The effect of bismuth on the lead acid battery system

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THE EFFECT OF BISMUTH ON THE LEAD-ACID BATTERY SYSTEM

by

Mark Johnson

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

January 1988

by Mark Johnson
The Work in this thesis has not been submitted, in full or in part, to this or any other institution for a higher degree.
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Finally, my appreciation extends to the staff and students involved with the Chaplaincy, who have been very supportive.
SUMMARY

The effect of bismuth on the electrochemistry of the lead-acid battery has been investigated using the techniques of linear sweep voltammetry, chronocoulometric and galvanostatic cycling, potentiostatic pulse experiments and corrosion measurements. Optical and scanning electron microscopy enabled a morphological examination of the electrodes to be carried out. The concentration of bismuth ranged from $5 \times 10^{-4}$ to 4.91 wt%. The effect of the presence of Bi was evaluated on both the negative and positive plates. On the negative, investigations were carried out into the hydrogen evolution reaction and on the effect of bismuth on the growth and development of the lead/lead sulphate active material. Research into aspects of positive plate performance have covered corrosion, oxygen evolution, pasted plates, electrocrystallisation and cycling of grid wires.

The effect of bismuth in increasing the hydrogen evolution overpotential and improving the nucleation of lead sulphate were noted on the negative plate. On the positive, bismuth had a generally deleterious effect; it increases the lead dioxide crystallisation overpotential, facilitates oxygen evolution, increases sulphation and leaches from the electrode. The advantages of bismuth on the positive are confined to improving the corrosion layer by making it more compact and, at low levels, improving the porosity and thus the utilization, of the pasted plates.

Thus it is recommended that bismuth be kept below 0.05% in the positive, but be allowed up to 1% in the negative.
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\[ E_{eq} \]  
Equilibrium Potential

\[ \Delta E_p \]  
Potential at which Maximum Current Density Occurs

\[ \Delta E_p^a \]  
Potential at which Maximum Current Density Occurs for the Forward Reaction

\[ \Delta E_p^c \]  
Potential at which Maximum Current Density Occurs for the Backward Reaction

\[ \Delta E_p/2 \]  
Potential at which Half of the Maximum Current Density Occurs

\[ E_{rat} \]  
Rational Potential

\[ F \]  
Faraday Constant

\[ G \]  
Gibbs Free Energy

\[ \Delta G \]  
Change in Gibbs Free Energy

\[ \Delta G^o \]  
Standard Gibbs Free Energy

\[ \Delta G_a^* \]  
Activation Energy of the Forward Process

\[ \Delta G_c^* \]  
Activation Energy of the Forward Process

\[ \Delta G_{oa}^* \]  
Standard Activation Energy of the Forward Process

\[ \Delta G_{oc}^* \]  
Standard Activation Energy of the Backward Process

\[ h \]  
Molecular Height

\[ I_p \]  
Maximum Current Density / A cm\(^{-2}\)

\[ I_p^a \]  
Maximum Current Density for the Forward Reaction / A cm\(^{-2}\)

\[ I_p^c \]  
Maximum Current Density for the Backward Reaction / A cm\(^{-2}\)

\[ i \]  
Current / A

\[ i_b \]  
Current Due to the Backward Reaction

\[ i_d(t) \]  
Diffusion Controlled Current

\[ i_f \]  
Current Due to the Forward Reaction

\[ i_{\text{max}}, i_m, i_m' \]  
Maximum Current

\[ i(r,t) \]  
Instantaneous Current Required to Expand the Growth
**LIST OF SYMBOLS**

A \quad \text{Electrode area}

A' \quad \text{First Order Nucleation Rate Constant}

A_F \quad N_0 \times A, \text{ the Nucleation Rate Constant}

\text{A}_F \quad \text{Arrhenius Constant for the Forward Reaction}

\text{A}_b \quad \text{Arrhenius Constant for the Backward Reaction}

\text{a}_0 \quad \text{Activity of the Oxidised Species}

\text{a}_E \quad \text{Activity of the Reduced Species}

C \quad \text{Charge} / \text{Coulombs}

C_{\text{diffuse}} \quad \text{Capacitance of the Diffuse Layer}

C_{\text{fixed}} \quad \text{Capacitance of the Fixed Layer}

C_1 \quad \text{Overall Double Layer Capacitance}

C_{H^+} \quad \text{Concentration of Hydrogen Ions in the Bulk}

C_0 \quad \text{Concentration of the Oxidised Species}

C_0^* \quad \text{Bulk Concentration of the Oxidised Species}

C_0(x,t) \quad \text{Concentration of the Oxidised Species Distance} \, x \, \text{from the Electrode at Time} \, t

C_R \quad \text{Concentration of the Reduced Species}

C_R^* \quad \text{Bulk Concentration of the Reduced Species}

C_R(x,t) \quad \text{Concentration of the Reduced Species Distance} \, x \, \text{from the Electrode at Time} \, t

D_0 \quad \text{Diffusion Coefficient}

E \quad \text{Electrode Potential}

E^\theta \quad \text{Standard Potential}
Centre of Radius $r$ at Time $t$

$i_0$  Exchange Current

$K$  Crystal Growth Constant

$K_c$  Reverse Reaction Rate Constant

$K_a$  Forward Reaction Rate Constant

$k_b$  Reverse Reaction Rate

$k_{b0}$  Apparent Standard Backward Reaction Rate

$k_f$  Forward Reaction Rate

$k_{f0}$  Apparent Standard Forward Reaction Rate

$k^o$  Intrinsic Rate Constant

$M$  Molecular Weight of the Substrate

$N$  Number of Molecules

$N_0$  Number of Active Nucleation Sites

$N(t)$  Rate of Appearance of Stable Nucleation Sites

$n$  Number of Electrons Transferred

$n_a$  Number of Electrons Transferred upto and Including the Rate Determining Step

$O$  Oxidised Species

$Q(r)$  Charge Required to Expand Growth Centre

$q$  Flux

$R$  Reduced Species

$R$  Gas Constant

$R_0$  Charge Transfer Resistance

$r(t)$  Radius of Crystal Centre at Time $t$

$S$  Area Covered by Crystal Growth

$S_{ext}$  Normalised Extended Area

$T$  Temperature / K
<table>
<thead>
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<th>Description</th>
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<tr>
<td>$t$</td>
<td>Time</td>
</tr>
<tr>
<td>$t_{\text{max}}, t_{m}$</td>
<td>Time to Maximum Current</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Charge Transfer Coefficient</td>
</tr>
<tr>
<td>$\alpha'$</td>
<td>Diffuse Layer Correction Factor</td>
</tr>
<tr>
<td>$\psi$</td>
<td>Effective Potential at Outer Helmholtz Layer</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Sweep Speed</td>
</tr>
<tr>
<td>$\nu$</td>
<td>$RT/F \ln 10$</td>
</tr>
<tr>
<td>$\gamma_{H^+}$</td>
<td>Activity Coefficient of Bulk Hydrogen Ions</td>
</tr>
<tr>
<td>$\gamma_{\text{ext}}$</td>
<td>Extended Surface Area</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Substrate Density</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Overpotential</td>
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CHAPTER 1

INTRODUCTION

The lead-acid battery has been around for many years, even so research into its detailed discharge/recharge mechanism, gas recombination, and the effects of alloying ingredients on performance (to name but a few), is still vigorously pursued. Currently between one and two papers a week are published on aspects of the lead-acid system. But a final all-encompassing explanation of the system is still elusive.

The research carried out and reported in this thesis concerns the effect of bismuth addition to all parts of the battery system and it attempts to understand and explain the resultant performance.

The history of the lead-acid battery - as recorded by Vinal (1) and Schallenberg (2) - is littered with ideas that at the time seemed to contribute to an improved battery. Some of the ideas, such as the use of FeCl$_3$ in the manufacturing process or Faure's "pasted plates" have been consigned to the commercial dustbin, while others such as Plante cells have undergone development to become important in today's market for rechargeable systems.

For over 120 years the lead-acid system has been the most important secondary power source available. The reasons for this success are easily discernable;

- it is cheap,
- the raw materials and the manufacturing process are inexpensive and use readily available technology,
- it has a good storage life, especially in the dry charge state,
- it has great versatility in providing high or low currents on demand.

Other batteries are now competing for the rechargeable market which highlight some of the lead-acid batteries disadvantages:

- low energy density,
- low utilization of theoretical capacity,
- use of toxic and/or noxious substances.

But this last point is not confined to just the lead-acid system. Table 1.1 (3,4) below shows the current "state of play" with reference to the competing and developing rechargeable systems.

However, despite all the time, money and effort put into other rechargeable energy sources, the lead-acid system still dominates.

The overall reaction of the battery can best be written as follows;

\[
\text{discharge} \quad \text{PbO}_2 + 2\text{H}_2\text{SO}_4 + \text{Pb} \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O} \quad E = 2.04 \text{ V}
\]

\[
\text{charge}
\]
<table>
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<tr>
<th>Battery System</th>
<th>Energy Density</th>
<th>Cycle Life</th>
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<td></td>
<td>Theoretical</td>
<td>Practical</td>
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<td>Lead-Acid</td>
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<td></td>
</tr>
<tr>
<td>Pasted Plate</td>
<td>25-35</td>
<td>1200-1300</td>
</tr>
<tr>
<td>Tubular</td>
<td>20-35</td>
<td>(starter 300)</td>
</tr>
<tr>
<td>Storage</td>
<td>25-35</td>
<td>1500+</td>
</tr>
<tr>
<td>Nickel-Cadmium</td>
<td>236</td>
<td></td>
</tr>
<tr>
<td>Pocket Plate</td>
<td>15-24</td>
<td>1000-2000</td>
</tr>
<tr>
<td>Sintered Plate</td>
<td>25-33</td>
<td>1000-2000</td>
</tr>
<tr>
<td>Nickel-Iron</td>
<td>304</td>
<td>2000</td>
</tr>
<tr>
<td>Nickel-Zinc</td>
<td>273</td>
<td>200-250(100%dis.)</td>
</tr>
<tr>
<td>Silver-Cadmium</td>
<td>400?</td>
<td>200</td>
</tr>
<tr>
<td>Silver-Zinc</td>
<td>460</td>
<td>10-200</td>
</tr>
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</table>

The generally accepted theory on the chemistry of the battery (5), indicating that PbSO₄ is the final product on discharge at both the anode and cathode, is called the "double sulphate" theory and was first proposed by Gladstone and Tribe (6). They found that, as the discharge proceeded, the electrolyte became weaker, thus showing that the
sulphuric acid is not only the electrolyte but also a reactant. Craig and Vinal (7) confirmed this thermodynamically, in 1940 and subsequent analysis by Beck, Lind and Wynne-Jones (8) and others (9,10) has shown this to be correct.

Depending on the use of a battery, the design can vary over a wide range, though the basic components are the same. The positive plate electrode is made up of porous PbO2 and the negative of "spongy" lead both on a lead or lead alloy backing grid. The grid acts as physical support for the paste and as current collector.

There are three main designs of lead-acid battery, first and foremost, for it is the most widely used, is the pasted plate described below, which is mainly used for starting, lighting and ignition (S.L.I.) applications. Secondly there is the tubular type, which is mainly utilized for traction, where a spine of lead or alloy is surrounded by active material held in by a separator. The rods are held in rows with the current take-off bar acting as positional support, and there is often a plastic former at the bottom of the case to help preserve the position of the rods. The negative is of a plate design and allows free passage of acid.

The third and final design is the Plante cell, which is a heavy battery and usually only used in stationary service, such as load levelling. The lead is cast in the form of a flat sheet, which is formed using a mixture of sulphuric and perchloric acids. The aggressive electrolyte converts the lead on the surface of the plate into sulphate, which is insoluble, and perchlorate, which is not. This leaves a layer of active material on a porous lead backing which can then be used in a battery environment.
The pasted plate design is the most widely manufactured and though mainly used for S.L.I., float charged stand-by power sources and traction applications have been tried, and with some success. Initially the plates are made up of a mixture of lead oxide and lead powder - called "leady oxide" - which is made either by the ball mill or Barton Pot methods. In the Barton Pot manufacturing process, air is blown over the surface and through a pool of molten metal and the oxide carried away for sizing.

The ball mill method is more popular and consists of lead or alloy ingots being tumbled together in a perforated steel drum, through which air is blown. Particles of lead are removed by collision and immediately oxidized and then size separated.

Typically 60 to 70% of both oxide streams is monoxide and 30% or so unoxidised lead. This is usually considered the optimum for paste production. From here the powder is mixed with sulphuric acid and water to form a paste which is spread onto the support grids. The plates are "cured" and dried to produce a lead monoxide/lead sulphate/basic lead sulphates mixture.

Formation of both positive and negative plates takes place in a tank of dilute sulphuric acid (S.G. 1.05 to 1.10 g cm⁻³, or molarity of between 0.3 and 0.7). Here the paste undergoes an electrochemical transformation under charge, to produce, on the negative plate a 'spongy' lead whilst on the positive plate, the paste is oxidized to PbO₂. After drying, the plates are assembled with alternating negative-positive plates, finishing with an extra negative plate. Separators are placed between the plates, these are good ionic conductors, electronic insulators, and are able to withstand the strong
chemical environment of battery electrolyte at temperatures of up to 70°C.

Prior to the 2nd World War, wood was the major separator, but as supplies neared exhaustion various artificial separators came into use. These are often polymeric microporous sheets such as Porvic (PVC), or Davak 5000, a phenol-formaldehyde resin polymer on a non-woven plastic fibre mat. Paper pulp or wood pulp stiffened with a phenolic-formaldehyde resin is sometimes used. More details can be found in Barak (11). These not only prevent shorting of the plates but also reduce the extent of "mossing" on the negative plate. Mossing is a term used to describe the development of dendrites on the negative, due to the dissolution-precipitation of PbSO₄ in the electrolyte.

Cycle life is usually considered to be limited by the positive plate (12) and over the past couple of decades, research into the positive plate has brought improvements in energy and power density of about 50% by the addition of alloying ingredients and electrode design.

Currently the trend is away from high (14%) antimonial alloys towards low (2-4%) and non-antimonial alloys. Antimony was added to pure lead to improve the castability, but it also reduces the grain size and amount of hot-tearing. A further advantage is that it has a beneficial effect on the structure and life of the positive plate, particularly on deep discharge. It is thought (13) that an antimony containing corrosion layer between the paste and the grid is more compact, has fewer voids and is mechanically more sound than the corrosion layer on a pure lead grid. As bismuth is in the same periodic group, it is important to note if these effects are reproduced when bismuth is present.

One disadvantage of using Sb is that it reduces the hydrogen
evolution overpotential on the negative plate. This would not matter to much if the antimony stayed on the positive plate, but this is not the case. While on overcharge, antimony can dissolve into the electrolyte in the +5 state. There are two paths that can be followed (14), it can either re-adsorb on the lead dioxide or it can migrate to the negative plate. There it is reduced to +3 and deposited. Reduction of the hydrogen overpotential then follows and significant water loss can occur. It is important that, in maintenance free batteries, this does not happen and new alloys have been developed to meet this need.

A second disadvantage (15) is the generation of antimony hydride (SbH$_3$) from the negative plate after antimony has been deposited. This usually occurs when the battery is either being float charged or on overcharge, for example if it is in use as a standby power source. Stibene is a toxic and flammable gas and build up of this can be particularly hazardous in an enclosed space, where there is a risk of an explosion. Lead has been successfully mixed with calcium and/or tin, and to a lesser extent magnesium and aluminium (16), to combat both of these problems. Again the effect of bismuth must be considered in such circumstances. Though the generation of bismuth hydride will be unlikely due to its thermodynamic instability and its extreme reactivity with water (17).

Lead as a raw material contains many impurities, and a major one is bismuth. Attempts to extract the bismuth are both time consuming and costly. Thus, if bismuth can be tolerated in the battery system, or if it has advantageous effects on the system then a cheaper raw material is gained.

Currently the Kroll-Betterson process is used to remove most of
the bismuth from the lead. By alloying calcium and magnesium to the molten lead, intermetallic compounds containing bismuth float to the top and are removed as dross. The level of residual bismuth is around 0.1%. To remove more of the impurity, as is usually specified by the battery manufacturers, the Jollivet process is employed. This uses potassium-magnesium drossing and levels down to $1 \times 10^{-3}$ wt% have been reported (18). Sodium is another reported alloy drossing agent (19). Alternatively the use of electrowinning is possible, but this is only economic when cheap electrical power is available.

Because of the expense of bismuth removal, some work has been carried out on electrochemical aspects of lead-bismuth alloys and this has been reviewed by Ellis et al. (20). The presence of bismuth in the lead-acid system has caused some controversy in the literature. Myers (21,22) and Devit et al. (23) have shown that bismuth has a beneficial effect by reducing the creep rate of an age-hardened alloy (21,22) and by decreasing the rate of self-discharge and gasing when compared to lead - antimony alloys (23). Kelly (24) confirmed these findings, whilst work done by Ritchie (25) at I.L.Z.R.O. contradicted the conclusions drawn by Kelly, Myers and Devit et al. Addition of bismuth to various binary alloys is a possibility and this has been studied by various authors (26,27,28), but is beyond the scope of the present research.

The main effort, for this thesis, has been to investigate fully the effect of bismuth on the lead-acid battery system. The conclusion and comparisons with antimonial alloys will be shown later, in particular whether bismuth can be tolerated in a commercially viable battery system.
2.1 The Electrode-Electrolyte Interphase

At the meeting place of two different phases there is a small but discernable region in which the bulk properties of either phase do not dominate, rather there is a mixing and overlap of properties. This area is known as the interphase. For electrochemists this region is usually that between the bulk electrode - where electrons carry the charge and the bulk electrolyte - where charge is carried by ions.

This transitional domain and its structure are very important in establishing the way electrode reactions proceed, though it is often only few microns across. It can be thought of as being similar to a capacitor, in which there is an "electrical double layer", or more often just "double layer", of charges and orientated dipoles. This double layer is usually found at the interphase between metal electrode and electrolyte.

The earliest model of this double layer was given by Helmholtz (29), his simple idea was that the excess charge on the electrode surface was balanced by a rigidly held layer of oppositely charged ions in the solution, Figure 2.1. This is equivalent to a simple parallel-plate capacitor. However, in order for the model of the double layer to be viable the following assumptions have to be made;

a) an electrostatic equilibrium holds the charges,
Fig. 2.1 Helmholtz Model of the Electrode/Electrolyte Interphase

Fig. 2.2 Gouy-Chapman Model of the Electrode/Electrolyte Interphase
b) there is no transfer of charge in either direction across the interphase with changes in electrode potential,

c) variation in electrode potential is mirrored in the solution near to the interphase,

d) thermal motion is not strong enough to break up the rigid array of charges.

This simple capacitive model implies no parallel resistive components and the electrodes which adhere to this projection are called "ideally polarizable" electrodes, e.g. Hg electrode in 1 mol dm$^{-3}$ KCl, but even here thermal motion causes the model to breakdown at room temperature.

A more comprehensive theory was developed independently by Gouy (30) and Chapman (31), here the idea of a diffuse double layer develops, allowing for both the thermal motion of ions and for the existence of ion pairs in the electrolyte. Thus the greatest concentration of excess charge is as close as possible to the electrode, where the electrostatic forces can overcome thermal motion. A general decrease in charge further away from the electrode, where thermal effects become dominant, Figure 2.2.

The major defect of the Gouy-Chapman theory is that ions are considered as point charges, this gives a very high value for the charge concentration close to the interphase. The variation in capacity with potential is also predicted, but with much greater values than found in practice.
Fig. 2.3  Stern-Model of the Electrode/Electrolyte Interphase
Stern (32) provided a suitable correction in the form of an absorbed layer of ions which have finite sizes and these could approach the electrode within a certain critical distance. There is now a division within this double layer such that next to the electrode is a region of firmly held ions of high field and low dielectric constant with a row of well attached charges, beyond which a diffuse layer extends from the plane of closest approach into the bulk electrolyte, Figure 2.3. This double layer can be treated as two capacitors connected in series i.e.

$$\frac{1}{C_1} = \frac{1}{C_{\text{fixed}}} + \frac{1}{C_{\text{diffuse}}} \tag{2.1}$$

Where

- $C_1$ = overall double layer differential capacitance
- $C_{\text{fixed}}$ = capacitance corresponding to the fixed layer
- $C_{\text{diffuse}}$ = capacitance corresponding to the diffuse layer

Grahame (33) also considered that the Helmholtz plane was divided into two regions, and allowing for dipoles from the water molecules suggested that there existed an inner and an outer layer, Figure 2.4. The inner plane is made up from specifically absorbed ions which have lost some of their hydration sheath and are, thus, closest to the electrode surface. An outer plane is present beyond this, with the charges fully hydrated, at their distance of closest approach.

Applying equation 2.1 to the modified Stern model shows that, as the electrolyte becomes more and more dilute, $C_{\text{diffuse}}$ becomes significantly larger than $C_{\text{fixed}}$. Subsequently the total double layer
Fig. 2.4  Grahame Model of the Electrode/Electrolyte Interphase
capacitance becomes independent of $C_{\text{fixed}}$ and at very low concentrations a plot of potential against $C_1$ gives a sharp minimum. This minimum is associated with the point of zero charge (p.z.c.) on the electrode.

Devanathan et al. (34) proposed a further refinement, after looking at the dielectric properties of the species in both Helmholtz planes. Their idea was that adsorbed solvated cations remained outside a layer of strongly orientated solvent dipoles. Thus penetration of the inner solvent layer by specifically adsorbed anions is thought to occur. Hence adsorbed water molecules have their negative poles pointing either away from or towards the electrode surface depending upon the potential, this is shown diagramatically in Figure 2.5.

The importance of the potential of zero charge was emphasised by Frumkin (35,36) explaining that the p.z.c. will move depending on ion adsorption. For anion adsorption the p.z.c. moves negative with the reverse being the case on cation incorporation. From this, the amount of charge on the electrode can be determined using $E_{\text{rat}}$ (rational potential). At positive values of $E_{\text{rat}}$ adsorption of negative ions is favoured and the opposite being true with $E_{\text{rat}}$ negative. Hence when $E_{\text{rat}}$ is small, there is little charge on the electrode and the adsorption of neutral molecules competes favourably with ionic crisis.

Since 1963 the majority of the work on the double layer theory has been concerned with the compact layer and subsequent orientations of the water molecules within the inner Helmholtz plane. Levine et al. (37), Damaskin and Frumkin (38) and Parsons (39) have all studied these areas.

In the late 1970's Cooper and Harrison (40-44) revised the thinking on the existence and structure of the double layer. Their new
Fig. 2.5  Davanathan Model of the Electrode/Electrolyte Interphase

COMPACT LAYER

Solvent Molecules

DIFFUSE LAYER

Solvated Cations

Specifically Adsorbed Anions

Inner Helmholtz Plane

Outer Helmholtz Plane
approach is to consider the interphase as one region with a shape formed from the innate differences between anions and cations, in an aqueous solution. With the distribution of charge such that it is considered to act at a mean distance from the electrode.

2.2 The Charge Transfer Process

The electrode processes which occur at the metal electrode-electrolyte interphase are coupled with the transfer of electric charge. These processes are often called heterogeneous reactions and the general formula below is a representation of this redox couple.

\[
\begin{align*}
O + ne & \xrightleftharpoons[\text{k}_b]{\text{k}_f} R \\
& \quad (2.2)
\end{align*}
\]

Where

- \(O\) = Oxidised species
- \(R\) = Reduced species
- \(k_f\) = forward reaction rate
- \(k_b\) = backward reaction rate

Thermodynamically speaking, as shown schematically in Figure 2.6, with the electrode at zero potential \(\Delta G_{oc}\) and \(\Delta G_{oa}\) correspond to the activation energies for the forward and backward processes respectively. Changing the potential of the electrode to the new value of \(E\) will result in a change in the activation energy by the amount \(-\frac{\Delta F}{E}\). Hence
Fig. 2.6 Thermodynamic Diagram Of The Reaction Scheme

\[ O + n e <\rightarrow R \]

Fig. 2.7 Perpendicular Diffusion Near an Electrode Surface
the reduction curve labeled "One" will move up or down by this amount. The dashed line in Figure 2.6 indicates the effect of making E more positive.

