Aspects of power sources based on lead-dissolving acids and the lead dioxide/lead couple

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ASPECTS OF POWER SOURCES BASED ON
LEAD DISSOLVING ACIDS AND
THE LEAD DIOXIDE/LEAD COUPLE

BY
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A thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Doctor of Philosophy of the Loughborough University of Technology

February 1973

Supervisor: DR. N.A. HAMPSON
Department of Chemistry

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I wish firstly to record my great debt to Dr. Hampson for continuous help, advice and instruction and, at times, very necessary encouragement.

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I am obliged to Prof. Phillips for his interest, support and, in particular, for providing the facilities which were necessary to me.

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SYNOPSIS

A comprehensive account is given of the work associated with the design, development and production of a high performance battery from the issuing of a new and demanding specification.

Theoretical considerations coupled with a survey of the field led to a choice of a suitable couple.

Laboratory methods for producing electrodes in quantity were worked out in order to enable the operating parameters of the cell to be optimised by a study of discharges under various conditions.

Production methods for the electrodes were developed and various problems, in particular those stemming from locked up stresses in electro-deposits, were solved in the laboratory.

The high performance specified could only be achieved by using perchloric acid electrolyte; important successes were achieved in reducing the fire and explosion hazard associated with this substance.

Thus far the final cell (and battery design) has proved eminently satisfactory not only in meeting specified performance but in maintaining activity after more than two years of dry storage. In addition full scale production, based on the methods evolved in the laboratory, is proceeding smoothly.
In the field of electrical engineering batteries connote devices for converting chemical energy into electrical energy. In broad terms these are referred to as primary batteries or secondary batteries; the primary batteries are used and, when the chemical energy is expended, they are discarded. The secondary batteries are capable of cycling, that is to say they can be discharged and the chemical reactions then reversed by connecting the battery up to the supply of direct current. In this way the secondary battery may be charged and discharged many times and is in truth an accumulator.

The work described in this thesis was initiated when it became necessary to design a special battery for use in powering certain missile devices. In such applications the factors which are of prime importance are as follows:

(i) The battery must be capable of delivering power at a high and specified rate for a period also specified.

(ii) The battery must be light in weight.

(iii) The battery must not be bulky.

(iv) The battery must be self contained.

(v) The battery must be capable of supplying the power almost instantly on demand.

(vi) For obvious reasons the battery must have excellent storage characteristics such that depreciation over a period of years should be only marginal.
The whole of the work was aimed to result ultimately in methods for producing a battery to meet a specification based on a quantification of the above criteria; in addition because the weapon in question was likely to be mass produced it followed that the battery should be so designed that it lent itself to large scale production.

Whilst there are quite a number of batteries in commercial production only three of these could be regarded as worthy of consideration in relation to this particular requirement. These are listed in the table below where the relative power densities in terms of weight and volume are shown assuming discharge in about 30 minutes: the figures in brackets are the performance assuming discharge to be complete in 5 minutes.

<table>
<thead>
<tr>
<th>Common Nomenclature</th>
<th>Couple</th>
<th>Watt.hrs/Kgm.</th>
<th>Watt hrs/ml.</th>
</tr>
</thead>
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<td>Leclanche 1</td>
<td>Zn/C(MnO₂&lt;sub&gt;2&lt;/sub&gt;, depolariser)</td>
<td>2.5</td>
<td>0.007</td>
</tr>
<tr>
<td>Alkaline 2</td>
<td>Cd/NiO(OH)</td>
<td>11 (6.9)</td>
<td>0.028 (0.018)</td>
</tr>
<tr>
<td>Lead acid 3</td>
<td>Pb/PbO₂</td>
<td>13 (8.3)</td>
<td>0.024 (0.015)</td>
</tr>
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</table>

The first battery type shown in table 1 is widely used in technology as the power source in transistorised devices and hand torches. The second type is largely limited in use to emergency lighting and stand-by power sources. The lead acid system presently has the widest application ranging from usage as small cells of ~1 Ah capacity in various miniature devices to cells of ~10⁴ Ah capacity used for telecommunication stand-by duty.
It is proposed to describe the three types in some detail and in view of the predominant position of the lead acid battery its technology will be fully discussed within the framework of general electrochemical theories. The general principles outlined in this description have been directly applied to the development of this research and the solution of problems which arose.

**The Leclanche Battery**

The Leclanche battery depends upon the old established principle of using a carbon rod as anode operating in an aqueous paste of ammonium chloride and starch contained in a zinc can which is the cathode. Surrounding the carbon anode is a depolarising mix consisting largely of manganese dioxide. Although this system is regarded as providing a primary and irreversible cell in which the zinc gradually forms oxychloride and the manganese dioxide is reduced to the divalent form during the drain of current from the system, in fact it can be recharged if care is taken. The system was quite unsuitable for the present application however because it is not appropriate for the very high rate of current demanded. The method of construction, involving large inter-electrode spacing, together with the high viscosity and comparatively low conductivity of the electrolyte, lead to large over-potentials when current densities are high, with a consequent serious fall in available power. It follows that in order to build a battery based on this system for the demand required, weight and bulk would have been out of all proportion.
The Alkaline Battery

Although there are several types of cell in current production based on alkaline electrolytes that using the nickel oxide/cadmium couple dominates this field.

The initial development of this system took place almost simultaneously in Sweden (Jungner) and the U.S.A. (Edison) and indeed the overlapping of patents, filed in January, 1901, led to litigation which almost overwhelmed Jungner.

The reaction at the nickel electrode is probably represented by the equation:-

\[
\text{Ni(OH)}_2 + \text{OH} \xrightarrow{\text{Charge}} \text{B} - \text{NiO OH + H}_2\text{O + e} \xrightarrow{\text{Discharge}} \\
\]

and the reaction at the cadmium electrode is almost certainly:-

\[
\text{Cd(OH)}_2 2\text{e} \xrightarrow{\text{Charge}} \text{Cd + 2 OH}^- \xrightarrow{\text{Discharge}} \\
\]

The positive electrode is made from nickel hydroxide (Ni(OH)_2) to which about 20% of graphite is added in order to promote electrical conductivity. It is also now common practice to add cobalt hydroxide (one to five atomic percent Co/Ni) as this results in increased capacity and life. The powder is contained in pockets made of perforated nickel plated steel sheet and these pockets are welded one to another in order to give a plate of the designed capacity.
The production of the negative electrode is not dissimilar from that of the positive except that cadmium hydroxide is used in place of the nickel compound. Some iron hydroxide (20%-30%) is added as otherwise the cadmium, in its reduced ("charged") metallic state, tends to agglomerate with a consequent loss of capacity.

Groups of negative and positive plates are assembled, usually by bolting together with mild steel bolts, and the plates are then interleaved and insulated from the facing plates of opposite polarity by insertion of plastic or rubber separating pins. Pole bolts of nickel plated mild steel are fitted when bolting up the plates.

The whole element is accommodated in a plastic or nickel plated steel container; in the latter event the element is suspended from the posts which pierce the cover through insulating glands.

The cells are then filled with potassium hydroxide solution (5m) and charged. Small amounts of lithium hydroxide are sometimes added to the electrolyte (1.2 mol./l) when frequent repetitive deep discharges are anticipated as this has been found to prolong the useful life of the cell.

The expensive raw materials make this battery very costly per ampere hour but, because of its resistance to long use, and even abuse, its employment can often be justified on the basis of cost per annum. In the present application however, where only one discharge is required, the nickel oxide/cadmium system is unattractive.
The Lead Acid Battery

In its modern form the lead acid battery consists of an assembly of cells connected in series. Each cell consists of an acid resistant container into which the essential element is fitted. This element consists of two groups of plates, denoted positive and negative, which are interleaved, * those of the positive group being insulated from those of the negative by the appropriate interposition of sheets of microporous insulating material, these sheets are known as separators.

* Footnote

A plate is a single electrode; a parallel array of plates is termed an element.

Throughout this thesis the term "negative" plate or element is used to denote that electrode which behaves as an anode during the discharge process and hence:

\[ \text{Pb} = \text{Pb}^{++} + 2e \]

and a cathode during the charge process.

The term "positive" plate or element is used to denote that which is connected to the terminal which is the more positive of the two terminals in the cell arrangement; it follows that a positive plate or element behaves as a cathode during the discharge process:

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

and an anode during the charge process.
The plates of the negative group are welded to a common lead alloy (usually 6% Sb) bar and those of the positive group similarly welded to another lead alloy bar. Provision is made for sealing the top of the cells with a suitable acid resistant cover at the same time permitting electrical connection to be made from the positive bar of one cell to the negative bar of the adjacent cell and so on in order to provide the complete series electrical circuit. Each cell is filled with sulphuric acid (B.S.S. 3031), of a concentration usually about 4.6 mol./L, such that the sulphuric acid solution is at a level just above the tops of the separators which in turn are just above the tops of the plates. This concentration relates to a battery in the fully charged condition.

The negative plates are formed by casting open grids in lead or lead alloy (usually 6% Sb) and filling the mesh with a paste formed from lead monoxide and sulphuric acid to which are added small quantities (fractions of one per cent) of barium sulphate and a derivative of lignin. After pasting the plates are held in a humid warm atmosphere until such time as the paste has developed some mechanical strength due to a cementation process following on the formation of basic sulphates of lead. The positive plates are formed in an almost identical manner except that no organic material is necessary in the paste mixture and the barium sulphate must be excluded at all costs.
After completion of the "cementation" process the plates are assembled in dilute sulphuric acid (0.3 mol./l) parallel to each other and in rows with positives and negatives alternating. They are then connected to a source of direct current the positives being connected to the positive poles. Current is allowed to flow for a period which may vary between one and three days at a rate such that the paste in the negative plate is almost completely converted to a mass of microporous spongy lead. At the same time the paste in the positive plates is oxidized to lead dioxide such that at the completion of this formation operation the positive plates contain a dark microporous chocolate brown material which is at least 85% lead dioxide. The plates are then withdrawn, washed and dried and, in the case of the negatives which tend to be pyrophoric, drying is effected in some form of inert atmosphere.

In former times the separators consisted of diaphragms of specially treated wood (many woods were tried for this purpose although the best without any question came from the Port Orford Cedar tree). In recent years this practice has been discontinued almost entirely and more efficient synthetic separators are used in modern batteries. Of the most popular of these modern separators are microporous hard rubber and microporous P.V.C.
On discharging a cell of this type the active materials in the positive and negative plates react with the electrolyte such that there is a gradual conversion of lead in the negative and lead dioxide in the positive to lead sulphate with a consequent fall in the sulphuric acid concentration in the electrolyte. It follows that the discharge of the cell can be followed by monitoring the specific gravity of the electrolyte. On recharging the cell or battery the lead sulphate in the negative element is converted back into spongy metallic lead and the sulphate in the positive is oxidised again to lead dioxide, the specific gravity of the electrolyte rising.

It is of interest here to make some reference to the use of barium sulphate and lignin derivatives in the negative paste. In the absence of barium sulphate the negative paste fairly quickly densifies as the cell is subjected to cycles of charge and discharge and in due course it is found that the capacity in terms of ampere hours which can be derived from the negative group has sunk to a very low value. Similarly the inclusion of the organic constituent permits the cells to be used at very low temperatures with considerable efficiency; in the absence of the organic material the performance of the negative group at low temperatures, that is to say at 0°C and below, is very poor. If a trace of the barium sulphate finds its way into the positive paste a very interesting phenomenon is observed; on cycling the battery rapid flaking or shedding of the positive paste occurs and complete loss of capacity results.
CHAPTER II. THEORETICAL PRINCIPLES

The central problem associated with the optimisation of cell performance is that of obtaining an output on discharge (and an input on charge) as nearly as possible equal to that predicted by the second law of thermodynamics for reversible behaviour that is

$$-\Delta G_0 = zFE_0$$

where $z$ is the number of electrons associated with the conversion of 1 mole of battery reactant to product. On open circuit (when no load is drawn from the terminals that is $i = 0$) this criterion is satisfied, however, as the load current is increased from zero the actual output departs from the theoretical. The principles which cause the divergence are well understood and form the basis of electro-dekinetics.

Polarisation and Overpotential

When a current passes through an electrode its potential changes from that when no current flows ($E(0)$), to $E(i)$. If $E(0)$ is the equilibrium potential $E^0$ then the difference $(E(i) - E(0))$ is termed the overpotential. If $E(0)$ is a mixed potential, that is when several exchange reactions are occurring simultaneously and are contributing towards the potential of the electrode at zero net current, then the difference $(E(i) - E(0)$ is termed the polarization. Thus:

$$\eta = E(i) - E^0 = \text{overpotential}$$
In this thesis the term "overpotential" will be used since it is not intended to examine mixed potential redox systems. On a commonly used convention a net cathodic current \( i \) (\( i_c - i_a = i \) where \( i_c \) and \( i_a \) denote the cathodic and anodic current densities) is designated positive and is associated with a negative overpotential.

The overpotential arises, on the passage of current, due to several factors. Each factor can be considered to be a resistive component which results in an overpotential on passage of current. Thus as discrete independent variables they form simple additive components of the overall overpotential \( \eta \).

There are five main component overpotentials which additively give the overall overpotential. These are charge transfer overpotential \( \eta_D \), diffusion overpotential \( \eta_d \), crystallization overpotential \( \eta_k \), reaction overpotential \( \eta_r \), and ohmic overpotential \( \eta_o \).

Thus \[ \eta = \eta_D + \eta_d + \eta_k + \eta_r + \eta_o \]

Charge transfer overpotential is the driving force behind the transfer of charge by electrons and ions across the double layer from electrolyte to electrode or vice versa.

For a simple redox reaction involving a metal \( Me \) and an \( Me^+ \) ion the simple relationship between the overpotential and the current passing across the electrode interphase is

\[ i = i_c - i_a = i_0 \left\{ \exp \frac{-\alpha ZF \eta}{RT} - \exp \frac{(1-\alpha)ZF \eta}{RT} \right\} \]  

(1)
\[ i_c + i_a = i_0 \] (when \( i = 0 \)) at the equilibrium potential

\( i_0 \) is the exchange current (strictly the apparent exchange current).

\( \alpha \) is the charge transfer coefficient.

The exchange current is also given by

\[ i_0 = ZFk^0 C_{Me}^{Z+} C_{Me}^{Z-} \] equation 2.

The constant \( k^0 \) is the apparent standard rate constant and the \( C \)'s refer to concentrations of the oxidised and reduced species respectively.

Equation 2 defines \( k^0 \) in terms of concentrations since activities are generally unknown.

(With an amalgam electrode \( C_{Me} \) can be varied by varying the concentration; with a pure metal this is not possible, it is convenient to assume that with a solid metal the activity of the metal component is unity). For the charge transfer step \( i_0 \) is a determinable quantity and its dependence on reactant activity enables \( \alpha \) to be determined and the electron transfer mechanism to be described.

Below an overpotential of about 7mV a linear relationship exists between overpotential and current density. Above 100 mV equation (1) conforms to the Tafel equation:-

\[ \eta = a - b \log_{10} i \] equation (3)

for the cathodic process

\[ a = \frac{2.3 \text{ RT}}{ZF} \log_{10} i_0 \] and \[ b = \frac{2.3 \text{ RT}}{ZF} \] equation (4)

\(-1-\alpha\) replaces \( \alpha \) for the anodic process.

- 12 -
The quantity
\[ \frac{d}{d_{i=0}} = \frac{R}{ZP} \frac{1}{i_0} \quad \text{equation (5)} \]
has the dimension of resistance and is called the reaction resistance, \( R_{D} \).

**Diffusion overpotential** arises purely from the difference in chemical potential stemming from a concentration of electroactive species. This gradient exists from just outside the fixed Helmholtz layer into the bulk of the electrolyte due to the electrode reaction increasing or reducing the concentration of these species and the diffusion coefficients for these ions being small enough to allow an appreciable gradient to be maintained.

**Crystallization overpotential** arises in a similar manner to diffusion overpotential. It is due to a difference in chemical potentials. It is found on solid electrodes where an electroactive ion from the electrolyte is to transfer charge and become incorporated in the lattice of the electrode, or if the lattice is to be broken down to produce the oxidised species. In some cases, when the ion is adsorbed on the electrode after charge transfer it moves about on the surface until it finds a point of relatively higher co-ordination number where it becomes completely integrated in the crystal lattice. The same diffusion across the surface occurs when the opposite reaction takes place on lattice disintegration, these surface diffusing particles are called adatoms or adions.
These diffusion currents produce concentration gradients of these adspecies on the surface at shorter reaction times and give rise to crystallization overpotential.

Reaction overpotential arises from a concentration effect on the electroactive species due to a prior or following slow chemical reaction involving the electroactive species in its equilibrium. The effect is identical to diffusion overpotential and the Nernst equation can be used to determine its magnitude.

Ohmic overpotential is a purely resistive component of the system. On passage of current the ohmic overpotential is directly proportional to the current density and is attributable to the resistance of the electrolyte and any surface film which may be present.

When a net current passes across the electrode interface the system changes from a dynamic equilibrium, where the rate of oxidation in the electrochemical reaction is equal to the rate of reduction, to an overall oxidation or overall reduction. Ohmic overpotential is set up virtually immediately since it involves the rapid movement of electrons. Likewise the transfer of charge across the interphase is so rapid that along with ohmic overpotential, charge transfer overpotential can be said to be time independent. However, the remaining factors, diffusion, crystallization and reaction overpotentials, depend on concentration effects which take an experimentally appreciable time to reach steady state.
For the most efficient performance of the lead acid battery it is clearly necessary to minimise $\eta$ during the charge and discharge process.

Fig. 1 depicts a standard cell typical of those used in lead acid batteries for automotive starting or light traction duties. The design is such that, as far as possible, the various components of overpotential are minimised so that utilisation of the stored energy may be as high as possible.

$\eta_a$ is reduced as far as possible by permitting sulphuric acid to circulate freely within the cell during the discharge process; in this way concentration gradients are trivial except at very high rates of discharge.

$\eta_a$ is controlled by reference to three factors. The plate pitch (separation) is made as small as possible consistent with satisfactory circulation of acid; the electrolyte concentration is chosen to be near that of maximum electrical conductivity and finally the separators which prevent physical contact of the plates are microporous and of high total porosity. The acid necessary for the reaction is mainly carried above the element.

$\eta_o$ is connected with the current density by an equation of the form of equation (1) thus if $i$ can be minimised then is small for constant current flowing in the cell. It is for this reason that the individual electrodes in the lead acid cell are made with a very highly porous structure so that the surface area is maximised.
Fig. 1

Monobloc lead/acid car battery. One cell sectioned to show internal arrangement of plates and separators.
CHAPTER III. PRELIMINARY EXPERIMENTAL WORK

CHOICE OF COUPLE

The selection of an appropriate couple had to take into account a number of factors but, transcending all others, the basic specification which the final production battery had to meet.

Design Requirement

The design requirements were as follows:

(a) The battery must yield a current of 600 amps. for 3 mins. at a voltage of at least 18.
(b) The battery must not weigh more than 50 Kgms. (i.e. 10.8 watts hrs./Kgm. at the 3 minute rate).
(c) The volume of the battery must not be greater than 30 litres (0.018 watt hrs./ml.)
(d) The battery must be capable of 5 years storage without appreciable loss of performance.

It is clear from Table 1 that if the design objectives are to be met a battery based on some more recherché couple will have to be developed. Moreover, because of the very severe demand on performance after long periods of storage, the design must be based on a known system in which electrolyte is admitted to a hermetically sealed cell unit by puncturing an electrolyte storage container. In summary it was necessary to select the system which would be capable of long periods of
shelf storage in the dry condition but which, immediately on
the admission of electrolyte, would activate with minimal
delay to give an unimpaired performance.

Chosen Systems

A comprehensive survey of the literature indicated
that with one significant exception the choice had to be
made of using couples which were only capable of high rate
performance at the cost of very great bulk or weight or
alternatively, and the silver oxide/zinc couple is an
admirable example, a high cost penalty had to be incurred.

The exception seemed to be the couple based on electro-
deposited lead dioxide operating against a negative of
metallic lead in an electrolyte of lead dissolving acid
such as perchloric; fluoboric,fluosilicic or nitric. In
addition to the data which suggested that cells based on
this system were capable of delivering energy at high
current density, whilst maintaining reasonable potential,
it also seemed that the production of the electrodes for
such cells might conceivably be developed to a point where
it was a more than feasible commercial operation. In short
from 'a priori' considerations it seemed that in this system
it would be possible to produce high performance batteries
capable of meeting the desired specifications using production
methods similar to those conventionally used in the battery
industry.
Negative Electrodes

It was considered from the outset that the manufacture of negative electrodes would present little or no problem as they could readily be made from lead sheet or lead alloy sheet suitably prepared and shaped or alternatively from lead electrodeposited onto supports of appropriate form and material.

Positive Electrodes

The production of the positives inevitably required a new approach from the conventionally oxidised pasted grids described above. Although it was known that lead dioxide could be anodically deposited from a variety of solutions onto a variety of substrate metals no data was available regarding the preparation and properties of anodically produced deposits nor was there any indication as to which of the possible methods might give the best electrodes for cells of this type.

