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A CONDUCTIVE FILM MODEL
FOR THE KINETICS OF THE LEAD ANODE
IN AQUEOUS SULPHURIC ACID.

A thesis submitted to the
University of Auckland for
the Degree of
Doctor of Philosophy.

by

Simon Berners Hall

Department of Chemistry
The University of Auckland
ACKNOWLEDGEMENTS

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Last, and by no means least, I acknowledge the many sacrifices my wife Karen has made in encouraging me to work towards this degree, especially during the months of preparation of this thesis.
The kinetics and mechanism of the anodic process on lead in aqueous 35% H₂SO₄ (4.65 mol L⁻¹) were studied. The lead anode is of interest as it is used in the form of the sponge lead negative plate in the lead-acid battery. Discharge of both planar and porous lead electrodes result in the electrocrystallisation of PbSO₄. In the past, the processes occurring at the lead electrode have been shown to include: dissolution, precipitation, and passivation.

The techniques used were cyclic voltammetry, potential-step, and potential-ramp/potential-hold. The resultant transients were recorded both as analogue and digital waveforms. Investigations were carried out at a constant acid strength over a range of temperatures (−18° to 30°C), and in the presence of additives.

Significant variation was found in cyclic voltammetry with regard to the cathodic potential prehistory immediately prior to measurements. After extreme cathodic polarisation (below −1500 mV vs SHE), voltammograms were recorded with relatively high anodic peak currents and charges. The extra charge was associated with the growth of a multilayer, and dissolution from the bare electrode. This multilayer is not reduced on subsequent moderate cathodic excursions (above −1000 mV). Hence for cyclic voltammograms in the absence of extreme cathodic polarisation one
observes relatively small currents and anodic charges. This is due to transmission of Pb²⁺ ions through the multilayer under resistance control. Passivation occurs in both cases by precipitation of microcrystalline PbSO₄ on the multilayer.

In contrast to cyclic voltammetry, potential-step transients were insensitive to cathodic polarisation and displayed current peaks due to growth of the surface film. One also observes a dissolution current from the bare electrode before it is covered by the growing film. The current first increases, passes through a maximum, and then decays with time. The increasing current was associated with growth of the multilayer, and the decaying current due to passivation by PbSO₄.

A new model was successfully applied to the potential-step and potential sweep results. The model consists of several charge-transfer reactions: growth of a multilayer, dissolution from the bare electrode, and transmission of Pb²⁺ through the multilayer. The kinetics of the multilayer are pivotal to the other charge-transfer reactions. The inclusion of film transmission is the novel aspect of this model. Quantitative analysis of the model resulted in a set of optimised parameters that follow plausible variation with anodic potential. Both the potential step and potential sweep transients are adequately described by the model.

The effect of chloride added to the electrolyte was studied. The anodic and cathodic peaks in cyclic voltammetry are enhanced by this anion (100% more anodic charge at higher chloride concentrations) and the cathodic to anodic charge ratio is markedly increased. The general form of the potential-step transients are not modified by chloride. Evidence of a monolayer of PbCl₂ was found \( q = 500 \, \mu \text{C cm}^{-2} \) in both cyclic
voltammetry and potential step experiments. The monolayer of PbCl₂ must underlie the subsequent growth of the multilayer as the monolayer is first-formed in potential-step experiments, and first to be reduced in cyclic voltammetry at a small underpotential.

The effect of methyl orange on the lead anode was explored and found to enhance the charge capacity. Battery tests confirmed these observations, but methyl orange was destroyed by the oxidising PbO₂ at the positive plate. Hence a derivative, designed to be insoluble in H₂SO₄, was synthesised. However, experiments on both planar and porous electrodes showed that the derivative, lauryl orange, C₁₂H₂₅NHC₆H₄NNH⁺C₆H₅SO₃⁻ (pKₐ = 4.06) was found to act as an inhibitor for the anodic reactions. In particular there was no contribution from multilayer growth in potential step experiments, and only dissolution (markedly diminished) and passivation were evident. Lauryl orange exhibited the required capabilities to bind to lead metal. The structure of lauryl orange was confirmed by n.m.r. and mass spectrometry.
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Colophon
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<th>Description</th>
<th>Unit</th>
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<tr>
<td>$a$</td>
<td>edge profile correction constant</td>
<td></td>
</tr>
<tr>
<td>$A$</td>
<td>geometric area of electrode</td>
<td>[cm$^2$]</td>
</tr>
<tr>
<td>$b$</td>
<td>radius of working electrode</td>
<td>[cm]</td>
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<tr>
<td>$c$</td>
<td>concentration</td>
<td>[mol L$^{-1}$]</td>
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<tr>
<td>$C_{dl}$</td>
<td>double-layer capacitance</td>
<td>[μF cm$^{-2}$]</td>
</tr>
<tr>
<td>$C_{dl\text{Hg}}$</td>
<td>double-layer capacitance of mercury</td>
<td>[μF cm$^{-2}$]</td>
</tr>
<tr>
<td>$C_p$</td>
<td>pseudo-capacitance</td>
<td>[μF cm$^{-2}$]</td>
</tr>
<tr>
<td>$d$</td>
<td>distance between Luggin and working electrode</td>
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<tr>
<td>$D$</td>
<td>diffusion coefficient</td>
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<tr>
<td>$E$</td>
<td>potential</td>
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<td>anodic potential limit (potential sweep)</td>
<td>[mV]</td>
</tr>
<tr>
<td>$E_{A_{\text{p}}}$</td>
<td>anodic peak potential</td>
<td>[mV]</td>
</tr>
<tr>
<td>$E_c$</td>
<td>cathodic potential limit (potential sweep)</td>
<td>[mV]</td>
</tr>
<tr>
<td>$E_{ct}$</td>
<td>cathodic limit prior to potential sweep</td>
<td>[mV]</td>
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<tr>
<td>$E_{C_{\text{p}}}$</td>
<td>cathodic peak potential</td>
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<td>$E_{eq}$</td>
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<tr>
<td>$E^*$</td>
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<td>$F$</td>
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<tr>
<td>$i$</td>
<td>current density</td>
<td>[mA cm$^{-2}$]</td>
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<tr>
<td>$i_{A_{\text{p}}}$</td>
<td>anodic peak current density</td>
<td>[mA cm$^{-2}$]</td>
</tr>
<tr>
<td>$i_{C_{\text{p}}}$</td>
<td>cathodic peak current density</td>
<td>[mA cm$^{-2}$]</td>
</tr>
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</table>
\[ i_d \quad \text{dissolution current} \quad [\text{mA cm}^{-2}] \\
\] \[ i_d^0 \quad \text{dissolution current at } t = 0 \quad [\text{mA cm}^{-2}] \\
\] \[ i_g \quad \text{multilayer growth current} \quad [\text{mA cm}^{-2}] \\
\] \[ i_t \quad \text{multilayer transmission current} \quad [\text{mA cm}^{-2}] \\
\] \[ i_m \quad \text{monolayer growth current} \quad [\text{mA cm}^{-2}] \\
\] \[ i_m^0 \quad \text{monolayer growth current at } t = 0 \quad [\text{mA cm}^{-2}] \\
\] \[ i_{\text{tot}} \quad \text{total theoretical current} \quad [\text{mA}] \\
\] \[ I \quad \text{current} \quad [\text{mA}] \\
\] \[ I_{\text{dl}} \quad \text{double-layer charging current} \quad [\text{mA}] \\
\] \[ I_f \quad \text{faradic resistance current} \quad [\text{mA}] \\
\] \[ I_1 \quad \text{battery discharge current} \quad [\text{A}] \\
\] \[ I_2 \quad \text{battery discharge current} \quad [\text{A}] \\
\] \[ J \quad \text{n.m.r. coupling constant} \quad [\text{s}^{-1}] \\
\] \[ k_t \quad \text{multilayer transmission constant} \quad [\text{mol cm}^{-2} \text{ s}^{-1}] \\
\] \[ k_g \quad \text{multilayer growth rate constant} \quad [\text{mol cm}^{-1} \text{ s}^{-1}] \\
\] \[ k_m \quad \text{monolayer growth constant} \quad [\text{s}^{-1}] \\
\] \[ k_2 \quad \text{rate constant for passive film} \quad [\text{cm} \text{ mV}^{-1} \text{ s}^{-1}] \\
\] \[ K_1 \quad \text{equilibrium constant} \quad [\text{mol L}^{-1}] \\
\] \[ K_2 \quad \text{equilibrium constant} \quad [\text{mol L}^{-1}] \\
\] \[ l \quad \text{passive film thickness} \quad [\text{cm}] \\
\] \[ l_A \quad \text{analysed depth in XPS} \quad [\text{cm}] \\
\] \[ l_m \quad \text{thickness of resistive film} \quad [\text{cm}] \\
\] \[ l_o \quad \text{passive film thickness} \quad [\text{cm}] \\
\] \[ l_o^* \quad \text{spontaneous passive layer thickness at } t = 0 \quad [\text{cm}] \\
\] \[ m \quad \text{number of equivalent monolayers in the multilayer} \quad [\text{cm}] \\
\] \[ M \quad \text{molar mass} \quad [\text{g mol}^{-1}] \\
\] \[ M^+ \quad \text{mass spectrometry molecular ion} \quad [\text{g mol}^{-1}] \\
\] \[ n \quad \text{number of electrons transferred} \quad [\text{mol}^{-1}] \\
\] \[ N_A \quad \text{Avogadro constant} \quad [\text{mol}^{-1}] \\
\] \[ N_o \quad \text{number of multilayer nucleation sites} \quad [\text{cm}^{-2}] \\
\] \[ N_{\text{Po}} \quad \text{number of lead atoms} \quad [\text{cm}^{-2}] \\
\] \[ N_{\text{Po}}^* \quad \text{number of lead atoms in a monolayer} \quad [\text{cm}^{-2}] \\
\] \[ q_{A1} \quad \text{charge of anodic peak A1} \quad [\text{mC cm}^{-2}] \\
\] \[ q_{C1} \quad \text{charge of peak C1} \quad [\text{mC cm}^{-2}] \\
\]
<table>
<thead>
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<th>Description</th>
<th>Unit</th>
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<td>monolayer charge</td>
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<td>$Q$</td>
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<td>$\lambda_{max}$</td>
<td>UV-visible absorption maximum</td>
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<tr>
<td>br</td>
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CHAPTER ONE
INTRODUCTION

1.1 Scope of this work.

The principal objective of this research project was to investigate the kinetics of the lead anode in aqueous sulphuric acid with the aim of determining the mechanism of the electrode reactions.

A number of previous investigations are outlined in Section 1.3 and discussed critically in later chapters. This thesis modifies and extends the existing models, removing inconsistencies.

The general approach in this thesis has been the use of two transient techniques: potential sweep and potential step. A detailed model is developed allowing quantitative fit to the experimental transients. The effect of temperature, anions, and adsorbates on the lead anode are examined.

This research closely identifies with the performance of the negative plate of the lead-acid battery, but is not a study of the overall battery as such.

Since good reviews on the lead-acid battery and electrode kinetics are available, this introduction will be confined to a brief outline. However a critical assessment of the previously published work on the lead anode kinetics is given in Chapters 3 and 4.
1.2 Relevance of the lead anode.

In 1859, Gaston Plante passed current through two strips of lead metal separated by rubber sheets immersed in 10% aqueous $\text{H}_2\text{SO}_4$.\textsuperscript{1-4} After a period of time, a two volt cell was formed. The cell was reversible, the discharged cell being recharged by application of an electric current in the opposite direction to that for the discharge. During recharge, sponge lead formed on the negative electrode and lead dioxide on the positive electrode. In 1860 Plante presented to the French Academy of Sciences a nine cell battery and a report entitled: "Nouvelle pile secondaire d'une grande puissance". The report heralded the arrival of the now familiar lead-acid battery.

The lead-acid battery is an integral component of modern life, providing an effortless means for automobile starting, lighting, and ignition (SLI), as well as many other uses such as standby power sources, remote area power storage, load levelling in electric power systems, electric vehicle traction, and portable power supplies. Recent advances have resulted in lead-acid batteries that require no maintenance by the user.

The use of the lead-acid battery has continued unabated. In 1961, in the midst of enthusiasm for fuel cell research, an article posed the question: "Is the lead-acid battery obsolete?".\textsuperscript{7} The battery was found not to be obsolete then, and is not obsolete today. The abundance of lead and the ease of recycling favour the lead-acid battery, as opposed to the high cost of fuel cell catalysts and the maintenance problems associated with sodium-sulphur batteries. In the future however, the emerging zinc-bromine and vanadium batteries may provide competition.

In a review of the lead-acid battery, Ruetschi\textsuperscript{3} discussed the
development in terms of three time periods. During the first period from 1860 to 1910, the most suitable electrode construction and practical manufacturing techniques were developed by the Edison method of trial and error. The second period from 1910 to 1950 resulted in the change to manufacture by high speed machinery and introduction of lignin expanders to the negative plates. The third period since 1950 has resulted in the use of polypropylene containers, shorter inter-plate spacing and optimisation of grid design. A series of reviews and texts detail these advances.1-7

The advances during these periods were technological rather than scientific in nature and progress of the latter has been relatively slow. Gladstone and Tribe in 1880 published the "double sulphate theory."8 According to this theory, the overall reaction is given by

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

During the second period, the precise thermodynamics for the lead and lead dioxide electrodes were established9-11 and the double sulphate theory substantiated.12-17 Research in the third period since 1950 has been facilitated by the development of improved electrochemical techniques, combined with diffraction, nuclear magnetic resonance, radiotracer, and electron spectroscopy techniques that have provided a better understanding of the solid surfaces involved.

Landers18,19 and Burbank20-22 established the presence of tetrahedral lead oxide (tet-PbO) in the anodic layer after polarisation of lead using X-ray diffraction analysis. Similarly Ruetschi and Cahan23,24 identified a second polymorph of lead dioxide on the positive electrode called \( \alpha-\text{PbO}_2 \). Pavlov et al25-27 confirmed these observations and proposed that the potential interval can be divided into three electrode
regions for the polarisation of Pb in H$_2$SO$_4$:

i) *lead sulphate electrode system* (PbSO$_4$). This is stable from -0.35 V to 0.22 V (vs SHE), an interval that is termed the "PbSO$_4$ potential region";

ii) *lead oxide/lead sulphate electrode system* (Pb/PbO/PbSO$_4$). This is stable from 0.22 V to 1.57 V, and is known as the "PbO potential region";

iii) *lead dioxide electrode system* (Pb/PbO$_2$). This occurs at potentials larger than 1.57 V, and is named the "lead dioxide potential region".

Pavlov and Dinev$^{28}$ have proposed a model based on the semi-permeability of the anodic layer to account for the formation of tet-PbO and α-PbO$_2$, species not predicted from Pourbaix diagrams to form in acidic media.$^{1,2}$

The PbO and PbO$_2$ potential regions in recent years have received much attention. This has mostly been due to the discovery of the semiconductor nature of tet-PbO$^{29}$ and the photo-electrochemical oxidation of Pb/PbO/PbSO$_4$ to Pb/PbO$_n$/PbSO$_4$ where $n$ is in the range $1 < n < 2$.$^{30}$

In contrast to this the PbSO$_4$ potential region has received relatively little attention and the kinetics are not well understood. The present work is devoted entirely to investigations in the PbSO$_4$ potential region.

1.3 Previous work in the lead sulphate region.

Previous publications on the kinetics of the PbSO$_4$ potential region are for the most part confined to the efforts of three main groups of
researchers: Archdale and Harrison, Hampson et al. and Danel and Plichon. These workers have employed both cyclic voltammetric and potential step methods to the lead anode. It has been established that the anodic reaction results in simultaneous formation of a solid phase and a soluble species that may diffuse irreversibly from the vicinity of the electrode. Danel and Plichon have summarised the reaction with the scheme:

\[
\begin{align*}
\text{Pb} & \rightarrow \text{solid PbSO}_4 \\
& \uparrow \text{at the electrode} \\
& \rightarrow \text{soluble Pb}^{2+} \\
& \text{at the electrode} \\
& \rightarrow \text{soluble Pb}^{2+} \\
& \text{in the bulk}
\end{align*}
\]

Potential step experiments yielded transients suggestive of a solid phase growth process on the electrode. Ring-disc electrode experiments established that the production of soluble Pb\(^{2+}\) species is progressively diminished by the solid phase growth process. Attempts to reconcile the growth process with theoretical growth laws has been largely unsuccessful. There is disagreement between the different groups of workers as to whether the solid phase growth should follow two- or three-dimensional growth laws.

The pertinent papers are reviewed in more detail in the appropriate chapters, where the literature findings will be critically assessed in the light of the results reported in this thesis.