The change in chemical energy must be equal to the amount of electrical energy the system produces. Hence the change in Gibbs energy is given by

$$\Delta G = -nFE$$  \hspace{1cm} (2.3)

and at equilibrium the standard Gibbs free energy change will be given by

$$\Delta G^0 = -nFE^0$$  \hspace{1cm} (2.4)

where $E^0$ is the standard potential at equilibrium. For the reaction in equation (2.2) to be taken to completion, the Gibbs free energy for the total reduction of the oxidised species O is given by the Van't Hoff isotherm

$$\Delta G = \Delta G^0 + RT \ln \frac{a_R}{a_O}$$  \hspace{1cm} (2.5)

which can be simplified to

$$\Delta G = \Delta G^0 + RT \ln \frac{[C_R]}{[C_O]}$$ \hspace{1cm} (2.6)

Now substituting for $\Delta G$ and $\Delta G^0$ from equations (2.3) and (2.4) gives
\[ E = E^\circ + \frac{RT}{nF} \ln \left( \frac{[C_0]}{[C_R]} \right) \]  

which is the Nernst equation and predicts the potential of the electrode, as well as defining the dependence of e.m.f. on concentration for this redox reaction. \( E^\circ \) is the equilibrium potential and is defined as the potential at which no net current flows.

A shift in potential from the equilibrium value to \( E = E \) gives the energy required for the forward process to become dominant over the reverse. We must now define the portion of energy required by each process, called - the charge transfer coefficient. This has a value from zero to unity, though for a reversible reaction it is typically 0.5. For the forward process at the potential \( E = E \) then

\[ \Delta G_c^+ = \Delta G_{oc}^+ - \alpha nFE \]  

and similarly for the reverse reaction

\[ \Delta G_a^+ = \Delta G_{oa}^+ - (1 - \alpha)nFE \]  

\( k_f \) and \( k_b \) have both previously been defined in equation (2.2), and assuming they fit an Arrhenius type equation, both forward and backward reactions can be described as

\[ k_f = \frac{\Delta G_c^+}{RT} \]  

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Expansion of the equations above in terms of activation energies from equations (2.8) and (2.9) gives

\[ k_f = A_f \exp \left( -\frac{\Delta G_{o_a}^+}{RT} \right) \exp \left( -\frac{\alpha nFE}{RT} \right) \]  

(2.12)

and

\[ k_b = A_b \exp \left( -\frac{\Delta G_{oa}^+}{RT} \right) \exp \left( \frac{(1 - \alpha) nFE}{RT} \right) \]  

(2.13)

Equations (2.12) and (2.13) above contain terms for the rate equations that are potential dependent and terms that are free of potential control. When \( E = 0 \) then the potential independent terms become equal to the rate constants and are as such called \( k_f^\theta \) and \( k_b^\theta \). Hence

\[ k_f = k_f^\theta \exp \left( -\frac{\alpha nFE}{RT} \right) \]  

(2.14)

\[ k_b = k_b^\theta \exp \left( \frac{(1 - \alpha) nFE}{RT} \right) \]  

(2.15)

The bulk concentration of the reactants in solution is denoted by
\( C_0^* \) and \( C_R^* \) but close to the electrode \( C_R(x,t) \) and \( C_0(x,t) \) are used, where \( x \) is the distance from the electrode and \( t \) is the time after the start of the reaction. At \( E = E^0 \), the standard equilibrium potential, the system is in equilibrium, with both reactants undergoing reactions at the same rate. Then

\[
C_0^* = C_R^* \quad (2.16)
\]

and hence

\[
k_F C_0^* = k_B C_R^* \quad (2.17)
\]

Then if equation (2.16) holds

\[
k_F = k_B = k^0 \quad (2.18)
\]

where \( k^0 \) is the intrinsic or standard rate constant. The potential independant term thence can be removed from equations (2.14) and (2.15). Thus for the forward reaction

\[
k_F = k^0 \exp \left[ \frac{-\alpha nF (E - E^0)}{RT} \right] \quad (2.19)
\]

and for the reverse process

\[
k_B = k^0 \exp \left[ \frac{(1 - \alpha) nF (E - E^0)}{RT} \right] \quad (2.20)
\]
In the investigation of an electrochemical reaction it is usually easier and more appropriate to measure current than rate constants. As current is a measure of the number of electrons passed, the following is true:

\[ i = nFkC \tag{2.21} \]

but with the forward and reverse reactions competing then the observed current is given by

\[ i = i_f - i_b \tag{2.22} \]

Substituting for \( i_f \) and \( i_b \) from equations (2.19) and (2.20)

\[ i = nFk^0 \left[ C_{0(0,t)} \exp \left[ \frac{-\alpha nF( E - E^\theta )}{RT} \right] - C_{R(0,t)} \exp \left[ \frac{(1 - \alpha) nF( E - E^\theta )}{RT} \right] \right] \tag{2.23} \]

which is known as the Butler-Volmer equation. This equation can be simplified under the correct conditions, i.e. when the bulk concentration is not significantly different from the surface value. This occurs when the solution is well stirred or the current density is low, as is given in equation (2.24) below.
\[ i = nFk^0C \left[ \frac{\exp \left( -\frac{\alpha nF(E - E^\theta)}{RT} \right)}{RT} \right] - \exp \left( \frac{(1 - \alpha)nF(E - E^\theta)}{RT} \right) \] \hspace{0.5cm} (2.24)

As \( E^\theta = E_{eq} \) under these conditions the overpotential is given by

\[ \eta = E - E_{eq} \] \hspace{0.5cm} (2.25)

also at this potential, it is noted that the exchange current density is given by

\[ i_0 = nFk^0C \] \hspace{0.5cm} (2.26)

We can substitute for \( i_0 \) and \( E = E^\theta \) to give

\[ i = i_0 \left[ \frac{\exp \left( -\frac{\alpha nFh}{RT} \right)}{RT} - \exp \left( \frac{(1 - \alpha)nFh}{RT} \right) \right] \] \hspace{0.5cm} (2.27)

which is known as the Erdy-Gruz and Volmer equation (45).

This equation can be simplified for two conditions:

a) Large Overpotentials \( (\eta > 100 \text{ mV}) \)

Equation (2.27) can be reduced to give Tafel behaviour as a limiting equation under these conditions.

As previously stated;

\[ i = i_f - i_d \] \hspace{0.5cm} (2.22)

Over-potential being defined by the difference between the working potential and the equilibrium potential.
with sufficient polarization of the electrode \( i_f \gg i_b \) and

\[
i = i_f \quad (2.28)
\]

\[
i = i_0 \exp \left( \frac{-anF\eta}{RT} \right) \quad (2.29)
\]

Taking logs of both sides in the above equation gives

\[
\ln i = \ln i_0 - \frac{anF\eta}{RT} \quad (2.30)
\]

This can be re-arranged to give, in cathodic form

\[
\eta = \left[ \frac{RT}{\alpha nF} \right] \ln i_0 - \left[ \frac{RT}{\alpha nF} \right] \ln i \quad (2.31)
\]

and similarly anodically,

\[
\eta = \left[ \frac{RT}{(1 - \alpha)nF} \right] \ln i_0 - \left[ \frac{RT}{(1 - \alpha)nF} \right] \ln i \quad (2.32)
\]

Equations (2.31) and (2.32) are known as Tafel equations (46).
b) Low Overpotentials \( ( \eta < 10/n \text{ mV} ) \)

The Erdey-Gruz and Volmer equation can be expanded if the current is so small that the third and subsequent terms of the exponential series are very close to zero,

\[
i = i_0 \left[ \left( \frac{(1 - \alpha)nF_n}{RT} \right) - \frac{1 + (1 - \alpha)nF_n}{RT} \right] \tag{2.33}
\]

Hence

\[
i = -i_0 \frac{nF_n}{RT} \tag{2.34}
\]

which shows a linear relationship between overpotential and current density at low overpotentials.

Re-arranging equation (2.34) gives

\[
i_0 = \frac{RT}{nF_n} \left( \frac{i}{\eta} \right) \tag{2.35}
\]

The ratio of \( \eta/i \) has dimensions of resistance and is often known as the charge transfer resistance \( R_0 \), i.e.

\[
R_0 = \frac{RT}{nF_n} \frac{1}{i_0} \tag{2.36}
\]

A numerical value for \( i_0 \) can be obtained from the value of \( R_0 \) and also from the extrapolation of the Tafel plots of \( \eta \) versus \( \ln i \), where
the intercept on the y-axis gives the value of $i_o$.

Returning to the Butler-Volmer equation, equation (2.23), under equilibrium conditions $k_f = k_b$ hence,

\[
nFk^0 C_0(x,t) \exp \left[ -\frac{\alpha nF(E_{eq} - \theta)}{RT} \right] \]

\[
= nFk^0 R_0(x,t) \exp \left[ \frac{1 - \alpha nF(E_{eq} - \theta)}{RT} \right]
\]

From this equation it can be deduced, because no net current flows at $E = E_{eq}$, that

\[
C_0(x,t) = C_0^* \quad (2.38)
\]

and

\[
C_R(x,t) = C_R^* \quad (2.39)
\]

substituting into equation (2.37) gives

\[
\exp \left[ \frac{nF(E_{eq} - \theta)}{RT} \right] = \frac{C_0^*}{C_R^*} \quad (2.40)
\]

after re-arrangement. Taking logs of both sides of equation (2.40) gives
\[ E = E^0 + RT \log \frac{C_R^*}{C_O^*} \]  
(2.41)

which is equivalent to equation (2.7). The kinetic derivation and proof are now in line with the thermodynamic approach.

By definition, the value of the exchange current density is given by the rates of the forward or reverse reactions at equilibrium:

\[ i_0 = i_f = i_b \]  
(2.42)

thus for a system in balance

\[ i_0 = nFk^0 C_O^* \exp \left[ -\frac{nF \eta}{RT} \right] \]  
(2.43)

raising equation (2.43) to the power of \( -\alpha \) gives

\[ \exp \left[ -\frac{nF \eta}{RT} \right] = \left[ \frac{C_O^*}{C_R^*} \right]^{-\alpha} \]  
(2.44)

and substituting back into equation (2.43) gives

\[ i_0 = nFk^0 C_O^* \left( 1 - \alpha \right) C_R^* \]  
(2.45)

Thus \( i_0 \) is proportional to \( k_0 \). \( k_0 \) is most easily interpreted as a measure of the ease of reaction, hence a system in which \( k_0 \) is small will take some time to come to equilibrium. But when \( k_0 \) is large, the
steady state condition will be rapidly achieved.

2.3 Mass Transport Processes

At the surface of an electrode, the redox reaction occurring can be represented by

\[
\begin{align*}
    k_f & \quad \text{O + ne} \rightarrow R \\
        & \quad \text{with} \quad k_d
\end{align*}
\]

and can be assumed to be made up of the following processes:

a) \( O_{\text{bulk}} \rightarrow O_{\text{electrode}} \)  
   \( \text{equation (2.46)} \)  
   \( \text{known as mass transport control.} \)

b) \( O_{\text{electrode}} + \text{ne} \rightarrow R_{\text{electrode}} \) 
   \( \text{equation (2.47)} \)  
   \( \text{called charge transfer control.} \)

c) \( R_{\text{electrode}} \rightarrow R_{\text{bulk}} \) 
   \( \text{equation (2.48)} \)  
   \( \text{known as chemical transformation rate control.} \)

These three processes may control the speed of the reaction, the slowest step obviously being dominant. These processes are
There are three types of mass transfer which normally occur and they are shown below:

1) Migration

Mass transfer is affected by the electrostatic forces between the charged particles and the electrode. This is very small when excess supporting electrolyte is present.

2) Convection

When a reactant is being used up, close to the electrode, natural convection will always occur, as a result of the formation of a density gradient. Other reasons for the disturbance of the system include thermal gradients or mechanical vibrations. Forced convection, via stirring, electrode rotation, bubbling gas etc., is often used.

3) Diffusion

Almost immediately after an electrochemical reaction starts, a concentration gradient will be produced as one of the reactants is used up. Whenever there is a concentration gradient then diffusion will follow.

In the study of the kinetics of electrode processes, rigidly defined conditions are usually employed and various mathematical models for describing the system are known. The most widely studied is that of diffusion.

In Fig. 2.7, an electrode with cross-sectional area A is undergoing a redox reaction, as described in equation (2.2). The number of molecules, $N$, of the species $O$, diffusing in time $dt$ is proportional to the concentration gradient of the diffusing species, as below.
\[
\frac{dN}{dt} = -D_0 \frac{\partial C_0}{\partial x}
\]

(2.49)

Equation (2.49) is known as Fick's First Law, and is a simple model describing the diffusion of a species to a planar electrode of infinite dimensions. \(1/A \frac{dN}{dt}\) is called the flux, and is the number of molecules diffusing through a unit area in unit time. \(D_0\) is known as the diffusion coefficient. Fick's law can be thus written as

\[
\frac{1}{A} \frac{dN}{dt} = \text{flux} = q = -D_0 \frac{\partial C_0(x,t)}{\partial x}
\]

(2.50)

While the reduction proceeds, the concentration of \(O\) in a volume element, \(dx\), decreases.

\[
\frac{\partial C_0(x,t)}{\partial t} = \begin{bmatrix} \text{amount of substance} \\ \text{No. of moles} - \text{No. of moles} \end{bmatrix} \begin{bmatrix} \text{entering} \\ \text{leaving} \end{bmatrix}
\]

(2.51)

in time \(t\),

\[
\frac{\partial C_0(x,t)}{\partial t} = \frac{q(x + dx) - qx}{dx}
\]

(2.52)

and as \(dx \rightarrow 0\), we can state

\[
\frac{\partial C_0(x,t)}{\partial t} = \frac{\partial q}{\partial x}
\]

(2.53)
Re-arrangement of Fick's first law gives

\[ q = \frac{D_0}{\alpha} \frac{\partial^2 C_0(x,t)}{\partial x^2} \]  

(2.54)

and differentiating with respect to \( x \) gives

\[ \frac{dq}{dx} = D_0 \frac{\partial^2 C_0(x,t)}{\partial x^2} \]  

(2.55)

Substituting for \( \frac{dq}{dx} \) in equation (2.53) gives

\[ \frac{\partial^2 C_0(x,t)}{\partial t} = D_0 \frac{\partial^2 C_0(x,t)}{\partial x^2} \]  

(2.56)

This equation is called Fick's second law and describes the behaviour of \( C_0 \) with time. For a particular set of boundary conditions, a solution to equation (2.54) allows a numerical value to be found for \( C_0(o,t) \) and subsequently the value of \( C_0 \) at any time after the start of the reaction.

The conditions for solving equation (2.54) are

(i) \( C_0(0,t) = 0 \) at \( t > 0 \)

(ii) \( C_0(x,t) \rightarrow C_0^* \) as \( x \rightarrow \infty \)

(iii) \( C_0(0,t) = C_0^* \) at \( t < 0 \)

where \( C_0^* \) is the bulk concentration of \( O \) and \( C_0(0,t) \) is the
concentration at the electrode surface.

A solution to equation (2.54) by integration is given by

\[ C_0(x, t) = C_0 \left[ \frac{x}{2D_0^{1/2} t^{1/2}} \right] \]

where the integral

\[ \int_0^z 2 e^{-y^2} dy \]

is called the error function of \( z \) or \( \text{erf} \ z \). \( z \) is substituted for

\[ \frac{x}{2D_0^{1/2} t^{1/2}} \]

and equation (2.57) can be simplified to

\[ C_0(x, t) = C_0 \times \text{erf} \ z \] (2.58)

The value of the error function depends only on \( z \) and the integral may be solved numerically or found in standard tables. The current of the reaction is proportional to the convective mass transport, thus

\[ i = nF \alpha \] (2.59)
and substituting into Fick's first law gives

\[
\frac{1}{A} \frac{dn}{dt} = D_0 \frac{\partial C_0(x, t)}{\partial x} = q = \frac{i}{nFA}
\]  

(2.60)

\( \frac{\partial C_0(x, t)}{\partial x} \) is the concentration gradient term and can be easily measured \( \frac{\partial C_0(x, t)}{\partial x} \)
as a current, hence

\[
i(t) = i_d(t) = nFAD_0 \left[ \frac{\partial C_0(x, t)}{\partial x} \right] \]  

(2.61)

where \( i_d(t) \) is the diffusion controlled current \( t \) seconds after the start of the reaction. Determination of the final term in equation (2.61) may be completed by differentiation of equation (2.58) with respect to \( x \) and by setting \( x = 0 \). Hence

\[
\frac{\partial C_0(x, t)}{\partial x} = \frac{C_0^*}{\pi D_0^{1/2} t^{1/2}}
\]  

(2.62)

Substituting from equations (2.61) and (2.62) for the concentration gradients gives

\[
i_d(t) = nFAD_0 \frac{1/2}{\pi} \frac{C_0^*}{t^{1/2}}
\]  

(2.63)

The above equation is known as the Cotrell equation and shows that the diffusion limited current at a planar electrode is inversely
proportional to the square root of time.

2.4 Porous Electrode Theory

The porous lead electrode's behaviour is complex and depends on many parameters, some of which are listed below:

1) temperature
2) rate of discharge
3) quantity of active material
4) concentration of electrolyte
5) quantity of electrolyte
6) electrode thickness
7) electrode porosity
8) electrode design

The mathematical modelling of such an electrode is a complicated task, and to account for all the factors involved would be extremely hard. However by using equations for the transport and kinetic phenomena occurring at the electrode a simplified but reasonably accurate result is obtained. Several reviews (47-50) exist of mathematical models and the majority of these use a uni-dimensional approach, ignoring the pore geometry.

Application of the macro-homogeneous model (51) to the lead-acid battery has been made by Micka and Rousar (52-54), Simonson (55) and others (56-58), using the steady-state approach to predict current distribution, discharge and depletion profiles.
CHAPTER 3

THEORIES OF RELEVANT ELECTROCHEMICAL TECHNIQUES

3.1 Linear Potential Sweep/Cyclic Voltammetry

Both of the above techniques involve the application of linear potential-time functions to an electrode. The current produced by the system under test is recorded as a property of the applied potential and the resultant trace is known as a voltammogram.

The simplest of the above experimental devices is linear sweep voltammetry (L.S.V.), in that the applied potential is swept from $E_1$ to $E_2$ and back again, at a rate $v$, Fig. 3.1. The experiment is stopped when the voltage reaches $E_1$ for the second time. Repetative sweeping between the potential limits is known as cyclic voltammetry.

Matheson and Nichols (59) were the first to use this type of experiment and the derivation of the fundamental equations was from work carried out by Delahay (60), Shain (61,62) and others (63-66). The two experimental methods have been used to elaborate and confirm data or reaction mechanisms, charge transfer processes and other complex electrode reactions. Cyclic voltammetry has often been used to study the formation and reduction of oxide layers on the surface of metal electrodes.

The main feature of a voltammogram, Fig 3.2, is the current peak at the voltage where a particular reaction takes place. The position and shape of the current peak obtained depend on many factors such as temperature, electrode material, sweep rate, solution composition and
Fig. 3.1  Linear Sweep Voltammogram Voltage - Time Trace

Fig. 3.2  Current Response to an L.S.V.
the concentration of the reactants.

The rate of change of the voltage can be varied within wide limits, as such, slow sweep rates are used to examine steady state reactions and fast sweeps are employed to view short lived or transient species. Only L.S.V.s can give accurate kinetic information because the equations derived apply only if there is no concentration gradient in the solution when \( t = 0 \). Cyclic voltammetry causes complex concentration gradients to prevail near the electrode surface, thus this style of experimental technique is best suited for the identification of steps in the overall reaction and new species which are formed during the electrolysis.

3.1.1 Reversible Reactions

If the rate of electron transfer in any particular electrochemical reaction is significantly greater than the rate of mass transport, then the reaction is said to be reversible. Under such conditions the peak current density, \( I_p \), is given by the Randles-Sevcik equation;

\[
I_p = - (2.69 \times 10^5) n^{2/3} C_0^* D_0^{1/2} v^{1/2} \text{ at } 25 \degree C
\]

where \( n \) = the number of electrons transferred in the overall electrode process

\( D_0 \) = diffusion coefficient (cm\(^2\) s\(^{-1}\))

\( C_0^* \) = bulk concentration of \( O \) (mol cm\(^{-3}\))

\( v \) = sweep rate (V s\(^{-1}\))

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and \( I_p \) = maximum current density ( A cm\(^{-2}\) )

It is obvious that \( I_p \) is proportional to the concentration of the reactive species, and \( I_p \) varies with the square root of both the sweep rate and the diffusion coefficient. The limiting conditions for reversibility of a system are tabulated below, Table 3.1:

<table>
<thead>
<tr>
<th>Table 3.1 - Conditions For a Reversible System</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) ( \Delta E_p = E_p^A - E_p^C = 59 \text{ mV} )</td>
</tr>
<tr>
<td>2) ( \left[ E_p - E_p/2 \right] = 59 \text{ mV} )</td>
</tr>
<tr>
<td>3) ( \left[ \frac{I_p^A}{I_p^C} \right] = 1 )</td>
</tr>
<tr>
<td>4) ( I_p \propto v^{1/2} )</td>
</tr>
<tr>
<td>5) ( E_p ) does not vary with ( v )</td>
</tr>
</tbody>
</table>

3.1.2 Irreversible Processes

The corollary to section 3.1.1 is that when the rate of electron transfer is not sufficient to maintain the surface equilibria the system is designated as irreversible. The peak current density is given by
\[ I_p = - (2.99 \times 10^5) n (q_a n_a)^{1/2} C_0 D_0^{1/2} v^{1/2} \text{ at } 25^\circ C \]  
(3.2)

where \( n_a \) = number of electrons transferred, up to and including the rate determining step.

Shain (61) showed that \( E_p \) varied with sweep rate in the relationship shown below:

\[ E_p = k + \frac{2.3RT}{2q_a n_a F} \log v \]  
(3.3)

where

\[ k = E_e^0 \cdot \frac{RT}{q_a n_a F} \left[ 0.78 + 2.3 \log \left( \frac{q_a n_a F D_0}{k^0^2 RT} \right) \right] \]  
(3.4)

Thus for a tenfold increase in sweep rate, \( E_p \), the peak potential would move by \( 30/n_a \) mV at \( 25^\circ C \). Also the value for \( E_p \) occurs beyond \( E_e^0 \), because of an activation overpotential related to \( k^0 \). Again the conditions for the irreversibility of the system are tabulated below, Table 3.2.

3.1.3 Quasi-Reversible Reactions:

The term was coined by Matsuda and Ayabe (64) for systems which show electron transfer kinetic limitations, similar to the irreversible case, but where the reverse reactions have to be considered. Thus the conditions for quasi-reversibility are shown below, Table 3.3.
Table 3.2 - Conditions for an Irreversible System

1) No reverse peak

2) \( I_p \propto \nu^{1/2} \)

3) \( E_p \propto \log \nu \)

4) \[ \left[ E_p - E_p/2 \right] = \left[ \frac{48}{a_n} \right] \text{mV} \]

Table 3.2 - Diagnostic Tests for a Quasi-Reversible System

1) \( I_p \) increases with \( \nu^{1/2} \) but it is not proportional to it

2) \[ \left[ \frac{I_p^a}{I_p^c} \right] = 1 \text{ if } a_c = a_a = 0.5 \]

3) \( \Delta E_p \) is greater than \( 59 \text{ mV} \)

4) \( \Delta E_p \) increases with increasing \( \nu \)

5) \( E_p \) moves more positive with increasing \( \nu \)
3.2 Potential Step Methods

3.2.1 Introduction

This technique is often used when investigating electrode surface phenomena such as electrocrystallisation, corrosion, passivation etc.

The method of changing the system is by instantaneously disturbing the working electrode potential and recording the resultant current as the system reverts to the steady-state. The rate controlling step can be either the diffusion of the electroactive species to the electrode or a solid state reaction with the active species on the electrode surface.

3.2.2 Diffusion Control

If the rate determining step is that of diffusion, the current trace shows a sharp peak as the potential is applied, followed by a decay as the electroactive species closest to the electrode is exhausted. The residual current then becomes limited by the rate of diffusion of the reactants to the electrode surface.

At high overpotentials, the rate of electron transfer is fast and as such the current will be determined by diffusion. Cottrell's equation is observed (Chapter 2.3) and the response is a linear $i v's t^{1/2}$.

With low overpotentials, neither process dominates and the decay of the curve is not so sharp. It has been shown (65) that in the limiting case, at long times
i = nFK_c \frac{C_0^* D_0^* t^{-1/2}}{\pi^{1/2} (K_c - K_a)} \tag{3.5}

and at short times

i = nFK_c C_0^* \left[ \frac{1 - nK_c + K_a}{\pi^{1/2} D_0^{1/2}} \right] t^{1/2} \tag{3.6}

3.2.3 Electrocrystallisation

In the charge and discharge of most electrochemical devices, some morphological change usually occurs. In the case of the lead-acid battery, the growth of lead sulphate on discharge, and the PbO_2 or lead on charge follow a complex set of steps in their nucleation and growth. It is important to investigate the development of the new phase and the nucleation and growth pattern it follows, with this data an improvement in the energy density etc. of the system may be gained.

Since the late 1950's renewed interest has been shown in the modelling and understanding of this phenomena (67,68). This has been built on the nucleation theory adopted in the 1960's of the instantaneous and progressive models.