THE PRODUCTION OF POSITIVE ELECTRODES

Electrodes formed by the electro-deposition of lead dioxide onto metallic bases (platinum, silver, nickel, cobalt and stainless steel) have been used for primary power source application and it was recognised that, for a successful production method of such electrodes, it was logical to confine attention to electrolytes (formation baths) based on lead compounds of relatively high solubility in order that rapid rates of deposition might be achieved. Studies were
therefore limited to solutions of lead perchlorate, fluoborate, nitrate, silicofluoride and plumbite. Preliminary experiments showed that satisfactory deposition rates (of the order of 30 mA/cm²) were unattainable with plumbite, fluoborate and silicofluoride electrolytes: at current densities above about 5 mA/cm² electrolytes based on these anions result in highly stressed, poorly adherent deposits which readily flaked, however electrolytes based on nitrate and perchlorate ion appeared to be promising.

Experimental

For the initial experiments sheets of various metals measuring 10 cm. x 5 cm. x 0.01 cm. were annealed to permit them to be flattened) and etched in a nitric (10%)/acetic (5%) bath. They were washed in distilled water and suspended symmetrically between stainless steel (18% Cr. 8% Ni. 74% Fe) cathodes 10 cm. apart in the required electrolyte. Current was switched conventionally and charge equivalent to the required deposit (0.043 gm/cm²) passed at the required rate. Electrolyte solutions were prepared using AR grade chemicals and distilled water.

Results

At low current densities lead dioxide is not deposited on the substrate (with the exception of platinum) instead the metal dissolves: the tendency is more pronounced with copper than with iron or nickel and under conditions of high acidity. For lead dioxide to deposit the basis must first be rendered passive, for the case of nickel the process:

\[ \text{Ni} \rightarrow \text{Ni}^{2+} + 2e^- \]  

(6)
changes to
\[ \text{Ni} + \text{H}_2\text{O} \rightarrow \text{NiO} + 2\text{H}^+ + 2\text{e} \]  \hspace{1cm} (7)

with the production of a passivating layer of oxide. The electrodepotential then rises to that necessary for the formation of lead dioxide.

\[ \text{Pb}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{PbO}_2 + 2\text{e} \]  \hspace{1cm} (8)

Optical photo-micrographs of prepared specimens show no trace of the passivating layer and similarly on the electron microscope no phase was discernible between the lead dioxide layer and the nickel base. None the less the reasoning is considered to be correct and one must assume that the oxide layer is limited in thickness to molecular dimensions.

It is necessary to control the pH of the electrolyte so that reaction (7) is favoured, if the pH is too low the passive layer may not be formed so that the anode continues to dissolve. In the presence of high $\text{H}^+$ it may be necessary to give a "flashing" treatment, that is the current is increased momentarily to a very high value, favouring reaction (7).

Lead Perchlorate electrolytes

Good adherent deposits of lead dioxide were obtained using electrolyte concentrations of the order of 2 mols./l of lead perchlorate and 1 mol./l of perchloric acid over fairly wide limits of lead ion concentration. Current densities of up to 50 mA/cm. were employed without unduly high internal stresses being encountered (plate distortion was slight), provided that hydrogen ion concentration did not rise above 1 mol./l. Acidity was controlled by continuous circulation through a bed of lead oxide.
Dendritic growth of lead on the cathode was a complicating factor, so that it was desirable to keep the cathode current density as low as possible. This was done by using cathodes of large area (5 times that of the anode).

Current efficiencies were approximately 100% based on the anodic oxidation.

**Lead Nitrate Electrolytes**

In lead nitrate solutions optimum conditions for the production of lead dioxide electrodeposits at a rate of 36 mA/cm² require 1.6 mol./l of lead nitrate in the electrolyte. Successive depositions in electrolyte at controlled pH show a decreasing faradaic efficiency. Thus four successive depositions gave efficiencies of 93.5%, 69.2%, 42.2% and 25.4%. It was also observed that with this progressive use of the bath the clear solution gradually developed a yellowish colour reminiscent of solutions of sodium nitrite and this suggested that the effect was due to the development of nitrite in the electrolyte which was confirmed by chemical analysis. The nitrite ion would be oxidised to nitrate at the anode and thus a mechanism, based on a nitrate/nitrite redox cycle, would exist for the continual reduction in the current efficiency of lead dioxide formation.

To test this theory electrodeposition experiments were carried out with solutions to which small amounts of nitrite ion had been added as sodium nitrite. The dependence of the deposition efficiency on the nitrite/nitrate ratio as determined from these experiments is shown in Fig. 2. This would support
Efficiency of lead dioxide electrodeposition from a lead nitrate solution as a function of nitrite ion concentration at 15°C.
Fig. 2.

\[
\frac{100[\text{NO}_2^-]}{[\text{NO}_3^-]} \quad \text{% Efficiency}
\]
the view that the nitrate ion is reversibly reduced to nitrite at the cathode and oxidised to nitrate at the anode according to the equation

\[ \text{NO}_3^- + 2\text{H}^+ + 2e^- = \text{NO}_2^- + \text{H}_2\text{O} \quad (9) \]

As might be expected, the amount of nitrite produced during the passage of a given quantity of electricity is found to depend on the cathodic current density. At low current density (of the order of 1 mA per cm.sq.) the deposition process was 100% efficient, at higher current density (of the order of 30 mA per cm.sq.) the efficiency fell markedly as nitrite was produced and at very high current densities (of the order of 100 mA per cm.sq.) ammonium ion is produced. Ammonium ion production 'takes over' from nitrite production as current density further increases. In the present experiments nitrite was removed from the system by oxidation with hydrogen peroxide or \( \text{Pb}_3\text{O}_4 \). This was coupled with pH control by pumping through an external circuit containing a bed of PbO and additions of hydrogen peroxide (drip feed) or solid \( \text{Pb}_3\text{O}_4 \).

**The Effect of Temperature**

It was found that within the temperature range of 15°C to 35°C there was little if any change in the appearance and performance on test discharge of the deposits produced in these baths (other parameters being maintained constant). This facilitated the development of laboratory equipment designed for the production of test electrodes in sufficient bulk to carry out the remainder of the work necessary for the provision of a sound basis for mass production of electrodes.
Laboratory Plant for Electrode Production

In order to produce fairly large numbers of test electrodes in the laboratory equipment was set up as shown in Figs. 3 and 4. In Fig. 3 (A) is a manifold through which lead nitrate or lead perchlorate solution is pumped to the various electrodeposition vessels (B). At the appropriate points on the glass manifold side tubes were blown with an air bleed at (C). In this way fresh electrolyte was continually fed to the vessels (B) in such a way that the entering fluid was broken up into droplets so that no electrical connection existed between the main body of the electrolyte in (B) and that circulating in (A). Similarly the overflow tube at (D) was provided with a constriction at its tip so that the efflux also fell as droplets into the PVC channel (E) which conveyed the liquor to the appropriate neutralisation bed and, when nitrate electrolytes were being used, oxidising bed. After passing through the rectifying beds the electrolyte was pumped up to a header tank which fed the manifold (A).

In Fig. 4 is shown the arrangement of the electrodeposition baths. The baths (D) were arranged in line and a long insulating rod of PVC covered steel (A) was provided with handles at each end and metal hooks at (B) insulated from the rod. The electrodeposition baths (D) were equipped with stainless steel cathodes (C) and the pre-treated specimens (conventionally called blanks) were hung from the hooks at (B). The pairs of cathodes were connected to sockets on a master plug and the hooks at (B) were
Fig. 3

Diagram of cell used for producing electrodes of electrodeposited lead peroxide on sheet metal bases.
Fig. 3.
Fig. 4

Diagram of laboratory plant for electrode production.
Fig. 4.
connected to pins on the male counterpart of the plug as shown at (E). It was found necessary to anneal the blanks as otherwise it was virtually impossible to flatten them: it will be appreciated that any significant curvature or distortion in the electrode is inimical to their subsequent assembly into "elements" consisting of parallel packs of positive and negative plates insulated from each other by 'separators' of minimal thickness. Etching of the blanks was also important as it resulted in a much better adhesion of the deposit to the basis. For example using nickel sheet "spalling" occurred from the unetched sheet very easily whereas, after etching, the dioxide layer was practically undisturbed when the electrode was bent around a radius of 2 times the basis thickness.

In order to prepare a set of test electrodes the rod was lowered, with the test electrodes already hooked on, into appropriate rests inserting the plug at (E) in order to complete the series circuit. Current was switched on and in this way all the electrodes received the same charge (6Ah) in solutions which were of constant composition. It was found that this method was satisfactory for the production of large numbers of test specimens under accurately controlled conditions with respect to temperature, current density and bath composition.
THE PRODUCTION OF NEGATIVE ELECTRODES

On Copper or Nickel Bases

Negative electrodes were made in a plant similar in all respects to that used for making positive electrodes excepting that no means were provided for the circulation and revivification of the liquor and secondly the auxiliary electrodes (anodes in this case) were made of lead sheet (0.3 cm thick, 99.5%). The electroplating solution used was lead fluoborate as experience had shown that this was the simplest solution to use if regular adherent deposits were to be obtained without difficulty.

The electrolyte consisted of a solution of lead fluoborate containing 40 gms./litre of free HBF$_4$ and made up to a specific gravity of 1.170. Glue was added (0.116 gms./litre) in order to ensure smooth deposits at 0.04 amperes per square cm.

In this way, and using copper or nickel blanks, perfectly satisfactory electrodes could be made which were entirely suitable for working with the positives made in the manner described. Some care was taken in cleaning and etching the metal blanks prior to the electrodeposition and, as a final operation, the electrodes were washed and dried. Otherwise no particular precautions were taken and at no time were any problems encountered from malfunctioning of electrodes so prepared.
Alternative "Self Supported" Electrodes

Because of economic considerations the use of lead sheet was considered at the earliest stages but, because of the impossibility of obtaining satisfactory rigidity in electrodes made in this way (unless thicknesses quite out of keeping with the coulombic demand were used) this idea had been abandoned. Subsequently however, attention was directed to the interesting properties of calcium lead alloys and in particular the rapidity with which such alloys age hardened. Age hardening is the property, possessed by some alloys, of increasing markedly in hardness during a few days (or sometimes hours) of storage at ambient temperature following casting. Thus an alloy of lead containing 0.08% calcium will have a Brinell Hardness Number (BHN) of about 3 or 4 immediately after casting. In four days at 15°C the BHN will increase to 9. Using binary alloys of between 0.06 and 0.09% calcium the initially soft castings developed quite remarkable hardness after periods of hours only at room temperature. Sample melts were therefore made and sheet was rolled from which electrodes were cut; it was found that these had satisfactory rigidity even when the thickness was only slightly in excess of that required for the operation of the cell in faradiac terms. Generally therefore all experiments were carried out with rolled calcium lead sheet negatives working against the positives of electrodeposited lead dioxide.

As the investigation progressed some problems were encountered which were a function of this method of preparing the negative plates; this will be discussed later in this thesis as it is in fact a peripheral effect for which as yet there is no adequate explanation.
CHAPTER IV. PROBLEMS ASSOCIATED WITH PLATE MANUFACTURE

Positive and negative plates were produced for the assembly of experimental cells and two problems of major importance were soon encountered. With the positive plates internal stresses in the deposit frequently caused severe buckling; in the negative plates cut from sheet calcium/lead alloy performance after dry storage was often disappointing though the electrodes made by electro-deposition were free from the defect.

Stress in Electrodeposits of Lead Dioxide

Positive plates were produced in large numbers using the equipment already described and it was soon found that the electrodeposits of lead dioxide frequently exhibited high internal stresses. These stresses were often sufficiently great to cause severe distortion of the nickel sheet onto which the deposit was made. Such "buckled" plates could not normally be used as the deposit flaked off on attempting to flatten them, nor could they be assembled into cells as face to face arrangement with close separation was precluded. It therefore became necessary to study the causes of high internal stresses in the deposit with a view to achieving a marked reduction, if not their total elimination. In order to achieve high electrical performance from the eventual cell the plates must be flat so that spacings may
be minimal without any risk of short circuits caused by contact of two opposing plates. In addition the reduction of internal stress in the deposit materially reduced the chance of flaking away. Finally it has been observed that highly stressed deposits are associated with inferior duration of discharge.

Existing Theory

It is by no means uncommon for electro-deposits to exhibit "locked-up" stress and indeed the literature particularly with respect to electroplated metal layers, gives many examples of studies of these phenomena. It is clear that the match/mismatch of the deposited lattice on the lattice of the substrate is not the only factor involved although it may be important in certain cases. Thus for the deposition of iron on a copper substrate orientated overgrowths are obtained even though there is a 12% mismatch in lattice spacings. Conversely, for the deposition of iron on gold, random deposits are obtained although no mismatch is involved. It is also noteworthy that copper on copper gives rise to a stressed deposit. It has also been reported that stress develops in deposits after the current has been switched off. For many metal/metal depositions, it has been suggested that hydrogen co-deposited during the electroplating process may give
rise to stress. The hydrogen may be present as inter-
stitially held hydrogen atoms or as an unstable hydride.

For the electrodeposition of lead dioxide on to nickel there is a considerable mismatch in structure of deposit and substrate. There is no likelihood of hydrogen co-deposition although oxygen co-deposition may occur.

In addition to the present technological application there is interest therefore, in the development of stress in lead dioxide deposits both with the object of stress control, in order to facilitate the production of acceptable plates, and in order to advance the general theory of the electrochemical development of stress. In the present work results of an investigation are presented using a lead nitrate based electrolyte because of its importance in the large scale production of battery electrodes.

**Lead dioxide electrodeposits**

Lead dioxide occurs in two forms; α-PbO$_2$ was described by Kameyama & Fukumoto and has an orthorhombic structure. β-PbO$_2$ has been known for a considerable time and has a tetragonal structure. Under acidic conditions, the β-form is produced. At low current densities, the product can be made exclusively β-PbO$_2$ but at the current
densities that are usually employed in technological processes, a small proportion of the $\alpha$-polymorph may be present in the electrodeposited. The $\beta/\alpha$ ratio of the deposit may be readily found using X-ray diffraction techniques. The essential difference is in the way in which the octahedra (at the centres of which lie the metal ions) are packed. Fig. 5.

Experimental

Lead dioxide was deposited from an aqueous acid solution of lead nitrate ($H^+ = 0.1$ mole/l.) The electrolytic cell (8 x 12 x 10 cm deep) was parallel sided and made of soda-glass; the electrolyte was continuously pumped through an external nitrite/hydrogen ion removal column packed with porcelain rings which supported a 2:1 mixture of red lead/lead monoxide. The rate of electrolyte circulation ($\sim 100$ ml/min) was varied to achieve optimum deposition conditions. Suspended solid was removed by filtering the return feed stream. The total volume of electrolyte was about two litres. A diagramatic illustration of the set up is shown in Fig. 6.

Stress Measurement

Two methods were employed:

(i) A fine rubber diaphragm was fixed over the end of a water-filled thistle funnel (3 cm dia).
Fig. 5

Structures of $\alpha$ and $\beta$ lead dioxide.
Fig. 5.

$\alpha\text{PbO}_2$
(orthorhombic)

$6 \times \text{Pb}-\text{O} = 2.16\,\text{Å}$
$2 \times \text{O}-\text{O} = 2.59\,\text{Å}$
$10 \times \text{O}-\text{O} = 2.92-3.35\,\text{Å}$

$\beta\text{PbO}_2$
(rutile)

$4 \times \text{Pb}-\text{O} = 2.15\,\text{Å}$
$2 \times \text{Pb}-\text{O} = 2.16\,\text{Å}$
$2 \times \text{O}-\text{O} = 2.67\,\text{Å}$
$8 \times \text{O}-\text{O} = 3.03\,\text{Å}$
$2 \times \text{O}-\text{O} = 3.38\,\text{Å}$
Fig. 6

Apparatus for examining the development of stress in electrodeposited layers of lead dioxide.
The diaphragm was coated with silver (from a silvering solution) and a layer of nickel (2 x 10^-3 cm) deposited from a nickel chloride/nickel sulphate bath on to the silver. The nickel deposit formed the basis for the deposition of lead dioxide. Compressive stresses in subsequent deposits on to the flexible substrate resulted in a rise in the water level in the stem of the funnel. Stress detection could be made very sensitive by the use of a capillary stem. The method was, however, suitable only for qualitative observations.

(ii) The second method was originally due to Naughton & Hothersall. An anode consisted of two thin (0.01 cm) annealed nickel plates clamped together forming two leaves (1 cm wide x 5 cm long). In practice it was convenient to coat the inner (facing) surfaces with an extremely thin layer of polyvinyl chloride. The complex anode was positioned in the cell exactly between two identical lead cathodes which were 12 cm apart in the electrolytic cell, so that the current distribution was uniform over the outer surfaces of the anode. During
the course of the anodic deposition, the leaves of the anode converged or diverged depending on whether the stress was compressive (+) or tensile (−). Stress is calculated from:

\[
\text{Stress} = \frac{Yd^2D}{3L^2t}
\]

where \( Y \) is Young's Modulus for nickel; \( L \) is the length of the anode (5 cm); \( d \) is the thickness of the anode (0.01 cm); \( t \) is the thickness of the deposit; and \( D \) is the difference in divergence of anode leaves before and after the deposition.

The stress in the deposited lead dioxide was studied as a function of current density, stirring and electrolyte composition. In addition, deformations of the electrodes (change in water level, method (i); change in \( D \), method (ii)); were followed throughout the course of the experiments. The majority of measurements were made in unstirred electrolytes at a current density of 30 mA/cm².

Results

Experiments were carried out under a variety of conditions and the results may be summarised qualitatively in the table below:
<table>
<thead>
<tr>
<th>Variable</th>
<th>Effect on Compressive Stress in Deposit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead nitrate concentration</td>
<td>Higher stresses in more dilute electrolytes.</td>
</tr>
<tr>
<td>Current Density</td>
<td>Significant reductions in stress at high current densities; films showed poor adhesion however.</td>
</tr>
<tr>
<td>Agitation of electrolyte</td>
<td>Very rapidly stirred electrolyte resulted in stress free deposits or even small tensile stresses</td>
</tr>
<tr>
<td>Organic acid anion concentration</td>
<td>Organic acid anions in the electrolyte caused reductions in compressive stresses and even, with large organic additions, tensile stresses</td>
</tr>
</tbody>
</table>

Fig. 7 shows the magnitude of the stress in electro-deposits obtained with electrolytes based on lead nitrate (1.21 mol./l) containing various concentrations of sodium acetate. At very high acetate concentration, a small amount of oxygen was evolved and the presence of a small proportion of gaseous organic product was evidence for a Kolbe-type reaction:

$$2\text{CH}_3\text{COO}^- = \text{C}_2\text{H}_6 + 2\text{CO}_2 + 2\text{e} \quad \text{(10)}$$

At sodium concentration 0.1 mol./l, no complications due to either oxygen evolution or reaction (10) were observed.
Fig. 7

The effect of sodium acetate additions to lead nitrate solutions on the stress developed in lead dioxide electrodeposited at 23°C.
Fig. 7.

Graph showing the relationship between stress, kg/cm², and the concentration of sodium acetate, mol/L, with a negative exponential trend.
At high sodium acetate concentrations the sign of the stress changes from compressive to tensile. The changeover concentration (0.366 mol/l) was checked by method (i). Fig. 8 shows the results for electrolytes based on 1.21, 0.755 and 0.303 mol./l lead nitrate, and in acetate-free electrolytes stresses were 590, 646 and 860 kg/cm², respectively. Acetate is more effective at low lead nitrate concentrations, that is, the ratio \[ \frac{[\text{NaAc}]}{[\text{Pb(NO}_3\text{)}_2]} \] is important.

In Fig. 9 is shown the effect of tartaric acid and citric acid on stress developed in electrolytes based on 1.21 mol./l concentration. The effect of the polybasic acids is much more pronounced than monobasic: at lower concentrations (0.05 mol./l), the polybasic acids are 80 times as effective as the monobasic sodium acetate. It was not possible to increase the concentration of citric and tartaric acid beyond 0.03 mol./l without adversely affecting the adherence of the deposit.

**Development of Stress**

Both methods (i) and (ii) allowed the development of stress to be observed during the course of the electrolysis. It was found that stress was produced only during the electrolysis and not after the current had been switched off. The magnitude of the stress was independent of the charge passed (thickness of electrodeposits).
Relation between stress and sodium acetate concentration for lead dioxide deposits produced from lead nitrate solutions of varying concentration at 23°C.
Fig. 9

Comparison of the stresses produced in lead dioxide electrodeposits using acetate, citrate and tartrate additions to the plating solution (23°C).
Fig. 9.

[Graph showing the relationship between stress and the concentration of organic anion. The x-axis represents the concentration of organic anion in mol/L x 10^-2, ranging from 0 to 3, and the y-axis represents stress in kg/cm² x 10^-2, ranging from -4 to 4. Two curves are shown, one for acetate.]
Nature of the electrodeposits

X-Ray analysis showed that the identity of the deposits was the same in all cases, mainly (90%) PbO₂.

There was no connection between the electrolyte constitution and the α/β ratio of the lead-dioxide deposit.

