The electrochemistry of Plante-formed lead dioxide electrodes

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THE ELECTROCHEMISTRY OF PLANTÉ-FORMED LEAD DIOXIDE ELECTRODES

by

Constantine Lazarides

Supervisor: Prof. N. A. Hampson


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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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Finally, I am grateful to my fellow research Electrochemists for their help and friendship.
To Claire and Miltos
The Planté process for the production of "stand-by" lead acid cells has been in operation since the 1900's. Absolute reliability is required for these stationary batteries since applications include, for example, usage in back-up systems for nuclear power stations.

Very little has been reported in the literature concerning the theoretical and practical considerations which form the basis of the present "code of practice". The aim of the research was therefore to derive the mechanisms governing the Planté process, and in turn evaluate the validity of the currently accepted techniques.

The investigation was carried out in two stages. First, the action of perchlorate (corrosive agent used in Planté positive plate formation) on lead was examined using \( \text{H}_2\text{SO}_4/\text{HClO}_4 \) mixtures.

Cyclic voltammetry showed that perchlorate promotes surface attack in the lead/lead sulphate region by displacing the passivating sulphate ion until a "self-stifling" effect is observed at higher concentrations.

In the lead dioxide region perchlorate possibly reduces the thickness of the passivating layer.

Rotating disc experiments showed a dissolution region for lead in \( \text{H}_2\text{SO}_4 \) and \( \text{H}_2\text{SO}_4/\text{HClO}_4 \) mixtures, however, it was proved that perchlorate does not influence the overall reaction in this region.

Potential step experiments with conditions similar to those used for Planté electrode production, showed that if the electrode
is not fully passive a relatively irregular attack occurs. The effect of perchlorate during the oxidation of Pb to PbO$_2$ was much more pronounced with a well defined electrode surface. The two-dimensional instantaneous nucleation process with H$_2$SO$_4$ becomes progressive nucleation with small additions of HClO$_4$. Higher perchlorate ion concentrations result in three-dimensional growth. An intermediate range of perchlorate concentrations shows PbO$_2$ steadily advancing into the metal indicating that the system can sustain a self-regenerating process.

The second part of the investigation involved an examination of fully formed Planté micro-electrodes. The electrodes were formed starting with pure lead following an eight-stage process according to the industrial specifications. Prior to any experimental work, formed electrodes were required to pass an industrially based capacity test.

Potential step experiments were made on the fully charged Planté electrodes by stepping from the rest potential to either more positive or more negative potentials. The results of similar experiments with partially charged electrodes were compared. These results and differences were interpreted in terms of current theories of electrocrystallisation.

The electrochemical processes occurring in the Planté electrodes at different states of charge were also examined by the a.c. impedance methods. Although the results are complicated due to the high porosity of these electrodes valuable information was obtained and a theory was proposed in order to explain the experimental evidence.
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LIST OF SYMBOLS

a    activity of adsorbate
A    electrode surface area
b    Tafel slope
C    Total differential capacitance
C_{comp} differential capacitance of the compact double layer.
C_{diff} differential capacitance of the diffuse double layer.
C_{dl, CL} double layer capacitance
C_{b, C_R} bulk concentration of O and R
C_{s, C_R} surface concentrations of O and R
D_{o, D_R} diffusion coefficient of O and R
E    electrode potential on a suitable reference scale
E^0  standard electrode potential
E_p  potential of peak or current density
E_r  reversible electrode potential (at i = 0)
E_{rat} rational potential
E_{1/2} polarographic half wave potential
F    Faraday's constant
h    height of nucleus
i    current or current density
i_d, i_t diffusion controlled current density
i_m, i_p peak current or current density
i_o  exchange current density
k_1  parallel growth rate constant
k_2  orthogonal growth rate constant
k_{a, k_c} potential dependent rate constants for the anodic and cathodic reactions
k_s  specific rate constant at E
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>k_{sh}</td>
<td>standard heterogeneous rate constant</td>
</tr>
<tr>
<td>k^{o}</td>
<td>apparent standard rate constant</td>
</tr>
<tr>
<td>L</td>
<td>inductance</td>
</tr>
<tr>
<td>M</td>
<td>molar mass</td>
</tr>
<tr>
<td>n</td>
<td>number of electrons</td>
</tr>
<tr>
<td>N</td>
<td>number of moles of reactant</td>
</tr>
<tr>
<td>N_{o}</td>
<td>number of nuclei</td>
</tr>
<tr>
<td>O</td>
<td>oxidised species</td>
</tr>
<tr>
<td>P_{f}</td>
<td>porosity factor</td>
</tr>
<tr>
<td>Q_{m}</td>
<td>maximum charge</td>
</tr>
<tr>
<td>q</td>
<td>charge on electrode, flux of diffusing species</td>
</tr>
<tr>
<td>r</td>
<td>radius of nucleus</td>
</tr>
<tr>
<td>R</td>
<td>gas constant, reduced species</td>
</tr>
<tr>
<td>R_{CT}, R_{D}</td>
<td>charge transfer resistance</td>
</tr>
<tr>
<td>R_{f}</td>
<td>roughness factor</td>
</tr>
<tr>
<td>R_{O}</td>
<td>ohmic resistance of electrolyte</td>
</tr>
<tr>
<td>S</td>
<td>electrode surface area</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
</tr>
<tr>
<td>t_{m}</td>
<td>time taken to reach maximum current</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
</tr>
<tr>
<td>u</td>
<td>age of the nucleus</td>
</tr>
<tr>
<td>W</td>
<td>Warburg impedance</td>
</tr>
<tr>
<td>\langle x \rangle, x</td>
<td>(mean) distance from the electrode</td>
</tr>
<tr>
<td>Z</td>
<td>total cell impedance</td>
</tr>
<tr>
<td>Z'</td>
<td>real part of electrode impedance</td>
</tr>
<tr>
<td>Z''</td>
<td>imaginary part of electrode impedance</td>
</tr>
<tr>
<td>a</td>
<td>charge transfer coefficient</td>
</tr>
<tr>
<td>\delta</td>
<td>diffusion boundary layer thickness</td>
</tr>
<tr>
<td>\eta</td>
<td>charge transfer overpotential</td>
</tr>
</tbody>
</table>
\( \theta \) surface coverage, phase angle, charge transfer coefficient

\( \nu \) kinematic viscosity, potential sweep rate

\( \rho \) density of deposit

\( \sigma \) Warburg coefficient

\( \phi \) potential difference between the electrode and solution

\( \omega \) angular velocity, angular frequency
Planté storage batteries have been in use since before the beginning of this century. The cells consist of solid lead positive electrodes and pasted lead negative electrodes. The positive plates are cast with large numbers of closely-pitched vertical lamelles in order to increase the surface area. The plates are then successively oxidised and reduced in sulphuric acid solution following the original Planté\textsuperscript{1,2} idea in order to obtain sponge lead and a final lead dioxide electrode of a large surface area. Today, however, a more efficient process is used to achieve the porous lead dioxide state required\textsuperscript{3,4}. This is possible with the use of a "forming agent" which when added to the sulphuric acid solution, hastens the corrosion of the pure lead plates. Lead-corroding acids like nitric, and perchloric may be used for this, but perchloric acid is the most popular.

The modern Planté process therefore, consists of two stages. First, the "attack" stage, during which the forming agent is used and the plates are first oxidised and then reduced. When this is done the plates are washed free from the corroding acid, dried and finally submitted to the second formation in pure sulphuric acid solution. After a series of oxidations and reductions, the fully formed lead dioxide plates are washed and dried. Figure 1.1 shows a positive Planté plate formed in this way.

It is immediately apparent that Planté type batteries made in this way would be too bulky and too heavy to be used, for example, in the automotive industry. They have, however, been of vital
Fig. 1.1 Plante positive electrode.
importance as stationary batteries providing emergency lighting to public buildings and hospitals etc., also switch operation and other similar duties in power stations and used extensively in telecommunications systems. In addition to these light standby services, the special properties of the Planté storage batteries, their long life and their absolute reliability make them ideal for use as standby sources of power in power stations. In these cases they would be expected to supply relatively large amounts of current for short periods, for example, in order to meet peak demands. In these cases, the battery would be submitted to a short deep discharge at a high rate, followed by a slow recharge making the reliability factor of paramount importance.

The recent interest in capturing solar power, in order to overcome future energy needs, has opened another field where Planté type cells are becoming important. Reliable storage cells have to be used in order to cater for the special requirements needed by a solar powered system. The battery will have to operate under conditions of regular charge and discharge cycles on one hand, and remain virtually discharged for long periods on the other, depending on the time of year.

There has been surprisingly little research on the theoretical and practical considerations of the Planté process, most of which has arrived at its present form by trial and error. This thesis investigates the mechanisms governing the Planté process and in turn evaluates the validity of the currently accepted techniques.

The research was carried out in two stages. In the first part, the action of the aggressive agent and the levels used during the plate formation are examined. This is important as an understanding
of the process could reduce time and manufacturing costs. Pure lead electrodes were employed for this investigation using cyclic voltammetry, rotating disc and potential step techniques.

The second part of the research was concentrated on studying the behaviour of fully formed Planté electrodes under laboratory conditions. In order to do this a method was devised for producing Planté microelectrodes in exactly the same way as the industrially produced ones. Potential step experiments and the a.c. impedance technique were used to examine fully and partially charged Planté electrodes. The importance of the results relative to the commercial use of the batteries is discussed.
CHAPTER 2

THEORETICAL PRINCIPLES

2.1 The Electrode-Electrolyte Interphase

Although two electrodes are required to form an electrolytic cell, it is important to isolate the effect of one of them during kinetic investigations. This can be done successfully by controlling the potential using a potentiostat and a Luggin capillary. Applying potential to a single electrode reveals a region where no current flows and the electrode is said to be perfectly polarisable. Change of potential in this region changes the charge of both sides of the electrode-electrolyte interphase. Interphase can be defined as the area between two phases in which the properties have not yet reached the bulk of either phase. The structure of the interphase is of paramount importance in establishing the actual mechanism by which ions are transferred from one side of the interphase to the other and thus the rate at which the electrochemical reaction is taking place. Therefore, it is essential that a description of the structure of the electrode-electrolyte interphase accompanies any discussion of electrode process.

The simplest model of the distribution of charged species at the interphase was proposed by Helmholtz\(^5\), who regarded the interphase as a "double layer" of charge; there being a layer of charge at the electrode that was equal in magnitude, but opposite in sign to a charged layer in the electrolyte. The system approximated to that of a parallel-plate condenser, made up of two thin layers of charge, separated by a distance of approximately 0.3 nm and having an electrical capacity \( C_{d1} \). The following assumptions are necessary for the acceptance of
the model:

(a) the separated charges at the interphase are in electrostatic equilibrium.
(b) there is no transfer of charge in either direction across the interphase with changes in electrode potential.
(c) the charge in the solution near the electrode interphase changes with changes in electrode potential.

It is therefore expected that the electrical behaviour of the double layer is purely capacitive and that there is no ohmic leakage resistance in parallel, corresponding to ion discharge. This is an idealised requirement as, in practice, the electrode-electrolyte interphase will have a small current passing, corresponding to the occurrence of some net electrode reaction. Electrodes which closely obey these conditions are termed "ideally polarisable", but a mercury electrode between the reversible hydrogen potential and 0.9 V (s.h.e.) is the only practical system approaching idealised conditions.

The Helmholtz model of a compact layer of ions in the electrolyte was later modified by Gouy and Chapman. They developed the concept of a diffuse layer which was necessary as Helmholtz neglected the thermal distribution of ions occurring at finite temperatures. However, even the improved model showed discrepancies between the theoretical and experimental results. This was because Gouy and Chapman considered ions as point charges which could approach to within infinitely small distances of the electrode surface.

The theory was further developed by Stern, who combined the previous two models. He showed that the diffuse part of the double layer extended from the bulk of the solution up to within a finite distance of the electrode surface. This is because of the finite
size of the ions. He further postulated that some ions could undergo adsorption by means other than electrostatic attraction. The overall picture of the double layer was now of a diffuse layer and a compact layer, close to the electrode surface.

Grahame eventually postulated that the Helmholtz compact plane is divided into two regions. The inner Helmholtz plane consists of specifically adsorbed ions and it is assumed that they have lost some of their water of hydration and so are closest to the electrode surface. The outer Helmholtz plane consists of normal hydrated ions at their distance of closest approach to the surface. The model thus consists of two parallel planes at different potentials, associated to the two different types of ions.

Figure 2.1 shows a representation of the Grahame model and the variation of potential, $\phi$, with distance through the interphase. Using this model of the double layer, Grahame showed that the double layer capacitance is given by:

$$\frac{1}{C_{dl}} = \frac{1}{C_{\text{diff}}} + \frac{1}{C_{\text{comp}}} \quad (2.1)$$

where

- $C_{dl}$ = total double layer capacitance,
- $C_{\text{diff}}$ = capacitance of the diffuse layer,
- $C_{\text{comp}}$ = capacitance of the compact layer.

The diffuse layer component becomes significantly larger than the capacitance associated with the compact layer, as the electrolyte becomes more dilute and $C_{dl}$ becomes virtually independent of $C_{\text{comp}}$. At very low concentrations a sharp minimum is obtained on a $C_{dl}$ versus potential plot. This minimum is associated with the point of zero charge (p.z.c.) on the electrode.
Fig. 2.1 Grahame Model of the Double Layer

Variation of Potential with distance through the Interphase predicted by the Grahame Model.
More recently Bockris\textsuperscript{10} has taken into account the predominant existence of the solvent in the interphase. In this case the inner Helmholtz plane extends from the average surface plane, to a region passing roughly through the centres of metal "adatoms", adsorbed orientated water molecules, adsorbed unsolvated anions and, in the case of a gas electrode such as s.h.e., adsorbed gas molecules. The outer Helmholtz plane passes through the centres of the solvated metal ions where positive charges constitute the outer plate of the electrical capacitor. Figure 2.2 illustrates that model. The electrical analogue of the interphase is not strictly correct as its capacitance is generally dependent on the potential drop across it. The analogy, however, is still useful for the analysis of electrode response to a.c. perturbations as we shall see later on.

Frakin\textsuperscript{11,12} discussed the importance of the p.z.c. mentioned earlier and indicated that for anion adsorption, it moves to more negative potentials and for cation adsorption the reverse applies. Where anion and cation adsorption occur, the direction of p.z.c. may be reversed by concentration changes. The quantity of charge on the electrode can be determined by $E_{\text{rat}}$ (rational potential). At positive $E_{\text{rat}}$, adsorption of negative ions is favoured and at negative $E_{\text{rat}}$, adsorption of positive ions is favoured. When there is little or no charge on the electrode, the magnitude of $E_{\text{rat}}$ is small and the adsorption of neutral molecules competes favourably with ionic adsorption.

The latest studies on the interphase structure have been mainly concerned with the orientation of the water dipoles in the compact layer\textsuperscript{13-15}. Cooper and Harrison\textsuperscript{16-20} have considered the structure of the interphase to arise specifically from the known differences between anions and cations in aqueous solution and the net distributed charge
Fig. 2.2 Model of the electrical double layer.

COMPACT LAYER

- Solvent Molecules

DIFFUSE LAYER

- Solvated Cations

- Specifically Adsorbed Anions

Inner Helmholtz Plane

Outer Helmholtz Plane
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.

The development of statistical theories for the distribution
of ions in the interphase, as well as the study of the differential
capacitance and a knowledge of the p.z.c., are important in understanding
experimental data and studying reactions at the electrode-electrolyte
interphase.

2.2 Mass Transport

The rate of an electrode reaction can be totally or partially
controlled by mass transfer. It is therefore necessary for this to
be taken into account when considering the rate of the overall
electrode reaction. The overall flow of electrons in a process
represented as:

$$0 + ne \rightarrow R$$ (2.2)
can be limited for two reasons. Firstly, the arrival of $0$ from
the bulk of the solution to the electrode might be slow, in which
case the overall reaction is mass transfer controlled. Secondly,
if the forward reaction of equation (2.2), at the electrode, is the
rate determining step, the reaction is charge transfer controlled,
as the process is limited by the rate of electron transfer. Finally,
if neither of the above processes are as slow as the chemical
transformation involving the electroactive species, the rate trans-
formation is the rate determining step.
Mass transport of reactants to the electrode and products away from it, occurs by three main processes, these being migration, diffusion and convection, which are going to be discussed in turn.

Migration

Mass transport by migration is the result of the force exerted on charged particles by an electric field. However, in the presence of a large excess of background or supporting electrolyte, migration of electroactive material is minimised to an extent where it can be neglected.

Diffusion

Diffusion is perhaps the most widely studied means of mass transport and exists whenever concentration differences are established. The extent of diffusion is measured by the diffusion coefficient which is dependent on the dimensions of the diffusing species and the viscosity of the solvent.

Consider the linear diffusion of reacting species to a plane electrode in a static solution (no migration or convection) with respect to the reaction shown in equation (2.2).

For electrolysis experiments carried out at constant potential, three experimental facts are noticeable; namely that the current is proportional to $C_0^b$ and to the electrode area, and that the current decreases with the time of electrolysis. These facts must be accounted for in any derived time/current relationship. Concentrations are denoted by $C_0$ and $C_R$, with the superscripts "s" and "b" to signify concentrations at the electrode surface and in the bulk of the solution.

The number of moles N of a substance diffusing across a given cross-sectional area (A cm$^2$) in a time dt is proportional to the
concentration gradient of the diffusing species:

\[
\frac{dN}{dt} = K A \frac{\partial C_o}{\partial x}
\]  

(2.3)

The proportionality constant, \(K\), is defined as the diffusion coefficient \(D_o\) hence:

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

(2.4)

This equation relates the diffusion rates to concentration and is known as Fick's first law. A useful modification is obtained if the number of moles diffusing through unit area in unit time, i.e., the flux of material is considered. The flux is usually defined as "\(q\)" and is given by:

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

(2.5)

If the electrolysis is considered over a period of time then \(C_o\), and hence \(\frac{\partial C_o}{\partial x}\) must vary and in fact \(C_o\) will decrease since "\(0\)" is being consumed at the electrode. It is, therefore necessary to know \(C_o\) both as a function of distance from the electrode and time. The change in \(C_o\) with time between two planes at distance \(x\) and \(x + dx\) from the electrode surface (\(x = 0\)) will be the difference between the number of moles of "\(0\)" entering the plane at \(x = 0\) and the number leaving at the plane \(x\), thus:

\[
\frac{\partial C_o}{\partial t} = \frac{q(x + dx) - q(x)}{dx}
\]  

(2.6)

but,

\[
\frac{\partial C_o}{\partial t} = \frac{\partial q}{\partial x} \quad \text{as} \quad dx \rightarrow 0
\]

Therefore,

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

(2.7)
This is Fick's second law and the fundamental equation for linear diffusion in solution. The instantaneous current associated with this process for a step in potential will be directly proportional to the flux at \( x = 0 \):

\[
i_t = nF AQ (0, t) = (nF A D_o \frac{\partial c_o}{\partial x}) o, t \quad (2.8)
\]

**Convection**

In any solution undergoing electrolysis, free or natural convection occurs spontaneously as a result of density differences which develop near the electrode. It may also be produced from thermal or mechanical disturbances. Finally, problems of forced convection can be caused by stirring the solution, bubbling gas near the electrode and rotating the electrode, which is an important consideration in rotating disc experiments discussed later on.

**2.3 Charge Transfer Process**

The transference of charge across the double layer in a metal ion electrode reaction requires that the reacting ion passes through the electrode-electrolyte double layer and is discharged at the electrode.

Consider the redox reaction

\[
O + n \text{ e}^{-} \xrightarrow{\text{kc}} \text{R}
\]

At the equilibrium potential charge is simultaneously being donated and accepted by the electrode in a dynamic equilibrium. According to the generally accepted theory of Volmer and Erdey-Gruz\textsuperscript{21} both cathodic and anodic processes are controlled by the potential dependent activation
energy barriers; this concept has been discussed elsewhere.

The partial currents associated with these two processes are given by:

\[ i_c = nF k_c C_o^s \]  
\[ i_a = nF k_a C_R^s \]  

where \( C_o^s \) and \( C_R^s \) are the electrode surface concentrations of the oxidised and reduced species and \( k_c \) and \( k_a \) are the potential dependent rate constants. The net current flowing through the system is given by:

\[ i = i_c - i_a \]

\[ i = nF (k_c C_o^s - k_a C_R^s) \]  

It was found that the variation of \( k_c \) and \( k_a \) with the electrode potential was exponential and the rate constants have the form:

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

where \( E \) is the potential of the electrode measured against any convenient reference electrode and \( k_c^0 \) and \( k_a^0 \) are the values of \( k_c \) and \( k_a \) at this reference potential. We therefore obtain:

\[ i = nF \left[ k_c^0 C_o^s \exp \left( \frac{-\alpha nFE}{RT} \right) - k_a^0 C_R^s \exp \left( \frac{(1-\alpha) nFE}{RT} \right) \right] \]

At the reversible potential \( E_R \), \( i = 0 \) hence:

\[ i_c = i_a = i_0 \]

\[ i_0 = nF k_c^0 C_o^s \exp \left( \frac{-\alpha nF E_R}{RT} \right) \]
\[ i_o = nF k_0^o c_R^o c_R^s \exp \left( \frac{(1-a) nFE_0}{RT} \right) \]  

(2.15b)

where \( i_o \) is the exchange current and the overpotential (\( \eta \)) is defined as:

\[ \eta = E - E_r \]  

(2.16)

Introducing equations (2.15) and (2.16) into equation (2.14) gives:

\[ i = i_o \left[ \exp \left( \frac{-a nF \eta}{RT} \right) - \exp \left( \frac{(1-a) nF \eta}{RT} \right) \right] \]  

(2.17)

Expression (2.17) has been verified using a quantum mechanical treatment by Horiuti and Polanyi\(^2\)

For low overpotentials (\( |\eta| \ll \frac{RT}{F} \)) the overpotential/current curve is linear and the proportionality between the overpotential and the current corresponds to an electrical resistance, the charge transfer resistance (\( R_D \)),

\[ R_D = - \left( \frac{\partial \eta}{\partial i} \right) \quad i \rightarrow 0 \]  

(2.18)

Differentiating equation (2.17) and putting \( \eta = 0 \) the expression becomes:

\[ \left( \frac{\partial i}{\partial \eta} \right)_{\eta=0} = - \frac{nF i_o}{RT} \]  

(2.19)

therefore,

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

(2.20)

Thus the exchange current density may be obtained from the charge transfer resistance at equilibrium (\( \eta = 0 \)).

For high cathodic overpotentials the Erdey-Gruz and Volmer equation (2.17) gives the Tafel relationship\(^2\):
\[ n = \frac{RT}{aF} \log i_o - \frac{RT}{(1-a) nF} \log i \quad (2.21) \]

Hence the magnitude of the exchange current density may also be obtained from high overpotential measurements by extrapolation of the current/potential curves back to the equilibrium potential \( E_r \).

The dependence of the exchange current on the reactant concentration has also been established and for the reaction (2,2) it can be shown that\(^25\):

\[ i_o = nFK_o a_R^\alpha a_o^{(1-\alpha)} \quad (2.22) \]

\( a_R \) and \( a_o \) are usually replaced by the corresponding concentrations, since activities are usually unknown. \( k^o \) is the apparent standard rate constant.
CHAPTER 3

THEORIES OF RELEVANT ELECTROCHEMICAL TECHNIQUES

3.1 Linear Potential Sweep/Cyclic Voltammetry

Since their introduction and theoretical analysis by Randles and Sevcik, these techniques have proved to be useful tools in obtaining detailed pictures of charge transfer systems and in examining reaction mechanisms. Cyclic voltammetry has also been useful in studying the formation and reduction of oxide layers on metal surfaces.

The method depends on applying a linear potential/time function to an electrode and observing the subsequent voltammogram. If only a single sweep is performed the technique is known as linear sweep voltammetry (L.S.V.), if the sweeps are repetitive, the technique is called cyclic voltammetry. The position and shape of current peaks obtained depend on many factors including solution composition and concentration, electrode material and sweep-rate used. The slow sweep rates are used to measure "steady-state" current/voltage curves on the assumption that the surface relaxes sufficiently rapidly and the system approaches the true steady state. On the other hand, very high sweep rates are used to test the existence of short-lived intermediates. Only the linear potential sweep can give accurate kinetic parameters, as the equations derived apply only if there are no concentration gradients in solution prior to the start of the sweep. Complex concentration gradients near the electrode surface are common with cyclic voltammetry and thus, it is better suited to the identification of steps in the overall reaction and of new species appearing during electrolysis. In spite of the
limitations cyclic voltammetry is very widely used for qualitative evaluation of intermediates formed in complex reaction processes. The expected results for various reaction schemes have been discussed in a review by Nicholson and Shain29.

For a simple electron transfer process, increasing the sweep rate (v) increases the peak current density (ip) at the corresponding potential (E_r). If the electron transfer rate is sufficiently high to maintain Nernstian equilibrium at the electrode surface, as would be the case for a reversible reaction, then the peak current density for the process at 25°C is given by:

\[ i_p = 2.72 \times 10^5 n^{3/2} D^{1/2} C^0 v^{1/2} \] (3.1)

where \( n \) is the number of electrons transferred in overall electrode process,
\( D \) is the diffusion coefficient (cm\(^2\) s\(^{-1}\)),
\( C^0 \) is the concentration in solution (mol cm\(^{-3}\))
\( i_p \) measured in A cm\(^{-2}\) and \( v \) in V s\(^{-1}\).

