potentiostatically charged. The lines shown in figure 7.17 are linear regression lines calculated from data showing the scatter normally observed from lead-acid negative plate behaviour. In fact, a slight increase in capacity was observed over the first three or four cycles for electrodes containing Indulin C.

The variation of end-of-charge voltages with cycle number and paste constitution is shown in the regression lines of figure 7.18. This figure shows that in the presence of Indulin C (Pastes 2 and 4), the end-of-charge voltage increases with cycle number, but decreases if Indulin C is omitted. This indicates that, in the presence of lignin, the active surface area of the electrode increases with cycle number; this confirms the results of figure 7.14 and the results of B.E.T. surface measurement and end-of-charge voltage measurements (35). Comparison of figures 7.17 and 7.18 indicates opposing trends for electrodes containing Indulin C; the capacity decreases with cycling but the active surface area increases. In Chapter 5, the effect of discharge rate on the capacity of the electrode was discussed. There are two competing processes on discharge: the conversion of all available lead to PbSO$_4$ and the plugging of pores in the electrode, which prevents the complete conversion of the available lead. It was found that, as the discharge rate increases, the effect of pore plugging becomes more noticeable. In the present experiments,
Figure 7.19a  Scanning electron micrographs of Paste 4 at 0 cycles

TOP: 6250X; bottoms: 1250X
Figure 7.19b  Scanning electron micrographs of Paste 4 at 15 cycles

TOP 6250X;  BOTTOM: 1250X
Figure 7.20  Scanning electron micrographs of Paste 2 at 15 cycles

TOP: 6250X;  BOTTOM: 1250X
Figure 7.21 Scanning electron micrographs of Paste 1 at 15 cycles

TOP: 6250X; BOTTOM: 1250X
Figure 7.22 Scanning electron micrographs of Paste 3 at 15 cycles

TOP: 6250X; BOTTOM: 1250X
a high rate of discharge was used and the effect of pore plugging would be significant. Figure 7.18 illustrates that the active surface area for hydrogen evolution progressively increases over the first fifteen cycles, but the capacity only increases over the first three or four cycles. This could indicate the progressive formation of a porous structure with pores of a smaller diameter, which are more easily plugged. In addition, the developing surface area for hydrogen evolution (and lead nucleation) is not necessarily available for PbSO₄ nucleation.

SEM studies largely bear out the above conclusions. Figure 7.19 shows that for Paste 4 (containing Indulin C and BaSO₄) there is some evidence for an increase in surface area/porosity over the first 15 cycles. This confirms the results of figure 7.14 obtained on a microelectrode. Comparison of figures 7.21 and 7.22 with figures 7.19 and 7.20 clearly demonstrates that, in the presence of Indulin C (lignosulphonate) a greater surface area/porosity develops. This confirms the end-of-charge voltage measurements of figure 7.18, and the significantly greater capacity observed for electrodes containing Indulin C (see figure 7.17).

It is interesting to note that the potentiostatic behaviours of the porous microelectrodes used in 7.3, and the battery plates used here, are similar. Potential step
studies were carried out on battery plates, which showed the same transient behaviour observed for the microelectrode. This validates the use of porous microelectrodes, and the extrapolation of the data obtained on them to the battery plate. Figure 7.16 also demonstrates that the potential of the negative electrode on discharge is always positive of the solution region. Therefore, under normal operating conditions the solution reaction will be an insignificant process in the discharge of the negative electrode. This contradicts the suggestion of Fleming and Harrison (227) that the solution reaction will be a significant reaction in the lead-acid battery.

7.5. Conclusions

1. There is a greater utilisable capacity in the presence of lignosulphonate; this is further improved by adding BaSO₄.
2. The utilisable capacity decreases as the rate of discharge increases.
3. In the absence of lignosulphonate, the porous lead electrode cannot be fully charged.
4. BaSO₄ provides nucleation centres for PbSO₄.
5. Carbon and lignosulphonate have no significant electrochemical effect on the discharge behaviour of the battery negative; the lignosulphonate effect is secondary and is caused by an increase in surface area/porosity.
6. Nucleation of lead is easier in the presence of lignosulphonate and is further improved by the addition of BaSO₄.

7. In the presence of lignosulphonate, the number of growth centres increases with cycle number owing to an increase in porosity/surface area.