Discussion

Electrodeposits obtained from simple lead nitrate electrolytes are notable for the magnitude of the compressive stress. For electrodeposited metals, values reported in the literature have rarely exceeded 300 kg/cm². It is clear from the effect of Pb²⁺ concentration on stress and from the effect of stirring that low compressive stress is favoured by high Pb²⁺ concentration.

The addition of acetate, tartrate and citrate ions can be regarded as controlling the acidity of the electrolyte; however, it is not possible to reconcile the magnitude of the relative effects of the three acids (Fig. 9) with simple buffer action. The effect of additions of organic acids appears to be most readily explicable in terms of adsorption at the electrode interphase. There is evidence that organic acid anions are adsorbed at the lead-dioxide electrode. The action of the anion can be considered as participation in the packing of the structural units that form the deposit. The greater is the surface concentration of the adsorbed ion, the greater is the proportion of the electrode surface which
cannot be used in the crystal growth process without displacing the adsorbate. A more open crystal structure then occurs, and the compressive stress is reduced and eventually reversed to become tensile as more adsorbate covers the surface.

It is interesting that there was no change in the ratio of the lead dioxide corresponding to the wide differences in deposit stress. It must be concluded that the parameters which determine the α or β arrangement are more fundamental than those which determine the nature of the stress. It is likely that the former may simply be the sign of the charge on the electrode (recent determinations of the zero point of charge of lead dioxide in nitrate electrolytes place it at \( \sim 1.0V \)). Thus, in acid electrolytes, the lead dioxide is deposited \( (E^0 = 1.45V) \) as \( \beta \)-PbO₂ under conditions of a positive charge on the electrode; in alkali, the lead dioxide is deposited \( (E^0 = 0.25V) \) as \( \alpha \)-PbO₂ with a negative charge on the electrode.

Analysis of electrodeposits does not preclude the possibility of the presence of hydrogen and additional oxygen in the electrodeposit. Values of ultimate formulae for systems of the present type are typically \( \text{PbO}_{1.95}^{(\text{OH})_{0.15}} \). Although the presence of hydrogen could not arise by the discharge of \( H^+ \), there is some evidence from kinetic
measurements that in acid electrolytes, H⁺ may be adsorbed even under conditions of positive surface charge. Hydrogen inclusion in the lattice could arise via a mechanism similar to that proposed for the formation of lead dioxide:

\[
Pb^{2+} + 2OH^- = Pb(OH)_2 \quad (11)
\]

\[
Pb(OH)_2 = Pb(OH)_2^{2+} + 2e \quad (12)
\]

\[
Pb(OH)_2^{2+} = PbO_2 + 2H^+ \quad (13)
\]

Reaction (12) is probably a 2-step process in the present experiments. Reaction (13) can be considered as the desorption of adsorbed H⁺, and it is possible that H⁺ could enter the lattice via this reaction. If organic acids or anions are adsorbed at the electrode, the stress may well be modified by the intrusion of the adsorption of the organic anion on reaction (13). Here again, the organic entity interferes with the lattice building process. Oxygen co-deposition and inclusion in the lattice is also a possibility at the potentials involved in the electrodeposition. It is not clear, however, how organic anions could participate in a process of oxygen co-deposition in such a way as to modify the stress in the manner observed.

The effect of very high current densities on the stress appears to agree with the other observations, since at the higher positive potentials involved at higher current densities, the adsorption of anions would be favoured.
CHAPTER V. LIMITATION OF ELECTRODE PERFORMANCE
BY PASSIVATION

Preliminary Discussion

Basic considerations suggest that, in a cell of the type under study, optimum performance on discharge, on both a weight and volume basis, would be achieved when the lead dioxide from the positive and the lead of the negative were completely converted into the perchlorate at the end of the discharge. At the same time the perchloric acid in the electrolyte should be completely converted into the lead salt.

Various factors militate against this happy consummation not least of which is the onset of passivity, consequent on the high current densities demanded by the application for which the batteries under development are intended.

The anodic dissolution of a metal in an acid is a consequence of the passage of metal ions from the lattice to the solution where they acquire a stabilising shell of water molecules (hydration). This process establishes a concentration gradient in the solution with the highest metal ion concentration at the electrode. With the continued passage of current the concentration increases until the
solubility limit is reached at the anode surface, in many cases a layer of the appropriate salt is then laid down on the metal surface effectively screening it from further attack.

Passivity of this type was first investigated systematically by Muller who referred to it as "Bedeckungspassivität" or "cover passivity" to distinguish it from chemical passivity where an oxide film or higher valency compound is formed.

In cells of the lead/sulphuric acid/lead dioxide type, the active material is prepared with a very large surface area so that a large amount of insoluble sulphate forms, and therefore a large output is achieved, before screening becomes effective in limiting the discharge. In cells of the pasted lead dioxide/sulphuric acid/zinc or more particularly electrodeposited lead dioxide/perchloric acid/lead types, where one or both electrodes have relatively undeveloped surfaces, it is of importance to know something of the factors which give rise to passivity in order that such cells may be operated at high efficiency. The passivation time of lead anodes in perchloric acid has been studied over a range of current densities. The experiments have been extended to study the effect of interruptions in the polarisation for which case a theoretical expression has been derived.
Sand has discussed the problem of concentration changes at an electrode subject to semi-linear diffusion and showed that if diffusion is the only mode of mass transport, then the time, $t_p$, for a limiting concentration to occur at the electrode at current, $i$, is given by an equation of the form:

$$i \sqrt{t_p} = \frac{zFCo}{2\pi D}$$

(14)

In this equation $z$ is the number of electrons involved in the process, $D$ is the diffusion constant (having dimensions $cm^2/sec$) and $F$ is the Faraday; $Co$ is the concentration at the electrode surface.

If the flow of current is discontinued, the accumulation of electroreactive species is reduced as diffusion occurs. Further passage of current after the interruption again increases the concentration at the electrode until passivation occurs. This routine is commonly encountered during the intermittent operation of energy storage devices.

**Theoretical Treatment**

First consider passivation (without interruption) of a system in which convection currents are eliminated and diffusion is uni-dimensional.

Consider a vertical cylindrical cell containing acid, the lower end of which consists of a metal anode of unit area. Let a current of $i$ amps. flow for a time $t$ secs. and let the cylinder be of sufficient height to be regarded as semi-
infinite. It is first necessary to find the concentration of metal ions at any height \( x \) cm. above the anode. The quantity \( C_{x,t} \) is then the solution of Fick's diffusion equation:

\[
\frac{\partial C_{x,t}}{\partial t} = D \frac{\partial^2 C_{x,t}}{\partial x^2} \quad \ldots \ldots \quad (15)
\]

with the boundary conditions

\[
D \frac{\partial C_{x,t}}{\partial x} = \frac{i}{\varepsilon F} \text{ at } x=0, \quad C_{x,t} = 0 \text{ at } x=\infty \quad \ldots \ldots \quad (16)
\]

The required solution is given by:

\[
C_{x,t} = \frac{2i}{F} \sqrt{\frac{t}{D}} \text{erfc} \frac{x}{2\sqrt{Dt}} \quad \ldots \ldots \quad (17)
\]

\[
\text{erfc} \ y = \frac{1}{\sqrt{\pi}} e^{-y^2} - \frac{2}{\sqrt{\pi}} \int_{y}^{\infty} e^{-\xi^2} d\xi \quad \ldots \ldots \quad (18)
\]

At the anode surface where \( x = 0 \)

\[
C_{0,t} = \frac{2i}{ZF} \sqrt{\frac{t}{D \pi}} \quad \ldots \ldots \quad (19)
\]
In acid of any given concentration, it is reasonable to suppose that the concentration of metal ions at the anode at the onset of passivity will be constant at constant temperature. Denoting this concentration by $C_P$ and the time to passivate as $\tau_P$, then

$$C_P = \frac{2i}{zF} \sqrt{\frac{t_P}{D\pi}} \ldots \ldots \ldots \ldots (20)$$

$$\therefore \tau_P = D\pi \left(\frac{C_PzF}{2i}\right)^2 \ldots \ldots \ldots \ldots (21)$$

which can be written as

$$\tau_P = \alpha \frac{C_P^2}{i^2}, \quad \alpha = \frac{D\pi z^2F^2}{4} \ldots \ldots \ldots (22)$$

**Experimental**

In order to measure passivation times at various current densities under conditions such as were assumed in developing the above theoretical treatment it becomes necessary to restrict diffusion to one dimension and to exclude as far as is possible side effects such as convection. To this end a simple cell was employed as shown in Fig.10. A is a glass cylinder of height 10 cm. and diameter 22 mm. and B is a disc of lead sheet (99.99% Pb); the construction of the gland permits the rubber ring C to be compressed so that a liquid tight seal is effected. D is a counter.
Apparatus for examining the rate of passivation of soluble anodes.
electrode of carbon (glassy or graphite). Temperature control was obtained by immersing the whole cell in a water thermostat but it was not always possible to eliminate faradaic heating effects. The perchloric acid electrolyte was of Analar quality.

By operating the electrode in this attitude with the electrolyte confined as shown thermal currents are limited as far as is possible (in the short term) and convention due to gravity changes caused by concentration variations is eliminated. In addition because the electrolyte is only allowed access to the horizontal surface of the electrode no spurious edge effects can influence the progression development of the linear concentration gradient in a vertical direction. This general principle of operation has been described in the literature.

A constant current was passed through the cell and constancy was maintained by taking it from a 100 V d.c. supply and using a large variable series resistor; owing to the high line voltage little adjustment was required. The voltage drop across the cell was measured on a high resistance 'Unipivot' instrument or electrometer and the onset of passivity could be detected quite accurately by the sudden rise in cell potential as shown in Fig. 11 at intersections of projected parts of the polarisation curve.
Fig. 11

Typical potential difference – time curves from passivation experiments at 20°C.
Fig. 11.

- 0.263 Amps./cm²
- 0.526 Amps./cm²
- 0.790 Amps./cm²
Results and Discussion

Typical voltage/time curves for the anodic dissolution of lead in perchloric acid are given in Fig. 11. The passivation times, \( t_p \), are plotted against reciprocals of \( i^2 \) in Fig. 12. It can be seen that the points lie closely along straight lines passing through the origin. Departure from linearity is due to the faradaic heating effects of the larger currents and delayed the onset of passivation.

The linear relation between \( t_p \) and \( i^{-2} \) and the increasing slope of the lines with decreasing concentration provides ample support for the supposition that the passivation process is diffusion controlled.

Quantitative Studies of Anodic Passivation

The time taken to passivate an anode increases rapidly with decreasing current density. This is clear when passivation time is plotted directly against the current flowing (Fig. 13) and when the charge required for passivation is plotted against the current (Fig. 14). The Theoretical lines in Figs. 13 and 14 were calculated from the following values of \( \alpha C_p^2 \) given with the corresponding strengths of perchloric acid: acid concn. 10%, 70.31; 20%, 51.62; 30%, 41.90; 40%, 33.20; 50%, 16.70; and 60%, 1.76. D was measured experimentally (and also calculated...
Fig. 12

Passivation of lead in perchloric acid.

Plot of time to passivate against the reciprocal of the square of the current ($20^\circ C$).
Fig. 12.

Graph showing the relationship between (amperes)$^2$ and seconds for different concentrations of HClO$_4$:
- 20% HClO$_4$
- 40% HClO$_4$
- 60% HClO$_4$
Fig. 13

Passivation time plotted against current density for lead in perchloric acid at 20°C.
Fig. 13.

- 40% HClO₄
- 50% HClO₄
- 55% HClO₄
- 60% HClO₄
Fig. 14

Passivating charge plotted against current density for lead in perchloric acid at 20°C.
Fig. 14.

% HClO₄

- 0  10
- 20
- 30
- 40
- 50
- 55
- 60

CHARGE (coulombs)

CURRENT (A/cm²)
by the Nernst formula), a value of $1.24 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ was obtained in reasonable agreement with the calculated figure of $0.97 \times 10^{-5}$.

From a consideration of the data of Figs. 13 and 14 the dependence of passivation time on the perchloric acid concentration is seen to be very pronounced: the reduction of the solubility of lead perchlorate by the common ion effect leading to very early passivation in the more concentrated acid.

In order to maximise the energy delivered by a cell based on this system it is necessary to have regard therefore, not only to the electrochemical equivalents of acid and active materials present, but also to the rate at which electric current must be supplied. The results of this particular work made it possible to select a 55% (8.1 mols./l.) solution of perchloric acid as optimal for the designated end use for which the battery was intended; data corresponding to this concentration are entered in Table 2 below:
<table>
<thead>
<tr>
<th>$i_A/$cm$^2$</th>
<th>$r_p$ secs.</th>
<th>$i^2t_p = \alpha C_p^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.147</td>
<td>286</td>
<td>616</td>
</tr>
<tr>
<td>0.147</td>
<td>308</td>
<td>6.64</td>
</tr>
<tr>
<td>0.147</td>
<td>275</td>
<td>5.95</td>
</tr>
<tr>
<td>0.153</td>
<td>276</td>
<td>6.40</td>
</tr>
<tr>
<td>0.174</td>
<td>222</td>
<td>6.67</td>
</tr>
<tr>
<td>0.200</td>
<td>170</td>
<td>6.76</td>
</tr>
<tr>
<td>0.200</td>
<td>173</td>
<td>6.87</td>
</tr>
<tr>
<td>0.240</td>
<td>106</td>
<td>6.06</td>
</tr>
<tr>
<td>0.245</td>
<td>110</td>
<td>6.30</td>
</tr>
<tr>
<td>0.354</td>
<td>46</td>
<td>5.70</td>
</tr>
<tr>
<td>0.358</td>
<td>49</td>
<td>6.22</td>
</tr>
<tr>
<td>0.580</td>
<td>21</td>
<td>7.14</td>
</tr>
<tr>
<td><strong>Mean</strong></td>
<td><strong>6.45</strong></td>
<td></td>
</tr>
</tbody>
</table>
Interrupted Discharges

For the case of interrupted polarisation, the above treatment is readily extended.

Let a current of \( i_1 \) Amps. flow for \( t_1 \) secs. and then let it be discontinued for a further \( t_2 \) secs. At this moment, current is again passed \( (i_2) \) for \( t_3 \) secs. It is now required to find the concentration of metal ions at any distance \( x \) cms. up the cylindrical cell \( (C_x, t) \).

The quantity \( C_x, t \) is again the solutions of Fick's equation subject to the boundary conditions:

(i) In the interval \( 0 - t_1 \) secs. the solution is given by equation (17).

(ii) In the interval \( t_1 - (t_1 + t_2) \) sec.,

\[
C_x, t = \frac{2i_1}{2F} \sqrt{\frac{t_1}{D}} \text{e}^{\frac{x}{\sqrt{D t_1}}} \\
D \frac{\partial C_x, t}{\partial x} = 0 \text{ at } x = 0.
\]

giving the required solution

\[
C_x, t = \frac{2i_1}{2F} \left[ \sqrt{\frac{t_1}{D}} \text{e}^{\frac{x}{\sqrt{D t_1}}} - \sqrt{\frac{t_2}{D}} \text{e}^{\frac{x}{\sqrt{D t_2}}} \right] \quad (32)
\]

(iii) In the interval \( (t_1 + t_2) - (t_1 + t_2 + t_3) \)

\( C_x, t \) is given by equation 32 at \( (t_1 + t_2) \) secs.

and

\[
D \frac{\partial C_x, t}{\partial x} = \frac{i_2}{2F} \text{ at } x = 0.
\]

giving the required solution

\[
C_x, t = \frac{2}{2FV} \left[ \frac{x}{\sqrt{D t_2}} \int e^{\frac{x}{\sqrt{D t_2}}} - \frac{x}{\sqrt{D t_3}} \int e^{\frac{x}{\sqrt{D t_3}}} \right] + \frac{x}{\sqrt{D t_2 + t_3}} \int e^{\frac{x}{\sqrt{D (t_2 + t_3)}}} - \frac{x}{\sqrt{D (t_2 + t_3)}} \int e^{\frac{x}{\sqrt{D (t_2 + t_3)}}} \quad (33)
\]
It will frequently occur that only the metal ion concentration at the electrode surface is of interest and, as \( \text{ierfc} \theta = \sqrt{\pi} \) it follows that:

\[
C_{o,c} = \frac{2}{zF/\sqrt{D}} \left[ i_2 \sqrt{\xi_3} + i_1 \sqrt{\xi_1 + \xi_2 + \xi_3} - i_1 \sqrt{\xi_2 + \xi_3} \right]^{(34)}
\]

If the current \( i_2 \) is allowed to flow until the electrode passivates, then \( C_p \) is given by Equation (34) and should be constant for a fixed set of conditions irrespective of the values of \( i_1, i_2, \xi_1, \xi_2 \). Thus:

\[
i_2 \sqrt{\xi_3} + i_1 \left( \sqrt{\xi_1 + \xi_2 + \xi_3} - \sqrt{\xi_1 + \xi_2} \right) = \frac{ZFC_P \sqrt{D \pi}}{2} = C_P \sqrt{\alpha}^{(35)}
\]

Experiments were carried out in which the initial current \( (i_1) \) was discontinued, before passivation occurred, and current was then switched on again \( (i_2) \) until passivation. The results are shown in Table 3.

The values of \( \alpha C_p^2 \) entered in the final column of Table 2 are calculated by the use of Equation (35); the approximate constancy of these figures for the wide ranges of current and time intervals employed, provides further support for the model assumed in the treatment of the 'interrupted' case.

The battery may well be required to give an interrupted discharge in service: the nature of the currents and durations
of discharge involved would be entirely determined by
the particular conditions operating at the time which
would create their own demand. The fact that the simple
diffusion mechanism of the model appears adequately to
match the test results provides a base for calculating
battery performance whatever the postulated sequence of
discharge (having regard to the fact that discharge rates
will always be high so that convection is limited by the
short time of the process).
TABLE 3
Passivation of lead in 60% perchloric acid by an intermittent current at 22.5°C

<table>
<thead>
<tr>
<th>$i_1$ A/cm²</th>
<th>$i_2$ A/cm²</th>
<th>$t_1$ secs.</th>
<th>$t_2$ secs.</th>
<th>$t_3$ secs.</th>
<th>$\alpha$ Cp²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.079</td>
<td>0.105</td>
<td>215</td>
<td>84</td>
<td>42</td>
<td>1.56</td>
</tr>
<tr>
<td>0.079</td>
<td>0.131</td>
<td>157</td>
<td>83</td>
<td>28</td>
<td>1.32</td>
</tr>
<tr>
<td>0.118</td>
<td>0.105</td>
<td>121</td>
<td>60</td>
<td>40</td>
<td>1.54</td>
</tr>
<tr>
<td>0.131</td>
<td>0.131</td>
<td>105</td>
<td>120</td>
<td>50</td>
<td>1.93</td>
</tr>
<tr>
<td>0.131</td>
<td>0.158</td>
<td>106</td>
<td>74</td>
<td>23</td>
<td>1.77</td>
</tr>
<tr>
<td>0.131</td>
<td>0.184</td>
<td>87</td>
<td>93</td>
<td>20</td>
<td>1.64</td>
</tr>
<tr>
<td>0.158</td>
<td>0.131</td>
<td>80</td>
<td>40</td>
<td>32</td>
<td>1.82</td>
</tr>
<tr>
<td>0.158</td>
<td>0.184</td>
<td>60</td>
<td>60</td>
<td>23</td>
<td>1.77</td>
</tr>
<tr>
<td>0.197</td>
<td>0.158</td>
<td>50</td>
<td>70</td>
<td>28</td>
<td>1.64</td>
</tr>
<tr>
<td>0.197</td>
<td>0.197</td>
<td>42</td>
<td>60</td>
<td>22</td>
<td>1.77</td>
</tr>
<tr>
<td>0.263</td>
<td>0.158</td>
<td>19</td>
<td>41</td>
<td>41</td>
<td>1.61</td>
</tr>
<tr>
<td>0.290</td>
<td>0.184</td>
<td>14</td>
<td>36</td>
<td>28</td>
<td>1.46</td>
</tr>
</tbody>
</table>

Mean 1.65
Experimental Measurement of
the Diffusion Constant 'D'

In order to measure D the diffusion coefficient of the lead ion in solutions of lead perchlorate in dilute perchloric acid a simple apparatus as shown in Fig. 15 was set up.

A is a J tube into the upper end of which is sealed a cylinder of pure lead B the lower surface of which was polished and etched in dilute nitric/acetic acid, washed and quickly dried. The tube is filled with the solution to be examined and the open end is immersed in a crystallising basin containing the same solution and equipped with a lead counter electrode of sheet formed into a cylinder C of relatively large surface area. By means of a battery and potentiometer a very small voltage (less than 0.2 volts) is applied across the electrodes and the current resulting measured at appropriate intervals on a galvanometer D of very low resistance.

The test electrode and electrode chamber (J tube) are arranged in this particular attitude in order to eliminate, as far as is possible, errors in measurement due to significant convection currents. In these experiments the lead ions in the solutions used were being deposited onto the electrode at the top of the J tube and hence specific gravity gradients were linear and such as to prevent convection. The applied voltage was chosen as small as was consistent with accurate current measurement in order to
Fig. 15

Apparatus for measuring diffusion constants of electrodepositing ions.
eliminate the possibility of hydrogen evolution becoming a substantial component of the cathodic reaction.