3.2.3.1 2-Dimensional Electrocrystallisation

By defining the number of active sites under particular experimental conditions as N_0, the rate of appearance of stable nucleation sites can be expected to follow first order kinetics (69),
Fig. 3.3  2 Dimensional Crystal Growth
\[ N(t) = N_0 \left(1 - \exp(-At)\right) \]  

(3.7)

if \[ At \gg 1 \] then equation (3.7) becomes

\[ N(t) = N_0 \]  

(3.8)

but for small values of \[ At \], \[ N(t) \] is given by

\[ N(t) = N_0 At \]  

(3.9)

or

\[ N(t) = A't \]  

(3.10)

In the above equations, \( A \) is the first order nucleation rate constant and equation (3.8) is the limiting case for instantaneous nucleation, i.e. where time for appearance of the nucleation centres is small compared to that of the double layer charging time.

Equation (3.10) is the limiting case for progressive nucleation such that the growth sites appear linearly with time.

The current at any time \( t \), for a single growth centre, will be given by equation (3.11), if we consider the simplest case of two-dimensional growth, Fig 3.3

\[ i(t) = nFKZ\pi rh \]  

(3.11)

where \( k \) is the rate of incorporation.
The charge required to expand the growth centre is

$$Q(r) = nhmP_0$$  (3.12)

where $\rho$ = density of the substrate

$M$ = molecular weight of the substrate

Differentiation with respect to time gives the instantaneous current required to increase the disc by radius $dr$

$$i(r,t) = \frac{2nhmP_0r(t)}{M} \cdot \frac{dr(t)}{dt}$$  (3.13)

The rate of radial expansion is thus as follows

$$\frac{dr(t)}{dt} = \frac{Mk}{\rho}$$  (3.14)

The radius at any time $t$ is, therefore, the integral of equation (3.14) i.e.

$$r = \frac{Mkt}{\rho}$$  (3.15)

Substituting for $r$ in equation (3.11) gives

$$i = \frac{2nmFr^2hMk}{\rho}$$  (3.16)
The current is only associated with the growth of a single disc on a planar surface. If there are \( N_0 \) nuclei then the current is

\[
i = 2 \pi r N_0 F K^2 \rho M \ \rho
\]  

in the instantaneous case (70).

For progressive nucleation, then not only is there the growth of the discs, but more nucleation centres appear with time. The current is given by

\[
i = \int_0^t i(u) \left[ \frac{dN}{dt} \right]_{t-u} du \tag{3.18}
\]

if \( i(u) \) is replaced by equation (3.16) and

\[
\frac{dN}{dt} = N_0 A = A \tag{3.19}
\]

then for progressive two-dimensional nucleation and growth

\[
i = \frac{nF \beta h A K^2 t^2}{\rho} \tag{3.20}
\]

which can be compared to equation (3.17).

The above equations refer to the growth of discrete centres with no overlap. This is true only at short times when the centres are widely spaced, but as growth proceeds the discs will come into contact, Figure 40.
3.3. This reduces the edge area. To account for the overlap Avrami (71) shows that the area covered, $S$, is related to the normalised extended area $S_{\text{ext}}$ by

$$S = 1 - \exp(-S_{\text{ext}}) \quad (3.21)$$

This approach was used by Bewick (72) to show that if the random overlap of the growth centres occurs then the fraction $\gamma$ of the surface covered by growing nuclei is related to the amount $\gamma_{\text{ext}}$ that would be covered by the absence of the collisions, Fig 3.4, by

$$\frac{d\gamma}{d\gamma_{\text{ext}}} = 1 - \gamma \quad (3.22)$$

Hence for instantaneous nucleation we can show that

$$\gamma_{\text{ext}} = N_0 \pi r^2 \quad (3.23)$$

and for progressive nucleation and growth

$$\gamma_{\text{ext}} = \int_0^t r(u)^2 \left[ \frac{dN}{dt} \right]_{t-u} du \quad (3.24)$$

Substituting for $r$ in terms of $t$ in equation (3.15) gives for instantaneous nucleation

$$\gamma_{\text{ext}} = \frac{\pi N_0 M^2 k^2 t^2}{\rho^2} \quad (3.25)$$
Fig. 3.4 2 Dimensional Crystal Growth Showing Overlap and Extended Area

Fig. 3.5 3 Dimensional Crystal Growth
Integrating equation (3.22) with respect to time and substituting into equations (3.25) and (3.26) gives for instantaneous nucleation

$$
\dot{\gamma} = 1 - \exp \left[ - \frac{\pi N_0 M K^2 \rho^2}{\rho^2} \right] \quad (3.27)
$$

and for progressive nucleation

$$
\dot{\gamma} = 1 - \exp \left[ - \frac{\pi N_0 M K^2 \rho^2}{3 \rho^2} \right] \quad (3.28)
$$

We can now arrive at current-time transient expressions allowing for overlap and thus at long time i.e. \( t > t_{\text{max}} \)

$$
i = \frac{2nF \pi h \rho N_0 K^2 t}{\rho} \exp \left[ - \frac{\pi N_0 M K^2 \rho^2}{\rho^2} \right] \quad (3.29)
$$

for two-dimensional instantaneous nucleation and growth and

$$
i = \frac{nF \pi h M K^2 A t^2}{\rho} \exp \left[ - \frac{\pi M^2 A K^2 t^3}{3 \rho^2} \right] \quad (3.30)
$$
for two-dimensional progressive nucleation and growth.

3.2.3.2 Three-Dimensional Electrocrystallisation

If the growth of a new phase on a substrate is not confined to the surface then we can consider growth as a right circular cone, Fig 3.5, with growth rates \( k_3 \) and \( k_3' \). The total current from one growing cone can be obtained by the integration of the contributions of a stack of discs with decreasing radii. By combining \( k_3 \) and \( k_3' \) as an aspect ratio, \( k \), then for short times \((73)\) when \( t < t_{\text{max}} \)

\[
i = \frac{2\pi F n M^2 N_0 k^3 t^2}{\rho^2} \tag{3.31}
\]

for instantaneous nucleation and

\[
i = \frac{2\pi F n M^2 \pi k^3 t^2}{3 \rho^2} \tag{3.32}
\]

for progressive nucleation. Following the same proof as for two-dimensional growth it can be shown \((74)\) that for \( t > t_{\text{max}} \) three-dimensional instantaneous nucleation and growth gives including a final passivation term

\[
i = n F k' \left [ 1 - \exp \left ( -\frac{\pi M^2 k^2 N_0 t^2}{\rho^2} \right ) \right ] \exp \left ( -\frac{\pi M^2 k^2 N_0 t^2}{\rho^2} \right ) \tag{3.33}
\]
and for three-dimensional progressive nucleation and growth

\[ i = nF K' \left( 1 - \exp \left[ -\frac{\pi M^2 K^2 A t^3}{3 \rho^2} \right] \right) \exp \left[ -\frac{\pi M^2 K^2 A t^3}{3 \rho^2} \right] \] (3.34)

Drawing together equations (3.31), (3.32), (3.33) and (3.34), the descriptions can be reduced to

i) \[ i = \alpha_1 t \exp (\beta_1 t^2) \] (3.35)

ii) \[ i = \alpha_2 t^2 \exp (\beta_2 t^3) \] (3.36)

iii) \[ i = \lambda_1 \left( 1 - \exp (\alpha_3 t^2) \right) \exp (\alpha_3 t^2) \] (3.37)

iv) \[ i = \lambda_2 \left( 1 - \exp (\alpha_4 t^3) \right) \exp (\alpha_4 t^3) \] (3.38)

and differentiation of the above with respect to time gives a single maximum \((i_m, t_m)\) at which \(\frac{di}{dt} = 0\), (74).

Thus the following values for the constants can be calculated

\[ \alpha_1 = \frac{i_m}{t_m} \exp (0.5) \] (3.39)

\[ \beta_1 = \frac{1}{2t_m^2} \] (3.40)

\[ \alpha_2 = \frac{i_m}{t_m^2} \exp (0.67) \] (3.41)
Fig. 3.6 Dimensionless Plot of the Predicted Current Response of a 2 Dimensional Instantaneous and a 2 Dimensional Progressive Nucleation and Growth Model
\[ \beta_2 = \frac{2}{3t_m^3} \quad (3.42) \]

\[ \lambda_1 = 4i_m \quad (3.43) \]

\[ \alpha_3 = \frac{\ln(1/2)}{t_m^2} \quad (3.44) \]

\[ \lambda_2 = 4i_m \quad (3.45) \]

\[ \alpha_4 = \frac{\ln(1/2)}{t_m^3} \quad (3.46) \]

By substituting the above constants back into equations (3.31-3.34), the equations are simplified to

\[ i_m = \frac{t}{t_m} \exp \left[ -\frac{1}{2} \frac{t^2}{t_m^2} \right] \quad (3.47) \]

for two-dimensional growth, instantaneous nucleation

\[ i_m = \left[ \frac{t}{t_m} \right]^2 \exp \left[ -\frac{2}{3} \frac{t^3 - t_m^3}{t^3} \right] \quad (3.48) \]

for two-dimensional progressive nucleation and growth.
Fig. 3.7  Dimensionless Plot of the Predicted Current Response of a
3 Dimensional Instantaneous and a 3 Dimensional
Progressive Nucleation and Growth Model

includes a passivation term
\[
d i = 4 \left( \frac{t^2}{t} \right)^2 \left( \frac{t^2}{t} \right)^2
\]

for three-dimensional growth, instantaneous nucleation and finally

\[
d i = 4 \left( \frac{t^3}{t} \right)^3 \left( \frac{t^3}{t} \right)^3
\]

for three-dimensional progressive nucleation and growth.

The above may be plotted out in a dimensionless graphical form, Figs 3.6 and 3.7, to which experimental data points can be fitted (74,75).

3.3 The Hydrogen Evolution Reaction on Lead

Investigations into the hydrogen evolution reaction (h.e.r.) on lead in sulphuric acid solutions have been conducted over a large number of years and several wide ranging reviews exist (76,77). It can be concluded from this published work that the kinetic data conforms to a process of rate control by charge transfer. Frunkin and Jafa (78) have shown that reactions of this kind can be represented for a range of acid concentrations by the equation below.
\[
\eta_H = \text{const.} + (1 - a^{-1}) \log C_{H^+} + \left[1 - \frac{a'}{a}\right] \log \gamma_{H^+} + (a^{-1} - 1) \psi_1 + \left[\frac{\nu}{a}\right] \log i \tag{3.51}
\]

where

- \(C_{H^+}\) = concentration of hydrogen ions in the bulk
- \(\gamma_{H^+}\) = activity coefficient of the hydrogen ions in the bulk
- \(a\) = cathodic transfer coefficient
- \(a'\) = "correction" factor for the diffuse layer
- \(\psi_1\) = the effective potential at the outer Helmholtz layer
- \(\nu = \frac{RT}{F} \ln 10\)

This equation has theoretical significance, however it is impossible to apply practically due to the lack of quantitative information concerning the majority of the variables. Jafa (79) has shown that the overpotential for lead in a range of sulphuric acid electrolytes from 0.05 to 0.005M conforms to the equation

\[
\eta = 1.52 + 0.118 \log i \tag{3.52}
\]

Where the cathodic overpotential is considered positive and using a S.H.E. reference. Further, the decrease in \(\eta\) with increase in sulphuric acid concentration was found to be less than expected from equation (3.51). The overpotential being almost independent of hydrogen ion concentration below about 5M and certainly less than the \(\frac{RT}{F} \ln 10 \log\)
C_H+ term in equation (3.51). Jafa (79) was also unable to find evidence for specific adsorption of sulphate ion on lead. Hence the need to examine the relationship between overpotential and sulphate concentration is removed.
CHAPTER 4

EXPERIMENTAL TECHNIQUES

4.1 Electrolytic Systems

4.1.1 Electrolyte Solutions

All electrolyte solutions used were prepared from Analar grade chemicals and triply distilled water from deionised stock. When required, degassing of the electrolyte was carried out for at least 15 minutes with white spot nitrogen.

For the hydrogen evolution work, the electrolyte was 0.05 M H$_2$SO$_4$ with 1 M Na$_2$SO$_4$. The sodium sulphate was added as a supporting electrolyte salt, to reduce the chance of any i-R drop.

5 M H$_2$SO$_4$ was adopted as standard for the potentiodynamic cycling, pulse work and corrosion studies. For the pasted plate experiments, two strengths of sulphuric acid were used. Firstly during formation and initial charging 0.5 molarity acid was employed. This was replaced with 5 M acid for the subsequent charge and discharge experiments.

4.1.2 Electrolytic Cells

All the cells used were made from borosilicate glass and all joints were lubrication free. Cleaning of the glassware was affected by total immersion in a 50:50 mixture of concentrated nitric and sulphuric
Three Component Cell
A = counter
B = working
C = reference
D = Luggin Capillary

Fig. 4.1 Diagram of a three limbed cell
acids for at least 24 hours. The acid was removed by repeated washing with triply distilled water.

A conventional three-limbed cell, Figure 4.1, was used for hydrogen evolution studies, cyclic voltammetry and potentiostatic pulse experiments. The working electrode was placed in the main cell compartment, 2 mm above the Luggin tip. The Luggin probe ensured that there was minimal i-R drop between the working and counter electrodes. The counter electrode was placed in the side limb marked A and the reference electrode in C.

The forming and galvanostatic charge and discharge of pasted plates took place in the cell shown in Figure 4.2.

Corrosion of the lead and lead-bismuth alloys used the cell shown, schematically, in Figure 4.3, which was contained in a light-proof Faraday cage.

4.2 Electrodes

4.2.1 Planar Electrodes.

These were constructed as shown in Figure 4.4. The lead and lead-bismuth alloy rods were machined to present a known surface area after insertion into the P.T.F.E. shrouds. A strong steel spring was soldered to the back of the electrode to enable a good electrical contact to be maintained between the alloy sample and the shaft of the rotating disc or other connecting rod. The screw thread enabled easy interchange of electrodes and removal of said electrode from the holder for optical and scanning electron microscopy.
Fig. 4.2 Diagram of Pasted Plate Charging Cell

Fig. 4.3 Diagram of Corrosion Cell
Electrode preparation consisted of polishing the samples on fine silicon carbide paper (600 and 1200 grit) using water as lubricant. The electrodes were then wiped with a tissue before being immersed in 10% HNO$_3$ for ten seconds. Finally all electrodes were washed with a jet of triply distilled water ahead of examination under an optical microscope to ensure that the surface was free of contamination by embedded SiC particles.

4.2.2 Electrodes for Corrosion Studies

These electrodes were constructed by taking 35 mm lengths of 7 mm diameter lead and lead alloy rods and soldering a wire connection to one end, as shown in Figure 4.5. Each electrode was placed in a mold and epoxy resin was added. After the polymer had set the mold was removed and the releasing agent subducted with acetone.

The electrodes had their surface area determined before being immersed in 10% HNO$_3$ for 10 seconds to remove any surface oxide layer. After washing with distilled water and acetone, the electrodes were dried and weighed before experimentation began.

4.2.3. Pasted Plate Electrodes.

The pasted electrodes consisted of a backing grid made from a lead, calcium (0.1%) and tin (0.32%) alloy, which was chosen in preference to an antimonial alloy, so that any effect of the bismuth contained in the paste would be easily discernable. The grids were cut from low maintenance S.L.I. battery plates, with dimensions as shown in
Fig. 4.4 Planar Electrode and Holder

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

Fig. 4.5 Corrosion Electrode

- Soldered Connection
- CONNECTING WIRE
- ALLOY SAMPLE
- EPOXY RESIN BLOCK
Fig. 4.6. No pre-treatment for the grids was considered necessary, as they receive none in commercial battery production.

The paste used was a standard battery type obtained from Chloride Advanced Research, with the designation P-10. This contained 78.8% total lead, in the form of free lead, basic sulphates and monoxide, with a nominal density of 4.3 g cm$^{-3}$.

The electrodes were made by taking the approximate amount of P-10, adding the correct amount of bismuth, in the form of Bi$_2$O$_3$, mixing, to obtain a good distribution of additives etc. The paste was applied to the grid, which was placed on a mat covered with polyester film, with a plastic spatula until an even distribution of the potential active material was obtained. The pasted grid was smoothed and weighed, before being cured and formed ready for cycling.

4.2.5 Counter and Reference Electrodes.

In the hydrogen evolution experiments, the counter electrode consisted of a 99.999% pure carbon rod, to exclude the presence of unwanted metal ions.

For the potentiodynamic cycling, pulse and corrosion work the counter consisted of pure lead (99.99+) in the form of rods, plaited wires or sheets.

With the work on the pasted plates, two previously formed negative plates were used. These were wrapped in a microporous separator to prevent mossing and subsequent shorting out of the cell.

The reference electrode used in the corrosion experiments was a lead dioxide/lead sulphate reversible electrode. This was made by
Fig. 4.6  Grid and Pasted Plate

Current Take-off Plate Suspended by P.T. F.E. Tape
Wire

Pb-Ca-Sn Grid

Active Material
plating lead dioxide on to a platinum gauze from a 2.25 M \( \text{Pb}^{2+} \) solution. The solution was made up from 2.25 moles of \( \text{PbO} \) and 4.5 moles of \( \text{HClO}_4 \). Plating took place at 60 °C with a nominal current density of 10 mA cm\(^{-2}\) until an even layer of \( \text{PbO}_2 \) had been formed, after approximately 3 hours. On testing, this electrode gave a potential of +1697 mV \( ' \)s S.H.E. in 5 M \( \text{H}_2\text{SO}_4 \). This is within 10 mV of the literature value (80) for the \( \text{PbO}_2/\text{PbSO}_4 \) reversible potential.

For the other electrochemical experiments the potentials were always measured by a Hg/Hg\(_2\text{SO}_4\) electrode in sulphuric acid of the same concentration as the working solution. Figure 4.7 shows a plan of the wick-type reference electrode used.

4.3 Electrical Circuits

4.3.1 Linear Sweep/Cyclic Voltammetry and Potentiostatic Step Experiments

The schematic diagram, Figure 4.8, shows the circuit used for this set of experiments. The potential was held by a potentiostat with subsequent voltage variation provided by the function generator. The resultant voltammograms or current-time transients were recorded by the x-y-t recorder and thence the data was transferred to a computer for further analysis.

4.3.2 Chronocoulometric Cycling Experiments

For the extensive chronocoulometric experiments a Z-80 based microprocessor, 64k R.A.M. system with twin 8" floppy disc drives was
Fig. 4.7 Wick Type Reference Electrode

Cu WIRE

B19 GROUND GLASS JOINT

PYREX HOLDER

PYREX TUBE

Hg POOL

Pt WIRE

Hg$_2$SO$_4$ SLURRY

SOLDER
used. In conjunction with a 12-bit Analogue to Digital (A.D.C.)
conversion board, the computer recorded the current generated by the
electrode. The potential control was obtained by use of a potentiostat
in addition to a digital ramp generator, as shown in Figure 4.9. The
charge was measured by a numeric integration method of the anodic part
of the linear sweep, this was displayed on screen and stored on floppy
disc for later use.

4.3.4 Corrosion Experiments

As shown in Figure 4.10, the experimental layout is very similar
to that of section 4.3.2 except that there is no function generator.
Again the current is measured by the A.D.C. board and stored on the
computer. A permanent record is held on floppy disc as well as displayed
on the V.D.U.

4.3.5 Pasted Plates

For galvanostatic cycling of pasted plates, it is necessary to
use relays to control the application of potentiostats, ramp generators
and galvanostats. The relays were built "in house" and had a switching
potential of +1.7 V. To supply this two digital to analogue converter
(D.A.C.s) boards were fitted (81) and controlled by the computer, Figure
4.11.

Under the correct software management, and use of a real time
clock, it is was possible to charge and then cycle the electrodes.
Fig. 4.8  Schematic Diagram of Layout for h.e.r. Experiments
4.4 Plate Paste Composition

A commercially available leady oxide paste, P-10 from Chloride Technical Ltd., was used. This had the following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount/Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gray Oxide (60% PbO, 40% Pb)</td>
<td>1080 kg</td>
</tr>
<tr>
<td>Polyester Fibres</td>
<td>0.9 kg</td>
</tr>
<tr>
<td>1.400 s.g. Sulphuric Acid;</td>
<td>140 litres</td>
</tr>
</tbody>
</table>

and a nominal density of 4.1 g cm$^{-3}$.

The paste used consisted of a mixture of monoxides and basic sulphates of lead, the amount of lead present was determined to be 78.8 wt. %, though the determination of the exact amounts of tri-basic lead sulphate could not be affected from the X-ray Powder Diffraction read-out due to the complex nature of the recorded data (82). The two levels of bismuth addition were fixed at 0.05 and 0.5 wt. % to the amount of lead. The bismuth was added in the form of Bi$_2$O$_3$, which would be the most likely form of the impurity after it had passed through the milling process. Thus the amount of Bi$_2$O$_3$ added was either 0.044g or 0.439g per 100g of P-10, depending on the required bismuth level.

4.5 Microscopy

4.5.1 Optical Microscopy

Use of a combined camera and optical microscope (Carl Zeiss Jana)
Fig. 4.9 Schematic Diagram of Layout for Chronocoulometry Experiments

- RAMP GENERATOR
- Z-80 BASED MICRO-
- A/D BOARD
- POTENTIOSTAT
- C.E. R.E. W.E.
- BUFFER AMPLIFIER
- SENSE RESISTOR
- WORKING ELECTRODE
- REFERENCE ELECTRODE
- COUNTER ELECTRODE
Fig. 4.10  Schematic Diagram of Layout for Corrosion Experiments

Fig. 4.11  Schematic Diagram of Layout for Pasted Plate Cycling Experiments
enabled photographs to be taken of cycled, etched or corroded samples.

4.5.2 Scanning Electron Microscopy

The availability of an S.E.M. enabled a good examination of the surface of many of the electrode samples. For the chronocoulometric examples, the objects were prepared by removing the electrode from its holder and washing with water and then methanol before storage in a desiccator. The samples were then coated with a thin layer of gold by diode sputtering to ensure conductivity before examination under S.E.M.

The corrosion samples were treated in a similar fashion, however it proved unnecessary to gold coat them before examination.
CHAPTER 5

THE EFFECT OF BISMUTH ON THE MICROSTUCTURE OF LEAD.

5.1 Introduction

The presence of bismuth in lead used for casting grids, will almost certainly alter the way the metal crystallizes on cooling, and it is often the case (81) that an impurity or alloying ingredient will be concentrated in the grain boundaries, simply because of the physical processes that occur (81) on solidification. Firstly dendrites, in this case of pure lead, grow outwards from nucleation sites until they meet other dendrites. The remaining liquid, which now has a higher impurity level, crystallizes on the dendrites until the whole is solid. This produces a polycrystalline structure, with the grain/crystal boundary containing the most impurity as they are the last sections to solidify. With certain alloys, e.g. antimony, there is the growth of segregated dendrites and these are included in the lead grains (82), though this leads to a very brittle alloy. Other alloying additives are simply insoluble and are dispersed through the alloy (83), e.g. Pb-Cd system.

Often, metals added to lead decrease the grain size, but this is not the case with bismuth (84), and little improvement is noted in this physical characteristic of the alloy produced. It was thought that the resultant system was a simple eutectic, but this is not the case (85), though an intermediate phase does not make its presence felt until the level of bismuth exceeds 22% (86), though this is well above what would be considered commercially important.
Fig. 5.1  Micrograph of Base Lead, x 70 Magnification

Fig. 5.2  Micrograph of 0.061% Bi, x 70 Magnification

Fig. 5.3  Micrograph of 0.117% Bi, x 70 Magnification
The casting of lead and lead alloy grids for batteries is now a highly automated process. The molten metal is poured into a partially water-cooled steel mould, thermostated at about 180 °C, which has been dusted with cork powder to prevent adhesion. The metal cools and solidifies within 5 seconds and the cast grid is then manually removed. The grid wires are not very thick and an accurate casting is required with the minimum of hot tearing. Bismuth has been added to improve the ease and precision castability of lead (87), and this from a metallurgical view point is advantageous.

The use of etchants to develop, and enhance, the grain structure of a metal surface is a standard technique, though there are some problems. Schreder (88), in her manual on etching "Atzheft", lists and categorises most of the common etchants and problems found with different materials. Problems can arise from the different solubilities of the etched products, which could cloud the surface, or a more general, severe, attack leaving the surface pitted and uneven. The main factor which is required of a good etchant is to remove the Beilby layer present after mechanical polishing and develop the grain boundaries.