The peak potential is independent of sweep rate and is related to the polarographic half-wave potential by:

\[ E_p = E_{1/2} - 1.109 \frac{RT}{nF} \] (3.2)

If the reaction is slow compared with the sweep rate, Nernstian response cannot be obtained. The peak characteristics change and the following limiting behaviour is approached at high rates under irreversible conditions:

\[ i_p = 3.01 \times 10^5 n \left( \frac{2.3 \frac{RT}{bF}}{nF} \right)^{1/2} D^{1/2} C^0 v^{1/2} \] (3.3)
where \( b \) is the Tafel slope \((V)\), and the peak potential in this case is given by:

\[
E_p = E_1 - b(0.52 - \frac{1}{2} \log \frac{b}{D} - \log k_s + \frac{1}{2} \log v) \tag{3.4}
\]

where \( k_s \) is the specific rate constant.

The dependence of \( E_p \) on \( v \) indicates the departure of the system from equilibrium. Provided that \( D \) is known, \( k_s \) at the standard potential and \( b \) can be calculated from a plot of \( E_p \) vs \( \log v \).

For a given system, as the sweep rate increases to the point at which the Nernstian equilibrium cannot be maintained, it will behave irreversibly. It is therefore possible to determine the specific rate constant from the characteristic sweep rate at which the transformation occurs.

3.2 The rotating disc electrode

In order to apply the kinetic equations derived in Chapter 2, it is necessary to restrict the range of mass transfer to that of diffusion. The rotating disc electrode is an example of a convective diffusion system where a complete hydrodynamic solution has been obtained. The electrode is rotated at a strictly controlled angular velocity, which eliminates the change of accidental convection, by forced mass transfer induced by forced convection. At the electrode surface the fluid flow is zero. Further away there is a velocity gradient, and eventually at a distance \( x \) perpendicular to the surface, the flow velocity has a value characteristic of the bulk of the solution, which is unaffected by the solid body. When concentration gradients exist, there will be diffusion and rotation of the electrode.
enables us to carry out experiments over long periods. In unstirred solutions the experiment would be restricted to very short times and the kinetic parameters obtained would necessitate approximations and lack precision.

Levich\textsuperscript{30} derived the mathematical solution for the hydrodynamic considerations in an experiment with a rotating disc electrode. He related the rate of transfer of a substance in solution to a rotating disc surface in terms of angular velocity of rotation $\omega$ (rads s\textsuperscript{-1}), the diffusion coefficient of the oxidised species $D_0$, the bulk concentration of the oxidised species $C_0^\infty$ and the kinematic viscosity (viscosity/density) $\nu$, giving the equation:

$$i = \frac{nF \bar{k} C_0^\infty}{1 + 1.61 \bar{k} \omega^{-1/2} \sqrt{\nu D_0^{-2/3}}} \quad (3.5)$$

where $\bar{k}$ is the potential dependant rate constant, with the diffusion boundary layer thickness $\delta$, given by:

$$\delta = 1.62 D_0^{1/3} \nu^{1/6} \omega^{-1/2} \quad (3.6)$$

Working at low overpotentials, $\bar{k}$ in equation (3.5) will be small and the rate of the electron transfer reaction will be small compared with the rate of mass transfer. In that case equation (3.5) becomes:

$$i = nF \bar{k} C_0^\infty \quad (3.7)$$

and the current will not vary with the rotation rate of the disc. Kinetic data can be directly calculated under these circumstances.

At large overpotentials, $\bar{k}$ will be large and the rate of mass transfer is the slowest step in the reaction sequence. Equation (3.5) is reduced to:

$$i = 0.621 nF D_0^{2/3} \sqrt{\frac{\nu}{C_0^\infty \omega^{1/2}}} \quad (3.8)$$
in this case and the current varies linearly with the square root of the rotation rate. In this case no kinetic data can be obtained.

For intermediate values of $k^*$, where mass transfer and the other process in the sequence are of similar rate, an extrapolation technique must be used to separate the rates of the two processes. Equation (3.5) is usually rewritten in the form:

$$\frac{1}{i} = \frac{1}{nFk^*C_0^\infty} + \frac{1.61 \sqrt{\nu}}{nFD_0^2\alpha C_0^\infty} \frac{1}{\omega^{1/2}} \quad (3.9)$$

The current depends on the rotation rate but an $i \text{ vs. } \omega^{1/2}$ plot is non-linear. The extrapolation to an infinite rate of mass transport is carried out by plotting $i^{-1} \text{ vs. } \omega^{-1/2}$, which should be linear. The intercept on the $i^{-1}$ axis gives the value for $k^*$.

For reversible reactions,

$$0 + ne \xrightarrow{k^*} R \quad (3.10)$$

the solution of the rotating disc equation is:

$$\frac{1}{i} = \frac{1}{nF(k^*C_0^\infty - kC_R^\infty)} + \frac{1.61 \sqrt{\nu}[(k^*D_0^{1/3} + (k^*D_0/D_R^{2/3})]}{nFD_0(k^*C_0^\infty - kC_R^\infty)\omega^{1/2}} \quad (3.11)$$

A plot of $i^{-1} \text{ vs. } \omega^{-1/2}$ is still linear and both rate constants can be obtained from the slope and intercept. Using this technique for a series of different potentials, the characteristics of the electron transfer reaction can be identified.
3.3 The potential-step method

3.3.1. Introduction

A large number of charge transfer reactions show no dependence of rate upon the hydrodynamic phenomena described above. In these cases, diffusion in solution plays little or no part in determining the kinetics of surface processes. The potential step method has proved to be a useful tool in studying such processes, which in cases like electrocrystallisation, corrosion, passivation and so forth are of technological importance.

The technique involves an instantaneous change of the working electrode potential, from a point where its state is well defined, to a new potential where the reaction of interest takes place. This is achieved with the aid of a pulse generator, and the current response against time can be recorded using a fast response recorder and/or a storage oscilloscope. The general form of the transient shows a spike attributed to the double layer, followed by a current decay.

When the diffusion is much faster than the electron charge transfer or any other reaction in the sequence, the current will be independent of time except for the charging current. Alternatively, when the diffusion is the rate determining step, the dependence of the falling current transients with time, can be given by the equation (2.8). It was shown that at high overpotentials, the whole transient yields a linear plot of \( i \) vs. \( t^{-1} \).

Under mixed control, the rates of diffusion and the other processes will be similar, and a falling transient is observed once more. However, the decay curve will fall less sharply, as diffusion is
only partially determining the rate of the electrode process. This will apply in the case of low overpotentials, in the steady state. The mass transfer will be fastest at short times and diffusion will control the current decay at long times. Thus, in the intermediate case the current density can be expressed by the equation:

\[ i = nF k_c C_o b \exp\left(\frac{k_c + k_a}{D}\right)^2 \alpha \text{erfc}\left[\frac{(k_c + k_a) t^{1/2}}{D^{1/2}}\right] \] (3.12)

and the limiting forms are,

(i) at short times the equation approximates to:

\[ i = nF k_c C_o b \left[1 - \frac{2(k_c + k_a)}{\pi^{1/2} D^{1/2}} t^{1/2}\right] \] (3.13)

and (ii) at long times it approximates to:

\[ i = \frac{nF k_c C_o b D^{1/2}}{\pi^{1/2} (k_c + k_a) t^{1/2}} \] (3.14)

Equation (3.13) shows that a linear plot is obtained from \( i \) versus \( t^{1/2} \) and kinetic data can be obtained by extrapolating to \( t=0 \) for short times. Equation (3.14) for long times should be linear for a plot of \( i \) versus \( t^{-1/2} \).

3.3.2 Electrocrystallisation

A. Two-dimensional model

The single pulse, potential step technique can be used very successfully for obtaining information on nucleation and growth of the electrochemical process. The crystal formation process on an electrode takes place in two distinct stages. First, there is an
incorporation of an atomic species into the crystal lattice. This can only occur where interaction can take place with several other species in the lattice (such as a kink site). The first stage thus requires an edge for the formation of nuclei. The second stage consists of the thickening of the deposited layer, by growth occurring at the peripheries of the formed nuclei.

The deposition of a new phase under controlled potentiostatic conditions has been studied in great detail and the theoretical interpretation of potentiostatic transients is well established. The following discussion will be concentrated on the nucleation and growth model (without edge effects), resulting in the equations governing the potentiostatic transient responses.

a) Without Diffusion

(i) Growth of Isolated Centres

Considering the simplest case, when the potential step is imposed, nuclei will form either instantaneously or progressively with time, at discrete centres. During their growth the nuclei can interact with one another but not with the boundary. Suppose we have a single two-dimensional nucleus growing laterally from the surface, and that the current (rate of growth) is proportional to the area (S) onto which deposition occurs. These assumptions permit the current to be written as

\[ i = nFkS \]  

where \( k \) is the rate constant (mol m\(^{-2}\) s\(^{-1}\)). The current is also equal to the rate of change of accumulated charge with time on the
Application of Faraday's law gives

\[ i = \frac{nFp}{M} \left( \frac{dV}{dt} \right) \]  \hspace{1cm} (3.16)

where \( \rho \) and \( V \) are the density and volume, respectively, of the deposited phase of molecular weight \( M \). When the radius \( r \) of the nucleus is taken into consideration, using equations (3.15) and (3.16), \( r \) can be obtained as a function of \( t \):

\[ \frac{dr}{dt} = \frac{MkS}{\rho (dV/dr)} \]  \hspace{1cm} (3.17)

For a nucleus of height \( h \), and substituting for \( S \) and \( V \) (\( S = 2\pi rh \), \( V = \pi r^2 h \)) the previous equation becomes

\[ \frac{dr}{dt} = \frac{Mk}{\rho} \]  \hspace{1cm} (3.18)

Assuming that \( r = 0 \) at \( t = 0 \), equation (3.18) is integrated w.r.t. time to yield the time dependence of the radius of a single nucleus:

\[ r = \frac{Mk}{\rho} t \]  \hspace{1cm} (3.19)

Thus, for deposition round the edge (\( S = 2\pi rh \)), using equations (3.15) and (3.19), the current for the growth of a single centre as a function of time is,

\[ i = nF 2\pi k^2 \frac{M}{\rho} t \]  \hspace{1cm} (3.20)

However, at a given time, a great number of nuclei will exist on
the macroscopic surface of a real substance. Consequently, it is necessary to introduce \( N_0 \), the total number of nuclei for the simplest case of instantaneous nucleation. Assuming that no new growth centres appear after the start of the pulse, equation (3.20) for the total current becomes

\[
i = \frac{nF N_0}{2\pi h k^2} \frac{M}{\rho} t
\]  

(3.21)

which predicts a linear dependence between \( i \) and \( t \).

An extension of the above equation to progressive nucleation can be obtained assuming that the population of nuclei is time dependent. The number of new growth centres should increase exponentially with time,

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

(3.22)

where \( N \) is the number of nuclei at any one time \( t \), \( N_0 \) is the initial number of nuclei and \( A \) is the nucleation rate constant. Since nucleation and growth occur simultaneously the resulting current at time \( t \) after the start of deposition is given by

\[
i = \int_0^t i(u) \left( \frac{dN}{dt} \right)_{t-u} \, du
\]  

(3.23)

where \( u \) is the age of the nucleus. If \( i(u) \) is represented by equation (3.20) with \( t \) replaced by \( u \), and \( dN/dt \) by

\[
\frac{dN}{dt} = N_0 A \exp (-At)
\]  

(3.24)
which can be approximated to (for small $t$),

$$\frac{dN}{dt} = N_0 A$$  \hspace{1cm} (3.25)

Thus, the total current for two-dimensional nucleation is given by

$$i = nF N_0 \Delta \pi h k^2 \frac{M}{\rho} t^2$$  \hspace{1cm} (3.26)

showing that $i$ can again be estimated as a function of $t$. Similar equations for an unbound electrode have been discussed by Thirsk and Harrison\textsuperscript{33}. The dependencies are all of the form $i \propto t^\beta$ and are rising transients, with $\beta$ depending on the geometry and type of nucleation.

(ii) Overlap of Growth Centres

Equations (3.21) and (3.26) for instantaneous and progressive nucleation respectively, predict an infinite increase of current with time. This cannot be true, since at some point during the two-dimensional growth process, neighbouring centres will overlap. As a result of that the area available for growth will decrease as overlap increases. For nuclei overlapping randomly, Avrami\textsuperscript{34} showed that

$$S_1 = 1 - \exp (-S_{1\text{ex}})$$  \hspace{1cm} (3.27)

where $S_{1\text{ex}} = \pi r^2$, is the top area of an isolated nucleus and $S_1$ is the actual area when considering overlap.
For instantaneous nucleation $S_{1\text{ex}}$ will be

$$S_{1\text{ex}} = N_0 \pi r^2 \quad (3.28)$$

and for progressive nucleation

$$S_{1\text{ex}} = \pi \int_0^t r(u)^2 \left( \frac{dN}{dt} \right)_{t-u} \, du \quad (3.29)$$

Substitution for $r$ in terms of $t$ using equation (3.19) yields for instantaneous and progressive nucleation respectively:

$$S_{1\text{ex}} = \pi N_0 k^2 \frac{M^2}{\rho^2} t^2 \quad (3.30)$$

$$S_{1\text{ex}} = \pi N_0 A k^2 \frac{M^2}{3\rho^2} t^3 \quad (3.31)$$

which can now be substituted in equation (3.27) giving

$$S_1 = 1 - \exp\left(-\pi N_0 k^2 \frac{M^2}{\rho^2} t^2\right) \quad \text{(instantaneous)} \quad (3.32)$$

and

$$S_1 = 1 - \exp\left(-\pi N_0 A k^2 \frac{M^2}{3\rho^2} t^3\right) \quad \text{(progressive)} \quad (3.33)$$

For circular two dimensional nuclei, the volume per unit area of total surface is $V = S_1 h$, which when substituted into equation (3.16) can give the current for instantaneous or progressive nucleation. Thus the expressions for the potentiostatic transients are,

for instantaneous nucleation:

$$i = nF N_0 2\pi h k^2 \frac{M}{\rho} t \exp\left(-\pi N_0 k^2 \frac{M^2}{\rho^2} t^2\right) \quad (3.34)$$
and for progressive nucleation:

\[ i = nF N_o A \omega h k^2 \frac{M}{\rho} t^2 \exp (-\pi N_o A k^2 \frac{M^2}{3\rho^2} t^3) \]  

(3.35)

Figure 3.1 shows the potentiostatic transients corresponding to the above equations. At very short times the current increases linearly with \( t \) for instantaneous and \( t^2 \) for progressive nucleation, as equations (3.34) and (3.35) are reduced to equations (3.21) and (3.26) respectively. The experimental \( i-t \) plots are of similar shape to the non-dimensional reduced plots shown in Figure 3.1.

The maximum current \( (i_m) \) and time \( (t_m) \) can be obtained by differentiating equations (3.34) and (3.35). It is shown that \( i_m \) increases and \( t_m \) decreases with increasing growth rate constant \( k \), and that the dependence is greater for instantaneous than for progressive nucleation. However, the value of \( (i_m t_m/Q_m) \) is independent of the potential dependence of \( k \), and has a constant value of 1.0 for progressive and 0.6 for instantaneous nucleation. \( Q_m \) is the maximum charge. Another diagnostic relationship between current and time can be obtained by dividing both the above equations by \( t \) and \( t^2 \) respectively. By taking logarithms of both sides of the equations we obtain

\[ \ln \left( \frac{i}{t} \right) = a - bt^2 \]  

(instantaneous)  

(3.36)

\[ \ln \left( \frac{i}{t^2} \right) = a' - b't^3 \]  

(progressive)  

(3.37)

Armstrong and Harrison\textsuperscript{35} extended the arguments implicit in equations (3.34) and (3.35) to layer by layer growth. This was necessary in order to account for the majority of cases where
Fig. 3.1 Theoretical current-time curves according to:

(a) equation (3.34)

(b) equation (3.35)

Fig. 3.2 Total current transient for layer by layer growth showing contribution from individual layers.
successive layers of deposit are observed. They achieved a solution by numerical integration, a method which was later refined by Armstrong and Metcalfe. It was shown that a limiting value for the current is reached after four or five monolayers. Figure 3.2 shows the contributions from the first five monolayers together with the total current observed.

b) With Diffusion

The situation can now be examined, whereby the nucleus considered in the previous section is growing by diffusion, two-dimensionally without overlap. The radius \((r)\) at time \(t\) was shown to obey the equation

\[ r = \theta (Dt)^{1/2} \]  

(3.38)

where \(\theta\) is a constant controlled by the potential, \(M\) and \(\rho\), and \(D\) is the solution diffusion coefficient.

By using the Avrami treatment for \(N_0\) number of nuclei overlapping we get, where \(q_m\) is the charge for the monolayer, for instantaneous nucleation:

\[ i = q_m \pi \theta^2 D \exp \left( -\pi \theta^2 DN_0 t \right) \]  

(3.39)

and for progressive nucleation:

\[ i = q_m \pi \theta^2 N_0 At \exp \left( -\frac{\pi \theta^2 DN_0 At^2}{2} \right) \]  

(3.40)

When the nuclei are surrounded by a fixed diffusion zone the value of \((i_m t_m/Q_m)\) is no longer a constant as was shown earlier. It is possible again to obtain a relationship for current-time with the existence of a fixed diffusion zone. This zone could arise either by adatom diffusion, where the diffusion zone is set
up by the electrochemical reaction on the clean surface, or by the preceding chemical reaction in the solution. However, a diffusion zone increasing with time, is due to two-dimensional metal deposition by diffusion in solution.

B. Three-dimensional Model

In principle three-dimensional growth can be obtained by layer-by-layer growth. Armstrong et al. have considered a three-dimensional model of growth of right circular cones where the rates of advance $V_1$, $V_2$, $V_3$ are defined as shown in Figure 3.3. A slice $x$ from the surface and height $dx$ will grow out horizontally, assuming that the nuclei are distributed at random on the surfaces and the interaction of slices at a height $x$ can be described by the Avrami equation. The current due to a layer comprising all the cylinders of height $dx$ is given by

$$di = f(x)dx = 2\pi FN_0 k_2 \left( t - \frac{x}{V_2} \right) \exp \left[ -\frac{\pi N_0}{\rho^2} k_1^2 M^2 \left( t - \frac{x}{V_2} \right)^2 \right] dx$$

(3.41)

for the case of instantaneous nucleation, where $V_2$ is the growth velocity perpendicular to the plane and $k_1$ is the rate constant parallel to the plane. Integration and replacement of $V_2$ by the related rate constant $k_2$ yields

$$i = nFk_2 \left[ 1 - \exp \left( -\frac{\pi N_0 k_1^2 M^2 t^2}{\rho^2} \right) \right]$$

(3.42)

At short times the current is given by

$$i = \frac{nFk_2^2 k_2 \pi N_0 M^2 t^2}{\rho^2}$$

(3.43)
Fig. 3.3 Three dimensional models

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

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

(c) current only flows into the uncovered area (passivation)
Equations (3.42) and (3.43) show that at short times \( i \) varies with \( t^2 \), whereas at long times it approaches \( nFk^2 \) asymptotically.

If progressive nucleation is considered the following expression is obtained:

\[
i = nFk^2 \left[ 1 - \exp \left( \frac{-\pi M^2 k^2 N_0 A t^3}{3\rho^2} \right) \right] \quad (3.44)
\]

This argument can be expanded to the case of three-dimensional growth leading to passivation. In this case the spread of a species from the electrode to the nucleation centres is essential for further expansion. The species will be considered to pass only through the uncovered area of the electrode. Thus, as time tends to infinity, the current reaches zero. It is not possible to derive an algebraic solution to this problem using a rigorous approach, but assuming that the velocity of advance orthogonal to the electrode \( (V_2) \) is proportional to the uncovered surface area, the following expression is obtained for progressive nucleation.

\[
i = nFk^2 \left[ 1 - \exp \left( \frac{-\pi M^2 k^2 N_0 A t^3}{3\rho^2} \right) \right] \exp \left( \frac{-\pi M^2 k^2 N_0 A t^3}{3\rho^2} \right) \quad (3.45)
\]

The above equation predicts a maximum in the \( i-t \) curve given by

\[
i_m = \frac{nFk^2}{4} \quad (3.46)
\]

and

\[
t_m = \left( \frac{3\rho^2 \ln 2}{\pi M^2 k^2 N_0 A} \right)^{1/3} \quad (3.47)
\]

Also

\[
i_m t_m = 0.208 \, nFk^2 \left( \frac{3\rho^2}{\pi M^2 k^2 N_0 A} \right)^{1/3} \quad (3.48)
\]
Fig. 3.4 Theoretical plot for 3-D progressive nucleation corresponding to eq. (3.45)

![Graph showing theoretical plot for 3-D progressive nucleation](image)

Fig. 3.5 Predicted i-t curves for 3-D progressive nucleation:
(A) without passivation, eq. (3.44)
(B) with subsequent passivation, eq. (3.45)

![Graph showing predicted i-t curves for 3-D progressive nucleation](image)
\( k_1, k_2 \) and \( N_0A \) can be eliminated if the above values are substituted into equation (3.45). A reduced plot can therefore be obtained shown in Figure 3.4. Finally, Figure 3.5 shows a comparison of predicted current-time transients for equation (3.44) corresponding to progressive three-dimensional growth without passivation and equation (3.45) where subsequent passivation occurs.

3.4 The A.C. Impedance Technique

3.4.1 Introduction

The a.c. impedance characteristics of electrochemical systems are important as their study enables us to measure the kinetic parameters of the cell. These can give indications of the type of reaction and transport mechanisms as well as an indication of the response to varying load conditions. The application of a.c. theory to reproducible liquid-metal electrodes has led to a better understanding of electrode reaction mechanisms. Reproducible values of exchange current densities and transfer coefficients have been obtained for simple charge transfer processes. The method is also being used successfully in evaluating more complex processes involving specific adsorption of reactants or products or chemical reactions before or after the charge transfer reaction.

Industrial investigations of electrode processes are usually concerned with solid or even porous electrodes, for example, those in fuel cells, batteries, electrochemical synthesis, electrolysis, electroplating etc. Although the results obtained on liquid electrodes are of limited use for these systems, the theoretical principles have been established for the interpretation of these measurements in terms of structure, exchange current density, double layer capacitance and surface area.
For the conventional electrochemical techniques, the voltage applied to the electrolytic cell is essentially kept constant during the measurement of current. In the alternating current technique, however, an alternating voltage \( v \) of relatively small amplitude (3 mV) is superimposed on the potential difference, and the current contains an alternating component of amplitude \( i \). When the amplitude of \( v \) varies sinusoidally with time \( t \), and with frequency \( f \), we may write

\[
\omega = 2\pi f
\]

\[
v = V_{\text{max}} \sin \omega t
\]

\[
i = I_{\text{max}} \sin(\omega t - \phi)
\]

and

\[
Z_{\text{cell}} = \frac{V_{\text{max}}}{I_{\text{max}}} \text{ arg} (\phi) = |Z_{\text{cell}}| \text{ arg} (\phi)
\]

where \( Z_{\text{cell}} \) is the impedance of the cell and \( \phi \) is the phase angle. Thus, the relationship between the current and voltage gives the a.c. impedance of the cell.

3.4.2 The Cell Impedance

The faradaic impedance of a cell was first calculated by Warburg\(^4\), but without taking into account the capacitance due to the double layer present at an electrode surface. Randles\(^5\) has finally established the impedance method for fast electrode reactions for a galvanic cell. A simple one step redox reaction takes place in the cell, the rate of which is controlled solely by charge transfer and diffusional mass transfer.
The impedance of an electrolytic cell can be represented as a rule by the network shown in Figure 3.6 often described as a Randles circuit. In this circuit $R_s$ is the ohmic resistance of the electrolyte solution between the electrodes, including the resistance of the metal leads to the electrodes, and $C_d$ the double layer capacitance which varies with d.c. potential depending on the concentration and nature of the electrolyte. $\Theta$ is the charge transfer resistance and it therefore represents the activation polarisation of the electrode reaction. $W$ ($W = R_d C_d$) the Warburg impedance, is the impedance to a.c. current due to the charged species diffusing to and from the electrode.

Solution of Fick's second law of diffusion, taking into account the appropriate boundary conditions, allows the Warburg impedance to be represented by a series combination of resistance and capacitive reactance:

$$W = \sigma \omega^{-\frac{1}{2}} - j \omega^{-\frac{1}{2}}$$  \hspace{1cm} (3.49)

where $\sigma$ is the Warburg coefficient and $\omega$ is the angular frequency of the alternating current.

$$\sigma = \frac{RT}{n^2 F^2 \sqrt{2}} \left[ \frac{1}{C_O D_O^{\frac{1}{2}}} + \frac{1}{C_R D_R^{\frac{1}{2}}} \right]$$  \hspace{1cm} (3.50)

where $C_O$ and $C_R$ are the concentrations of oxidised and reduced forms of reacting species in the bulk of the solution, and $D_O$ and $D_R$ are the diffusion constants of the reacting species.

The activation polarisation resistance is related to the concentrations $C_O$ and $C_R$ and the reaction rate constant $k_{sh}$ by:
Sluysers$^4$ and Sluysers-Rehbach$^5$ finally interpreted the total impedance of the cell in terms of $R_Q$, $C_L$, $\theta$ and $\sigma$ and represented the frequency dependant impedance of the simple electrode by plotting the impedance as a vector in the complex plane. The method entails plotting the real component ($Z'$) and the imaginary component ($Z''$) of the cell impedance against each other as a function of some varied parameter (frequency, concentration or d.c. voltage).