The current flowing is determined by a number of factors and may be considered as varying with time during three phases as follows:-

(1) If the applied voltage is \( V \), and the initial resistance of the cell and circuit \( R \), then there is an immediate current \( i_0 = \frac{V}{R} \) which is the instantaneous starting current.

(2) At the applied voltages used the current is uniquely determined by the rate of deposition of lead ions on the cathode \( B \): the current is therefore (by Fick's law) determined by the concentration gradient of lead ions at \( B \) since there is no activation overvoltage associated with this electrode reaction. During this phase we may regard the current as a measure of the rate of transition from a situation in which there is no concentration gradient to one in which there is a smooth well defined gradient to infinity. This is illustrated graphically in Fig. 16.

(3) In the final phase the current diminishes with increasing time according to the well established equation where:

\[
i = zFC_A\sqrt{\frac{D}{\pi \tau}} \quad \ldots \ldots \ (23)
\]

Here \( z \) is the charge on the ion, \( F \) the Faraday, \( A \) the electrode area, and \( D \) the diffusion constant.

- 52 -
Fig. 16

Notional relationships between concentrations of ions in solution and distance from electrode.
Fig. 16.

[Graph showing ion concentration as a function of distance from electrode]
Considering these three phases in the process the initial current is given by \( \frac{E}{R} \) and stays sensibly at this value until the concentration of lead ions at the electrode surface is reduced to zero: it follows that the duration of this primary phase is extremely brief. Let \( \frac{E}{R} = \frac{I_0 A}{R} \) where \( A \) is the electrode area and the initial uniform concentration of lead ions \( C_0 \). Then from the commencement of the experiment to time \( T \) the concentration of ions at a distance \( x \) from the electrode is given by:

\[
C_{x,t} = C_0 - \frac{2I_0}{F} \sqrt{\frac{\varepsilon}{D}} \sinh \frac{\varepsilon x}{2\sqrt{D}t} \cdots \cdots \( 24 \)
\]

Eventually the concentration at the electrode surface is reduced to zero and at this point:

\[
C_{o,t} = 0 = C_0 - \frac{2I_0}{F} \sqrt{\frac{\varepsilon}{D}} \sinh 0
\]

\[
= C_0 - \frac{2I_0}{F} \sqrt{\frac{\varepsilon}{D}}
\]

And hence:

\[
t = \frac{C_0^2 F^2 D\pi}{4I_0^2} \cdots \cdots \( 25 \)
\]

This value of \( t \) is the length of the first phase of the process in which the concentration at the electrode surface is reduced to zero. It follows that the concentration at any point distant \( x \) from the electrode at the end of the first phase is given by:

\[
C_x = C_0 \left[ 1 - \sqrt{\pi} \sinh \frac{x I_0}{C_0 D F \sqrt{\pi}} \right] \cdots \( 26 \)
\]
The second phase begins at the moment when the concentration at the electrode reaches zero: at any time \( t \) after this the concentration at a distance \( x \) from the electrode \( (C_{x,t}) \) is given by:

\[
C_{x,t} = \frac{C_0}{2\sqrt{\pi Dt}} \int_0^\infty \left[ e^{-\frac{(x-x')^2}{2Dt}} - e^{-\frac{(x+x')^2}{2Dt}} \right] dx'
\]

Differentiating within the integral we obtain:

\[
\frac{\partial C_{x,t}}{\partial x} = \frac{C_0}{2\sqrt{\pi Dt}} \int_0^\infty \left( 1 - \sqrt{\pi} i e^{-\frac{x+x'}{\sqrt{D}t}} \frac{x'I_0}{DC_0\sqrt{\pi}} \right)
\]

\[\left( (\frac{x+x'}{\sqrt{D}t}) e^{-\frac{(x-x')^2}{2Dt}} - (\frac{x-x'}{\sqrt{D}t}) e^{-\frac{(x+x')^2}{2Dt}} \right) dx',\]

At \( x = 0 \) the expression can be integrated to give:

\[
\left( \frac{\partial C}{\partial x} \right)_{x=0} = \frac{I_0}{D} \left( 1 - \frac{2}{\pi} \tan^{-1} \frac{2I_0}{C_0\sqrt{D\pi}\sqrt{t}} \right) \ldots (27)
\]

Now the current at time \( t \) is given by:

\[
I_t = zFD \left( \frac{\partial C}{\partial x} \right)_{x=0}
\]

and therefore:

\[
I_t = zFI_0 \left( 1 - \frac{2}{\pi} \tan^{-1} \frac{2I_0}{C_0\sqrt{D\pi}\sqrt{t}} \right) \ldots (28)
\]
Thus
\[ \frac{\partial I_t}{\partial (l_0)} = 2F \frac{4C_0 I_0 \sqrt{D\pi}}{4\pi I_0 + \pi^2 C_0^2 \pi} \] (29)

Thus when \( t \) becomes large (phase 3) we have:

\[ \frac{\partial I_t}{\partial (l_0)} = 2FC_0 \sqrt{D \pi} \] (30)

This equation on integration gives:

\[ I_t = 2FC_0 \sqrt{\frac{D}{\pi \epsilon}} + \text{Const.} \] (31)

which differs from that generally accepted in the integration constant.

Results

Using various concentrations of lead perchlorate and perchloric acid experiments were carried out in order to test the validity of the above reasoning and also to measure the diffusion constant of the lead ion in these conditions.

In Fig. 17 is shown a family of curves derived from equation (28) and assuming varying applied voltages. In Fig. 18 are shown actual experimental curves: the upper curve using an applied voltage of 0.2 deviates from the theoretical slope as the values of \( t \) become large. This is due to the evolution of hydrogen.
Fig. 17

Theoretical curves showing current density as a function of $t^{-\frac{1}{2}}$ for systems under consideration.
Fig. 17.

![Graph showing current density vs. (seconds)^{-1/2} for different values of I_0: 6.3, 3.14, and 1.57.](image-url)
Fig. 18

Typical experimental curves of current $t^{1/2}$ against $t$ at 25°C.
Fig. 18.

\[ [\text{Pb}^{2+}] = 0.04 \text{ mols./L.} \]
\[ [\text{HClO}_4] = 0.846 \text{ mols./L.} \]
\[ \text{TEMP.} = 25^\circ\text{C} \]
becoming the alternative discharge mechanism when the supply of lead ions to the surface becomes inadequate to support the applied voltage.

In Table 4 below are entered the results from a number of experiments with the value of \( D \) derived from the limiting slope of the graph of \( i \) against \( \sqrt{E} \):

\[
\begin{array}{|c|c|c|c|}
\hline
[\text{Pb}^{2+}] \text{mols./l} & [\text{HClO}_4] \text{mols./l} & \text{Limiting Slope} & D \times 10^5 \\
\hline
0.04 & 0.846 & 20.7 & 1.31 \\
0.04 & 1.692 & 23.5 & 1.68 \\
0.08 & 0.846 & 41.5 & 1.25 \\
0.08 & 1.692 & 39.0 & 1.20 \\
0.08 & 2.538 & 40.5 & 1.24 \\
0.16 & 1.692 & 78.6 & 1.18 \\
\hline
\end{array}
\]

We can calculate \( D \) from the Nernst equation:

\[
D_i^o = \frac{RT}{F^2} \lambda_i^o
\]

when we obtain the value \( 0.97 \times 10^{-5} \) at 25°C in satisfactory agreement with the mean result obtained in the experiments (Fig.19).
Fig. 19

Plot of $\frac{\partial I}{\partial [\text{ion}]}$ against lead ion concentration. Electrode area 1.31 cm$^2$, temperature 25°C.
Fig. 19.

\[ \frac{\partial I}{\partial \tau} \text{ M. Amps. /Secs.}^2 \]

\[ [Pb^{++}] \text{ Mols./L.} \]

Slope = 4.95

\[ \therefore D = 1.20 \times 10^{-5} \]
CHAPTER VI
PRELIMINARY CELL DESIGN CONSIDERATIONS

Introduction

It is frequently the case that, when battery power is required for a particular project, not merely the electrical output but also the volume and shape of the power unit are specified. In the case of the battery with which the studies in this thesis are associated the initial requirements were especially stringent in respect of bulk: the cavity into which the battery had to fit was immutable and in the form of a right cylinder. It was therefore decided that the individual cells, each with an upper reservoir containing electrolyte and priming arrangement, should be fitted side by side in the compartment leaving a space above for the mechanical priming gear and a space below for terminals and bus bars. The arrangement is shown schematically in Fig. 20.

Two points require comment, one on account of the unusual arrangement and the other because of its bearing on the work here described.

(i) The terminals are taken through the bottom of the cells: this facilitates quick priming by permitting free ingress of the electrolyte once the bottom of the acid container is breached.

(ii) The shape of the individual plate is decided by the need to fit cell, acid container, and auxiliaries into the space shown. The plate dimensions were finalised at 14.2 cm. x 6.4 cm. The profile is shown in Fig. 26.
Fig. 20

Diagram showing cross section of battery receptacle with cells in position.
Fig. 20.

- ACID VESSEL
- CELL
- BUS BARS
Performance Specification

The lengthy specification, which was eventually agreed, which the battery had to meet had the following salient clauses:

Low rate discharge 250A at 15°C
Initial voltage 21 V
Final voltage 18 V
Duration of discharge to exceed 16 min.

High rate discharge 750A at 15°C
Initial voltage 18 V
Final voltage 16 V
Duration of discharge to exceed 3.25 min.

Maximum weight of battery with electrolyte = 50 kg.

Dimensions
Battery to fit in a cavity of cylindrical shape measuring 66 cm. long by 40.5 cm. diameter.

The performance required at the 3 1/2 minute rate of discharge is equivalent to 14.5 watt hours/kg. (assuming a mean voltage during discharge of 17 V) which is in excess of the power available from better known systems at this rate (as shown in tables 1 and 2).
Determination of Cell Number

Single Plate Testing

The open circuit voltage of the system under study is slightly in excess of 2 V and, as soon as significant current is taken from the cell, the various elements of overpotential corresponding to the particular current density combine to reduce this voltage markedly as discussed in Chapter II. In order to gain more precise information a cell for the study of single plate discharges was devised as shown in Fig. 21 in which a positive plate (having rubber bands positioned on it so as to act as separators) situated between two negative plates was discharged through a selected resistance under controlled conditions.

The vessels, in which these discharges were carried out, were constructed of hard rubber (i.e. rubber which has been fully vulcanised with sulphur) sheet as this material was found to be quite resistant to the acids used under the conditions of the test discharges. Sheets of lead 0.025 cm. thick, containing 0.08% calcium as alloying addition, were inserted in the outer slots and were connected as shown through resistances of Nichrome wire cooled in baths of glycerol. $V_1$ and $V_2$ are voltmeters so that, on filling the vessel with an appropriate electrolyte, the discharge begins and each side of the positive plate can be tested independently.
Fig. 21

Sketch of single plate test cell.
**Working Current Density**

At the high rate of discharge we can expect that the capacity of the cell will be determined by the time to passivate. Approximate calculations can be made providing that the time taken to passivate is not too long assuming that diffusion is the only mode of mass transport. Thus using the data in table 2:

\[
\left( \frac{i}{A} \right)^2 t = 6.45
\]

we can calculate the number of positive plates of the prescribed shape which will be necessary to sustain a current of 750 A for 3.25 m. Thus:

Area of plate (14.2 cm. x 6.4 cm.) = 182 cm².

Then if \( N \) positive plates are necessary we have:

\[
\left( \frac{750}{A^{2}} \right)^2 = 6.45
\]

\[A = 182 \text{ and } t = 195\]

Thus \( N = 22.6 \)

As a first approximation therefore we may base our paper design on a cell using 23 positive plates or a working current density of 0.18 A cm⁻².

**Results of Single Plate Tests**

Three single plate test cells were used which differed only in the spacing between the negative auxiliary electrodes; these spacings were 0.34 cm, 0.58 cm, and 1.19 cm, respectively and corresponded with volumes of electrolyte of 59 ml, 85 ml and 150 ml. The choice of the two larger
cell dimensions was somewhat arbitrary but the smallest was based on the electrode spacings, and electrolyte volumes, which could be accommodated assuming that twelve cells each having 23 positive and 24 negative plates, would be near optimal in meeting the high rate electrical performance specified for the battery.

A number of positive plates were tested in the smallest cell using 55\% w/v perchloric acid as electrolyte. Resistances of 0.08 ohm were used which, at a final cell voltage of 1.33, correspond with the current required to give 750 A. from a cell embodying 23 such positives: twelve cells connected in series and discharging to a final voltage of 1.33 would, in this regard, conform to the battery specified final voltage of 16 at the high rate of discharge. In addition the choice of this method of test rather than pure galvanostatic discharge had the advantage that it more nearly corresponded to service conditions.

Under these conditions, and at a temperature of 15\degree C, it was found that the initial voltage on discharge was always between 1.52 and 1.58: therefore the selected parameters for the cell and battery design were thus far
consistent with the specification for the high rate
discharge. These test discharges of single plates were
initiated by pouring the electrolyte into the cell after
electrical connection had been made, this eliminated the
need for switching heavy currents (with all its attendant
problems) and indeed simulated the eventual battery
operating mode.

Typical discharges are shown in table 5 from
which it will be seen that significant variations in
the duration of the discharge from each side of the
positive plate were frequent. This was attributed to
small variations from symmetry in the arrangement
caused by the plates not being truly planar; the end
point of the discharge is brought about by passivation
but there is of course some convection which serves to
delay the onset of film formation. Even slight
variations in the gap between the tested positive plate
surface and the negatives would have a profound effect
on the convection process.
TABLE 5

<table>
<thead>
<tr>
<th>Discharge</th>
<th>Time in seconds for voltage to fall to 1.33</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Side A</td>
</tr>
<tr>
<td>1</td>
<td>175</td>
</tr>
<tr>
<td>2</td>
<td>170</td>
</tr>
<tr>
<td>3</td>
<td>150</td>
</tr>
<tr>
<td>4</td>
<td>140</td>
</tr>
<tr>
<td>5</td>
<td>150</td>
</tr>
<tr>
<td>6</td>
<td>145</td>
</tr>
</tbody>
</table>

Although the durations were much less than the 205 s. required in the final cell it will be realised that the specified performance is at a constant current corresponding to the current delivered by the single plate test cell at the end-point of the discharge. At the commencement of the tests the currents are much higher than the pro rata values because of the high initial voltage.

Prototype Cell Test

Two prototype cells were made using 23 positive and 24 negative plates and arrangements were made to discharge these at 750 A at 15°C. The method used to maintain such a large current constant is shown in Fig. 22. The cell under test a is connected in series with a variable resistor b and a large capacity battery c of
Fig. 22

Circuit used for discharging cells at constant current.
Fig. 22.
much higher voltage than the EMF of the test cell. Appropriate adjustment of the resistor then permits the current to be held at a predetermined value as the cell voltage gradually falls.

The cell was connected into the circuit and the discharge commenced immediately following addition of the electrolyte (1040 ml 55% v/v perchloric acid): the results of the two tests are entered in table 6.

**TABLE 6**

<table>
<thead>
<tr>
<th>Time Elapsed</th>
<th>Cell Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cell 1</td>
</tr>
<tr>
<td>Min. S.</td>
<td></td>
</tr>
<tr>
<td>0 0</td>
<td>2.04</td>
</tr>
<tr>
<td>0 2</td>
<td>1.54</td>
</tr>
<tr>
<td>0 5</td>
<td>1.54</td>
</tr>
<tr>
<td>0 10</td>
<td>1.54</td>
</tr>
<tr>
<td>0 15</td>
<td>1.52</td>
</tr>
<tr>
<td>0 30</td>
<td>1.50</td>
</tr>
<tr>
<td>1 0</td>
<td>1.48</td>
</tr>
<tr>
<td>1 30</td>
<td>1.47</td>
</tr>
<tr>
<td>2 0</td>
<td>1.47</td>
</tr>
<tr>
<td>2 30</td>
<td>1.46</td>
</tr>
<tr>
<td>3 0</td>
<td>1.43</td>
</tr>
<tr>
<td>3 30</td>
<td>1.41</td>
</tr>
<tr>
<td>4 0</td>
<td>1.37</td>
</tr>
<tr>
<td>4 18</td>
<td>1.33</td>
</tr>
</tbody>
</table>
It will be noted that both cells gave a considerable margin over the required duration at this rate of discharge; this was not thought to be excessive as the specification presupposes some period of storage before use and it was therefore desirable to have an in-built reserve of capacity in order to cope with any losses which might result from storage.

Although one expected the high rate performance to be the more demanding a further cell was tested at the 250 A rate, and the results are entered in table 7. The specified performance was again met with ample margin.

**Conclusion**

On the basis of the evidence accrued it was decided to plan a battery made up from twelve cells connected in series. Each cell would have 23 positive and 24 negative plates and would require 1040 ml of 55% v/v perchloric acid.
<table>
<thead>
<tr>
<th>Time Elapsed</th>
<th>Cell Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min. S.</td>
<td></td>
</tr>
<tr>
<td>0 0</td>
<td>2.04</td>
</tr>
<tr>
<td>0 5</td>
<td>1.74</td>
</tr>
<tr>
<td>2 0</td>
<td>1.74</td>
</tr>
<tr>
<td>4 0</td>
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<tr>
<td>10 0</td>
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<td>1.66</td>
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<td>14 30</td>
<td>1.65</td>
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<td>15 0</td>
<td>1.63</td>
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<td>1.58</td>
</tr>
<tr>
<td>17 0</td>
<td>1.54</td>
</tr>
<tr>
<td>17 20</td>
<td>1.50</td>
</tr>
</tbody>
</table>
CHAPTER VII
DISCHARGES IN FLUOBORIC AND FLUOSILICIC ACIDS

Introduction

Throughout the preliminary work on this project the explosion risk, when using perchloric acid in contact with organic materials, was constantly in mind and there was soon evidence forthcoming to show that this system could be very dangerous. In Chapter VIII this aspect of the overall investigation is dealt with in some detail but, before the chosen system was made safe, thought was given to possible electrolytes which would be intrinsically free from these hazards.

It was realised that it was unlikely that any other electrolyte would permit a cell performance comparable with that obtained with perchloric acid, on account of the outstanding solubility of lead perchlorate. The lead salts of fluoboric and fluosilicic acids were known to be very soluble however and it was decided to test these acids, in various concentrations, in order to establish whether or not one or other could be used instead of perchloric acid without a serious reduction in the electrical output of the cell. Cells based on the lead/lead dioxide couple and using fluoboric acid as electrolyte, have found use in more than one field; nothing closely comparable with this present requirement has yet been met by this system however.
Experimental Results

Using the single plate test equipment described in the last chapter and illustrated in Fig. 21 a number of tests were made on standard positive plates discharging in fluoboric and fluosilicic acids of various concentrations. Most of the experimental discharges were made in the cell having an 0.34 cm. electrode spacing, a few however were carried out in the larger cells: in all these tests the currents were maintained constant using a large battery and series resistor as described in Chapter VI.

In table 8 are shown the results of discharging plates in fluoboric acid of varying concentrations using a range of current densities: these figures are also displayed graphically in Fig. 23.

In table 9 are shown similar results from discharges carried out in fluosilicic acid over a range of concentrations and current densities: the graphs based on these figures are in Fig. 24.

It will be remarked that, at the higher current densities, the curves of output (in Ah) against acid concentration pass through maxima: the relevant figures are entered in table 10. It is of interest to speculate on the reason for this general effect and this will be discussed later.
Fig. 23

Single plate discharges in HBF$_4$ at various constant currents and electrolyte concentrations.
Fig. 23.

Graph showing data with markers and curves labeled 6A, 9A, 12A, 15A, 20A, and 30A.
Fig. 24

Single plate discharges in H$_2$SiF$_6$ at various constant currents and electrolyte concentrations.
Fig. 24.
A few discharges were made using the two larger test cells and the results of these experiments are entered in tables 11 and 12 in the case of fluoboric acid and 13 and 14 for fluosilicic acid.

Discussion

In assessing the potentialities of these two acids, as electrolytes for batteries to meet the specification, the difficulties stem from the number of variables involved. Volume, weight, current, ampere hours have all to be reconciled with each other and with the minimum design requirements. Some simplification results from concentrating on the high rate requirement of 750A for 3.25 min., to a final voltage of 16, equal to 40.6 Ah.

Inspection of table 10 enables us to make trial calculations as follows:

At 15A per positive plate in fluoboric acid of concentration 6.7 mols./l the capacity per plate is 2.5 Ah. Fifty plates would be necessary to yield the 750A discharge current but the capacity of the cell would be 125 Ah or three times the requirement. The initial voltage of 1.52 would be satisfactory for the twelve cell battery but each cell would be more than twice as large as the provisional design based on perchloric acid.
At 20 A per plate the capacity of 1.85 Ah per plate is again more than adequate but 38 plates would be necessary for each cell and, though a twelve cell battery would meet the initial voltage requirement the margin would be small.