5.2 Experimental

Rods of base lead and alloy, with a diameter of approximately 10mm, were cast in polymethyl methacrylate blocks. These were then machined to a suitable size, surface preparation began on 600 and 1200 grit emery paper, subsequently a mechanical polisher was used with a svelte-type cloth disc, with 5 and 0.3 micron alumina, was used to polish the samples, with water as lubricant. After polishing, the sample
Fig. 5.4  Micrograph of 0.26% Bi, x 70 Magnification

Fig. 5.5  Micrograph of 0.565% Bi, x 70 Magnification

Fig. 5.6  Micrograph of 1.061% Bi, x 70 Magnification
was washed with triply distilled water and then acetone, before being dried in a stream of warm air followed by storage in a desiccator, to reduce the chance of oxy-hydroxide film formation.

Two types of etching solutions were used, firstly a 10% $\text{HNO}_3$ solution was used on samples of up to 0.5% bismuth. Secondly, for higher bismuth concentration, a mixture of glacial acetic acid (25 cm$^3$), $\text{H}_2\text{O}_2$ (30%, 20 cm$^3$), $\text{HNO}_3$ (20 cm$^3$) and 100 cm$^3$ $\text{H}_2\text{O}$ was utilized. Several drops of the either etchant were placed on each sample until the grain structure was clearly visible. The samples were washed with water and then acetone, before being dried, in warm air, and placed under the optical microscope. Photographs of each sample were then taken at different magnifications.

5.3 Results and Discussion

The photomicrographs of lead and lead-bismuth alloys are shown below, Figs 5.1 - 5.6.

By comparing the microstructure with that of the base lead, Fig 5.1, it is easy to see how the addition of bismuth alters the grain structure. Fig 5.2 shows a polished and etched sample containing 0.061% bismuth, and the change is quite dramatic, from small regularly shaped grains to large rectilinear ones. It is possible that the impurities in the base lead act as nucleating centres, but when Bi becomes dominant then a change occurs and the resultant structure, as shown in Fig 5.2, appears.

Further additions of bismuth, unto 0.5%, give rise to little change, Figs 5.3 and 5.4. But on reaching 0.5% Bi a further modification
occurs, Fig 5.5, the recrystallization of the worked surface is, now, clearly visible. This has been reported before (89), and is present in all the alloys with a concentration of bismuth above 0.5%, e.g. Figs 5.6, though the change in grain size is minimal with the increased presence of bismuth.

5.4 Conclusion

The addition of bismuth to lead for casting in grids improves the accuracy of the casting and reduces the amount of hot tearing. The alteration in the grain size with the presence of bismuth means that bismuth, concentrated in the grain boundaries, will be present on the surface and is, thus, easily accessible for any electrochemical reactions that may occur, such as corrosion. The effect of this will be described later, though the presence of Bi would seem, here, to have a beneficial effect.
6.1 Introduction

Considerable work, stretching back into the last century, has been carried out on the nature of hydrogen evolution on lead electrodes. Until recently, however, the importance of the purity of reactants and system remained unrecognised. Thus most of the early experimental work done by people such as Caspari (92), Tafel (46), Newbury (93) etc. must be considered to be of dubious reliability. At least three good reviews exist on the suitability, and accuracy (or otherwise), of work carried out on hydrogen evolution (46,94,95).

Problems arise due to the low activity of hydrogen on lead, and subsequent magnification of any effects of impurities. Away from the purely academic side of obtaining correct values for the kinetic constants as such, there is a very important technological point. The development, and even pre-eminence, of the maintenance-free battery system in recent years has sparked investigations into the mechanism and effect of impurity levels (96) on the hydrogen evolution reaction.

The value of the hydrogen overpotential, where the overpotential is defined by;

$$ n = ( E_{i=0} - E_{i} ) $$

(6.1)

determines not only the rate of self-discharge (97) on the negative
plate, but also the current efficiency on recharge. If the hydrogen overpotential is low, due to the presence of impurities (Sb is a well-known example) open circuit losses occur because of hydrogen evolution from impurity centres in concert with the transformation of PbSO\(_4\) to porous lead.

The addition of alloying ingredients to battery support grids is a conventional process for obtaining properties required by the battery manufacturer, both for production and end product performance. Antimony is added to improve the castability and to give good deep-cycling capacity for the positive plate, but the migration of Sb\(^{5+}\) ions to the negative plate, and the reduction in hydrogen evolution overpotential that this causes, means that the elimination of Sb is desirable. Bismuth is in the same periodic group as Sb, and its effect on the hydrogen overpotential is of some import when considering the level of bismuth that can be allowed in the electrode material.

6.2 Experimental

The electrodes used in this study of hydrogen evolution were made from polycrystalline rods of lead and lead-bismuth alloy which had been aged for at least one month prior to use. The compositions of the alloys are listed in Table 6.1, below. The electrodes were prepared as described in Chapter 4.

The electrolyte used was as described in Chapter 4.1.1, 5 M H\(_2\)SO\(_4\) (approximately battery strength acid) was not used because the large concentration of H\(^+\) ions would lead to very rapid, excessive hydrogen evolution, limiting the amount of extractable data.
Fig. 6.1  Current Response to a L.S.V. into the Hydrogen Evolution Region
The sweeping experiments were made between -1200 mV and -2300 mV, versus Hg/Hg₂SO₄ reference electrode, at 100 mV s⁻¹. This sweep rate gave reproducible results with little sign of intruding gas interference.

Table 6.1  Working Electrode Composition

<table>
<thead>
<tr>
<th>Pure Pb %</th>
<th>&quot;Base&quot; Pb %</th>
<th>&quot;Pure&quot; Bi %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb &gt; 99.999</td>
<td>Pb &gt; 99.973</td>
<td>Bi &gt; 99.95%</td>
</tr>
<tr>
<td>(Aldrich, Gold Label)</td>
<td>Bi' = 5 x 10⁻⁴</td>
<td>(Johnson-Mathey, Mathey Reagent)</td>
</tr>
<tr>
<td>Fe &lt; 0.001</td>
<td>Cu &lt; 0.003</td>
<td></td>
</tr>
<tr>
<td>Sb &lt; 0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As &lt; 0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag &lt; 0.0025</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn &lt; 0.001</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6.2 Results and Discussion

Figure 6.1 shows a typical L.S.V. for the evolution of hydrogen on pure lead. There is one major peak which corresponds to mass transport limited hydrogen ion reduction. The decrease in current occurs as this species in the region close to the electrode is depleted, and the pseudo-peak at the switching potential is due to the reduction of the water in the electrolyte.

By taking data from the foot of the potentiodynamic wave, points
Fig. 6.2  Graph of Current Density Against Potential for Lead
which are not mass transport limited can be accumulated. Figure 6.2

Table 6.2  
Alloy Composition

<table>
<thead>
<tr>
<th>Alloy Label</th>
<th>Pb %</th>
<th>Bi %</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>99.725</td>
<td>0.275</td>
</tr>
<tr>
<td>G</td>
<td>99.455</td>
<td>0.565</td>
</tr>
<tr>
<td>H</td>
<td>98.937</td>
<td>1.063</td>
</tr>
<tr>
<td>I</td>
<td>97.891</td>
<td>2.109</td>
</tr>
<tr>
<td>J</td>
<td>96.413</td>
<td>3.587</td>
</tr>
<tr>
<td>K</td>
<td>95.091</td>
<td>4.909</td>
</tr>
</tbody>
</table>

shows the potential-current density data for lead. The Tafel slope, i.e. the value of 'b' in the Tafel equation, was found from the reasonably straight lower portion of the curve. The constant 'b' had the value of -0.13 V and the ordinate, 'a', at the reversible potential (referred to S.H.E.) was determined to be -1.31 V. These values agree fairly well with the work carried out by Aguf, Dasoyan and other Russian workers (76,79,98), in H₂SO₄ of equivalent sulphate concentrations to the supported electrolyte of the present work, where the measured values of 'a' and 'b' were only slightly altered by sulphate concentration changes. The value of 'b' has been reported to vary quite considerably (76), between -0.11 and -0.16 V, the reasons that have been put forward to explain this variation include electrolyte purity, sulphate adsorption (94) and grain structure.
Fig. 6.3 Graph of Current Density Against Potential for Alloys 1, 2 and 3.

Log $[A/cm^2]$

$E/mV$ vs $Hg/Hg_{SO_2}$

- + - Alloy 1
- - Alloy 2
- ▲ - Alloy 3

-1275 -1430 -1585 -1740 -1895 -2050
Figures 6.3 and 6.4 show the current density-potential curves for typical alloys of lead and bismuth from the series above. Again values of $i_o$, 'a' and 'b' were calculated from the lower, approximately straight sections of the curves. Table 6.3 gives the values of $i_o$ measured against the hydrogen reference electrode together with 'a' and 'b'; for comparison with the earlier published data.

The linear sweep voltammograms recorded on sweeps with less negative limits, show a hysteresis which is produced by the slow establishment of an adsorption equilibrium, as discussed by earlier workers (99,100). Figure 6.5 illustrates a closed loop potential-current density plot for pure lead. On the same axis are plotted the data points for the upward sweep on the 4.91% Bi alloy, showing the disparity between lead and the maximum bismuth containing alloy.

The values in Table 6.3, below, show that the presence of bismuth in lead alloy does not increase the rate of the hydrogen reaction. An indication that the h.e.r. on bismuth alloys might be slow arises from the work on pure bismuth by Kilimnik et al. (101), who reported Tafel coefficients of the order of -1.1 V and -0.12 V respectively for 'a' and 'b'. This value of 'a' is close to that obtained for the alloys in the work reported here, however, the Tafel slopes found are generally increased by the addition of Bi to lead.

As an aside, an investigation into the electrochemistry of pure bismuth in battery strength electrolyte showed hydrogen evolution beginning some 50 mV more cathodic than for pure lead.

Addition of small amounts of bismuth give rise to significant changes in both Tafel constants. But further addition of Bi appears to have little if any effect on 'a' or 'b'. It seems likely that the small
Fig. 6.4 Graph of Current Density Against Potential for Alloys 4, 5 and 6

- Alloy 4
- Alloy 5
- Alloy 6

E/mV vs Hg/Hg\textsubscript{2}SO\textsubscript{4}

log \(i/Acm^{-2}\)
variations observed are due either to surface preparation of different specimens or reflect differences in adsorption of hydrogen/proton and anions on heterogeneous alloy surfaces.

Table 6.3 Kinetic constants for the h.e.r. on various Pb-Bi alloys in 0.05 M H₂SO₄ and 1.0 M Na₂SO₄ at 22 °C

<table>
<thead>
<tr>
<th>Label</th>
<th>&quot;b&quot;/V</th>
<th>Log10 i₀</th>
<th>&quot;a&quot;/V</th>
<th>i₀/10-11 A cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-0.13</td>
<td>- 9.80</td>
<td>-1.31 ± 0.04</td>
<td>15.8</td>
</tr>
<tr>
<td>F</td>
<td>-0.14</td>
<td>-10.96</td>
<td>-1.58 ± 0.04</td>
<td>1.10</td>
</tr>
<tr>
<td>G</td>
<td>-0.15</td>
<td>-10.37</td>
<td>-1.59 ± 0.03</td>
<td>4.27</td>
</tr>
<tr>
<td>H</td>
<td>-0.14</td>
<td>-10.68</td>
<td>-1.53 ± 0.04</td>
<td>2.09</td>
</tr>
<tr>
<td>I</td>
<td>-0.15</td>
<td>-10.41</td>
<td>-1.51 ± 0.01</td>
<td>3.89</td>
</tr>
<tr>
<td>J</td>
<td>-0.16</td>
<td>- 9.83</td>
<td>-1.54 ± 0.04</td>
<td>14.8</td>
</tr>
<tr>
<td>K</td>
<td>-0.14</td>
<td>-10.91</td>
<td>-1.51 ± 0.01</td>
<td>1.23</td>
</tr>
</tbody>
</table>

6.3 Conclusions

From the data in Table 6.3 it can be seen that the addition of bismuth to the alloy electrode decreases the rate of hydrogen evolution and increases the value of n, the overpotential. Thus bismuth alleviates hydrogen evolution. This is rather unexpected when considering the effect of the addition of Sb on hydrogen gassing and bodes well for the inclusion of bismuth into the negative electrode.

Since there is little change in either of these variables with bismuth concentration, the conclusion must be drawn that somewhere
Fig. 6.5  
Graph of Current Density Against Potential for Alloy 6 and Hysteresis Loop for Pure Lead
between zero and 0.27% there is a critical level of bismuth which triggers this effect.
CHAPTER 7

POSITIVE CYCLED PLANAR LEAD AND LEAD-BISMUTH ELECTRODES

7.1 Introduction

The criteria for the development of alloys for the positive electrode, in the lead-acid battery, has often been a trade off between the electrochemical properties, such as good cycle life, good paste retention and so forth, and production requisites, e.g. few voids or hot tears on casting and such like. This has sometimes lead to a compromise situation in which neither property is present.

Methods of testing alloys for their suitability for use as positive plate material have been discussed at international levels, and various standard tests have been instituted, e.g. Society of Automotive Engineers (S.A.E.), Battery Council International (B.C.I.) and most recently through the battery section of the International Electrotechnical Commission (I.E.C.). Even so, individual researchers have applied their own tests, where appropriate (102-105), to highlight particular aspects of corrosion or performance. However, they require the use of full scale plates, if not complete batteries. The cost, in time and money, of manufacturing battery systems, of the particular alloy under investigation is greater than can be born in the case of most research and thus a "cheap and easy" solution is required.

At Loughborough University, the answer to the question posed is to take polycrystalline rods of lead and lead alloys and embed them in P.T.F.E. (27,106), as described in Section 4.2.1. This method of testing
alloys has proved to be effective (27,106,107) in the investigation of electrochemical phenomena and surface processes that occur during charge and discharge of an electrode. There are some common points, in comparing what seem like the two disparate situations of pasted grid wire and test piece. Firstly, after initiating a layer of PbO₂ on the electrode, the potentiodynamic cycling which occurs, leads to the build up of a porous layer of lead sulphate, lead dioxide or a mixture, depending on the potential applied.

Secondly, the layer is subject to the internal stresses which build up because of the change in volume between the sulphate and dioxide. This can cause cracking and isolation of particular areas of the electrode. Thirdly there is oxygen evolution, where bubbles of gas formed on the PbO₂ active mass could partially restrict the pores. Finally, as the layer develops and thickens, the sulphuric acid may not be able to penetrate to the electrode surface. This can give rise to an increase in pH, which will affect the formation of a corrosion layer between the active mass and the alloy backing.

There are several limitations to the test, which can reduce the effectiveness of the experimental method, though they are not so constraining as to render the data useless (108). The problems are, firstly, that the sulphuric acid is in excess. This is not a problem in flooded batteries, though many of today's battery designs are "electrolyte starved" and the problem will then arise. Secondly, there is no paste into which a corrosion layer can be accommodated. Thirdly, no vibration of the electrode, as found in, for example, S.L.I. batteries, and fourthly, the limits of the voltage and rate of change of the potential.
Fig. 7.1  L.S.V. of Lead Sulphate to Lead Dioxide

Fig. 7.2  L.S.V.s for Pure Lead After Various Cycle Numbers
7.2 Experimental

The electrodes were made from rods of polycrystalline lead and lead-bismuth alloy, with composition as listed in Table 7.1. The working, counter and reference electrodes and electrolyte were prepared as described in Chapter 4. The experimental set up is as shown in Fig. 4.9, and the cell used was of a standard three-limbed design.

The data was recorded by an analogue to digital conversion board on a Z-80 based microcomputer, using in-house written software, Appendix 1. A graphics tablet (Watanabe), and in-house software were used for graphic representation of the results.

The electrodes were cycled between +600 and +1350 mV, at 50 mV s\(^{-1}\), though the initial cycle was extended to 2000 mV (108), to initiate a layer of lead dioxide on the electrode, the high overpotential for nucleation of dioxide on lead making this necessary. After the cycling experiment was completed, the electrodes were removed from the acid solution, washed in distilled water, then acetone, before being stored in a desiccator in preparation for optical and scanning electron microscopy.

Each alloy was tested at least twice (using separate electrodes) and the results, in Figs. 7.2 to 7.12 are the average of these runs, this helped to eliminate any extraneous preparative effects.

7.3 Results and Discussion

As before, all potentials quoted are measured against Hg/Hg\(_2\)SO\(_4\)/electrolyte solution. There are three main features in the
Fig. 7.3 Graph of Bismuth Concentration against Oxygen Evolution Current After 100 and 1000 Cycles

Graph shows the relationship between Bismuth concentration and oxygen evolution current after 100 and 1000 cycles. The concentration is indicated on the y-axis, while the percentage of Bismuth in the alloy is shown on the x-axis. Symbols 'o' represent 100 cycles, and '+' represent 1000 cycles.
Fig. 7.4  Graph of Bismuth Concentration against Oxygen Evolution Current After 2000 and 3000 Cycles

$O_2$ Current (mA cm$^{-2}$) vs. %age Bi in Alloy

- 2000 Cycles
- 3000 Cycles
Fig. 7.5  
Graph of Bismuth Concentration against Oxygen Evolution Current After 4000 and 5000 Cycles
results obtained from the potentiodynamic cycling of the lead and alloy electrodes. These are

i) the change in linear sweep voltammograms with cycle number,

ii) the change in the L.S.V.'s with bismuth addition,

and

iii) the change in capacity with cycle number and bismuth level.

Table 7.1

<table>
<thead>
<tr>
<th>Label</th>
<th>%age Lead (±0.008)</th>
<th>%age Bismuth (±0.008)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>99.999</td>
<td>-------</td>
</tr>
<tr>
<td>B</td>
<td>99.999</td>
<td>5 x 10^-4</td>
</tr>
<tr>
<td>C</td>
<td>99.9439</td>
<td>0.061</td>
</tr>
<tr>
<td>D</td>
<td>99.883</td>
<td>0.117</td>
</tr>
<tr>
<td>E</td>
<td>99.795</td>
<td>0.205</td>
</tr>
<tr>
<td>F</td>
<td>99.735</td>
<td>0.265</td>
</tr>
<tr>
<td>G</td>
<td>99.435</td>
<td>0.565</td>
</tr>
<tr>
<td>H</td>
<td>98.937</td>
<td>1.063</td>
</tr>
<tr>
<td>I</td>
<td>97.891</td>
<td>2.109</td>
</tr>
<tr>
<td>J</td>
<td>96.413</td>
<td>3.587</td>
</tr>
<tr>
<td>L</td>
<td>95.091</td>
<td>4.909</td>
</tr>
</tbody>
</table>

7.3.1 Development and change in the L.S.V.'s

The first factor to note is that the L.S.V. shows a relatively sharp oxidation peak, Fig 7.1, as the lead sulphate is converted to
dioxide. However, the reduction sweep shows a much shallower curve as the reverse process takes place, this is due to the fact that the lead sulphate formed has a high resistance, and forms a protective layer around the crystals of PbO₂. Thus to convert the shielded dioxide, higher overpotentials are required.

As the cycling progresses, there is a change in the L.S.V. as shown in Fig 7.2. At 100 cycles, that is after 50 mins., the anodic peak is relatively sharp, showing that the layer of active material next to the electrode is reasonably planar. By 1000 cycles, the cycling time being 8 hrs. 20 mins., the oxidation curve has broadened quite considerably, and the peak current is at a maximum. This represents the maximum capacity for the electrode, with almost all of the porous active mass being used and the counter-acting sulphation process only just beginning to take effect. On reaching 2000 cycles, 16 hrs. and 40 mins. into the experiment, the peak current has dropped and the oxidation peak has become much broader. This indicates, firstly, that sulphation of the active matrix is becoming dominant and blocking the pores, thus reducing the amount of electrolyte that can penetrate to the active electrode surface. And secondly, the porous nature of the active mass spreads out the current response to the changing voltage. This general reduction in capacity continues as the cycling of the electrode proceeds, though the development of the porous mass continues with some variation in the rate depending on the access of the acid to the electrode surface, temperature and other physical factors.

Also, it should be noted that the current does not drop to zero at the most positive switching potential. This is due to the evolution of oxygen on the lead dioxide, Figs. 7.3 to 7.5 show the oxygen
Fig. 7.6 L.S.V. of Alloy J After Various Cycle Numbers

Fig. 7.7 L.S.V.s of Lead and Low Lead-Bismuth Alloys After 100 Cycles
evolution current at +1350 mV against cycle number. There are three points which can be deduced from these figures. Firstly, the amount of oxygen evolved depends on the amount of PbO₂ present, thus the evolution current is low after 100 cycles compared to the other times, simply because there is not as much PbO₂ present. Secondly, there is a critical level of bismuth concentration of around 0.6%, which gives rise to two separate areas on Figs. 7.3 to 7.5. When the level of bismuth is below 0.6%, the evolution current is similar to that of pure lead. But above 0.6% a change occurs with the current doubling from around 0.6 mA cm⁻² to 1.2-1.3 mA cm⁻². This suggests that bismuth present in the active mass promotes the generation of O₂. Finally, Figs. 7.3 to 7.5 show a decrease in i with an increase in cycle number. This suggests that as the cycling progresses, the bismuth is leached out of the positive into the solution from where it can be plated onto the negative, reducing any catalytic oxygen evolution effect of Bi. The gradual sulphation of the active mass will also contribute to the lowering of the oxygen current.

7.3.2 Effect of addition of bismuth on the L.S.V.'s

Fig. 7.6 shows the L.S.V.'s of a lead-bismuth alloy electrode, there are several similarities when comparing it with Fig. 7.2. For instance, the peak becomes broader as cycling progresses and the maximum capacity is reached at around 1000 cycles before falling away. However there are two important differences, in the first instance, after 1000 cycles the voltage at which the maximum current occurs moves to less positive values.

The second important point is that the presence of bismuth alters
Fig. 7.8  L.S.V.S of Lead and High Lead-Bismuth Alloys After 1000 Cycles
Fig. 7.9  
Graph of Bismuth Concentration Against Peak Potential After 100, 1000 and 2000 Cycles
Fig. 7.10  Graph of Bismuth Concentration Against Peak Potential After 3000, 4000 and 5000 Cycles
the peak current potential \( E_p \), in such a way as to push the value higher, this is shown in Figs 7.7 and 7.8. The L.S.V.'s recorded after 100 and 1000 cycles show quite clearly that the presence of bismuth, even in small amounts, inhibits the formation of lead dioxide on lead sulphate. This is best shown in Figs 7.9 and 7.10, which show a linear increase in the crystallization overpotential up to levels of around 0.5% bismuth, followed by a levelling off, in the case of 100, 1000, and 2000 cycles (Fig. 7.9) this is shown to be only temporary in Fig 7.10, with the fall continuing as cycle number increases. There seems to be a critical concentration of bismuth, because there is another fall in \( E_p \) on reaching 4.9% bismuth. This maybe due, however, to the porous matrix not being so well developed, i.e. the inhibiting effect of the alloying addition restricts the build up of the matrix of active material and hence reduces the electrochemical charge required to convert the active mass.

7.3.3 The Change in Capacity with Cycle Number and Bismuth Concentration

Figs. 7.11 and 7.12 show the results of the potentiodynamic cycling of lead and lead-bismuth alloys. The resultant trace is the numeric integration of the anodic current from each sweep. The Figs 7.11 and 7.12 show that all the electrodes follow a similar route, with a build up of porous active mass giving a peak in capacity at around 800 to 1000 cycles. The capacity subsequently falls away as sulphation and isolation of areas of the active matrix occurs. A level capacity region at around 60-80% of the maximum follows.

Taking pure lead as a comparison, the effects of the addition of
Fig. 7.11  Graph of Cycle Number Against Capacity For Pure Lead and Alloys C to E
bismuth can be clearly seen. The bismuth has two effects, when considering the capacity of the electrode, in the first case, the addition of bismuth inhibits the formation of the porous matrix, this is confirmed by the previous observations with the effect of bismuth addition on $E_p$. This inhibition, or crystallisation overpotential, slows down the development of the matrix, hence a lower capacity for the alloys in the range 0.061% to 0.27%, with sulphation of the porous mass occurring at the same rate.

The second effect of bismuth is that it is leached from the electrode. Experiments with pure bismuth in 5 M $\text{H}_2\text{SO}_4$ give a reversible potential of $-403 \text{ mV}$ at 20 °C, with subsequent oxidation and dissolution at potentials more positive than this. Thus with the electrode under test being cycled between +600 and +1350 mV, it is not surprising that the alloying ingredient is removed from the test piece. The leached bismuth can either reside in the active mass or it can dissolve into the electrolyte. Given a reversible potential of $-403 \text{ mV}$, any bismuth that escapes into the electrolyte is almost certain to plate out on the counter electrode.

By removing the bismuth, which will probably have been concentrated in the grain boundaries (83), the surface area is increased and fresh lead exposed, ready for oxidation. This effect is in opposition to the one above, hence, with the amount of bismuth above 0.3%, this second trend begins to counteract the inhibition of matrix formation. This leads to an increase in the capacity from 0.57% to 2.10% bismuth alloy electrodes. However the inhibiting effect is still present, and the peak capacity is reached some 150 to 200 cycles later than for pure lead.
Fig. 7.12  Graph of Cycle Number Against Capacity For Pure Lead and Alloys F to K
Increasing the amount of bismuth once more, up to 3.50%, leads to the situation where the first factor again dominates. Thus the capacity drops, and the peak is reached some 200 cycles later than for pure lead. Even adding more bismuth, up to 4.91%, leads to no improvement in performance. Thus the opening up of the surface has been effectively neutralised by the crystallisation overpotential of the bismuth and sulphation.