1.4 Outline of this thesis.

This thesis is arranged in a number of chapters in which different
aspects of the anodic behaviour of Pb in H₂SO₄ are investigated.

The experimental apparatus for electrochemical experiments is described in Chapter 2. This is followed by a detailed presentation of experimental results using the techniques of cyclic voltammetry in Chapter 3 and the potential step transient in Chapter 4.

A conductive thin film model is developed in Chapter 5 to account for the results obtained from potential step and cyclic voltammetry experiments. Computer simulation has been used to fit the theory to experiment in a quantitative fashion. The mechanism proposed has a number of novel features, and represents a considerable advance on previous published work on the lead anode.

In Chapter 6, the effect of chloride on the lead anode is explored using both cyclic voltammetry and potential step techniques. Chapter 7 describes the investigation of simple sulphonic acids as models for lignin expanders. A sulphonic acid is designed, synthesised, and characterised for this purpose. The synthetic procedure is described at the end of Chapter 7.

Chapter 8 provides a conclusion to the present work.
2.1 Introduction.

This chapter deals only with the electrochemical methods. Organic synthesis and spectroscopic details are described in succeeding chapters.

The techniques employed in the present study were cyclic voltammetry and potential step experiments. Cyclic voltammetry is a technique in which the electrode potential, monitored with respect to a reference electrode, is made to cycle as a triangular function of time. The resulting current-potential curve is recorded. The main variables for this technique are the potential sweep rate and the limits of the potential excursion.

Potential step experiments are where the potential of the working electrode is made to instantaneously change from one value to a new value. The ensuing current transient is recorded, usually over a short time interval.

The specific details of cyclic voltammetry (CV) and potential step experiments are dealt with in detail in Chapters 3 and 4 respectively.

2.2 Instruments and Circuit.

A conventional three-electrode potentiostatic circuit was used. The
three electrodes were the working electrode, reference electrode, and the auxiliary or counter electrode. A Princeton Applied Research (PAR) Model 173 Potentiostat/Galvanostat fitted with a PAR Model 178 Electrometer Probe was the central component of the circuit and was controlled in one of two ways depending on the type of experiment in progress.

For experiments where analogue output was required, the potentiostat was programmed by a PAR Model 175 Universal Programmer and the current was measured with a PAR Model 179 Digital Coulometer fitted into the potentiostat (Fig. 2.1). Potential-current curves were recorded on a Hewlett Packard 7046A X-Y recorder and a Tekronix 5223 digitising oscilloscope fitted with two 5A22N differential amplifiers and a 5B25N digitising time-base amplifier. Potentials and currents were monitored using a Hewlett Packard 3466A and Metravo 464 digital multimeters respectively. The charge passed in a transient experiment was determined by either manual operation of the Model 179 digital coulometer or by using a microcomputer for data capture. In the latter method, the PAR 179 Coulometer provided a BCD digital output which was processed with an Apple IIe computer and an ISAAC Cyborg 91A digital-to-analogue (D/A) and analogue-to-digital (A/D) converter.

For experiments where the output was digitised a second potentiostat was employed (Fig. 2.2). A PAR Model 363 Potentiostat/Galvanostat was controlled by the Model 175 Universal Programmer to provide preconditioning CV cycles to the working electrode. Subsequent potential step and CV experiments were performed and the resulting current transients were digitised using the Model 173 Potentiostat/Galvanostat with a PAR Model 276 Digitising Interface connected. The interface was
Fig. 2.1 Block diagram of the apparatus used for experiments where analogue output is required.
Fig. 2.2  Block diagram of the apparatus used for experiments where the output is digitised.
controlled by an Apple IIe computer, data and programme files were stored to disk on this machine. The digitised binary data files were converted to ASCII character format and transmitted to an Exzel AT personal computer via an RS232c serial communication cable, filing and data processing were subsequently performed on the Exzel AT computer using software developed during the course of this research (see Section 2.8). Current transients were also captured by the digitising oscilloscope and plotted on the X-Y recorder.

2.3 Electrodes.

2.3.1 Working electrodes

The lead electrodes consisted of rods of 99.999% pure lead (Koch Chemicals Ltd.) 0.45 cm in diameter. Fig. 2.3 shows the construction of the electrode. The lead rod was press-fitted into a PTFE cylinder with a screw tapped brass fitting soldered to the rear of the rod for electrical and mechanical connection. Two types of electrode holder were designed and both are shown in Fig. 2.3. The first (Electrode Holder I) consists of a stainless steel shaft press-fitted into a PTFE cylinder of same diameter as the electrode, the shaft was tipped by a threaded piece which attached firmly to the brass base of the working electrode. This electrode holder was employed for all experiments, except the temperature controlled potential step experiments where the second holder was utilised. The second holder (Electrode Holder II) was similar to the first in that it consisted of a PTFE cylinder with a threaded stainless steel tip. The long stainless steel shaft is replaced by a flexible wire to allow complete immersion of the cell in the temperature controlled ethanol bath.
Fig. 2.3  Electrode and holder construction.
2.3.2 Reference electrodes.

Two types of reference electrodes were employed. A mercury / mercurous sulphate reference electrode was constructed (Fig. 2.4) and used for all potential step experiments. The potential of this electrode against the standard hydrogen electrode (SHE) is given by the polynomial expression in equation 2.1.\(^{53,54}\)

\[
E/mV = 676.26 - 73.595x - 30.531x^2 - 30.552x^3 - 12.045x^4
\]  
(2.1)

where \(x = \log m\) with \(m\) being the molality of sulphuric acid (3.64 mol kg\(^{-1}\) for 35% H\(_2\)SO\(_4\)). A saturated calomel reference electrode (SCE) was used for the experiments in Chapter 5 where traces of chloride from the electrode would disturb the potential of the Hg/Hg\(_2\)SO\(_4\) electrode. Conversion of the potential from the SCE to the SHE scale was effected with equation 2.2:

\[
E_{(\text{SHE})} = E_{(\text{SCE})} + 244.4 \text{ mV} - 2.5(T - 298)
\]  
(2.2)

where \(T\) is in kelvin.\(^{55}\) The mercurous sulphate reference electrode is preferred for variable temperature experiments as the potential for this electrode has identical dependence as the working electrode.\(^{55}\) In both cases a Luggin capillary was used to minimise the solution resistance; no compensation for IR drop was used.

2.3.3 Counter electrode

The counter electrode was either a platinum sheet electrode
Fig. 2.4  Mercury/mercurous sulphate reference electrode construction.
(A = 3.5 cm$^2$) or a sheet of lead foil 99.95% pure (May & Baker Ltd., A = 8 cm$^2$). The lead counter electrode was employed in the experiments reported in Chapter 5, because chloride ions promote the formation of soluble tetrachloroplatinate and hexachloroplatinate anions that result in platinum electrodeposition on the working electrode.

2.4 Cell apparatus.

The reaction cell was a 250 mL cylindrical vessel with four ground inlet necks (Fig. 2.5). The lower neck carried the lead working electrode which was oriented in the inverted position. One of the side necks located the tip of the Luggin/reference combination 3 mm above the working electrode face to minimise ohmic drop. The Luggin was filled with electrolyte common to the reaction vessel. The other side neck positioned the thermometer bulb in the electrolyte at the same height as the working electrode face. The top neck provided entry for the gas bubbler and exit for the exhaust gas.

2.5 Solutions and chemicals.

All the water used, for cleaning and for solution preparation was deionised water further purified by passing through a Milli-Q resin filter system.

Chemicals were of analytical grade (BDH or May & Baker), used without further purification.

Prior to all experimental runs, the electrolyte was deoxygenated in the reaction cell by sweeping with dry nitrogen (N2) free of oxygen.
Fig. 2.5  The electrochemical cell.
2.6 Evaluation of the surface roughness.

Charge density and current density values throughout this thesis are calculated by the ratio of the observed charge or current, to the geometrical area of the electrode. The true surface area of the electrode however, will invariably be greater than the geometrical area, due to microscopic roughening caused by polishing or electrochemical activity. The degree of roughening is related to the geometrical surface area, $A$, by

$$A_0 = \gamma A$$

(2.3)

where

$A_0$ is the true surface area [cm$^{-2}$], and

$\gamma$ is the roughness factor [ ].

A common method for the estimation of $\gamma$ is to calculate the ratio of the measured double-layer capacitance to the double-layer capacitance of the liquid mercury electrode, where it is assumed that $\gamma$ is unity.$^{58}$ The double-layer capacitance is determined by superimposition of a rapid triangular waveform upon a potentiostatically controlled potential, $E$, at which the electrode is film free.$^{59,61}$ The current response is a distorted square-wave which may be related to an equivalent circuit consisting of a resistance and capacitance in parallel; the resistance being faradaic and the capacitance due to the charging of the double-layer. Thus the current consists of two components, $I_{dl}$ and $I_r$, the capacitance and resistance current respectively. $I_{dl}$ is related to the double-layer capacitance by

$$C_{dl} = \frac{I_{dl}}{\nu A}$$

(2.4)
where

- $v$ is the potential sweep rate [V s$^{-1}$],
- $C_{dl}$ is the double-layer capacitance [F cm$^{-2}$], and
- $I_{dl}$ is the double-layer charging current [C s$^{-1}$ cm$^{-2}$].

The double-layer capacitance for liquid mercury, $C_{dl}$ (Hg), is taken to be 20 µF cm$^{-2}$.$^{58,62}$ It is assumed that the double-layer capacitance of the true surface of the lead electrode will have the same value as mercury. Birss and Smith$^{63}$ have shown that this assumption works well for the silver electrode. The roughness factor, $\gamma$, may then be calculated from the ratio of the capacitances according to

$$\gamma = \frac{C_{dl}}{C_{dl} (Hg)}$$

(2.5)

Typical current responses for roughness factor calculations are shown in Fig. 2.6. The roughness factor was frequently determined and a typical sample yields an average of 3.18 and a standard deviation of 0.11 for 93 measurements.

The faradaic resistance, $R_f$, at any point in the distorted square-wave is given by

$$R_f = \frac{\Delta E}{\Delta I_f}$$

(2.6)

where

- $\Delta E$ is the potential excursion of the triangular wave-form [V], and
- $\Delta I_f$ is the corresponding change in $I_f$ [C s$^{-1}$]
Fig. 2.6 Typical current-time curves for triangular potential sweeps.

$E = -356 \text{ mV}$, 20 mV peak-to-peak potential waveform, $v = 10 \text{ V s}^{-1}$, $A = 0.159 \text{ cm}^{-2}$, a) $\gamma = 3.23$, b) $\gamma = 3.27$. 
2.7 Electrode surface morphology.

The working electrodes were polished with emery paper (600 grit followed by 1200 grit) and tissue paper, and then rinsed with water and 35% H$_2$SO$_4$ prior to experiments.

Scanning electron microscopy (SEM) shows in Fig. 2.7 that the polishing material becomes embedded in the smooth, but smeared, lead surface (the particles were confirmed to be silicon carbide by X-ray fluorescence). The particles are mostly removed during cathodic polarisation as is shown in Fig. 2.7, presumably by the vigorous evolution of hydrogen from the surface. Hence SiC particles would not be present in significant amount in the kinetic experiments.

2.8 Computer software.

Computer software was developed for both the Apple IIe and Exzel AT computers. The programming languages employed were LABSOFT BASIC and BASIC for the Apple IIe, and GW-BASIC and TURBO PASCAL for the Exzel AT. A brief outline of the uses for the programs and the languages employed are listed below.

i) PENLIFT: controls the X-Y plotter during cyclic voltammetry experiments. Specific cycle number voltammograms can be selected for plotting. LABSOFT BASIC.

ii) QCHARGE: provides the charge either by integrating the analogue current signal or by digital interrogation of the PAR Model 179 Coulometer. LABSOFT BASIC.

iii) CVSCOPE: triggers the oscilloscope capture of transients at specified potential and potential ramp direction for CV pseudo-
Fig. 2.7 Scanning electron micrographs of lead electrodes: a) immediately after polishing, and b) two cyclic voltammetry cycles after polishing, with the potential sweep terminated at the cathodic limit in the potential region for hydrogen evolution.
capacitance and faradaic resistance experiments. LABSOFT BASIC.

iv) **COULOMET**: calculates current density, anodic and cathodic charge, peak-picks anodic and cathodic waves, smooths (using the five-point Savitsky-Golay algorithm\(^{64}\)), and prepares plotting files for digitised cyclic voltammograms. TURBO PASCAL.

v) **POTSTEP**: calculates current density, smooths (using the five-point Savitsky-Golay algorithm\(^{64}\)), and prepares plotting files for digitised potential step transients. TURBO PASCAL.

vi) **PLOTCRV**: calculates theoretical potential step transients for the model described in Chapter 5, lists the optimised parameters for the theoretical transient. TURBO PASCAL.

vii) **CVSIM**: simulates theoretical cyclic voltammograms using the optimised parameters calculated in **PLOTCRV**. TURBO PASCAL.

In addition to the listed programs, numerous additions and alterations were made to existing commercial software packages to allow data transfer from the Apple IIe to the Exzel AT computer using RS232c serial port communication.
CHAPTER THREE
CYCLIC VOLTAMMETRY

3.1 Introduction.

The electrochemical behaviour of the lead electrode in aqueous 35% sulphuric acid (4.65 mol L\(^{-1}\)) was examined. The technique used was cyclic voltammetry (CV) where the potential was swept between \(E_c\) and \(E_a\), the cathodic and anodic potential limits respectively. No stirring of the electrolyte or rotation of the electrode was employed. With the exception of the temperature dependence measurements described in Sections 3.8 and 3.13, all experiments were conducted at room temperature (18 ± 2°C).

3.2 First and subsequent cycles.

Cyclic voltammograms for the first seven and seventieth cycles of a freshly polished Pb electrode are shown in Fig. 3.1. In this typical set of voltammograms an anodic peak A1, due to Pb oxidation develops on the forward (or anodic) scan, the maximum current for this peak is denoted \(i_{A1}\). After the maximum the current diminishes rapidly as solid, insulating, PbSO\(_4\) deposits on the electrode eventually resulting in zero current. The electrode is said to be passivated. On the reverse (or cathodic) scan a cathodic current evolves due to PbSO\(_4\) reduction. The potential at which the cathodic current first appears is close to that for the first appearance
Fig. 3.1  Successive cyclic voltammograms for a freshly polished electrode. \( v = 20 \text{ mV s}^{-1}, \ E_c = -756 \text{ mV}, \ E_a = 244 \text{ mV}, \) analogue data. \( [\text{H}_2\text{SO}_4] = 4.65 \text{ mol L}^{-1} \). \( T = 18 \pm 2^\circ \text{C} \). In this and all subsequent experiments \( i \) is the apparent current density uncorrected for the roughness factor \( \gamma \).
of the anodic current on the forward sweep. The cathodic current develops into a peak $C_1$ with a current maximum $i_{c_1}$. The cathodic current due to reduction of PbSO$_4$ is superimposed on a cathodic current due to H$^+$ reduction and this latter reaction becomes increasingly more dominant at potentials close to the cathodic limit, $E_c$. Fig. 3.1 shows that cycle numbers three to seventy result in coincident voltammograms. The voltammogram recovered for cycle one indicates that the potential at which the anodic peak begins to develop is at a potential more anodic by 10 mV than the anodic peaks for the coincident cycles. The anodic peak current for the first cycle is approximately 10% larger than those for cycles three to seventy. The rising slope of the anodic peak for the first cycle is steeper than for the coincident cycles. The $A_1$ peak for cycle two falls between the $A_1$ peaks for cycle one and cycles three to seventy. The $C_1$ peak like the $A_1$ peak becomes coincident on the third cycle.

3.3 Electrode reproducibility.

A comparison between the fourth CV cycles for four experiments performed at different times on a freshly polished electrode is shown in Fig. 3.2. Typically the variation in peak current, $i_{A_1}$ is less than 10%. The size of the $C_1$ peak however varies markedly between different preparations of the electrode. It is noted in Section 3.2 that the $C_1$ peak becomes coincident for sequential cycles on a polished electrode. This is an indication that the $C_1$ peak may only be directly compared with confidence for experiments performed on an electrode for the same polishing. Fig. 3.2 however shows that the $A_1$ peak may be readily compared for different experiments.
Fig. 3.2 Fourth cyclic voltammograms for four freshly polished electrode surfaces. $v = 20 \text{ mV s}^{-1}$, $E_c = -756 \text{ mV}$, $E_a = 244 \text{ mV}$, analogue data.
3.4 Cathodic treatment.