At 30 A per plate only 25 plates per cell would be necessary but the capacity at 38.75 Ah (25 x 1.55) is inadequate. Moreover the initial voltage at 1.44 would involve the use of 13 cells in order to meet the initial battery voltage of 18 specified for the 750 A rate of discharge.

It will be seen from table 10 that, although the initial voltages using fluosilicic acid are somewhat higher than with fluoboric, the difference is not sufficient to offset the further reduction in capacity.

**Conclusion**

It was decided that, in view of the disappointing but not unexpected performances with fluoboric and fluosilicic acid electrolytes, efforts should be made to reduce the risks associated with the use of perchloric acid electrolyte. It was considered that any alternative course could only be pursued if very significant relaxation in the specification could be tolerated; at this stage such a request would have been premature.
TABLE 8

Capacity (amp. hours) and Initial Voltages for Single Plate Discharges in Fluoboric Acid

<table>
<thead>
<tr>
<th>Fluoboric Acid Concentration (mols./l.)</th>
<th>Current in Amperes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>I.V.</td>
</tr>
<tr>
<td>3.45</td>
<td>1.575</td>
</tr>
<tr>
<td></td>
<td>1.55</td>
</tr>
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<td></td>
<td>1.525</td>
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</tr>
<tr>
<td></td>
<td>1.455</td>
</tr>
<tr>
<td></td>
<td>1.425</td>
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</table>
# TABLE 9

Capacity (amp. hours) and Initial Voltages for Single Plate Discharges in Fluosilicic Acid

<table>
<thead>
<tr>
<th>Fluosilicic Acid Concentration (mols./l)</th>
<th>Current in Amperes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6</td>
</tr>
<tr>
<td>2.09 I.V.</td>
<td>1.63</td>
</tr>
<tr>
<td>2.93 A.H.</td>
<td>2.10</td>
</tr>
<tr>
<td>2.93 I.V.</td>
<td>1.63</td>
</tr>
<tr>
<td>2.93 A.H.</td>
<td>2.65</td>
</tr>
<tr>
<td>3.60 I.V.</td>
<td>1.68</td>
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<tr>
<td>3.60 A.H.</td>
<td>3.15</td>
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<tr>
<td>4.53 I.V.</td>
<td>1.70</td>
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<tr>
<td>4.53 A.H.</td>
<td>3.80</td>
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</table>

- 72 -
TABLE 10
Values of Capacity, Initial Voltage and Acid Concentration at the Maxima of the Curves in Figs. 23 and 24

<table>
<thead>
<tr>
<th>Current (A)</th>
<th>Fluoboric Acid</th>
<th>Fluosilicic</th>
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<tbody>
<tr>
<td></td>
<td>AH</td>
<td>Volts</td>
</tr>
<tr>
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<td>1.52</td>
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<td>1.51</td>
</tr>
<tr>
<td>30</td>
<td>1.55</td>
<td>1.44</td>
</tr>
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</table>
TABLE 11

Discharges in Fluoboric Acid with Auxiliary Electrodes spaced at 0.58 cm. (85 ml. electrolyte)

<table>
<thead>
<tr>
<th>Fluoboric Acid Concentration (mols./l)</th>
<th>Current in Amperes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>I.V.</td>
</tr>
<tr>
<td>3.45</td>
<td>1.52</td>
</tr>
<tr>
<td></td>
<td>2.1</td>
</tr>
<tr>
<td>4.01</td>
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<td></td>
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<td></td>
<td>2.9</td>
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<tr>
<td>6.09</td>
<td>1.56</td>
</tr>
<tr>
<td></td>
<td>3.4</td>
</tr>
</tbody>
</table>
### TABLE 12

**Discharges in Fluoboric Acid with Auxiliary Electrodes spaced at 1.19 cm. (150 ml. electrolyte)**

<table>
<thead>
<tr>
<th>Fluoboric Acid Concentration (mols./l)</th>
<th>Current in Amperes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>9</td>
</tr>
<tr>
<td>3.45</td>
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<tr>
<td>I.V.</td>
<td>1.55</td>
</tr>
<tr>
<td>A.H.</td>
<td>4.12</td>
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<tr>
<td>4.01</td>
<td></td>
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<tr>
<td>A.H.</td>
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<td>1.55</td>
</tr>
<tr>
<td>A.H.</td>
<td>4.35</td>
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<tr>
<td>6.09</td>
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<tr>
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<td>8.37</td>
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<td>I.V.</td>
<td>-</td>
</tr>
<tr>
<td>A.H.</td>
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</tr>
</tbody>
</table>
TABLE 13

Discharges in Fluosilicic Acid with Auxiliary Electrodes spaced at 0.58 cm. (85 ml. electrolyte)

<table>
<thead>
<tr>
<th>Fluosilicic Acid Concentration (mols./l)</th>
<th>Current in Amperes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<tr>
<td>I.V.</td>
<td>1.53</td>
</tr>
<tr>
<td>A.H.</td>
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</tr>
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</tr>
<tr>
<td>A.H.</td>
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</tr>
<tr>
<td>I.V.</td>
<td>1.57</td>
</tr>
<tr>
<td>A.H.</td>
<td>1.9</td>
</tr>
<tr>
<td>I.V.</td>
<td>1.58</td>
</tr>
<tr>
<td>A.H.</td>
<td>2.6</td>
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</table>
**TABLE 14**

Discharges in Fluosilicic Acid with Auxiliary Electrodes spaced at 1.19 cm. (150 ml. electrolyte)

<table>
<thead>
<tr>
<th>Fluosilicic Acid Concentration (mols./l)</th>
<th>Current in Amperes</th>
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</thead>
<tbody>
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<td>1.88 I.V.</td>
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<td>1.51</td>
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</tr>
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</tr>
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<td>0.75</td>
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</table>
Further Discussion

The maxima shown by the curves relating to the higher current densities in Figs. 23 and 24 may be explained as follows:-

(1) Although the vertical attitude of the electrodes in these single plate test cells permits some convection, at sufficiently high current densities the discharge will be terminated by the formation of a passive film of reaction product.

(2) The greater the acid concentration the less will be the solubility of the reaction product.

(3) Since the capacity is measured by the time taken, at a fixed current, to reach an arbitrary final voltage, the high resistivity of dilute electrolytes will tend to restrict the discharge.

Considering these three factors we should expect the measured capacity at a given current, to increase with increasing electrolyte concentration until the advantages of reducing resistivity were overtaken by the declining solubility of the reaction product. Increasing the current would merely displace the curve downwards as is seen in Figs. 23 and 24.
Using greater electrode separations, and incidentally more electrolyte, permits much freer convection and thus delays the onset of passivation. One would therefore anticipate that the general shape of the curves would be the same but that, at any given current and electrolyte concentration, capacities would increase with electrode separation. An inspection of tables 11, 12, 13 and 14 reveals that this is generally so and in Fig. 25 typical results have been plotted for fluoboric acid electrolyte at the 30 A. rate of discharge for the three separations. In the case of fluosilicic acid at the 30 A. rate passivation occurs so rapidly that the convection process has little modifying effect.
Fig. 25

Curves illustrating discharge performance of single plates in HBF$_4$ at various concentrations and electrode separations.
**Fig. 25.**

Graph showing the relationship between capacity ($C_{IH}$) and $[HBF_4]$ concentration ($\text{mols./L.}$) for different electrode spacings. The spacings are labeled as follows:

- 0.34 cm.
- 0.58 cm.
- 1.19 cm.

The graph demonstrates a peak capacity at a specific concentration for each spacing, with the capacity decreasing as the concentration increases or decreases from the peak point.
CHAPTER VIII. THE STABILITY OF POSITIVE PLATES WHEN IMMERSED IN 55% PERCHLORIC ACID

Introduction

Casual observation showed that if positive plates, made by electrodeposition lead dioxide onto nickel sheet, were immersed in 55% w/v perchloric acid, after the lapse of a few hours flakes of lead dioxide began to detach themselves from the substrate metal. It was noted that the process became more rapid at higher temperatures though this was a general observation as the onset of the shedding mechanism differed markedly in time from plate to plate.

One of the earliest batteries, assembled from cells embodying these plates, exploded a few hours after accidental priming with electrolyte. Initially it was not easy to suggest a reason but, on observing the propensity of positive active material to "spall" under these conditions, a ready explanation for the explosion was forthcoming. The flakes of dioxide are large enough effectively to bridge the small gap between adjacent positive and negative plates, an electronic conductor is thereby established and the cell begins to discharge. The temperature rises and further short circuiting current paths are formed until, in the final stage, boiling and sometimes ignition with explosion occurs.
A programme of work was therefore designed aimed at determining the factors which could influence the reaction of positive plates with electrolyte.

**Experimental Programme**

The first essential, to work aimed at elucidating the important factors influencing the production of "good" plates, was to devise a test for measuring the quality of a plate in terms of resistance to immersion in perchloric acid electrolyte.

As it had been noted that warm acid caused a more rapid shedding of the dioxide layer the use of 60% w/v acid at 60°C was decided upon as the standard medium for conducting these accelerated tests. The specimen, consisting of a positive plate as shown in Fig. 26, was suspended by the take-off lug from an acid resistant cover to a container of acid maintained at 60°C in a thermostat. At intervals samples of acid were withdrawn for lead ion determinations and the potential of the electrode with reference to a small lead wire, partially immersed in the acid, was measured continuously.

The results of a typical test are shown graphically in Fig. 27. It will be seen that both the lead ion concentration and the potential-difference measurement provide a reliable guide to the end of the stability period.
Positive plate profile
Fig. 27

Curves displaying onset of "instability" of positive plates immersed in HClO$_4$. 
Fig. 27
It was then decided that the effect of varying the conditions during positive plate formation should be investigated, using the single plate stability test as described, to determine the sensitivity of the "stability period" with respect to various parameters, these are given in the list below:-

(a) Method and degree of etching of nickel blanks prior to electrodeposition of lead dioxide.
(b) Current density for deposition.
(c) Temperature of electrodeposition bath.
(d) Acidity of bath.
(e) Presence of suspended matter in the electrodeposition solution.

The examination of solutions varying with respect to suspended solids was decided upon as a result of a qualitative observation that plates seemed less stable when produced in solutions clouded by suspended lead carbonate particles (from the neutralising stack).

**Experimental Results**

At the time of starting this particular investigation the plates were all being produced from nickel blanks measuring 14.2 cm. x 6.4 cm. electrolytically etched in sulphuric acid (sp.gr. 1.250) containing 20% by weight of sodium dichromate and using an alternating current of 6 amperes for 10 minutes.
After washing the blanks were immersed in a solution of lead perchlorate (1.55 - 1.60 sp.gr.) at a temperature of 45°C and containing free perchloric acid in the range 0.2 to 0.4 M. A current of 6 amperes was then passed for 1 hour to give a deposit of lead dioxide weighing 26.4 g. approximately.

a) Varying etch procedures

A set of eighteen plates was made in three groups of six. The first group was standard, the second was etched in sulphuric acid free from sodium dichromate and the third was etched in 1.250 sp.gr. sulphuric acid which, having been used many times, was rich in nickel ions. The results are entered in table 15 and it will be seen that the plates were similar in respect of stability performance irrespective of the etching procedure.
The "old" etchant used for the specimens in Group 3 was liquor which would normally have been discarded on account of the low acidity, due to more than half the H⁺ having been replaced by Ni²⁺.
Supplementary tests showed that, using the standard etch method (Group (1)), the stability period of the plates was not influenced by varying the etching time between 5 and 30 minutes.

b) **Filtered plating electrolytes**

It was observed that plates made in baths using electrolyte which was continuously filtered through ceramic candles, were much more resistant than those from baths containing suspended particles. Because of this observation all the remaining work was carried out using solutions so filtered; the magnitude of the effect is shown in table 16.

c) **Varying Current Density**

A set of ten plates was prepared using standard conditions (filtered electrolyte) except that the current was varied in the range 1.5 to 9.0 A. In each case 6.0 Ah were used to "form" the positive plate.

The results of the stability tests on these plates are entered in table 16 and shown graphically in Fig. 28 and it will be seen that the stability of the plate is sensitive to current density and that in reducing the current from 9.0 A to 1.5 A the stability period is about doubled.
Fig. 28

Positive plate stability as a function of PbO$_2$ electrodeposition current.
Fig. 28.
d) Varying Bath Temperature

Ten plates were prepared under conditions which were standard in all respects except that the temperature was varied in the range 15°C to 60°C. The results of stability tests are entered in table 17 and a graph of these appears in Fig. 29. The great influence of bath temperature on stability can be seen.
Fig. 29

Positive plate stability as a function of electrodeposition bath temperature.
Fig. 29.
### Table 17

<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>1</td>
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</tr>
<tr>
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<td>27</td>
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<tr>
<td>3</td>
<td>38</td>
<td>10.4</td>
</tr>
<tr>
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<td>49</td>
<td>12.2</td>
</tr>
<tr>
<td>5</td>
<td>60</td>
<td>14.0</td>
</tr>
</tbody>
</table>

#### e) Varying Bath Acidity

The acidity of the lead perchlorate electroplating solution can be controlled by controlling the rate of circulation of the electrolyte through the neutralising tower. The acid generated during the plating process stabilizes at a concentration level roughly proportional to the reciprocal of the circulation rate.

Eight plates were prepared in baths ranging in perchloric acid content from 0.2 M to 0.8 M.
The results of stability tests on these plates are entered in table 18; there is no apparent relationship between stability and acidity.

**TABLE 18**

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Concentration of Acid in solution/M</th>
<th>Stability Period/hr.</th>
</tr>
</thead>
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<td>1</td>
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<td>11.5</td>
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<tr>
<td>2</td>
<td>0.2</td>
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</tr>
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<td>0.4</td>
<td>9.7</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.6</td>
<td>8.7</td>
</tr>
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<td>6</td>
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<tr>
<td>8</td>
<td></td>
<td>11.0</td>
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</tbody>
</table>

**Conclusion**

It was clear from these results that substantial improvements in the intrinsic quality of the plates could be made by comparatively simple changes in process. It was therefore decided to alter the electroplating conditions by:

(a) Raising the bath temperature to 60°C.

(b) Filtering continuously the liquor after neutralisation.

(c) Reducing the size of the cathodes so that they were smaller in height and width than the positive plate blanks.
Two points need explanation. Firstly the current density was not reduced from 6A. per plate because, although this would have resulted in some further gain in stability, it was thought that sufficient had been gained to permit us to omit a step which would have slowed down the output from each plating plant materially.

Secondly during the tests on single plate stability it was observed that flaking usually began at the plate edges where the deposit of lead dioxide was thicker due to locally higher current densities. By reducing the size of the auxiliary electrodes in the plating bath this was avoided. It is noteworthy that this improvement was achieved at no additional cost.

Three tests carried out on plates made by this modified process all gave stability periods in excess of 24 hours, it was therefore decided to make a number of full size cells and carry out comparative tests on these.
Briefly the stability of standard cells, when primed with 55% perchloric acid and held at 60°C, was such that rapid temperature rise could be anticipated at any time after five hours, it was always necessary to terminate the test within eight hours to avoid the possibility of a rapid reaction which might lead to an ignition.

Using the modified process (but allowing the plating bath temperature to vary between 48°C and 60°C) the stability of full size cells was markedly improved as shown below (table 19).

**TABLE 19**

<table>
<thead>
<tr>
<th>Temperature of bath (°C)</th>
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<th>52</th>
<th>54</th>
<th>60</th>
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<tbody>
<tr>
<td>Cell stability (hours)</td>
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<td>13.1</td>
<td>14.5</td>
<td>13.0</td>
<td>19.5</td>
</tr>
<tr>
<td></td>
<td>13.2</td>
<td></td>
<td></td>
<td></td>
<td>23.0</td>
</tr>
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<td></td>
<td>16.5</td>
<td></td>
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</tr>
</tbody>
</table>

**Recommendation**

Following on this work it was decided that all the process modifications detailed above be introduced and, in particular, that the temperature of the plating liquor be maintained accurately at 60°C.
Additional Studies on Stabilisation using Sulphate Additions

It is well established that the addition of ions to corroding systems often reduces the rate of corrosion if the added ion is able to form an insoluble film at points of attack. In the present study in order to reduce the corrosion which doubtless begins at pores in the lead dioxide film it was considered that some ion should be added which is able to produce an insoluble compound of lead. Lead sulphate provides an ideal material for mechanical corrosion protection because of its great insolubility and its very high specific resistance.

Experimental

Experiments were made in which sulphuric acid (1%) was added to an electrolyte of primed cells and the whole cell maintained at a temperature of 60°C. The results were surprisingly good. The time the cells were able to stand on test without any pronounced reaction due to excessive corrosion occurring was increased markedly and in some cases indefinitely. Capacity tests on cells containing sulphuric acid additions showed that the effect of the sulphate was both fundamental and important. Both positive and negative plates were found to be adversely affected in as much as the on-load
potential of both plates (against a reference electrode) were markedly reduced in such a way that capacity requirements referred to in earlier chapters could not be fulfilled. It is likely that the same process which retarded the rate of the corrosion reaction retarded the discharge process, that is by the formation of an insoluble film of lead sulphate at both electrodes.

In view of the very beneficial action of the sulphate ion experiments were made in which at the bottom of the cell container small amounts of sodium sulphate and sodium carbonate (60g. 50/50 mixture) protected by a film of Cellophane (nitrocellulose film) were disposed. The time taken for the acid to destroy the nitrocellulose covering was somewhat greater than the time the cell would normally be required to operate. The process envisaged by the above arrangement was as follows. Some minutes after priming, the acid penetrates the nitrocellulose and the stirring caused by the \( \text{CO}_2 \) evolution results in the rapid dissolution of the sodium sulphate in the perchloric acid electrolyte, hence if a cell is primed accidentally the stabilising influence of the sulphate ion comes into operation protecting against corrosion failure. When the cell operates under normal conditions the discharge is completed at higher rates and practically completed (greater than 80%) in the case of lower rates before the
sulphate is released. It is noteworthy that at the lower rates the effect of sulphate ion on discharge behaviour was not so pronounced as at higher rates, thus confirming that the effect of sulphate was via the high resistance film of insoluble material at the electrodes.

**Practical Implications**

The results recorded above provided the basis for the design and manufacture of inhibitor cartridges which were fitted into the bottom of all the early production cells. Subsequently the improved plate quality permitted this practice to be discontinued; the additional volume of acid thereby accommodated was beneficial in as much as it resulted in a small increase in capacity.
CHAPTER IX

FINAL CELL DESIGN AND PERFORMANCE
OF PRODUCTION UNITS

Introduction

Considerations of the results of the work described in Chapters V, VI and VIII, together with the performance required from the battery as specified by the Ministry from whom the original demand came, lead to a final design based on the following salient features:

(i) The plates were made to the profile shown in Fig. 26.

(ii) The element was based on 23 positive and 24 negative plates.

(iii) The positive plates were produced by the deposition of lead dioxide (equivalent to 6 Ah) on etched nickel blanks.

(iv) The negative plates were blanked out from sheets of rolled calcium/lead alloy containing 0.08 - 0.09% Ca.

(v) The electrolyte consisted of 1040 ml. of 55% w/v perchloric acid.

(vi) The plates of each group (positive and negative) were pitched at 0.34 cm. centres.

(vii) The cell containers were made of hard rubber 0.15 cm. wall thickness.

(viii) The upper acid containers were made of general purpose (GP) polystyrene of wall thickness 0.1 cm.

(ix) The battery comprised twelve cells arranged in two contiguous rows of six.

- 94 -
The cells were assembled in a light sheet steel frame and were secured in position by a cover which also carried a complicated priming mechanism. Priming was effected by a simultaneous release of twelve spring loaded bolts which quickly and cleanly pierced the bottom of the acid containers permitting a rapid entry of electrolyte into the cell.

**Cell Performance**

**Electrical Capacity**

As the batteries were designed for dry storage, priming only immediately before use, it was essential to sample the product frequently in order accurately to monitor production quality and thus ensure a minimal failure rate in service. During a representative year of production capacity tests were made on 222 cells, a sampling rate of 10%. Although this figure was high it was thought necessary at the outset in order to obtain a reliable estimate of the variations in product quality and thereby a measure of the probability of any battery being sub-standard.

Of the cells tested 178 were tested at the high rate by connecting to a resistance of 0.00178 ohms and initiating the discharge by filling the acid reservoir, with 1040 ml electrolyte, and firing a bolt (similar to
those fitted to the battery cover): the value of the resistance was chosen to give a current of 750A at a cell voltage of 1.33. The remaining 44 cells were tested at the low rate using a resistance calculated to pass 250A at the cut off voltage of 1.50, (i.e. the minimum current was 250A). The results are shown as histograms in Figs. 30 and 31 and the mean values and standard deviations of the two sets of results are respectively:

- 750A discharge
  \[ \bar{x} = 4.051 \text{ min.} \]
  \[ \sigma = 0.194 \text{ min.} \]

- 250A discharge
  \[ \bar{x} = 17.480 \text{ min.} \]
  \[ \sigma = 0.625 \text{ min.} \]

The quantities \( \bar{x} \) and \( \sigma \) are respectively the best estimates of the mean and standard deviation computed from the data (n observations) as follows:

\[
\bar{x} = \frac{\sum x}{n}
\]

\[
\sigma = \sqrt{\frac{\sum (x - \bar{x})^2}{n-1}}
\]

These two statistics uniquely determine the equation to the normal Gaussian distribution curve and, for errors so distributed, divergences from the mean of \( \pm \sigma \), \( \pm 2\sigma \) and \( \pm 3\sigma \) have associated probabilities of occurrence of 0.32, 0.045 and 0.0026. It follows that the probability of an error of known sign is half that of the corresponding figure for the absolute value of that error.
Fig. 30

Histogram of high rate capacities of production cells.
Figure 30.