The variation in capacity of each of the cycled electrodes is quite large. This is particularly true of the pure lead, where the dispersion of the results is between +30% and +10% depending on the cycle number. At the peak capacity, the variation is up to 30%, this could mean that almost all the alloy capacity plots, Figs 7.11 and 7.12, will be covered by the spread of the results for pure lead, though this is unlikely. It does show that even a nominally identical method of electrode preparation can give rise to a large diversity in the results.

The fluctuation in the capacity of different electrodes falls to around 10% at 5000 cycles, such that the surface variation has been, to a large extent, countered by the build up of the layer of active material.

At this point in the cycle life, the results for lead and lead alloy are more directly comparable, with less room for statistical variation. But this difference only indicates that there is some uncertainty in explaining the effect of bismuth, it does not invalidate the results and conclusions drawn above, and the two aspects of the addition of Bi to lead still prevail.
Fig. 7.13 Electron Micrograph of Pure Lead Electrode After Cycling, 5000 x Magnification

Fig. 7.14 Electron Micrograph of Alloy D After Cycling, 5000 x Magnification
Fig. 7.15  Electron Micrograph of Alloy I After Cycling, 5000 x Magnification

Fig. 7.16  Electron Micrograph of Alloy K After Cycling, 5000 x Magnification
7.3.4 Scanning electron micrographs of the electrodes.

After cycling, the electrodes were examined under a S.E.M., the results are shown in Figs 7.13 to 7.16. The sulphate film on the pure lead sample (Fig. 7.13), shows a coherent film with regular shaped crystals. Fig. 7.14 shows the sulphate film that has developed on an electrode containing 0.11% Bi, the difference is quite large, there is a greater range of crystal sizes, with a fine, almost amorphous layer on which large lead sulphate crystals are scattered. This trend is continued with increases in the amount of bismuth, see Figs. 7.15 and 7.16. Bismuth might be promoting the nucleation of sulphate, which will give rise to the amorphous layer of lead sulphate. The large crystals are either above lead rich areas or are due to the dissolution and reprecipitation of sulphate (110). This makes passivation and/or isolation of the dioxide from the electrode much easier, leading to a drop in capacity.

7.4 Conclusions

The efficiency of this method as a quick means of analysis of the suitability of an alloy is confirmed, though more than three runs are required at each impurity level, to smooth out any variation in the surface of the electrode, and subsequently in the recorded capacity. The addition of bismuth has four main effects when added to the positive electrode. Firstly it inhibits the oxidation of lead sulphate to lead dioxide, in contrast to Sb (107). Secondly it increases the amount of oxygen evolved, in line with antimonial alloys (84). Thirdly it is
leached from the electrode, leading to its incorporation in the active material and plating out on the negative, again directly comparable to antimony. And finally, it prevents the formation of a more open sulphate film on the surface of the electrode, the microcrystallites forming a barrier between the active surface and the electrolyte.
8.1 Introduction

The active material supported by the grids in the lead acid battery, accounts for around 35% of the total weight of the battery (111) and generates most of the power. It would, therefore, seem unreasonable not to investigate the effect of the addition of bismuth to the paste, and considering that most of today's batteries are positive plate limited, research into the effect of bismuth on the positive active material is important.

A large amount of research has been carried out into all aspects of the positive plate and its active material. Several comprehensive reviews exist, in particular Burbank et al. (19), Ruetschi (112) and Ellis et al. (113). The results of these suggest that failure of the positive plate is due to three main reasons (113);

a) Isolation of the active material,

b) Increase in the ratio of macropores to micropores, (loss of active surface area)

and c) Grid corrosion.

But the cycle-life of the active material can be increased by;

a) Compression of the active material.

b) Addition of antimony to the positive grid,

c) Higher operating temperatures,
and d) Improved plate preparation, in particular, the improvement of the initial ratio of $\alpha: \beta PbO_2$.

The major problems with the positive active material (P.A.M.) are, firstly, that the lead sulphate formed on discharge acts as an insulator limiting the utilization of the P.A.M. to between 25% and 60 percent of the theoretical capacity, though modern batteries can extract over 50%. Secondly, the resultant volume change of 92% (114), on reduction of lead dioxide to lead sulphate disrupts the layer of active material and must become a determining factor in the life of the plate.

Hampson et al. (115-117) investigated the effect of the interphase between the active material and the grid and suggested that the nature of the corrosion layer and its conductivity affected the recharge characteristics. This corrosion layer was influenced by the composition of the alloy support, given that the paste composition was the same every time. Thus, antimony additions to the grid give rise to a higher porosity of the P.A.M. (117) and give instantaneous nucleation on oxidation as compared with progressive nucleation for lead and lead - calcium - tin. The effect of grid alloys has been reviewed by Dasoyan and Aguf (100).

The composition of the P.A.M. will vary depending on the position in the charge/discharge cycle and the previous history of the cycling of the battery. The greater the depth of discharge on each cycle, the more sulphate will be produced, this could, and often does in non-antimonial grids, lead to a premature loss of capacity. Various additives have been used to improve the performance of the P.A.M. Dietz et al. (118,119) have carried out a thorough investigation of paste additions such as carbon black, silica gel and short length fibres. These improve the
mechanical strength of the P.A.M., and in the case of carbon black also improve the paste conductivity. A relatively small amount of work seems to have been done on the addition of chemical compounds (120,121), which confirms that the addition of barium sulphate will be deleterious because it helps to nucleate lead sulphate, this increases the self-discharge and helps the breakdown of the crystallite structure leading to excessive loss of active material.

8.2 Experimental

The plates used were prepared as described in Chapter 4. All plates were pasted and cured at the same time to try and minimise any variation in performance due to differences in production (particularly paste aging). The composition of the pastes used is shown in Table 8.1 below.

Each plate was measured for thickness in seven places to give an average value for the volume, this was done before and after curing and formation and after cycling. Each plate was formed in an excess of 0.5 M sulphuric acid, a diagram of the apparatus employed is shown in Fig 4.11. The forming regime employed was C/15 for 16 hours, under computer control. There followed two hours rest, four hours charge, two hours rest and finally four hours charge, this gives an overcharge of 9 hours.

Following formation the plate was removed from solution and the electrolyte replaced with an excess of 5 M H₂SO₄. The plate was replaced and equilibrium established, the second potentiostat and relay were installed and the control program loaded. Cycling of the plates was carried out under the following conditions; at a rate of C/5, the
electrode was charged until the potential against a Hg/Hg$_2$SO$_4$ reference electrode varied by less than 2 mV in four minutes above +1500 mV, this was followed by a 20 minute overcharge period. Ten minutes rest was considered necessary to allow the re-establishment of the electrolyte through-out the P.A.M. The discharge of the plate was also at C/5 until the potential of the plate fell to +800 mV, this cut-off potential was chosen as it is just below the shoulder of the discharge voltage profile, after which little capacity would be gained and the cell would be close to going into reversal.

After the discharge cut-off potential was reached, a 10 minute rest period was allowed before the cycle was repeated. The use of a computer enabled all these functions to be carried out automatically and recording of the data, such as time for discharge etc., to be compiled. It was decided that the plate would be deemed to have failed when its discharge capacity fell below 80% of the maximum capacity achieved during cycling.

After failure, the plate was removed and its thickness measured, the acid was washed out with distilled water, taking care not to dislodge any active material, and the plate dried at 95 °C for 16 hours. When the plate had cooled its weight was determined.

8.3 Results and Discussion

It was felt that the rather arbitrary failure level of 80% of the maximum time for discharge gave sufficient indication of plate life within a reasonable time limit. The use of lead - calcium - tin grids was chosen to avoid any complications with antimony in the plates. The
Fig. 8.1 Cycle Number v's Discharge Time

Fig. 8.2 Cycle Number v's Time For Charge
advantages of using a computer, under real time control, were very evident. The computer was able to note the potentials and times of the working cycle on, as well as control the formation of, the plate. Five pieces of information were stored on floppy disc for each cycle, they were; time for charge, potential before and after overcharge, potential at the end of the rest period and time for discharge. Lack of time prevented the complete investigation of the range of bismuth addition to a series of plates.

The voltage across the cell, on overcharge, was recorded manually and found to be between 2.5 and 2.65 V, depending on the plate and length of time into overcharge. A significant problem was found with gassing of the electrodes, the air-borne sulphuric acid condensed on the connecting wires and surrounds leading to corrosion of the electrical connections, stand and equipment near by. The condensed acid also leached through to the connecting wires causing embrittlement, acid attack and failure. A piece of separator was lightly laid across the top of the cell to reduce the dispersion of the aerosol and prevent contamination of the electrolyte from the precipitated run-off.

Table 8.1, below, lists the physical characteristics of each plate.

Looking at the discharge performance of each plate, Fig. 8.1, there are no outstanding features, except for the dramatic fall in capacity of Plate H, which was due to failure of the reference electrode. All the plates show their peak capacity within the first few cycles before declining, with increasing rapidity, to the point of failure. Indeed, on the basis of this small set of experiments it would
Fig. 8.3 Cycle Number v's Top of Charge Voltage

Fig. 8.4 Plate Thickness v's Cycle Number
Table 8.1  
Physical Characteristics of Plates Used

<table>
<thead>
<tr>
<th>Label</th>
<th>Paste Type</th>
<th>Paste wt. / g</th>
<th>Paste density / g cm(^{-3}) (ave.)</th>
<th>Plate Thickness (ave.) / mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>P-10 + 0.5% Bi</td>
<td>38.74</td>
<td>4.38</td>
<td>2.2</td>
</tr>
<tr>
<td>D</td>
<td>P-10 + 0.05% Bi</td>
<td>35.24</td>
<td>4.62</td>
<td>1.9</td>
</tr>
<tr>
<td>E</td>
<td>P-10 + 0.05% Bi</td>
<td>27.26</td>
<td>3.94</td>
<td>1.8</td>
</tr>
<tr>
<td>F</td>
<td>P-10 only</td>
<td>21.55</td>
<td>3.82</td>
<td>2.1</td>
</tr>
<tr>
<td>G</td>
<td>P-10 only</td>
<td>38.86</td>
<td>4.28</td>
<td>2.2</td>
</tr>
<tr>
<td>H</td>
<td>P-10 only</td>
<td>26.78</td>
<td>3.77</td>
<td>1.8</td>
</tr>
</tbody>
</table>

be almost impossible to draw any conclusions on the effect of bismuth, in the pastes, on capacity. Similarly, with Fig. 8.2, which shows the time for charge against cycle number for each plate, there is little to distinguish the paste types (and the rapid rise of Plate F is again due to problems with oxygen evolution and the reference electrode).

Fig. 8.3 shows the top of charge voltage, at the end of the overcharge period, and the broad spread of the results is such that no particular trend can be seen for the presence of Bi in the paste mixture.

Comparing the data for paste density against number of cycles or maximum time for discharge, as in Table 8.2 below, shows that the low bismuth plates give a better than expected maximum time for discharge for their density.

When comparing the results to plate thickness instead of paste density, some important features can be seen. Fig. 8.4 shows a plot of plate thickness against number of cycles. The results are interesting
Fig. 8.5 Plate Thickness v's Maximum Discharge Time

![Graph showing the relationship between plate thickness and maximum discharge time.]

Fig. 8.6 Plate Thickness v's Utilization

![Graph showing the relationship between plate thickness and utilization.]

**Paste Type**
- △ P-10
- X P-10 + 0.05 T S1
- □ P-10 + 0.57 S1

**Plate Thickness**
- 0.17
- 0.18
- 0.19
- 0.20
- 0.21
- 0.22
- 0.23

**Maximum Discharge Time**
- 170
- 160
- 150
- 140
- 130
- 120
- 110

**Utilization**
- 5.5
- 5.0
- 4.5
- 4.0
- 3.5
- 3.0
because they suggest that, as expected, cycle life increases with plate thickness, but with 0.05% Bi the number of cycles is improved for the same thickness of plate. This suggests that at this level, bismuth has a beneficial effect. Increasing the amount of Bi to 0.5% has the opposite effect and the thicker plate B gives fewer cycles than expected. In Fig 8.5 the maximum time for discharge is plotted against thickness, the resultant graph shows that the time for discharge decreases with increasing plate thickness, which is to be expected. The addition of a small amount of Bi, though following the trend, decreases the maximum time for discharge. Adding 0.5% Bi, however, moves the discharge time back in line with the P-10 standard.

Table 8.2 Results for All Plates

<table>
<thead>
<tr>
<th>Plate</th>
<th>Paste Density / g cm⁻³</th>
<th>No. of Cycles</th>
<th>Max. Time for Discharge / mins.</th>
<th>Max. Time for Charge / mins.</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>4.38</td>
<td>13</td>
<td>119</td>
<td>178</td>
</tr>
<tr>
<td>D</td>
<td>4.62</td>
<td>16</td>
<td>141</td>
<td>217</td>
</tr>
<tr>
<td>E</td>
<td>3.94</td>
<td>10</td>
<td>146</td>
<td>209</td>
</tr>
<tr>
<td>F</td>
<td>3.82</td>
<td>17</td>
<td>137</td>
<td>196</td>
</tr>
<tr>
<td>G</td>
<td>4.28</td>
<td>18</td>
<td>112</td>
<td>179</td>
</tr>
<tr>
<td>H</td>
<td>3.77</td>
<td>8</td>
<td>165</td>
<td>---</td>
</tr>
</tbody>
</table>

Table 8.3, below, shows the total discharge and total charge times together with plate thickness. The results from the lower bismuth addition indicate that these plate give more discharge capacity for their thickness than P-10 or P-10 with 0.5% Bi, but that the ratio of
Fig. 8.7 Paste Density v/s Utilization

Fig. 8.8 Cycle Number v/s Percentage Overcharge Plates D and F
total discharge time to total charge time, i.e. charging efficiency, is the same.

Examining the utilisation of the paste, as shown in Fig. 8.6, against thickness, shows that when compared to standard P-10, less

<table>
<thead>
<tr>
<th>Plate</th>
<th>Thickness (ave) / mm</th>
<th>Total Time for Discharge / mins.</th>
<th>Total Time for Charge / mins.</th>
<th>Ratio TFD/TFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>2.2</td>
<td>1404</td>
<td>1976</td>
<td>0.71</td>
</tr>
<tr>
<td>D</td>
<td>1.9</td>
<td>2082</td>
<td>2792</td>
<td>0.75</td>
</tr>
<tr>
<td>E</td>
<td>1.8</td>
<td>1306</td>
<td>1712</td>
<td>0.76</td>
</tr>
<tr>
<td>F</td>
<td>2.1</td>
<td>2154</td>
<td>2875</td>
<td>0.75</td>
</tr>
<tr>
<td>G</td>
<td>2.2</td>
<td>1890</td>
<td>2737</td>
<td>0.69</td>
</tr>
<tr>
<td>H</td>
<td>1.8</td>
<td>1136</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

charge per gram per cycle can be extracted with the 0.05% Bi paste. Plotting density against utilisation, Fig 8.7, shows that increasing the paste density lowers the utilisation, but with 0.05% bismuth the utilisation is improved.

The reason why bismuth has this, seemingly, contradictory behaviour is because it has three effects. Firstly, it improves the nucleation of lead sulphate, secondly it retards the development of PbO2 on recharge and thirdly, it is removed from the paste. This leaching leads to increased plate porosity, which, in turn gives better acid penetration, greater total discharge time (i.e. the sum of the discharge times for each cycle) and more cycles than ordinary P-10. However, the
promotion of sulphate formation, and the inhibition of dioxide nucleation and/or growth, mean that the maximum time for discharge is reduced when plotted against plate thickness. The increase in porosity which occurs due to the removal of Bi from the plates gives an improvement when the results are plotted against plate density.

The physical properties of the plates will obviously affect the performance and thus it is important to try and compare plates that are similar, but have different paste compositions. Thus taking plates D and F, it is possible to directly compare the performance and note any differences that arise from the presence of bismuth. Fig. 8.8 shows a plot of percentage overcharge against the cycle number, that there is very little difference between the two and this suggests that the efficiency of the charge/discharge reaction is not affected. Plate D is, however, denser than F, while F is thicker, therefore, from the extrapolated data above F should give more cycles and less capacity if the above hypotheses hold true and this is seen to be the case.

8.4 Conclusions

From the earlier work in Chapter 6 the concentration of bismuth in the positive electrode is reduced when electrochemical reactions take place, thus most of the bismuth added to the paste will be removed on the initial formation of the plate. Some will be trapped in the pores or surrounded by electro-inactive material, allowing it to affect the cycling studies.

The small amount that remains in the paste, initially containing 0.05% Bi, will still enhance the nucleation of lead sulphate. This will
lead to an increase in the amount of active material isolation and reduce the utilization. The bismuth which is present will still be subjected to the electrochemical forces and, in the process of being leached, will rupture the PbSO$_4$ layer and increase the porosity; hence the 0.5% Bi sample will have a higher utilization than expected.

Porosity decreases with increasing density and removal of bismuth from the paste will increase the porosity. This will lead to an increase in utilization of the active material and pastes containing bismuth will therefore give an improved performance when compared to ordinary P-10. The increased concentration of bismuth also increases sulphate formation which, in the confinement of high density paste, will restrict porosity. The increase in oxygen evolution seen before in the L.S.V.s may also restrict the movement of the acid. Further work could include O$_2$ evolution from the plates versus cycle number.

The increase in oxygen evolution is also linked to an increase in the amount of grid corrosion, which in turn will reduce the cycle life, and this may be the case in plate B. Also it is possible that a decrease in the top of charge voltage may be due to the presence of Bi lowering the oxygen overpotential.

Considering the results above, one can conclude that the presence of Bi between 0 and 0.05% has no effect on the lifetime capacity or the recharge efficiency, that is there is no increase in O$_2$ evolution. Further work should include the following; self-discharge, oxygen evolution versus cycle number and the effect of Bi in both the grids and the paste, leading to the development of the corrosion layer as found in a real battery situation.
9.1 Introduction

In comparison with the positive plate, the negative electrode has received substantially less research. The main areas of investigation have been the hydrogen evolution reaction, grid disintegration, and the action of expanders, such as lignin and barium sulphate, on the capacity and cycle life of the negative plate. Part of the reason for this must lie in the fact that most of today's batteries are positive plate limited and the major failure modes are therefore linked with this plate and the active material it carries.

However to understand the effect of the addition of bismuth to the integral battery, some work must be done on the effects of the intruding element. The hydrogen evolution work, carried out in Chapter 5 is part of this, but it was felt that the investigations into the negative electrode must include some cycle life studies.

Looking at the electrochemistry of the negative plate, there are several papers (80,106,122-124) which describe, in detail, the reactions, species and ions, that are to be found. The process of passivation and sulphation which a lead electrode, when placed in sulphuric acid, is subjected to was not investigated, however, the solid state and dissolution/precipitation processes that occur are adequately described in Refs. (80,122).

The discharge of the pasted lead electrode can best be described
by the equation below

$$\text{Pb} \rightarrow \text{Pb}^{2+} + 2e^- \rightarrow \text{PbSO}_4$$  \hspace{1cm} (9.1)

This scheme initially involves the dissolution of the lead to the divalent cation; (124,125) this is subsequently followed by the formation of a non-conducting surface film of lead sulphate. The impedance of the film has been measured at approximately $10^{10}$ ohm cm$^{-1}$, and its presence ultimately restricts the Pb$^{2+}$ ion production. There is a parallel reaction, to the above dissolution-precipitation mechanism, which involves direct attack on the lead by adsorbed sulphate anion on the lead surface (124). This mechanism relies on the production of Pb$^{2+}$ on the surface, which immediately attracts the adsorbed sulphate. A mechanism can only be described as dissolution/precipitation if the lead ions move from the surface into the solution, and in this case, this does not occur. However, the above mechanism requires a critical potential, and the reaction cannot be initiated if the potential remains negative of this limit.

Work by Archdale and Harrison (124,126-128) indicates that a soluble lead-complex solution species is formed. Detection of this was confined to a small potential region that was negative of the critical potential for the solid state formation of PbSO$_4$ mentioned previously. The existence of this region has been confirmed (122). The suggested mechanisms of lead dissolution also include a Pb(1) species either in a one electron step with disproportionation (129) or in a dimeric form (130) to give Pb$^{2+}$ and electrons.

In concert with this, measurements on concentrated Pb(Hg) amalgam (127), i.e. a simulation of surface and mechanical defect-free lead,
Fig. 9.1 Typical L.S.V. for Lead to Lead Sulphate

Fig. 9.2 L.S.V.s for Pure Lead After Various Cycle Numbers
showed that as the formation of lead sulphate increased, the concentration of soluble lead dropped. This suggests that lead goes into solution between the crystals of lead sulphate and not through them. On taking a planar polished lead electrode, the oxidation and reduction voltage sweeps show a discrepancy in the amount of charge returned. This suggests the presence of nucleation sites for the reductive process, leading to the isolation of some sulphur and depleting the amount of active material available for subsequent cycles.

At low dissolution rates, lead is passivated by PbSO$_4$ only, e.g. when left at its rest potential. With further anodic oxidation and thickening of the layer, some basic lead sulphates and lead monoxide can form. Burbank (131) has studied the composition of such films, as have Pavlov and others (132,133). This film appears to be a semi-permeable membrane (134,135), allowing access for H$^+$ and H$_2$O but not SO$_4^{2-}$, this could lead to the alkalization of the interior, giving some unexpected chemistry with anodic corrosion of the lead electrode.

The use of small area, planar electrodes, enables the monitoring of the development of the sulphate layer and also easy access for any micrographical work that needs to be done.

9.2 Experimental

The electrodes were made of polycrystalline, pure lead and lead-bismuth alloy as described in Chapter 4. The electrolyte used was 5 M H$_2$SO$_4$, and the cell was thermostated at 25 ± 1 $^\circ$C.

The equipment was arranged as shown in Fig 4.9 and, as for the work in Chapter 7, the data was recorded by a 2-80 based microcomputer,
Fig. 9.3 L.S.V.s for Alloy D After Various Cycle Numbers

Fig. 9.4 L.S.V.s For Pure Lead and All Alloys After 2000 Cycles
The electrodes were prepared as described in Chapter 4, and were placed in the electrolyte at -1300 mV v's a Hg/Hg$_2$SO$_4$ reference electrode. The counter electrode was pure lead with a relatively large area.

The electrodes were cycled between -1300 and -500 mV at 50 mV s$^{-1}$ for several thousand cycles. At the termination of the experiment the electrodes were removed and washed with water and acetone before being stored in a desiccator, prior to microscopic examination.

Table 9.1 Electrode Composition.

<table>
<thead>
<tr>
<th>Label</th>
<th>%age Pb</th>
<th>%age Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>99.9999</td>
<td>-0.008%</td>
</tr>
<tr>
<td>B</td>
<td>99.939</td>
<td>0.061</td>
</tr>
<tr>
<td>C</td>
<td>99.883</td>
<td>0.117</td>
</tr>
<tr>
<td>D</td>
<td>99.735</td>
<td>0.265</td>
</tr>
<tr>
<td>E</td>
<td>99.435</td>
<td>0.565</td>
</tr>
<tr>
<td>F</td>
<td>98.937</td>
<td>1.063</td>
</tr>
<tr>
<td>G</td>
<td>97.891</td>
<td>2.109</td>
</tr>
<tr>
<td>H</td>
<td>95.091</td>
<td>4.909</td>
</tr>
</tbody>
</table>

9.3 Results and Discussion.

The composition of the electrodes used is shown in Table 9.1.
Fig. 9.5  Graph of Percentage Bismuth Against Peak Height for Various Cycle Numbers
this range enables a full exploration of the effect of the addition of bismuth.

Similarly to the positive cycling experiments, the data recorded by the computer includes the charge passed, when the current is positive, and a linear sweep voltammogram at regular intervals. Six L.S.V.'s were recorded, at 100, 1000, 2000, 3000, 4000 and 5000 cycles. These correspond to run times of 53 minutes 20 seconds and multiples of 8 hours 53 minutes 20 seconds respectively into the experiment.

Figure 9.1 shows a typical L.S.V., after 2000 cycles. There are several points of interest. Firstly, as the potential is swept from -1300 mV, the reduction of the final amount of lead sulphate occurs. On reaching around -950 mV the current changes sign and the oxidation of the lead alloy begins. This proceeds smoothly, with the current profile being a regular shape, until passivation is reached at around -800 mV. This is caused by a layer of lead sulphate completely covering the electrode surface, the very high resistance of the film making further current flow very unlikely.