From the Randles circuit (Fig. 3.6) the cell impedance can be given by

$$Z = R_Q + \frac{1}{j\omega C_L + \frac{1}{[1/(\theta + \sigma^{-1} + j\sigma^{-1})]}} \quad (3.52)$$

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

$$Z = Z' - jZ'' \quad (3.53)$$

where $Z'$ and $Z''$ are given by

$$Z' = R_Q + \frac{\theta + \sigma^{-1}}{(\sigma^{-1}C_L+1)^2 + \omega^2C_L^2(\theta + \sigma^{-1})^2} \quad (3.54)$$

and

$$Z'' = \frac{\omega C_L(\theta + \sigma^{-1}) + \sigma^{-1}(\sigma^{-1}C_L+1)}{(\sigma^{-1}C_L+1)^2 + \omega^2C_L^2(\theta + \sigma^{-1})^2} \quad (3.55)$$
Fig. 3.6 Electrical analogue of the electrode interphase

![Electrical analogue of the electrode interphase](image)

\[ R_d + C_d = W \]

Fig. 3.7 Complex plane display - diffusion control

![Complex plane display](image)
Fig. 3.8 Complex plane display - charge transfer control

Fig. 3.9 Complex plane display - mixed control
At low frequencies, when the effects of the double-layer capacitance may be neglected, the impedance $Z$ from equation (3.53) reduces to:

$$Z = R_\infty + \theta + \sigma \omega^{-\frac{1}{2}} - j(\sigma \omega^{-\frac{1}{2}} + 2\sigma^2 C_L) \quad (3.56)$$

Thus, the value of the impedance tends to that of $W$, discussed earlier. A complex plot of $Z''$ against $Z'$ shows a straight line of $45^\circ$ slope (Fig. 3.7).

At higher frequencies and with a fairly irreversible electrode reaction, the concentration polarisation can be neglected and equation (3.53) reduces to:

$$Z = R_\infty + \frac{\theta}{1 + \omega^2 C_L^2 \theta^2} - j \frac{\omega C_L \theta^2}{1 + \omega^2 C_L^2 \theta^2} \quad (3.57)$$

Figure 3.8 shows that, in this case, when the real and imaginary parts are plotted against each other, a semicircle is obtained. The semicircle arises from the range of values of frequency for which $\omega$ shrinks to a value small enough for the analogue to behave as a resistance and capacitance in parallel. The diagram shows that $R_\infty$ and $\theta$ can be easily obtained from such an experiment. In addition, from the frequency at the top of the semicircle, $\omega = 1/\theta C_L$, the value of the double-layer capacity, $C_L$, in the presence of the redox-system can be computed.

At lower frequencies, the diffusion polarisation gives rise to a distortion of the circle. Figure 3.9 shows that at low frequencies a $45^\circ$ slope will be obtained.
3.4.3 Practical considerations

Many systems investigated by the a.c. impedance method have shown deviations in behaviour from that expected from the Randles circuit shown in Figure 3.6. The simple process has been extended, to incorporate the effects of surface processes, by Grahame\textsuperscript{46}, but more significantly by Sluyters\textsuperscript{45}. Thus, the adsorption of species is represented by incorporating extra resistances and capacitances in the electrode analogue. If the adsorbed species are able to undergo a redox reaction, it is necessary to add extra components to the analogue, in effect shunting the double-layer\textsuperscript{47}. A review by Armstrong et al\textsuperscript{48} extends the discussion of complex reactions to passivity, nucleation and growth processes. It was shown that differences in the impedance spectra can be used to distinguish between cases of two-dimensional nucleation and growth and adsorbed intermediates.

Impedance measurements are also being carried out on complete cells\textsuperscript{49,50}. The impedance spectra show gross changes occurring as the cells are discharged. This means that it may well be possible to develop a state-of-charge test which will be based on a frequency-response experiment. Finally, the requirement of high surface area material for storage cells, means that the modifications to the planar electrode behaviour introduced by the high porosity are gross\textsuperscript{51}. Thus, an extension of the existing impedance theory would give a better understanding of the behaviour of commercial cells. Difficulties arise from the recognition that, in principle, for a planar electrode, the current lines are vertical to the electrode surface, where for a porous electrode they are effectively parallel to it. A consequence of that is that the Warburg impedance in the porous electrode is
dependent on terms proportional to $\omega^{-1/4}$ rather than $\omega^{-1}$ in equation (3.49). Similarly, the high frequency semicircle which cuts the real axis normally for the plane electrode, comes off at $\pi/4$ in the case of the porous one. The most convenient method of dealing with the porous electrode is to use the method of "squaring"$^{51}$. In this, the phase angle in the locus of the impedance is doubled and the amplitude is squared. A further interesting feature observed in porous impedance experiments is the inductive behaviour seen at high frequencies. Darby$^{52}$ showed that inductive impedances arise when mass transport and electrochemical reactions can occur simultaneously over a distributed region of the electrode, Gutmann$^{53}$, who also observed the inductive region, ascribed it to geometrical effects of the electrode pores. It was suggested that the inductive part of the frequency spectrum arose due to the time elapsed between the arrival of the signal at the mouth of the electrode pore and its reaching the bottom. Similar observations have been made by others$^{49,54}$ and the inductive behaviour at high frequencies will be discussed more extensively in a later chapter.
4.1 Introduction

Positive plates for the lead-acid battery can be prepared by one of two methods. In the more common process a paste of leady oxides is oxidised in dilute sulphuric acid. In the original process, the lead dioxide was prepared by the electrooxidation of a piece of lead. The Plante process, as mentioned in the Introduction, is based on this original process. The formation process, which consists of a series of charges and discharges, will be described fully in the next Chapter. The active PbO₂ material is produced from the pure lead base. During service lead dioxide is gradually lost from the positive plate of a lead-acid cell. In the case of pasted electrodes this loss is irretrievable. However, in the case of the Plante positive the loss is made good from the lead base. It is this quality that gives the Plante electrode its long life.

4.2 The Lead Electrode

The Plante storage battery and lead-acid systems in general have been used commercially over one hundred years. It is therefore not surprising that a number of reviews have been written on the lead-acid cell\(^55\text{--}57\).

In the Plante process pure lead is converted to lead dioxide via a lead sulphate state:

\[
Pb + SO_4^{2-} \xrightarrow{\text{Discharge}} PbSO_4 + 2e^- \quad (4.1)
\]
The oxidation of lead in sulphuric acid has been studied using both constant current and constant potential experiments and Hampson and Lakeman have reviewed the electrochemistry of porous lead\textsuperscript{58}.

The capacity of the porous lead electrode is determined by the following factors:

- a) the amount of active material in the electrode;
- b) the thickness of the electrode;
- c) the rate of discharge;
- d) the temperature;
- e) quantity and concentration of electrolyte;
- f) porosity;
- g) electrode design;
- h) previous history of the electrode.

The oxidation of porous lead electrodes in sulphuric acid showed no rotation speed dependence\textsuperscript{59}. This proved that the oxidation current arose from the inner porous structure. Potential step studies showed that although planar electrodes exhibited an initial proportionality between current and time, the porous electrode showed a half-power time dependence\textsuperscript{60,61} in keeping with the porous electrode theory.

The reduction of lead sulphate has similarly been examined using a potential step technique\textsuperscript{62}. Both planar and porous electrodes behaved in similar manner, showing a current transient rising at \((\text{time})^b\). This observation indicates that in both cases the surfaces can be regarded as porous. In addition the electrocrystallisation process was found to be two-dimensional instantaneous nucleation for both the oxidation and reduction sequences.
Studies on cycled negative plates\textsuperscript{63} showed that there was a relationship between the size of the lead sulphate crystals in the reduced plates and capacity. As the PbSO\textsubscript{4} crystal size decreased with cycling, so did the capacity of the plate suggesting the occurrence of passivation.

4.2 The Lead Dioxide Electrode

The positive electrode of a lead-acid cell is the electrode which under normal conditions limits the discharge capacity of the cell.

The reaction at the positive plate may be written as

\[ \text{PbO}_2 + \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e} \rightleftharpoons \text{PbSO}_4 + 2\text{H}_2\text{O} \quad (4.2) \]

However, the discharge capacity is at best 50\% of what should be expected from the above equation. Capacity limitations are due to similar factors to those mentioned before. Literature shows examples of these effects due to the crystallite size and surface area\textsuperscript{64}, modification of lead dioxide (\(\alpha\) or \(\beta\))\textsuperscript{64,65} acid starvation effects\textsuperscript{64}, pore size distribution\textsuperscript{64} and passivation by lead sulphate\textsuperscript{64,66}.

Analysis of the elementary processes occurring within the electrode matrix, such as transport and charge transfer, have been used to provide a mathematical model for the porous electrode\textsuperscript{51,67-69}. The achievement of a model can provide design criteria for the perfectly optimised electrode. When the distances over which there is significant variation in concentration and potential are large compared with the pore size, the pore geometry can be ignored. The majority of flooded
porous electrode models therefore use a one-dimensional representation and may be divided into three categories, (a) the pore model, (b) the analogue model and (c) the macrohomogeneous model.

The pore model is represented by parallel cylindrical pores of constant radius, perpendicular to the outer surface, whereas the analogue model makes use of equivalent circuits, with the resistance of carrier materials and electrolytes in conjunction with polarisation resistance. Both these models have disadvantages. In the first case the geometric complexity of the electrodes causes complications arising from the possible direction of the pores. The analogue model on the other hand using a linearised polarisation equation does not apply for high current densities as the polarisation equation becomes of the exponential type.

The work of Newman and Tobias showed that using the macrohomogeneous approach, the need for detailed uniformity of the porous matrix could be neglected while retaining a realistic representation of the porous electrode. 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. The model is 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.

At a given time, there will be a large range of reaction rates within the pores. This rate distribution directly influences the net
power available from a battery and will change during the course of charge/discharge reactions. 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.\textsuperscript{75} who investigated flooded porous metal electrodes undergoing structural change by anodic dissolution. Alkire and Place\textsuperscript{76} 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\textsuperscript{77, 78} 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.

Specific applications of the macrohomogeneous model to the lead-acid cell have been made by Micka and Rousar\textsuperscript{79-81}, Simonsson\textsuperscript{82-85} and others\textsuperscript{86-88}, using the steady-state approach to predict current
distributions, discharge profiles and acid depletion profiles.

Weisener and Reinhardt\textsuperscript{89} working on Pb accumulator positive electrodes found that the electrode content of $\alpha$-PbO$_2$ decreased, with an increase for the $\beta$-form, during cycling. $\alpha$ and $\beta$ PbO$_2$ are products of the oxidation of lead\textsuperscript{90,91} and it was concluded that $\alpha$-PbO$_2$ is found adjacent to the metal due to the high pH at the lead/corrosion product interphase\textsuperscript{91,93}.

When an aggressive agent is used in the anodic oxidation of lead, the anodic film consists of $\alpha$ and $\beta$ PbO$_2$, and the diffusion of oxygen carrying species like $\text{H}_2\text{O}$, $\text{OH}^-$, $\text{O}_2^-$, or (O) into the interior of the film is involved\textsuperscript{94}. Anions such as $\text{ClO}_4^-$ may influence the permeability of the anodic films and thus penetration of the protective sulphate layer is the basis of the "forming agent" action. The penetration of the PbO$_2$ layer produces pitting corrosion of the lead. The degree of corrosion is influenced by the ratio of $\text{ClO}_4^-$ to $\text{SO}_4^{2-}$\textsuperscript{95}. The influence of the perchlorate ion in the Planté formation process will be discussed fully in the following chapters.
CHAPTER 5

EXPERIMENTAL TECHNIQUES

5.1 Electrolytic Systems

5.1.1 Electrolytic Cells

All cells were made from borosilicate glass fitted with ground glass joints. All glassware was cleaned by total immersion in a 50:50 mixture of nitric and sulphuric acid for a minimum period of three days. The acid was then removed by thoroughly washing with tri-distilled water.

The type of cell used for all the experimental techniques was a conventional three-limb cell shown in Figure 5.1. The design also enabled the passage of nitrogen through the cell in order to deoxygenate the electrolyte. White spot nitrogen was used which was first deoxygenated by passing over copper at 400°C. The reference electrode was connected to the working electrode compartment via a Luggin capillary and a ground-glass joint.

A different type of cell, shown in Figure 5.2, was used for the actual formation of the Planté microelectrodes. The working electrode was formed in the upward facing position in order to avoid retention of gas in its porous matrix. The counter electrode, the reference electrode and a cooling finger were introduced at the top of the cell.

5.1.2 Working Electrodes

The working electrodes used throughout this work were made from pure lead rods (99.999%) supplied by Koch-Light. The lead was
Fig. 5.1 Electrolytic Cell.
Electrode compartments: A, counter; B, working; and C, reference.
D, Luggin capillary.
Fig. 5.2 Formation Cell.
Electrodes: A, counter; B, reference; C, working.
machined to produce rotating disc electrodes \((A = 0.071 \, \text{cm}^2)\) which were set firmly in Teflon receptors. A stout spring was then soldered to the back of the electrode, ensuring good electrical contact and the receptor was screwed onto a hollow Teflon holder with a liquid tight sealing. This arrangement enabled the simple removal of the working electrode for S.E.M. examination (Figure 5.3).

A rotating disc assembly was required for the dissolution region experiments but it was in fact used in all the electrochemical studies, checking for rotation speed dependence, and allowing for the removal of gas from the electrode surface. The complete working electrode unit was secured onto a stainless steel shaft, by means of a screw on the Teflon holder. A copper wire dipped into a mercury pool at the top of the steel shaft formed the terminal for the working electrode.

The working electrodes used in the aggressive ion \((\text{ClO}_4^-)\) investigation were pretreated by polishing on roughened glass, using tri-distilled water as a lubricant. Immediately prior to an experiment, the electrodes were etched \((60\, \text{s}; \, \text{HNO}_3, 1.58 \, \text{M})\) and thoroughly washed with tri-distilled water before immersing them, still wet, into the electrolyte solution.

The Planté microelectrodes used in the second part of the work were formed galvanostatically following the industrially accepted procedure. The electrodes were polished as before on roughened glass and then introduced into the formation cell. The electrolyte used for the first formation was sulphuric acid \((1.075 \, \text{s.g.})\) containing potassium perchlorate \((7.5 \, \text{g/l})\). The electrodes were first cathodically "cleaned", and this was followed by the two oxidation-reduction cycles. The electrolyte temperature was kept
Fig. 5.3 Working electrode

- Stainless-steel Grub screw
- Threaded Teflon Electrode holder
- Metal Electrode
- Threaded Teflon Electrode shroud

Fig. 5.4 Reference Electrode

- Cu wire
- B 19
- pyrex
- solder
- HgSO₄
- Pt wire
- Hg
below 16°C as industrial practice has shown that this is essential in order to obtain the required performance from the completed plate. The reduced electrodes were thoroughly washed in stirred, warm, tri-distilled water, for a minimum of half an hour, to ensure the removal of the perchlorate from the porous matrix. They were then dried slowly in a cool oven (around 40°C), to allow the "sponge" lead to oxidise.

The second formation was carried out in pure sulphuric acid (1.210 s.g.). It should be noted at this stage that AnalaR grade reagents were used throughout this work. The electrodes underwent a long oxidation (third cycle), followed by a series of charge and discharge cycles. The electrodes were finally fully charged and a ten-hour capacity test was performed on them. Only electrodes that passed this test by exhibiting capacities greater than 10h were used for further study. Details of times and currents used in the Plante formation process are shown in Table 5.1.

5.1.3 Counter and Reference Electrodes

The counter electrodes used throughout were pure lead rods, coils or sheets of large surface area.

The reference electrode was a wick-type mercury/mercurous sulphate in sulphuric acid, of the same concentration as that of the cell electrolyte, (Figure 5.4). All potentials in this thesis were measured against this reference electrode.
<table>
<thead>
<tr>
<th>FORMATION STEPS</th>
<th>TIME (h)</th>
<th>CURRENT DENSITY (mAcm⁻²)</th>
<th>ELECTROLYTE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathodic Cleaning</td>
<td>0.5</td>
<td>1.380</td>
<td>(\text{H}_2\text{SO}_4 (1.075 \text{ s.g.}) + \text{KClO}_4 (7.5 \text{ g/l}))</td>
</tr>
<tr>
<td>FIRST FORMATION:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1st Cycle (oxidation)</td>
<td>20</td>
<td>1.725</td>
<td>&quot;</td>
</tr>
<tr>
<td>2nd Cycle (reduction)</td>
<td>20</td>
<td>1.725</td>
<td>&quot;</td>
</tr>
<tr>
<td>SECOND FORMATION:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3rd Cycle (oxidation)</td>
<td>30</td>
<td>1.845</td>
<td>(\text{H}_2\text{SO}_4 (1.210 \text{ s.g.}))</td>
</tr>
<tr>
<td>FIRST DISCHARGE</td>
<td>6</td>
<td>0.949</td>
<td>&quot;</td>
</tr>
<tr>
<td>RECHARGE</td>
<td>7</td>
<td>1.449</td>
<td>&quot;</td>
</tr>
<tr>
<td>SECOND DISCHARGE</td>
<td>9</td>
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<td>&quot;</td>
</tr>
<tr>
<td>FULL RECHARGE</td>
<td>20</td>
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</tr>
<tr>
<td>TEST DISCHARGE</td>
<td>10</td>
<td>0.791</td>
<td>&quot;</td>
</tr>
</tbody>
</table>
5.2 Electrical Circuits

5.2.1 Cyclic Voltammetry, Potentiostatic Pulse and Rotating Disc Studies

Potentiostatic control was obtained using a scanning potentiostat (Kemitron, type P.03/SG.2) which could be operated in sweeping or steady-state potentiostat modes. The unit was also supplied with an inbuilt liquid crystal voltmeter. A pulse generator (Kemitron PM3) was interphased to the potentiostat for the potentiostatic pulse experiments.

Potentiodynamic profiles for cyclic voltammetry were recorded on an x-y recorder (Bryans Series 26000) or a y-t recorder (Bryans Series 27000). In the case of rotating disc experiments, the currents were monitored using a digital multimeter (Gould Advance). Figure 5.5 shows the block diagrams of the experimental set-up used.

The rotating disc electrode was strictly controlled using a servo drive unit (Chemical Electronics RD1) which was calibrated using a stroboscope (Dawe, type 1200 E).

5.2.2 Planté electrode formation

The electrodes were formed galvanostatically using a double D.C. Power Supply (Advance PP.3) in conjunction with a 24h timer and a relay that allowed automatic reversal of the current. The charging and discharging current levels were set using a digital ammeter (Sinclair, DM 450) in series with the electrolytic cell. The complete process was monitored with a y-t recorder (Kipp and Zonen, BD 8) measuring the potential difference between the working and the reference electrode, and Figure 5.6 shows a schematic
Fig. 5.5  (i) L.S.V and potentiostatic pulse circuit

(ii) Rotating disc electrode circuit
Fig. 5.6 Circuit for PLANTÉ electrode formation
representation of the experimental arrangements.

5.2.3 Faradaic impedance measurements

The experimental set-up used for a.c. impedance measurements is shown in Figure 5.7. It was based on the Solatron 1172 Frequency Response Analyser (F.R.A.) with a Solatron 1182 Interphase used as a potential controller. The F.R.A. consists of a programmable generator that provides the perturbing sinusoidal signal, the response of the system examined is analysed with the aid of a correlator and the results obtained are finally displayed.

The F.R.A. has the advantage of rejecting all harmonics present in the output of the system and minimises the effect of random noise. The generator is programmed to sweep through a large frequency range by choosing suitable values of maximum frequency (up to 10 kHz for the S.1172 F.R.A.), the minimum frequency (down to 0.1 mHz) and the number of points per frequency decade at which measurements are to be taken. The instrument then takes measurements sequentially in either direction, at equally spaced intervals, over the designated range. The response is given once a measurement has been completed and can be displayed in one of three possible notations: amplitude (A) and phase angle (θ) relative to the output signal, log (A) and θ, or the real and imaginary parts of the impedance. The results (together with the measurement frequency) are then transferred to a teletype printer and tape punch. Simultaneously, the results can be plotted on an x-y recorder (Bryans 26000, A3) to give the impedance spectrum directly. A schematic diagram of the experimental circuit can be seen in Figure 5.8.
Fig. 5.7  The a.c. impedance system.

Fig. 5.8  Schematic diagram of the a.c. impedance measurement and data collection system.
The punch tape facility allowed the results of the a.c. impedance experiments to be fed into the PRIME 400 University computer. A graphics terminal (TEKTRONIX) was then used to obtain the complex plane plots and Randles plots. This enabled parts of the impedance spectrum, of special interest, to be expanded to show the exact shape of the curve. Similarly, this facility enabled the use of a computer program to obtain theoretical model fits for the experimental results. This technique will be discussed more extensively in the relevant chapter.
PART 1

THE PERCHLORATE EFFECT
CHAPTER 6

BEHAVIOUR OF THE LEAD/SULPHATE/PERCLORATE SYSTEM ON CYCLING

6.1 Introduction

Recently, Azim and co-workers\textsuperscript{95-97} have reported galvanostatic and potentiostatic measurements on lead systems in which the perchlorate-assisted oxidation was studied. These workers have identified the pitting corrosion process as the mechanism of the aggressive ion attack and have described the general features of the process in terms of the possible displacement of sulphate by perchlorate. This explanation is along the general lines for the theory of pit growth\textsuperscript{98}.

An interesting and important aspect of the electrochemistry of the lead/sulphate/perchlorate system is the behaviour on cycling, since one cycle of charge and discharge takes place during Plant\textsuperscript{6} plate production. Additionally, the examination of the cyclic behaviour can give a greater insight into the mechanism of the Plant\textsuperscript{6} process. The cyclic voltammetry of lead in sulphuric/perchloric acid has therefore been examined.

6.2 Experimental

The electrolytes used in these experiments contained various concentrations of perchloric acid in 0.5M sulphuric acid. The perchlorate concentrations examined were: 1 mM, 10 mM, 54 mM, 100 mM, 200 mM. All experiments were carried out at room temperature (23\textdegree C) in the presence of the atmosphere.
For the experiments in the potential region of lead sulphate formation, the electrode was held at a cathodic potential close to the potential required for the onset of hydrogen evolution for one hour, to minimise the chances of the development of any sulphate film. Cycling was then carried out at various sweep rates between the limits of -1250 mV and -450 mV.

The experiments in the lead dioxide region consisted of cycling to a constant response (approx. 1 hour), by sweeping between 400 mV and 1500 mV. The electrode was momentarily brought up to 2000 mV at the start of the experiment to "initiate" the reaction in order to produce lead dioxide\textsuperscript{99,100}.

Sweep rates used for both types of experiments were usually in the range 200 mVs\textsuperscript{-1} to 3 mVs\textsuperscript{-1}, starting with high sweep rates and cycling to a constant response before moving to a lower sweep rate.
6.3 Results and Discussion

6.3.1 Investigation of the whole region, from H₂ to O₂ evolution.

Polarisation of lead in sulphuric acid over a very extensive range of potentials from that of hydrogen evolution to the potential of oxygen evolution shows two regions connected with the electrochemistry of lead. The first represents the Pb to PbSO₄ reaction and occurs at about -900 mV, while the second occurs at a much more positive potential and represents the oxidation of PbSO₄ to PbO₂. This is shown clearly in Figure 6.1 which is the first sweep in a slow L.S.V. experiment on lead in 0.5M H₂SO₄. The anodic peak observed at about 1000 mV in the cathodic sweep can be interpreted in terms of the production of a layer of oxygen or related adsorbed species during the potential excursion into the oxygen region, which disrupts the lead sulphate layer. On sweeping back, the desorption of oxygen exposes parts of the lead surface which can undergo attack by the electrolyte, requiring an anodic current flow to produce a passivating film.

Figure 6.2 shows the effects of a sweep with 0.5M H₂SO₄ containing 100 mM ClO₄⁻. We can see that the potentiodynamic curve is significantly affected, specifically the peak for the oxidation of Pb to PbSO₄ is enhanced around the trailing edge and indeed a subsidiary peak is observed at approx. -700 mV. This peak indicates further oxidative attack of the lead surface at potentials more positive than the PbSO₄/Pb equilibrium potential under the influence of the perchlorate ion. It seems likely that the electrode initially passivates (at ~ -900 mV) at the lead sulphate potential and at somewhat more positive potential, the sulphate film is penetrated aggressively by the ClO₄⁻ ion and a further quasi active
Fig. 6.1 L.S.V. curve for lead in 0.5M $\text{H}_2\text{SO}_4$; sweep rate 50 mVs$^{-1}$.

Fig. 6.2 L.S.V. curve for lead in 0.5M $\text{H}_2\text{SO}_4$ containing 100 mM $\text{HClO}_4$; sweep rate 50 mVs$^{-1}$.
region is observed. Alternatively, the current falls but relatively slowly over a large potential range, indicating a pitting attack (pitting corrosion). No discrete peak for PbO₂ formation appears due to the oxygen evolution reaction intruding into the PbO₂ formation reaction.

On increasing the positive limit of the sweep, PbO₂ is produced, as shown by the occurrence of a reduction peak (at ~ 900 mV) in the reverse sweep from the positive limit. However, as soon as the discharge is completed, there is evidence for the active dissolution of the underlying base Pb as shown by the anodic current at approx. 600 mV. The explanation for this is that the discharge of PbO₂ produces a PbSO₄ layer which is not perfect enough to completely render immune the surface from the aggressive attack, and so the lead surface is attacked. This anodic current was quite large in early experiments (e.g., the first cycle) but was reduced in subsequent cycling. The peak for the reduction of PbSO₄ to Pb appears to be normal. It is to be concluded that the perchlorate ion has affected both the Pb to PbSO₄ reaction and also the PbSO₄ to PbO₂ oxidation; the significant effect is, however, the penetration of the PbSO₄ layer by the perchlorate ion.

6.3.2 The Lead - Lead Sulphate Region

This potential region was investigated under the conditions which might be expected for Plante formation. Electrodes were subjected to cyclic voltammetry at a series of sweep rates.

Figure 6.3 shows a stabilised cyclic voltammogram for a system free from perchlorate ions. The trace is similar to many which appear in the literature and consists of a peak in the positive-going direction.
Fig. 6.3 Stabilised cyclic voltammogram (in the Pb-PbSO₄ region) for lead in 0.5M H₂SO₄; sweep rate 50 mVs⁻¹.
Fig. 6.4 $i_p$ vs. $\sqrt{t}$ relationship for cyclic voltammograms (in the Pb-PbSO$_4$ region) for lead in 0.5M H$_2$SO$_4$ containing:

Δ, 0 mM HClO$_4$; ■, 1 mM HClO$_4$; ▲, 10 mM HClO$_4$;
○, 54 mM HClO$_4$; □, 100 mM HClO$_4$; ○, 200 mM HClO$_4$. 