8. The current decay rate on potentiostatic reduction depends on porosity/surface area.

9. The cycling behaviour of the negative electrode is optimised by the incorporation of both BaSO₄ and lignosulphonate.
CHAPTER 8

THE OXIDATION AND REDUCTION OF SOLID AND POROUS LEAD ELECTRODES AT LOW TEMPERATURE

8.1. Introduction

In Chapters 4 to 7, the electrochemistry of solid and porous Pb electrodes in H$_2$SO$_4$ at ambient temperature was investigated. The formation of PbSO$_4$, and the reduction of PbSO$_4$ to Pb, conformed to nucleation and growth mechanisms, which were rate-limited by crystallisation and growth processes. In a small region of potential positive of the Pb/PbSO$_4$ potential, lead was found to freely dissolve in H$_2$SO$_4$, and was detected by rotating-disc experiments on the planar Pb electrode.

A knowledge of the processes occurring at the negative electrode at low temperatures is important because of the poorer charge acceptance of the lead-acid battery under these conditions$^{(157)}$. Literature on the electro-chemistry of the negative electrode at low temperature is scarce. Chang et al$^{(228)}$ discussed the cyclic voltammetry of lead at temperatures between 25$^\circ$C to -40$^\circ$C. These authors found that decreasing the temperature reduced: (a) the separation between the lead sulphate reduction peak and hydrogen evolution, and (b) the charge in the sulphation peak. An increase in separation of the oxidation and reduction peaks was also observed with decreasing temperature.
In this Chapter, the potentiostatic behaviours of solid and porous Pb electrodes in deoxygenated 5M $\text{H}_2\text{SO}_4$ at $-30^\circ \text{C}$ are investigated.

8.2. Experimental

8.2.1. Solid electrodes

The construction and preparation of solid Pb electrodes is described in Chapter 3. After polishing and etching, electrodes were reduced at $-1400\text{mV}$ in the experimental cell containing 5M $\text{H}_2\text{SO}_4$ at $-30^\circ \text{C}$, until a minimal current was measured. LSV studies and potentiostatic oxidation pulses were then carried out.

For potentiostatic reduction pulses, the electrode was reduced, as described above, and then potentiostatted at $-800\text{mV}$ for two hours before stepping to various potentials.

8.2.2. Porous electrodes

Electrodes were prepared (using Paste A) and cycled to constant response as described in Chapter 3. After fitting in the electrochemical test cell, electrodes were reduced at $-1050\text{mV}$ at ambient temperature for at least 16 hours, until a constant, minimal current was recorded. Electrolyte temperature was then reduced to $-30^\circ \text{C}$ and potentiostatic oxidation pulse experiments were carried out.

For potentiostatic reduction pulses, the electrodes were reduced (as above) and then potentiostatted at $-800\text{mV}$ for 2 hours (at $-30^\circ \text{C}$) before stepping to various potentials.
8.3. Results and Discussion of Experiments on the Solid Pb Electrode

Figure 8.1 depicts LSV curves obtained at 0.1 and 10 \text{Vs}^{-1} after sweeping from -1.4 to -0.4V in 5M H$_2$SO$_4$ at -30°C. It is obvious that at least two peaks are apparent in the current of the positive-going sweep. Generally, one major peak at more negative potentials were observed, and the second peak was of variable magnitude, but was more noticeable at higher sweep rates. In the negative-going sweep, one major peak is observed with two secondary peaks, with the hydrogen evolution reaction occurring at more negative potentials (see figure 8.1A). The ratio $Q_A/Q_C$ (Charge in oxidation/Charge in reduction) was found to decrease with increasing sweep rate, as can be observed in figure 8.1. This confirms the observations of Willhnganz (157) that smaller crystals of lead sulphate, as formed at higher discharge rates (see figure 5.2a), are easier to reduce. Table 8.1 shows that the charge, $Q_A$, in the oxidation peak decreases with increasing sweep rate, $v$.

**TABLE 8.1**

<table>
<thead>
<tr>
<th>Sweep rate, $v$ \text{Vs}^{-1}</th>
<th>Charge in oxidation, $Q_A$ \text{mC cm}^{-2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.003</td>
<td>33.1</td>
</tr>
<tr>
<td>0.003</td>
<td>21.1</td>
</tr>
<tr>
<td>0.01</td>
<td>15.8</td>
</tr>
<tr>
<td>0.03</td>
<td>9.2</td>
</tr>
<tr>
<td>0.1</td>
<td>4.3</td>
</tr>
<tr>
<td>0.3</td>
<td>3.5</td>
</tr>
</tbody>
</table>
Figure 8.1. LSV curves obtained after sweeping a solid Pb electrode in 5M H2SO4 at -30°C from -1.4 to -0.4V

(A) 0.1 Vs⁻¹  (B) 10 Vs⁻¹
Figure 8.2. A log current versus potential plot obtained from the foot of an oxidation wave of an LSV curve run at 0.01 \text{Vs}^{-1}. Line drawn at 32mV decade$^{-1}$. 
Figure 8.3. The dependence of oxidation peak parameters on sweep rate (A) $E_p$ versus $v^{1/2}$ (B) $I_p$ versus $v^{1/2}$. 