Following this the current is almost zero, anodic corrosion of the lead backing could occur, but the passivating layer is present for only a short time and any perm-selective equilibria is unlikely to have time to develop. Trapped acid will reduce even further the alkalisation of the interior of the film and the subsequent electrochemical reaction of the lead is prevented by the high resistance of the sulphate film.

The reduction of the film does not begin until the potential reaches around -970 mV, when the current becomes negative. In contrast to the oxidation peak, the reduction profile is shallow and elongated. This is due to the nature of the sulphate film, and the way the lead
Fig. 9.6  Graph of Percentage Bismuth Against Peak Potential for Various Cycle Numbers
recrystallises at the lead/lead sulphate/sulphuric acid interphase (106). There is evidence for the growth of lead dendrites (123), from the electrode surface and piercing the sulphate layer, concomitant with progressive dissolution of PbSO₄. Vetter (136) has suggested a solution-precipitation mechanism for the charge and discharge reactions, though both Lakeman (106) and Mitchell (81) failed to experimentally prove this. Both authors suggested, however, that it was a potentially valid mechanism, and the idea was indirectly supported by the work of Harrison and Thirsk (67). Another idea would be the consideration of a surface diffusion mechanism for lead, though this would be difficult to prove. The diffusion of lead, within a small radius, to the lead crystal growth centres on recharge is considered a practical possibility (81,106).

This only goes part-way to explaining the shallowness of the reduction peak. As the reduction proceeds, lead dendrites cross and merge leading to areas of sulphate being trapped and the escape of sulphuric acid is limited, thus slowing the kinetics of the reaction. Though the oxidation of lead to sulphate takes approximately 4 seconds (Fig. 9.1), after 2000 cycles, the subsequent reduction, back to lead, requires almost 13 seconds, 3 times the oxidation time, and even then, the current does not fall to zero.

Figures 9.2 and 9.3 show a series of L.S.V.'s for pure lead and alloy D (0.26% Bi). There are several similarities that can be seen. Firstly both figures show the development of porous layers of lead, such that the current densities must be considered nominal. Secondly, the symmetrical oxidation peaks, though there is some variation in both peak height, peak width and position of the peak potential. Finally, the
Fig. 9.7  Graph of Cycle Number Against Capacity For Pure Lead and All Alloys
presence of bismuth affects the reduction peak current and gives rise to a slight negative shift to $E_p$ at higher cycle number potential.

Figure 9.4 illustrates the difference in the size and shape of the current profiles for a range of alloys after 2000 cycles, i.e. 17 hours 46 minutes. The conclusions that can be drawn are:

i) the presence of bismuth helps in the distribution of the current as the passivating layer forms and,

ii) it is also probable that nucleation is enhanced thus leading to a tighter, more compact layer.

These two forces are in opposition, the first facilitates the development of a porous layer, leading to an increase in capacity whilst the second, improving the formation of a blanket of sulphate across the electrode surface, denies access to the electrolyte.

Plotting the peak height against bismuth level, Figure 9.5, illustrates that the maximum capacity is obtained with 0.3% bismuth, however, even with 4.9% bismuth present, the peak height is still greater than for pure lead. The potential for the peak current ($E_p$), as illustrated in Figure 9.6, shows a general trend of becoming more negative, i.e. easier nucleation of the sulphate and formation of the layer with increasing bismuth levels. Compactness of the sulphate layer, which is the direct result of the increased availability of nucleation sites, then works against this trend and pushes $E_p$ more positive.

The result of this is shown when plotting the capacities of each alloy against cycle number, Fig. 9.7. Here the capacity climbs with
Fig. 9.8  Electron Micrograph of the Sulphate Layer on Pure lead, 300 x Magnification

Fig. 9.9  Electron Micrograph of the Sulphate Layer on Alloy E, 300 x Magnification
cycle number, levelling out at different levels for each alloy. Though the rate of increase in capacity seems to be larger for the two higher alloys.

Using scanning electron microscopy there are two important features that come to light. Firstly it is interesting to note that the surface of the electrode is riddled with defects as shown in Figs. 9.8 and 9.9, (low power magnifications of the general electrode surface for samples A and E). This is important because not only could an estimate be made of the surface roughness, but it suggests that the method used to polish the electrodes is inefficient and will lead to a considerable variation in capacity. The presence of SiC, from the polishing process, does not seem to alter the size or shape of the lead sulphate crystals and seems to take no part in the electrochemistry. However, their presence will lead to a reduction in the active area of the sample. This does not seem to be the case with the electrodes used for positive cycling, where the surface of the electrode is covered to some depth.

Secondly the previously mentioned micrographs show that on a macro level the development of the sulphate layer does not mask the defects and thus the layer is not very thick and corrosion of the underlying lead electrode seems to be minimal. This is to be expected as lead sulphate is essentially insulating and the Pb$^{2+}$ ions will usually be found close to the electrode.

Increasing the magnification shows that even at 5000 times the original size there is little difference in crystal size between lead (A), in Fig. 9.10, and 2.1% Bi (G), Fig. 9.11. This suggests that the development of the layer is from many individual nucleation centres and the presence of bismuth on the electrode surface helps this process.
Fig. 9.10  Electron Micrograph of the Sulphate Layer on Pure lead,  
5000 x Magnification

Fig. 9.11  Electron Micrograph of the Sulphate Layer on Alloy G,  
5000 x Magnification
9.4 Conclusions

There are two main conflicting effects of bismuth on the negative electrode in this situation. The improvement in nucleation leads to a tighter and more compact layer which limits the development of the sulphate layer, though the lead sulphate layer itself is never particularly thick. And secondly, it helps in the distribution of current, acting as a connection from the electrode to, and through, the sulphate layer on and above the electrode surface.
CHAPTER 10

ELECTROCRYSTALLISATION

10.1 Introduction

The growth and development of a new phase on an electrode surface is always of considerable interest and when that new phase is related to the electrochemical performance of a lead-acid battery plate, the interest is enhanced. There are several investigative techniques for the examination of alloy effects on the electrocrystallisation mechanisms on lead. The investigation into the electrocrystallisation mechanisms of the active mass are complicated by the size and shape of the pores and other physical factors.

Renewed interest in the formation and growth of phases on the electrodes has been shown in the last two decades. Work by Thirsk, with Harrison (67) and Fleischmann (68), along with that of Armstrong et al. (137), has been extended and enhanced by many researchers, to provide mathematical modelling of the current transients (138,139). These present a more comprehensive picture of the nature of the transient response. The treatment of nucleation theory has, however, remained essentially the same; thus there are two types of nucleation, instantaneous and progressive. Instantaneous nucleation occurs when the nuclei for crystal growth are produced within a very short time relative to the current trace. Once these nuclei are formed, the number of nucleation centres remains effectively constant. In progressive nucleation, the nuclei develop with time, so new centres of growth are
forming throughout the experiment, the originators of these ideas on nucleation were Fleischmann and Thirsk (69,140). Once the nucleation type has been initiated, it is the resultant current response which indicates the type of electrochemical process occurring.

The growth transients can be categorised into one, two or three dimensional crystal growth. In certain circumstances, it is possible to get one dimensional growth, for example the growth of lead sulphate down the channels in a porous matrix of active material. However, this is often complicated due to pore branching and convolution. In two dimensional growth, the new phase simply covers the surface of the electrode, effectively as a monolayer. And in three dimensional growth, the directional expansion is not only across the electrode surface, but also into and away from it. This has sometimes been referred to as "2 1/2" dimensions, as growth, in this case, into the electrode is restricted. Chapter 3.2.3 gives a theoretical derivation of the equations used to model the processes described.

Various transient techniques have been used to gain an insight into the growth and development of the new phase. In particular, work by Carslow and Jaeger (141) and Frank (142) have looked at the rates of mass transport, and their effect on the processes when in unstirred solutions. This work has been complimented by Astley et al. (143) and Hills et al. (144), on the effect of diffusion control.

Research by Bialaki et al. (145), Webster et al. (146) and Hampson et al. (147) has cast light on the effect of the battery alloy on the nature of electrocrystallisation mechanisms. The work described below draws on this research and attempts to explain the effect of Bi on the electrocrystallisation mechanisms.
10.2 The Discharge Processes

10.2.1 Introduction

During discharge of a lead-acid cell, there is a reductive process at the positive plate and an oxidative process at the negative plate, both of which lead to the formation of lead sulphate. Today almost all lead-acid batteries are made positive plate limited, i.e. the capacity of the negative plate exceeds that of the positive. However, if the negative plate has a slow oxidation mechanism, then the rate of discharge will be limited by this. A comparison of the reduction processes of the positive plate and the oxidation of the negative plate, with and without bismuth, is therefore required.

10.2.2 Experimental

The electrodes were prepared, as described in Chapter 4, though final polishing was on 5 and 0.3 micron alumina to give a more even finish. The electrodes, in their P.T.F.E. shrouds were then mounted in the holder. A list of the compositions of the electrodes is shown in Table 10.1, note that the alloys were made up from the base lead, B, plus the required amount of bismuth.

Electroreduction of PbO₂ to PbSO₄ was studied by placing the electrodes in 5 M sulphuric acid at +500 mV vs Hg/Hg₂SO₄. The potential applied to the electrode was swept to +2020 mV and held there for five seconds to initiate a layer of lead dioxide on the electrode surface. The potential was then swept to +1200 mV and held until the residual
current reached a steady value. With the current constant, the potential was stepped down to +500 mV and the resultant current trace recorded on a chart recorder. The rise time of the pulse generator was determined to be less than 2.5 μs. A schematic diagram of the experimental equipment, for both investigations, is shown in Figure 4.9.

For the electro-oxidation of lead to lead sulphate, the concurrent process to the one above, the sample preparation was the same. The electrodes were placed in the 5 M sulphuric acid electrolyte at -1000 mV, which prevented the formation of any sulphate or oxy-sulphate layer on the sample surface. When the current had fallen to a small and constant value, the potential was stepped to -930 mV and the current trace recorded.

10.2.3 Results and Discussion

The potential step for the electroreduction process could be seen as excessive and it would represent, in battery terms, a particularly deep discharge. However, it was felt that only this type of extreme test would reveal if there was an alloy effect. This depth of discharge has been successfully used by various other researchers, eg Kelly (27) and Webster (84). From previous work, Chapter 7, it could be expected that the longer the electrode was in the sulphuric acid or the more cycles it underwent, the lower the bismuth concentration would become and its effect, if any, would be diminished.

Figure 10.1 shows a typical current response to the voltage step from +1200 to +500 mV, for a sample of pure lead (A). Comparing this with Fig 10.2, which is of a lead-bismuth alloy (G), one sees few
Fig. 10.1 Current Response of a Pure Lead Electrode Stepped From +1200 mV to +600 mV
Fig. 10.2 Current Response of Alloy G Electrode Stepped From +1200 mV to +600mV
noticeable differences, and indeed, any difference in the time to reach
the maximum current are masked by the variation due to sample
preparation (see Table 10.1).

<table>
<thead>
<tr>
<th>Label</th>
<th>%age Bismuth</th>
<th>Time / s x 10^-3</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>± 0.008%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>--</td>
<td>1.4</td>
<td>0.5</td>
</tr>
<tr>
<td>B</td>
<td>5 x 10^-4</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>C</td>
<td>0.061</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>D</td>
<td>0.117</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>E</td>
<td>0.205</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>F</td>
<td>0.265</td>
<td>1.6</td>
<td>0.4</td>
</tr>
<tr>
<td>G</td>
<td>0.565</td>
<td>1.0</td>
<td>0.4</td>
</tr>
<tr>
<td>H</td>
<td>1.063</td>
<td>0.9</td>
<td>0.2</td>
</tr>
<tr>
<td>I</td>
<td>2.109</td>
<td>1.1</td>
<td>0.4</td>
</tr>
<tr>
<td>J</td>
<td>3.587</td>
<td>1.1</td>
<td>0.1</td>
</tr>
<tr>
<td>K</td>
<td>4.909</td>
<td>1.0</td>
<td>0.3</td>
</tr>
</tbody>
</table>

It would seem difficult to devise a more reproducible method of
surface preparation. Use of a microtome would be possible but the effect
of the P.T.F.E. holder and the softness and ductility of the samples,
mean that it is impossible to get a similar finish on every run. There
is, however, a minimum in the time to $I_{\text{max}}$ with alloy G, even allowing
for the large standard deviation. This suggests that Bi facilitates the
reduction of lead dioxide, even though at the potentials applied, it would be expected for the bismuth present to leach from the electrode.

To view any change in the mechanism of electocrystallisation, there is an alternative way of utilising the data; and that is to use dimensionless plots and compare the four theoretical models (2 dimensional instantaneous, 2 dimensional progressive, 3 dimensional instantaneous and 3 dimensional progressive nucleation and growth) with that of the actual transient. Because of the variation due to surface preparation, at least four transients were run for each sample. The resultant, averaged dimensionless plots, shown in Figs 10.3 to 10.5, are compared with two theoretical current responses, three dimensional instantaneous nucleation and growth and two dimensional progressive nucleation and growth (Figures 3.6 and 3.7 show all four theoretical models).

Fig. 10.3 shows the results for pure lead (A), and from this it can be seen that the actual recorded profile varies between three dimensional instantaneous and two dimensional progressive nucleation and growth. This indicates that, because of the volume change or change in other physical properties that occur on reduction, there is uncertainty as to the actual mechanism. This is evidence for a proposed "2 1/2" dimensional growth mechanism, where some crystal growth away from the electrode surface is possible but is dependant on the vertical vector of the growth cone. After $t_{max}$, the current decay is closest to three dimensional instantaneous nucleation and growth, however, $I/I_{max}$ begins to plateau at around $t/t_{max} > 1.5$ - this could be ascribed to one dimensional growth, i.e. the sulphation down the pores on the semi-porous surface.
Fig. 10.3 Dimensionless Plot of the Current Response For a Pure Lead Electrode

Fig. 10.4 Dimensionless Plot of the Current Response For Alloy G Electrode
Fig. 10.5  Dimensionless Plot of the Current Response For Alloy K Electrode
Moving onto Fig. 10.4, which is for alloy F, there is a subtle, but definite change. Now the current trace is biased toward two dimensional progressive nucleation and growth, though as before, after the current maximum, the curve approaches three dimensional instantaneous nucleation and growth. Fig. 10.5 shows the result for K, that is the maximum bismuth concentration, the trend is continued, with the transients moving closer to the two dimensional progressive nucleation and growth line. It is important to note that the difference, in dimensionless plot terms, between two dimensional progressive and three dimensional instantaneous modes of nucleation and development, is marginal and it is possible that a hybrid "2 1/2" dimensional growth mechanism may become dominant, as suggested above. The trend on the downward part of the curve is, again, toward three dimensional instantaneous, though the levelling out of the current at \( t/t_{\text{max}} > 1.5 \) and the one dimensional growth idea this suggests may have an influence earlier as the transient peaks.

The addition of bismuth seems to have a marginal effect, facilitating nucleation of lead sulphate on discharge of lead dioxide.

On the oxidation of lead to lead sulphate, the potential step from -1000 mV to -930 mV, is much less severe. The value of 70 mV change was chosen because it gave a reproducible transient. A typical current response is shown in Fig. 10.6.

It is interesting to note the shape of the curve, there is an initial spike, which is due to a combination of double-layer charging and nucleation of the sulphate centres. The current then falls before rising again to a maximum and tailing away. Analysis of the time to peak current, as listed in Table 10.2 shows little, if any, consistancy, though all the
Fig. 10.6  Current Response of a Pure Lead Electrode Stepped From
-1000 mV to -930 mV
times of the alloys are less than pure lead (A).

Table 10.2 Time to Imax for Oxidation of Lead to Lead Sulphate

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Average Time / s</th>
<th>Deviation / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>71 ±16</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>50 ±6</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>33 ±7</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>44 ±11</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>31 ±12</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>61 ±26</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>58 ±18</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>54 ±13</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>42 ±11</td>
<td></td>
</tr>
<tr>
<td>J</td>
<td>48 ±2</td>
<td></td>
</tr>
</tbody>
</table>

The variation between the times for the same alloy, upto 26%, ensures that some overlap is inevitable, however, the trend implies that Bi promotes the formation and/or growth of lead sulphate crystals. This variation in Imax is probably due to two factors. Firstly, the preparation of the sample, that is the "roughness" of the electrode, and secondly, the presence of O2 in the electrolyte. Work by Flemming et al. (148) and Baugh and Bladen (149), for example, give ample evidence for the effect of dissolved oxygen in the electrolyte. Investigations were carried out in aerated solutions which are similar to those found in the battery system in real applications, degassing the electrolyte would
have removed this.

One possible explanation for the changes in time to $I_{\text{max}}$ is the competition between two antagonistic factors. When the bismuth is added to the lead, the grain size increases after cooling, this should reduce the ease of nucleation as the number of defect sites on the grain boundaries will fall. Hence, the presence of Bi must act as a nucleation promoter. As the level of bismuth increases, the grain size also increases, see Chapter 5, and this then becomes the dominant factor.

10.3 The Recharge Processes

10.3.1 Introduction

Inhibition of the kinetics of this process means that more energy will be required to bring the system back up to full charge, thus, reducing efficiency of charging and increasing the time to top of charge. This will be more of a problem for load levelling than for S.L.I. or standby batteries.

10.3.2 Experimental

The electrodes used in the investigation of the recharge process, PbSO$_4$ to PbO$_2$, were prepared in the standard way and were subjected to the discharge process described above. Once the current from the previous step had fallen to a small and constant value, the recharge potential step, to +1200 mV, was applied and the current was recorded on a y-t recorder.
Fig. 10.7  Current Response of a Pure Lead Electrode Stepped From
+600 mV to +1200 mV

Fig. 10.8  Current Response of a Pure Lead Electrode Stepped From
-930 mV to -1000 mV
For lead sulphate to lead, the electrodes were, again, those used in the discharge experiments of lead to lead sulphate, described above. The potential was pulsed back from -930 mV to -1000 mV and the current transient stored on the y-t recorder.

10.3.3 Results and Discussion

10.3.3.1 Lead Sulphate to Lead Dioxide

A typical i-t transient for the recharge of lead sulphate to lead dioxide is shown in Fig. 10.7. The electrode probably undergoes a similar potential jump at the start of the recharge process in the actual battery system, as explained in Chapter 8. The trace shows an initial sharp current rise on the change in the potential, due to double layer charging and nucleation, followed by a gradual rise as the transformation takes place at the individual crystal growth centres. The current falls away as these centres overlap and the sulphate is converted. The current does not fall to zero because some oxygen evolution occurs from the PbO2 mass. The layer to be oxidised must now be considered as somewhere between planar and completely porous.

The results tabulated, Table 10.3, below show the time to the maximum current.

It is difficult to draw any definite conclusions from the above data (due to the variation encountered), except to note that the time for maximum current seems to go through a minimum at around 0.56% Bi. This suggests that a modification in the mechanism of nucleation and growth of the dioxide layer occurs. Any beneficial effect becomes
masked, however, as the level of bismuth rises above 1%. The inhibition of the formation of lead dioxide on lead-bismuth alloy supports has been discussed previously in Chapter 7, though the effect seems to be delayed here. This could be due to the preparation of the electrodes or more effective removal of the bismuth on the surface than with the cycled planar electrodes. With the minimum at 0.56%, an explanation is required for the "improvement" in time to $I_{\text{max}}$. This is probably due to the formation of the initial sulphate layer and its effect on the subsequent morphology of the dioxide, as described in Chapter 7. The results for alloy J are anomalous.

The effect of bismuth on the nucleation of lead sulphate has been discussed and as Bi enhances PbSO$_4$ crystallisation the crystals will be

Table 10.3 Time to Maximum Current for the Oxidation of Lead Sulphate to Lead Dioxide

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Time / s</th>
<th>Variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.9</td>
<td>±0.1</td>
</tr>
<tr>
<td>F</td>
<td>3.4</td>
<td>±0.8</td>
</tr>
<tr>
<td>G</td>
<td>3.0</td>
<td>±1.4</td>
</tr>
<tr>
<td>H</td>
<td>3.4</td>
<td>±0.8</td>
</tr>
<tr>
<td>I</td>
<td>4.5</td>
<td>±0.9</td>
</tr>
<tr>
<td>J</td>
<td>2.4</td>
<td>±0.4</td>
</tr>
<tr>
<td>K</td>
<td>4.7</td>
<td>±1.2</td>
</tr>
</tbody>
</table>
smaller which will indirectly improve the nucleation of the lead dioxide. At low levels, the Bi will be leached out and the results will then be similar to those of pure lead. But with more bismuth present, its inhibitive effect on the nucleation of PbO\textsubscript{2} will predominate.

It is interesting to note that the potential limit for the reduction process is only +1200 mV, this suggests that, as the current response indicates, there are isolated centres of PbO\textsubscript{2} within the semi-porous surface layer and thus even a substantial excursion into the sulphate region, in the electrode pre-treatment, does not completely reduce the PbO\textsubscript{2} crystallites. This can be explained by the insulating nature of the lead sulphate film.

10.3.3.2 Lead Sulphate to Lead

On conversion of lead sulphate to lead, the resultant current-time trace shows a single very sharp peak, as shown in Fig. 10.8. The time to $t_{\text{max}}$ is very short, indicating that the recharge of lead sulphate to lead will not affect the cell efficiency.

The results for the alloys are shown below in Table 10.4.

There are two conclusions which can be drawn from the data in Table 10.4. Firstly, there is quite a difference between pure lead (A) and base lead (B), that is the refined lead used as the base for making the alloys. Though it could be argued that the result bucks the general trend, as the value is some 80% greater than those on either side; it is possible that the trace impurities retard the kinetics of the reaction. The second point is that bismuth appears to alleviate this, with the initial drop in $t_{\text{max}}$ when alloy C is reached. Increasing the amount of
Table 10.4  Time to $I_{\text{max}}$ for the Reduction of Lead Sulphate to Lead

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Time to $I_{\text{max}}$ / s</th>
<th>Variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.20 ±0.20</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2.22 ±0.05</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>1.32 ±0.27</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>1.37 ±0.10</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>1.55 ±0.05</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>1.42 ±0.20</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>1.30 ±0.10</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>0.83 ±0.05</td>
<td></td>
</tr>
<tr>
<td>J</td>
<td>0.75 ±0.25</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>0.50 ±0.07</td>
<td></td>
</tr>
</tbody>
</table>

Bismuth up to alloy H, has little effect, the large values for the standard deviation suggest that alloys in the range C to G can be grouped together. These alloys now give a similar time to that of A and the bismuth helps to overcome the retardant properties of the trace impurities. At 2.1% Bi, there is a sudden drop to around 60% of the previous time. The kinetics of the reaction are dependant on the size of the lead sulphate crystals so an increase in time from A to B is probably due to an increase in crystal size. It is also possible, however, that a new alloy phase has formed when the Bi level exceeds 2%. Though this is not reported in the phase diagram, possibly because it is a surface effect, the crystal structure would be affected confirming the
ideas in Chapter 9.

The reduction in $t_{\text{max}}$ could be due to the bismuth acting as a nucleation point for the growth of lead crystallites, or providing a conductive pathway through the lead sulphate layer. This effect is then superseded when the level of Bi reaches a critical point which causes the size of the sulphate crystals to be reduced significantly. Thus as far as recharge is concerned, low levels of Bi, up to 0.2% have no detrimental effect in performance and high levels of bismuth, greater than 1%, give distinct improvements in the recharge characteristics.

One idea would be that bismuth forms an inter-metallic complex of the form shown in Eqn. (10.1) shown below. Confirmation of this would be difficult to obtain, but the presence of bismuth on the electrode surface is known and the use of micro-probe analysis could cast some light on the idea.

\[
Pb/\text{Bi} \\
PbSO_4 \overset{\text{---------}}{\longrightarrow} PbBi_x
\]  

(10.1)

10.4 Quasi-porous Cycled Electrodes

10.4.1 Introduction

In order to overcome the difficulties associated with crystallisation studies employing planar electrodes, a Plante style process can be used to generate a quasi-porous electrode surface. This has the advantage of being more representative and, hopefully, more reproducible than the planar electrode. The major disadvantage, especially when dealing with soluble impurities such as bismuth, is that
the leaching of the alloying ingredient with cycling, will lead to a lower impurity concentration and diminished alloy effect. If this is the case, then all of the different alloy samples will give similar responses. Webster (84) has looked into the response of some cycled lead, lead-tin-calcium and lead-antimony alloys and reached the conclusion that the alloy effect, although limited by the development of the porous matrix, is still present and comparisons between different alloys were therefore valid.