It was established that the shape of a voltammogram for a stable multi-cycled electrode is influenced by potential steps to extreme cathodic potential limits, denoted $E_{ct}$, prior to initiation of subsequent CV cycles from the cathodic limit, $E_c$. Fig. 3.3 displays the fifth voltammogram for a freshly polished electrode. The Al peak is similar to those shown in Figs. 3.1 and 3.2. The second voltammogram (b) in this figure is that for a cycle after the fifth cycle where the potential sweep is halted at $E_c$, stepped to a potential $E_{ct}$ of $-1756$ mV for 20 sec, stepped to $E_c$ and then the potential sweep is continued as before. The Al peak for (b) is similar to that for the first cycle shown in Fig. 3.1 in that the development of the Al peak is shifted to more positive potentials and the forward slope is steeper than for the stable voltammogram after many cycles. The anodic peak current for the cathodically stepped case (b) is more than twice that for the multi-cycled voltammogram. The Cl peaks in this figure follow identical development but the current continues to a larger peak for (b) due to the greater amount of PbSO$_4$ deposited on the electrode during the previous forward scan. The larger cathodic current for (b) on the forward scan at potentials more cathodic to the anodic peak is due to H$_2$ evolution. Further experiments established that after such a potential excursion into the extreme cathodic region the electrode could be cycled many times in the potential region from $E_c$ to a potential 20 mV more positive than the first appearance of the anodic current ($-316$ mV) and a subsequent cycle from $E_c$ to $E_a$ would result in a voltammogram identical to scan (b) in Fig. 3.3. If the electrode was cycled further than 20 mV into the anodic region then a subsequent cycle from $E_c$ to $E_a$
Fig. 3.3    a) fifth cyclic voltammogram for a freshly polished electrode, b) next cyclic voltammogram recorded after a) but after the potential sweep was terminated at $E_c$, stepped to $-1756$ mV for 20 sec, stepped to $-756$ mV and then restarted. $\nu = 20$ mV s$^{-1}$, $E_c = -756$ mV, $E_a = 244$ mV.
results in a voltammogram identical to that for a many-cycled electrode.

Fig. 3.4 shows the stable many-cycled voltammograms for an electrode cycled to a constant anodic limit, $E_a$, from a varied cathodic limit, $E_c$, where $E_c$ is in the potential range $-756$ mV to $-1756$ mV. The first appearance and forward slope of A1 is identical for $E_c$ in the range $-756$ mV to $-1056$ mV but at more cathodic limits the development of the current moves to more anodic potentials and the slope becomes steeper. This continues until the rising portion of A1 becomes identical to that for voltammogram (b) shown in Fig. 3.3. The anodic peak current, $i_{A1}$, steadily increases with more cathodic values of $E_c$, but for $E_c$ limits more cathodic than $-1456$ mV the peak current becomes coincident. All the C1 peaks show identical slope but the peak currents increase with the increase of $i_{A1}$ indicating the greater quantities of PbSO₄ available for reduction. The cathodic current due to H⁺ reduction increases with more cathodic $E_c$.

3.5 Sweep rate dependence.

The sweep rate dependence was investigated for electrodes both cycled between $E_c$ and $E_a$ of $-756$ mV and $244$ mV respectively, and for electrodes cycled between these limits but stepped to $-1756$ mV prior to each sweep similarly to that shown in Fig. 3.3. The two sets of voltammograms are displayed in Figs. 3.5 and 3.6 respectively.

The forward slopes of the A1 peaks in Fig. 3.5 are at increasingly more anodic potentials for decreasing sweep rates. The slopes however are similar in magnitude. The peak current, $i_{A1}$, is increasingly higher and passivation occurs at more anodic potentials for greater sweep rates. The C1 peak potential, $E_{C1}$, appears at more cathodic potentials with
Fig. 3.4 Successive cyclic voltammograms for a many cycled electrode where the cathodic potential limit for each cycle is varied from -756 to -1756 mV. $v = 20 \text{ mV s}^{-1}$. $E_a = 244 \text{ mV}$, analogue data.
increasing sweep rates.

The Al peaks for voltammograms recorded after a cathodic potential step, shown in Fig. 3.6, display coincident positions for the forward slope for all sweep rates investigated, with only minor differences at the foot of the peak. The values for $i_{Al}$ increase with sweep rate as before but the magnitude of this current is greatly increased over that displayed in Fig. 3.5. The Cl peaks show a similar dependence on sweep rate to that in Fig. 3.5. The H$^+$ reduction shows more pronounced dependence on sweep rate and is of larger value than that evident in Fig. 3.5. The lack of coincidence of the H$^+$ reduction on the forward and reverse sweeps does not allow integration of the Cl peak to give a charge due to reduction of PbSO$_4$ alone.

The anodic charges were determined for the Al peaks in Figs. 3.5 and 3.6. The data are listed in Table 3.1 and Fig. 3.7 displays the sweep rate dependence. The sweep rate dependence shows a hyperbolic form with the anodic charge being similar in value at low sweep rates for both cases. At higher sweep rates the charge decreases more for the cycled electrode than for the electrode stepped to $-1756$ mV prior to sweeping. Fig. 3.8 shows the dependence of the anodic charge on the inverse of the sweep rate. The plot shows that charge tends towards zero at infinitely high sweep rates. Fig. 3.9 shows the plot of the anodic peak current, $i_{Al}$, versus the square root of the sweep rate, the data being listed in Table 3.2. The electrode stepped to $-1756$ mV displays a linear dependence while the cycled electrode exhibits two linear sections.
Fig. 3.5 Cyclic voltammograms for a many cycled electrode where the sweep rate is varied from 2 to 100 mV s\(^{-1}\). \(E_c = -756\) mV, \(E_a = 244\) mV, analogue data.
Fig. 3.6  Cyclic voltammograms for a many cycled electrode where the sweep rate is varied from 2 to 100 mV s\(^{-1}\). Prior to each recorded voltammogram the potential is held at \(E_c\), stepped to -1756 mV for 20 sec, stepped to \(E_c\) and then the sweep is initiated. \(E_c = -756 \text{ mV}\), \(E_a = 244 \text{ mV}\), analogue data.
Table 3.1  Anodic charge for peak Al at different sweep rates and cathodic pretreatment. $E_c = -756$ mV, $E_a = 244$ mV, data are plotted in Figs. 3.7 and 3.8, analogue data.

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Fig. 3.7  Plot of the anodic charge for peak Al, $q_{Al}$, versus the sweep rate. ○ Voltammograms cycled between $E_c$ and $E_a$ (Fig. 3.5). △ Voltammograms recorded after the potential is stepped to -1756 mV and then cycled between $E_c$ and $E_a$ (Fig. 3.6). $E_c = -756$ mV, $E_a = 244$ mV, data are listed in Table 3.1, analogue data.
Fig. 3.8  Plot of the anodic charge for peak A1, \( q_{A1} \), versus the inverse of the sweep rate. ○ Voltammograms cycled between \( E_c \) and \( E_a \) (Fig. 3.5). △ Voltammograms recorded after the potential is stepped to \(-1756 \text{ mV}\) and then cycled between \( E_c \) and \( E_a \) (Fig. 3.6). \( E_c = -756 \text{ mV}, \ E_a = 244 \text{ mV} \), data are listed in Table 3.1. analogue data, peak integration by PAR 179 Coulometer.
Table 3.2  Dependence of anodic peak current on sweep rate and cathodic pretreatment. $E_c = -756$ mV, $E_a = 244$ mV. data are plotted in Fig. 3.9, analogue data.

<table>
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Plot of the anodic peak current, $i_{\text{A}}$, versus the square root of the sweep rate. ◯ Voltammograms cycled between $E_c$ and $E_a$ (Fig. 3.5). △ Voltammograms recorded after the potential is stepped to $-1756$ mV and then cycled between $E_c$ and $E_a$ (Fig. 3.6). $E_c = -756$ mV, $E_a = 244$ mV, data are listed in Table 3.2, analogue data.
3.6 Potential-ramp/potential-hold.

An experiment was developed during the course of the present work in which the potential of the Pb electrode is ramped from a cathodic limit, $E_\text{c}$, to an anodic potential, $E_\text{h}$, at which it is then held. Until the potential $E_\text{h}$ is reached the current time transient is identical to that observed for a cyclic voltammetry experiment. After the potential is held at $E_\text{h}$ the transients are similar in form to those for potential step experiments. Figs. 3.10 and 3.11 depict the transients for this experiment for a multi-cycled electrode cycled between $E_\text{a}$ and $E_\text{c}$, and for an electrode stepped to $E_\text{at} = -1756$ mV prior to each ramp/hold experiment, respectively. The results for the multi-cycled electrode in Fig. 3.10 show rapidly diminishing current transients after $E_\text{h}$ is attained. Conversely the transients depicted in Fig. 3.11 show for electrodes pre-treated to $-1756$ mV that an initial increase in current is evident after $E_\text{h}$ is attained, followed by a peak and a gradual decrease in current.

3.7 Pseudo-capacitance and Faradaic resistance during cyclic voltammetry experiments.

The pseudo-capacitance and faradaic resistance of the electrode during cyclic voltammetry experiments were determined by a method related to that described in Section 2.6 for the evaluation of the electrode roughness factor. A $\pm 15$ mV triangular waveform with a sweep rate of 10 V s$^{-1}$ was superimposed onto a 20 mV s$^{-1}$ cyclic voltammetry waveform. The resulting current waveform due to capacitance and resistance was captured on the storage oscilloscope by filtering the oxidation and reduction current signals; these having frequency less than 1 Hz. The
Fig. 3.10 Potential-ramp/potential-hold transients for a many-cycled electrode. Potential is ramped from $E_c$ to a potential $E_h$ at which it is then held. $v = 20 \text{ mV s}^{-1}$, $E_c = -756 \text{ mV}$, analogue data.
Fig. 3.11  Potential-ramp/potential-hold transients for an electrode potential ramped from $E_c$ to a potential $E_h$ at which it is then held. Prior to each ramp the potential is stepped to $-1756$ mV for 20 sec, stepped to $E_c$ and then the ramp is initiated. $v = 20$ mV s$^{-1}$, $E_c = -756$ mV, analogue data.
oscilloscope capture was triggered by the computer program CVSCOPE (see Section 2.8). The pseudo-capacitance and faradaic resistance were calculated from the recorded transient as described in Section 2.6. Experiments were performed for both a multi-cycled electrode and for an electrode cycled after stepping to an extreme cathodic potential. The data are listed in Tables 3.3 and 3.4 and plotted in Figs. 3.12 and 3.13 respectively.

Fig. 3.12 shows that the pseudo-capacitance passes through sharp maxima on both the forward and the reverse sweeps. The maximum on the forward sweep is at a potential in the voltammogram (Fig. 3.5) at which the forward slope of the Al peak is beginning to curve away from linearity. The maximum on the reverse sweep is at a potential at which a cathodic current is first evident. The faradaic resistance has a parabolic shape with broad minima on both the forward and reverse sweeps but with deviations near the potential limits, passing through local maxima. The minimum on the forward sweep is at a potential in the voltammogram where the anodic peak is reached. On the reverse sweep the minimum is at a potential just after the cathodic current first appears. A clear local maximum is found at -500 mV.

Fig. 3.13 shows that the form of the pseudo-capacitance and faradaic resistance are similar to that for Fig. 3.12. The maximum for the pseudo-capacitance on the forward sweep is at a potential in the voltammogram at which the anodic peak is reached. On the reverse sweep the maximum is at a potential just prior to the cathodic peak. The minimum for the faradaic resistance on the forward sweep is at a potential just after the anodic current has decreased after the anodic peak. On the reverse sweep the
Table 3.3 Dependence of the faradaic resistance and pseudocapacitance on potential for both the forward and reverse sweeps of a cyclic voltammetry experiment for a multi-cycled electrode. $\nu = 20 \text{ mV s}^{-1}$, $E_c = -756 \text{ mV}$, $E_a = 244 \text{ mV}$, data are plotted in Fig. 3.12, analogue data.

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Table 3.4 Dependence of the faradaic resistance and pseudocapacitance on potential for both the forward and reverse sweeps of a cyclic voltammetry experiment. The electrode was held at $E_{ct} = -1756 \text{ mV}$ for 20 sec prior to each sweep. $v = 20 \text{ mV s}^{-1}$, $E_c = -756 \text{ mV}$, $E_a = 244 \text{ mV}$, data are plotted in Fig. 3.13, analogue data.

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Fig. 3.12  Plot of faradaic resistance and pseudo-capacitance for a many cycled electrode.  ⊙ Pseudo-capacitance on the forward sweep.  ▲ pseudo-capacitance on the reverse sweep.  ■ faradaic resistance on the forward sweep.  ◇ faradaic resistance on the reverse sweep.  $v = 20 \text{ mV s}^{-1}$, $E_c = -756 \text{ mV}$, $E_a = 244 \text{ mV}$, data are listed in Table 3.3, analogue data.
Fig. 3.13 Plot of faradaic resistance and pseudo-capacitance for a many cycled electrode between $E_c$ and $E_a$ after being stepped to -1756 mV for 20 sec prior to each measurement. ○ Pseudo-capacitance on the forward sweep. △ pseudo-capacitance on the reverse sweep. ■ faradaic resistance on the forward sweep. ◆ faradaic resistance on the reverse sweep. $v = 20$ mV s$^{-1}$, $E_c = -756$ mV, $E_a = 244$ mV. data are listed in Table 3.4, analogue data.
minimum is at a potential at the foot of the cathodic slope. A local maximum in the faradaic resistance is again found at approximately -500 mV on both the forward and reverse sweeps.

3.8 Temperature dependence.

The temperature and sweep rate dependence of a multi-cycled electrode was determined for temperatures in the range -16°C to 30°C and for sweep rates from 10 mV s⁻¹ to 200 mV s⁻¹. The voltammograms were digitised and the experiments were controlled by the PAR 276 interface. The parameters of the interface do not allow collection of voltammograms at sweep rates less than 10 mV s⁻¹. The data was smoothed using the five point Sovitsky Golay algorithm. The lowest attainable stable temperature was -16°C.

Voltammograms from the limits of the temperature region explored are shown in Figs. 3.14 and 3.15. The voltammograms in Fig. 3.14 are those recorded for experiments performed at -16°C. The forward slopes of the Al peak are identical for all the sweep rates. The values for the peak current, $i_{Al}$, show no clear dependence on sweep rate and are very low in magnitude. The Cl peak is not well resolved against the H⁺ reduction wave indicative of the small amounts of PbSO₄ deposited on the surface. The hydrogen evolution current at the cathodic potential limit shows only slight dependence on sweep rate. All these observations are in opposition to those described for Fig. 3.5.

Fig. 3.15 displays the voltammograms recorded at 30°C. The form of the transients are identical to those described for Fig. 3.5 and as such require no further comment.
Fig. 3.14  Cyclic voltammograms for a many-cycled electrode at \( T = -16^\circ C \) for sweep rates between 10 and 200 mV s\(^{-1}\). \( E_c = -880 \) mV, \( E_a = 120 \) mV, digital data.
Fig. 3.15 Cyclic voltammograms for a many-cycled electrode at
$T = 30^\circ\text{C}$ for sweep rates between 10 and 200 mV s$^{-1}$. $E_c = -880$ mV, $E_a = 120$ mV, digital data.
A more convenient method of displaying the temperature dependence is to compare voltammograms for one sweep rate at each temperature. Fig. 3.16 shows voltammograms for a sweep rate of 100 mV s\(^{-1}\). The forward slope to the A_1 peak is found at more anodic potentials for decreasing temperatures. The anodic peak current, \(i_{A_1}\), is decreased with decreasing temperature but at the higher temperature values the temperature dependence becomes less pronounced. The slope of the C_1 peak is steeper and the peak current, \(i_{C_1}\), is larger with increasing temperature. The hydrogen evolution current at the cathodic limit is larger at higher temperatures.

The anodic passivating charge, \(q_{A_1}\), and the anodic peak current, \(i_{A_1}\), are tabulated in Table 3.5 and displayed in Figs. 3.17 and 3.18, and Figs. 3.19 and 3.20 respectively. Fig. 3.17 shows that the hyperbolic variation of anodic charge with sweep rate is evident for each temperature, but that the magnitude of the charge is less for lower temperatures. The variation of anodic charge with temperature for each sweep rate is linear as is shown in Fig. 3.18. There is no common intercept of the lines of best fit with the temperature axis. Fig. 3.19 displays the anodic peak current plotted as a function of the square root of the sweep rate. At the lowest temperature there is no clear dependence in contrast to the results in Fig. 3.9 at room temperature. As the temperature is increased a curvilinear relationship is established with linear dependence at low sweep rates and excursion from this at high sweep rates. A true linear relationship is established at 30°C. Fig. 3.20 shows the anodic peak current plotted as a function of temperature for each sweep rate. The dependence of \(i_{A_1}\) on temperature is greater for
Fig. 3.16 Cyclic voltammograms for a many-cycled electrode at 100 mV s\(^{-1}\) for temperatures between -16 and 30°C. \(E_c = -880\) mV, \(E_a = 120\) mV, digital data.
Table 3.5 Dependence of the anodic peak current and anodic charge on sweep rate and temperature for cyclic voltammetry experiments. $E_e = -880$ mV, $E_a = 120$ mV. data are plotted in Figs. 3.17 to 3.20, digital data.