(A) 

(Ep in mV) vs. $\sqrt{v/\sqrt{S}}$

-800
-700
-600

5 10

(B) 

($i_p$ in mA/cm$^2$) vs. $\sqrt{v/\sqrt{S}}$

50 0

2 4 6
Figure 8.2 shows that a plot of log current versus potential from the foot of the oxidation wave gave a Tafel slope of 32 mV decade\(^{-1}\). This would conform to a slope of \(~40\text{mV decade}^{-1}\) at \(22^\circ\text{C}\) and suggests that electron transfer occurs by two one-electron steps, the second being rate-determining. This suggestion confirms the rotating-disc experiments of Chapter 4; this transfer mechanism is theoretically treated by equations 2.20 to 2.24 of Section 2.2. The measured Tafel slope observed in the present experiments is unlikely to be influenced by the increased resistivity of the electrolyte as \(E\) is proportional to log \(i\), and is not linear with \(i\).

Figure 8.3 demonstrates that the potential, \(E_p\), of the major oxidation peak, and its corresponding current, \(i_p\), varies with the square root of sweep rate. This behaviour is consistent with the passivation model of Müller\(^{(229)}\); \(\text{PbSO}_4\) nucleates on the surface and spreads laterally across the \(\text{Pb}\) surface until a small fraction of \(\text{Pb}\) surface remains uncovered. Therefore, the area available for reaction decreases with time until the rate of reaction is limited by the resistance of the solution in the pores of the \(\text{PbSO}_4\). This model was also observed using potential oxidation steps at ambient temperature (see Chapter 5). This situation has been mathematically described by Macdonald\(^{(230)}\) to give the following expression for peak current:

\[
i_p = \left(zF\rho_{\text{K/M}}\right)^{\frac{1}{2}} a(1-H_p)v^{\frac{1}{2}}
\]

(8.1)
where \( \kappa \) is solution conductivity, \( p \) is the density of \( \text{PbSO}_4 \), 
\( M \) is the molecular weight of \( \text{PbSO}_4 \), \( a \) is electrode area, 
and \( H_p \) is the degree of coverage of the \( \text{Pb} \) by \( \text{PbSO}_4 \) at 
the oxidation peak. The potential at which the current 
peak occurs is given by:

\[
E_p = \left( zFp\kappa/M \right)^{\frac{1}{2}} \left[(h/M) + 2a(1-H_p)\right] v^{\frac{1}{2}}
\]  

(8.2)

where \( h \) is film thickness and \( z \) is the resistance of the 
solution external to the film.

Therefore, if \( H_p \) is independent of sweep rate, then 
\( i_p \) and \( E_p \) should vary linearly with \( v^{\frac{1}{2}} \) as demonstrated 
by figure 8.3. At sweep rates greater than \( \sim 0.1 \text{Vs}^{-1} \), 
a plot of \( E_p \) versus \( I_p \) gives a value of \( \sim 25 \Omega \text{cm}^2 \) for 
\( Z_p \), the resistance of the solution in the pores of the 
\( \text{PbSO}_4 \) film. At sweep rates \( \leq 0.03 \text{Vs}^{-1} \), plots of \( I_p \) and 
\( E_p \) against \( v^{\frac{1}{2}} \) have a different slope, and a plot of \( I_p \) 
versus \( E_p \) yields a value for \( Z_p \) of \( \sim 200 \Omega \text{cm}^2 \). Therefore, 
at higher sweep rates a thinner and more porous \( \text{PbSO}_4 \) 
film is formed, which probably makes the formation of a 
second phase easier. Potentiostatic oxidation steps at 
\( \sim 22^\circ \text{C} \) showed a change in the model for nucleation and growth 
of lead sulphate at different rates of discharge (see 
section 5.3). At low overpotentials (discharge rates), 
an instantaneous nucleation and 3-D growth model was observed, 
which yielded a thicker film. At higher overpotentials, an 
instantaneous nucleation and 2-D growth model was observed.
yielding a thinner film; this model approximates to the model for passivation of Müller\(^{(229)}\).