10.4.2 Experimental

An investigation into aged, at least one month old, polycrystalline lead and lead bismuth samples was carried out. Five test pieces were used, they were A, B, G, I, and K. Each sample was polished in the usual way and placed in the electrolyte at +700 mV, v's Hg/Hg₂SO₄. The samples were then swept to +2020 mV on the first cycle, to initiate a layer of lead dioxide, before being potentiodynamically swept between +600 and +1350 mV at 50 mV s⁻¹.

At specific times, the potential on the down sweep was halted at +1200 mV. After the current had stabilized, the electrode was discharged by stepping the potential down to +600 mV and the current transient was recorded on a y-t recorder.

After the resultant current had stabilized, the reverse process (to +1200 mV) was recorded. Cycling was then recommenced until either 24 hours of cycling were completed or the cycle number reached for the next pulse sequence.
Fig. 10.9  Current Response of a Quasi-Porous Pure Lead Electrode
Stepped From +1200 mV to +600 mV

Fig. 10.10  Current Response of a Quasi-Porous Pure Lead Electrode
Stepped From +600 mV to +1200 mV
10.4.3 Results and Discussion

The shape of both the reduction and oxidation current responses of the cycled electrodes, Figs. 10.9 and 10.10, are very similar in shape to that of the planar electrodes. The areas of difference will come in measuring the time to maximum current or similar property, where the physical nature of the electrode surface is important.

The time at which the pulses were taken varied, but the approximate times were 4 hours (450 cycles), 8 hours (900 cycles) and 24+ hours. This gave time for the porous matrix to develop and then sulphate, as described in Chapter 7.

Table 10.5 shows the time to the maximum current, $t_{\text{max}}$, for the reduction of the lead dioxide layer on each of the samples, along with the cycle number at which the reduction was carried out. There are two points which can be deduced, firstly, the general trend that as the cycle number increases, the value for $t_{\text{max}}$ increases, within each alloy. This is to be expected as the development of a more complex porous layer will increase the time to $I_{\text{max}}$. Secondly, the variation within the alloy range, as shown in Fig 10.11, illustrates that the presence of the base impurities, i.e. sample B, reduces the value for $t_{\text{max}}$, while the addition of bismuth, in samples G, I, and K, gives rise to an increase in $t_{\text{max}}$. Problems arise with any attempt to determine the time of discharge. Firstly, with the development of the porous layer, when the potential of the electrode is stopped at $+1200$ mV, the oxidation proceeds and lead sulphate conversion will continue, except for the "hard" sulphate, thus the snapshot discharge picture becomes complicated. A second complication will arise from the variation in the
Fig. 10.11 Cycle Number vs Time to $I_{\text{max}}$ for Discharge Pulse

Fig. 10.12 Cycle Number vs Time to $I_{\text{max}}$ for Recharge Pulse
### Table 10.5

<table>
<thead>
<tr>
<th>Label</th>
<th>Cycle Number</th>
<th>Time / s x 10^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>529</td>
<td>0.85</td>
</tr>
<tr>
<td>A2</td>
<td>860</td>
<td>0.93</td>
</tr>
<tr>
<td>A3</td>
<td>1701</td>
<td>0.87</td>
</tr>
<tr>
<td>B1</td>
<td>669</td>
<td>0.76</td>
</tr>
<tr>
<td>B2</td>
<td>942</td>
<td>0.76</td>
</tr>
<tr>
<td>B3</td>
<td>2925</td>
<td>0.77</td>
</tr>
<tr>
<td>G1</td>
<td>525</td>
<td>0.83</td>
</tr>
<tr>
<td>G2</td>
<td>1076</td>
<td>0.67</td>
</tr>
<tr>
<td>G3</td>
<td>2538</td>
<td>0.90</td>
</tr>
<tr>
<td>I1</td>
<td>500</td>
<td>0.78</td>
</tr>
<tr>
<td>I2</td>
<td>938</td>
<td>0.89</td>
</tr>
<tr>
<td>I3</td>
<td>2657</td>
<td>0.91</td>
</tr>
<tr>
<td>I4</td>
<td>3200</td>
<td>1.00</td>
</tr>
<tr>
<td>K1</td>
<td>461</td>
<td>0.73</td>
</tr>
<tr>
<td>K2</td>
<td>1017</td>
<td>0.73</td>
</tr>
<tr>
<td>K3</td>
<td>3053</td>
<td>1.12</td>
</tr>
</tbody>
</table>

Roughness of the sample, which will affect the rate of development of the porous matrix, as described in Chapter 7, where up to 30% variation in capacity could be found. Thirdly, impurities may inhibit the formation of the porous matrix, in particular if any insoluble compounds are formed. The only way to overcome these would be to run a large
Fig. 10.13  Dimensionless Plot of the Current Response of the Discharge of the Quasi-Porous Pure Lead Electrode After 529 Cycles

Fig. 10.14  Dimensionless Plot of the Current Response of the Discharge of the Quasi-Porous Pure Lead Electrode After 860 Cycles
Fig. 10.15 Dimensionless Plot of the Current Response of the Discharge of the Quasi-Porous Pure Lead Electrode After 1701 Cycles

Fig. 10.16 Dimensionless Plot of the Current Response of the Discharge of the Quasi-Porous Alloy B Electrode After 669 Cycles
number of each alloy, however, time did not allow this.

Table 10.6  
Time to Maximum Current for Oxidation of 
Lead Sulphate to Lead Dioxide.

<table>
<thead>
<tr>
<th>Label</th>
<th>Cycle Number</th>
<th>Time / s</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>529</td>
<td>1.66</td>
</tr>
<tr>
<td>A2</td>
<td>860</td>
<td>2.87</td>
</tr>
<tr>
<td>A3</td>
<td>1701</td>
<td>2.61</td>
</tr>
<tr>
<td>B1</td>
<td>669</td>
<td>3.70</td>
</tr>
<tr>
<td>B2</td>
<td>942</td>
<td>2.20</td>
</tr>
<tr>
<td>B3</td>
<td>2925</td>
<td>4.58</td>
</tr>
<tr>
<td>G1</td>
<td>525</td>
<td>2.93</td>
</tr>
<tr>
<td>G2</td>
<td>1076</td>
<td>4.72</td>
</tr>
<tr>
<td>G3</td>
<td>2538</td>
<td>3.82</td>
</tr>
<tr>
<td>I1</td>
<td>500</td>
<td>2.81</td>
</tr>
<tr>
<td>I2</td>
<td>938</td>
<td>4.07</td>
</tr>
<tr>
<td>I3</td>
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<td>3.74</td>
</tr>
<tr>
<td>I4</td>
<td>3200</td>
<td>4.07</td>
</tr>
<tr>
<td>K1</td>
<td>461</td>
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<tr>
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<td>1017</td>
<td>6.52</td>
</tr>
<tr>
<td>K3</td>
<td>3053</td>
<td>6.15</td>
</tr>
</tbody>
</table>

Moving on to look at the recharge pulse, Table 10.6 shows the value for $t_{\text{max}}$ for each sample at the respective cycle numbers. It can be seen that, in general, the value of $t_{\text{max}}$ peaks or plateaus at 900 to
Fig. 10.17  Dimensionless Plot of the Current Response of the Discharge of the Quasi-Porous Alloy B Electrode After 942 Cycles

Fig. 10.18  Dimensionless Plot of the Current Response of the Discharge of the Quasi-Porous Alloy B Electrode After 2925 Cycles
Fig. 10.19 Dimensionless Plot of the Current Response of the Discharge of the Quasi-Porous Alloy G Electrode After 525 Cycles

Fig. 10.20 Dimensionless Plot of the Current Response of the Discharge of the Quasi-Porous Alloy G Electrode After 1076 Cycles
1000 cycles before falling away as the cycle number increases. The only alloy to buck this trend is B.

A second factor to notice is that the time to the peak current increases with the addition of bismuth. Even after 3000 cycles, the value of $t_{\text{max}}$ is at least 30% greater than the projected value for pure lead. The presence of bismuth has a two-fold effect, as it is leached from the alloy it will increase the development of the porous matrix, but it will inhibit the formation of PbO$_2$. These factors are clearly shown to be at work in Table 10.6, and the larger the initial amount of Bi, then the longer the inhibitive effect will last. With alloys K and I, it can be seen that the time to $I_{\text{max}}$ levels out with cycle number, but for alloy G it drops away with the continuation of cycling. Again sample B provides a rogue result. The important point to be made here, is that bismuth inhibits the recharge of the porous matrix, and the more bismuth, the greater the degree of inhibition. This is shown graphically in Fig 10.12.

Before considering the charge passed on each electrode, it is worth examining the crystallisation mechanisms which occur for both the discharge and charge potential steps on the porous electrodes, the use of dimensionless plots helps to cast some light on the possible mechanisms.

Figure 10.13 shows the dimensionless plot for the discharge response of sample A1, it is quite similar in shape to that in Fig 10.3 (that of the "planar" pure lead) but the current response approximates more closely to that of two dimensional nucleation and growth than the planar lead. After $t_{\text{max}}$ reaches 1, the current decay is between two dimensional progressive and three dimensional instantaneous but tends to
Fig. 10.21  Dimensionless Plot of the Current Response of the Discharge of the Quasi-Porous Alloy B Electrode After 2538 Cycles

Fig. 10.22  Dimensionless Plot of the Current Response of the Discharge of the Quasi-Porous Alloy K Electrode After 461 Cycles
Fig. 10.23  Dimensionless Plot of the Current Response of the Discharge of the Quasi-Porous Alloy K Electrode After 1017 Cycles

Fig. 10.24  Dimensionless Plot of the Current Response of the Discharge of the Quasi-Porous Alloy K Electrode After 3053 Cycles
one dimensional as $t/t_{\text{max}}$ approaches 2. Further cycling produces little change in the mechanism, as shown in Figs. 10.14 and 10.15 for A2 and A3 respectively. The levelling out of the current after $t/t_{\text{max}} > 1.5$ is consistent and, as the cycling progresses, the final current becomes higher. This is indicative of an increase in the porous nature of the active layer.

In comparison with the pure lead, the base lead plots show some variation, Figs. 10.16 to 10.18. With sample B1, Fig. 10.16, the resultant response is closer to two dimensional progressive nucleation and growth than A1. After $t/t_{\text{max}} = 1$, the current decay approaches that of the predicted three dimensional instantaneous nucleation and growth, though as $t/t_{\text{max}}$ reaches 2, the current levels off and a one dimensional model would be a better representation. As before, the porosity increases with cycling and a strong preference for a one dimensional model follows this trend.

Comparing the results for base lead (B) with those for the bismuth containing alloys (G, I, and K) gives rise to several interesting points. Fig 10.19 shows the response for G1 and the graph is very similar to that of B1; except with the rising part of the transient where the curve is even closer to two dimensional nucleation and growth. The rest of the results for G, Figs. 10.20 and 10.21, confirm the development of a three dimensional instantaneous response after $I_{\text{max}}$ and the increase in porosity gives a higher final current. The results for K confirm these observations.

When the percentage of bismuth reaches 4.9% however, there is a change in response, as shown in Figs. 10.22 to 10.24. The result for K1 shows close agreement with the three dimensional instantaneous
Fig. 10.25 Dimensionless Plot of the Current Response of the Recharge of the Quasi-Porous Pure Lead Electrode After 529 Cycles

Fig. 10.26 Dimensionless Plot of the Current Response of the Recharge of the Quasi-Porous Pure Lead Electrode After 860 Cycles
Fig. 10.27  Dimensionless Plot of the Current Response of the Discharge of the Quasi-Porous Pure Lead Electrode After 1701 Cycles

Fig. 10.28  Dimensionless Plot of the Current Response of the Recharge of the Quasi-Porous Alloy G Electrode After 525 Cycles
nucleation and growth model on the transient decay. But there is no increase in porosity with cycling, Figs. 10.23 and 10.24, this suggests that above 2.1% bismuth, the inhibition of lead dioxide formation and the increase in sulphate nucleation, as described in Chapters 7, 9 and above, reduces or limits the porosity. In fact, the increase in the correlation between the falling part of the transient and three dimensional instantaneous nucleation and growth mechanism of the other alloys may be due to the increased porosity, from the leaching of bismuth, and the subsequent effect of a one dimensional type of crystal growth on the current response.

Fig. 10.25 shows the current-time trace for the potential step from +600 to +1200 mV on sample Al. There is an initial peak as the potential is applied, which is probably due to oxygen evolution from the lead dioxide centres, the lead sulphate crystal structure surrounds a kernel of lead dioxide, and acts as a semi-permeable membrane which lets only small ions and molecules such as \( \text{H}_2\text{O} \), \( \text{OH}^- \), and \( \text{H}^+ \) through. This leads to the possibility of the alkalisation of the internal structure, thus when the potential step is applied it is quite feasible that oxygen will be generated. After this initial jump in current, there is a fall as the water is used up, then the transformation of the lead sulphate to dioxide begins. Fig. 10.26 shows the translated current response in dimensionless form, the closest fit for a theoretical model is that of three dimensional progressive nucleation and growth. This concurs with the theory that the conductive lead dioxide grows through-out the lead sulphate porous matrix (150). As before, there is some deviation as \( t/t_{\text{max}} \) exceeds 1.5, with the current levelling off. This is due to a constant amount of oxygen evolution added with the effect of the porous
Fig. 10.29 Dimensionless Plot of the Current Response of the Recharge of the Quasi-Porous Alloy K Electrode After 461 Cycles
Fig. 10.30 Cycle Number v's Charge Reduction Pulse

![Graph showing charge reduction pulse with cycle number]

Fig. 10.31 Cycle Number v's Charge Oxidation Pulse

![Graph showing charge oxidation pulse with cycle number]
nature of the lead sulphate matrix.

Continued cycling reveals little change, except for the increase in porosity as expected. Figure 10.27 shows the dimensionless plot for A3. With the addition of bismuth, there is little or no difference, as indicated in Figs. 10.28 and 10.29 of G2 and K2 respectively.

Another area of investigation considers the amount of charge passed on each charge/discharge pulse and compare the ratio of the capacity on reduction to that on oxidation. To make the values comparable, however, only the current passed within the time limit of two times \( t_{\text{max}} \) was used. The resultant values are also corrected for the variation in electrode size, such that charge is per 3 mm diameter electrode.

Looking first at the charge passed on reduction of lead dioxide to lead sulphate, Fig. 10.30. Essentially the trend is, within each alloy, that the first pulse gives the largest capacity, however both K and B are different, with the second discharge giving the maximum value. From this it could be said that the composition of K and B delay the development of the porous matrix, with sulphation affecting all of the samples as the cycle number increases. The maximum charge, which is considerably higher than that for pure lead (A), is shown with alloy G.

Considering the capacity on oxidation or recharge, Fig. 10.31, the trend is one of a peak in the charge on the second pulse, that is as the capacity of the porous matrix reaches its maximum. Again the maximum charge passed is shown with G, though the second value for G is slightly less than the first. Variations are likely, due to factors such as wait time between pulses. No experiments were carried out to see if increasing the time between current stabilization and pulse application
Fig. 10.32 Cycle Number vs Oxid^{n}\text{-}Redc^{n} Capacity

- Sample A
- Sample B
- Sample C
- Sample I
- Sample K
caused any difference in the recorded trace, charge passed or time to
\[ I_{\text{max}} \]

In Fig. 10.32 (the ratios of discharge capacity to charge capacity) the points of interest are, firstly, that the ratio is low, that is less than 0.4. This is probably due to a combination of three things; oxygen evolution from the lead dioxide, \( \text{PbO}_2 \) formation overpotential and the enhanced formation of lead sulphate. Secondly, in the initial stages, lead is the most efficient, but this soon fades and all the other alloys overtake A.

10.5 Conclusions

Dimensionless plotting has shown that bismuth levels of up to 2.1% improve the porosity of a electrode, however the effect on nucleation and crystal growth mechanisms is inconclusive.

In the discharge process, the effect of bismuth is that, in general, to decrease \( t_{\text{max}} \) on the planar and, in low levels, on the porous electrodes.

When considering the recharge process, bismuth inhibits the change of lead sulphate to lead dioxide, but facilitates lead sulphate to lead.
CHAPTER 11

CORROSION OF LEAD AND LEAD-BISMUTH ALLOYS

11.1 Introduction

The corrosion of lead and its alloys in the lead-acid battery has attracted a large amount of work, (131,133,151-156). The principle areas of investigation have been the relative performance of the positive plates in areas such as weight loss, charge passed and so forth. The relevance, or otherwise, of these standards of corrosion and corrosion resistance has been called into question (155,157), but the overall suitability of a particular alloy is dependent on several points, as described below.

Simon (158) looked at the development of the corrosion layer in pasted lead-antimony plates. Initially, the lead corroded uniformly to give a cohesive film, but once a critical corrosion layer thickness was established, a change occurred. The corrosion began to accelerate at the grain boundaries and at the interface of the primary lead dendrites with the eutectic. This second stage gave a corrosion product of higher specific volume than the lead dioxide previously formed which resulted in more stress being applied to the grain boundaries and other areas of micro-crack propagation. The extra stress forced cracks to appear in the thin grid spars, leading to loss of capacity. The reason for the development of a second type of layer seems to be due to a reduction in the acidity of the electrolyte at the lead interface which is produced by the perm-selectivity of the dioxide layer (82) (similar to that found
with sulphate (159)).

The above constitutes one of the major factors in the corrosion of lead and its alloys. A second important factor is that of the potential of the electrode. Leander (133,152) showed that peak corrosion of lead occurred at mild overcharge, corresponding to the potential of "float charge" in stand-by batteries. The introduction of Pb-Ca alloys, by Haring and Thomas (22), exploited the fact that, at this potential, Pb-Sb grids corrode much faster than either pure lead or Pb-Ca positives and thus had inferior cycle lives. Data has been obtained for various alloy compositions, including the ones used today (161). The relevance of such information though, depends on the application of the battery.

A third factor that affects the suitability of alloys for grid construction is the microstructure. Valeriote (105) and co-workers (159) examined the corrosion behaviour of low antimony anode lead, calcium and tin alloys. Their results show the effects of different preparative methods as well as the differences inherent in the addition of alloying ingredients. The conclusions reached are that during corrosion, stresses are produced across grain boundaries by intergranular corrosion products. Using a low tin:calcium ratio, discontinuous precipitation occurs, and this forms an interlocking grain network with high stress resistance.

It must be noted that some corrosion of the electrode is required to ensure adhesion of the paste to the plate, and this is facilitated in the early stages of curing when the relative humidity is around 100%. Restriction and control of grid corrosion is, therefore, a crucial factor in determining the longevity of the plate when in an active
environment. Elements such as Mg, Sr and even Li (162) have been added as alloying ingredients, to regulate the growth and development of the corrosion layer.

The presence of bismuth, both as an alloying ingredient and as a basic impurity, has been examined by several researchers with reference to its effect upon the corrosion of electrodes (24,147,163). All workers have reported an increase in weight, particularly of coupons.

The corrosion resistance of the lead-bismuth electrodes, tested by Kelly (24,147) passes through a maximum at between 0.17 and 0.2%. This region of bismuth concentration does not correspond with any special phase in the phase diagram (161), but the diagram is inaccurate at such low Bi levels (86). Kelly suggests that, using work by Zener (164), the grain growth will stop when the average grain size is equal to the average inclusion diameter over the fraction of the volume of the inclusion in the alloy. These particular conditions will be met when the amount of bismuth is between 0.14 and 0.19%, therefore, incorporation of Bi into the lead lattice could be the reason.

The object of this investigation was to determine if the amount of Bi in the alloy sample had a detrimental effect on the performance of the grid. Investigations are also required into the sites of attack on the surface of the grid wire. Work by Schonborn and Aumayer (165) shows that the corrosion of battery grids goes through a maximum at the PbO$_2$/PbSO$_4$ reversible potential, before increasing again at +0.2 V and greater. They used samples of wrought and cast low antimonial, calcium and calcium-tin alloys, though no pure lead comparison was tested.

Their experimental method was used for the exploration of the corrosion of the lead and lead bismuth samples under consideration.
The samples consisted of polycrystalline rods of lead and lead-bismuth alloys, the composition of which is shown in Table 11.1, partially embedded in epoxy resin blocks as described in Chapter 4. The reference electrode was PbO₂ electrodeposited on a platinum mesh, and all potential are referred to this (unless otherwise stated), the counter electrode used was pure lead sheet, of large area.

The cell is described in Chapter 4.3.4, and was kept at room temperature, 23 ± 2 °C, in a light proof, earthed Faraday cage, to remove the possibility of, both, photo-electric currents and the superposition of stray A.C. interference. A schematic diagram of the equipment is shown in Fig. 4.10. The electrolyte used was 5 M H₂SO₄, and the volume of acid used was recorded so that the level of bismuth in solution after the experiment could be monitored.

The electrodes were prepared by immersion in 10% HNO₃ for 10 seconds, followed by a wash with distilled water and then acetone. Subsequent to this the test pieces were dried, weighed and their surface area determined. The electrodes were placed in the electrolyte at 0 mV and the current was monitored by the computer at 30 second intervals. Each sample was corroded for at least 5 days, before being removed from the cell. The samples were washed with water, then methanol before being stored in a desiccator to await weighing and both scanning electron and optical microscopic examination.

After the test pieces had been viewed, the corrosion layer was removed by placement in 5 M ammonium acetate solution for 24 hours. Following this treatment, the samples were again washed and dried then
weighed before being placed back in a desiccator for further microscopic investigation.

Measurement of the presence and amount of bismuth in the electrolyte was obtained by using atomic adsorption. Samples of the electrolyte from each run were compared with standard solutions.

Table 11.1 Composition of Lead and Lead-Alloy Test Pieces

<table>
<thead>
<tr>
<th>Label</th>
<th>%Bi (±0.008)</th>
<th>%Pb (±0.008)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>---</td>
<td>99.999</td>
</tr>
<tr>
<td>F</td>
<td>0.265</td>
<td>99.735</td>
</tr>
<tr>
<td>G</td>
<td>0.565</td>
<td>99.435</td>
</tr>
<tr>
<td>H</td>
<td>1.063</td>
<td>98.937</td>
</tr>
<tr>
<td>I</td>
<td>2.109</td>
<td>97.891</td>
</tr>
<tr>
<td>K</td>
<td>4.909</td>
<td>95.091</td>
</tr>
</tbody>
</table>

11.3 Results and Discussion

Using the computer to record and store the corrosion current data, enabled easy data manipulation. Figures 11.1 to 11.4 show the current/time plots for lead and lead-bismuth alloys. The pure lead sample, shown in Fig. 11.1, gives the classic current profile of a thickening and passivating layer, with the exponential decay most prominent over the first 24 hours. The decline of the current continues, and after the first few days, the gradient is so shallow as to be
Fig. 11.1  Graph Of Time Against Current for the Corrosion Current of Pure Lead

Fig. 11.2  Graph Of Time Against Current for the Corrosion Current of Alloy F

Fig. 11.3  Graph Of Time Against Current for the Corrosion Current of Alloy H
almost flat. The growth of a totally passivating layer could take up to 30 days (165), though the definition of total passivation is open to some questioning (see the discussion section of Ref. 165).

A sharp change from the typical curve shape can be seen on the addition of bismuth to the test sample. Though the exponential-decay is still present, the difference is that the peak current is reached after some time at the corrosion potential, and this time is dependant upon the amount of bismuth present in the alloy, cf. Figs. 11.2 to 11.4. The reason for this delay in reaching the maximum current must be due to the inhibiting effect of bismuth, as the preparation and initial treatment of each sample was similar.

The chemical composition of the layer must be considered to be, at least initially, PbSO₄ (110), with the possibility of Bi₂(SO₄)₃ being present. The actual presence, and the starting concentrations, of bismuth both affect the recorded corrosion current, thus if bismuth promotes the formation of a fine, cohesive layer of PbSO₄ over the electrode surface, then explanation of the above phenomena can be postulated: i.e., the more Bi, the better the cohesion of the film. The film now provides a barrier that has to be surmounted, giving resistance to further growth of a corrosion layer and preventing any Bi ions dissolving into solution.

Another consideration must be that the layer, newly formed, may act as a semi-permiable membrane, if the crystals are fine enough. This will restrict the access of large ions such as SO₄²⁻ and HSO₄⁻, but not H₂O, which would reduce the acidity of the interior and lead to the production of monoxide and basic lead sulphates. The development of these products behind the membrane will lead to the build up of internal...
Fig. 11.4  Graph of Time Against Current for the Corrosion Current of Alloy K

Fig. 11.5  Graph of time Against Total Charge Passed for Pure Lead
stresses which can only be accommodated by fracturing the corrosion layer thus demolishing the membrane. This will allow access to the acid, and the subsequent acidification of the interior will lead to a rise in current, as the freshly uncovered alloy surface corrodes. The electrochemistry of bismuth is such that it will go into solution at potentials more positive than -1490 mV vs a PbO₂/PbSO₄ reference electrode. Hence, at the potentials at which these experiments were run, the bismuth in the alloys will leach into solution.