$i/\mu A$ vs. $\sqrt{t}$/s$^{1/2}$
Fig. 6.5 \( i_p \) vs. \( v \) for cyclic voltammograms (in the Pb-PbSO\(_4\) region) for lead. Code as for Fig. 6.4.
representing the oxidation of Pb to PbSO₄, followed by a cathodic peak in the reverse sweep. The effect of increase in the sweep speed is to amplify the current. However, there was a simple correlation between peak height and rate of potential change in the oxidation peak.

It is clear from the Figure 6.4 that $i_p$, the current maximum in the anodic going sweep, is proportional to $v^{1/2}$, where $v$ is the sweep rate. However, aside from the perchlorate free system, all the lines had a positive intercept on the current axis. The currents in these sweeping experiments were found to be independent of electrode rotation speed and confirm that the reaction is independent of diffusion of Pb(II) products in solution. We are therefore forced to conclude that the reaction must be a solid-state one. The square root sweep rate - peak current relationship could represent a controlling diffusion process in the solid state, possibly diffusion through a porous PbSO₄ layer.

If the products of the reaction remain at the electrode as a film of PbSO₄ of constant thickness, then we could expect that the peak current would be a linear function of the sweep rate. Figure 6.5 shows that this is not so, and the passivating PbSO₄ film contains a variable amount of charge, depending on the sweep rate. Moreover, the curvature of this plot (away from the axis) indicates thinner films at higher sweep speed. This might well be expected for at high sweep rate (higher currents - higher reaction rates), the crystals produced will be smaller as they would not have time to grow. Consequently, complete blocking of the lead surface would be achieved more efficiently than at lower speeds.
The addition of HClO₄ amplified the current up to a maximum at 54 mM which thereafter decreased. Once more, the current is sweep rate dependent in exactly the same way as in absence of perchlorate ions. This is shown by the cyclic voltammogram in Figure 6.6.

The concept that the presence of aggressive anions in solution is the cause of the breakdown of passive films is well known. According to Russian workers⁹⁸, the adsorptive displacement of passivating species from the surface occurs when anion concentration has attained a critical value. The anions cause intense destruction of the underlying metal by the formation of complexes with the metal surface species passing into solution. The localised nature of the process depends on non-uniform current distribution and also structural non-uniformity.

In the general picture, an important step is the transport and interconversion of ions within the pit formed in the localised attack, forming what might be thought of as a feedback process. The principle is that at the surface, sulphate ions are displaced by ClO₄⁻ so that PbClO₄⁻ complexes can move off into the double layer. However, once outside the double layer region, precipitation occurs. Lead sulphate is formed and perchlorate ion is regenerated to displace further sulphate ions at the lead surface. As more perchlorate is introduced into the system, the process of displacement and precipitation is increased. This is shown by the curves of Figure 6.5, where currents are amplified at the higher concentrations.

As the perchlorate ion concentration is still further increased, the amount of current in the stabilised potentiodynamic curve goes through
Fig. 6.6  Stabilised cyclic voltammograms (in the Pb-PbSO$_4$ region) for lead in 0.5M H$_2$SO$_4$ containing 54 mM HClO$_4$.
Sweep rates, 1,200; 2,100; 3,50; 4,20 and 5,5 mVs$^{-1}$.

Fig. 6.7  Stabilised cyclic voltammogram (in the Pb-PbSO$_4$ region) for lead in 0.5M H$_2$SO$_4$ containing 200 mM HClO$_4$; sweep rate 200 mVs$^{-1}$. 
a maximum, somewhere in the region of 54 mM in 0.5M H₂SO₄. Further addition caused reduced currents at all the sweep rates and potentials. This is an interesting observation for it suggests that at bulk concentrations in excess of about 50 mM, there is insufficient sulphate ion in the advancing pits to completely precipitate all the lead perchlorate and lead sulphate is formed nearer the pore entry, causing early passivation by plugging up the pore. This effect is enhanced at higher perchlorate ion concentration and the current in the oxidation peak decreases. It should be emphasised, however, that we are only observing the electrochemistry of the "available" electroactive material. Further PbSO₄ may be present on the electrode, but isolated from the electric current, Figure 6.7 shows the stabilised cyclic voltammogram for a 200 mM HClO₄ solution. An interesting feature of this Figure is that on the reverse sweep, the potentiodynamic curve shows an active anodic region in the cathodic direction. This indicates that the film undergoes aggressive attack by the perchlorate ion and the normally passive sulphate film is broken down.

It should be noted that the simple theory that PbSO₄ films are permeable to ClO₄⁻ ions and that lead dissolves anodically in the form of Pb(ClO₄)₂ cannot be correct in view of the appearance of the maximum at 54 mM.

6.3.3 The Lead Sulphate - Lead Dioxide Region

In this region, which is near the oxygen evolution potential, the presence of oxygen gas in the solution was of no consequence and unavoidable in any case. Figure 6.8 shows a typical cycle-stabilised potentiodynamic curve for lead sulphate/lead dioxide
Fig. 6.8 Stabilised cyclic voltammogram (in the PbSO₄-PbO₂ region) for lead in 0.5M H₂SO₄; sweep rate 50 mVs⁻¹.

Fig. 6.9 Stabilised cyclic voltammogram (in the PbSO₄-PbO₂ region) for lead in 0.5M H₂SO₄ containing 54 mM HClO₄; sweep rate 50 mVs⁻¹.
in 0.5M H₂SO₄. A small, well-defined peak at around 1000 mV was observed in early experiments, developed to a maximum after about 2h cycling at 50 mVs⁻¹ and then reduced to a virtual plateau. This is interesting and different from the observations²⁰⁰ in 5M H₂SO₄ and is possibly the development of significant amounts of α-PbO₂ under the higher pH conditions formed in the more dilute solution. With prolonged cycling of a stabilising structure, this α-component is evidently transformed to β.

Figure 6.9 shows a typical cycle-stabilised L.S.V. curve for 0.5M H₂SO₄ containing 54 mM ClO₄⁻. Comparison with the data of Figure 6.8 shows important differences. Surprisingly, the current in the reduction "loop" of the curve is less than the corresponding one in the perchlorate free system. There is no sign whatever of the small peak at around 1000 mV. The rise of oxygen evolution and PbO₂ formation is enhanced. The peak potential of the reduction process is shifted to more negative potentials by the perchlorate ions. However, the redox reactions commence at about the same potentials.

Above 54 mM ClO₄⁻ concentration it was not possible to get a steady response at potentials greater than 400 mV. The unsteadiness was apparently due to the evolution of oxygen from a surface which was not completely passive. Thus a rise in current was followed by a rapid fall in current, presumably as the "quasi passive" film was broken down by the aggressive attack of the perchlorate and then was healed by sulphate formation at higher potential. This behaviour has been observed by others²⁹⁸ who described potential oscillations occurring in galvanostatic charging experiments carried out in H₂SO₄/IIClO₄ mixtures. Another feature of the curves was
Fig. 6.10. \( ip \) vs. \( \nu \) for cyclic voltammograms (in the PbSO\(_4\)-PbO\(_2\) region) for lead in 0.5M H\(_2\)SO\(_4\) containing:

- \( \Delta \), 0 mM HClO\(_4\);
- \( \blacksquare \), 1 mM HClO\(_4\);
- \( \blacktriangle \), 10 mM HClO\(_4\);
- \( \blackcircle \), 54 mM HClO\(_4\).

\[ 10^{-3} \text{ i/\(\mu\text{A} \)} \]

\[ 0 \text{ to } 150 \text{ V/mVs}^{-1} \]
that the small polarisable region between PbO$_2$/O$_2$ formation and PbO$_2$ discharge (reduction) was eliminated by the ClO$_4^-$ ion.

For the reduction curve (negative going sweep) there was no satisfactory relationship between peak current and sweep speed. The data is shown in Figure 6.10, addition of ClO$_4^-$ decreases the peak current for the reduction of PbO$_2$. Moreover, this reduction is progressive in the experimental range available.

It is clear from the curves that the formation of PbO$_2$ is complicated by the oxygen evolution reaction.

The reduction of the formed PbO$_2$ is clearly highly irreversible as shown by the shifts in peak potential to lower values at the higher sweep rates. The fall in reduction current caused by ClO$_4^-$ ions is clearly proportional to the quantity of PbO$_2$ which is available for electrochemical reduction, rather than revealing the total oxidation which has occurred. We are forced to conclude that the effect is therefore to cause a thinning of the formed and available PbO$_2$ layer. It must be recognised, however, that the total quantity of oxidised product increases with ClO$_4^-$ concentration as previously recorded$^{97,100}$. Since this reducible material must be in contact with the electrode, we are observing the lead sulphate passive layer which has been oxidised to PbO$_2$. This available layer is apparently thinner, the more ClO$_4^-$ in the bulk, possibly through a poorer contact with the substrate,
CHAPTER 7

THE PERCHLORATE ASSISTED FORMATION OF LEAD DIOXIDE ON LEAD

7.1 Introduction

Previous work on aggressive ions has indicated that the effect of the aggressive ion on the oxidation process occurs at potentials when the electrode is covered with a layer of lead sulphate. This layer when formed in sulphuric acid alone effectively covers the lead surface and passivates the electrode. When the electrode is introduced to positive enough potentials to produce lead dioxide, the PbSO₄ layer is transformed to PbO₂. The first sign of the influence of the perchlorate ion on the reaction was seen in the previous chapter. The results showed that the anodic current on the positive facing slope of the active/passive transition increased on addition of perchlorate. This indicated that as soon as the electrode contains surface lead sulphate some degree of depassivation is effected by the perchlorate ion.

This chapter examines the electrochemical effects of the perchlorate ion, using potential-step experiments, in the region of potential where the formation of lead dioxide from lead sulphate occurs.

7.2 Experimental

Pure lead electrodes (A = 0.071 cm²) were used once more and sulphuric acid (0.5M) was the base electrolyte with added perchloric acid (up to 200 mM).
The electrode was introduced to the cell at 700 mV and was maintained at this potential for 1 hour, during which time the current passing through the electrode had fallen within the range 1 to 3 µA. At this point we considered that the electrode was completely blocked by lead sulphate and the underlying lead satisfactorily protected from further oxidative attack.

The lead sulphate layer produced at 700 mV was therefore sufficiently coherent to ensure that a satisfactory surface for the study of its further oxidation was available\textsuperscript{102}.

The electrode was finally stepped to a more positive potential and the current-time transient was recorded.

Replicate experiments were made, each time using a freshly polished, etched and passivated electrode.
7.3 Results and Discussion

Figure 7.1 shows the resulting current-time transient obtained by stepping the electrode from 700 mV, in the PbSO₄ region, to 1400 mV, in the PbO₂ region. It is similar to other curves observed for the oxidation of PbSO₄ on base lead₁⁰⁵. It consists of a rising part in which the current is proportional to the time and after going through a maximum, begins to fall again. However, the current does not fall to zero, but to a steady state value. This steady state current is due to the evolution of oxygen from the product PbO₂. Evidence for the onset of this is obtained during the course of the experiment, as the development of a "noisy" signal indicates the presence of gaseous oxygen on the porous PbO₂.

Similar results have been previously reported₁⁰⁶ for the oxidation of massive lead. They indicate that the process is a two-dimensional growth with instantaneous nucleation of PbO₂ on lead sulphate which follows the equation (3.34) described in Chapter 3.

This was tested by comparing the equation with the experimental data in the form of the non-dimensional plot of \(i/i_m\) versus \(t/t_m\) (Figure 7.2), showing that the results fit the theoretical curve. Further proof can be obtained by analysing the falling part of the current-time transient. It was necessary to first subtract the current going into the oxygen evolution reaction \(i_\infty\) and this was done with the assumption that this reaction was fully developed throughout the "long time" part of equation (3.34). Plotting \(\log_{10} [(i-i_\infty)/t]\) versus \(t^2\) indicates that this assumption is justified as shown in Figure 7.3.

The addition of perchlorate ion to the system had a fundamental effect. The results of the stepping experiments with 5 mM ClO₄⁻
Fig. 7.1 Potentiostatic pulse experiment for pure lead between 700 mV and 1400 mV; 0.5M $\text{H}_2\text{SO}_4$. 

![Graph showing the potentiostatic pulse experiment](image-url)
Fig. 7.2 Reduced plots for pure lead stepped from 700 mV to:
0, 1300; ▲, 1325; □, 1350; ●, 1375 and △, 1400 mV;
0.5M H₂SO₄. Line drawn, theoretical 2D-instantaneous nucleation.

Fig. 7.3 \( \log_{10}[(i-i_\infty)/t] \) vs. \( t^2 \) for the falling part of transient
shown in Fig. 7.1.
Fig. 7.4 Current-time transients for pure lead stepped from 700 mV to: (a) 1250; (b) 1300; (c) 1350; (d) 1375 and (e) 1400 mV; 5 mM HClO₄ in 0.5M H₂SO₄.
Fig. 7.5 Current-time transient for pure lead stepped from 700 - 1400 mV; 20 mM HClO₄ in 0.5M H₂SO₄.

Fig. 7.6 Current-time transient for pure lead stepped from 700 - 1400 mV; 30 mM HClO₄ in 0.5M H₂SO₄.
Fig. 7.7 Current-time transients for pure lead stepped from 700 - 1400 mV in 0.5M H$_2$SO$_4$ containing: (a) 54; (b) 75; (c) 100 and (d) 200 mM HC10$_4$.

Fig. 7.8 Reduced plots for pure lead stepped from 700 mV to: 0, 1300; ▲, 1325; □, 1350 and △, 1400 mV; 20 mM HC10$_4$ in 0.5M H$_2$SO$_4$. Line drawn, theoretical 2D-progressive nucleation.
were very interesting for they indicated that this concentration marked the threshold of the gross perchlorate ion attack (Figure 7.4). The peak currents \(i_m\) increase with potential until the 700 to 1350 mV step, thereafter a decrease is observed. This increase and decrease in \(i_m\) can be interpreted if the extent of the PbO\(_2\) film is increased at high potential and at the same time becomes tighter and thus more passivating. The increased secondary rise at high overpotential indicates that ClO\(_4^-\) ions (probably adsorbed) are able to penetrate the passive layer under the influence of the potential to promote further corrosion.

Figures 7.5-7.7 show a series of transients corresponding to stepping from 700 mV to 1400 mV for a number of solutions containing perchlorate. The results show that the currents in the transients increase even with small perchlorate additions, however, when 20 mM ClO\(_4^-\) was added the shape of the transients alter significantly. Particularly is this true of the "falling" part which exhibits a progressively greater "steady state" value. The falling part is completely absent in the 30 to 40 mM perchlorate range. Thereafter, although the current maximum continues to increase somewhat with added ClO\(_4^-\), a well defined trailing part is apparent once more. The well-defined tail is apparent up to 200 mM ClO\(_4^-\) concentration.

The initial parts of the perchlorate system transients also change progressively with concentration. Although below 20 mM the transients resemble Figure 7.1, a concavity develops at this perchlorate concentration when the results are plotted in the reduced form. This indicates a change to a two-dimensional progressive process following the equation (3.35), and Figure 7.8
shows how the reduced plots compare with the theoretical instantaneous nucleation process and the progressive two-dimensional process.

The growth law for the PbO₂ development throughout the range of potentials is not very consistent; at low potentials the progressive process gives the better fit, at higher potentials the process reverts to the instantaneous two-dimensional law. This indicates that at low potentials insufficient nucleation centres are available for growth corresponding to the available arising potential and as the reaction proceeds further additional growth points become activated. At high potentials the driving voltage activates every possible growth point.

As the concentration of the aggressive ion is increased the reaction becomes progressively nucleated, all instantaneously nucleated two-dimensional character being lost. In addition the current in the "nucleation part" of the transients is everywhere increased by the ClO₄⁻ (Table 7.1). This indicates that the perchlorate ion produces a thicker layer of PbO₂ of which the late developing regions grow with nucleation which occurs after the initial nucleation of the PbO₂ film has started.

The results for the 54 mM ClO₄⁻ concentration given in the reduced form in Figure 7.9, shows considerable three-dimensional nucleation character. This is clearly a change from a layer growth of a passivating phase to the in-depth growth of a non-passive layer.

The initial currents begin to be rectilinear with t², (Figure 7.10), and ultimately t³ (Figure 7.11) and the final (corrected) falling parts of the higher ClO₄⁻ concentrations also conform to a linear relationship between log₁₀ i/t³ versus t³. This verifies the
Table 7.1

Variation of $i_m$ with HClO$_4$ concentration for potential step experiments from 700 mV.

<table>
<thead>
<tr>
<th>HClO$_4$ (mM) in 0.5 M H$_2$SO$_4$</th>
<th>Current maximum, $i_m$ (µA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>700-1250 (mV)</td>
</tr>
<tr>
<td>0</td>
<td>25</td>
</tr>
<tr>
<td>5</td>
<td>40</td>
</tr>
<tr>
<td>20</td>
<td>54</td>
</tr>
<tr>
<td>30</td>
<td>500*</td>
</tr>
<tr>
<td>40</td>
<td>450*</td>
</tr>
<tr>
<td>54</td>
<td>1150</td>
</tr>
<tr>
<td>75</td>
<td>600</td>
</tr>
<tr>
<td>100</td>
<td>1400</td>
</tr>
<tr>
<td>200</td>
<td>1920</td>
</tr>
</tbody>
</table>

* Current levels off, no falling part to the transient.
Fig. 7.9 Reduced plots for pure lead stepped from 700 mV to:
- o, 1250; o, 1300; □, 1350 and Δ, 1400 mV; 54 mM 
  HClO₄ in 0.5M H₂SO₄. Broken line, theoretical 2D-
  progressive nucleation; continuous line, theoretical 
  3D-progressive nucleation.

Fig. 7.10 i vs. t² for rising transients for pure lead stepped 
from 700 - 1350 mV: o, 30 and □, 40 mM HClO₄ in 0.5M H₂SO₄.
Fig. 7.11  $i$ vs. $t^3$ for rising transients for pure lead stepped from 700 - 1350 mV: 
- 54 and ■ 75 mM HClO$_4$ in 0.5M H$_2$SO$_4$. 

![Graph](image-url)
change to three-dimensional progressive nucleation (Figure 7.12) for which the current-time relationship was shown in equation (3.45). The Figures 7.11 and 7.12 show that in the region 54 mM to 75 mM the data fit this three-dimensional process quite satisfactorily.

The "plateau region" around 30-40 mM ClO$_4^-$ ion concentration is interesting. At these conditions, the preceding reaction forms a front which progressively advances in the same manner as for the electrodeposition of a metal from solution, in which a layer by layer growth occurs. We are dealing under these circumstances with a system which can sustain a self-generating reaction which follows the sequence:

\begin{align*}
Pb + \text{SO}_4^{2-} & \rightarrow Pb\text{SO}_4(s) + 2e \quad \text{(7.1)} \quad \text{(Very fast at this potential)}

Pb\text{SO}_4(s) + 2\text{H}_2\text{O} & \rightarrow Pb\text{O}_2 + \text{HSO}_4^- + 3\text{H}^+ + 2e \quad \text{(7.2)} \quad \text{(Slow, crystallisation controlled)}

Pb\text{O}_2(s) + Pb + 4\text{HClO}_4 & \rightarrow 2Pb(\text{ClO}_4)_2 + 2\text{H}_2\text{O} \quad \text{(7.3)} \quad \text{(Fast, chemical reaction)}

Pb(\text{ClO}_4)_2 + \text{H}_2\text{SO}_4 & \rightarrow 2\text{HClO}_4 + Pb\text{SO}_4(s) \quad \text{(7.4)} \quad \text{(Regeneration of reactants)}
\end{align*}

with the propagating sequence (7.2) - (7.4).

Provided that the layers can be penetrated by the ionic species of H$_2$SO$_4$ and HClO$_4$ in the optimum concentrations, then the reaction is self perpetuating. If insufficient HClO$_4$ is present then the reaction tends towards the simple reaction in H$_2$SO$_4$, as observed. If the optimum concentration of ClO$_4^-$ is exceeded then equation (7.4) does not produce sufficient lead sulphate for continuation of the chain and a passivating layer of PbO$_2$ is formed from solution soluble...
Fig. 7.12 \( \log_{10}\left(\frac{i_i - i_\infty}{t^3}\right) \) vs. \( t^3 \) for falling parts of transients for pure lead stepped from 700 mV to:
- ○, 1300 mV; 54 mM HClO\(_4\) and □, 1400 mV; 75 mM HClO\(_4\) in 0.5M H\(_2\)SO\(_4\).

Fig. 7.13 Current-time transients for pure lead stepped from 700 mV to: (a) 1250; (b) 1300; (c) 1350; and (d) 1400 mV; 200 mM HClO\(_4\) in 0.5 H\(_2\)SO\(_4\).
Potential dependencies of $i_m$ and $t_m$ for curves shown in Fig. 7.13:

(a) $\log_{10} i_m$ vs. $E$

(b) $\log_{10} t_m$ vs. $E$. 

---

Fig. 7.14  Potential dependencies of $i_m$ and $t_m$ for curves shown in Fig. 7.13:

(a) $\log_{10} i_m$ vs. $E$

(b) $\log_{10} t_m$ vs. $E$. 

---

Figure 7.14: Potential dependencies of $i_m$ and $t_m$ for curves shown in Fig. 7.13:

(a) $\log_{10} i_m$ vs. $E$

(b) $\log_{10} t_m$ vs. $E$.
Pb\textsuperscript{2+} species by electrodeposition\textsuperscript{107}. It is the generation of this quality of electrodeposited PbO\textsubscript{2} which presumably accounts for the ultimate three-dimensional current limitation.

Above 75 mM although the shapes of the curves remain the same (Figure 7.13) the currents are slightly decreased at high potentials. This effect is rather obscure, however, we can attempt an explanation if the higher solution concentration of Pb\textsuperscript{2+} in the higher ClO\textsubscript{4}\(^{-}\) containing solutions produce a more efficient passivation and the maximum current becomes less.

This gross solution process is to be distinguished from that at low ClO\textsubscript{4}\(^{-}\) concentration when the reaction takes place in the adsorbed state. The undulating character of the currents at long times must be evidence for the growth of different layers of PbO\textsubscript{2}.

The position of the transients was dependent upon the potential to which the electrode was stepped. Differentiation of equation (3.45) yielded equations (3,46) and (3,47) which predicted $i_m$ and $t_m$ respectively.

The potential dependencies of $i_m$ and $t_m$ can be obtained by plotting $\log_{10} i_m$ against $E$ (Figure 7.14a) and $\log_{10} t_m$ against $E$ (Figure 7.14b). These give slopes of 514 mV/decade and -350 mV/decade respectively.

Thus for $k_1$ the parallel growth rate constant, the potential dependence of $t_m$ is -350 mV/decade which implies a potential dependence of 525 mV/decade; and for $k_2$, the orthogonal rate constant, a potential dependence of 514 mV/decade.
These potential dependencies of the growth rate constants are much less than the values of those corresponding to systems free of perchlorate ions\textsuperscript{105}. Bearing in mind that the current densities in the perchlorate systems are considerably greater than for the perchlorate free systems, that is, the reactions are occurring in considerably greater depth; this decrease reflects the increased extent of the field over which the reaction is driven,
8.1 Introduction

In the previous chapter the electrochemistry of the Planté formation process was studied under controlled conditions. Thus, the investigation of the specific effect of the formation of lead dioxide was achieved by carefully growing a layer of lead sulphate on lead. In doing so, a well-defined pre-electrode state was obtained before stepping the electrode into the region where lead dioxide could be formed.

The industrial process by which the Planté formation is carried out is not well-controlled in the above sense. The current is galvanostatically controlled and the electrode potential takes care of itself. From our investigation of the industrial process it appears that the effect of the current is to immediately passivate the surface for lead dissolution and solid phase lead sulphate formation, for the potential immediately rises to that for the development of PbO₂. In order to study the industrial process under laboratory conditions the electrode was immediately introduced to the region of lead dioxide formation without prior formation of a lead sulphate phase.

8.2 Experimental

The electrodes were pretreated in the normal way and then introduced to the cell at the potential required in the lead dioxide formation region. Perchlorate concentrations of up to 200 mM were again examined.
8.3 Results and Discussion

8.3.1 Perchlorate-free Electrolyte Solutions

Figure 8.1 shows a typical current-time curve for lead in sulphuric acid. At all potentials in the experimental range 1100 mV - 1300 mV the forms of the current-time curves were similar. After a sharp rise and fall, due to double layer effects, a slow increase in current was followed by a decrease indicating the growth of solid phase lead dioxide. Thereafter, an increase in current was observed over the remainder of the time of the experiment. This increase was due almost exclusively to an increase in the oxygen evolution reaction from the lead dioxide surface. The form and magnitude of the current-time curves were independent of the speed at which the electrode was rotated. This fact indicated the lack of participation of a current controlling reaction via the agency of the solution. Had such processes been present, then the currents would have increased with the speed of rotation. This is because the diffusional processes occur more rapidly at high rotation speed when the hydrodynamic diffusion layer is thin.

This conclusion is confirmed by the rising and falling transient attained as the formation reaction proceeds, which indicates the presence of a solid state crystallisation process. Initially the current is low (ideally it starts from zero), as the requirement that the rate of crystallisation is proportional to the area of growing phase present, controls the current. The current increases as the growth of the new phase occurs. However, the current goes through a maximum as the growing centres overlap.