Linearity of \(E_p\) and \(I_p\) with \(v^{\frac{1}{2}}\) has been observed by other workers for different passivation reactions\(^{(231,232)}\) but in the present case the sharp fall in current predicted by the above model of Macdonald\(^{(230)}\) is not observed. This is particularly true at high sweep rates and is due to the occurrence of a second oxidation peak which represents the formation of a second phase. The formation of a second phase indicates that the primary passivation layer must be highly porous. This is confirmed by Table 8.2, which shows the effect of cycling the electrode. The reduction peak was always minimal, and it is assumed that a \(\text{PbSO}_4\) film was always present prior to the next oxidation, which resulted in an increasingly compact \(\text{PbSO}_4\) film.

### Table 8.2

The effect of cycle number on the charge in the anodic oxidation peak, \(Q_A\) (sweep rate = 0.01 \(\text{Vs}^{-1}\)).

<table>
<thead>
<tr>
<th>Cycle Number</th>
<th>Charge in oxidation, (Q_A) mC cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.8</td>
</tr>
<tr>
<td>2</td>
<td>13.5</td>
</tr>
<tr>
<td>3</td>
<td>7.7</td>
</tr>
<tr>
<td>4</td>
<td>7.3</td>
</tr>
<tr>
<td>6</td>
<td>6.8</td>
</tr>
</tbody>
</table>
LSV studies by other workers on lead in $H_2SO_4$ at $22^\circ C$ (228, 233-235) have shown only one $PbSO_4$ oxidation peak, and it is concluded that at $-30^\circ C$ the $PbSO_4$ film formed during LSV is more porous. The present results confirm those of Chang et al (228) that decreasing the temperature increases the separation between oxidation and reduction peaks. A reduction of the charge in the reduction peak was also observed which confirms the observation (157) that lowering the temperature makes the rechargeability of the lead-acid battery more difficult.

Potential oxidation steps resulted in complex current-time transients of five limiting forms (see figure 8.4). At potentials between -880 and -940mV, the transients were of the form shown in figure 8.4A, the second peak being small at low overpotentials. Between $\sim -840$ and -550mV a single rising and falling transient is observed; at more negative potentials this takes the form of figure 8.4B, but the rising portion is gradually lost and the transient becomes increasingly distorted so that only a falling transient is observed (see figure 8.4C).

Figure 8.4A indicates that, initially a nucleation and growth process is observed; the initial transient has a negligible rising portion, suggesting the pre-existence of nucleation centres. This initial transient is succeeded by a further rise and fall, probably indicating the formation of a second layer of $PbSO_4$ on top of a highly porous first...
Figure 8.4. Typical oxidation transients obtained using a solid Pb electrode in 5M H$_2$SO$_4$ at -30°C after stepping from -1200 mV to (A) -850mV, (B) -830mV (C) -700mV, (D) -500mV, and (E) -400mV.
Fig. 8.4 continued
layer. As the driving potential is increased, only the second transient is observed (see figures 8.4B and 8.4C). The rising portion of this transient always extrapolates to positive current intercepts at zero time, indicating the pre-existence of nucleation centres. Distorted oxidation transients were observed at 22°C (see figure 5.1C), and it is inferred that nucleation could occur during the double-layer charging process, or, owing to the low solubility of PbSO₄ at -30°C, nucleation centres pre-exist the potential step. Distorted transients have also been observed by Fleischmann et al.(224), who demonstrated that this phenomenon may arise if adspecies diffusion became rate determining at higher overpotentials. In the present case, the solubility of PbSO₄ at -30°C, and the possible development of porosity at long times, makes this explanation unlikely.

At potentials between ~ -550 and -450, a falling transient showing a slight current arrest is observed (see figure 8.4D). At potentials more positive than -450mV, this current develops into a rising and falling transient (see figure 8.4E). The potential of these transients coincides with the potential at which the growth of PbO has been observed under the primary passivating PbSO₄ layer(26); this is schematically illustrated in figure 1.5.

The results of the integration of the current-time transients at various potentials are shown in figure 8.5. Assuming a charge of 325 μC cm⁻² for the formation of a
Figure 8.5. A plot of charge in the oxidation transients versus E; charge is expressed as monolayer equivalents of PbSO$_4$ results obtained at (▲) 22°C (●) -30°C.
Figure 8.6. A typical reduction transient after stepping a sulphated lead electrode from -800 to -1200mV.