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Fig. 3.17  Plot of the anodic charge, $q_{A1}$, versus sweep rate for different temperatures. $\Box$ -16°C, $\bigcirc$ -10°C, $\triangle$ -5°C, +0°C, $\times$ 5°C, $\diamondsuit$ 10°C, $\otimes$ 15°C, $\circledast$ 20°C, $\times$ 25°C, $\star$ 30°C. Data are listed in Table 3.5, digital data.
Fig. 3.18 Plot of the anodic charge, $q_{AI}$, versus temperature for different sweep rates. □ 10 mV s$^{-1}$, ○ 20 mV s$^{-1}$, △ 50 mV s$^{-1}$, + 100 mV s$^{-1}$. ◊ 200 mV s$^{-1}$. Data are listed in Table 3.5. digital data.
Fig. 3.19  Plot of the anodic peak current, $i_{M}$, versus the square root of the sweep rate for different temperatures. □ -16°C, ⊗ -10°C, △ -5°C, + 0°C, × 5°C, ◊ 10°C, ⊠ 15°C, ♦ 20°C, × 25°C, ♣ 30°C. Data are listed in Table 3.5, digital data.
Fig. 3.20  Plot of the anodic peak current, $i_{pA}$, versus the temperature for different sweep rates. □ 10 mV s$^{-1}$, ○ 20 mV s$^{-1}$, △ 50 mV s$^{-1}$, + 100 mV s$^{-1}$, ◊ 200 mV s$^{-1}$. Data are listed in Table 3.5, digital data.
higher sweep rates.

3.9 Comparison of experimental data with previous work.

Previously reported investigations of the lead anode in sulphuric acid by cyclic voltammetry have been confined to the work by three main groups of researchers: Hampson et al.,37,38,45 Archdale and Harrison,31,33,34 and Danel and Plichon.47-49 The results of the present work will be discussed in the light of these references.

The difference between the first and subsequent cycles, as shown in Fig. 3.1, has been previously been reported. In all cases the Al peak for the first cycle is found at potentials more anodic than those for the subsequent cycles. The ratio of the peak currents for the first and following cycles varies widely and may reflect the various polishing techniques employed. Danel and Plichon47-49 used mechanical polishing followed by a cathodic treatment in the electrolyte. Hampson et al.37,38,45 polished with carborundum paper and then electropolished in 10% aqueous perchloric acid, and Archdale and Harrison31,33,34 polished with 1-5 μm γ-alumina and then electropolished in a 10% perchloric acid/ethyl alcohol and diethyl ether mixture. The present work employs mechanically polished electrodes. Thus in the present work the peak current for the first cycle is similar to that for the third and ensuing cycles, while Danel and Plichon48 report a peak current for the first cycle more than three times greater than for the third cycle. The similarity between the form of the first and subsequent cycles for polished electrodes and for cycled electrodes cathodically treated (as in Figs. 3.1 and 3.3 respectively) may be found in the work by previous authors.38 but it also must be recognised...
that Danel and Plichon\textsuperscript{48} employed cathodic treatment during the polishing regime and therefore their results may be considered as being similar to those depicted in Fig. 3.3. Brennan and Hampson\textsuperscript{38} achieved similar results by holding the potential at the negative potential limit for a fairly long, but unspecified, time until the cathodic current diminished to a small steady value. Danel and Plichon\textsuperscript{48} have shown that this behaviour is independent of sulphuric acid concentration and have stated that this indicates that there is a common mechanism operating at all concentrations.

The voltammograms displayed in Fig. 3.4 are unique in that they are the first investigation into the variation of the A1 peak with the cathodic potential excursion limit. The voltammograms clearly show that the A1 peak shifts steadily to more anodic potentials and the peak current increases with more cathodic limit to an invariant position and height for cathodic limits lower than \(-1456\) mV. That the transition is not achieved suddenly at a specific potential excursion limit is indicative that the response may be due to the time for which the potential is below a certain value so that a relatively slow reaction may take place.

3.10 Previous approaches to interpretation of the cyclic voltammetry data.

Having established the difference between the first and subsequent cycles all the previous workers have only investigated the behaviour of the first cycle for elucidation of the mechanism. Thus the sweep rate dependence of the electrode has been solely reported for the first cycle of cathodically pretreated or polished electrodes.\textsuperscript{31,33,34,38,45,47-49}
Therefore the previous reported voltammograms may be identified with those depicted in Fig. 3.6 for the cathodically treated electrode in the present work. Danel and Plichon\textsuperscript{48} have reported very similar voltammograms to those shown in Fig. 3.6. The forward slopes of the Al peak are coincident at all sweep rates and the peak current is progressively higher with increasing sweep rate. Alternatively the present work has explored the sweep rate dependence of the stable voltammograms that develop for multi-cycled electrodes. The voltammograms displayed in Fig. 3.5 are the first reported for the sweep rate dependence of the multi-cycled electrode. The voltammograms in this figure differ significantly from those shown in Fig. 3.6. The forward slopes of the Al peak are now not coincident but move to more positive potentials at lower sweep rates. The eventual slopes however are independent of sweep rate and are of similar value. The charge and peak current for the Al peak are markedly different as can be readily seen in Figs. 3.7 and 3.9 respectively. Brennan and Hampson\textsuperscript{38} have previously reported the form of the anodic charge vs sweep rate and the present work shows similar hyperbolic dependence in Fig. 3.7. This however is the first comparison between the charge for the first cycle and the stable multi-cycled case. The plot indicates that the charge for the multi-cycled electrode is less and displays more dependence on the sweep rate, diminishing to lower values more rapidly at higher sweep rates, than for a cathodically treated electrode. Brennan and Hampson\textsuperscript{38} have suggested that the passivating anodic charge tends to a limiting value at high sweep rates. If this is correct a plot of the anodic charge vs the inverse of the sweep rate should then produce a relationship with an intercept with the charge axis. Fig. 3.8 however shows that such a
plot results in a curve that tends towards the origin rapidly at high sweep rates thereby refuting this proposal.

The relationship between the peak current and the sweep rate has previously been investigated by most of the authors mentioned.\textsuperscript{34,37,38,45,48,49} The results however differ between, and even within, research groups. In general the results fall into two distinct groups: linear $i_A \text{ vs } v^{1/2}$, and $i_A \text{ vs } v^{1/2}$ with two linear sections.

Researchers finding a linear relationship,\textsuperscript{34,45} have analysed the data in two different ways. The earlier work on Pb amalgam electrodes by Archdale and Harrison\textsuperscript{34} related the linear dependence of $i_A \text{ vs } v^{1/2}$ to the equation derived by Delahay and co-workers for the reversible reduction of a soluble electroactive species to form an insoluble deposit\textsuperscript{65,66}

$$i_A = -3.67 \times 10^5 \ n^{3/2} \ c \ D^{1/2} \ v^{1/2} \quad (3.1)$$

where

$D$ is the diffusion coefficient [cm$^2$ s$^{-1}$].

$c$ is the concentration of the electroactive solution species [mol cm$^{-3}$], and

the units of the constant are [C mol$^{-1}$ V$^{-1/2}$].

Hampson \textit{et al} \textsuperscript{37} had previously noted that a similar equation could be written for the anodic reaction but did not furnish it. Archdale and Harrison\textsuperscript{34} employed equation 3.1 modified only by a sign change for the anodic reaction on lead amalgam and used an independently determined value for $D,$\textsuperscript{67} and stated that this was the appropriate equation to use
based on Hampson et al.\textsuperscript{37} Their choice of equation 3.1 was doubly unfortunate as immediately prior to the use of this equation they stated: "Based on previous experiments (no references) the curves are expected to analyse as a reversible two-electron dissolution with the limiting step the diffusion of Pb in Hg."\textsuperscript{34} Thus they employed an equation for the reduction of an electroactive species to form an insoluble product to describe an oxidation of a surface species controlled by diffusion of a non-electroactive counter ion, after they had described the reaction as being controlled by diffusion of the Pb within the liquid amalgam.

Hampson and Lakeman\textsuperscript{45} on finding a linear $i_{A1}$ vs $v^{1/2}$ relation at $-30^\circ$C on solid electrodes related their data to the Müller passivation model\textsuperscript{68} where the rate of reaction is controlled by the ohmic resistance of the electrolyte within the pores or intercrystalline spaces of the insoluble non-conducting deposit on the electrode. The peak current for this situation has been derived mathematically by Macdonald\textsuperscript{69} to give the following expression

$$i_{A1} = \left(\frac{nF\kappa}{M}\right)^{1/2} (1 - \theta_p) v^{1/2} \quad (3.2)$$

where

- $\kappa$ is the solution conductivity [\(\Omega^{-1} \text{ cm}^{-1}\)],
- $\rho$ the density of PbSO$_4$ [g cm$^{-3}$],
- $M$ the molar mass of PbSO$_4$ [g mol$^{-1}$],
- and $\theta_p$ the fractional coverage of the Pb by PbSO$_4$ at the oxidation peak [ ].

If $\theta_p$ is independent of sweep rate then $i_{A1}$ should vary linearly with $v^{1/2}$. 
However the voltammograms do not show the same form as those previously found for other passivation systems which have been successfully analysed using this model.\textsuperscript{70,71} In these cases the current rapidly diminishes to zero after the peak as the pore resistance controls the reaction. The Müller model will be discussed and its applicability to the system in the light of the present work will be refuted in Chapter 5.

Two linear sections in the plot of $i_{A1}$ vs $v^{1/2}$ is more commonly found.\textsuperscript{37,38,48} Hampson et al\textsuperscript{37} discussed the linear slope through the origin at low sweep rates as being due to control by diffusion of $SO_4^{2-}$ to the electrode surface. Deviation to another linear relationship at higher sweep rates was interpreted as being due to control by formation of a solid layer. The movement of the deviation or 'knee' to progressively lower sweep rates at higher [$H_2SO_4$] was interpreted by these workers as being a result of the following: At lower sweep rates and low [$H_2SO_4$] current limitation is caused by a shortage of anions. At higher [$H_2SO_4$] there are always sufficient anions present so this cannot be rate determining. The knee between the two linear sections moves to lower sweep rates at higher [$H_2SO_4$] as limitation of diffusion by the anions becomes more unlikely and the other process takes control. Danel and Plichon\textsuperscript{48} duplicated the results of Hampson et al\textsuperscript{37} and stated that the plot of $i_{A1}$ vs $v^{1/2}$ is essentially meaningless as more than one process is occurring; oxidation (by possibly more than one simultaneous reaction), and decrease in the surface area from passivation.

The results from the present work at room temperature shown in Fig. 3.9 indicate that the plot of $i_{A1}$ vs $v^{1/2}$ may give both linear and dual linear relationships depending on the cathodic potential treatment.
When the electrode is cycled between $E_c$ and $E_a$ a dual linear relationship is found with the knee between 10 and 20 mV s$^{-1}$. The slope below 10 mV s$^{-1}$ gives a straight line tending towards the origin. Conversely cathodic treatment to $E_{ct} = -1756$ mV prior to the experiment yields a linear $i_{rt}$ vs $v^{1/2}$ relationship passing through the origin. Clearly for both sets of experiments the acid concentration remains constant so arguments similar to that put forward by Hampson et al.$^{37}$ cannot be employed here. Therefore it is proposed that the rate controlling reactions are greatly different between the cathodically treated and the multi-cycled electrodes.

The proposal is further reinforced by the transients shown in Figs. 3.10 and 3.11. An experiment was devised in which a potential ramp is applied to the electrode until a potential $E_a$ in the anodic region is achieved, this potential being then held constant and the resultant current transient recorded. The experiment is termed the 'potential-ramp/potential-hold' experiment. Fig. 3.10 displays the transient recovered for a multi-cycled electrode ramped from $E_c$ to $E_a$ and Fig. 3.11 shows the transient for an electrode stepped to a cathodic limit, $E_{ct}$, of $-1756$ mV prior to each potential ramp. The form of the transients for the two sets of experiments are clearly different. In Fig. 3.10 the current diminishes rapidly from the point at which the potential is held. Conversely in Fig. 3.11 the current continues to increase with time after the potential, $E_a$, has been attained, the current passing through a maximum and then decreasing with time. Applying the interpretation of potential step experiments, to which the present experiment is related, an increasing current transient is due to growth of a phase on the electrode surface where the current is dependent on the rate of growth of the new phase.
Peter et al.\(^{72}\) have shown that such a transient cannot be an artifact due to uncompensated solution resistance, as in such situations only shoulders on current transients develop. The falling transients in Fig. 3.10 may be due to precipitation of passivating PbSO\(_4\) on the electrode.

### 3.11 The case for a completely new mechanism.

To summarise so far: the first or cathodically pretreated voltammograms differ from subsequent cycles; the cathodic current due to hydrogen evolution is always greater for the first or cathodically treated cycle than for subsequent cycles. Potential-ramp/potential-hold experiments show growth of a rate controlling phase evident in cathodically treated cycles and the absence of this in multi-cycled electrodes. Therefore it is proposed from the present work that the first cycle (either freshly polished or cathodically treated) differs from the subsequent cycles in that a rate controlling phase is developed on the first anodic sweep but not reduced on the subsequent scan (see Fig. 3.21). Thus the current observed for subsequent anodic sweeps arises from electrochemical reactions operating through this phase (Fig. 3.21b). The presence of the phase accounts for the decrease in hydrogen evolution after the first cycle as the protons have restricted contact with the unoxidised lead surface. The phase is not reduced during cathodic scans to \(E_c = -756\) mV, but on stepping to \(E_{ct} = -1756\) mV or by decreasing \(E_c\) to \(-1756\) mV the phase is either electrochemically reduced or physically removed by vigorous gas evolution.

Hampson et al.\(^{37}\) in an early paper suggested that the control of the total reaction rate could be due to summation of two processes:
Fig. 3.21 Schematic of the surface film model and the film-free electrode. Charge transfer in the film-free case (a) initially results in a soluble Pb(II) species, Pb$^{2+}_{(aq)}$, that diffuses away from the electrode. Film growth and passivation by microcrystalline PbSO$_4$ is not indicated in this scheme. Charge transfer in the presence of the surface film (b) results in a Pb$^{2+}$ ion at the metal/film interface that migrates through the film, emerging from the film/electrolyte interface as Pb$^{2+}_{(aq)}$. This species both diffuses away from the electrode and precipitates on the film as passivating microcrystalline PbSO$_4$. 
the diffusion of $\text{SO}_4^{2-}$ and $\text{HSO}_4^-$ to the electrode.

(ii) the transport of mass and charge through an insoluble layer of PbSO$_4$ on the electrode.

These workers equated diffusion of Pb$^{2+}$ through an insoluble layer with formation of a passivating layer on the electrode. Thus these workers rejected the possibility of a mediating film because of the low conductivity of PbSO$_4$. However an insoluble, non-equilibrium, non-stoichiometric, ionically conducting layer of PbSO$_4$ can be visualised at an interface between the solid electrode and the electrolyte for a dynamic system. Delayed crystallisation phenomena of PbSO$_4$ have previously been reported by Danel and Plichon$^{47}$ when Pb(NO$_3$)$_2$ is introduced to sulphuric acid. The supersaturation of PbSO$_4$ (ratio of the actual concentration of Pb$^{2+}$ to the concentration in equilibrium with PbSO$_4$) was found to have a value of 9 in 4.7 mol L$^{-1}$ H$_2$SO$_4$ in a later report by these authors.$^{49}$

In the present work it is also proposed that Pb$^{2+}$ forms solvation products preferentially with H$_2$O, since SO$_4^{2-}$ is only poorly coordinated to Pb$^{2+}$. The ion pair [Pb$^{2+}$][SO$_4^{2-}$] has a relatively low formation constant$^{73}$ ($K_1 = 10^{2.62}$). That the foot of the anodic peak is at a potential 10 mV more cathodic for the cycled electrode in the presence of the insoluble layer than the clean electrode indicates that the film results in an underpotential for oxidation. That is, the ionic charge transfer from the lead metal to the insoluble layer is energetically more favoured than charge transfer from the metal to form a dissolved Pb$^{2+}$ species. This may be related to the relative change in environment for each case, for the multi-cycled electrode charge transfer at the metal/film interface merely
results in movement of that interface into the metal (Fig. 3.21b), whereas in the film-free case charge transfer requires solvation, desorption, and diffusion (Fig. 3.21a).