A secondary factor will be that as the bismuth is removed, more lead is exposed for corrosion. Hence, an increase in the total charge, Q, passed will occur. This can be seen with alloy H onwards. The inhibiting effect of the bismuth may counter, to some extent, the increase in current due to the leaching of bismuth, the acidification of the interior and the exposure of the unreacted electrode surface. The final current for the pure lead sample is higher than for any of the alloy samples, see Table 11.2 below. This is due to the increased compactness of the corrosion layer with increase in bismuth level.

After the test pieces had been corroded, scanning electron micrographs were taken of the surface of the corrosion layer. Fig 11.9 shows a porous crystalline corrosion layer, for pure lead, made up almost exclusively of lead sulphate, with a range of crystal sizes. There is a clear difference in the structure of the layer when bismuth is present, for example the 0.265% Bi alloy (Fig 11.10). As suggested above, the surface consists of a much more amorphous structure, with cracks present and large crystals of lead sulphate distributed across the surface, in a seemingly random fashion. The presence of lead sulphate in such large crystals suggests that a
Fig. 11.6 Graph of time Against Total Charge Passed for Alloy F

Fig. 11.7 Graph of time Against Total Charge Passed for Alloy H
Fig. 11.8  Graph of time Against Total Charge Passed for Alloy K
Fig. 11.9  Electron Micrograph of Pure Lead, 1000 x Magnification

Fig. 11.10  Electron Micrograph of Alloy F, 1000 x Magnification

Fig. 11.11  Electron Micrograph of Alloy G, 1000 x Magnification
Table 11.2  End of Day Average Current for 5 Days of Corrosion

<table>
<thead>
<tr>
<th>Label</th>
<th>Current / A x 10^-6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Day 1</td>
</tr>
<tr>
<td>A</td>
<td>10.65</td>
</tr>
<tr>
<td>F</td>
<td>11.46</td>
</tr>
<tr>
<td>G</td>
<td>9.95</td>
</tr>
<tr>
<td>H</td>
<td>16.09</td>
</tr>
<tr>
<td>I</td>
<td>20.83</td>
</tr>
<tr>
<td>K</td>
<td>25.00</td>
</tr>
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</table>

dissolution/precipitation mechanism is present (166) with excess Pb^{2+} ions migrating through the layer and precipitating on the surface. The amorphous nature of the underlying stratum suggests that Bi improves nucleation, but not the growth of PbSO_4. This seems to be the case no matter how much Bi is present, though the number of lead sulphate crystals on the surface of the other alloys increases after alloy G, as shown in Figs 11.11 to 11.13.

After removal of the layer, the exposed metal shows where the attack was strongest. Fig 11.14 shows an optical micrograph of pure lead, this reveals that the attack was of a generalised nature, but deep pits were formed where innate weaknesses are present. The lack of depth of field restricts the amount of the picture which is in focus. Scanning electron micrographs of the samples show some interesting features. Figure 11.15 reveals the pitted and corroded surface of a pure lead electrode. Even a ten fold increase in magnification, to 1000 times as shown in Fig. 11.16, supports the idea of a general attack on the
Fig. 11.12  Electron Micrograph of Alloy I, 1000 x Magnification

Fig. 11.13  Electron Micrograph of Alloy K, 1000 x Magnification
electrode surface, though some areas of lead show some resistance in the form of small crystallites protruding on the surface.

The addition of a small amount of bismuth has the effect of changing the area of attack, as shown in Figs. 11.17 and 11.18, where sample F shows corrosion generally over the electrode surface, but also a particularly deep pit along the grain boundary, which is where the bismuth is likely to be concentrated. A further increment in the amount of Bi reveals this even more starkly, Fig 11.19, and the resistance of certain crystal arrangements of lead is also shown.

Increasing the bismuth content to 1%, as in sample H, reveals an intensification in the mode of attack. Figures 11.20 and 11.21 show this quite dramatically with a mass of small crystals, or grains, standing in relief with the grain boundaries etched away, thus bismuth has affected the way the grains grew when the sample was cooled. Stepping the level of alloy addition up another level to 2.1%, I, reveals a change in the stripped backing. This time, as in Fig. 11.22, the surface has resorted to a much more uniform corrosion attack with some attack at the grain boundaries. Finally, when the Bi level reaches 4.9%, the change is almost complete and the bismuth seems to be leached evenly across the electrode surface, but with the grain boundaries still revealed. This indicates that the bismuth is almost entirely mixed with the lead to produce a uniform phase.

The weight loss after the removal of the corrosion layer, tabulated below in Table 11.3, shows considerable variation within each alloy band, however, an overall trend can be detected. Considering that the weight loss is around 13 mg cm$^{-2}$, on average, and the mean surface area is 5.85 cm$^{-2}$, the mean weight loss per sample is in the order of 76
Fig. 11.14  Optical Micrograph Pure Lead Stripped of Corrosion Layer,
            70 x Magnification

Fig. 11.15  Electron Micrograph of Pure Lead Stripped of Corrosion
            Layer, 100 x Magnification

Fig. 11.16  Electron Micrograph of Pure Lead Stripped of Corrosion
            Layer, 1000 x Magnification
Any error in this is compounded by the weight of each sample of around 50g, including the resin. The limit of the surface area, especially when compared to the work done by Schonborn and Aumayer (165) and Valeriote (105,159), means that the data can, at best, only be taken as indicative.

Table 11.3 Weight Loss After Removal of the Corrosion Layer for Lead and Lead-Bismuth Alloys

<table>
<thead>
<tr>
<th>Label</th>
<th>Wt. Loss / mg cm(^{-2})</th>
<th>&quot;Spread&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>24.53</td>
<td>11.8</td>
</tr>
<tr>
<td>F</td>
<td>5.89</td>
<td>1.05</td>
</tr>
<tr>
<td>G</td>
<td>6.74</td>
<td>1.25</td>
</tr>
<tr>
<td>H</td>
<td>10.15</td>
<td>3.45</td>
</tr>
<tr>
<td>I</td>
<td>15.50</td>
<td>5.66</td>
</tr>
<tr>
<td>K</td>
<td>16.24</td>
<td>5.96</td>
</tr>
</tbody>
</table>

The trend which can be deduced, from the table above, essentially suggests some resistance to corrosion for the lead-bismuth alloys, when compared to pure lead. The growth of the corrosion product, in weight terms, is reduced by the presence of bismuth which contradicts the charge-time plots (Figs 11.5 to 11.8). These show a minimum of corrosion occurring at 0.565 % Bi, before climbing to a peak with alloy I, but the final current is again lower for all Bi samples than for pure lead, Table 11.2.

So why is the corrosion layer weight loss greater for pure lead
Fig. 11.17  Electron Micrograph of Alloy F Stripped of Corrosion Layer, 300 x Magnification

Fig. 11.18  Electron Micrograph of Alloy F Stripped of Corrosion Layer, 1000 x Magnification

Fig. 11.19  Electron Micrograph of Alloy G Stripped of Corrosion Layer, 1000 x Magnification
than for Pb-Bi alloys, when both the loss of bismuth and the total charge passed would seem to indicate the reverse? The answer must lie in the nature of the corrosion layer. Thus if the composition of the layer is such that more electrons are required to form the 'sulphate' layer on lead-bismuth than on pure lead, the difference in valence can easily outperform the difference in weight loss.

\[
\begin{align*}
-2e & \quad \text{Pb} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 \\
-6e & \quad 2\text{Bi} + 3(\text{SO}_4^{2-}) \rightarrow \text{Bi}_2(\text{SO}_4)_3
\end{align*}
\]

(11.1)  

(11.2)

With the alloys H and onwards there is both an increase in charge passed and in the weight loss after stripping the corrosion product. This can be explained by the larger amount of Bi being leached, which has a moderating influence on the increasing corrosion charge due to the initial presence of bismuth.

The solubility of bismuth has been commented on above, and it was deemed appropriate to determine whether the leached bismuth remained in solution or plated out on the negative electrode. Visual evidence indicated that the bismuth was, indeed, electrodeposited on the counter electrode, but this required confirmation. A.A.S was performed on samples of the electrolyte and compared with standard solutions of 5, 10 and 50 ppm Bi\(^{3+}\). The results are shown in Table 11.4 below.

The results show that the level of bismuth in the electrolyte is less than 5 ppm, confirming that the electrodeposition of the free Bi
Fig. 11.20  Electron Micrograph of Alloy H Stripped of Corrosion Layer; 300 x Magnification

Fig. 11.21  Electron Micrograph of Alloy H Stripped of Corrosion Layer, 1000 x Magnification

Fig. 11.22  Electron Micrograph of Alloy K Stripped of Corrosion Layer, 1000 x Magnification
ion on the counter electrode is almost total.

Table 11.4 Results from the A.A. Studies on Corrosion Electrolytes

<table>
<thead>
<tr>
<th>Label</th>
<th>Absorbance / A.U.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.15 ± 0.05</td>
</tr>
<tr>
<td>B</td>
<td>0.18 ± 0.07</td>
</tr>
<tr>
<td>C</td>
<td>0.18 ± 0.03</td>
</tr>
<tr>
<td>D</td>
<td>0.16 ± 0.02</td>
</tr>
<tr>
<td>E</td>
<td>0.16 ± 0.03</td>
</tr>
<tr>
<td>F</td>
<td>0.17 ± 0.04</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Absorbance / A.U.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 ppm std.</td>
<td>0.19 ± 0.2</td>
</tr>
<tr>
<td>10 ppm std.</td>
<td>0.47 ± 0.7</td>
</tr>
<tr>
<td>50 ppm std.</td>
<td>&gt; 1</td>
</tr>
</tbody>
</table>

11.4 Conclusions

The conclusions which can be drawn are that bismuth decreases the amount of corrosion by creating a more compact lead sulphate layer over the electrode surface. This is not a good thing in a battery system because it would, if allowed to form, create a resistance between the grid and the paste, however, the nature of the curing process will negate the effect of the bismuth.

A second factor is that the presence of bismuth in the grain boundaries, particularly at low levels, will mean that increased stress
will be placed on the grid members as the Bi is leached away. This will be detrimental to the plate performance, and will lead to a loss in capacity. This disadvantage along with the formation of the tighter sulphate film will probably outweigh any advantages gained with reduced weight loss or final corrosion current.

Comparing the results to those obtained with antimony (12), the corrosion layer on an antimonial alloy surface is more compact, has fewer voids and is mechanically more sound than that on pure lead. But the addition of Bi does not lead to this, thus it is inferior to Sb. A second point is that the corrosion of Pb-Sb alloys, upto 5% antimony, is uniform, which is not the case with Bi. Hence the addition of bismuth to the positive electrode will have, in general, a detrimental effect on performance.
By examining the effect of the addition of bismuth to the constituent parts of the lead-acid cell, it is possible to gain an insight into the problems that could arise without the expense of manufacturing and field-testing a complete set of batteries. The problem then becomes one of assessing the relative importance of each of the individual parts in relation to the whole system. It could be that a major improvement in the performance of one aspect will be completely swamped by the combination of several, less dramatic disadvantages.

The results from the voltammograms of the lead-bismuth alloys give some clue to the effect of bismuth on the electrochemistry. These suggest that the Bi will be leached from the positive and deposited on the negative, the rise in concentration of bismuth will increase the effects beyond initial expectations. When investigating the effect of bismuth on the hydrogen evolution reaction, the initial levels of bismuth do not change but in the real system they will increase. The results show that even with higher levels of bismuth than normally encountered, the h.e.r. is suppressed. The solubility of bismuth salts in sulphuric acid solutions is in no doubt, Latimer (167) has shown that Bi exists in the form of a hydrated BiO⁺ ion in strong acid solutions and not as Bi³⁺ so its migration from the positive to the negative plates will be inhibited by the P.A.M. and separators.

The effect of Bi on the kinetics of both discharge and charge reactions on the negative plate becomes all the more important with this
concentrating factor. The results from the work carried out in Chapters 9 and 10 show that bismuth addition improves the cycling of the negative electrode and gives an improvement in the electrokinetics for both charge and discharge reactions when compared to pure lead. But the presence of Bi increases the compactness of the sulphate layer and this will probably be detrimental, leading to the isolation of active material and loss of capacity.

On balance it is probable that the presence of bismuth is an advantage on the negative plate, though further work must include investigations into the oxygen reduction properties, for maintenance free applications and gas recombinant technology and hydrogen evolution in battery strength electrolyte. Similarly areas such as corrosion resistance on standing and determination of the effect of Bi on the pasted plate will require greater exploration.

The presence of bismuth in the positive active material has three effects and it would be hard to say which dominates. The problems will tend to resolve themselves, however, as the bismuth is leached into the electrolyte, albeit slowly. Indeed, it may well be that as long as the initial concentration of Bi is kept below 0.05%, then the effect will be negligible. The improvement in the porosity which occurs will lead to greater utilization of the plate, however, it has been shown that the presence of bismuth improves the nucleation of lead sulphate. While this will give a higher initial discharge current, the overall effect will enhance the isolation of active material and reduce the plate capacity. A second disadvantage is the inhibiting effect that bismuth has on the oxidation of PbSO₄. From the L.S.V.'s of the lead-bismuth alloys, one can see that increasing the concentration of Bi increases the peak
potential. The retardation of the kinetics becomes important for applications such as load levelling rather than automotive use where a constant topping-up charge is available from the alternator. It would be difficult to suggest which will dominate, but the enhanced nucleation of sulphate and inhibition of oxidation would certainly be more important in the first few cycles. Future work in this area should include a full investigation into the porosity and paste density with and without Bi, plus more extensive cycling of the plates. The question of the effect of bismuth on the recharge properties will also need further exploration.

The use of bismuth to improve the casting properties has been noted, but its presence in the positive grid will give rise to other effects. The most notable of these must be the development of the corrosion layer and, though this is necessary to ensure good adhesion of the paste to the grid, it becomes a problem when the insulative effects predominate. The nature of the compact corrosion layer seen in Chapter 11 does not bode well, but it is possible that the corrosion layer would form differently when cured rather than when placed in an acid environment. The lowering of the oxygen evolution overpotential also gives cause for concern. Current theories on the nature of corrosion (168) suggest that the diffusion of oxygen through the semi-porous membrane is the rate limiting step. If after an overcharge period, there is a concentration of oxygen around the positive grid, then corrosion can more easily take place.

The leaching of the bismuth into either the electrolyte or the paste presents further problems. Its removal from the grid presents a second important area where failure of the current collector could
arise. The gaps in the grid surface left vacant by the loss of Bi will become focal points for the growth of micro-cracks and increased corrosion as the lead sulphate product fills the hole and applies extra stress. The loss of the thin grid spars will lead to the isolation of areas of P.A.M. and a drop in capacity, though full scale trials would be needed to establish the level of attack and loss of conductivity. Indeed the results from the corrosion work, Chapter 11, show preferential attack along the grain boundaries. A significant point of weakness will become open to attack, especially with the use of thin grid spars in most modern automotive batteries.

Further problems with the presence of bismuth include a decrease in the oxygen evolution overpotential. This will mean a loss of efficiency when the electrode is being recharged, and when combined with the inhibition of the recharge of PbSO\textsubscript{4} to PbO\textsubscript{2}, as described above, will pose a potentially serious problem. The leaching of the Bi from the grid and into the P.A.M. will only help to increase these problems. Investigations and experimental work will be required to try to determine if there is a lower limit below which the presence of bismuth is tolerable in the positive plate and paste.

In conclusion, the amount of bismuth which can be tolerated in either the positive plate or the paste is 0.05%. In the negative plate, the limit is much higher, upto 1%, little, if any, detrimental effects were found. Though above this level, some problems were encountered in the sulphate cycling.
REFERENCES


87] D. Soloman and W. Morris-Jones, Phil. Mag., 11, (1931), 1090.


10 REM LEAD DIOXIDE TO LEAD SULPHATE CYCLING PROGRAM, STORING L.S.V.s AT 100, 1000, 2000, 3000, 4000 AND 5000 CYCLES.
20 REM DATA STORED ON DISC FOR EASY ACCESS
30 PRINT "ENTER FILE NAME FOR DATA STORAGE": INPUT ST$: ST$=LEFT$(ST$, 4)
40 DIM Q(1000), W(100), V(100)
50 INPUT "What is the amplification set on the UNI-AMP? BF";
60 INPUT "What is the value of the sensing resistor (in Ohms)"; BG
70 INPUT "What is the diameter of the electrode (in mm)"; BH: BI=3.14159: BK=1500.77: BL=32.5
80 INPUT "What file name is to be used to store the LSV'S"; CA$: CA$=LEFT$(CA$, 4)
90 PRINT "OK. TO RUN THE REST OF THE PROGRAM HIT (CR)";
100 X$=INPUT$(1)
110 OUT 19,139: OUT 22, 15: OUT 21, 160: OUT 20, 0
120 PRINT "RUNNING"
130 REM MAIN SUMMING LOOP
150 IF FLA=1 THEN FOR W=1 TO U: TOT=TOT+((Q(W)+BJ)/BZ)*BY): NEXT W: IF TOT (0.00009)
160 REM SUM STORAGE ROUTINE
170 REM LSV STORAGE SUBROUTINE
180 CA=CA+1: AC$=STR$(CA): CA$=CA$+RIGHT$(AC$, LEN(AC$)-1): CODE$=1
190 OPEN "R", £1, CA$, 128
200 FIELD £1, 128 AS CB$: CA$=LEFT$(CA$, 4): PRINT $"Gone sub 2000"
210 OUT 16, 1: AZ=INP(0): A=INP(1): B=INP(2): D=(B AND 15)*CON+A: IF B AND 54 THEN V(C)=D ELSE V(C)=-D
230 CODE$=CODE$+1: STRI$="": NEXT C: CODE$=1
240 COUNT=COUNT+2: PRINT "$LST STORED."; CLOSE £1: C=1: RETURN
REM PASTED PLATE GALVANOSTATIC CYCLING PROGRAM FOR K-3000
30 REM DATA TO BE STORED ON DISC.......
40 PRINT CHR$(26);"Cycling program for pasted plates. Before running this program ensure that M/C routine for access to the real time clock is in place"
45 REM" Version 1.6. Dated 30-09-87"
50 DIM M(85,5):CYCLE=1:OUT 19,139:OUT 16, O:B=INP(17):C=INP(18):D=INP(20)
60 PRINT"All relays will be set open ....":GOSUB 3000:GOSUB 5000
70 PRINT"Data will be stored on disc for easy access. The following times and voltages are stored in this order:...
1)T.O.C. voltage 2)T.O.C. voltage after O/C. 3) Rest potential 4) Time for charge. 5) Time for discharge."
80 INPUT "What is the file name for data storage" ;F$
90 IF LEN(F$)7 THEN PRINT" File name too long, try again...":GOTO 80
100 PRINT"Ready to run?":Q$=INPUT$:REM START TIME AND SWITCH IN,RELAY
110 PRINT"Charging cycle CYCLE; started at ;Z1;: ;Y1;: ;X1;");Z0=Z1:YO=Y1:XO=X1
115 PRINT"Voltage is ;E; mV at time ;Z1;: ;Y1;: ;X1;:CHR$(13);".GOSUB 1000:PRINT"Voltage above 1500 mV..."
120 IF E>1500 THEN PRINT CHR$(10):CHR$(13)"Voltage fell below previous maximum times, going back to recharge":GOTO 170
130 PRINT"Time to switch to rest potential...":CHR$(10):CHR$(13);"Overcharge period ended!":GOSUB 3000
140 REM SAVE FINAL TIME
150 REM TOP OF CHARGE REACHED 20 MINS ON O/C
160 F0=0:GOSUB 1000:IF F0 THEN PRINT"Voltage fell below previous m ax;":F$; times, going back to recharge":GOTO 170
170 IF F0 THEN PRINT"Relay switched out final voltage after O/C is ;E; :CHRS$(13);"EM SAVE FINAL TIME
180 REM REST PERIOD
190 GOSUB 1000:IF F0 THEN PRINT"Overcharge period ended!!":GOSUB 3000:REM REST PERIOD
200 GOSUB 1000:PRINT"Current time is ;Z1;: ;Y1;: ;X1;:CHR$(13);"
400 IF Y4=Y1 AND X4=X1 THEN 410 ELSE 390
410 REM END OF REST PERIOD. TAKE POTN.
420 GOSUB 6000:GOSUB 6000:EN=E
430 PRINT CHR$(10):CHR$(13);"Now on discharge period.":"GOSUB 1000:X5=X1:Y5=Y1:Z5
440 GOSUB 4000:PRINT "Current voltage is ";E;" mV and time is ";Z1;":"
450 IF E<800 THEN 460 ELSE 440
460 REM END OF DISCHARGE
470 Z6=Z1:Y6=Y1:X6=X1:REM SAVE TIME
480 GOSUB 5000:IF Z6<Z5 THEN Z6=Z6+24:
490 Z7=Z6-Z5:IF Y6<Y5 THEN Y6=Y6+60:Z7=Z7-1
500 Y7=Y6-Y5:PRINT CHR$(10):CHR$(13);"Time for discharge is ";Z7;" Hrs and ";Y7
" mins."
510 TOT=(Z7*50)+Y7:IF TOT<TOT1 THEN
520 REM END OF DISCHARGE
530 Z5=Z1:Y6=Y1:X6=X1:REM SAVE TIME
540 GOSUB 5000:IF Z6-Z5<0 THEN Z6=16+2.4:
550 Z7=Z6-Z5:IF Y6-Y5<0 THEN Y6=Y6+60:Z7=Z7-1
560 Y7=Y6-Y5:PRINT CHR$(10):CHR$(13);"Time for discharge is ";Z7;" Hrs and ";Y7
" mins."
570 TOT=(Z7*50)+Y7:IF TOT<TOT1 THEN
580 REM END OF DISCHARGE
590 Z7=Z6-Z5:Y6=Y5:Z6=Z7:Y5=Y7:Z7=Z6:
600 PRINT "Maximum time for discharge is ";TOT1;" mins.":IF TOT<TOT1*0.8 THEN
610 IF FLA=1 THEN PRINT"T.F.D. is < 80% of max. All data stored, progran to end."
620 FOR N=1 TO CYCLE:PRINT N;" time for charge";M(N,4);", time for discharge";M(N,5);" and t.o.c. voltage";M(N,2); NEXT N
630 IF FLA=1 THEN END
640 CYCLE=CYCLE+10
650 REM DATA STORE ON DISC - ....
660 PRINT"Data will now be stored on disc and as an array"
670 Y8=Y3-YO:IF Y8<0 THEN Y8=Y3+60:
680 Z3=Z3-1:
690 IF Z3<Z0 THEN Z3=Z3+24
700 Z8=Z3-Z0
710 TFC=(Z8*50)+Y8
720 M(CYCLE,1)=E1:M(CYCLE,2)=E2:M(CYCLE,3)=E4:M(CYCLE,4)=TFC:M(CYCLE,5)=TOT:
730 OPEN "O",#1,F$:PRINT #1,CYCLE:FOR N=1 TO CYCLE:FOR 0=1 TO 5:PRINT #1,M(N,D>:
740 NEXT 0:NEXT N:CLOSE #1
750 IF FLA=1 THEN PRINT"T.F.D. is < 80% of max. All data stored, progran to end."
760 FOR N=1 TO CYCLE:PRINT N;" time for charge";M(N,4);", time for discharge";M(N,5);" and t.o.c. voltage";M(N,2); NEXT N
770 IF FLA=1 THEN END
780 CYCLE=CYCLE+10
790 REM END OF DISCHARGE WAIT
800 GOSUB 150
810 REM TIME SUBROUTINE
820 TMX=6&HDD000:A=6&HDD00:CALL TMX:X$=CHR$(PEEK(A))+CHR$(PEEK(A+1))+Y$=CHR$(PEEK(A
830 +2))+CHR$(PEEK(A+3))+Z$=CHR$(PEEK(A+4))+CHR$(PEEK(A
840 +5)):X1=VAL(X$):Y1=VAL(Y$):Z1=VAL(Z$)
850 RETURN
860 REM CHARGE RELAY CLOSE
870 OUT 48,10:OUT 49,10:OUT 50,10:OUT 51,10:RETURN
880 REM CHARGE RELAY OPEN
890 OUT 48,0:OUT 49,0:OUT 50,0:OUT 51,0:RETURN
900 REM DISCHARGE RELAY CLOSE
910 OUT 112,10:OUT 113,10:OUT 114,10:OUT 115,10: RETURN
920 REM DISCHARGE RELAY OPEN
930 OUT 112,0:OUT 113,0:OUT 114,0:OUT 115,0:RETURN
940 REM ADZ READ AND CONVERT
950 OUT 16,0:BIN(17):C=INP(18):D=INP(20):E=(C AND 15)*256+B:IF C AND 64 THEN
960 E=E ELSE E=-E
970 E=(E+45)/1.5996:E=INT(E+.5):RETURN