Frequency

Duration of DISCHARGE (Mins.)
Fig. 31

Histogram of low rate capacities of production cells.
Fig. 31.

**Duration of Discharge, (Mins.)**

<table>
<thead>
<tr>
<th>Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>10</td>
</tr>
</tbody>
</table>
These results were considered to be very satisfactory as, not only was the variation about the mean reasonable, the actual level of performance was such as to provide a margin over the specified figure which was probably adequate for any foreseeable contingency. The doubt implicit in this statement stems from the need for the batteries to meet specification after, possibly, years of storage.

The specification calls for a duration of discharge at the 750 A rate of 3.25 mins. that is to say 0.801 mins. less than the mean value of the test result. As this discrepancy is over 4 times the standard deviation it follows that cells only very rarely will fail to meet the requirement (less than one in ten thousand assuming a normal distribution).

Stability

The batteries were eventually required to meet a stability test which was defined by the Ministry as follows:

The cell held at 60°C must be filled with electrolyte at that temperature and maintained in a suitable ambience at 60°C; the rise in cell temperature during the succeeding eight hours must not exceed 20°C.
During the year under review a total of 163 production cells were tested in this way: of these six failed to meet specification as the temperature had reached the end point after:

- 6 hrs. 16 mins.
- 6 hrs. 40 mins.
- 7 hrs. 10 mins.
- 7 hrs. 10 mins.
- 7 hrs. 15 mins.
- 7 hrs. 15 mins.

Of the remainder the lowest recorded stability period was 9 hrs. 20 mins. and the highest 108 hours. Usually the test was discontinued after 16 or 24 hours frequently without any rise in temperature having been observed.

The cells for stability test were made from plates produced in one production batch, a failure of a cell on this test resulted in the batch being scrapped. In spite of this severe approach to quality the plant performance was very satisfactory.

Storage

It is not as yet possible to specify the performance required from these batteries after storage because not enough is known of the behaviour with time of such units under conditions of dry inactivity. In addition it would be desirable to have the freedom to store for periods as long as ten years or even longer if performance were not thereby severely impaired.
It was therefore agreed by the Ministry that batteries should be tested at intervals after storage under dry temperate conditions whilst sealed in large polyethylene bags.

The first three batteries so examined were taken from store after 2½ years and two were tested at the 750A rate and one at the lower rate. The results are entered in table 20 together with the specified performances.

**TABLE 20**

<table>
<thead>
<tr>
<th></th>
<th>Cell 1</th>
<th>Cell 2</th>
<th>Cell 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discharge current</td>
<td>750A</td>
<td>750A</td>
<td>250A</td>
</tr>
<tr>
<td>Initial voltage</td>
<td>1.52</td>
<td>1.54</td>
<td>1.72</td>
</tr>
<tr>
<td>Specified initial voltage</td>
<td>1.50</td>
<td>1.50</td>
<td>1.67</td>
</tr>
<tr>
<td>Duration</td>
<td>3.73 min.</td>
<td>4.09 min.</td>
<td>19.95 min.</td>
</tr>
<tr>
<td>Specified Duration</td>
<td>3.25 min.</td>
<td>3.25 min.</td>
<td>16.0 min.</td>
</tr>
</tbody>
</table>

It will be noted that there was no detectable change in performance following on the storage period (having regard to the statistics quoted earlier) in fact the performance of cell 3 was so good as to be extraordinary.
Conclusion

At this point it could fairly be said that, following on laboratory work and pilot plant operation, a production process and battery design had been achieved which met the specification on all points. In due time, and with the increasing knowledge and experience of battery behaviour in service, it is conceivable that the specification may be tightened or extended.
CHAPTER X
CONTINUING WORK PROGRAMME

Introduction

In most research and development programmes the upward progress is punctuated by the occasional plateau which permits an appraisal to be made: it is at these times that the course of the project may be reshaped and, on occasion, profitable use made of the work thus far completed. In the present case such a position has been reached and eminently satisfactory batteries are being produced in a small factory, further work must now be undertaken however as indicated briefly below.

Plate Production

Positive Plates
Continuing production of stress free (and therefore flat) positive plates, which are of more than satisfactory quality in respect of electrical performance and stability, demonstrates the essential soundness of the preparatory work. There is an outstanding problem however and this lies in the brittle nature of the deposited lead dioxide layer. Of necessity the plates are handled many times between production and assembly into cells and some are damaged and perforce scrapped. The proportion of plates so discarded is too high; the principal cause of rejection is exposure of small areas of the bare nickel due to small pieces of the brittle coating becoming dislodged when the sheet is inadvertently flexed.
It has been observed that the susceptibility of plates to loss of flakes of lead dioxide in this way is very variable. Inadequate etching prior to plating is an established cause of poor adhesion which leads to high scrap rates. There are however undoubtedly other important factors as yet unidentified and, it is now proposed to undertake their elucidation.

The programme of work is not at this time definite but the following stages are of primary importance:

(i) Establish methods for measuring the strength of the adhesion of the lead dioxide layer to the substrate.

(ii) Establish methods for measuring the flexibility of the deposit.

(iii) Develop means for masking, for example by the use of inert varnishes, the defective areas on the plates.

Negative Plates
It had been considered that the negative plates were uncomplicated and, provided that they were clean, no problems need be expected. In the event a peculiar effect was observed in service.

Although the battery was not designed for low temperature operation some trials were made at a temperature of 0°C; it was found that the voltage developed too slowly as the electrolyte poured into the cells on releasing the priming mechanism.
Replacing the negatives (of lead/calcium alloy sheet) by lead plated nickel of the original design eliminated the trouble.

The punching of negative plates from lead alloy sheet had obvious advantages and some tests were carried out to determine how such plates could be made to respond as quickly (on priming the cells) as the original type. In the table below is a summary of the results of the first exploratory experiments.

<table>
<thead>
<tr>
<th>Cell No.</th>
<th>Treatment of negative plates</th>
<th>Cell Voltage on 750A discharge at various times after priming (seconds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Degreased in trichlorethylene</td>
<td>0.23  1.10  1.43</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>0.37  1.18  1.48</td>
</tr>
<tr>
<td>3</td>
<td>Wire brushed under trichlorethylene</td>
<td>0.50  1.35  1.55</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>0.39  1.20  1.47</td>
</tr>
<tr>
<td>5</td>
<td>As above and then cathodically degreased</td>
<td>0.25  1.16  1.50</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>0.40  1.31  1.52</td>
</tr>
<tr>
<td>7</td>
<td>As above then etched in HNO₃(2 mols/l)</td>
<td>0.45  1.31  1.52</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>0.42  1.31  1.52</td>
</tr>
<tr>
<td>9</td>
<td>Degreased then &quot;flashed&quot; in lead plating bath.</td>
<td>0.50  1.31  1.51</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>0.47  1.31  1.52</td>
</tr>
</tbody>
</table>
A few batteries have been made using negative plates of sheet Pb/Ca alloy which had been "flashed" and these have responded quickly after cold priming.

It appears that the surface of the calcium/lead alloy is such that it significantly increases some component of the polarisation at the negative plate; this subject must receive further study.

**Cell Design**

Naturally there remains a wish to use some electrolyte in these cells which is intrinsically safer than perchloric acid.

It is thought that fluoboric acid at a temperature appreciably in excess of 15°C might prove satisfactory in so far as the cells would then meet the performance specified. Work is to be begun with the dual aims of determining the acceptable working temperature and of developing suitable methods of heating the electrolyte prior to priming.

**Diffusion Coefficients**

The work on diffusion of electrolytes has generated interest in this matter per se and some thought has been given to a rapid method of measuring the diffusion coefficient of ions which can be electrodeposited. The practical importance of such measurements in battery technology is widely appreciated and indeed the discussions in Chapter V indicate this very clearly.
It is proposed to use an apparatus as shown in Fig. 32 where A is an electrode of copper at the base of a short parallel sided tube B. The whole of B and the surrounding vessel C is filled with copper sulphate solution at a concentration of about 0.1 mol/l.

Using the circuitry shown a current of the order of $10^{-2} \text{ A/cm}^2$ is passed and the potential difference between electrodes A and D followed. A sharp break in the volts x time curve is to be expected when the copper ion concentration at the surface of electrode A reaches zero. At this point we have from equation (25):

$$t = \frac{\pi C^2 F^2 D}{4I^2}$$

If C is of the order of $10^{-4}$ (mols/ml), D about $10^{-5}$ and I about $10^{-2}$, then $t$ will approximate to 10 seconds.

A series of determinations may be made rapidly by stirring the solution after each experiment.
Fig. 32

Proposed apparatus for rapid measurement of D for electro-depositing ions.
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APPENDIX
PUBLISHED WORK

A number of published papers are submitted in addition to the work already described. These are set out in the table below:--

1. C.J. Bushrod and N.A. Hampson, 'The Anodic Electrodeposition of PbO,

2. C.J. Bushrod and N.A. Hampson, 'Anodic Behaviour of Lead in Perchloric Acid

3. C.J. Bushrod and N.A. Hampson, 'Stress in Anodically Formed Lead Dioxide',


5. C.J. Bushrod and N.A. Hampson, 'The Anodic Behaviour of Zinc in KOH Solution.
In addition to the papers 1, 2 and 3 two other contributions arose directly from discussions during the development of the presently described research and from general discussions during the study period (1967-1973).

4. "The Differential Capacitance of Polycrystalline Antimony in Aqueous Solution"

Although much data exists on the double layer structure at lead electrodes published work on antimony is scarce. The use of lead antimony alloys for battery grids is now generally accepted practice since it enables strength, conductivity, castability, creep resistance and many other favourable properties to be conferred on the finished battery plate. In addition however, certain undesirable properties arise and one of these is the process by which antimony is lost from the alloy in the form of stibine. This occurs when the metal is in a state of high negative polarisation and causes much concern due to its effect on personnel (submarine operation): much argument has been conducted in technological circles in order to try to settle the mechanism by which stibine is produced from the alloy.
5. 'The Anodic Behaviour of Zinc in KOH Solution. 

V; Galvanostatic polarization with an interruption'

It was realised from the mathematical treatment outlined in Chapter V that equations describing the incremented passivation time experiments could only apply to a situation which was completely dominated by diffusion in solution. Conversely it followed that if the system conformed mathematically to this equation then diffusion in solution must be the rate controlling process for the passivation. Therefore, a decision as to whether a passivation process was caused first by a diffusion process, followed by a back precipitation (as discussed by Muller), or whether a solid film built up on the electrode surface from the time of switching on the current could be made. Battery technology, in connection with the silver oxide zinc cell, had been perplexed by the question of whether precipitation diffusion or diffusion precipitation was responsible for terminating the growth of zinc oxide on a discharged (passivated) zinc negative electrode in alkali. The equation of Chapter V was applied to the zinc electrode in KOH solution in order to show that a solution precipitation process is the mode by which zinc anodes become passive. The experimental data was provided in part by a number of students of the Chemistry Department of the University using apparatus and circuits designed by the author.
Discussion highlighted the fact that there was no data whatsoever on the evolution of stibine from antimony itself. Consequently it was decided to investigate the double layer structure of polycrystalline antimony in aqueous solution in order to provide some background data. The work was undertaken in part by the author and in part by M.A. Goulden working in the laboratories at Loughborough. This work was extended at a later date by Carr and Calvert to lead antimony alloys and it is intended that in subsequent years the work will continue so that the specific effects of antimony on the lead/lead sulphate exchange reaction in sulphuric acid can be assessed.

Recently a further factor has emerged in connection with the use of more dilute alloys (antimony below 6%) where it is found that the adhesion of lead dioxide material to such alloys is extremely bad. It is hoped that these continuing studies will also provide data in this area.
THE DIFFERENTIAL CAPACITANCE OF POLYCRYSTALLINE ANTIMONY IN AQUEOUS SOLUTION

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(Received 7th August 1970)

INTRODUCTION

The structures of certain electrode/electrolyte interphases have been correlated with the properties of the electrode materials. It is clearly desirable to extend our knowledge to all types of electrode. Data have been slowly accumulating as a result of many investigations. However, there still exists a number of metals for which data are lacking. Antimony may be included among these.

Wu and Lin have reported differential capacitance results for antimony in 0.01 N HCl. Using an a.c. bridge method, at frequencies 1000–5000 Hz, they estimate the p.z.c. to be $-0.19 \pm 0.02$ V (NHE), which corresponded to a deep minimum in the $C_L$ vs. $E$ curve. Alekseeva et al. have also studied the differential capacitance of antimony–gallium alloys in a eutectic LiCl/KCl melt. At a frequency of 50 Hz, for antimony, a capacitance minimum of 30 $\mu$F cm$^{-2}$ at $-0.18$ V was observed.

The antimony/aqueous solution interphase is complicated by oxide (or hydroxide) films under conditions of high pH, and even in acid solutions oxide films may be present at positive potentials. The following reactions are known to occur in acid solutions:

\[
\begin{align*}
\text{Reaction} & \quad E^0 \\
\text{SbH}_3 (g) & \rightarrow \text{Sb} + 3 \text{H}^+ + 3 e & -0.51 \text{ V} \\
2 \text{Sb} + 3 \text{H}_2\text{O} & \rightarrow \text{Sb}_2\text{O}_3 + 6 \text{H}^+ + 6 e & +0.152 \text{ V} \\
\text{Sb}_2\text{O}_4 + \text{H}_2\text{O} & \rightarrow \text{Sb}_2\text{O}_5 + 2 \text{H}^+ + 2 e & +0.479 \text{ V} \\
2 \text{SbO}^+ + 3 \text{H}_2\text{O} & \rightarrow \text{Sb}_2\text{O}_5 + 6 \text{H}^+ + 4 e & +0.581 \text{ V}
\end{align*}
\]

It is therefore clear that the antimony/aqueous solution interphase may be studied in a small range of potential around 0.0 V (NHE).

In this paper differential capacitance results are presented for polycrystalline antimony in aqueous HNO$_3$, H$_2$SO$_4$ and H$_3$PO$_4$ electrolytes.

EXPERIMENTAL

Electrical circuit

The electrode interphase was matched as a series combination of resistance and capacitance ($R_E$ and $C_L$) using a Schering bridge.
Electrolytic system

The electrolytic cell in which the electrolyte is subjected to continuous purification by adsorption of impurities on charcoal has been described previously. The test electrode (4.01 x 10^-2 cm²) was prepared from spectroscopically pure antimony (Johnson Matthey Co. Ltd.) which was melted under an atmosphere of nitrogen and cast in glass. The electrode was then mounted in polythene and cut at right angles to the long axis.

Electrode pretreatment

The electrode was mechanically polished on carborundum paper using bidistilled water as a lubricant, and freed from SiC particles by etching. Various chemical etches were used; a 5-s etch in concentrated HCl or a 4-s etch in concentrated HNO₃ were found to give reproducible results. Longer etches in HNO₃ and electropolishing in HClO₄ were found to produce a film on the electrode surface.

RESULTS

Figure 1 shows characteristic faradaic current vs. potential curves for HNO₃, H₂SO₄ and H₃PO₄ electrolytes. This indicates an experimentally accessible polarisable region for H₂SO₄ and H₃PO₄ from -0.05 to +0.4 V. For H₂SO₄ and H₃PO₄ electrolytes over the range +0.35 to 0.5 V there was little change in the curve before a significant increase in faradaic current density was observed. The curve for HNO₃ shows an initial increase in faradaic current; however, at more positive potentials the curve was similar to those observed for the other electrolytes. Experimentally it

Fig. 1. Faradaic current–potential curves, polycrystalline antimony, 23°C: (▲) 0.5 mol l⁻¹ H₂SO₄, (●) 0.071 mol l⁻¹ HNO₃, (○) 0.063 mol l⁻¹ H₃PO₄. Electrode area 4·01 x 10⁻² cm².

was found that stable impedance readings could be taken at potentials more negative than \(-0.05\) V; the ultimate limit was defined by the process of gas evolution at \(\sim -0.5\) V.

Chemically etched electrodes were generally satisfactory. Both HNO\(_3\) and HCl (30\%) gave consistent results, although for more dilute solutions there was evidence that stability was reached in a shorter period of time of electrode/electrolyte contact using HCl etches.

The times of electrode/electrolyte contact required to give stable values of electrode impedance for H\(_2\)SO\(_4\) and H\(_3\)PO\(_4\) electrolytes were from 2 h for the more concentrated solutions to \(7\frac{1}{2}\) h for the more dilute solutions. Generally for HNO\(_3\) electrolytes, less than half the time for H\(_2\)SO\(_4\) and H\(_3\)PO\(_4\) electrolytes was required to reach equilibrium.

Electrodes forced to potentials at the extremes of the experimental polarisable region (\(+0.3\) to \(-0.45\) V) required some time to revert to equilibrium. Hysteresis at the positive limit of potential was greater than at the negative limit; in both cases \(\sim 20\) min was required for the impedance measurements to return to the initial values. Hysteresis became more pronounced in dilute solutions and the effect was particularly marked where capacitance changes were large for small deviations in potential.

Black-grey films were observed when the electrode was forced to potentials more positive than \(+0.3\) V in relatively concentrated (0.05 mol l\(^{-1}\)) H\(_2\)SO\(_4\) electrolytes. Visible films were not observed in H\(_3\)PO\(_4\) electrolytes and the more dilute H\(_2\)SO\(_4\) electrolytes. Films were also produced in HNO\(_3\) electrolytes; when the potential was forced to \(-0.95\) V a substantial film was observed (Fig. 2).

Figures 3, 4 and 5 show typical differential capacitance curves for polycrystalline antimony in H\(_2\)SO\(_4\), HNO\(_3\) and H\(_3\)PO\(_4\) electrolytes. The variation of \(R_E\) with potential is also shown for each electrolyte. A maximum in capacitance occurs in the range 0.05 to 0.15 V. A minimum is also observed from \(-0.05\) to \(-0.25\) V in all cases.

---

**Fig. 2.** Differential capacitance curves for polycrystalline antimony, 23°C; electrode area 4.01 \(\times\) 10\(^{-2}\) cm\(^2\): (●) 0.0114 mol l\(^{-1}\) HNO\(_3\), 310 Hz; (○) 0.063 mol l\(^{-1}\) H\(_3\)PO\(_4\), 310 Hz. \(R_E\) vs. potential curves: (△) 0.0114 mol l\(^{-1}\) HNO\(_3\), 310 Hz; (▲) 0.063 mol l\(^{-1}\) H\(_3\)PO\(_4\), 310 Hz.

*J. Electroanal. Chem.*, 30 (1971) 59–65
Some frequency dispersion was observed; however this was no more than expected for a polycrystalline metal surface.

DISCUSSION

Figure 1 indicates that in the experimentally accessible region the electrode behaviour is not ideal. Although the negative limit of the experimental region is well defined (sharp increase in faradaic current), it is difficult to decide the positive limit since no abrupt increase in the current density is observed.

A sharp peak is observed in the capacitance curves (Figs. 3, 4 and 5) at ~ 0.1 V. This may be an adsorption peak preceding the formation of an antimony oxide^{10}, Sb$_2$O$_3$ (eqn. 2). At these potentials, capacitances were observed to be unstable with

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CAPACITANCE OF ANTIMONY IN AQUEOUS SOLUTION

Fig. 4. Differential capacitance curves for polycrystalline antimony, 23°C; electrode area 4.01 \times 10^{-2} \text{ cm}^2: (●) 0.025 mol l^{-1} \text{ H}_2\text{SO}_4, 310 \text{ Hz}; (○) 0.0081 mol l^{-1} \text{ H}_2\text{SO}_4, 310 \text{ Hz}. R_\text{e} vs. potential curve: (▲) 0.025 mol l^{-1} \text{ H}_2\text{SO}_4, 310 \text{ Hz}.

time. This is consistent with the formation of a surface film and may account for the fact that the magnitude of the capacitance peak does not decrease with electrolyte concentration as expected, although the general shapes of the curves followed the expected trend.

Studies of lead–acid battery systems\textsuperscript{14,15} have shown that stibine is evolved from antimony during cathodic polarisation at the potential corresponding to hydrogen evolution and occurs simultaneously with the process of hydrogen evolution. In all cases a rapid increase in capacitance is observed at -0.4 to -0.5 V and it is not possible to detect any change in electrode capacitance which could be ascribed to SbH\textsubscript{3} formation.

Previous work\textsuperscript{7,8} indicates that the p.z.c. should occur at -0.18 V. In all capacitance curves observed a broad minimum was obtained. It is therefore likely, as discussed by Frumkin\textsuperscript{16}, that the p.z.c. is masked by a minimum which represents a transition from preferential anion to preferential cation adsorption. Consequently the p.z.c. can only be estimated as -0.15 \pm 0.1 V.