Plots of $\log_{10} i$ against $\log_{10} t$ for the first rising transient throughout the experimental range (Figure 8.2) indicated that the
Fig. 8.1 Current-time transient for pure lead in 0.5M H₂SO₄.
Potential, 1150 mV.

Fig. 8.2 \( \log_{10} i \) vs. \( \log_{10} t \) for rising parts of transients for pure lead in 0.5M H₂SO₄; •, 1150 mV and ■, 1300 mV.
current increases initially in an ill-defined way, plots curving upwards especially at the less positive potentials. However, the slope of the lines was generally near to unity. This suggests an instantaneous, two-dimensional, nucleation process. Testing the dimensionality of the process by examining the falling part of the transient showed that for the two-dimensional instantaneous process the expected plot of $\log_{10}(i/t)$ vs $t^2$ was not a straight line. However, that corresponding to the two-dimensional progressive behaviour ($\log_{10}(i/t^2)$ vs $t^3$) (Figure 8.3) gave a straight line.

It should be noted that in the present analysis of the results, a correction was made to the current magnitude, due to the presence of a pseudosteady-state current at long times. This current is due to the oxygen evolution reaction occurring from product PbO₂ when it is formed. The validity of the progressive nucleation for the oxidation process under investigation was tested by plotting the transient data in terms of units corresponding to the maximum, i.e. $i/i_m$ was plotted against $t/t_m$ (here again, $i$ was corrected for the oxygen evolution). The results of this are shown in Figure 8.4 and the reduced plot is compared with theoretical equations for both the instantaneous and progressive two-dimensional processes. It is clear that the progressive process fits the experimental facts most satisfactorily. This behaviour differs from that observed with well-formed lead sulphate surfaces, discussed in the previous chapter, where the instantaneous two-dimensional process predominates.

We can interpret this difference in terms of the electrochemical reactions:
Fig. 8.3 $\log_{10}(i/t^2)$ vs. $t^3$ for falling transient corresponding to Fig. 8.1 (Current corrected for oxygen evolution).
\[
Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e \quad (8.1)
\]
\[
PbSO_4 + 2H_2O \rightarrow PbO_2 + HSO_4^- + 3H^+ + 2e \quad (8.2)
\]

occuring simultaneously rather than (8.2) taking place on a fully passivated lead sulphate surface,

At the oxidation potentials used, reaction (8.1) would be very rapid initially; however, as soon as a significant layer of PbSO_4 is formed, some reduction in the rate of reaction (8.1) would occur. On oxidation and transformation of PbSO_4 to PbO_2, as reaction (8.2) proceeds, an incomplete film of PbSO_4 is produced and we can obtain the chemical redox process,

\[
PbO_2 + Pb + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O \quad (8.3)
\]

whereby the corrosion reaction can penetrate further into the metal surface. The initial response of the electrode will be an instantly nucleated two-dimensional process on a lead sulphate layer which has not been fully developed. The formation of PbSO_4 by the redox reaction (8.3) requires the nucleation of new PbO_2 centres for the reaction to proceed. The electrocrystallisation reaction therefore, becomes progressively nucleated. The transition between an equation of the instantaneous form to the progressive form is to be expected and the progressive process will then dominate in the long time. This explanation is consistent with the induction periods present in this series of experiments, which were absent from experiments on well-developed PbSO_4 surfaces. The time taken before the current started to rise was long in the case of stepping to potentials just inside the lead dioxide region (\(\sim 1100 \, mV\)) and decreased as the potential was stepped to more
Fig. 8.4 Reduced plots for current-time transients for pure lead in 0.5M H₂SO₄; ●, 1150 mV and □, 1300 mV. (Current at long times corrected for oxygen evolution). Broken line, theoretical 2D-instantaneous nucleation; continuous line, theoretical 2D-progressive nucleation.

Fig. 8.5 Current-time transient for pure lead in 0.5M H₂SO₄ containing 10 mM HCIO₄. Potential, 1275 mV.
positive values. This is in accord with the need to form a film of PbSO$_4$ on the lead suitable for oxidation to PbO$_2$. At more positive potentials this took much less time so that the induction period was short.

8.3.2 Perchlorate-containing Electrolyte Solutions

Figure 8.5 shows the effect of adding 10 mM of perchlorate ion in the form of HClO$_4$ to the dilute sulphuric acid. This causes shortening of the induction periods and the broadening of the electrocrystallisation peaks. The previous chapters have shown that perchlorate ions tend to displace sulphate ions from the surface of the lead and this is possibly the cause of the shorter induction time, a passive layer resulting more readily in the presence of the mixed ion environment. At higher final potentials the induction period was very short indeed and the electrocrystallisation peak became quite sharp. However, large and rising currents were observed at long times. Figures 8.6(a), (b) and (c) show the kinetic plots for the analysis of Figure 8.5 type transients. The process is clearly a two-dimensional progressively nucleated process under all conditions. This is similar to the behaviour of well-developed layers of PbSO$_4$ on lead, however, the difference in the lengths of the induction periods marks the distinction between the two systems which can be identified with the incomplete PbSO$_4$ layer on which PbO$_2$ must eventually grow.

The presence of around 30 mM concentration of perchlorate on a completely passive lead sulphate surface (Chapter 7) gave a current response which consisted of a rising transient followed by
a steady current. In the present experiments it was found that, in this region, a rising response was observed which peaked and then gave a steady state current at a value somewhat lower than the peak, shown in Figure 8.7. The response and the correlations, which show the electrocrystallisation to be a three-dimensional process with progressive nucleation are shown in Figures 8.8(a) and (b).

The results show a similar behaviour to the case of the passivated electrode, where the system can sustain a self-generating reaction following the sequence (7.1) - (7.4). Under the present conditions, however, the addition of perchlorate ion has caused a change from a two-dimensional, progressively nucleated process to a three-dimensional process which is advancing uniformly into the metal lattice.

When the concentration of added perchlorate ion was increased to the region of 100 mM, current responses of similar shape to those obtained at ~ 50 mM were observed. The current maxima, however, were lower than those for the 54 mM concentrations. This is an interesting observation, for it confirms that there is an optimum perchlorate ion addition for the most efficient "attack" on the lead substrate.

It was observed that the current responses to the changes in potential were smooth provided that the concentrations of added perchlorate remained below 100 mM. Above this limit the currents were rather erratic, changing abruptly about a mean value. We interpreted this as oxygen evolution which from time to time altered the effective electrode area, as bubbles grew and then.
Fig. 8.6 Data corresponding to Fig 8.5:
(c) reduced plot; line indicates the theoretical 2D-progressive nucleation.

Fig. 8.7 Current-time transients for lead in 0.5M H$_2$SO$_4$ containing 54 mM HClO$_4$; (a) 1225 mV and (b) 1250 mV.
Fig. 8.8 Data corresponding to Fig. 8.7:

(a) i vs t for rising parts of the transients;
- , 1225 mV; ▐, 1250 mV.

(b) reduced plot; line indicates the theoretical 3D-progressive nucleation. - , 1225 mV; ▐, 1250 mV.
Information obtained from current-time transients on unpassivated lead

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<td>175</td>
<td>40</td>
<td>-</td>
<td>1500</td>
<td>10</td>
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</table>

S, slope of log₁₀i vs log₁₀t for the rising part of transient.

i_m, current maximum (µA)

t_m, time (min.) at maximum current.

*, in 0.5M H₂SO₄.
suddenly detached. The increased oxygen evolution reaction was presumably caused by the change in the electrolyte medium. Progressive additions of perchlorate produced more erratic currents in line with continued lowering of the oxygen evolution potential. Table 8.1 shows the results obtained. These results confirm that increasing concentrations of perchlorate do not produce ever increasing rates of attack on lead.
CHAPTER 9

THE ANODIC DISSOLUTION OF LEAD IN H₂SO₄/HClO₄ SOLUTIONS

9.1 Introduction

The anodic oxidation of lead in sulphuric acid solutions has been very extensively studied and it has revealed a small potential region in which lead dissolves freely into the electrolyte solution⁵⁹,⁹₂,¹⁰₈,¹⁰⁹.

The dissolution of lead has also been studied in a number of other solutions. Johnson et al.¹¹⁰ have postulated a mechanism in KN⁶³, Pb(Ac)₂ and NH₄Ac solutions involving Pb(I) species. Data on the Pb(II)-Pb exchange in perchlorate ion solutions containing soluble lead salts are not common. Gioda et al.¹¹¹, however, have recently reported kinetic studies in various perchlorate ion solutions. Their results were interpreted in terms of the formation of Pb(I) dimers which eventually cross the double layer to form divalent lead ions¹¹². It was suggested¹¹¹,¹¹² that this mechanism might be preferred for the dissolution of a number of sp. metals, although this contradicts a principle that such processes are most favoured by particles of low charge number, preferably zero¹¹³.

Another difficulty associated with the study of lead has been identified by Fleming and Harrison¹⁰₈ who were unable to identify the solution species arising from the oxidation of lead in sulphuric acid solution due to difficulties arising from lack of knowledge of the ionic activities of SO₄²⁻ and HSO₄⁻.
Furthermore they concluded that the reaction could not be investigated in the presence of an inert electrolyte, as most of the ions commonly used (possibly even $\text{ClO}_4^-$) complex more strongly with $\text{Pb}^{2+}$ than $\text{SO}_4^{2-}$. Fleming et al.\textsuperscript{11} have reported that the electrode impedance of lead in sulphuric acid in the region of free solubility of oxidised species shows only diffusion characteristics. Hampson and Lakeman\textsuperscript{59,60} have also made measurements in the lead dissolution region and their results indicated that the oxidation process was not solely controlled by diffusion in solution.

In view of the limited number of electrochemical investigations with perchlorate solutions in the dissolution region of lead, it was decided to examine the effect of the perchlorate ion in this region. The dissolution behaviour of lead in sulphuric acid may be sufficiently different from that in perchloric acid\textsuperscript{108}, when the electrolytes are examined separately. It was therefore important to determine the mechanism of the $\text{Pb}^{2+}$-$\text{Pb}$ exchange reaction in sulphuric acid and the possible perchlorate assisted dissolution in mixed electrolyte solutions, if the Planté formation process is to be better understood.

### 9.2 Experimental

Rotating disc experiments were performed on pure lead electrodes using dilute sulphuric acid solutions and solutions containing up to 200 mM perchloric acid.

Experiments were made under purified nitrogen after the system had been purged with nitrogen and whilst the working electrode was held in the hydrogen region. This procedure is necessary if sulphate
film formation is to be avoided.

Potentiostatic experiments were made beginning with the most negative potential. Steady state currents were recorded after a constant value had been maintained for 30 s.
Figure 9.1 shows plots of $i^{-1}$ against $\omega^{-1/2}$ for lead in 0.5M H$_2$SO$_4$. Figures 9.2 - 9.6 show similar data obtained with additions of perchloric acid. The straight lines obtained indicate that the current density increases with rotation. The plots also show a potential dependence. Figure 9.7 shows plots of $\log_{10} i_\infty$ against $E$ which have slopes of approximately 30 mV per decade. The currents at infinite rotation speed ($i_\infty$) were obtained by extrapolating the lines, for each set of results, to the $y$-axis. The slopes of the lines which were plotted as $\log_{10}s$ against $E$ (Figure 9.8) also gave straight lines with gradients of approximately -15 mV per decade. Table 9.1 shows the results obtained for all the concentrations examined.

For a completely reversible reaction in the thermodynamic sense, the $i^{-1}$ vs $\omega^{-1/2}$ lines should pass through the origin. It is clear from the data of Figures 9.1 - 9.6 that this does not apply in our case, indicating that the Pb(II)-Pb exchange in sulphuric acid and Planté formation electrolytes cannot be a 2e reversible process. Conversely, the 30 mV Tafel slope indicates that the charge transfer steps are indeed fast.

A mechanism which is consistent with the experimental data is that proposed by Hurlen$^{112}$:

\begin{align}
\text{Pb} & \rightarrow \text{Pb(I)} + e \\
2\text{Pb(I)} & \rightarrow [\text{Pb(I)}]_2 \\
[\text{Pb(I)}]_2 & \rightarrow 2\text{Pb}^{2+} + 2e
\end{align}

\[(9.1)\]  
\[(9.2)\]  
\[(9.3)\]
Fig. 9.1 $i^{-1}$ vs $\omega^{-1/2}$ for Pb in 0.5M H$_2$SO$_4$: O, -953; A, -950; □, -945; ●, -940 and △, -935 mV.

Fig. 9.2 $i^{-1}$ vs $\omega^{-1/2}$ for Pb; 5 mM HClO$_4$ in 0.5M H$_2$SO$_4$. O, -958; A, -955; □, -950; ●, -945 and △, -940 mV.
Fig. 9.3  \( \frac{1}{i} \) vs \( \omega^{-1/2} \) for Pb; 40 mM HClO₄ in 0.5M H₂SO₄.
0, -960; ▲, -955; □, -950; ●, -945 and Δ, -940 mV.

Fig. 9.4  \( \frac{1}{i} \) vs \( \omega^{-1/2} \) for Pb; 60 mM HClO₄ in 0.5M H₂SO₄.
Code as Fig. 9.3.
Fig. 9.5  \( i^{-1} \) vs \( \omega^{-1/2} \) for Pb; 100 mM HClO\(_4\) in 0.5M H\(_2\)SO\(_4\).

Code as Fig. 9.3.

Fig. 9.6  \( i^{-1} \) vs \( \omega^{-1/2} \) for Pb; 200 mM HClO\(_4\) in 0.5M H\(_2\)SO\(_4\).

Code as Fig. 9.3 plus ■, -935 mV.
Fig. 9.7 Tafel plot; $\log_{10}i_\infty$ vs $E$ from data of Fig. 9.1 and 9.5.
$\bullet$, Pb in 0.5M $\text{H}_2\text{SO}_4$; $\bigcirc$, Pb in 0.5M $\text{H}_2\text{SO}_4$ containing 100 mM $\text{HClO}_4$. Line drawn 30 mV/decade.

![Graph showing Tafel plot with data points and a linear line.]

Fig. 9.8 $\log_{10}(3i^{-1}/3\omega^{-1})$ vs $E$ from data of Fig. 9.1 and 9.5.
Code as Fig. 9.7. Line drawn -15 mV/decade.

![Graph showing $\log_{10}(3i^{-1}/3\omega^{-1})$ vs $E$.]
**TABLE 9.1**

Tafel gradients and gradients of $3i^{-1}/3\omega^{-1/2}$ against $E$ for lead in

$\text{HClO}_4$-free and $\text{HClO}_4$-containing $\text{H}_2\text{SO}_4$

<table>
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<th>$\text{H}_2\text{SO}_4$ concentration (M)</th>
<th>$\text{HClO}_4$ concentration (M)</th>
<th>$\Delta E/\Delta \log_{10} i_{\infty}$ (mV per decade)</th>
<th>$\Delta E/\Delta \log_{10} S$ (mV per decade)</th>
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<td><strong>Mean results</strong></td>
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<td><strong>29.6</strong></td>
<td><strong>-13.9</strong></td>
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</table>
This mechanism was based upon a stoichiometric number of 0.5, indicating that for each occurrence of the rate determining step the reaction goes twice to completion. Following Bockris and Reddy\textsuperscript{115}, a quasi-equilibrium one-electron charge transfer provided a plausible explanation.

For this mechanism the rate of reaction (9.2) determines the current flowing in the reaction and if $k -$ is the rate constant for the oxidation

$$i_2 = 2Fk_2 [\text{Pb}(I)_{ad}]^2$$

(9.4)

with the Pb(I) concentration determined by the Nernst equation since reaction (9.1) is reversible:

$$\frac{[\text{Pb}(I)]}{[\text{Pb}_{lat}]} = \exp \left( \frac{F}{RT} \right) (E - E^\theta)$$

(9.5)

so that equation (9.4) becomes

$$i_2 = 2Fk_2 [\text{Pb}_{lat}]^2 \exp \left( \frac{2F}{RT} \right) (E - E^\theta)$$

(9.6)

The total controlled current in reaction (9.2) is

$$i_\infty = 4Fk_2 [\text{Pb}_{lat}]^2 \exp \left( \frac{2F}{RT} \right) (E - E^\theta)$$

(9.7)

since reaction (9.3) is reversible and simply doubles the current.

The slopes of the $i^{-1}$ vs $\omega^{-1}$ lines contain information which allows the calculation of the stoichiometric number. When the complete (anodic and cathodic) reaction is considered we have\textsuperscript{115}
\[
i/2F = \frac{k}{4} \left[ \text{Pb(I)}_{ad} \right]^2 - \frac{k}{4} \left[ \text{Pb(I)}_{2ad} \right] \tag{9.8}
\]

which when written in terms of solution species and the electrode, through equations (9.1) and (9.3) and the Nernst equation, becomes

\[
\frac{i}{4F} = k \left[ \text{Pb}^{2+} \right]_{ad} \exp \left( \frac{2F}{RT} \right) \left( E - E^\theta \right) - k \left[ \text{Pb}^{2+} \right]_{2ad} \exp \left( \frac{2F}{RT} \right) \left( E^\theta - E \right) \tag{9.9}
\]

since

\[
\frac{1}{i} = \frac{1}{i_\infty} - \frac{S}{u^2} \tag{9.10}
\]

we obtain

\[
S = \frac{k \delta_{\text{Pb}^{2+}} \exp \left( \frac{4F}{RT} (E^\theta - E) \right)}{4F k \left[ \text{Pb}^{2+} \right]_{ad} D_{\text{Pb}^{2+}}} \tag{9.11}
\]

We would therefore expect a 30 mV Tafel slope \((dE/d\log_{10}i_\infty\) from equation (9.7)) and a slope dependence of -15 mV per decade for \(\log_{10} (\beta_i^{-1}/u^{2}) \) versus \(E\). Table 9.1 shows that these relationships are indeed observed experimentally.

Figures 9.1 - 9.6 show that the reaction is not unduly affected by even quite high concentrations of the perchlorate ion. In the solutions containing the higher concentrations of perchlorate ion in which the \(\text{Pb}^{2+}\) species had a greater solubility it would have been very interesting if the reverse deposition reaction of \(\text{Pb}^{2+}\) onto lead in this same dissolution region could be studied. However, attempts to carry out these experiments resulted in a
large proportion of the current going into the hydrogen evolution reaction. It is clear from these results that the perchlorate ion does not participate in any corrosion promotion reaction in this dissolution region.

The important and interesting feature of this investigation in common with that of Gioda et al\textsuperscript{111} is the identity of the species which are involved in equation (9.2), that is, those involved in the surface reaction to give an entity containing two Pb(I) species. This association has been postulated by Hurlen (as mentioned earlier) for both zinc and iron exchange reactions on the basis of the experimentally obtained stoichiometric number of 0.5. Similar cases have been reported for iron in acidic media by Kabanov et al\textsuperscript{116a} and later by Husler\textsuperscript{116b}, Gerischer\textsuperscript{116c} and Lorenz et al\textsuperscript{116d} where they have all suggested such species as $[\text{Fe-OH-Fe}_{\text{ads}}]$ as intermediates in the electrode process. In the present case we should note that an apparent order of reaction with respect to $\text{H}_2\text{SO}_4$ can be calculated if the data of Fleming et al\textsuperscript{114} and Hampson and Lakeman\textsuperscript{59} are taken together. These, with the present data, give a value of unity which rules out the possibility of an initial step of the form:

$$\text{Pb} + \text{OH}^- \rightleftharpoons \text{PbOH}_{\text{ad}} + e \quad (9.12)$$

which would be expected to have a negative order for the anodic step with respect to increasing sulphuric acid concentration.

We suggest that the initial step may well be

$$\text{Pb}_{\text{lat}} + \text{HSO}_4^- \rightleftharpoons \text{PbHSO}_4^-_{\text{ad}} + e \quad (9.13)$$
which would give an increase in current as a result of an increasing \( \text{H}_2\text{SO}_4 \) concentration. It is interesting that with perchloric acid Gioda et al\(^{111} \) found from the reaction orders that \( \text{ClO}_4^- \) apparently did not enter into the intermediate reaction. The rate determining bimolecular reaction could be therefore

\[
2[(\text{Pb}^\text{I} \text{HSO}_4)_\text{ad}] \longrightarrow [\text{Pb}^\text{I} - \text{SO}_4 - \text{Pb}^{\text{I} \text{ad}} + \text{H}_2\text{SO}_4
\]

(9.14)

The complex intermediate is possible due to the expected increased basic strength of the \( \text{Pb}(\text{I}) \) ion compared with the low basicity of the \( \text{Pb}(\text{II}) \) ion. An alternative to this step

\[
[(\text{Pb}^\text{I} \text{HSO}_4)_\text{ad}] + \text{Pb}_{\text{lat}} \longrightarrow [\text{Pb}^\text{I} - \text{SO}_4 - \text{Pb}^\text{I}_{\text{ad}} + \text{e} + \text{H}^+
\]

(9.15)

appears to be ruled out by the 30 mV Tafel slope.

It is reasonable to conclude that the first electron is readily lost as a reversible step from a lattice atom at a convenient kink site\(^{116} \). The univalent particle is stabilised by the \( \text{HSO}_4^- \) ion to form a neutral entity. It is interesting why this should not pass directly across the double layer. Gioda et al\(^{111} \) consider that in the perchlorate system chemical interaction occurs to form a more suitable species for the second charge transfer. This cannot be the complete explanation, for another interesting point is the apparent reversibility of the step (9.3) in the electrode process. There exists a formidable body of evidence to show that in stepwise reactions the final electron transfer to form the solution species provides the highest energy.
barrier. This is due to the hydration energy for a given element, in different oxidation states, increasing as the charge on the cation increases\textsuperscript{117-118}. The speed of reaction (9.3) must indicate that a considerable degree of solvation already exists for the ionic species and it must be concluded that the presence of the di-lead (I) intermediate facilitates this. In other words the kinetically hindered combination of $[\text{Pb}^{I}\text{HSO}_4]_{\text{ad}}$ species followed by the reversible charge-transfer provides less of an energy barrier than the direct transfer of the Pb(I) species with an energetically unfavourable final condition to Pb(II).
PART 2

THE FULLY FORMED

PLANTÉ ELECTRODE
10.1 Introduction

Following the investigation of the effect of the aggressive agent in the Planté formation process, it was a natural progression to devote the second part of the project to the electrochemistry of fully formed Planté electrodes.

The Planté microelectrodes were examined using the potential step technique under various states of charge. The identification of the processes taking place during conditions similar to the operating duties of the Planté cell are necessary if a better understanding of the Planté storage battery is to be achieved.

10.2 Experimental

The Teflon mounted electrodes were formed according to the process described in Chapter 5. Following the capacity test the Planté microelectrodes were fully charged (at the 10h rate) and then discharged to different levels of charge for the potential step experiments.

Following the above procedure the electrode was removed from the formation cell and was immediately introduced to a conventional three-compartment cell with the facility to spin the electrode in order to remove any retained gas from the pores. It was then allowed to settle down to the reversible potential, (+ 1078 mV)
on open circuit, before being stepped from this voltage, to
either the fully charged state (+1378 mV), or to more negative
potentials. The electrodes were fully charged after the end of
each experiment and then discharged again to the required level
in order to ensure that the correct amount of charge was always
present.

All experiments were carried out in sulphuric acid of the same
concentration as that used in the second formation Plante process
(3.58 M).
10.3 Results and Discussion

Figure 10.1 shows the initial part of the current-time transient obtained by stepping a fully charged Planté electrode from the open circuit voltage (OCV) to a more negative potential. The curve consists of a rising part with a sharp peak due to the double layer charging combined with a transient response of a species which Reacts more readily than the bulk material. This is followed by a small shoulder, due possibly to the interaction of the reaction of the above species with the phase formation reaction, for which the main transient represents the current output. The current thereafter falls to zero. Figure 10.2 shows a similar current-time transient for a pulse 90 mV negative of the OCV. In this case however, the current starts rising again after the initial fall. A broad peak is eventually formed before the current once more falls to zero. Figure 10.3 shows the fast part of the current-time transient for a potential step to a potential 160 mV negative of the OCV. In this case the current starts rising immediately after the double layer spike has been formed, producing a peak within three seconds of the start of the experiment. Finally, Figure 10.4 shows a similar, but much sharper response, obtained when the electrode was stepped 200 mV negative of the OCV. Figure 10.5 shows that the current response for the rising part of the first peak is proportional to time. Extrapolating to zero time a zero current intercept was observed for all these responses. This is to be expected as the electrode surface would be uniformly covered with PbO₂, no PbSO₄ being present prior to the potential step experiments. The current starts increasing from its zero value as lead sulphate starts forming.
Figure 10.6 shows the complete current-time transient for fully charged Plant6 microelectrodes at various potentials negative of the OCV. The curves show that the deeper the electrode is stepped into the lead/lead sulphate region, the higher the currents are, and the sharper the peaks observed. Analysis of the falling parts of the curves, indicated the type of nucleation process taking place.

Figures 10.7 and 10.8 show plots of falling parts of the transients for the fully charged electrodes. A \( \log_{10}(i/t) \) plot vs. \( t^2 \) gave the best straight lines showing that the process is a two-dimensional (2-D) instantaneous growth of lead sulphate which follows the equation (3.34). Electrodes discharged by small amounts (10%, 20%) gave similar results to the fully charged electrodes.

Figure 10.9 shows that the initial rising part of the first peak is still proportional to time. This suggests that the initial growth is again two-dimensional, with instantaneous nucleation. The long time parts of the current-time transient are shown in Figure 10.10. Analysis of the falling parts of these transients, Figure 10.11, indicates that the process is still a two-dimensional, instantaneous, nucleation. Higher currents are observed again as the electrode is stepped further into the lead sulphate region. These currents are also higher than the equivalent values obtained with the fully charged electrode.

Figure 10.12 shows that the rising part of the first peak remains proportional to time for various potential step experiments with electrodes discharged to much higher levels. It is interesting to note that only the fully charged electrodes (Figure 10.5) show
Fig. 10.1 Current-time transient for a fully charged electrode stepped from 1078 to 1003 mV. Electrolyte; $\text{H}_2\text{SO}_4$ (3.58 M).