3.12 Interpretation of the pseudocapacitance and faradaic resistance.

The pseudocapacitance and faradaic resistance determined during cyclic voltammetry experiments are shown in Figs. 3.12 and 3.13 for a multi-cycled electrode and a cathodically treated electrode respectively. The results are best discussed in relation to an equivalent electrical circuit adapted from the circuit described by Conway for an adsorbed intermediate on an electrode. The equivalent circuit from Conway is shown in Fig. 3.22a. The circuit consists of the double layer capacitance, $C_{dl}$, in parallel with an $R-C$ circuit describing the adsorbed behaviour. In both the film-free cathodically-treated electrode and the electrode in the presence of the film a capacitance term due to the adsorption at the electrode is present. The capacitance (called the pseudocapacitance, $C_p$) arises from charge separation at the metal/film or metal/electrolyte interface due to the adsorbed $\text{Pb}^{2+}$ species on the metal. The pseudocapacitance is less adequately described by a capacitor than the double layer, though it will still behave electrically like a capacitor. The pseudocapacitance is charged by a charge-transfer step, represented by a resistance, $R_1$, which may be non-ohmic. $C_p$ corresponds to a surface coverage by an intermediate and at least one more subsequent step is required to remove the steady state coverage to give either film formation, mass transport through the film, or dissolution from the surface. Hence $C_p$ is short circuited by a second non-ohmic resistance component, $R_2$. The combination of $C_p$, $R_1$, and $R_2$ must
Fig. 3.22 Equivalent circuits for the lead electrode: a) basic circuit for charge-transfer step and pseudocapacitance discharged by following rate determining step; b) simplification of a) for analyses of transients. After Conway;\textsuperscript{74} Conway, B.E., Theory and Principles of Electrode Processes, The Ronald Press Company, New York, 1965, p.139.
be in parallel with $C_{dl}$, since they provide a leakage path across the double layer.

Conway\textsuperscript{74} stated that the pseudocapacitance charging resistance, $R_1$, is the faradaic resistance. It may however be more appropriate to describe $R_1$ as the pseudocapacitance loading resistance, $R_2$ as the pseudocapacitance shunt resistance, and the summation $R_1 + R_2 = R_{eq}$ as the apparent faradaic resistance. In the steady state the current passes through $R_1$ and $R_2$ and is more likely to be limited by $R_2$. The capacitance will be dominated by $C_p$. Thus the equivalent circuit may be simplified, as shown in Fig. 3.22b, by a parallel circuit consisting of $R_{eq}$ and $C_p$ where $R_{eq}$ is the apparent faradaic resistance and $C_p$ the sum of the pseudo and double layer capacitances. The current transients were analysed for this simplified circuit and the results are shown in Figs. 3.12 and 3.13.

In the previous discussion it was assumed that the multi-cycled electrode is covered by a conductive, insoluble layer of a Pb(II) compound. On the forward sweep $R_{eq}$ follows a parabolic relationship with potential. A broad minimum is centered at a potential where the anodic current passes through a maximum. $C_p$ passes through a maximum just prior to the potential for the anodic peak. $R_{eq}$ approximates the shunt resistance, $R_3$, across $C_p$ and is expected to decrease in value as the potential approaches the anodic region and to further decrease with increasing overpotential. This resistance is indicative of the reaction rate across the metal/film interface. Precipitation of PbSO$_4$ onto the conductive film occurs however and tends to increase $R_{eq}$ because of the passivation by this phase. This is evident by an increase in $R_{eq}$ at potentials more anodic than just prior to the anodic peak. This indicates the point at which
passivation begins to dominate. $C_p$ increases in the anodic region as the charge separation across the interface increases. In a similar manner to $R_t$, $C_p$ is altered by precipitation of passivating PbSO$_4$ on the film. Thus $C_p$ is found to diminish rapidly after the anodic peak.

In the film-free case for cathodically treated electrodes another charge transfer is taking place; that of the formation of the conductive, insoluble, Pb(II) solid film. The approximation is made that the pseudocapacitance and the load and shunt resistances for the metal/electrolyte interface are of a similar character to that for the metal/film interface so that the equivalent circuit shown in Fig. 3.22b is still applicable.

As is shown in Fig. 3.13, $R_t$ decreases with increase in potential approaching the anodic region as film building and dissolution occurs and as before is increased by the onset of passivation. The resultant increase is more abrupt in Fig. 3.13 than in Fig. 3.12 and also occurs after the anodic peak. This suggests that a substantial portion of the anodic charge is associated with film building and that the anodic peak is dominated by the completion of the film rather than passivation. That the minimum for $R_t$ occurs well after the anodic peak shows that deposition of passivating PbSO$_4$ becomes important relatively late in the peak when compared to the multi-cycled case. The ring-disc results reported by Danel and Plichon indicate that the ring current, due to soluble Pb$^{2+}$ reduction, passes through a maximum before the anodic peak and thus it is now proposed that film building is the predominant reaction from this point to the anodic peak. In accordance with this $C_p$ passes though a maximum at the same position as the $R_t$ minimum after the anodic peak. The peak value for $C_p$ is three
times larger for the cathodically treated case than for the multi-cycled electrode, indicative of the extra charge separation associated with film building.

The reverse scans for both multi-cycled and cathodically treated electrodes are very similar. This is consistent with the proposal that in both cases reduction of PbSO₄ occurs leaving the conductive film layer for a subsequent cycle. \( R_f \) decreases as the potential scan approaches the cathodic region and a minimum is reached at the foot of the cathodic peak. \( C_p \) passes through a maximum at the same position.

For both cases at potentials near the anodic sweep limit \( R_f \) varies markedly, this may be due to delayed crystallisation phenomena in the passivating layer. Near the cathodic sweep limit \( R_f \) passes through an ill-defined local maximum at \(-550 \text{ mV}\) in both cases. This potential region is close to the reported values for the potential of zero charge for lead, \(-0.60 \text{ V (SHE)}\). It is also the potential at which cathodic hydrogen evolution begins to predominate and the measured \( R_f \) may represent the faradaic resistance for this reaction.

3.13 The effect of temperature on the anodic process.

The temperature dependence of cyclic voltammetry experiments was determined for multi-cycled electrodes. Figs. 3.14 and 3.15 display the voltammograms for the sweep rate dependence at the lower and upper limits of the temperature range explored, \(-16\degree \text{C}\) and \(30\degree \text{C}\) respectively. The voltammograms in Fig. 3.14 have coincident forward slopes for the A1 peak unlike those in Fig. 3.15 where the position of the slope is found at more anodic potentials at lower sweep rates. The relative position of the
coincident forward slope in Fig. 3.14 can be seen in Fig. 3.16 where the variation of voltammograms for one sweep rate with temperature are shown. The voltammograms at lower temperature are found to have slopes at more anodic potentials. Hampson and Lakeman\textsuperscript{45} have noted that linear slopes on the A1 peak are to be expected if the oxidation process is controlled by a resistance. The present work has given rise to a proposed conductive thin film which is in agreement with this concept. However the sweep rate dependence has shown that at and near room temperature a simple ohmic control is not operating alone as the linear slopes on the A1 peak are moved to more anodic potentials at lower sweep rates. At high sweep rates the current develops into a linear region as soon as oxidation takes place. In contrast to this at low sweep rates a non-linear current is evident initially and a linear dependence develops only at a higher potential. At low temperatures the linear region is independent of sweep rate and the position of the slope is similar to that for low sweep rates at room temperature. The present understanding of the system is insufficient to explain this behaviour.

The peak current values, \( i_{A1} \), at \(-16^\circ C\) show only slight variation with \( v \) as can be seen in Fig. 3.14 and the plot of this parameter in Figs. 3.19 and 3.20. Variation of \( i_{A1} \) with \( v \) develops with increase in temperature and a linear \( i_{A1} \) vs \( v^{1/2} \) relationship is found at \( 30^\circ C \) as is shown in Fig. 3.19. Fig. 3.20 displays the variation of \( i_{A1} \) with \( T \) for each sweep rate and it is evident that the higher sweep rate voltammograms are more dependent on \( T \) than are the lower. The form of the temperature dependence for each sweep rate in Fig. 3.20 is that of an increase in \( i_{A1} \) levelling off to a plateau where temperature independence is observed. The
plateau is attained at lower temperatures for lower sweep rates. This is indicative of a process controlling $i_{A1}$ that has more time to operate at low sweep rates and consequently reaches a stable value (and hence temperature independence) at a lower temperature than do high sweep rate voltammograms.

The plots of $i_{A1}$ vs $u^{1/2}$ are difficult to analyse, as noted above and by Danel and Plichon, since they relate to the summation of several different processes.

The variation of the anodic charge, $q_{A1}$, with $u$ is shown in Fig. 3.17 and follows the hyperbolic behaviour as previously shown in Fig. 3.7, and by Brennan and Hampson. The curves are progressively moved to lower charge values at lower temperatures. The progression is linear with temperature for a given sweep rate as is shown in Fig. 3.18.

Both $q_{A1}$ and $i_{A1}$ arise from a combination of more than one separate reaction. Thus elucidation of a mechanism based on the measurement of these two parameters is difficult.

3.14 Conclusions.

A conductive film model is proposed for the stable multi-cycled electrode in cyclic voltammetry experiments. Charge transfer is proposed to take place at the metal/film interface to produce Pb$^{2+}$ ions in the solid state, which then diffuse through the film. An alternative description with a different frame of reference involves consideration of movement of the metal/film interface by migration of the counter ions into the metal lattice. By either process, Pb$^{2+}$ ions emerge through the film/electrolyte interface and diffuse into the electrolyte as solvated aquo ions. A
supersaturation of solvated ions in the presence of $\text{SO}_4^{2-}$ ions results in precipitation of microcrystalline PbSO$_4$ due to the solubility product being exceeded. The distance travelled by the diffusing $\text{Pb}^{2+}_{(\text{aq})}$ is small so that precipitation of the insulating PbSO$_4$ crystals occurs on the underlying conductive film. Thus the electrode becomes electrically insulated and the charge-transfer rate decreases. The passivation rate increases with time after the initial precipitation, since the crystalline deposit of PbSO$_4$ on the film will provide sites for growth by addition of further Pb$^{2+}$. The conductive film is not reduced on subsequent cathodic scans but is removed by polishing or extreme cathodic treatment. Removal in the latter case would be by either electrochemical reduction or physical dislodgement by vigorous hydrogen evolution.

The first cycle after polishing or cathodic treatment is different from the subsequent or multi-cycled cases in that there is no surface film present on the electrode. Initially, charge transfer at the metal/electrolyte interface results in soluble $\text{Pb}^{2+}_{(\text{aq})}$ as is shown by the ring-disc experiments performed by Danel and Plichon.$^{49}$ After an appropriate overpotential is reached, film building is postulated to occur by combination of solvated Pb$^{2+}$ ions with counter ions to form an insoluble, non-crystalline, non-stoichiometric phase. It can be assumed that this phase does not crystallise to form PbSO$_4$ due to non-stoichiometry; it is relatively thin and conductive. During and after completion of the phase formation, diffusion of Pb(II) to the film/electrolyte interface takes place and solvated $\text{Pb}^{2+}_{(\text{aq})}$ ions diffuse away from the electrode. As in the case of the multi-cycled electrodes a supersaturation point is exceeded and passivating PbSO$_4$ deposits on the film stifling the charge-transfer
reaction.

Thus far, the hypothesis of two types of anodic pathways, depending on the presence or absence of a thin conducting surface film, has been based on a qualitative interpretation of the cyclic voltammetry results. In Chapter 5, a mathematical formulation of the model will be presented, and it will be shown that a quantitative treatment of the data in terms of the model is quite successful.
CHAPTER FOUR
POTENTIAL STEP EXPERIMENTS

4.1 Introduction.

Potential step experiments were used to elucidate the anodic behaviour of Pb in aqueous 35% H₂SO₄ (4.65 mol L⁻¹). Investigations were carried out at room temperature (18 ± 2°C) and over the temperature range -16 to 30°C at 5°C intervals. Electrodes were polished as described in Section 2.7. Prior to performing potential step experiments the electrodes were electrochemically cycled using the cyclic voltammetry technique between the potential limits $E_c$ and $E_a$ of -880 and 120 mV respectively at a sweep rate of 20 mV s⁻¹ for 10 minutes. All the transients were initially observed visually with the storage oscilloscope and recorded digitally using the Model 276 interface for later data handling. The data was smoothed, current densities calculated, and plotting files generated using the computer program POTTSTEP (Section 2.8).

4.2 Potential-step experimental sequence.

A standardised potential step sequence was employed for all the experiments and is shown in Fig. 4.1. The potential is initially held at a cathodic value, $E_{pc}$, for 10 s. $E_{pc}$ is in the potential region where solid PbSO₄ is reduced (typically -756 mV). The variation in the transients for
Fig. 4.1 Scheme for the standardised potential step sequence. 

$E_{pc}$ is a cathodic potential at which any Pb$^{2+}$ material is reduced. $E_1$ is a cathodic potential at which only a small current passes due to H$^+$ reduction, and $E_2$ is the stepping potential into the anodic region. Elapsed time in later figures is measured from the instant when $E_2$ is reached. 

$E_{eq}$ is the equilibrium potential of Pb in 4.65 mol L$^{-1}$ (−316 mV).
different values of $E_{pc}$ is given in Section 4.4. The potential is stepped
to another cathodic potential, $E_1$, for 15 s at which only a small current
flows due to H$^+$ reduction. The next potential step is to $E_2$ which is in
the anodic region and in this text is referred to as the 'anodic stepping
potential'. The current-time transient measurements are initiated from the
time at which $E_2$ is reached. The potential is held at $E_2$ for 35 s.
Variation of the transients with $E_2$ is described in Sections 4.5 and 4.6.
The potential is stepped back to $E_{pc}$ to cathodically remove the corrosion
products resulting from the preceding anodic step in preparation for
subsequent experiments. The parameters of the Model 276 interface are
such that for an 80 s experiment the smallest time interval between
digitised points is 20 ms.

4.3 Reproducibility of the transients and quality of the digitising.

A series of transients for a sequence of potential step experiments
for the same values of $E_{pc}$, $E_1$, and $E_2$ and for the same electrode
polishing interval are shown in Fig. 4.2. The transients are very similar in
shape and the peak current differs by 6%. In contrast to this Fig. 4.3
displays a series of transients for a new, but again common, value of $E_2$
and the same values of $E_{pc}$ and $E_1$ as before but with the electrode
polished (and electrochemically precycled) between experiments. The
transients differ greatly in both shape and peak height. The four
transients in this figure also illustrate the varying quality of the digitised
signal. The signal to noise ratio seemed dependent on the electrical
activity in the immediate environs. There was a noticeable increase in
noise during the installation of the Brüker AM400 Nuclear Magnetic
Fig. 4.2  Current-time transients recorded after stepping to $E_2$ for an electrode with no polishing between experiments. $E_{pc} = -756$ mV, $E_1 = -456$ mV, $E_2 = -256$ mV. $T = 18^\circ C$, $[H_2SO_4] = 4.65$ mol L$^{-1}$, digitised data.
Fig. 4.3 Current-time transients recorded after stepping to $E_2$ for experiments performed on an electrode polished at different times using the same polishing technique. $E_{pc} = -756$ mV. $E_1 = -456$ mV. $E_2 = -276$ mV. $T = 18^\circ$C. digitised data.
Resonance Spectrometer. Also several banks of fluorescent light tubes appeared to be responsible for some noise. For this reason potential step experiments were performed at night or during weekends and public holidays with noisy lights turned off. Transients of poor quality such as the worst example depicted in Fig. 4.3, that were occasionally measured were discarded and the experiment repeated if possible.

In view of the high degree of variability caused by re-polishing the electrode (Fig. 4.3), the strategy for obtaining quantitative transients was to perform a complete set of experiments without repolishing. The resulting data set gave good reproducibility (see Fig. 4.2), and could be used to determine the effect of variables such as $E_{pc}$, $E_1$, and $E_2$.

4.4 Variation of the transients with cathodic reduction stepping potential, $E_{pc}$

The variation of transients with different values of $E_{pc}$, measured for the same value for $E_2$ and without re-polishing are shown in Fig. 4.4. The shapes of the transients are very similar and the overall variation in the peak current is 14%. The variation in peak current does not follow a clear correlation with the value for $E_{pc}$.