\[ 10 \text{mAcm}^2 \]

\[ 2.5 \text{ms} \]
Figure 8.7. Typical $i$ versus $t^{-\frac{1}{2}}$ plots obtained from reduction transients after stepping to various potentials.
monolayer of PbSO₄, the charge is expressed as monolayer equivalents of PbSO₄; previous results from figure 5.2 are also shown. At -30°C, rising and falling transients characteristic of a nucleation and growth process were not observed at potentials more negative than ~880 mV, whereas at ~22°C transients were observed at potentials as negative as -930 mV. The reason for this is due to the measured $E_f$ for Pb/PbSO₄; at ~22°C this potential was found to be ~-970 mV, but was ~-935 mV at -30°C. Also, at -30°C an increased driving potential of ~15 mV is necessary before the nucleation and growth of lead sulphate can proceed. At potentials between -400 and -200 mV a significant increase in the charge taken out of the electrode is observed, owing to the formation of second phase. This phase is probably PbO, which is able to form under a porous layer of PbSO₄ at higher discharge rates (higher porosity at higher rates of discharge is suggested by the LSV studies above).

Figure 8.6 shows a typical current-time transient recorded after a potentiostatic reduction step. Falling transients were observed over a wide range of reduction potentials, and figure 8.7 shows that the current decayed as $t^{-1/2}$ at short times. This current-time behaviour would indicate an electrochemical reaction which is rate-limited by mass-transport of a reactive species. Because rising
transients are not observed it must be assumed that nucleation centres are available for the growth of Pb on reduction of PbSO₄. This does not seem unreasonable as it has been shown above that the PbSO₄ film is relatively porous. The PbSO₄ film formed had a charge of 28 mC cm⁻², and the charge under the transients during the duration of the plots shown in figure 8.7 was only 0.1% of this value. It is likely, therefore, that the growth of lead from lead sulphate is rate-limited by mass transport through a thick film. The plots of figure 8.7 do not extrapolate to zero current at infinite time, but rather the intercept occurs at shorter times as the overpotential is increased. This indicates the hindrance imposed on mass-transport by the PbSO₄ film as the driving potential (charge rate) is increased. At longer times, the current deviates from the extrapolations of figure 8.7 to more positive values and probably represents the intrusion of the hydrogen evolution reaction. This renders impossible the determination of the amount of PbSO₄ reduced to Pb.

In all experiments described above, the current in the oxidation and reduction reactions was always rotation-speed-independent, except for the hydrogen evolution reaction. It is concluded that in the formation of PbSO₄ from Pb, and the formation of Pb from PbSO₄, current limitation is not due to diffusion in solution of a reactive species. Experiments were also carried out in
5\text{M } \text{H}_2\text{SO}_4 \text{ to determine the presence of the solution region found at room temperature (see section 4.3). The presence of a solution region could not be detected by rotating disc studies. This is due to the low solubility of PbSO}_4 \text{ at -30}^\circ \text{C. The trend of decreasing solubility with decreasing temperature is well illustrated by figure 1.1.}

8.4. Results and Discussion of Experiments on the Porous Pb Electrode

Figure 8.8 shows a typical oxidation transient, recorded on the porous Pb electrode at -30\(^\circ\)C, which is profoundly different from those recorded on the planar electrode under similar conditions (see figure 8.4). Comparison with other oxidation transients recorded on porous electrodes at ambient temperature also show some differences (see figures 5.6 and 7.1) although figure 8.9 demonstrates that the current in the transient again rises as \(t^\frac{2}{3}\). Comparison of the plots in figure 8.9 with corresponding ambient temperature ones in figures 5.8 and 7.2 to 7.4 emphasises the significantly lower currents recorded at -30\(^\circ\)C.

Figure 8.9 also shows that the \(i-t^\frac{2}{3}\) plots intercept the current axis at \(t=0\), indicating the pre-existence of nuclei for the growth of PbSO\(_4\). These nuclei probably result from the BaSO\(_4\) addition to the active material. However, it is envisaged that the low solubility of PbSO\(_4\) at -30\(^\circ\)C will also have a significant effect, because the slopes of the \(i-t^\frac{2}{3}\) plots, and the values of \(i(t=0)\), are both potential-dependent.
Figure 8.8. A typical oxidation transient recorded on the porous Pb electrode after stepping from -1050 mV to -780 mV in 5M H₂SO₄ at -30°C.
Figure 8.9. Typical \( i-t^{1/2} \) plots taken from oxidation transients recorded on a porous Pb electrode, after stepping from -1050 mV, in 5M \( \text{H}_2\text{SO}_4 \) at -30°C, to -830mV, -850mV, and -880mV.

![Graph](image)

Figure 8.10. The double layer charging transient for the porous lead electrode after stepping the potential from -1050 mV to -1200 mV, with \( i-t^{1/2} \) as inset.