Fig. 10.2 Current-time transient for a fully charged electrode stepped from 1078 to 988 mV. Electrolyte; $\text{H}_2\text{SO}_4$ (3.58 M).
Fig. 10.3  Current-time transient for a fully charged electrode stepped from 1078 to 918 mV. Electrolyte; H₂SO₄ (3.58 M).

Fig. 10.4  Current-time transient for a fully charged electrode stepped from 1078 to 878 mV. Electrolyte; H₂SO₄ (3.58 M).
Fig. 10.5  $i$ vs $t$ for initial rising parts of transients for potential step experiments on fully charged electrodes from the OCV (1078 mV) to: △, 1003; □, 978 and ○, 951 mV.

Fig. 10.6 Series of long time transients for potential step experiments on fully charged electrodes from the OCV (1078 mV) to: (a) 1003; (b) 978; (c) 938; (d) 918; (e) 898 and (f) 878 mV. Electrolyte: $\text{H}_2\text{SO}_4$ (3.58 M).
Fig. 10.7  $\log_{10}(i/t)$ vs $t^2$ for the falling part of transient (b) in Fig. 10.6.

Fig. 10.8  $\log_{10}(i/t)$ vs $t^2$ for the falling part of transient (f) in Fig. 10.6.
Fig. 10.9 i vs t for initial rising parts of transients for potential steps, from 1078 to 953 mV, on electrodes discharged by: □, 10% and ○, 20%.

Fig. 10.10 Current-time transients for 10% discharged electrodes stepped from 1078 mV to: (a) 978 and (b) 928 mV. Electrolyte; H₂SO₄ (3.58 M).
Fig. 10.11 $\log_{10}(i/t)$ vs $t^2$ for falling parts of Fig. 10.10. 
\[ \Box, (a); \Box, (b). \]

Fig. 10.12 $i$ vs $t$ for rising transients obtained by stepping partially discharged (D.) Planté electrodes from 1078 mV to:
- ■, 953 mV and ●, 928 mV (40% D.);
- □, 953 mV and △, 928 mV (50% D.);
- ●, 928 mV (75% D.).
a zero intercept. In theory we would expect the partially discharged electrodes to show a positive intercept due to the fact that there will be some lead sulphate already present. This process is apparently influenced by the fact that the initial discharge was carried out galvanostatically, which would drive the reaction at a fixed rate, irrespective of the relative reactivities of the forms of lead dioxide present and independent of the size of the nucleation centres. The response to a subsequent potentiostatic experiment would be conditioned by the galvanostatic experiments until sufficient new surface (PbSO₄) had been formed. The first part of the potentiostatic transient contains a major contribution arising from the galvanostatic conditioning of the surface. Later on in the experiment the current rises in the expected manner. The extrapolation to the time axis rather than the current axis reflects this.

Analysis of the falling parts of the transients, proved to be more complicated for the highly discharged electrodes, i.e. those containing a large proportion of PbSO₄. Electrodes discharged by 40% and 50% gave straight line plots for both instantaneous and progressive two-dimensional nucleation and growth (Figures 10.13(a) and 10.13(b)), with slightly better correlation coefficients obtained from the progressive nucleation plots, for which the current-time equation (3.35) was given in Chapter 3.

For the 75% discharged electrode, however, the plots for the falling parts of the transients showed that the process taking place was a three-dimensional progressive nucleation and growth (Table 10.1), for which the current-time relationship shown in equation (3.45) applies, for the case of the growth of right circular cones.
Fig. 10.13(a) $\log_{10}(i/t)$ vs $t^2$ for falling transient obtained by stepping a 50% discharged electrode from 1078 to 978 mV.

Fig. 10.13(b) $\log_{10}(i/t^2)$ vs $t^3$; details as Fig. 10.13(a).
TABLE 10.1

Summary of nucleation and growth processes obtained for potential-step experiments from the OCV to potentials in the PbSO₄ region.

Asterisks (*) indicate observed model.

<table>
<thead>
<tr>
<th>% Discharge</th>
<th>Growth</th>
<th>Nucleation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2D</td>
<td>3D</td>
</tr>
<tr>
<td>0</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>20</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td></td>
<td>*</td>
</tr>
</tbody>
</table>
Figures 10.14(a) and 10.14(b) show that again there was some indication that the process was a two-dimensional progressive nucleation one, i.e. there was indication of some two-dimensional progressive character to the three-dimensional (3-D) process. This could arise if the rate constants for the three-dimensional process were very small in one of the three directions.

Potential step experiments were also carried out by stepping from the open circuit voltage to 1378 mV. This potential was chosen as this was the voltage attained by the fully formed Planté microelectrodes when they were galvanostatically charged to their fully charged state.

Figures 10.15 - 10.18 show the current-time responses for such experiments using fully and partially charged Planté electrodes.

An initial spike is again observed in these experiments and is followed by a second peak with considerable overlap by the first. The current finally decays to zero, indicating completion of the growth of solid phase PbO₂. It is interesting to note that in addition to these responses, longer time transients for the same experiments show an extra hump for the 40% discharged electrode and two humps for the 75% discharged electrode. These indicate the occurrence of additional electrocrystallisation processes in the cases of highly discharged electrodes.

The current magnitudes in these and all other experiments were independent of rotation speed of the electrode. This indicated the lack of any current controlling reaction via the solution.

An exhaustive examination of the falling parts of the transients for the reoxidation of the reduced electrodes was undertaken in
Fig. 10.14(a)  $\log_{10}(i/t^2)$ vs $t^3$ for falling transient obtained by stepping a 75% discharged electrode from 1078 to 953 mV.

Fig. 10.14(b)  $\log_{10}(i/t^3)$ vs $t^3$; details as Fig. 10.14(a).
Fig. 10.15  Current-time transient for a fully charged electrode stepped from 1078 to 1378 mV. (a) Fast and (b) Slow response. Electrolyte; H₂SO₄ (3.58 M).

Fig. 10.16  Current-time transient for a 10% discharged electrode. Details as Fig. 10.15.
Fig. 10.17  Current-time transient for a 40% discharged electrode.
Details as Fig. 10.15.

Fig. 10.18  Current-time transient for a 75% discharged electrode.
Details as Fig. 10.15.
order to see if these contained information about the crystallisation processes.

The clear picture obtained with the lead dioxide reduction process was not evident in these cases. There was no conformation to the classical two-dimensional or three-dimensional processes. An attempt to correct the transient data for electrode porosity was made by "square-rooting" the time dependencies as described by de Levie\textsuperscript{51} and also discussed by Lakeman\textsuperscript{61}. This relatively crude correction produced success in a limited number of cases as typified by the data of Figure 10.19 for 10\% discharge which shows that the falling transient at long times could be interpreted as a two-dimensional, instantaneous process occurring on the inner surfaces of the porous electrode. Such well-defined cases were rare, however, and the data from electrodes discharged to a greater extent yielded no clear picture. The method used by Casson can be used to show the form of the current decay, that is, a simple $\log_{10}i/i_m$ versus $\log_{10}(t-t_m)$ presentation. Our data showed two straight line parts (Figure 10.20) in a similar manner to the data obtained by Casson\textsuperscript{105} but with more negative exponent values, indicating a more gradual current decay. Finally, Figure 10.21 shows the falling transients presented in terms of $\log i$ versus $\log t$ for which straight lines were observed.

These results could be explained in terms of gradual removal of randomly dispersed lead sulphate from a lead dioxide matrix. The number of points on the lead sulphate which can be transformed to lead dioxide is clearly sufficiently large for the nucleation process not to be a current limiting factor since no initial rising transient is observed. The kinetics correspond to the removal
Fig. 10.19  $\log(i/t^b)$ vs $t$ for falling part of transient of Fig. 10.16.

Fig. 10.20  $\log(i/i_m)$ vs $(t-t_m)$ for falling part of transient of Fig. 10.15.
Fig. 10.21 $\log_{10} i$ vs $\log_{10} t$ for the falling parts of transients for electrodes stepped from 1078 to 1378 mV. 0, fully charged; □, 10%; △, 40%; ●, 50% and ■, 75% discharged electrodes.
of the final traces of lead sulphate particles of varying sizes which have been randomly nucleated by the galvanostatic process. The current might be expected to fall in accordance with the Avrami equation\textsuperscript{34} which would predict the exponential decay of the type observed.

It does not seem, therefore, that a suitable model exists for the electrocrystallisation process for the reoxidation of galvanostatically reduced Planté lead electrodes. This is interesting, for the continuation of the reduction process, by a potentiostatic step, behaves in the manner expected. The difference probably lies in the different conductivities of the two phases. In the case of the reduction, an insulating phase is being created whereas in the oxidation a conducting phase is produced. We must conclude that in the presence of significant amounts of lead dioxide, lead sulphate is oxidised, unhampered by nucleation processes, to give a simple falling transient of the form predictable by Canagaratna et al\textsuperscript{119}. 
A.C. IMPEDANCE STUDIES ON A PLANTÉ PbO₂
ELECTRODE AT VARIOUS STATES OF CHARGE

11.1 Introduction

The a.c. impedance of massive PbO₂ (electroplated onto Pt) in sulphuric acid has already been reported¹¹⁹,¹²⁰ and the behaviour observed has been compared with that due to simple porous films produced by the electrooxidation of basic lead sulphate formed upon lead¹²⁰ and lead alloys¹²¹. The appearance of a high frequency semi-circle in the frequency spectrum enabled certain kinetic constants for the β-PbO₂/PbSO₄, H₂SO₄ electrode to be calculated. This electrode showed a considerable time dependency, for it was found that the charge-transfer resistance changed continuously with time, due apparently to a lead sulphate layer which progressively developed on the massive β-PbO₂. For the porous electrode an inductive region was observed at high frequency¹²¹. Keddam et al¹⁴⁹ have also observed these effects with lead-acid cells and have suggested that geometrical effects could be the cause of the inductances. On the other hand the work of Darby⁵² has shown that inductive components of the total electrode impedance can arise if the reaction can take place over a distributed region especially if gas reactions are involved. An investigation of the impedance of PbO₂ formed by a simple potential excursion of lead and lead alloys into the PbO₂ region showed that there were considerable differences between the response of PbO₂ formed from pure lead and that formed from alloys containing Sb and Bi¹²¹. It was considered of interest to investigate the a.c. impedance of PbO₂ formed in
depth from pure lead, as is the case with the Planté formed microelectrodes. This chapter shows the results of an impedance study with these electrodes, at the reversible potential, at various states of charge. The effect of cycling these electrodes was also examined.

11.2 Experimental

The electrode was fully formed in the way described in Chapter 5. It was then introduced to the impedance cell containing sulphuric acid (3.58 M) and allowed to settle down to the reversible potential, on open circuit, before being connected to the a.c. apparatus.

Impedance measurements were made at the open circuit voltage (zero current potential) in the range of 10 kHz to 10 Hz, at ten intervals per decade. This was achieved with the use of a frequency response analyser (Solatron 1172) and a potentiostat interphase (Solatron 1186).

After the end of the experiment the electrode was removed, introduced to the formation cell once more and discharged by 10% of its nominal capacity. It was then returned again to the impedance cell and allowed to settle down to its zero current potential before the start of the impedance measurements. This procedure was repeated until the electrode was completely discharged. It was essential to use the same electrode throughout these experiments in order to eliminate problems due to possible variations in capacity.

In order to examine the electrodes under more realistic conditions, the a.c. impedance of cycled electrodes at various
states of charge was also investigated. The fully formed Planté electrodes were discharged by 10%, 25%, 50% and 75% and then cycled. The electrodes underwent eighty cycles (discharge/charge, ±10% of their nominal capacity) ending with the charging part of the sequence. The a.c. impedance of these electrodes was similarly measured at the reversible potential. The electrodes were finally washed free of sulphuric acid with acetone and dried under vacuum prior to scanning Electron Microscope (Cambridge Stereoscan, Model 2A) examination.
11.3 Results and Discussion

Figure 11.1 shows the impedance plot for an electrode completely free of PbSO$_4$ (100% charged). It consists of a very well-defined inductive region extending from the highest available frequency to about 1 kHz. As the frequency is further reduced, the impedance locus crosses the zero out-of-phase axis and further reduction in frequency results in a capacitive component. This impedance loci is rather different from previously reported data. The fairly well-defined, approximately circularly shaped, high frequency part of the impedance spectrum, due to a partially discharged electrode, is clearly not observed\textsuperscript{122}. Similarly, the response does not conform to the simple line of increasing slope, corresponding to the pure Pb electrode, overlayed with PbO$_2$ by polarisation at 1250 mV and then returned to the reversible potential (~ 1.00V)\textsuperscript{123}. In both these cases the impedance spectra were free from any inductive regions.

On discharging (reducing) the electrode in 3.58M sulphuric acid (s.g. = 1.210 conforming to industrial practice) the overall shape did not change, however, the curve was displaced in such a way that the inductive region was reduced in frequency range (from 10 kHz). This is shown in Figures 11.2 - 11.9. At the discharged level which represents the removal of 70 - 80% of the recoverable charge the inductive region at 10 kHz was not observable as shown by Figures 11.8 and 11.9. On the removal of all the recoverable charge the shape of the impedance loci changed dramatically (Figure 11.10) now conforming to the shapes reported for the system PbO$_2$/PbSO$_4$,$H_2$SO$_4$ in the PbSO$_4$ region of potential\textsuperscript{122,123}. The reversible potential of the electrode (0.948 V) was significantly
Fig. 11.1  Complex-plane plot for a fully charged Planté microelectrode. a.c. impedance experiment at the OCV in H_2SO_4 (3.58 M); 23°C; ●, experimental points; full line, computer fit. Frequencies marked in Hz.

Fig. 11.2  As Fig. 11.1; 10% discharged Planté electrode.
**Fig. 11.3** As Fig. 11.1; 20% discharged Planté electrode.

**Fig. 11.4** As Fig. 11.1; 30% discharged Planté electrode.
Fig. 11.5  As Fig. 11.1; 40% discharged Planté electrode.

Fig. 11.6  As Fig. 11.1; 50% discharged Planté electrode.
Fig. 11.7 As Fig. 11.1; 60% discharged Planté electrode.

Fig. 11.8 As Fig. 11.1; 70% discharged Planté electrode.
Fig. 11.9  As Fig. 11.1; 80% discharged Planté electrode.

Fig. 11.10  As Fig. 11.1; totally discharged Planté electrode.
affected by this final process.

The inductive region at high frequency is of considerable interest. The only explanation in terms of the electrochemistry appears to be that due originally to Darby\textsuperscript{52}. He showed that inductive reactances can arise when mass transport and electrochemical (faradaic) reactions can occur simultaneously over a distributed region of the electrode. A geometrical (spatial) explanation was given somewhat earlier by Gutmann\textsuperscript{53}, whose observation of lagging currents in porous electrode systems was treated as analogous to viscoelastic phenomena. He suggested that they arose effectively because a certain time elapsed between the arrival of the signal at the mouth of the electrode pore and its reaching the bottom. According to these two views, the magnitude of the inductive reactance attributable to this cause is frequency dependent, however, whereas the Darby theory, where the behaviour can be considered as uncoupled, predicts a complex dependence on frequency, the Gutmann proposal predicts a constant inductance, $L$.

A further interesting feature of the impedance curves is that the low frequency tail rises with a dihedral angle greater than $\pi/4$. Moreover the slope gradually increases as the frequency is decreased. This can be interpreted in terms of a layer of PbSO\textsubscript{4} at the electrode which contributes an extra capacitance in series with the faradaic reaction and the electrolyte resistance. The presence of lead sulphate at the electrode is clearly essential if the reversible potential of the electrode of the second kind PbO\textsubscript{2}/PbSO\textsubscript{4}, H\textsubscript{2}SO\textsubscript{4} is to be established. Assuming that the faradaic reaction is charge transfer controlled then the simplest analogue of the electrode is shown in Figure 11.11. This last assumption
Fig. 11.11 Analogue circuit consisting of a simple Randles circuit plus an external capacitor ($C_X$) and inductance ($L$).
is open to considerable doubt at long times for there is now much unequivocal evidence to support the view that in the second range of times (frequencies ~ 10 Hz) the processes of nucleation and growth are rate limiting, especially where the PbO₂ electrode is relatively free of PbSO₄. For this reason in the present discussion the frequency range has been limited to 10 Hz.

A computer method has been devised for matching the theoretical response of the best analogue to the experimental data points. The matching was carried out by writing equations for the cell analogue and using the complex number handling capabilities of the PRIME 400 computer to separate out the real and imaginary parts (R equation and C equation). The impedance data can now be matched on the basis of either of these equations; in practice both are used and an internal check of the results is provided by the agreement between the computer predictions. The process we use is to expand about approximate values (x') of the circuit elements (x) such that x = x' + Δx. Using Taylor's theorem two linear equations result

\[ R = R' + \sum \left( \frac{dR}{dx} \right) Δx \]  \hspace{1cm} (11.1)

and \[ C = C' + \sum \left( \frac{dC}{dx} \right) Δx \]  \hspace{1cm} (11.2)

The n experimental data points (frequency) each provide one linear equation. These can be reduced by the method of least squares to the number of normal equations needed to calculate Δx. The process is repeated until Δx is small enough to be neglected.
It was found that only the highly reduced PbO₂ electrodes could be satisfactorily matched. In many cases, especially at unreduced PbO₂ or where only limited reduction had occurred, the curving region appeared to bend too shallowly. We have corrected this behaviour by allowing for the porosity of the electrode. This was done by using a modification of the "halving" technique for the time dependent processes which occur in the porous structure. Essentially, because the current arrives parallel to the plane of the porous electrode rather than normal to it (as would occur at a planar electrode) for a porous electrode with semi-infinite pores, the time dependent responses of the electrode become "halved". Rather than use a formal halving of the phase angle and a square rooting technique for the amplitude for those components affected by the porosity, we introduced a "porosity factor" $P_f$ and calculated $P_f$ as the power to which the amplitude was raised (or the appropriate multiplier of the phase angle). The electrode inductance was not corrected for the porosity as was the electrode reaction and double layer elements in the first instance and it was found that there was no need to include this correction.

The results of the computations are shown in Table 11.1 and the fitted curves are shown as the unbroken lines in Figures 11.1 - 11.10.

The electrode response can clearly be matched to a very high precision, by the analogue previously shown, when the porosity factor is taken into account. This was also confirmed by Randles plots, showing that experimental and calculated curves were coincidental with respect to the frequency parameter. Figures 11.12 - 11.14 show typical examples of these plots. It is to be expected
Fig. 11.12  Randles plot corresponding to Fig. 11.1.

Fig. 11.13  Randles plot corresponding to Fig. 11.6.
Fig. 11.14  Randles plot corresponding to Fig. 11.9.
TABLE 11.1

Mean values for electrode characteristics obtained from matched computer data for C and R equations

<table>
<thead>
<tr>
<th>Charge (%)</th>
<th>Charge (C/cm²)</th>
<th>OCV (%)</th>
<th>R_R (Ω)</th>
<th>θ (Ω)</th>
<th>C_L (μF)</th>
<th>σ (Ωs⁻¹)</th>
<th>P_F</th>
<th>C_X (μF)</th>
<th>L (μH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>28.47</td>
<td>1.078</td>
<td>1.812</td>
<td>0.024</td>
<td>4375.0</td>
<td>1.83</td>
<td>0.690</td>
<td>48552</td>
<td>2.530</td>
</tr>
<tr>
<td>90</td>
<td>25.62</td>
<td>1.077</td>
<td>1.647</td>
<td>0.030</td>
<td>5173.9</td>
<td>1.47</td>
<td>0.593</td>
<td>30384</td>
<td>2.543</td>
</tr>
<tr>
<td>80</td>
<td>22.78</td>
<td>1.080</td>
<td>1.649</td>
<td>0.047</td>
<td>4000.7</td>
<td>1.92</td>
<td>0.5414</td>
<td>24417</td>
<td>2.408</td>
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<tr>
<td>70</td>
<td>19.93</td>
<td>1.080</td>
<td>1.805</td>
<td>0.050</td>
<td>1723.0</td>
<td>3.83</td>
<td>0.5581</td>
<td>21335</td>
<td>2.468</td>
</tr>
<tr>
<td>60</td>
<td>17.08</td>
<td>1.080</td>
<td>1.834</td>
<td>0.081</td>
<td>592.3</td>
<td>7.70</td>
<td>0.623</td>
<td>18175</td>
<td>2.591</td>
</tr>
<tr>
<td>50</td>
<td>14.23</td>
<td>1.080</td>
<td>2.121</td>
<td>0.168</td>
<td>203.8</td>
<td>12.39</td>
<td>0.913</td>
<td>(27395)*</td>
<td>2.051</td>
</tr>
<tr>
<td>40</td>
<td>11.38</td>
<td>1.080</td>
<td>2.206</td>
<td>0.205</td>
<td>147.2</td>
<td>16.35</td>
<td>1.000</td>
<td>9687</td>
<td>1.922</td>
</tr>
<tr>
<td>30</td>
<td>8.54</td>
<td>1.080</td>
<td>2.503</td>
<td>0.134</td>
<td>64.3</td>
<td>25.87</td>
<td>0.888</td>
<td>4675</td>
<td>2.537</td>
</tr>
<tr>
<td>20</td>
<td>5.69</td>
<td>1.077</td>
<td>3.245</td>
<td>0.258</td>
<td>43.5</td>
<td>62.36</td>
<td>1.000</td>
<td>(25999)*</td>
<td>1.632</td>
</tr>
</tbody>
</table>

* No reason could be found for these values obtained by the computer matching technique. With such values, a small error in the experimental data results in large magnitude difference in C_X.
that the system is unchanged in character by progressively transforming PbO₂ to PbSO₄ and indeed the relative constancy of the reversible potential of the electrode indicates that the process of reduction leaves this electrode of the second kind unaffected.

The development of lead sulphate in the electrode has a very marked effect on the electrochemical characteristics (Table 11.1). All the electrode parameters change in the way expected if the initially large area lead dioxide electrode was progressively covered with lead sulphate which blocked-off the electrode reaction. The values of the porosity factor, Pₑ, are of special interest. Either the values are around 0.5, for the electrode containing relatively little lead sulphate, or are around 1.0, for the higher lead sulphate content electrodes. This change is not accompanied by any change in electrode potential and it must be concluded that the originally porous electrode has become essentially planar on the conversion of about half of the available PbO₂ to PbSO₄. It is also of interest to note that the magnitude of the inductance has not changed during this process. It is clear that whatever process gives rise to the inductive region, it cannot be explained by the Gutmann reasoning, since effectively, the electrode porosity has been changed considerably by the reduction of PbO₂ to PbSO₄.

On the other hand, the potential of the reversible oxygen electrode is some 400 mV less positive than the reversible lead dioxide electrode in sulphuric acid. Thus the inductive effect could arise from the oxygen redox reaction over a distributed region of the electrode. If the electrode is forced to a value of ~100 mV more negative than the reversible potential, the inductive component cannot be detected. This again confirms that the effect is unlikely to be explained by the Gutmann reasoning. We may conclude therefore,
that the inductive region is associated with an electrochemical process and this is likely to be the oxygen redox reaction. This confirms the observations made earlier at polarised lead in sulphuric acid where it was shown that the impedance becomes increasingly reactive at higher positive potentials.

Figures 11.15 - 11.20 show how the values of the circuit elements change with the state of charge. The values of the double layer capacitances show a drastic fall from the unreduced condition (100% PbO$_2$). Initially, however, the values of the double layer capacitance are fairly constant as lead sulphate is generated. As the convertible lead dioxide is reduced below 80%, the double layer capacitance falls very rapidly and below 50% it becomes of the order of that expected for a metal in 5M H$_2$SO$_4$. When only 20% of the lead dioxide remains, the magnitude of this is low even for a plane solid metal. Values of both $\theta$, the charge-transfer resistance, and $\sigma$, the Warburg coefficient, change in a way complementary to this. At about 70% PbO$_2$ there is a marked change in magnitude. This can be explained if the surface of the lead dioxide is being covered by insulating lead sulphate in such a way that the electrochemically active area is effectively reduced as conversion continues. Confirmation of this is obtained from the values of the porosity factor. These are shown plotted against % PbO$_2$ in Figure 11.19. The data form a sigmoidal curve. At high lead dioxide contents the porosity factor is approximately half, corresponding to a semi-infinitely porous system, at lower lead dioxide contents (< 50% charge) the electrode appears planar. This is an interesting observation for it can be taken as evidence for pore blocking. This was tested by "correcting" the values of $\theta$ and $\sigma$ for the loss
Fig. 11.15  Plot of computed electrolytic resistance $R_\Omega$ (mean value for C&R equation) versus state of charge for experiments shown in Figs. 11.1 - 11.9.

Fig. 11.16  As Fig. 11.15; charge transfer resistance, $\theta$, versus % charge.
Fig. 11.17  As Fig. 11.15; double layer capacitance, $C_L$, versus % charge.

$C_L / \mu F$

20  40  60  80  100
% charge

Fig. 11.18  As Fig. 11.15; Warburg coefficient, $\sigma$, versus % charge.

$\sigma / \Omega \cdot \mu F$

20  40  60  80  100
% charge
Fig. 11.19  As Fig. 11.15; Porosity factor, $P_f$, versus % charge.

Fig. 11.20  As Fig. 11.15; External capacitance, $C_x$, versus % charge.
of surface area. If the "quality" of electrode blocking was the same throughout the range, then $6C_L$ and $9C_L$ should be constant throughout. Table 11.2 shows that they are fairly constant when at low lead sulphate contents, but after about 30% of the lead dioxide has been converted, the values progressively fall to low values. Clearly the argument is substantiated.