4.5 Transient dependence on the anodic stepping potential, $E_2$

A series of current-time transients for experiments performed for different values for $E_2$ and same values of $E_{pc}$ and $E_1$ on an electrode without re-polishing are shown in Fig. 4.5. The transients are typified by an initial current at time $t = 0$, followed by an initially linearly increasing current with time. The double-layer charging peak at short times (1 ms) is
Fig. 4.4  Current-time transients recorded after stepping to $E_2$ for different values of the cathodic reduction potential, $E_{pc}$. $E_1 = -456$ mV, $E_2 = -266$ mV. $T = 18^\circ$C, digitised data.
not shown in any of these figures. The increasing current passes through a maximum, and then the current diminishes with time. Both the initial current, terminated $i_0^o$, and the initial current-time gradient, $(d i/d t)_{t=0}$, increase with more anodic values of $E_2$. This is more clearly shown in an expanded plot of the transients at shorter times in Fig. 4.6. At the lowest value for $E_2$ the current gradient approaches zero and no current maximum is observed. The time for the current maximum to be reached is shorter, and the current after the peak diminishes more rapidly, for more anodic values for $E_2$. The values for $i_0^o$ and $(d i/d t)_{t=0}$ from Figs. 4.5 and 4.6 are listed in Table 4.1 and displayed in Fig. 4.7. The semi-log plot of $i_0^o$ vs $E_2$ shows two linear regions with a slope of 29 mV decade$^{-1}$ for $E_2$ below -266 mV and 65 mV decade$^{-1}$ for $E_2$ above this value. The semi-log plot of $(d i/d t)_{t=0}$ vs $E_2$ shows a smooth curve with a larger potential dependence at less anodic values for $E_2$.

4.6 Temperature and anodic stepping potential dependence of the transients.

A strict regime was employed for the investigation of the temperature dependence. For each temperature the electrode was polished and then placed in the cell with the degassed electrolyte pre-cooled or heated to the required operating temperature. The electrode was potentiodynamically cycled using cyclic voltammetry as described in Section 4.1. The cyclic voltammery behaviour was then determined (as reported in the previous chapter, Section 3.8) and then the potential step experiments were performed. Polishing was required between temperature settings as it was inconceivable to allow the employment of only one
Fig. 4.5  Current-time transients recorded after stepping to $E_2$ for different values of $E_2$ on an electrode within the same polishing period. $E_{pc} = -756$ mV, $E_1 = -456$ mV. $T = 18^\circ$C, digitised data.
Fig. 4.6  Expanded view of the current-time transients displayed in Fig. 4.5 recorded after stepping to $E_2$ for different values of $E_2$ on an electrode within the same polishing period. The initial slope, $(di/dt)_{t=0}$, is indicated by the solid line for each transient and $x$ denotes the digitised data points. For clarity the transient recorded after stepping to $E_2 = -306$ mV is not included. $E_{pc} = -756$ mV, $E_1 = -456$ mV. $T = 18^\circ$C. digitised data.
Table 4.1  Dependence of the initial current and the initial current gradient on the anodic stepping potential. \([\text{H}_2\text{SO}_4] = 4.65 \text{ mol L}^{-1}\). \(T = 18^\circ\text{C}\), \(E_{pc} = -756 \text{ mV}\), \(E_i = -456 \text{ mV}\), data are plotted in Fig. 4.7, digital data.

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Fig. 4.7 Plot of the logarithms of the initial current at $t = 0$, $i^0$, and the initial current-time gradient at $t = 0$, $(di/dt)_{t=0}$, versus the stepping potential, $E_2$, for the transients shown in Fig. 4.5. □ $\log (i^0 \text{ mA cm}^{-2})$, △ $\log ((di/dt)_{t=0} \text{ mA cm}^{-2} \text{ s}^{-1})$. $T = 18^\circ\text{C}$. Data are listed in Table 4.1.
polishing over a period of several days. Experiments during the course of the present work have shown the build-up of irreducible corrosion products on the surface of the electrode over several hours.

The transients were of the same form as those shown previously. The parameters of interest are the initial current, \( i_0 \), and the initial slope, \( (di/dt)_{t=0} \), these are listed in Table 4.2. Fig. 4.8 shows the semi-log plot of \( i_0 \) vs \( E_2 \) for each temperature. The plot shows that the initial current increases with increasing potential as was evident in Fig. 4.7 and in general also increases with temperature. Fig. 4.9 shows the semi-log plot of \( i_0 \) vs \( T \) for each potential. This figure shows that there is a greater temperature dependence at lower potentials. Fig. 4.10 depicts the semi-log plot of \( (di/dt)_{t=0} \) as a function of potential for each temperature. In general \( \log(di/dt)_{t=0} \) increases with increasing potential as before, and the relationship is non-linear, with greater curvature at the lowest temperatures. Fig. 4.11 shows the semi-log plot of the initial slope as a function of temperature for each potential. This figure shows the sharp discontinuity at \(-16^\circC\) where no finite current-time slopes are found.

### 4.7 A summary of the behaviour of the potential-step transients.

The transients displayed in Figs. 4.2 and 4.3 show that experiments may be only directly compared for the same polishing period. The transients in Fig. 4.2 show good reproducibility for the initial current, the initial slope, peak position and height, and for the gradual decay after the peak. Conversely the transients depicted in Fig. 4.3 for repeated polishing treatments show marked variation in the above mentioned features. The
Table 4.2 Dependence of the initial current and the initial current gradient on the anodic stepping potential and electrolyte temperature. 

\[ [H_2SO_4] = 4.65 \text{ mol L}^{-1}, \quad E_{pc} = -756 \text{ mV}, \quad E_i = -456 \text{ mV}, \]  

data are plotted in Figs. 4.8 to 4.11, digital data.

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Fig. 4.8  Plot of the logarithm of $i_0^*$ versus $E_2$ for different electrolyte temperatures.  $T$.  $\bigcirc -16^\circ C$, $\square -10^\circ C$, $\triangle -5^\circ C$, $+$ $0^\circ C$.  $\times 5^\circ C$, $\diamond 10^\circ C$, $\times 15^\circ C$, $\ast 20^\circ C$, $\times 25^\circ C$, $\star 30^\circ C$.  data are listed in Table 4.2.
Fig. 4.9  Plot of the logarithm of $i_d^0$ versus $T$ for different stepping potentials, $E_2$. $\bigcirc$ -300 mV, $\square$ -290 mV, $\triangle$ -280 mV, $+$ -270 mV, $\times$ -260 mV, $\Diamond$ -250 mV, $\ast$ -240 mV, $\bigstar$ -230 mV, data are listed in Table 4.2.
Fig. 4.10  Plot of the logarithm of \( (di/dt)_{t=0} \) versus \( E_2 \) for different electrolyte temperatures, \( T. \) □ -10°C, △ -5°C, + 0°C, × 5°C, ◊ 10°C, × 15°C, ※ 20°C, × 25°C, ⦿ 30°C. data are listed in Table 4.2.
Fig. 4.11 Plot of the logarithm of \((dt/dt)_{t=0}\) versus \(T\) for different stepping potentials, \(E_2\). \(\bigcirc\) -300 mV, \(\blacklozenge\) -290 mV, \(\bigtriangleup\) -280 mV, + -270 mV, \(\times\) -260 mV, \(\bigcirc\) -250 mV, \(\bigstar\) -240 mV, \(\bigstar\) -230 mV. Data are listed in Table 4.2.
variation is greater than that observed for the variation in cyclic voltammograms for different polishings discussed in the previous chapter. This is indicative that the potential step technique is inherently more sensitive to surface preparation than cyclic voltammetry.

The effect of the cathodic pretreatment on cyclic voltammetry experiments was a feature of the last chapter and the effect of the cathodic limit $E_{pc}$ was investigated for potential step experiments. Fig. 4.4 shows that there is no pronounced variation in the experimental transients with variation in $E_{pc}$ (for the same anodic stepping potential). The variation in the peak current value is only slightly greater than that for the transients in Fig. 4.2 where identical sequential experiments were performed. This marginally larger variation may be ascribed to the presence of hydrogen bubbles on the surface of the electrode. The lack of any significant variation with $E_{pc}$ is in direct contrast to the results for cyclic voltammetry.

The variation of experimental transients with the anodic stepping potential, $E_2$, is shown in Figs. 4.5 and 4.6. The features are that the initial current, $i_0^o$, and the initial current-time slope, $(di/dt)_{1-o}$, increase with $E_2$. The increasing current passes through a maximum at shorter times and the following decaying current diminishes more rapidly with increasing $E_2$. At the lowest potential explored for $E_2$ no increasing current gradient is observed and the current follows only a decaying transient with time.

The temperature variation of the potential step transients are depicted in Figs. 4.8 to 4.11. Direct comparison between data at different temperatures is not available due to the need to polish the electrode
between temperature settings. In general it is evident the initial current is more influenced by temperature at lower values for $E_2$ and that the failure to observe positive values for the initial slope is moved to progressively more positive values for $E_2$ with lower temperature.

4.8 Previous reports on potential-step transients.

Previous authors$^{31,33-37,40-42,76}$ have shown that the electrochemical oxidation of lead in sulphuric acid in the lead/lead sulphate potential region as described by Pavlov et al$^{25-27}$ can be divided into two further potential regions. At low anodic potentials, oxidation results in soluble Pb$^{2+}$ species that diffuse away from the electrode.$^{31}$ At more anodic potentials, rising current transients characteristic of a charge-transfer reaction controlled by growth of a solid phase are found. The dissolution reaction is not replaced by the formation of the solid phase but operates simultaneously. Archdale and Harrison$^{31}$ have proposed that in 1.0 mol L$^{-1}$ H$_2$SO$_4$ the dissolution reaction may result in diffusion of several Pb(II) species away from the electrode, that of Pb$^{2+}$$_{(aq)}$ (presumably solvated) and soluble PbSO$_4$$_{(aq)}$:

$$\text{Pb} - 2e^- \rightarrow \text{Pb}^{2+}$_{(aq)}$ \quad \rightarrow \text{D}_1 \rightarrow \text{PbSO}_4$_{(aq)}$ \quad \rightarrow \text{D}_2$$

These workers also proposed that at higher concentrations dissolution via the species Pb(SO$_4$)$_2$ was viable. Danel and Plichon$^{48}$ have summarised the solid and solution reactions with a scheme:
Archdale and Harrison\textsuperscript{31} have confirmed with ring-disc electrodes that the solution reaction is diminished as the solid reaction proceeds.

All previous studies of the potential-step transients have reported linear relationships between $i$ and $t$ near the beginning of the transients. Archdale and Harrison\textsuperscript{31} however, reported an initially decreasing current at short times before the linear $i$ vs $t$ dependence was evident. This initially decreasing current is not to be confused with the double-layer charging transient which is completed at very short times. Other workers\textsuperscript{40-42} have reported similar transients to those depicted in the present work.

Previous authors have not commented on the variation of the potential-step transient parameters of the initial current and initial slope on the anodic stepping potential. Fig. 4.7 depicts the dependence of these parameters and shows that the slope becomes increasingly more dependent on potential for low values of $E_0$, at the lower limit the dependence is of the order of 10 mV decade$^{-1}$.

Interpretation of the transients due to the solid reaction has resulted in conflicting mechanisms being presented for the charge-transfer reaction. Brennan and Hampson\textsuperscript{39} have proposed that the development of the solid phase is governed by a two-dimensional instantaneous nucleation and growth process as described by the Bewick, Fleischmann, and
Thirsk\textsuperscript{50,51} (BFT) model. This model involves the lateral growth of a surface layer from the random nucleation and subsequent expansion of two-dimensional patches under perimeter control. The BFT model predicts linear $i$ vs $t$ transients until overlap of the expanding patches begins to reduce the perimeter available for growth. Conversely Archdale and Harrison\textsuperscript{31} postulated that the growth of the solid phase should be governed by a three-dimensional nucleation and growth process as the two-dimensional growth did not adequately account for the charge associated with the solid phase deposited on the electrode. Fleming and Harrison\textsuperscript{35} in a later study suggested progressive nucleation of a three-dimensional phase. Hampson and Lakeman\textsuperscript{41} concluded that the nucleation is progressive and either two- or three-dimensional growth, despite both these mechanisms predicting non-linear $i$ vs $t$ transients. The linear slope was considered to be a misleading artifact due to the contribution by direct dissolution from the surface. In a later paper Hampson and Lakeman\textsuperscript{43} discussed the transients in the light of two models:

1) instantaneous nucleation and growth of three-dimensional centres, and

2) instantaneous nucleation and growth of two-dimensional centres.

The fit of the experimental transients to the models was superior for the two-dimensional case.

Hampson and Lakeman\textsuperscript{45} have reported transients for potential step experiments performed at $-30^\circ$C. Little comment was made on the form of the transients but by direct comparison with the published figures in their earlier work at room temperature\textsuperscript{43} it can be seen that they obtained similar results to the present study.
In summary, previous authors having found good agreement with the BFT model of instantaneous nucleation and two-dimensional growth have discarded the notion as too unlikely, due to the large number of equivalent monolayers deposited on the surface. Thus they have insisted that the growth must be three-dimensional and that the simultaneous dissolution reaction was destroying any chance of elucidation of the mechanism. The results presented in this study will be discussed in the following chapter in terms of a kinetic model for instantaneous random nucleation and growth of a three-dimensional layer on the surface that obeys equivalent rate laws to the BFT model for instantaneous nucleation and growth of a monolayer. The kinetic model also includes consideration of the solution reaction and eventual passivation of the electrode.

4.9 Comparison with potential sweep experiments.

The potential step transients are similar in form to the potential-ramp/potential-hold transients for extreme cathodic pretreatment discussed in the previous chapter (Section 3.6). Rising linear transients followed by a peak and then gradual decay in current are evident in both sets of transients. In the previous chapter it was concluded that the transients were due to growth of a conductive layer of PbSO₄ (Section 3.11). When the electrode was not cathodically pretreated to extreme limits then only falling transients were evident. This was interpreted as the film already being present (due to lack of reduction on previous cathodic treatment). Hence charge-transfer was operating through the film, this being diminished with time by passivation.

In the potential step experiments reported in this chapter, growth
transients were found for every cathodic pretreatment explored. This is in direct contrast to the potential-ramp/potential-hold experiments of Chapter 3. It should be noted that current peaks indicating surface film growth were obtained in the potential-step experiments even if the potential was first swept to $E_{pc}$, rather than simply holding $E_{pc}$ constant for 10 s (Section 4.1).

There is a clear discrepancy between the cathodic pretreatment dependence results for potential-ramp/potential-hold and potential-step experiments: potential-step shows only nucleation and growth type transients while potential-ramp/potential-hold exhibits growth behaviour and a further response which is attributed to precipitation only. There is no apparent explanation for this dichotomy.

4.10 Conclusion.

In conclusion, potential step experiments show transients due to growth of a solid phase except at low values for $E_2$ where only the dissolution reaction is present. The initial slope is linear, indicative of a charge-transfer controlled by a two-dimensional growth law. In contrast to the cyclic voltammetry experiments there is not good reproducibility between different polishing times and there is no variation in the transients with cathodic pretreatment at various values of $E_{pc}$. The transients will be discussed in light of a kinetic model in the following chapter.
CHAPTER FIVE

MODELLING OF THE ANODIC BEHAVIOUR FOR CYCLIC VOLTAMMETRY AND POTENTIAL STEP EXPERIMENTS.

5.1 Introduction.

The previous two chapters have explored the electrochemical reaction of the lead anode in sulphuric acid using the potential control techniques of potential step and cyclic voltammetry. The conclusion drawn from the results was that the anodic behaviour of lead is mediated by the presence of a conductive thin film on the surface of the electrode. Potential-ramp/potential-hold experiments displayed transients suggestive of nucleation and growth of this phase when the electrode was cathodically pretreated to extreme potentials. In contrast to this potential step experiments showed growth transients for all cathodic pretreatment potentials. Section 5.2 presents a model for the potential step anodic behaviour and the deconvoluted results are discussed. The new model contains elements which have been suggested by previous authors but never quantified to the extent shown in this section. The resulting parameters for the potential step model are applied to the cyclic voltammetry experiment for cathodically pretreated electrodes in Section 5.3. A resistance model is proposed in Section 5.4 for the multi-cycled cyclic voltammetry experiments in which the conductive thin film is present prior to the bulk oxidation of the metal lattice. The existing
resistance models based on the work by Müller and subsequent modification by Birss and Wright for control of charge-transfer rate by solution resistance in a porous passivating layer, are shown to be inadequate. An alternative model is proposed based on the changing electrode resistance caused by passivation of a conductive thin film.