![Graph](image)
In Chapters 5 and 6, the $i^{-\frac{1}{2}}$ behaviour of the porous electrode was explained in terms of de Levie porous electrode theory (43). The $i^{-\frac{1}{2}}$ behaviour at the porous electrode is equivalent to the $i-t$ behaviour at a solid electrode. Consequently, the formation of PbSO$_4$ occurs by an instantaneous nucleation and 2-D growth process. This is equivalent to the passivation process already discussed in section 8.3 for the solid electrode.

At long times in the current decay of figure 8.8, there is a sudden change in the $i-t$ relationship. This change was more gradual at lower overpotentials, and is substantially different from the change in $i-t$ behaviour observed for a porous electrode containing no lignosulphonate at ambient temperature (see figure 7.1). This current decay did not conform to any simple relationship, except that at low overpotentials and intermediate times, some $i^{-\frac{1}{2}}$ behaviour was observed (c.f. figures 5.9 and 7.6). This accelerated current decay rate has a significant effect on the charge required to passivate the electrode (the capacity) as shown in Table 8.3.
TABLE 8.3
The variation of the electrode capacity with oxidation potential at -30°C

<table>
<thead>
<tr>
<th>E/mV</th>
<th>Capacity/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>-880</td>
<td>3.9</td>
</tr>
<tr>
<td>-870</td>
<td>3.4</td>
</tr>
<tr>
<td>-860</td>
<td>2.9</td>
</tr>
<tr>
<td>-830</td>
<td>2.2</td>
</tr>
<tr>
<td>-810</td>
<td>2.0</td>
</tr>
<tr>
<td>-800</td>
<td>1.8</td>
</tr>
</tbody>
</table>

The theoretical capacity of the electrode is 16.85C, and results for a similar lignosulphonate-containing electrode at ambient temperature are shown in Table 5.2. At -30°C capacities are significantly lower, especially when it is remembered that the Pb/PbSO₄ potential is \( \sim -935 \text{mV} \) at -30°C. Also, the capacity decreases significantly more with potential (discharge rate) at -30°C, owing to the acceleration in decay rate shown in figure 8.8. At ambient temperature, the discharge of a porous electrode was described as two competitive processes: passivation and pore plugging by product PbSO₄. At -18°C, Winsel et al (67) demonstrated that, at high discharge rates, these two processes were accelerated by the presence of ice crystals, in addition to the PbSO₄. These ice crystals are formed when the isothermal dilution of the pore liquid causes its concentration to coincide with the solidus curve of the H₂SO₄/H₂O phase diagram (see figure 1.3). If the pore electrolyte falls to a concentration of \( \sim 3.5 \text{M} \) at -30°C, ice crystals will form...
having a volume about eight times larger than that of the PbSO₄ which is generated simultaneously.

It is concluded that discharge at -30°C effects electrolyte depletion in the pores of the electrode, and this causes the formation of ice crystals which accelerate the passivation and pore plugging processes. This ice passivation is reflected in the sudden change in decay rate of the i-t transient shown in figure 8.8.

Figure 8.10 shows a typical double layer charging transient for the porous electrode at -30°C. This figure shows that the current again decays as t⁻¹/₂ (c.f. figure 5.7). Therefore, the porous electrode theory discussed in Chapters 1, 4, 5 and 6 is still obeyed at -30°C. The i-t⁻¹/₂ plot shows that the intercept occurs at shorter times than for the same electrode at 23°C (c.f. figure 5.7). Because of the even greater ohmic resistance of the electrode preventing an infinite current density at zero time, the intercept occurs at even shorter times. The double layer capacitance was found to be only 2% of the ambient temperature value. The fall in double layer capacitance with temperature has been observed elsewhere (236'), and in this case arises owing to stronger adsorption forces, and the possibility of ice crystal in the interphase.

On reduction of a passivated porous Pb electrode at -30°C, rising transients were not observed at potentials more positive than -1080mV. At ambient temperature, rising transients were observed at overpotentials of 20mV. This low temperature behaviour is confirmed by the LSV results.
Figure 8.11 A typical reduction transient recorded after stepping a sulphated porous (Pb) electrode from -800mV to -1100mV in 5M $\text{H}_2\text{SO}_4$ at -30°C.
Figure 8.12. A plot of $i$ vs $t^{3/2}$ from the rising transient of figure 8.11
of the planar electrode in section 8.3, where the reduction peak was shifted substantially (see figure 7.1) towards the hydrogen evolution region.