It is interesting to note that only in HNO\textsubscript{3} electrolytes, at ~0.9 to 1.0 V does

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the capacitance rise after a gradual decrease. Inspection of the electrode showed a substantial black film on the surface. This feature was not observed in H$_2$SO$_4$ and H$_3$PO$_4$ electrolytes. In these electrolytes the interphase may be complicated by adsorption to form complex species at the surface.

ACKNOWLEDGEMENTS

The Science Research Council and Cheshire County Council are thanked for financial support (to R.J.L. and M.A.G.). M.I. Gillibrand (E.P.S. Ltd.) is thanked for discussion.

SUMMARY

The results of measurements of the differential capacitance of the solid ant-

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mony/aqueous solution interphase for the electrolytes, HNO$_3$, H$_2$SO$_4$ and H$_3$PO$_4$ are presented.

The electrode is not ideally polarisable. However an accessible experimental region exists from +0.3 to −0.5 V. The p.z.c. can only be estimated as −0.15±0.1 V since the interphase is complicated by the adsorption of anionic and cationic species.

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Technical Note

The Anodic Electrodeposition of PbO₂

C. J. Bushrod* and N. A. Hampson

Department of Chemistry, Loughborough University of Technology

MS received 12 March 1970

SUMMARY—Lead dioxide may be deposited on suitable bases from aqueous solutions of lead salts. For commercial production only two electrolytes are suitable: nitrate and perchlorate. Of these the lead perchlorate bath is the simpler to operate.

INTRODUCTION

ELECTRODES formed by the electrodeposition of PbO₂ onto an inert basis (Pt, Ag, Ni, Cu, stainless steel) have been used for primary power source applications and are of interest in the field of electro-organic oxidation.

Electrolytic systems suitable for electrodeposition must utilize a soluble lead salt as electrolyte. This requirement limits the choice of a suitable anion to a small group of which the most readily available are perchlorate, nitrate, fluoborate, silicofluoride and plumbite. Under carefully controlled conditions satisfactory deposits may be obtained using these electrolytes.

For commercial applications to achieve satisfactory deposition at a reasonable rate (~30 mAcm⁻²) plumbite, fluoborate, silicofluoride and plumbite are unsuitable as electrolytes. At current densities above about 5 mAcm⁻² electrolytes based on these anions result in highly stressed, poorly adherent deposits which readily flake.

This note summarizes the results of experiments conducted with perchlorate and nitrate electrolytes.

EXPERIMENTAL

Metal bases (10×5×0.01 cm) were annealed and etched. Washed (distilled water) bases were suspended symmetrically between cathodes (stainless steel—10 cm apart) in the electrolyte. Current was switched conventionally and charge equivalent to the required deposit (0.43 gm cm⁻²) passed at the required rate.

RESULTS AND DISCUSSION

With the exception of platinum, if the current density is low, PbO₂ is not deposited, rather the basis dissolves. This tendency is more pronounced with metals such as copper and under conditions of high acidity. For PbO₂ to be deposited the basis must first be rendered passive for the basis metal dissolution process. The basis (anode) dissolves until the point of passivation is reached, when a passive layer is formed, for the case of nickel when the process

\[ \text{Ni} = \text{Ni}^{2+} + 2e \]

changes to

\[ \text{Ni} + \text{H}_2\text{O} = \text{NiO} + 2\text{H}^+ + 2e \] (1)

the electrode passivates with the production of an insoluble layer of nickel oxide. The electrode potential then rises to that required for the formation of PbO₂.

\[ \text{Pb}^{2+} + 2\text{H}_2\text{O} = \text{PbO}_2 + 4\text{H}^+ + 2e \] (3)

PbO₂ electrodeposits on metals other than platinum therefore incorporate a passive layer between the basis and the PbO₂.

It is necessary to control the pH of the electrolyte so that reaction (2) is favoured; if the pH is too low the passive layer may not be formed, so that the anode continues to dissolve. In the presence of high [H⁺] it may be necessary to give a ‘flashing’ treatment, that is the current is increased momentarily to a very high value, favouring reaction (2).

LEAD PERCHLORATE ELECTROLYTES

We have obtained good adherent deposits of PbO₂ using electrolytes of ~2 mol 1⁻¹ lead perchlorate and 1 mol 1⁻¹ perchloric acid. Over fairly wide limits of [Pb⁺²] current densities of up to 50 mAcm⁻² have been employed without unduly high stresses being encountered, provided that [H⁺] does not rise above 1 mol 1⁻¹. Acidity was controlled by continuous circulation through a bed of PbO₂.

Dendritic growth of lead on the cathode was a complicating factor, so that it was desirable to keep the cathode current density as low as possible. This was done by using cathodes of large area (five times that of the anode).

Current efficiencies were ~100% based on the anodic oxidation.

LEAD NITRATE ELECTROLYTES

Optimum conditions for the production of PbO₂ electrodeposits at a rate of 36 mAcm⁻² require 1.6 mol 1⁻¹ lead nitrate electrolyte. Successive depositions in electrolyte at controlled pH show a decreasing faradic efficiency. Thus four successive depositions gave efficiencies of 93.5%, 69.2%, 42.2% and 25.4%. The effect is due to the presence of nitrite in the electrolyte (Fig 1), the nitrate ion is reversibly reduced to nitrite at the cathode and oxidized to nitrate at the anode.

\[ \text{NO}_3^- + 2\text{H}^+ + 2e = \text{NO}_2^- + \text{H}_2\text{O} \] (4)

As might be expected, the amount of nitrite produced during the passage of a given quantity of electricity is found to depend on the cathodic current density. At low
Fig 1. Effect of the nitrite ion on the faradaic efficiency for the anodic electrodeposition of PbO₂ from lead nitrate electrolyte.

current density (≈ 1 mA cm⁻²) the deposition process was 100%, at higher current density (≈ 30 mA cm⁻²) the efficiency fell markedly as nitrite was produced and at very high current densities (≈ 100 mA cm⁻²) ammonium ion is produced. Ammonium ion production ‘takes over’ from nitrite production as current density further increases. In the present experiments nitrite was removed from the system by oxidation with H₂O₂ or Pb₃O₄. This was coupled with pH control by pumping electrolyte through an external circuit containing a bed of PbO and additions of H₂O₂ (drip feed) or solid Pb₃O₄.

A certain residual stress in deposits obtained from nitrate electrolytes was corrected by the addition of buffers.²

The Effect of Temperature

With nitrate and perchlorate electrolytes investigated variation between 20° and 40°C does not materially affect the character of the deposit or anode efficiency.

Acknowledgment

We thank the Directors of EPS Ltd for permission to publish this paper.

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7 C. Dratschmann, Batteries, 1964, 17, 569.

Erratum—It is regretted that owing to a technical oversight during printing, the micrographs comprising Fig 11 of the paper by J. K. Dennis and J. J. Fuggle entitled The Effect of Metallic Contamination on Electrodeposited Nickel: Pt II—Appearance and Surface Topography (Trans Inst Metal Finishing, 1970, 48, 79) are shown upside down and in reverse order.
The anodic behaviour of zinc in KOH solution. V: Galvanostatic polarization with an interruption

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Received 2 December 1970

Galvanostatic polarization experiments, in which the current flow is interrupted and re-established, show that the process of passivation is controlled by the transport of mass in the solution phase.

Introduction

The dissolution of Zn anodes in aqueous alkali

$$\text{Zn} + 4\text{OH}^- \rightarrow \text{Zn(OH)}_4^{2-} + 2e$$

has been the subject of many investigations reported in the literature [1]. The mechanism of the active-passive transition for the Zn/CH$^-$ system has also been extensively investigated [1, 2]. Passivation of the Zn occurs when the electrode is no longer oxidized to Zn(II) and the potential rises to that required for the o.e.r. It is generally agreed that the formation of a layer of ZnO or Zn(OH)$_2$ occurs at the instant of the active-passive transition. Two possibilities exist for the formation of the film (a) precipitation, in which the passivating layer is formed by precipitation from the electrolyte layers immediately surrounding the electrode and (b) direct, in which the passivating layer is formed directly on the surface as a solid phase. It has been intuitively accepted, if not always stated explicitly, that the composition of the electrolyte in the vicinity of the anode is the factor determining the onset of film formation by either (a) or (b). The passivity which may ultimately be attained by zinc in alkali is then formally similar to 'cover passivity' as discussed by Müller [3] who distinguished between this and 'chemical passivity' where a higher valency metal compound is formed at the electrode surface.

The identity of the process of film growth ( (a) or (b) ) under galvanostatic conditions in general does not alter the kinetics of the attainment of the passive state since as soon as the electrolyte conditions at the electrode are 'critical', passivation occurs and the potential rises. It has been shown theoretically [4, 5] that if diffusion is the only mode of mass transport then

$$i = k$$

where $t$ is the time to passivation from initially closing the circuit at a current density $i$; $k$ is a constant for a given set of composition and temperature conditions. Equation (2) has been thoroughly justified experimentally under conditions where diffusion is the only significant mode of mass transport [6]. When diffusion is the major mode of mass transport but some other minor modes (e.g. convection) are present a limiting current $i_l$ is observed [7] ($i$ must be replaced by $(i-i_l)$ in Equation (2)).

Equations of the form (2) can fit data due to controlling mechanisms other than diffusion in solution as, for example, if the transition between the active dissolution and the passive electrode state occurs at a definite potential and the products of polarization in the active region remain (either (a) completely or (b) partly) as an insoluble film at the electrode surface [8]. The
purpose of this note is to present data which satisfactorily precludes these other possibilities.

The experimental situation

The quantitative treatment of a completely diffusion controlled system to the point of passivation in two distinct steps each separated from the other by an open circuit period has already been given [9]. Assuming semi-linear infinite diffusion it was shown that for the case of an electrode which became passive due to the Müller mechanism:

\[ I_2 \sqrt{I_3 + I_1 (\sqrt{I_3 + I_2 + I_3 - \sqrt{I_2 + I_3}})} = k' \]  

where \( I_1 \) is the initial current flowing for time \( t_1 \), followed by an open circuit period for time \( t_2 \), and finally polarized at \( I_2 \) until passivation occurs after a time, \( t_3 \). It is clear that (3) reduces to (1) when \( t_2 \) and \( t_3 \) are zero; \( k' \) in Equation (3) is equal in magnitude to \( k \) in Equation (2) (= \( \frac{1}{2} D \sqrt{2\pi} \), where \( D \) is the diffusion coefficient of the electrode product and \( C^* \) is the concentration of electrode product required to bring about passivation).†

Experimental

The experimental arrangement in which horizontal sheet anodes orientated with the bulk of the solution vertically above so that convection is effectively suppressed (at least in the experimental time range) has been described [10]. Zinc sheet (99.95%) was degreased (CCL\(_4\)) and etched (\( \sim 2 \text{ mol}^{-1} \text{H}_2\text{SO}_4 \)) immediately before the electrolyte was introduced into the cell. Cell electrolytes were prepared from AR grade KOH and doubly distilled water.

Passivation experiments were made both with and without an open circuit period interposed in the active dissolution region. From uninterrupted polarization data \( I-t^{-1} \) curves were drawn all of which were straight lines and extrapolated through the origin; the slope of these lines \( k \), was measured geometrically. From

† At the point of passivation a very considerable degree of supersaturation occurs; consequently it is not possible to assess the relative significance of the variables \( C^* \) and \( D \) as [KOH] increases [11].

### Table 1

<table>
<thead>
<tr>
<th>( \text{KOH} )</th>
<th>( \text{Electrode Area} )</th>
<th>( k' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 mol ( \text{KOH} )</td>
<td>( 1.76 \text{ cm}^2 )</td>
<td>0.12</td>
</tr>
<tr>
<td>( I_1 )</td>
<td>( I_2 )</td>
<td>( I_3 )</td>
</tr>
<tr>
<td>0.015</td>
<td>0.020</td>
<td>30</td>
</tr>
<tr>
<td>0.020</td>
<td>0.025</td>
<td>30</td>
</tr>
<tr>
<td>0.025</td>
<td>0.020</td>
<td>15</td>
</tr>
<tr>
<td>0.015</td>
<td>0.025</td>
<td>30</td>
</tr>
</tbody>
</table>

| 2 mol \( \text{KOH} \) | \( 1 \text{ cm}^2 \) | 0.38 |
| \( I_1 \) | \( I_2 \) | \( I_3 \) | \( t_1 \) | \( t_2 \) | \( t_3 \) |
| 0.024 | 0.045 | 60 | 30 | 35 | 0.41 |
| 0.042 | 0.046 | 40 | 30 | 35 | 0.28 |
| 0.015 | 0.052 | 30 | 30 | 45 | 0.55 |
| 0.056 | 0.045 | 15 | 30 | 63 | 0.46 |
| 0.056 | 0.051 | 20 | 40 | 40 | 0.40 |

| 3 mol \( \text{KOH} \) | \( 1 \text{ cm}^2 \) | 0.95 |
| \( I_1 \) | \( I_2 \) | \( I_3 \) | \( t_1 \) | \( t_2 \) | \( t_3 \) |
| 0.025 | 0.018 | 180 | 30 | 158 | 1.17 |
| 0.010 | 0.014 | 120 | 20 | 77 | 0.97 |
| 0.020 | 0.030 | 30 | 30 | 18 | 0.97 |
| 0.025 | 0.033 | 20 | 30 | 18 | 0.96 |

| 4 mol \( \text{KOH} \) | \( 1 \text{ cm}^2 \) | 1.16 |
| \( I_1 \) | \( I_2 \) | \( I_3 \) | \( t_1 \) | \( t_2 \) | \( t_3 \) |
| 0.003 | 0.0088 | 60 | 30 | 158 | 1.23 |
| 0.0086 | 0.0054 | 60 | 30 | 117 | 1.22 |
| 0.088 | 0.0099 | 60 | 30 | 97 | 1.14 |
| 0.094 | 0.0099 | 60 | 30 | 88 | 1.16 |
| 0.099 | 0.0105 | 60 | 30 | 92 | 1.25 |

| 5 mol \( \text{KOH} \) | \( 1 \text{ cm}^2 \) | 2.55 |
| \( I_1 \) | \( I_2 \) | \( I_3 \) | \( t_1 \) | \( t_2 \) | \( t_3 \) |
| 0.030 | 0.030 | 14.5 | 300 | 14 | 1.39 |
| 0.025 | 0.025 | 14.5 | 300 | 36 | 1.23 |

| 6 mol \( \text{KOH} \) | \( 1 \text{ cm}^2 \) | 3.32 |
| \( I_1 \) | \( I_2 \) | \( I_3 \) | \( t_1 \) | \( t_2 \) | \( t_3 \) |
| 0.20 | 0.20 | 60 | 60 | 95 | 1.32 |
| 0.20 | 0.20 | 60 | 60 | 95 | 1.33 |
| 0.20 | 0.20 | 60 | 60 | 95 | 1.26 |
| 0.20 | 0.20 | 60 | 60 | 45 | 1.26 |
| 0.30 | 0.30 | 30 | 60 | 36 | 1.23 |

| 7 mol \( \text{KOH} \) | \( 1 \text{ cm}^2 \) | 4.55 |
| \( I_1 \) | \( I_2 \) | \( I_3 \) | \( t_1 \) | \( t_2 \) | \( t_3 \) |
| 0.075 | 0.075 | 204 | 200 | 39 | 1.27 |
| 0.130 | 0.130 | 132 | 200 | 58 | 1.26 |
| 0.30 | 0.30 | 14.5 | 200 | 14 | 1.39 |

| 8 mol \( \text{KOH} \) | \( 1 \text{ cm}^2 \) | 3.32 |
| \( I_1 \) | \( I_2 \) | \( I_3 \) | \( t_1 \) | \( t_2 \) | \( t_3 \) |
| 0.20 | 0.20 | 60 | 60 | 95 | 1.32 |
| 0.20 | 0.20 | 60 | 60 | 95 | 1.33 |
| 0.20 | 0.20 | 60 | 60 | 95 | 1.26 |
| 0.20 | 0.20 | 60 | 60 | 45 | 1.26 |
| 0.30 | 0.30 | 30 | 60 | 36 | 1.23 |

| 9 mol \( \text{KOH} \) | \( 1 \text{ cm}^2 \) | 7.77 |
| \( I_1 \) | \( I_2 \) | \( I_3 \) | \( t_1 \) | \( t_2 \) | \( t_3 \) |
| 0.15 | 0.20 | 30 | 60 | 82 | 1.13 |
| 0.20 | 0.15 | 30 | 30 | 98 | 0.98 |
| 0.20 | 0.25 | 30 | 30 | 45 | 1.13 |
| 0.25 | 0.10 | 20 | 50 | 452 | 1.28 |

Notes:
(i) Units \( I_1, I_2, I_3; t_1, t_2, t_3; s; k'; \text{Acm}^{-2} \text{s}^{-1} \)
(ii) All measurements were made at 23°C.
interrupted polarization data $k'$ was calculated numerically. The results are shown in Table 1.

Discussion

The values of $k$ are in good agreement with previously reported data [6]. The agreement between $k$ and $k'$ is very satisfactory, particularly since the experiments deal with solid metal systems.

It can be concluded that mass transport in solution is the controlling process for the passivation of smooth electrodes in KOH solution (this conclusion does not necessarily apply to microporous electrode systems [8]).

Acknowledgment

Our thanks are due to final year students (Electrochemistry Elective 1970) who provided the experimental data.

References

Measurements of the stress in lead dioxide deposits formed anodically on a nickel substrate are reported for acid lead nitrate electrolytes. In simple acid electrolytes, the electrodeposited stress is compressively stressed, high stress is favoured by low (PbO\textsubscript{2}\textsuperscript{+}). The effect of additions of organic acid anion is pronounced; depending on the concentration of the organic anion, stress may be partly or completely relieved. Addition of sufficient organic anion causes a reversal of the stress from compressive to tensile. The results may be interpreted in terms of adsorption at the electrode.

### Stress in Anodically Formed Lead Dioxide

**by C. J. Bushrod* and N. A. Hampson†**

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(Revised manuscript received 17 June, 1970)

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**Introduction**

Lead dioxide (PbO\textsubscript{2}) may be deposited anodically from Pb(II) solutions:

\[ \text{Pb}^{2+} + 2\text{H}_2\text{O} = \text{PbO}_2^- + 4\text{H}^+ + 2\text{e}^- \]  \hspace{1cm} (1)

and such electrodeposits of lead dioxide are frequently stressed. Stressed deposits are undesirable for primary power source applications not only because of the tendency for cracking and detachment of the deposit from the substrate but also because stressed deposits of lead dioxide are frequently inferior in duration of discharge under galvanostatic conditions. This latter phenomenon is probably simply explained by stress engendering asymmetrical discharge over the area of the electrode, stress relieved areas having a lower exchange current density than highly stressed areas.

Literature concerning the development of stress in electrodeposits (mainly metals) already exists. It is clear that the match/mismatch of the deposited lattice on the lattice of the substrate is not the only factor involved although it may be important in certain cases. Thus for the deposition of iron on a copper substrate orientated overgrowths are obtained even though there is a 12\% mismatch in lattice spacings. Conversely, for the deposition of iron on gold, random deposits are obtained although no mismatch is involved. It is also noteworthy that copper on copper gives rise to a stressed deposit. It has also been reported\textsuperscript{1} that stress develops in deposits after circulation of the electrolyte through lead monoxide; in this paper, results are presented of such an investigation made with nitrate-supported electrolytes.\textsuperscript{2,3}

For the electrodeposition of lead dioxide on to nickel there is a considerable mismatch in structures of deposit and substrate. There is no likelihood of hydrogen co-deposition although oxygen co-deposition may occur.

There is interest, therefore, in the development of stress in lead dioxide electrodeposits both technologically, with the object of stress control, and scientifically, in the advancement of general theory of the electrochemical development of stress. In this paper, results are presented of such an investigation made with nitrate-supported electrolytes.

### Lead dioxide electrodeposits

Lead dioxide occurs in two forms; \( \alpha-\text{PbO}_2 \) was described by Kameyama & Fukumoto\textsuperscript{4} and has an orthorhombic structure.\textsuperscript{4} \( \beta-\text{PbO}_2 \) has been known for a considerable time and has a tetragonal structure. Under acidic conditions, the \( \beta \)-form is produced. At low current densities, the product can be made exclusively \( \beta-\text{PbO}_2 \) but at the current densities that are usually employed in technological processes, a small proportion of the \( \alpha \)-polymorph may be present in the electrodeposit.\textsuperscript{7-10}

The \( \beta: \alpha \) ratio of the deposit may be readily found using X-ray diffraction techniques.\textsuperscript{11}

### Experimental

**Deposition of lead dioxide on to nickel**

Lead dioxide was deposited from an aqueous acidic (1\% = 0-1 mole/l) solution of lead nitrate. In this electrolyte, the current efficiency of the deposition is a function of the nitrite ion concentration due to a subsidiary reaction:

\[ \text{NO}_2^- + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{O} + \text{NO}_2^- \]  \hspace{1cm} (2)

The NO\textsubscript{2}\textsuperscript{-} takes part in a NO\textsubscript{3}\textsuperscript{-}/NO\textsubscript{2}\textsuperscript{-} cycle, oxidation occurring at the anode and reduction at the cathode. When the [NO\textsubscript{3}\textsuperscript{-}] rises to \( \sim 5\% \), current efficiency falls to \( \sim 20\% \); for this reason NO\textsubscript{2} was removed by continuous oxidation of the electrolyte by circulation through lead red.

\[ \text{PbO}_2^- + \text{NO}_2^- + 5\text{NO}_2^- + 6\text{H}^+ = 3\text{Pb}(\text{NO}_3)\text{H} + 3\text{H}_2\text{O} \]  \hspace{1cm} (3)

With an efficient circulation cycle, current efficiency could be maintained at 98\%.