5.2 Model for the anodic reaction in potential step experiments.

5.2.1 Introduction.

The model is based on the processes shown in Fig. 5.1. Each feature is considered in turn and the appropriate current density determined. The summation of all the terms yields a theoretical current transient. The parameters of the individual terms were optimised so that the theoretical and observed transients are coincident. The overall anodic reaction consists of five separate processes which are coupled according to their separate rate laws. Only three of the processes contribute to the current directly.

i) A multilayer is developed, assumed to be a compact layer of non-stoichiometric PbSO₄. This layer is imagined to grow as expanding circular patches of constant thickness to eventually cover the surface. The rate constant for growth is potential dependent, the surface fractional coverage of the multilayer is given by \( \theta \), and the current density arising from the growth is given by \( i_g \).

ii) There is a zone of fractional coverage \( \phi \) surrounding the multilayer, in which the multilayer has not reached its full thickness, but there is sufficient PbSO₄ on the surface to prevent direct
Fig. 5.1 Schematic of the processes proposed for the potential step model. The charge-transfer reactions are: a) instantaneous nucleation and growth of multilayer cylinders, b) dissolution of soluble Pb$^{2+}$ species away from the electrode, c) transmission through the multilayer. Process d) accounts for precipitation of PbSO$_4$ on the multilayer and e) provides an edge profile correction to the growing multilayer centres.
dissolution. This zone is considered to be a small correction factor to the profile of expanding multilayer cylinders: a trapezoidal cross section phase is more natural than a sharp boundary at the growing edge. It is thus termed the 'edge profile correction'.

iii) There is dissolution directly from the bare lead surface. The current density, \( i_d \), due to this dissolution is proportional to the fractional area of the bare electrode, including a correction for the edge profile, thus \( i_d \) is proportional to \( (1 - \theta - \varphi) \).

iv) A three-dimensional bulk phase of passivating PbSO\(_4\) of fractional coverage \( \psi \) is developed by precipitation of crystallites from the saturated solution of Pb\(^{2+}\) adjacent to the electrode. This phase is constrained to grow on regions of the electrode already covered by the multilayer (in cases where the critical multilayer formation potential is not achieved, then three-dimensional PbSO\(_4\) may grow on the bare lead surface).

v) There is dissolution through the multilayer due to the transmission of Pb\(^{2+}\) ions by the applied electric field. The transmission of ions is possible due to the non-stoichiometry of the PbSO\(_4\) in the multilayer. The current density, \( i_l \) is proportional to \( (\theta - \psi) \), the fractional area of multilayer upon which no bulk phase is yet established.

These features identify the physical properties of the model. The time dependence of \( \theta, \varphi, \psi \), and the length of the multilayer perimeter must be determined to calculate the theoretical current transient.
5.2.2 Nucleation and growth of a multilayer controlled by two-dimensional kinetics.

The nucleation and growth current, \( i_g \), as described by the Bewick, Fleischmann, and Thirsk model\(^{50,51}\) is proportional to the perimeter of the expanding growth centres. In the present model the rate or current is dependent on the perimeter of the completed multilayer cylinders. The following derivation follows closely the method originally used by Bewick et al.\(^{51}\)

\[
i = N_e n_F k_g (2\pi r)
\]  
(5.1)

where:

- \( N_e \) is the surface density of nucleation sites [cm\(^{-2}\)]
- \( n \) is the electron number
- \( k_g \) is the rate constant for the growth per unit length of perimeter [mol cm\(^{-1}\) s\(^{-1}\)] and
- \( r \) is the radius of the expanding site [cm]

Bewick et al\(^{51}\) related the growth current with the rate of change of the volume, however in the present model the rate of change of charge has been employed, thus

\[
\dot{i}_g = q_g \frac{d\theta}{dt}
\]  
(5.2)

where:

- \( q_g \) is the charge density required for the phase completion [C cm\(^{-2}\)]
- \( \theta \) is the fractional coverage of the surface of the growing phase
At short times before overlap of the cylinders becomes significant:

\[ \theta = N_0 \pi r^2 \]  

(5.3)

differentiation of (5.3) with respect to \( t \), substitution into (5.2) and equating with (5.1) yields:

\[ N_0 \pi q_br \frac{dr}{dt} = N_0 nFk_s 2\pi r \]  

(5.4)

thus

\[ \frac{dr}{dt} = nFk_s / q_s \]  

(5.5)

and integration with respect to \( t \) yields

\[ r = nFk_s t / q_s \]  

(5.6)

substituting for \( r \) in (5.1) results in

\[ i_s = 2\pi N_0 n^2 F^2 k_s^2 t / q_s \]  

(5.7)

Bewick et al.\textsuperscript{51} adapted the theory by Avrami\textsuperscript{78} to show that if random overlap occurs between expanding centres, then the actual fractional coverage, \( \theta \), is related to the fractional coverage in absence of
overlap, $\theta_{\text{ext}}$, by

$$\theta = 1 - \exp(-\theta_{\text{ext}})$$  \hspace{1cm} (5.8)

where

$$\theta_{\text{ext}} = N_0 \pi r^2$$  \hspace{1cm} (5.9)

substituting for $r$ using (5.6) yields

$$\theta = 1 - \exp(-N_0 \pi n^2 F^2 k_r^2 t^2 / q_a^2)$$  \hspace{1cm} (5.10)

now substituting (5.10) into (5.2) achieves the desired result

$$i_g = (2\pi N_0 n^2 F^2 k_g^2 t / q_a) \exp(-N_0 \pi n^2 F^2 k_g^2 t^2 / q_a^2)$$  \hspace{1cm} (5.11)

5.2.3  \hspace{0.5cm} \textit{Edge profile of the expanding multilayer centres.}

The growing two-dimensional centres are described in 5.2.1 as cylinders. This assumes that the rate of growth of this phase perpendicular to the surface is many times larger than the rate of growth laterally given by (5.5). It is more reasonable to assume that these two rates are comparable. Therefore a correction to the edge profile can be applied. This is a zone of fractional coverage $\phi$ that surrounds the completed growing centres in which the multilayer is incomplete. The growth current, $i_g$, operates in this region and direct dissolution is not
possible. It is proposed that $\phi$ is proportional to $\theta$ but is also diminished by the overlap factor $(1 - \theta)$

$$\phi = a\theta(1 - \theta)$$

(5.12)

where $a$ is a dimensionless proportionality constant.

Since $\phi$ is relatively small, changes in $\phi$ make no significant contribution to the overall current. It should be noted that the rate of the growing multilayer (5.11) is not proportional to the leading edge of the growing phase but rather proportional to the perimeter of the multilayer which has reached its full thickness.

5.2.4 Dissolution from the bare lead surface.

The dissolution current, $i_d$, is assumed to be proportional to the uncovered fraction of the electrode, with $i_d^0$ being the value at $\theta = 0$.

$$i_d = i_d^0(1 - \theta - \phi)$$

(5.13)

or

$$i_d = i_d^0(1 - \theta(1 + a) + a\theta^2)$$

(5.14)

5.2.5 Transmission through the multilayer.

Lead ions are able to migrate through the multilayer due to the assumed non-stoichiometry of this phase. The transmission is constrained to occur through the completed multilayer in regions not covered by
passivating PbSO$_4$. Therefore the current due to this transmission, $i_t$, is proportional to $(\theta - \psi)$:

$$i_t = k_t(\theta - \psi) \quad (5.15)$$

where $k_t$ is the transmission rate constant [mol cm$^{-2}$ s$^{-1}$]

5.2.6 Growth of the passivating layer.

The rate of growth of the passivating layer is proportional to the fractional coverage of the electrode covered by the multilayer and as yet uncovered by the passivating layer, the multilayer providing a substrate for growth of the crystalline PbSO$_4$. The growth relationship is given by

$$d\psi/dt = k_p(\theta - \psi) \quad (5.16)$$

where $k_p$ is the passivation constant [s$^{-1}$]. Equation (5.16) cannot be integrated to give an equation for $\psi$ in terms of $t$ as a single variable. Therefore the solution for this relationship was determined numerically using the finite difference method at short time intervals ($\Delta t = 0.001$ s).

For potentials at which no multilayer formation occurs the three-dimensional passivating layer of microcrystalline PbSO$_4$ grows on the bare lead surface. The expression for the rate of coverage is now controlled by the fractional coverage of the electrode as yet uncovered by the crystalline PbSO$_4$ and is given by

$$d\psi/dt = k_p(1 - \psi) \quad (5.17)$$
or rewritten as

$$\psi = 1 - \exp(-k_{\ell}t)$$  \hspace{1cm} (5.18)

At these potentials the absence of a conductive film means that film transmission cannot take place, therefore \(i_\ell = 0\) and the expression for dissolution from the bare lead is

$$i_\ell = i_\ell^\circ (1 - \psi)$$  \hspace{1cm} (5.19)

5.2.7  \hspace{1cm} Total current and derivation of initial slope.

The total observed current, \(i_{\text{tot}}\), is given by

$$i_{\text{tot}} = i_g + i_\ell + i_f$$  \hspace{1cm} (5.20)

Since \(d\theta/dt = 0\) at \(t = 0\), from (5.10), it can be shown that differentiation of (5.20) with respect to \(t\) at \(t = 0\) yields

$$\left(\frac{dk_{\text{tot}}}{dt}\right)_{t=0} = 2\pi N_0 n^2 F^2 k_g^2 / q_g$$  \hspace{1cm} (5.21)

Differentiation of (5.11) under identical conditions gives the same result indicating that

$$\left(\frac{dk_{\text{tot}}}{dt}\right)_{t=0} = \left(\frac{di_g}{dt}\right)_{t=0}$$  \hspace{1cm} (5.22)
Therefore at short times it possible to evaluate the \(i \text{ vs } t\) gradient to determine the growth rate constant by rearranging (5.21) with respect to \(k_g\). However the nucleation site surface density, \(N_0\), is an unknown parameter. Fortunately the product \(N_0k_g^2\) need never be separated into the individual factors to solve for \(i_g\) and \(i_f\).

5.2.8 Fitting of the model to the potentiostatic transients.

The parameters for the model were evaluated for the set of experimental transients depicted in Figs. 4.5 and 4.6 and discussed in Section 4.5. The product \(N_0k_g^2\) was determined from the experimental values of \((di/dt)_{t=0}\) listed in Table 4.1 using equation (5.21). The computer program \textsc{plotcrv} (Section 2.8) was employed to provide a manual interactive method for the optimisation of the parameters. The theoretical transient, together with the transients for the three contributing charge-transfer processes, were plotted on the Exzel AT computer screen simultaneously with the experimental transient. The parameters were manipulated until the theoretical transient was coincident with the experimental transient. Typical results are shown in Figs. 5.2 and 5.3. The fit for the special case at the lowest value for \(E_2\) is shown in Fig. 5.4; here only one term \(i_f\) contributes to the current. The edge profile correction constant \(a\) has a constant value of 0.5 for all potentials at which multilayers develop. The three remaining fitted parameters increase with increasing \(E_2\) and are listed in Table 5.1. The normal plot for \(q_g\) and the semi-log plots for \(k_p\) and \(k_f\) are shown in Fig. 5.5.
Fig. 5.2  Plot of the simulated transient for the model optimised for the experimental data (denoted by x). The individual charge-transfer transients are included. $E_I = -456$ mV, $E_2 = -276$ mV, $E_{pc} = -756$ mV. $T = 18^\circ$C, digitised data.
Fig. 5.3  Plot of the simulated transient for the model optimised for the experimental data (denoted by x). The individual charge-transfer transients are included. $E_1 = -456 \text{ mV}$, $E_2 = -266 \text{ mV}$, $E_{pc} = -756 \text{ mV}$, $T = 18\text{°C}$, digitised data.
Fig. 5.4  Plot of the simulated dissolution transient for the special case at $E_2 = -306$ mV where nucleation and growth and film transmission are not evident. Experimental data points denoted by x. $E_1 = -456$ mV, $E_{pc} = -765$ mV, $T = 18^\circ$C, digitised data.
Table 5.1   List of the optimised parameters for the potential step model. The parameter $m$ denotes the number of equivalent monolayers in the multilayer. The parameter $N_0k_s^2$ for multilayer growth is not tabulated, but can be readily obtained from the data for $(di/dt)_{t=0}$ in Table 4.1 by using equations (5.21) and (5.22), with the values for $q_s$ below. Data are plotted in Fig. 5.5.

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Fig. 5.5  Plot of the multilayer charge $q_*$ and the semi-log plots of the film transmission and passivation constants, $k_t$ and $k_p$ respectively, vs $E_2$. Data are listed in Table 5.1.
5.2.9 Discussion.

The model is found to be of good fit over the potential range explored as is evident in Figs. 5.2 to 5.4. There is an inherent weakness in the model in that it requires three parameters to be optimised (a fourth parameter, a, is found to be constant). This is unavoidable as the system is complicated with several simultaneous processes. A point in favour of the model is that the three charge-transfer processes are dependent on the instantaneous nucleation and growth reaction. Thus the transients are not being optimised to the sum of three independent processes. The uniqueness of the optimised parameters for each transient was tested rigorously by selection of vastly differing starting values. Optimisation was manual in that there was a human choice in the parameter changes for each theoretical transient calculated by the computer. A fully computerised optimising program SIMPLEX was initially employed but it was found that this program sacrificed the important features of the initial slope and peak to minimise the sum of the least squares differences.

The model developed from consideration of a theoretical transient defined only by a nucleation and growth current as described in 5.2.2 and a dissolution current, \( i_d \), given by

\[
    i_d = i_d^0 (1 - \theta)
    \]  

(5.23)

This limited model adequately described the observed current until the current peak was attained after which the theoretical transient decayed too quickly. Investigation of the relationship between the current
unaccounted for after the peak and the coverage by the multilayer. This showed that a direct correlation was initially evident followed by a gradual decrease. The model was developed to allow for these features, namely the film transmission current which at short times is proportional to the coverage of the multilayer, and the precipitation of crystalline PbSO₄ that progressively stifles the transmission. The final fine tuning of the model required consideration of the 'edge profile correction'. This zone is requisite for two reasons: firstly the growth current needs a region to operate in and it is most unlikely that it would operate in the same area as direct dissolution; secondly, the charge of the multilayer is equivalent to many monolayers and it is inconceivable that rigid profiles could be considered.

The optimised 'edge profile correction' parameter, \( a \), is found to have a constant value of 0.5. This implies that, at short times when overlap of the growing multilayer centres is not significant, the rate of growth of the edge of the multilayer is 1.5 times the rate of growth of the full multilayer. Thus the rate of growth laterally along the electrode surface is greater than the rate of growth vertically.

Figs. 5.2 and 5.3 show that at the beginning of the transient the processes that dominate are nucleation and growth and dissolution from the bare surface. At longer times the transmission current dominates and is under control by precipitation only as the multilayer is completed. The separation of the regions in which the different charge-transfer components dominate facilitates deconvolution.

The initial linear current dependence at short times is retained despite the rapidly diminishing dissolution reaction due to the small, but
increasing, transmission current. The diminishing dissolution current predicted by this model is consistent with the ring-disc electrode experiments reported by Archdale and Harrison\textsuperscript{32} where the ring current due to reduction of soluble Pb\textsuperscript{2+} diminishes with the progression of the nucleation and growth process. Furthermore their results suggest that the soluble Pb\textsuperscript{2+} species, formed as a result of the transmission current, is for the most part captured by the growth of the passivating microcrystalline PbSO\textsubscript{4} layer.

Since the specific charge $q_{s}$ for the multilayer film increases linearly with $E_{2}$ (Fig. 5.5) it follows that the thickness of this phase increases linearly with potential. The thickness can not be determined with confidence as the density of this phase is unknown. However, the equivalent number of monolayers at each potential is given in Table 5.1 assuming a charge of 325 $\mu$C cm\textsuperscript{-2} is required to form a monolayer (as for orthorhombic PbSO\textsubscript{4}).\textsuperscript{43} The variation of $q_{s}$ with potential is consistent with the theory proposed by Chao et al\textsuperscript{80} that suggests that such a film would mediate the potential drop across the film by having a constant field.

The semi-log plots of the rate constant for the film transmission current, $k_{f}$, vs $E_{2}$ and of the passivation constant, $k_{p}$, vs $E_{2}$ are shown in Fig. 5.5. The slopes of the linear regions have slopes of 26 and 37 mV decade\textsuperscript{-1} respectively.
5.3 Model for the anodic reaction in cathodically pretreated cyclic voltammetry experiments.

5.3.1 Introduction.

It has been reported in the previous two chapters that for extreme cathodically pretreated cyclic voltammetry experiments, potential-ramp/potential-hold experiments display transients akin to nucleation and growth potential-step transients. Therefore it is appropriate that the model derived for the potential step experiments be adapted to apply to cathodically pretreated cyclic voltammetry experiments.