Figure 8.11 shows that on reduction, a transient is recorded which is substantially different from those recorded at room temperature (c.f. figure 6.4). In the low temperature case, there is a rapid rise and fall in current as the double layer charges, followed by slow rise in current. This rising electrocrystallisation transient is substantially slower than its ambient temperature counterpart. Also, the current rise follows an $i \propto t^{3/2}$ relationship as shown in figure 8.12. The current rise is shallow, and the $i-t^{3/2}$ plots intercept the current axis at zero time. Therefore, Pb nucleation centres pre-exist the nucleation and growth phase, and subsequent growth of lead occurs at a relatively low rate. The pre-existence of nucleation centres is not surprising in view of the porous nature of the PbSO$_4$ film observed for the solid electrode in section 8.3. However, rising transients were never recorded after a potentiostatic reduction step on the sulphated solid Pb electrode at -30°C. Therefore, significantly less nucleation centres must be available for Pb growth on the porous Pb electrode. This would be the case if the pores of the electrode were plugged with PbSO$_4$ (and ice crystals), preventing the reaction of the inner active surface.

The current rise in the transient as $t^{3/2}$ can be explained in the light of the porous electrode theory already discussed$^{(43)}$, which would lead to an $i \propto t^3$. 

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relationship at a solid electrode. Armstrong et al (203) have demonstrated this relationship for progressive nucleation and 3D growth, although this model predicts a current which rises asymptotically to a current maximum. These authors also demonstrated that the current would fall if the electrode was being progressively passivated. This is clearly not the case here, and the fall in current is difficult to explain on the basis of this model.

It is possible that the "progressive nucleation and 3D growth" is an artefact owing to the progressive dissolution of ice crystals of relatively large volume as the electrolyte concentration increases. The observed transient is, therefore, a complex phenomenon resulting from the reduction of PbSO₄ to Pb, the dissolution of ice crystals, and the hydrogen evolution reaction. The i-t relationship of the falling transient did not fit any simple mathematical equation, and a substantial current at long times was recorded as the result of the hydrogen evolution reaction. It is probable that hydrogen bubbles in the electrode caused some current decay by a pore blocking mechanism.

The significance of expander additions at -30°C is reduced by the ice crystallisation phenomenon, although it is envisaged that discharge capacity would be substantially lowered by their omission. There is some evidence that BaSO₄ again provides nucleation centres for PbSO₄. Also,
an electrode manufactured without lignosulphonate will have a lower surface area/porosity (see Chapter 7), leading to a lower cold discharge capacity, and a poorer low temperature charge acceptance.

8.5. Conclusions

1. The formation of PbSO₄ at solid Pb electrodes at -30°C occurs by the same passivation mechanism, involving the lateral spread of PbSO₄ across the surface, observed at ambient temperature.

2. At high discharge rates (oxidation potentials), the PbSO₄ was significantly more porous; this factor led to the formation of PbO under the PbSO₄.

3. Tafel slopes from LSV curves suggest that electron transfer on oxidation occurs by two one electron steps, the second being rate-determining.

4. Growth of Pb on the sulphated solid Pb electrode was rate-limited by mass transport through the PbSO₄ film.

5. The capacity of the porous Pb electrode at -30°C is substantially lower than at 23°C.

6. Capacity at -30°C is limited by ice passivation.

7. Nucleation and growth of PbSO₄ at -30°C follows
the same i-t relationship for the porous electrode as observed at \( \approx 23^\circ C \), and therefore conforms to the mechanism observed on the solid Pb electrode at \(-30^\circ C\).

8. The current in the double layer charging transient decayed as \( i \propto t^{-\frac{1}{2}} \), conforming to porous electrode theory (43) given by equation (1.9).

9. The double layer capacitance was found to be 2% of the value measured at \( \approx 23^\circ C \).

10. The reduction of PbSO\(_4\) to Pb on the porous Pb electrode at \(-30^\circ C\) is complicated by ice dissolution and hydrogen evolution.
CHAPTER 9

FINAL DISCUSSION

9.1. The Negative Electrode of the Lead-Acid Battery

The lead-acid battery has been in use for over a century. If it is to remain viable in an age of new energy storage systems, the performance has to be improved. This is particularly true in the electric vehicle field, because the battery has a low energy density.

The present work has considered the negative electrode, where there is obvious scope for improvement because ~50% of the active material is utilised on discharge (energy production). Therefore, energy density could be substantially improved by efficient utilisation of the active material.

The optimisation of the porous lead electrode is most efficiently achieved by mathematical modelling, to balance the relevant parameters. Therefore, the fundamental processes occurring at the porous lead electrode must be known so that this data can be used to refine the modelling procedure.