Initial anodic passivation of the nickel substrate via the formation of an oxide layer is required before PbO\textsubscript{2} is deposited. Excess H\textsuperscript{+} may inhibit the formation of the passive layer and result in dissolution of the nickel instead of the formation of lead dioxide. H\textsuperscript{+} is readily controlled by circulation of the electrolyte through lead monoxide; in practice it is convenient to add lead monoxide to the red-lead bed.

**Electrolytic system**

The electrolytic cell (8 x 12 x 10 cm deep) was parallel sided and made of soda-glass; the electrolyte was continuously pumped through an external NO\textsubscript{3}\textsuperscript{-}/H\textsuperscript{+} removal column packed with porcelain rings which supported a 2:1 mixture of red lead/lead monoxide. The rate of electrolyte circulation (\( \sim 100 \text{ mI/min} \)) was varied to achieve optimum deposition conditions. Suspended solid was removed by filtering the return feed stream. The total volume of electrolyte was \( \sim 2 \text{I} \).

**Stress measurement**

Two methods were employed:

(i) A fine rubber diaphragm was fixed over the end of a water-filled thistle funnel (3 cm dia). The diaphragm was coated with silver (from a silvering solution) and a layer of nickel (2 x 10\textsuperscript{-3} cm) deposited from a nickel chloride/nickel sulphate bath on to the silver. The nickel deposit formed the basis for the deposition of lead dioxide. Compressive stresses in subsequent deposits on to the flexible substrate resulted in a rise in the water level in the stem of the
funnel. Stress detection could be made very sensitive by the use of a capillary stem. The method was, however, suitable only for qualitative observations.

(ii) The second method was originally due to MacNaughton & Hothersall. An anode consisted of two thin (0.01 cm) annealed nickel plates clamped together forming two leaves (1 cm wide x 5 cm long). In practice it was convenient to coat the inner (facing) surfaces with an extremely thin layer of polyvinyl chloride. The complex anode was positioned in the cell exactly between two identical lead cathodes which were 12 cm apart in the electrolytic cell, so that the current distribution was uniform over the outer surfaces of the anode. During the course of the anodic deposition, the leaves of the anode converged or diverged depending on whether the stress was compressive (+) or tensile (−). Stress is calculated from:

\[
\text{Stress} = \frac{Y d^3 D}{3 L^2 t}
\]

where \( Y \) is Young's Modulus for nickel; \( L \) is the length of the anode (5 cm); \( d \) is the thickness of the anode (0.01 cm); \( t \) is the thickness of the deposit; and \( D \) is the difference in divergence of anode leaves before and after the deposition.

The stress in the deposited lead dioxide was studied as a function of current density, stirring and electrolyte composition. In addition, deformations of the electrodes (change in water level, method (i); change in \( D \), method (ii); were followed throughout the course of the experiments. The majority of measurements were made in unstirred electrolytes at a current density of 30 mA/cm².

Results

Effect of lead nitrate concentration

Electrodeposits formed from electrolytes containing 1·2–0·3 mole/l of lead nitrate were compressively stressed. The magnitude of this stress was 600–900 kg/cm², higher stresses occurring in the more dilute electrolytes.

Effect of current density

Changes in current density below ∼70 mA/cm² had no effect on the magnitude of the observed stress. Significant reductions in the compressive stress were observed, however, at higher current densities; films of poor adhesion resulted at these rates, however.

Effect of stirring

Very rapidly stirred electrolytes gave rise to stress-free deposits or deposits having tensile stresses. These experiments were only qualitative since it was not possible in the present experiments to measure the actual rate of electrolyte flow at the electrode.

Effect of organic acid anions

Fig. 1 shows the magnitude of the stress in electrodeposits obtained with electrolytes based on lead nitrate (1·21 mole/l) containing various concentrations of sodium acetate. At very high acetate concentration, a small amount of oxygen was evolved and the presence of a small proportion of gaseous organic product was evidence for a Kolbe-type reaction:

\[
2\text{CH}_3\text{COO}^- = \text{C}_2\text{H}_4 + 2\text{CO}_2 + 2e
\]

At sodium acetate concentration <0·1 mole/l, no complications due to either oxygen evolution or reaction (5) were observed.

At high sodium acetate concentrations the sign of the stress changes from compressive to tensile. The changeover concentration (0·366 mole/l) was checked by method (i). Fig. 2 shows the results for electrolytes based on 1·21, 0·755 and 0·303 mole/l lead nitrate, and in acetate-free electrolytes stresses were 590, 646 and 860 kg/cm², respectively. Acetate is more effective at low lead nitrate concentrations, that is, the ratio [NaAc]/[Pb(NO₃)₂] is important.

In Fig. 3 is shown the effect of tartaric acid and citric acid on stress developed in electrolytes based on 1·21 mole/l concentration. The effect of the polybasic acids is much more pronounced than monobasic: at lower concentrations (∼0·05 mole/l), the polybasic acids are ∼80 times as effective as the monobasic sodium acetate. It was not possible to increase the concentrations of citric and tartaric acid beyond 0·03 mole/l without adversely affecting the adherence of the deposit.

Development of stress

Both methods (i) and (ii) allowed the development of stress to be observed during the course of the electrolysis. It was found that stress was produced only during the electrolysis and not after the current had been switched off. The magnitude of the stress was independent of the charge passed (thickness of electrodeposits).

Nature of the electrodeposits

\( X \)-Ray analysis showed that the identity of the deposits was the same in all cases, mainly (∼90%) \( \beta \)-PbO₂. There was no connexion between the electrolyte constitution and the \( \alpha:\beta \) ratio of the lead-dioxide deposit.

Discussion

Electrodeposits obtained from simple lead nitrate electrolytes are notable for the magnitude of the compressive stress. For electrodeposited metals, values reported in the literature have rarely exceeded 300 kg/cm². It is clear from the effect of Pb²⁺ concentration on stress and from the effect of stirring that low compressive stress is favoured by high Pb²⁺ concentration.

The addition of acetate, tartrate and citrate ions can be regarded as controlling the acidity of the electrolyte; however,
it is not possible to reconcile the magnitude of the relative effects of the three acids (Fig. 3) with simple buffer action. The effect of additions of organic acids appears to be most readily explicable in terms of adsorption at the electrode interface. There is evidence\textsuperscript{15,16} that organic acid anions are adsorbed at the lead-dioxide electrode. The action of the anion can be considered as participation in the packing of the structural units that form the deposit. The greater is the surface concentration of the adsorbed ion, the greater is the proportion of the electrode surface which cannot be used in the crystal growth process without displacing the adsorbate. A more open crystal structure then occurs, and the compressive stress is reduced and eventually reversed to become tensile as more adsorbate covers the surface.

It is interesting that there was no change in the $\alpha$:$\beta$ ratio of the lead dioxide corresponding to the wide differences in deposit stress. It must be concluded that the parameters which determine the $\alpha$ or $\beta$ arrangement are more fundamental than those which determine the nature of the stress. It is likely that the former may simply be the sign of the charge on the electrode (recent determinations\textsuperscript{17} of the zero point of charge of lead dioxide in nitrate electrolytes place it at $\sim$1.0 V). Thus, in acid electrolytes, the lead dioxide is deposited ($E^\circ = 1.45$ V) as $\beta$-PbO$_2$ under conditions of a positive charge on the electrode; in alkali, the lead dioxide is deposited ($E^\circ = 0.25$ V) as $\alpha$-PbO$_2$ with a negative charge on the electrode.

Analysis of electrodeposits does not preclude the possibility of the presence of hydrogen and additional oxygen in the electrodeposits. Values of ultimate formulæ\textsuperscript{18} for systems of the present type are typically PbO$_2$,$\delta$(OH)$_{\delta-}$\textsuperscript{15}. Although the presence of hydrogen could not arise by the discharge of H$^+$, there is some evidence from kinetic measurements\textsuperscript{18} that in acid electrolytes, H$^+$ may be adsorbed even under conditions of positive surface charge. Hydrogen inclusion in the lattice could arise via a mechanism similar to that proposed\textsuperscript{18} for the formation of lead dioxide:

- $\text{Pb}^{2+} + 2\text{OH}^- \rightarrow \text{Pb(OH)}_2$ \hspace{1cm} (6)
- $\text{Pb(OH)}_2 = \text{Pb(OH)}_2^{+} + 2e^-$ \hspace{1cm} (7)
- $\text{Pb(OH)}_2^{+} = \text{PbO}_2 + 2\text{H}^+$ \hspace{1cm} (8)

Reaction (7) is probably a 2-step process in the present experiments.\textsuperscript{18} Reaction (8) can be considered as the desorption of adsorbed H$^+$, and it is possible that H$^+$ could enter the lattice via this reaction. If organic acids or anions are adsorbed at the electrode, the stress may well be modified by the intrusion of the adsorption of the organic anion on reaction (8). Here again, the organic entity interferes with the lattice building process. Oxygen co-deposition and inclusion in the lattice is also a possibility at the potentials involved in the electrodeposition. It is not clear, however, how organic anions could participate in a process of oxygen co-deposition in such a way as to modify the stress in the manner observed.

The effect of very high current densities on the stress appears to agree with the other observations, since at the higher positive potentials involved at higher current densities, the adsorption of anions would be favoured.

Acknowledgments

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Anodic Behaviour of Lead in Perchloric Acid
I. Continuous and Interrupted Polarisation

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The passivation time \((t_p)\) of polycrystalline lead anodes in perchloric acid has been studied over a range of current densities \((i)\).

When diffusion is the only mode of mass transport, the equation \(i\sqrt{t_p} = C_p\sqrt{\pi}\) is obeyed where \(C_p\) is the concentration of metal ions at the anode at the onset of passivity. The effect of an interruption (at time \(t_1\) for a period \(t_2\)) during the polarisation (at \(t_1\)) followed by further polarisation (at \(t_2\)) until passivation occurs \((t_3 = t_1 + t_2 + t_3)\) is considered. The relationship:

\[t_3\sqrt{t_3} + t_3(\sqrt{t_1} + t_2 - \sqrt{t_2} + t_3) = C_p\sqrt{\pi}\]

is derived theoretically and shown to apply in practice.

Consider a vertical cylindrical cell containing acid, the lower end of which consists of a metal anode of unit area. Let a current of \(i\) A flow for a time \(t\) sec and let the cylinder be of sufficient height to be regarded as semi-infinite. It is first necessary to find the concentration of metal ions \(C_{x,t}\) at any height \(x\) cm above the anode. The quantity \(C_{x,t}\) is then the solution of Fick's diffusion equation:

\[\frac{\partial C_{x,t}}{\partial t} = D \frac{\partial^2 C_{x,t}}{\partial x^2}\]  

with the boundary conditions

\[D \frac{\partial C_{x,t}}{\partial x} = \frac{i}{zF} \text{ when } x = 0 \text{ and } C_{x,t} = 0 \text{ when } x = \infty.\]

In these equations, \(z\) is the number of electrons involved in the process, \(D\) is the diffusion constant (having dimensions \(\text{cm}^2\text{sec}^{-1}\)) and \(F\) is the Faraday.

The required solution is given by:

\[C_{x,t} = \frac{2i}{zF} \sqrt{\frac{t}{D}} \text{erfc} \left(\frac{x}{2\sqrt{D}t}\right)\]

where \(\text{erfc} = \frac{1}{\sqrt{\pi}} \int_{y}^{\infty} e^{-y^2} dy\).

At the anode surface where \(x = 0\):

\[C_{x,0} = \frac{2i}{zF} \sqrt{\frac{t}{D\pi}}\]

In acid of any given concentration, it is reasonable to suppose that the concentration of metal ions at the anode at the onset of passivity will be constant at constant temperature. Denoting this concentration by \(C_p\) and the time to passivate as \(t_p\), then

\[C_p = \frac{2i}{zF} \sqrt{\frac{t_p}{D\pi}}\]

or \(t_p = D\pi \left(\frac{C_p z F^2}{2i}\right)^2\)

which can be written as

\[t_p = \frac{\alpha C_p^2}{i^2}\]  

where \(\alpha = D\pi z^2 F^2 / 4\).

The passivation time \((t_p)\) of polycrystalline lead anodes in perchloric acid has been studied over a range of current densities \((i)\).

Introduction

The anodic dissolution of a metal in an acid is a consequence of the passage of metal ions from the lattice to the solution where they acquire a stabilising shell of water molecules (hydration). This process establishes a concentration gradient in the solution with the highest metal ion concentration at the anode. With the continued passage of current the concentration increases until the solubility limit is reached at the electrode until passivation occurs.

This routine is commonly encountered during the intermittent operation of energy storage devices.

Theoretical

First consider passivation (without interruption) of a system in which convection currents are eliminated and diffusion is uni-dimensional.

Consider a vertical cylindrical cell containing acid, the lower end of which consists of a metal anode of unit area. Let a current of \(i\) A flow for a time \(t\) sec and let the cylinder be of sufficient height to be regarded as semi-infinite. It is first necessary to find the concentration of metal ions \(C_{x,t}\) at any height \(x\) cm above the anode. The quantity \(C_{x,t}\) is then the solution of Fick's diffusion equation:

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In these equations, \(z\) is the number of electrons involved in the process, \(D\) is the diffusion constant (having dimensions \(\text{cm}^2\text{sec}^{-1}\)) and \(F\) is the Faraday.

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where \(\text{erfc} = \frac{1}{\sqrt{\pi}} \int_{y}^{\infty} e^{-y^2} dy\).

At the anode surface where \(x = 0\):

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In acid of any given concentration, it is reasonable to suppose that the concentration of metal ions at the anode at the onset of passivity will be constant at constant temperature. Denoting this concentration by \(C_p\) and the time to passivate as \(t_p\), then

\[C_p = \frac{2i}{zF} \sqrt{\frac{t_p}{D\pi}}\]

or \(t_p = D\pi \left(\frac{C_p z F^2}{2i}\right)^2\)

which can be written as

\[t_p = \frac{\alpha C_p^2}{i^2}\]  

where \(\alpha = D\pi z^2 F^2 / 4\).
For the case of an interrupted polarisation, the above treatment is readily extended. Let a current of $i_1$ A flow for $t_1$ sec and then let it be discontinued for a further $t_2$ sec. At this moment, current is again passed ($i_2$ A) for $t_2$ sec. It is now required to find the concentration of metal ions at any distance $x$ up the cylindrical cell ($C_{x,T}$).

The quantity $C_{x,T}$ is again the solution of Pick's equation subject to the boundary conditions:

(i) In the interval $0 \rightarrow t_1$ sec, the solution is given by Equation (2)

(ii) In the interval $t_1 \rightarrow (t_1 + t_2)$ sec,

(A) $C_{x,t} = \frac{2i_1}{zF\sqrt{D}} \frac{x}{2\sqrt{Dt_1}}$ at $t_1$ .

(B) $D \frac{\partial C_{x,t}}{\partial x} = 0$ at $x = 0$

giving the required solution:

$$C_{x,t} = \frac{2i_1}{zF\sqrt{D}} \left[ \frac{t_1}{2\sqrt{Dt_1}} \text{erfc} \frac{x}{\sqrt{2Dt_1}} \right]$$

(iii) In the interval $(t_1 + t_2) \rightarrow (t_1 + t_2 + t_3)$ sec,

(A) $C_{x,t}$ is given by Equation (11) at $(t_1 + t_2)$ sec

(B) $D \frac{\partial C_{x,t}}{\partial x} = \frac{i_2}{zF}$ at $x = 0$

giving the required solution:

$$C_{x,t} = \frac{2i_2}{zF\sqrt{D}} \left[ \frac{t_1}{2\sqrt{Dt_1}} \text{erfc} \frac{x}{\sqrt{2Dt_1}} + \frac{t_2}{2\sqrt{Dt_2}} \right]$$

It will frequently occur that only the metal ion concentration at the electrode surface is of interest and, as $\text{erfc} \ 0 = 1/\sqrt{\pi}$ it follows that:

$$C_{o,t} = \frac{2i_2}{zF\sqrt{D\pi}} \left[ \frac{t_2}{\sqrt{t_1 + t_2 + t_3}} \right]$$

If the current $i_2$ is allowed to flow until the electrode passivates, then $C_o$ is given by Equation (5) and should be constant for a fixed set of conditions irrespective of the values of $i_1$, $i_2$, $t_1$ and $t_2$. Thus:

$$i_2 \sqrt{t_3} + i_1 \left( \sqrt{t_1 + t_2 + t_3} - \sqrt{t_2 + t_3} \right)$$

$$= \frac{zFC_p\sqrt{D\pi}}{2} \frac{\partial C_{o,t}}{\partial x}$$

### Experimental

The principle of orientating electrodes in a horizontal plane with the electrolyte confined in such a way that it formed a vertical right cylinder above the electrode has been described in the literature. In this way convection can be suppressed as long as the experiment is not too protracted. In the present experiments, the circular electrode (99.99% Pb of 22 mm dia.) was enclosed in a glass cylinder (10 cm) so that 'edge effects' were eliminated. The counter electrode was carbon (glassy or graphite). Temperature control was obtained by immersing the whole cell in a water thermostat but it was not always possible to eliminate faradaic heating effects. The perchloric acid electrolyte was of Analar quality.

A constant current was passed through the cell and constancy was maintained by taking it from a 100 V d.c. supply and using a large variable series resistor; owing to the high line voltage little adjustment was required. The voltage drop across the cell was measured on a high resistance ‘Unipivot’ instrument or electrometer and the onset of passivity could be detected quite accurately by the sudden rise in cell potential as shown in Fig. 1 at intersections of projected parts of the polarisation curve.

![Fig. 1. Polarisation curves for lead in 40% perchloric acid at 20°C](image)

![Fig. 2. Passivation of lead in perchloric acid at 20°C](image)
Results and discussion

Typical voltage/time curves for the anodic dissolution of lead in perchloric acid are given in Fig. 1. The passivation times, $t_p$, are plotted against reciprocals of $i$ in Fig. 2. It can be seen that the points lie closely along straight lines passing through the origin. Departure from linearity is due to the faradaic heating effect of the larger currents and delayed the onset of passivation.

The linear relation between $t_p$ and $i^{-1}$ and the increasing slope of the lines with decreasing concentration provides ample support for the supposition that the passivation process is diffusion controlled.

Experiments were carried out in which the initial current ($i_1$) was discontinued, before passivation occurred, and current was then switched on again ($i_2$) until passivation. The results are shown in Table I.

The values of $\alpha C_f$ entered in the final column of Table I are calculated by the use of Equation (15); the approximate constancy of these figures for the wide ranges of current and time intervals employed, provides further support for the treatment of the 'interrupted' case.

Quantitative studies of anodic passivation

The time taken to passivate an anode increases rapidly with decreasing current density. This is clear when passivation time is plotted directly against the current flowing (Fig. 3) and when the charge required for passivation is plotted against the current (Fig. 4). The theoretical lines in Figs 3 and 4 were calculated from the following values of $\alpha C_f$ given with the corresponding strengths of perchloric acid: acid concn. 10%, $\alpha C_f$ 70·31; 20%, 51·69; 40%, 31·30; 50%, 16·70; and 60%, 1·77. $D$ was measured experimentally and also calculated by the Nernst formula. A value of $1·24 \times 10^{-8}$ cm$^2$ sec$^{-1}$ was given by both methods.

From a consideration of the data of Figs 3 and 4, it is clear that the effect of increasing the perchloric acid concentration is to decrease the passivation time. This is due to the lowered solubility of Pb(ClO$_4$)$_2$ in perchloric acid due to common ion effects. For primary energy conversion applications, it is necessary to consider the total acid concentration; in the experiments reported here this was not done since excess acid was always present. Consideration of the electrolyte/active material balance required for a viable unit indicated that for the anodic dissolution of lead for primary power source applications, the optimal concentration of perchloric acid is 55% (8·1 mole l$^{-1}$; 12·3 mole kg$^{-1}$). Data corresponding to this concentration are shown in Table II.

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mean = 6·45

Fig. 3. Passivation time vs. current density data for lead in perchloric acid at 20°C


TABLE I

Passivation of lead in 60% perchloric acid by an intermittent current at 22·5°C

Fig. 4. Passivating charge vs. current density data for lead in perchloric acid at 20°C

Conclusions

For the anodic dissolution of lead in perchloric acid, for times less than 1000 sec, convection may be effectively suppressed by suitably orientating the electrode.

The process of anodic passivation is controlled by the process of mass transport in solution; when diffusion is the only mode of mass transport the \( \sqrt{t} \) relationship is obeyed.

The effect of a discontinuity in the anodic polarisation may be treated quantitatively.

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