The external capacitance $C_x$, which we have suggested represents the effective thickening of the film of lead sulphate, shows no such abrupt change in character. This can be understood if the development of the PbSO$_4$ film affected the 'external' capacitance according to the flat capacitor theory. As more lead sulphate is produced the dielectric layer thickens and $C_x$ is diminished. A simple trivial mathematical treatment using the macrohomogeneous approach of Newman indicates that a linear relationship should exist between the PbSO$_4$ (dielectric) content and the capacitance. That this is so is shown in Figure 11.20.

The most interesting point about this work is the identity of the inductance. With such a complex system it does not seem possible at present to press the interpretation further without further high-frequency data, not presently available.

The frequency independence of the inductance agrees with the complete cell observations of Keddam et al., however this is not invariably so with porous PbO$_2$ electrodes. It is possible that over a frequency range extending to higher values a more complex shape would result.

The a.c. impedance experiments on the cycled electrodes gave very similar spectra to the ones already described (Figures 11.21 -
### TABLE 11.2

Variation of $\theta C_L$ and $\sigma C_L$ with charge.

<table>
<thead>
<tr>
<th>Charge %</th>
<th>$\theta C_L$ ($\Omega \ \mu F$)</th>
<th>$\sigma C_L$ ($\Omega \mu F \ s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>106.30</td>
<td>7920.41</td>
</tr>
<tr>
<td>90</td>
<td>147.70</td>
<td>7140.40</td>
</tr>
<tr>
<td>80</td>
<td>181.70</td>
<td>7593.36</td>
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<td>70</td>
<td>86.30</td>
<td>6574.17</td>
</tr>
<tr>
<td>60</td>
<td>47.28</td>
<td>4542.76</td>
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<td>34.42</td>
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<td>1652.51</td>
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<tr>
<td>20</td>
<td>11.24</td>
<td>2716.18</td>
</tr>
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</table>

### TABLE 11.3

Partially discharged and cycled Plante electrodes

Mean values for electrode characteristics obtained from matched computer data for $C$ and $R$ equations

<table>
<thead>
<tr>
<th>Charge %</th>
<th>$R_Q$ ($\Omega$)</th>
<th>$\theta$ ($\Omega$)</th>
<th>$C_L$ ($\mu F$)</th>
<th>$\sigma$ ($\Omega s^{-1}$)</th>
<th>$P_f$</th>
<th>$C_X$ ($\mu F$)</th>
<th>$L$ ($\mu l$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>3.250</td>
<td>0.033</td>
<td>2613</td>
<td>3.12</td>
<td>0.704</td>
<td>45750</td>
<td>2.465</td>
</tr>
<tr>
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Fig. 11.21  a.c. impedance of a 10% discharged, cycled Planté electrode (80 cycles, ± 10% of nominal capacity). Details as Fig. 11.1.

Fig. 11.22  As Fig. 11.21; 25% discharged, cycled Planté electrode.
Fig. 11.23  As Fig. 11.21; 50% discharged, cycled Planté electrode.

Fig. 11.24  As Fig. 11.21; 75% discharged, cycled Planté electrode.
The same theoretical model was used (Figure 11.11) and the values obtained for the various circuit elements are shown in Table 11.3. These values, unlike the case of the uncycled electrodes remained fairly constant. The only significant feature was that of the porosity factor which showed an average value of 0.75. This is interesting in view of the distinct changes in porosity observed with the uncycled electrode (Figure 11.19). In the case of the cycled electrodes, instead of the pore blocking observed with the uncycled electrode at low states of charge, an intermediate value between that of a semi-ininitely porous and a planar system was obtained.

Figures 11.25 - 11.28 show S.E.M. photographs of the electrodes examined. Figure 11.25 shows the electrode surface evenly covered by PbO₂ crystals providing the expected porosity of a semi-infinite porous system. Figures 11.26 - 11.28 on the other hand show the electrode surface for the cycled electrodes. It is likely that the duplex structure of the large crystals observed accounts for the retention of some of the porous character at low states of charge.
Fig. 11.25 100% charged Plante electrode; magnification x550.

Fig. 11.26 25% discharged, cycled Plante electrode; magnification x550.

Fig. 11.27 50% discharged, cycled Plante electrode; magnification x630.

Fig. 11.28 50% discharged, cycled Plante electrode; magnification x2200.
CHAPTER 12

THE A.C. IMPEDANCE OF THE PLANTÉ PbO₂ ELECTRODE POLARISED IN SULPHURIC ACID

12.1 Introduction

The impedance of Planté formed porous PbO₂ electrodes at the reversible potential was examined in the preceding chapter. In an excess of sulphuric acid solution, it was shown that the reversible potential was independent of the lead sulphate content of the electrode. The changes of the impedances of electrodes measured under these conditions were interpreted as resulting from the development of insulating phase PbSO₄ inside the porous structure and at the front of the electrode. This investigation did not yield any kinetic data since the presence of the lead sulphate on the electrode surface introduces considerable uncertainty in addition to the uncertainties of the porous structure.

Some experiments were also made in which the potential of an electrode initially free of PbSO₄ was forced from the equilibrium and the impedance immediately determined. The results of these experiments are discussed in this chapter.

12.2 Experimental

The Planté microelectrode was fully charged and then allowed to settle down to its reversible potential on open circuit (1078 mV). The electrode was recharged after each experiment.

The potential was rapidly forced from the equilibrium to a more negative value, and the impedance spectrum was measured as
as rapidly as possible. The experiments were therefore made with an a.c. perturbation on top of the d.c. level corresponding to the potential at which the electrode was poised. The experiments were again carried out using the Solatron 1172 F.R.A. together with the Solatron 1186 Potentiostat interphase. The electrolyte used was sulphuric acid (AnalaR; 3.58 M) and the impedances were measured in the range 10 kHz to 0.001 Hz.
12.3 Results and Discussion

The results could be divided into two groups. First, the overpotential range extending from OCV to OCV -50 mV was considered. Here, the high frequency part of the impedance spectrum resembled the results obtained in the previous Chapter, and the plots could be interpreted using the same model. The model consisted of the basic Randles circuit, with the addition of an external capacitor and inductor, and Table 12.1 contains the relevant electrode magnitudes of the circuit elements. Figures 12.1 - 12.5 show the impedance loci for the same experiments.

The charge-transfer resistance increased as the electrode was forced to more negative values. This is a rather unexpected observation, for under reduction conditions we would expect,

$$\frac{d \ln \theta}{dE} = + \frac{RT}{aZF}$$  \hspace{1cm} (12.1)$$

showing that $\theta$ should decrease as the potential became more negative. The explanation for the increase is in terms of the development of a layer of lead sulphate across the front of the electrode. The consequence of this sulphate layer is to block off the active surface and thus obscure the reaction. The effect of this is readily seen on the double layer capacitance which is drastically reduced as the electrode is made more negative. The relationships are most conveniently expressed as logarithmic plots against the potential. Figures 12.6 and 12.7 show the relationships for which we can calculate respectively,

$$\frac{d \log \theta'}{dE} = -45 \text{ mV/decade}$$  \hspace{1cm} (12.2)$$
Fig. 12.1 High frequency complex-plane plot for a fully charged Planté microelectrode. a.c. impedance experiment at 1078 mV (OCV); in H₂SO₄ (3.58 M), 23°C. •, experimental points; full line, computer fit. Frequencies marked in Hz.

Fig. 12.2 As Fig. 12.1; impedance measurements at 1068 mV.
Fig. 12.3  As Fig. 12.1; impedance measurements at 1058 mV.

Fig. 12.4  As Fig. 12.1; impedance measurements at 1048 mV.
Fig. 12.5  As Fig. 12.1; impedance measurements at 1028 mV.
Fig. 12.6  $\log_{10} \theta'$ versus $E$, mean values (from C&R equations) from computed data for Figs. 12.1 - 12.4.

Fig. 12.7  As Fig. 12.6; $\log_{10} C_L$ versus $E$. 
<table>
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<tr>
<th>$V'$-ve of $E_T$ (mV)</th>
<th>R (Ω)</th>
<th>$θ$ (Ω)</th>
<th>$C_L$ (μF)</th>
<th>$α$ (Ωs⁻¹)</th>
<th>$P_F$</th>
<th>$C_X$ (μF)</th>
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<td>0.820</td>
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</tr>
</tbody>
</table>
and

\[ \frac{d \log C_L}{dE} = 20 \text{ mV/decade} \quad (12.3) \]

where \( \theta' \) is the apparent charge transfer resistance.

The value obtained from equations (12.2) and (12.3) can be combined if we consider the double layer capacitance to give a true value of available electrode surface to yield:

\[ \frac{a \log \theta}{aE} = -36 \text{ mV/decade} \quad (12.4) \]

This value can be compared with others obtained for systems where PbSO\(_4\) was formed on thin layers of PbO\(_2\) overlaying Pb\(^{122}\) or PbSO\(_4\) on PbO\(_2\) electrodeposited on Pt\(^{120}\). These values were considerably higher than the corrected value of 36 mV found here. This is probably due to the fact that the previous work\(^{120,122}\) was carried out on a thin layer of lead dioxide which, when passivated, provided a fairly continuous, well-characterised film, which efficiently covered the electrode surface. In the present case, the deposit of PbO\(_2\) is very thick and the electrode is formed in depth. Inside the porous structure diffusion is limited by the pore geometry and even though the front of the electrode may be effectively covered by lead sulphate, the interstices will be relatively free. This is because the change in electrode conditions required by the Nernst equation can be achieved in the short term by the reduction in the concentration of sulphuric acid. For a thin (or electrodeposited) lead dioxide layer on the other hand the concentration change is swamped out by diffusion. Therefore over the time scale of the
experiment the inner regions of the electrode, from which the majority of the current arises, provide sufficient areas of PbO₂ for the electrochemistry of lead dioxide to occur on areas not complicated by PbSO₄. Under these conditions, the effect of the (growing) film of lead sulphate can be satisfactorily removed through the application of the double layer capacitance correction.

The value of the Tafel slope of \(-36\, \text{mV per decade}\) increase in current density agrees well with established data on the lead-acid battery positive as determined by Simonsson³ using potential step methods on complete lead-acid cells. His value of \(-30\, \text{mV per decade}\) is a rather surprising value, as for a two electron change a greater value would have been expected for this electrode. Nevertheless, this work is to be taken as confirmation of his result.

The inductance which is needed to match the electrode impedance data is observed to be fairly constant throughout the small potential range. The argument that this is due to the oxygen reaction distributed within the porous structure can still be maintained, for the experiments are being conducted at a potential remote from the reversible oxygen potential. The remainder of the features of this potential region follow naturally from the theory that an increasingly thick layer of lead sulphate is progressively developing at the front of the electrode. Eventually, the reaction is driven more deeply into the porous structure as the potential is forced to increasingly more negative potentials. Thus, \(R_\Omega\) increases and \(C_x\) remains fairly constant in agreement with the preferential development of PbSO₄ at the electrode front. The porosity factor is constant over the potential range of interest. This is to be expected since there will be little change in sulphuric acid
content of the porous interior with potential.

When the frequency range was increased down to a few mHz, impedance spectra shown in Figures 12.8 - 12.13 were obtained. It was considered that especially in the cases where a significant step function is applied to the electrode, any effects due to the creation of new PbSO$_4$ phase would be apparent from the earliest instants. Therefore there was little point in attempting to avoid such complications. Indeed it is probably the intrusion of these effects into the experimental frequency range that limited the range of application of the relatively simple electrode analogue.

The low frequency impedance data for experiments close to the OCV reveal a curvature towards the real axis producing a semicircle which gradually decreased in size and a shallow Warburg line is observed (Figures 12.8 - 12.10). With experiments 60 - 300 mV negative of the OCV the impedance loci become much more complex and difficult to interpret. Figure 12.11 shows the impedance loci corresponding to a potential of 978 mV. It consists of a line initially inductive at 10 kHz which has a dihedral angle of $\sim 36^\circ$ and which rises more steeply at lower frequencies. This broadly similar shape is maintained throughout the potential region, down to 820 mV with the exception that the inductive part is lost for potential excursions more negative than 978 mV. The high frequency points in these cases consist of a fairly flat part which shows some curvature as the electrode is introduced to more negative potentials, shown in Figures 12.12 and 12.13.

The disappearance of the inductive character for impedance measurements at 10 kHz can be interpreted using either of the theories
Fig. 12.8  As Fig. 12.1; but for full frequency spectrum; a.c. at 1068 mV.

Fig. 12.9  As Fig. 12.1 but for full frequency spectrum; a.c. at 1058 mV.
Fig. 12.10 As Fig. 12.1 but for full frequency spectrum; a.c. at 1028 mV.

Fig. 12.11 As Fig. 12.1 but for full frequency spectrum; a.c. at 978 mV.
Fig. 12.12  As Fig. 12.1 but for full frequency spectrum; a.c. at 878 mV.

Fig. 12.13  As Fig. 12.1 but for full frequency spectrum; a.c. at 778 mV.
mentioned in the previous chapter. Using Gutmann ideas, the formation of lead sulphate would be formed preferentially at the front of the electrode and would destroy the in-depth porosity of the electrode. On the other hand, the reduction in the potential of the electrode would drive the electrode out of the oxygen region. On account of both theories therefore, the extent of the inductive component should diminish. However, it is not possible, on the present evidence, to decide which of these two proposals is the correct one.

At low frequencies all the impedance loci approximate to a line at $45^\circ$ to the real axis representing diffusion of the molecules of $\text{H}_2\text{SO}_4$.

We can conclude therefore that the experiments can only be satisfactorily interpreted within $-50$ mV of the reversible potential. The development of lead sulphate films at more negative potentials obscures the electrochemistry.
13.1 Introduction

Previous impedance work\textsuperscript{122} for thin films of PbO\textsubscript{2} electroformed on Pb, showed that the mode of PbSO\textsubscript{4} passivation was by a spreading, rather than thickening process. It was considered important to carry out similar measurements on Planté electrodes where the lead is overlayed by a thick film of PbO\textsubscript{2}.

The problem of a well-defined pre-electrode state is always present in cases where it is intended to polarise an electrode of the second kind. The development of the insoluble phase which occurs as a consequence of the potential excursion interferes with the electrode impedance. One can quickly change the potential and determine the impedance spectrum assuming that the electrode conditions are not changing. The complimentary method is to polarise potentiostatically until no further current flow occurs and then determine the impedance spectrum corresponding to the steady-state conditions. This latter was the procedure chosen for the present experiments in view of the very high currents which flow from the porous electrode as a consequence of a small change in potential.

13.2 Experimental

The Planté electrode was fully charged at the start of the experiment and was recharged prior to each successive experiment. The electrolyte was sulphuric acid (3.58 M).
The electrode was introduced to the system at a potential negative to the open circuit voltage and the impedance was measured only when the electrode reduction current had fallen to zero. In this way the impedances, at the potentials of interest, were measured at well-defined pre-electrode states. Three-hundred millivolts negative of the OCV was the maximum limit for these experiments as beyond this range a Planté battery would be considered discharged and therefore any results would be of little significance.
13.3 Results and Discussion

The shape of the impedance spectra changed dramatically with the change in potential. In the range of potentials from the OCV (1078 mV) up to 30 mV negative of it, the high frequency part of the complex plots showed an inductive part, similar to that previously observed, which did not show significant potential dependence within the limited range (Figures 13.1 and 13.2). The inclusion of this inductor made the analogue difficult to handle, and in addition, the unduly long times required to ensure that the electrode was at the zero current point at these small overpotentials introduced considerable uncertainty. Consequently a full decomposition of the electrode over the whole of the experimental range was not attempted in this potential region. As the potential was forced to more negative potentials and PbSO₄ progressively developed, the electrode became free from inductive effects and it was possible to obtain an approximate match of the electrode data using the analogue shown in Figure 13.3. The high frequency data was matched using the analogue described in Chapter 11 (Figure 11.11).

When the whole frequency spectrum is considered, it is immediately apparent that the initially rising line at low frequencies observed at OCV, gradually curves towards the resistance axis reaching a limit at 30 mV negative of the rest potential and Figure 13.4 shows the fully formed semicircle. Figure 13.5 shows a complex plot for an experiment 40 mV negative of the OCV. The inductive part at the high frequency end has now disappeared, but, perhaps more significantly, the overall shape of the plot has changed. After an initial slight curvature the low frequency points produce a Warburg line with a slope of approximately 20°.
Fig. 13.1 High frequency complex-plane plot for a fully charged Planté microelectrode. a.c. impedance experiment at 1078 mV (OCV) in H₂SO₄ (3.58 M); 23°C. ⋄, experimental points; full line, computer fit. Frequencies marked in Hz.

Fig. 13.2 As Fig. 13.1 but electrode poised at 1048 mV until zero current was observed before starting the impedance experiment.
Fig. 13.3 Analogue circuit consisting of a simple Randles circuit with the addition of an external capacitor ($C_X$).
Fig. 13.4  As Fig. 13.2; a.c. at 1048 mV; whole frequency spectrum.

Fig. 13.5  As Fig. 13.2; a.c. at 1038 mV; whole frequency spectrum.
In the experiments from 50 mV to 300 mV negative of the rest potential, the complex plots follow a distinct pattern. Figure 13.6 shows a flat high frequency region parallel to the resistance axis up to about 60 Hz, followed by a Warburg line of 30°. This eventually increases to 45° as the electrode is driven to more negative potentials (Figure 13.7). The high frequency region gradually curves until at 150 mV negative of the OCV a properly defined semicircle is observed. The radius of the semicircle is progressively increased as more negative potentials are reached and Figures 13.8 - 13.13 show characteristic complex plots. The model used to match these plots was identical to that used for the high frequency inductive Sluyters plots, with the exception that the inductor was eliminated from the circuit (Figure 13.3).

A completely satisfactory fit of the data to the theoretical model was obtained only if the effect of surface roughness or porosity was taken into account. This was done by a general procedure used in Chapter 11, of raising the modulus of the impedance to a power \( R_f \) and reducing the amplitude by the same factor. It is probably not possible to interpret with any certainty intermediate values of \( R_f \), however, using the computer technique, it allows the unbiased calculation of \( R_f \). In the present series of experiments using both the capacitance data and the resistance data, all values of \( R_f \) calculated in the potential region 1003 mV to 878 mV (Figures 13.8 - 13.13) turned out to be 0.5 within experimental limits. This shows unequivocally that the electrode is porous and that the pores may be considered semi-infinite.

Table 13.1 shows the salient details of the decomposition of the high frequency impedance data for experiments close to the rest
Fig. 13.6 As Fig. 13.2; a.c. at 1028 mV; whole frequency spectrum.

Fig. 13.7 As Fig. 13.2; a.c. at 1018 mV; whole frequency spectrum.
Fig. 13.8  As Fig. 13.2; a.c. at 1003 mV.

Fig. 13.9  As Fig. 13.2; a.c. at 978 mV.
Fig. 13.10  As Fig. 13.2; a.c. at 953 mV.

Fig. 13.11  As Fig. 13.2; a.c. at 928 mV.
Fig. 13.12  As Fig. 13.2; a.c. at 903 mV.

Fig. 13.13  As Fig. 13.2; a.c. at 878 mV.
**TABLE 13.1**

Mean values for electrode parameters
from C and R equations using analogue of Figure 1

<table>
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<tr>
<th>$E$ (mV)</th>
<th>$R$ ($\Omega$)</th>
<th>$\theta$ ($\Omega$)</th>
<th>$C_L$ (F)</th>
<th>$\sigma$ (ns$^{-1}$)</th>
<th>$R_f$</th>
<th>$C_X$ (F)</th>
<th>$L'$ (H)</th>
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**TABLE 13.2**

Mean values for electrode parameters
from C and R equations using analogue of Figure 2

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potential. Figures 13.14 and 13.15 show typical Randles plots corresponding to Figures 13.1 and 13.2, confirming the agreement between experimental and computed data for C and R equations. In this potential range the presence of the inductive component may be ascribed to two causes, both already discussed in Chapter 11 (Darby\textsuperscript{52} and Gutmann\textsuperscript{53}). In the present case the reversible potential of the electrode is about 300 mV more positive than the reversible oxygen reaction. So that even in H\textsubscript{2}SO\textsubscript{4} solution of this concentration the electrode is in the oxygen evolution reaction (O.E.R.) region. A crucial point is that the electrode is still porous (R\textsubscript{f} = 0.5), throughout the experimental region so that any retardation in the sense of Gutmann, would be expected to be essentially constant throughout the whole of the potential region and it would be expected that the inductive component would be constant throughout. On the other hand using the Darby concept the inductive component would diminish as the potential becomes more negative i.e. as the electrode is driven progressively out of the oxygen region. This confirms the previous work and consequently it can be concluded that the inductive component arises from the distributed O.E.R. in the porous matrix.

The fact that throughout the experimental potential range (down to 870 mV) the electrode behaves as a semi-infinitely porous electrode (R\textsubscript{f} = 0.5) is interesting. It was shown in Chapter 11 that under galvanostatic conditions (when the reducible capacity of the electrode is withdrawn over 10h) the electrode becomes planar after about 50% of the conversion to lead sulphate has been effected. In that case it was argued that pore blockage produced a non-porous electrode which behaved more akin to a planar one. In that situation moreover, the time of the reaction ensured that diffusion provided for the effective pore filling process. In the present case the effect of
Fig. 13.14  Randles plot corresponding to Fig. 13.1.

Fig. 13.15  Randles plot corresponding to Fig. 13.2.
driving the electrode to more negative potentials forces the conversion to PbSO₄ (thermodynamically the reduction of the sulphuric acid concentration in the porous matrix). In addition, higher reduction potential tightens the PbSO₄ film on the PbO₂ and inhibits the reaction. The interpretation which most effectively describes the situation is of a film of lead sulphate spreading progressively over the pores of the matrix without pore blocking taking place. The establishment of a thin, mechanically perfect, blocking layer in the sense of Muller¹²⁶, at lower potentials is indicated by the data shown in Table 13.2, and Figures 13.16 and 13.17 are typical Randles plots, confirming again the agreement between experimental and computed data.

It is interesting to note that the kinetic data abstracted from the computer (Table 13.2), all gave an exponential relationship with the potential. Figures 13.18 - 13.20 show these relationships for which dE/dlogÇL, dE/dlogΘ and dE/dlogΘ were found to be respectively 80 mV dec⁻¹, -65 mV dec⁻¹ and -40 mV dec⁻¹. If we assume, as seems sensible, that as the potential is decreased, a fairly uniformly thin layer of lead sulphate is formed which blocks-off the reaction by a dielectric of very low conductivity, then we can use the reduction in the double layer capacitance to correct the experimental value of Θ for the area by considering the change in ÇL with potential. This is shown in Figure 13.21 to be a straight line with a slope of -100 mV dec⁻¹ for the best straight line which agrees with the value calculated from the two separate Tafel curves. This value compares with a value of -36 mV dec⁻¹ which was obtained from the impedance measurements described in the previous chapter, where the electrode was polarised rapidly at the desired potential immediately after forcing it to the experimental potential. This value compares
Fig. 13.16  Randles plot corresponding to Fig 13.9.

Fig. 13.17  Randles plot corresponding to Fig. 13.11.
Fig. 13.18  Semilogarithmic plot of the double layer capacitance (C_L) versus E from data of Table 13.2.

Fig. 13.19  Semilogarithmic plot of the Warburg coefficient (σ) versus E from data of Table 13.2.
Fig. 13.20  Semilogarithmic plot of the charge transfer resistance ($\Theta$) versus $E$ from data of Table 13.2.

Fig. 13.21  Semilogarithmic plot of $\Theta C_L$ versus $E$ from data of Table 13.2.
with $-30 \text{ mV dec}^{-1}$ obtained from galvanostatic measurements on large cell systems by Simonsen. This seems to be the most reasonable value so that the additional slope in the present Tafel curves must be ascribed to the increase in potential across the passivating layer due to the tightening of the PbSO$_4$ film.
14.1 The Perchlorate Effect

Cyclic voltammetry experiments, used to identify the region of pronounced perchlorate influence, showed that the perchlorate ion displaces the sulphate ion from the electrode in the lead - lead sulphate region. At high perchlorate ion concentrations lower currents are observed indicating that insufficient sulphate ion reaches the pores of the electrode. In the lead sulphate - lead dioxide region similar experiments showed that the ClO$_4^-$ ion reduces the thickness of the passivating layer. At high perchlorate ion concentrations, the system was not passive due to the "aggressiveness" of the forming agent.

Potential step experiments showed that with low levels of perchlorate in solution the reaction involved a two-dimensional instantaneous nucleation, for the production of PbO$_2$. Above a 20 mM perchlorate concentration, the reaction followed the two-dimensional progressive nucleation process. With perchlorate molarities greater than $\sim$ 50 mM the nucleation became three-dimensional progressive. Above 75 mM lower current densities were observed. This was attributed to a higher Pb$^{2+}$ solution concentration in the high perchlorate containing solutions. If this is the case, then a more efficient passivating layer results, reflecting the lower currents.

With perchlorate concentration of 30 - 40 mM, a "plateau" was observed in the current-time transients. This observation is
important in the industrial formation process. It means that although the current densities, at these concentrations, are lower than for the concentrations used in the industrial process, the sustained reaction can produce a more efficiently formed plate.

A different set of potential step experiments, carried out with electrodes that were not passivated by lead sulphate, indicated the difficulties arising due to non-defined electrode states. This procedure, simulating industrial practice, showed that the two-dimensional instantaneous nucleation for lead to lead dioxide (in $\text{H}_2\text{SO}_4$, 0.5 M), observed earlier, becomes two-dimensional progressive. High perchlorate concentrations again resulted in three-dimensional progressive nucleation and growth processes.

It was confirmed once more that increasing the perchlorate ion concentration does not produce ever-increasing rates of attack. This was attributed to the fact that $\text{ClO}_4^-$ displaces the $\text{SO}_4^{2-}$ ion from the lead surface, inhibiting the regeneration reaction.