It is important to note in this regard, that the behaviour of the porous Pb microelectrode can be explained in terms of well-established semi-infinite porous electrode theory\(^{(43)}\). The relevance of the porous Pb microelectrode to the behaviour of the battery plate has been established experimentally, and the input parameters investigated in
this project will be briefly reviewed in terms of
electrochemistry, expander action, and low temperature
behaviour.

9.1.1. Electrochemistry

The presence of a solution region has been
demonstrated in 1M\(\text{H}_2\text{SO}_4\), but in 5M\(\text{H}_2\text{SO}_4\) (normal battery
concentration) the solubility of \(\text{PbSO}_4\) is much lower, and
the solution reaction less significant; solubility also
decreases with decreasing temperature. E-t measurements
at high and low rate discharge also indicate that the
electrode does not operate in this potential region.

The formation of solid \(\text{PbSO}_4\) at porous and solid
\(\text{Pb}\) electrodes occurs by instantaneous nucleation and lateral
spread across the metal surface, with slow growth into
solution. Therefore, to increase the capacity, the
surface area of the electrode must be increased, or the
velocity of the lateral spread lowered (by increasing \(\text{PbSO}_4\)
solubility).

On recharge, \(\text{Pb}\) probably starts to grow at the
\(\text{Pb/\text{PbSO}_4/\text{H}_2\text{SO}_4}\) interface. Growth is probably in the form
of dendrites, with the concomitant progressive dissolution
of \(\text{PbSO}_4\).

The solution-precipitation mechanism of Vetter\(^{68}\)
for the charge and discharge reactions could not be
confirmed under normal battery conditions, and the processes
probably do occur, particularly on reduction when lead must diffuse from the PbSO$_4$ to the sites of growth. Certainly, the $i \propto t^{\frac{1}{2}}$ relationship observed here for the reduction of PbSO$_4$ at the planar Pb electrode, has been observed elsewhere$^{(201)}$ for electocrystallisation under diffusion control. However, quantitative analysis of the experimental data in Chapter 6 showed that solution-diffusion was not a rate-limiting process. Surface diffusion of Pb is also a possibility, but difficult to prove experimentally.

9.1.2. Expander action

The use of a porous microelectrode in conjunction with the potential step technique was found to be a cheap and efficient means of expander assessment. In this way, additives can be screened to assess their potential, and optimal concentrations can be established.

The major function of lignosulphonate is to increase the surface area/porosity of the electrode, and may be a means of improving the active material utilisation. Lignosulphonate acts by promoting Pb nucleation (and possibly delaying PbSO$_4$ nucleation); adsorption must play an important role in this. BaSO$_4$ provides nucleation centres for PbSO$_4$ and acts synergistically with the organic in increasing the surface area for sulphation; this also makes the PbSO$_4$ film thinner and easier to reduce.
9.1.3. **Low temperatures**

At low temperatures the rate of PbSO$_4$ nucleation increases and its solubility decreases. The effect of ice is significant and must be considered in the optimisation of the lead-acid battery.

9.2. **Further Work**

1. The elucidation of the mechanism of lignosulphonate action is crucial in predicting the potential use of other compounds. Compounds could be screened and their optimal concentration established.

2. The use of a model pore is recommended for the confirmation and further investigation of processes already established. Porous electrode theory needs to be further developed to explain the behaviour of experimental electrodes undergoing progressive phase change.

3. The active material utilisation must be improved for better energy density, and two approaches are recommended:

   (a) the concept of penetration depth should be mathematically developed to define optimal electrode thickness, and

   (b) different methods for controlled active material manufacture should be investigated.
4. Further studies at low temperature are recommended to improve low temperature performance, which is limited by ice crystal formation.
REFERENCES

85. W. Stein, Naturwissenschaften, 45 (1958) 459.
110. Fauré, French patent 141,057 (1881).


154. W. Peukert, Elektrotechn. Z., 18 (1897) 287.
166. D.L. Chapman, Phil. Mag., 25 (1913) 475.
186. A. N. Frumkin, Z. Physik, 35 (1926) 792.
51 (1955) 71.
224. M. Fleischmann, J.A. Harrison, and H.R. Thirsk,
227. A. N. Fleming and J.A. Harrison, in A.T. Kuhn (Ed.), "The
231. A.J. Calandra, N.R. de Tacconi, R. Pereiro, and A.J. Arvis,
232. J. Ambrose, R.G. Barradas, K. Belinko, and D.W. Shoesmith,
233. H.S. Panesar, in D.H. Collins (Ed.), Power Sources 3,
236. G.W. Herzog, W. Sitte, and O. Fruhwirth, Surface Technol.,
9 (1979) 337.