Rotating disc experiments proved that the perchlorate ion does not exert an influence on the reaction in the lead dissolution region.

The interpretation of the results from the rotating disc showed that univalent surface species, adions and adatoms, are formed at the electrode. Eventually, these species combine to form dimers which eventually undergo reversible oxidation to $\text{Pb(II)}$ species. The rate of this combination controls the current.

The rotating disc experiments showed that the mobility of $\text{Pb}$ atoms at the negative electrode during the operation of the lead cell can be readily understood in terms of the adsorbed intermediates.
The lack of dependence on rotation speed in all other experiments proved that the lead dioxide formation reaction is a solid state one. Finally, the collective results indicated that the "forming" action is concentrated in the lead dioxide region.

14.2 The fully formed Planté electrode

Potential step experiments carried out using partially charged Planté formed electrodes showed that excursions into the lead sulphate region produced different nucleation and growth characteristics, depending on the state of charge of the electrodes.

Small discharges gave a two-dimensional instantaneous nucleation response which changed to a progressive one for electrodes discharged up to 50%. With even higher levels of discharge, the nucleation and growth changed to a three-dimensional process.

Experiments where the partially charged microelectrodes were stepped from the rest potential to the lead dioxide region did not show a clear picture. No suitable model was observed for the re-oxidation of galvanostatically reduced electrodes.

The difference in behaviour between oxidation and reduction indicates the different conductivities of the two phases. In the case of reduction an insulating phase is created, whereas during oxidation a conducting phase is produced. It can be concluded that in the presence of significant amounts of lead dioxide, lead sulphate is oxidised, unhampered by nucleation processes.

A.C. impedance experiments carried out at the OCV showed that electrodes exhibited planar characteristics when discharged by more than 50%. It is interesting to note that similar experiments on
cycled Plante microelectrodes, showed an average value for the electrode porosity over the whole range of charges examined. These later experiments represent a closer simulation of the working conditions of a Plante cell. A porosity value between those of porous and planar electrodes is, therefore, possibly closer to the true situation.

The reversible potential in the above experiments remains constant showing that the process of reduction leaves the electrode unaffected.

An interesting feature of these experiments was the appearance of an inductive component to the impedance at high frequencies. This was visible in all experiments down to 20% of charge. The inductive part was attributed to the oxygen reaction.

The impedance spectra for experiments with electrodes polarised negative of the OCV again showed an inductive region, which disappeared in experiments where overpotentials greater than 50 mV were applied. This was again interpreted in terms of the oxygen reaction. The remainder of the parameters obtained from these experiments showed an agreement with the theory of an increasingly thick PbSO$_4$ layer developed at the front of the electrode. The development of PbSO$_4$ films at more negative potentials obscured the electrochemistry. The disappearance of the inductive part is due either to the formation of films at the front of the electrode (destroying the in-depth porosity), or, more simply, to the shift away from the oxygen region.

With a.c. experiments on electrodes that had achieved steady-state conditions at potentials negative of the OCV, the electrodes showed porous behaviour under all experimental conditions. Once more,
the inductive region observed at low overpotentials is attributed to the oxygen evolution reaction.

It is concluded that the current limiting process is essentially the growth and tightening of the lead sulphate film. It is also concluded that the charge-transfer process is only a minor current limitation.
14.3 Further Work

The recent interest in harvesting solar energy means that Planté-type storage cells can play an important new role. In order to do that, their behaviour under different states of charge must be fully understood.

In operation as a buffer battery in a solar powered system, it is conceivable that cycling of cells occurs to the exigencies of supply (from solar cells) and demand (from the grid) at any state of charge of the cells. This imposes a new set of operating conditions upon the electrodes; whereas standby duty implied an initially fully charged cell, the buffer battery must be capable of operating in a charge/discharge mode at all states of charge. The effect of cycling around various states of charge should be therefore thoroughly investigated, using potential-step experiments, the a.c. impedance method and close examination of the fully formed microelectrodes using S.E.M.

The observation of sustained currents obtained with ClO₄⁻ concentrations lower than those industrially used should be further investigated. It is suggested that microelectrodes are formed using these lower concentrations. Comparisons of the results obtained with those described in this thesis should yield useful information. It would also be of interest to employ the a.c. technique in order to examine the effect of perchlorate concentration on the impedance spectra of lead electrodes. This would provide confirmation for the conclusions already obtained.

Further information about the electrocrystallisation process could be obtained employing the a.c. impedance technique. It would
also be interesting to study the inductive region observed during the a.c. experiments under higher frequencies. Unfortunately, the capabilities of the Solatron 1172 frequency response analyser limited the analysis to a maximum frequency of 10 kHz.

Moving to a more empirical approach to research, the industrial experience of better plate performance obtained with "aged" formation electrolyte should be investigated.

Finally, the examination of cells of commercial proportions using the a.c. technique and S.E.M. could produce important links to help in the understanding of the Planté cell.
A.1 Introduction

The reliability of the Planté standby storage battery is well known. The possibility that the cell could be used as a buffer battery for "solar technology", as discussed earlier, necessitates research into the performance of the industrial size cells, under the new working conditions.

It is axiomatic in the lead battery industry that cells should not be allowed to stand in the discharged condition and that frequent stabilising charges are required if efficient use is to be made of, for example, traction cells. It is important to know whether or not these limitations would apply to Planté cells on the Solar regime which may involve these conditions.

This work reports the results of tests made to investigate this type of duty.

A.2 Experimental

The experiments were carried out using Planté cells of 100 Ah nominal capacity (Tungstone Type HBP9). After an initial discharge at the 10A rate (to 1.6 V.P.C.) each cell was cycled for 80 cycles of charge and discharge in the following four states-of-charge.
Group a  |  Group b  |  Group c  |  Group d  
90% ↔ 80%  |  75% ↔ 65%  |  50% ↔ 40%  |  25% ↔ 15% 

Based on the recoverable capacity on the 1st rating discharge of the cells, these are equivalent to the following (c.f. Table A.1),

93% ↔ 87%  |  82% ↔ 75%  |  65% ↔ 58%  |  43% ↔ 35%

i.e. for 75/65; 2.5h discharge at 10A from the fully charged state followed by 10h discharge at 1A and 10h at 1A recharge. After cycling, the cells were recharged at a constant potential of 2.25 V.P.C. for 140h and capacities were determined at 10A to 1.6 V.P.C. A final capacity test was made after the cells were fully charged galvanostatically at 7A to a constant cell voltage over 2h. In this connection it is recognised that the low capacity cells may have received some overcharge. At this point, however, it was thought unwise to try to adjust this slight asymmetry. The cycles of operation are shown in the following scheme,

CYCLE 80X → FLOAT → DISCHARGE 1 → RECHARGE → DISCHARGE 2

Fig. A.1  |  Fig. A.2  |  Fig. A.3  |  Fig. A.4

The positive electrodes were sampled for S.E.M. examination at various points in the cycles of electrochemical operation. This was done by cutting sections from electrolyte soaked electrodes from the centre of the bottom of the plate, and washing them free of sulphuric acid solution with acetone. In this way the worst conditions for the development of sulphate phases were imposed.
It was important not to wash the sulphuric acid out with water because the establishment of a PbO₂/PbSO₄ system at two different H₂SO₄ concentrations would provide sufficient driving potential (in the Nernstian sense) to alter the PbO₂/PbSO₄ ratio at different areas on the electrode. When free from aqueous solution the specimens were dried and appropriate samples examined in the S.E.M. (Cambridge Stereoscan, model 2A).
Table A.1

Initial cell capacities at 10A

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<thead>
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<tbody>
<tr>
<td>a</td>
<td>15 h</td>
<td>8 m</td>
</tr>
<tr>
<td>b</td>
<td>14 h</td>
<td>4 m</td>
</tr>
<tr>
<td>c</td>
<td>14 h</td>
<td>7 m</td>
</tr>
<tr>
<td>d</td>
<td>13 h</td>
<td>10 m</td>
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Table A.2

Cell capacities (% of initial capacities)

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<tbody>
<tr>
<td>a</td>
<td>11h 31m/15h 8m</td>
<td>76.1%</td>
</tr>
<tr>
<td>b</td>
<td>11h 52m/14h 4m</td>
<td>84.4%</td>
</tr>
<tr>
<td>c</td>
<td>9h 31m/14h 7m</td>
<td>67.4%</td>
</tr>
<tr>
<td>d</td>
<td>6h 36m/13h 10m</td>
<td>50.1%</td>
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Table A.3

Capacities after galvanostatic recharge (% of initial capacity)

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<tbody>
<tr>
<td>a</td>
<td>13h 20m/15h 8m</td>
<td>88.1%</td>
</tr>
<tr>
<td>b</td>
<td>12h 45m/14h 4m</td>
<td>90.6%</td>
</tr>
<tr>
<td>c</td>
<td>12h 7m/14h 7m</td>
<td>85.8%</td>
</tr>
<tr>
<td>d</td>
<td>11h 47m/13h 10m</td>
<td>89.5%</td>
</tr>
</tbody>
</table>
A.3 Results and Discussion

Table A.1 shows the initial capacity at the nominal 10h rate and these data indicate that all cells were satisfactory at the start of the experiments.

Table A.2 shows the capacity available after the 80 cycles and after a constant potential charge. There is a serious reduction in electrochemical storage capacity for all groups, with a marked deterioration of the group c and d cells.

Following this discharge, the cells were given a galvanostatic charge and the data of Table A.3 shows that much more capacity was obtained on the subsequent discharge after recharge.

It can be concluded from these electrometric results that cycling in a restricted state-of-charge range below 100%, results in a loss in immediately recoverable storage capacity. This loss is greater after a constant potential (potentiostatic) recharge, for times approaching one week, than after a galvanostatic recharge.

A possible explanation for this behaviour can be given in terms of the development of large crystals of lead sulphate in the electrode as a result of the cycling tests. Earlier work\textsuperscript{127} has once more proved that such large crystals are more difficult to oxidise and indeed the electro-oxidation of reduced lead dioxide in 5M H\textsubscript{2}SO\textsubscript{4} yields response curves which may be deconvoluted such that the component curves may be identified with crystals of different sizes. In the present case it appears that cycling in the restricted ranges has produced crystals of PbSO\textsubscript{4} which are difficultly oxidised to PbO\textsubscript{2} and that the deterioration is aggravated at low levels of charge.
The examination of the electrodes using the S.E.M. technique confirmed this conclusion. The Figures A.1 (a, b, c and d) show the condition of the electrode immediately after cycling for 80 complete cycles and finishing in the highest level of charge (i.e. a, 90%; b, 75%; c, 50%; d, 25%).

It is clear from these pictures that in all cases the electrodes appear to be completely choked with PbSO₄ with not very much evidence for the small prismatic PbO₂ particles. Even for the case of Figure A.1.a the surface quite evidently contains considerably more PbSO₄ than the 10% which might be expected from energetic considerations. It is quite possible that this conclusion applies only to the surface of the electrode and that the cycling process has resulted in a redistribution of lead sulphate so that the surface of the electrode is very heavily sulphated. The appearance of the electrodes is towards the development of a surface consisting of large PbSO₄ particles almost submerged with fine material (Figure A.1.d). The maximum sizes of the visible lead sulphate crystals do not seem to be related to the state of charge. This seems to be a contradiction to current ideas, however, the appearance of the electrodes after a subsequent constant potential recharge considerably clarify the position. The photomicrographs corresponding to the completion of the constant potential charge are shown in Figure A.2 (a - d). Whereas the cell cycled in the highest state of charge (Figure A.2.a) shows some evidence of the presence of PbSO₄ crystals, at lower states of charge an increasing amount of lead sulphate material of increasing crystal size is clearly evident. We can conclude from this that the prolonged constant potential charge (140 h) at 2.25V is ineffective in converting the large crystals of PbSO₄ to PbO₂. We propose that for each size of crystal there
exists a critical potential below which the conversion to PbO₂ is difficult, probably kinetically hindered. Figure A.2.d supports this view for the field shows that all the small PbSO₄ crystals have been converted and that only very large crystals remain.

That the surface under normal discharge conditions returns to a fine-grained (small crystal) texture is shown in the Figures A.3. These were obtained at the termination of a 10h rate discharge to a final cell voltage of 1.6 V.P.C. Here the whole of the surface is covered by small PbSO₄ crystals with an occasionally large crystal visible (Figure A.3.c).

Following a galvanostatic charge the electrodes in the higher states-of-charge return to the condition expected of cycled electrodes. Relatively small PbO₂ particles of fairly uniform shape can be readily seen in the micrographs A.4 (a - d). However, those electrodes from the lowest (25%) state of charge were rather untypical. Apparently the large PbSO₄ crystals had been oxidised to lead dioxide but with considerable damage to the structure and disruption of the electrode. This is shown typically in Figure A.4.d. Areas of quite satisfactory lead dioxide structure are visible but there are also disrupted areas of PbO₂ and even some residual PbSO₄. It was considered unlikely that this effect was due to the disruption of 1 or 2 crystals as it was not observed generally. This condition of the surface again emphasises the difficulty in converting lead sulphate from prolonged cycling at a low state-of-charge to something approaching a fully charged condition. However, this is difficult to accomplish and results in damage to the surface structure.

We finally conclude that restricted cycling of Planté positives in a low state-of-charge (especially ~ 25% and below) is to be
avoided for it makes complete recharging difficult and results in
deterioration of electrode structure.

A final comment arises from this investigation. For solar
applications and other duties of this type where limited cycling
around the 50% discharge level may occur, a float voltage of
approximately 2.25 is perhaps on the low side. A more realistic
value of 2.3V per cell would clearly be better. However, the
optimum would be to galvanostatically recharge from time to time.
There is no doubt that whatever battery is used for solar purposes,
considerable thought will have to be given to the operational scheme
of usage.
Fig. A.1.a  Positive Plante electrode surface at completion of 80 cycles of charge/discharge (90% ↔ 80%); magnification x300.

Fig. A.2.a  Electrode surface at completion of float recharge at 2.25 V.P.C. Initial charge 90%; magnification x280.

Fig. A.3.a  Electrode surface at completion of discharge after recharge. Initial charge 90%; magnification x260.

Fig. A.4.a  Electrode surface at completion of galvanostatic recharge. Initial charge 90%; magnification x260.
Fig. A.1.b  As Fig. A.1.a; 75% ←→ 65% charge;
magnification x300.

Fig. A.2.b  As Fig. A.2.a; initial charge 75%;
magnification x300.

Fig. A.3.b  As Fig. A.3.a; initial charge 75%;
magnification x320.

Fig. A.4.b  As Fig. A.4.a; initial charge 75%;
magnification x270.
Fig. A.1.c  As Fig. A.1.a; 50% $\leftrightarrow$ 40% charge;
magnification x260.

Fig. A.2.c  As Fig. A.2.a; initial charge 50%;
magnification x260.

Fig. A.3.c  As Fig. A.3.a; initial charge 50%;
magnification x260.

Fig. A.4.c  As Fig. A.4.a; initial charge 50%;
magnification x280.
Fig. A.3.c

Fig. A.4.c
Fig. A.1.d  As Fig. A.1.a; 25% $\leftrightarrow$ 15% charge;
magnification x260.

Fig. A.2.d  As Fig. A.2.a; initial charge 25%;
magnification x280.

Fig. A.3.d  As Fig. A.3.a; initial charge 25%;
magnification x260.

Fig. A.4.d  As Fig. A.4.a; initial charge 25%;
magnification x270.
THE FREQUENCY DISPERSION AT LEAD ELECTRODES

B.1 Introduction

The frequency dispersion of capacitance (and resistance) at solid electrodes, which arises as a consequence of surface heterogeneity, can be calculated using conventional equations when some assumptions are made regarding the magnitude of the capacitance of different electrode areas\(^{128,129}\). This approach was tested\(^{130}\) using microcrystalline tin electrodes and the data were in good agreement with the heterogeneity conception. The effect of the electrode roughness was considered in this work and "scratched" surfaces were examined in order to see if dispersion due to surface roughness in the sense of de Levie\(^{131}\) made a significant contribution to frequency dispersion in the experimental frequency range from 50 kHz to 20 Hz. According to de Levie, at sufficiently high frequency, even sub-grooved and rough electrodes would be expected to behave as a porous electrode. It was found that dispersion arising from this source was relatively minor and that the electrode heterogeneity was due either to partial filming or the exposure of a number of areas of different crystal plane index (different coordination and hence different thermionic work function).

A possible explanation of why the "porosity" dispersion was not apparent may be the relatively soft and low melting character of tin. Such a surface might conceivably possess sufficient surface mobility to modify the fine structure of the electrode. The metals which are available for study are limited to the few which possess
resistance to oxidative attack and a high hydrogen overvoltage. Lead has a rather higher melting point than tin and is in the other two respects rather similar, consequently capacity dispersion at lead might be expected to be made dependent on the physical surface characteristics. This would be especially true of porous lead which is a well characterised and stable surface. This section describes capacitance measurements on such surfaces.

B.2 Experimental

Two types of electrodes were used. The solid lead electrodes were identical to those described in Chapter 5. The porous lead electrodes were produced from pure lead following the Planté formation procedure. The fully formed electrodes were reduced and washed thoroughly to convert the surface to porous lead. The thickness of the porous lead was equivalent electrochemically to $10^5$ atomic layers. However, it was not possible to determine the effective surface area.

The electrolyte used throughout this work was 1M NaClO$_4$ and all potentials were measured against a saturated sodium calomel electrode. It was necessary to purify the electrolytes by circulation through exhaustively extracted charcoal$^{132,133}$. Measurements were made under nitrogen using a conventional a.c. bridge set-up. The classical a.c. bridge method for finding the double layer capacitance is well documented and has been previously described by Farr and Hampson$^{132}$. 

- 131 -
B.3 Results and Discussion

B.3.1 The massive lead electrode

A satisfactory polarisable region between -0.55 and -1.60V was observed i.e. no d.c. flow due to electrochemical reaction occurring, as shown in Figure B.1. There are two extremes, high cathodic potentials produce hydrogen evolution and at anodic potentials there is lattice dissolution. The experimental work was carried out between these two extremes.

Measurements obtained for the impedance of the analogue at a series of frequencies showed that the bridge was satisfactorily accurate over a frequency range 10 kHz - 20 Hz. The maximum error was at 10 kHz, \( \sim 10\% \). Since data on metal electrodes is unlikely to be reproducible to better than 5 - 10\% it was considered that no further refinements to the bridge circuit was required as most of the measurements would be made at around 1 kHz (error \( \sim 2\% \)). Figure B.2 shows a typical double layer capacitance for the electrode at a pH \( \sim 4.5\% \); the U shaped curve is relatively featureless except near the trough where some ripples occur at about -1.1V indicating that the electrode is effectively blocked by some impurities from the solution. This condition is achieved by the formation of a layer of material that has been removed from the solution by the adsorptive forces of the electrode. The identity of the intruding species is difficult to judge, but it cannot be removed by pre-electrolysis or by oxidative/reductive processes. It has been suggested by Hampson and Larkin\(^{13}\) that borate from the glass can have this effect although this has not been definitely proven.

What is certain is that the results in Figure B.3 obtained some
Fig. B.1  Polarisation curve for polycrystalline (solid) lead in 1 M NaClO₄. 23°C.
Fig. B.2  Differential capacitance curve for polycrystalline lead in 1 M NaClO$_4$, 23°C. Filmed electrode due to adsorption of solution impurities.
Fig. B.3 Differential capacitance curve for polycrystalline lead in 1 M NaClO₄; 23°C. The electrode is free from adsorbed films.

Fig. B.4 The dispersion of capacitance at polycrystalline lead electrodes.
eight weeks after Figure B.2 are typical of the system free from complications induced by intruding films. It can be concluded therefore that it has taken eight weeks circulation through purified charcoal for a satisfactory control of the impurity level and for the true interphase structure to be revealed.

The most reasonable theory for the slow cleaning process is that the intruding impurities are adsorbed on the glass walls of the electrolytic cell and the activated charcoal removes the impurities from the walls via the solution. Eventually a satisfactory impurity level is attained when the deposition of the intruding film onto the electrode is not sufficient to affect the results over the time scale of the experiment. Once the cell had been cleaned it was not allowed to dry; on replacement of the electrolyte with a new solution it was found that the charcoal was more efficient in exerting control over residual contaminants in the cell.

The concentration of the electrolyte solution in this investigation was kept at 1 M so that it was not possible to identify the potential of zero charge (PZC) by the appearance of the characteristic diffuse layer minimum at low concentrations. However, there was a local maximum at -0.9V which compares well with the reported P.Z.C. of -0.796V of Larkin and which could well be the appearance of the hump which we would expect to occur at this potential. This curve in general agrees with Larkin and therefore the results have satisfactorily confirmed established data.

Figure B.4 shows frequency dispersion data corresponding to clean electrodes, the curves are very encouraging as they are very similar to those expected from the heterogeneous surface theory of frequency dispersion advanced by Leek and Hampson. If $C_F$ is
the differential capacitance, $C_{E_0}$, is the capacitance at zero frequency.

Then the magnitude of the ratio of $C_E/C_{E_0}$ in this case indicates conformity to the Hampson and Leek model\textsuperscript{130} of the lead surface containing elements of three different types of surface with equal areas corresponding to each type.

### B.3.1 The porous lead electrode

The porous electrode data was surprisingly readily obtained. It had been anticipated that the electrode would be difficult to prepare and characterise. Preparation was as described in the experimental section, and the resultant porous electrode seemed to be of high quality, as the double layer capacitance results were always completely free, as far as could be judged, from intruding films. One probable reason for this would undoubtedly be due to the prolonged cleaning of the electrolyte and cell from the earlier experiments with the solid lead electrode. However, it is surprising that such excellent results as shown in Figure B.5 could be obtained with the minimum of trouble; the form of the curve is what theory and analogy with the mercury system would have us believe is the behaviour of all polarisable metals in the region of the P.Z.C., it consists of a well defined hump in the region of about $-0.9V$ followed by a further fall and a capacitance rise on the cathodic branch to hydrogen evolution. This curve is very superior to the solid metal with very clear features and agrees with Hampson and Larkin\textsuperscript{134}. The magnitude of the capacitance is about 50 times that of the planar electrode. A reasonable explanation appears to be that in this case the intruding impurities in the solution are only able to adsorb on a fraction of the available area in the time scale of the experiment, leaving the rest of the surface clean. (The outer surface of the
Fig. B.5  Differential capacitance curve for porous lead 1 M NaClO₄. 23°C.
porous mass effectively "getters" the residual solution impurity so that the inner surface remains clean).

Figure B.6 indicates the effect of frequency on the double layer of the porous lead electrode. These effects are gross, proportionally they are considerably greater than those obtained with the flat electrode, but this agrees only qualitatively with de Levie's micro-roughness explanation\textsuperscript{131,134}. According to this theory, as the frequency increases from zero to an infinite value a sigmoidal change in the capacitance magnitude occurs over about 4 decades of frequency. Figure B.7 shows that the curves have a similar form to the solid lead (Figure B.5), however, curvature is much more pronounced and indicates a much more heterogeneous surface which we would expect from the preparations and structure of the electrode. We can interpret the results if the pores are not "semi-infinite". De Levie\textsuperscript{131} has shown under these conditions the change in the magnitude of the phase angle is only relatively small, less than the 50\% decrease as demanded by the infinitely deep pore. As frequency is increased there exists a limit in which all pores ought to appear infinite in depth, however, before this could be observed inductive effects (see below) obscured the behaviour. We can conclude at this stage that the extent of the frequency dispersion on porous lead (Figure B.6) appears to be double that of the smooth surface. The mode of preparation of porous electrodes may have something to do with this heterogeneous surface since solid lead is prepared by mechanical smoothing and careful chemical etching. Porous electrodes are prepared by a successive series of redox processes which is expected to produce a more active surface with considerable roughening on an atomic basis.

An interesting feature of the differential capacitance when taken
Fig. B.6 The effect of frequency change below 1 kHz on the data of Fig. B.5.
Fig. B.7  The dispersion of capacitance at porous lead in the form of Fig. B.5.

Fig. B.8  The high frequency inductive effect of porous lead electrodes.
over all the frequency range is the change in capacitance as the frequency is increased from 1 kHz to 10 kHz. Instead of the decrease in capacitance being maintained, the capacitance goes through a minimum then increases (Figure B.8).

This behaviour is very interesting as it confirms once more the presence of the inductive region observed during the a.c. impedance experiments on the Planté PbO₂ electrodes. Darby⁵² has shown mathematically that the inductive response would occur increasingly at high frequencies. At low frequencies with more charge going into each wave of a.c. the reaction is throttled down by the polarisation produced by hydrogen species adsorbed at the electrode.

The maximum inductive effect will occur when the potential is such that the concentration of oxidising/reduced species, when multiplied together, produce a maximum value according to the equation

\[ i_o = ZF K_o C_{H^+}^{1-a} C_{H_2}^a a/2 \]  

(B.1)

\( a \) is a transfer coefficient.
In other words the rate of increase of the inductive component is expected to go through a maximum.

Examination of Figure B.8 shows this is true. A maximum occurs at about -0.9V, i.e. 0.6V more negative than the equilibrium potential \( H^+/H_2 \) reaction. Presumably at more negative potentials the concentration of the reduced species, i.e. adsorbed hydrogen, predominates and at more positive potentials the concentration of \( H^+ \) predominates.

Leek has shown a mathematical link to a term equal to charge
transfer resistance $e^{i\theta}$ where $\theta$ is the charge transfer resistance for the hydrogen evolution reaction.

The alternative explanation of the inductive region by Gutmann$^{53}$ in terms of retardation of the a.c. signal in the porous structure does not agree with our results. If this was true we would expect, in such inductive regions, to return to the real axis rather than continually diverging as in the present case. It must be concluded therefore, that the most likely explanation of the present behaviour is in terms of the hydrogen evolution reaction occurring in the distributive region of the electrode.
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