5.3.2 Description of the model.

The individual rate equations for the nucleation and growth, dissolution, and film transmission charge-transfer reactions are identical to those described in Section 5.2. The rate constants and parameters however now vary with potential, and hence time, in the cyclic voltammetry experiment. Several assumptions are made:

i) The semi-log plots of \( k_p \) and \( k_f \) follow linear dependence on \( E \) at potentials beyond that explored in potential step experiments. Similarly it is assumed that the multilayer charge density, \( q_s \), varies linearly with potential for all potentials. These assumptions mean that values of the parameters \( k_p \), \( k_f \), and \( q_s \) can be attained over the whole range of the cyclic voltammetry experiments.

ii) For facile manipulation of the equations the product \( N_0 k_s^2 \) needs to be separated into the individual terms. There is no information available to determine \( N_0 \), the density of nuclei giving
rise to the growing centres. It is assumed that the density of nuclei $N_0$ is constant with potential and has a value of $6.25 \times 10^8 \text{ cm}^{-2}$. This results in an average spacing of $0.4 \text{ \mu m}$, a figure which is approximately eight times the maximum thickness of the multilayer observed in Section 5.2 (assuming a similar density to stoichiometric PbSO$_4$).

$\text{iii)}$ The growing multilayer cylinders do not need to complete the requisite charge or equivalent number of monolayers prior to increase of the multilayer. The rate of increase of the radius is controlled by equation (5.5). It is assumed that the inner regions of the multilayer formed at lower potentials, and hence a smaller number of equivalent monolayers, are 'filled in' by the transmission current until a constant field is formed through this phase.

The equations employed for the variation of $q_\phi$, $k_\rho$, $k_\tau$, $i_0^\circ$, and $(di/dt)_{t=0}$ with potential are derived from the least squares linear fit to the data depicted in Figs. 4.6 and 5.5. The multilayer growth constant, $k_\phi$, is determined via a rearrangement of equations (5.21) and (5.22)

$$k_\phi = (q_\phi (di/dt)_{t=0} / 2\pi N_0 r^2 F^2)^{1/2}$$

(5.24)

The time is incremented by small steps ($\Delta t = 0.001 \text{ s}$) so that the parameters may be determined and hence the charge transfer reactions may be calculated. The algorithm employed in the computer program CVSIM (Section 2.8) used to calculate the theoretical transient consisted of: incrementing the time, calculating the potential, calculating the radius and
charge $q_a$ of the expanding centres, determining the constants $k_p$ and $k_q$, and then calculating the individual current terms.

5.3.3 Results.

The dynamic cyclic voltammetry model was solved for sweep rates in the range 5 to 100 mV s$^{-1}$. The resulting transients for the Al peak are depicted in Fig. 5.6. The transients are of similar form to those shown in Fig. 3.6 for cathodically pretreated voltammograms. Fig. 5.7 displays digitised versions of the experimentally measured transients on the same scale as those determined by the present model. Fig. 5.7 shows that the experimental anodic waves have nearly coincident forward slopes to the Al peak with slightly higher current for successively lower sweep rates. The computer simulated transients follow closely this behaviour with very similar position and magnitude of the current and even predict the marginally higher current at lower sweep rates. The peak current value, $i_{A1}$, for both the experimental and simulated waves are given in Table 5.2 and plotted in Fig. 5.8 as a function of the square root of the sweep rate. The experimental transients show linear dependence as is described in Section 3.5. The simulated transients however display exponential dependence of $i_{A1}$ on $\nu^{1/2}$ and at high sweep rates this feature is markedly larger than that determined experimentally. At sweep rates in the range 5 to 20 mV s$^{-1}$ the simulated transients follow more closely the experimental transients. The sharp decrease in current after the anodic peak observed experimentally is not predicted by the model and only gradual passivation occurs. Fig. 5.9 displays the simulated Al peak and the individual contributions from nucleation and growth, dissolution, and film
Fig. 5.6  Plot of the simulated anodic peaks for a cathodically pretreated electrode in cyclic voltammetry experiments at various sweep rates.
Fig. 5.7  Plot of the experimental anodic peaks for a cathodically pretreated electrode in cyclic voltammetry experiments at various sweep rates. $E_c = -756$ mV, $E_a = 244$ mV, digitised data.
Table 5.2  List of experimental and predicted values for the anodic peak current $i_{A1}$ in cathodically pretreated cyclic voltammograms. Data are plotted in Fig. 5.8. The experimental data is similar to that listed in Table 3.2 and plotted in Fig. 3.9 for cathodically pretreated voltammograms.

<table>
<thead>
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<th>$v$/mV s$^{-1}$</th>
<th>experimental</th>
<th>model</th>
</tr>
</thead>
<tbody>
<tr>
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<td>86.9</td>
<td>143.4</td>
</tr>
<tr>
<td>50</td>
<td>58.6</td>
<td>85.5</td>
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<tr>
<td>20</td>
<td>36.8</td>
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<td>10</td>
<td>25.2</td>
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</tr>
<tr>
<td>5</td>
<td>16.2</td>
<td>13.4</td>
</tr>
</tbody>
</table>
Fig. 5.8 Plot of the anodic peak current $i_{\text{a1}}$ for both experimental (△) and simulated (□) transients shown in Figs. 5.6 and 5.7. The data are listed in Table 5.2.
Fig. 5.9  Plot of the simulated anodic peak for a sweep rate of 20 mV s⁻¹. The current contribution for the individual processes are included.
transmission, for a sweep rate of 20 mV s\(^{-1}\). This figure shows that at short times the Al peak is dominated by the dissolution reaction. Multilayer growth requires a significant time to develop and this charge-transfer largely controls the centre of the anodic wave. As the multilayer develops the resulting film transmission becomes more significant and after completion of the multilayer film, transmission and subsequent passivation govern the wave.

5.3.4 **Discussion.**

The computer model shows a good fit to the forward slope of the Al peak, both in the position and magnitude of the current wave. The model also predicts the slightly larger currents observed experimentally on the forward slope at progressively lower sweep rates. This slightly larger current may be explained by consideration of the time integral for each sweep rate. For a given potential on the forward slope the rate laws of multilayer growth are identical but the lower sweep rates have larger coverage when compared with high sweep rates as there has been sufficient time to grow this phase. As a consequence the total perimeter length of the growing multilayer centres is greater and hence the growth current is larger for lower sweep rates. This is mostly offset by a decreased dissolution current but contribution by the resultant film transmission current yields an overall larger current at lower sweep rates. The model does not describe the peak current or peak current variation well at high sweep rates and provides only moderate agreement at low sweep rates. The sharp passivation observed experimentally is also not adequately predicted by the model. An explanation for both these features
not being well described may be because these events occur in the potential region at which the parameters are derived by extrapolation rather than experimentation (especially at high sweep rates) and the semi-log and linear assumptions may be inaccurate. Furthermore the passivation event in the experimental transient is clearly a rapid event rather than a progressive phenomenon as predicted by the potential step experiments. This rapid event may be due to a recrystallisation or phase transition event at large anodic overpotentials, specific to the cyclic voltammetry experiment.

The dissolution component of the simulated wave shown in Fig. 5.9 shows remarkably good agreement with the ring current measured for the reduction of soluble Pb²⁺ species in ring-disc cyclic voltammetry experiments reported by Danel and Plichon.⁴⁹ These workers reported that the ring current increases with the forward slope of the A1 peak but passes through a maximum and decreases at potentials where the disc current is still increasing. As a consequence the ring and disc current maxima are not coincident. The contribution to the ring current by reduction of Pb²⁺_(aq) formed as a result of film transmission (according to the scheme depicted in Fig. 5.1) is diminished due to capture of this species by the development of the passivating microcrystalline PbSO₄ layer. This is consistent with the ring-disc potential step experiments reported by Archdale and Harrison⁴² and interpreted in Section 5.2.9 in which it is proposed that the only soluble Pb³⁺ species apparent in ring-disc experiments are a result of the dissolution charge-transfer process. The maximum for the simulated iₓ wave is also coincident with the maximum for the pseudo-capacitance depicted in Fig. 3.16.
5.4 Model for the anodic reaction for multi-cycled cyclic voltammetry experiments.

5.4.1 Introduction.

The waveforms for the multi-cycled electrode in cyclic voltammetry experiments (Sections 3.4 and 3.5) are not well understood. The potential-ramp/potential-hold experiments (Fig. 3.10) show only decaying transients. This is indicative of the lack of growth of a multilayer, since no peak is observed, and the most probable event would be control of the anodic dissolution reaction by precipitation of passivating PbSO₄. The Al peak occurs at a potential 15 mV more cathodic than the Al peak for cathodically pretreated electrodes, and the forward slopes are at progressively more anodic values with decreasing sweep rate. A description was proposed at the conclusion of Chapter 3 (Section 3.11) that advanced the theory that the Al peak represents oxidation of the Pb electrode through a conductive thin film under resistance control. Passivation then occurs by precipitation of stoichiometric PbSO₄ onto this film.

A number of models have previously been suggested concerning cyclic voltammetry reactions controlled by ohmic resistance and subsequent precipitation. It is appropriate initially to discuss the present work with regard to these models. In general the resistance has been calculated by consideration of the solution resistance within the porous passivating layer. Section 5.4.2 presents two of these models and concludes that neither is applicable to the present work due to the high conductivity of H₂SO₄. A new model is proposed in Section 5.4.3 based on the changing resistance of a preformed conductive thin film as it becomes progressively passivated.
by PbSO₄.

5.4.2 The Müller/Arvia model and modifications.

The Müller passivation model predicts that for some systems the anodic reaction is controlled by a resistance comprising of the solution resistance, \( R_s \), and the resistance, \( R_p \), of the electrolyte within the pores of the growing passive layer (Fig. 5.10). It is assumed that dissolution of soluble oxidation products is negligible and thus the charge of the passive layer at any time is the integral of the anodic current to that time. The insoluble passive film nucleates at certain points and extends outwards over the whole surface as a layer of uniform thickness \( l_0 \). The pore resistance is given by

\[
R_p = l_0 / (\kappa A (1 - \xi))
\]

where

- \( l_0 \) is the uniform thickness of the film [cm],
- \( \kappa \) is the solution conductivity [S cm\(^{-1}\)],
- \( A \) is the area of the electrode [cm\(^2\)], and
- \( \xi \) is the coverage of the passive film.

Arvia et al. have adapted the resistance function to the potentiodynamic case and it can be shown that

\[
d\xi/dt = vt/(\kappa s (R_s + R_p))
\]
Fig. 5.10 Schematic of the passivation process defined by the Müller/Arvia pore resistance model.\textsuperscript{68,81} Oxidation of the Pb electrode results in growth of a passivating layer of PbSO\textsubscript{4} with surface coverage $\xi$ and a constant thickness $l_0$. 
and

\[ I = k_o \, d\xi/dt \]  \hspace{1cm} (5.27)

where \( k_o \) is a constant equivalent to the charge at the experimental anodic peak where \( \xi \) is assumed to be 0.99 using

\[ k_o = nF\rho A_l / M = Q/\xi \]  \hspace{1cm} (5.28)

where

\( Q \) is the anodic charge [C] and
\( \rho \) is the density of the growing phase [g cm\(^{-3}\)]

The thickness of the passive layer is also determined by equation (5.28).

The model predicts an anodic wave where the forward slope is initially linear under control by the solution resistance \( R_s \). As the coverage of the passive layer increases the current deviates from the linear slope, resulting in a rapid passivation as \( \xi \) approaches unity. The forward slopes are predicted to be sweep-rate independent and Macdonald\(^{69}\) has shown that the peak current should show linear dependence on \( v^{1/2} \).

The model was applied to the present work for the multicycled electrode. The solution resistance, \( R_s \), between the working electrode and the Luggin capillary is given by the Newman equation

\[ R_s = (2\pi \rho b) \tan^{-1}(d/b) \]  \hspace{1cm} (5.29)
where
\[ d \text{ is the vertical distance between the Luggin and the working electrode [cm] and} \]
\[ b \text{ is the radius of the electrode [cm].} \]

The conductivity of the electrolyte has previously been found to be 0.76 S cm\(^{-1}\).\(^82\) The parameters \( d \) and \( b \) are 0.20 cm and 0.22 cm respectively indicating that the solution resistance \( R_s \) is approximately 0.6 \( \Omega \). \( R_s \) may also be estimated experimentally using the IR compensation on the Model 276 interface and was found to be approximately 0.5 \( \Omega \). Using an average \( R_s \) of 0.6 \( \Omega \) the model was evaluated for the present results. The theoretical transients are shown in Fig. 5.11. A constant linear slope of 1.7 mA/mV is found until a sharp passivation event is observed. The model is inadequate for several reasons when compared with the transients shown in Fig. 3.5.

1) The model predicts coincident rising slopes for each sweep rate.
2) The predicted slope and peak current are too high.
3) The passivation event is too rapid.

Birss and Wright\(^77\) proposed a modification to the Müller/Arvia model to alleviate the sharp passivation event. The modification allows for the passive film to thicken with overpotential \( \eta \) according to:

\[ \frac{dl}{dt} = 2k_2 \eta \]  \hspace{1cm} (5.30)
Fig. 5.11 Theoretical anodic peaks determined by the Müller/Arvia pore resistance model.\textsuperscript{68,81} The forward slopes are coincident and the peak current for each sweep rate overestimates the experimental transients (see Fig. 3.5)
thus

\[ l = k_2ut^2 + l_0' \]  \hspace{1cm} (5.31)

where

- \( l \) is the passive layer thickness [cm],
- \( l_0' \) is the initial spontaneous thickness at \( t = 0 \) [cm], and
- \( k_2 \) is a rate constant [cm mV\(^{-1}\) s\(^{-1}\)].

These workers found a more satisfactory fit to the experimental data for this model than for the simple Müller/Arvia model for the anodic growth of AgBr in 1.0 mol L\(^{-1}\) NaBr in 5.1 mol L\(^{-1}\) NaClO\(_4\). The peak current was better resolved and the passivation event was less abrupt. In the present work it was found that the Birss-Wright modification gave almost identical results to that for the Müller/Arvia model. Both models fail to adequately describe the behaviour of the lead anode in H\(_2\)SO\(_4\) because of the high conductivity of the electrolyte.

\section*{5.4.3 Film transmission model.}

Digitised transients for the anodic wave for a multicycled electrode are shown in Fig. 5.12. For each sweep rate on the forward slope an approximately linear \( I \) vs \( \eta \) region is evident. Extrapolation of the linear region to the overpotential axis yields a common intercept \( \eta_f \) for each sweep rate of 39 ± 1 mV. The slopes of the linear section increase with sweep rate and may be related to a resistance \( R_c \)

\[ R_c = (\eta - \eta_f)/I \]  \hspace{1cm} (5.32)
Fig. 5.12 Plot of the Al peaks for experimental cyclic voltammograms for multi-cycled electrodes. The voltammograms are similar to those shown in Fig. 3.5. The linear least squares fit to the linear section of the forward slopes are included. Equations for the linear region are listed in Table 5.3. $T = 18^\circ$C, $A = 0.159 \text{ cm}^2$, $\eta = 0$ at $E = -332 \text{ mV}$. 
Table 5.3  List of the equations determined by linear-least-squares for the linear current-overpotential section of the forward slope to the experimental transients displayed in Fig. 5.12. The intercept with the overpotential axis $\eta_0$, the anodic charge prior to the linear forward slope $\mathcal{Q}_f$, and the equivalent resistance of the slope $R_e$ are also listed. The plot of $R_e$ vs $\mathcal{Q}_f$ is given in Fig. 5.13. $A = 0.159$ cm, $\eta = 0$ at $E = -332$ mV.

<table>
<thead>
<tr>
<th>$\nu$/mV s$^{-1}$</th>
<th>$I$/mA</th>
<th>$\eta_0$/mV</th>
<th>$\mathcal{Q}_f$/10$^{-4}$ C</th>
<th>$R_e$/$\Omega$</th>
</tr>
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<tr>
<td>200</td>
<td>0.183 x ($\eta - \eta_0$) - 7.19</td>
<td>39.4</td>
<td>1.55</td>
<td>5.47</td>
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<tr>
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<td>2.52</td>
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<td>50</td>
<td>0.159 x ($\eta - \eta_0$) - 6.34</td>
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<td>3.95</td>
<td>6.29</td>
</tr>
<tr>
<td>20</td>
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<td>38.4</td>
<td>5.95</td>
<td>8.29</td>
</tr>
<tr>
<td>10</td>
<td>0.096 x ($\eta - \eta_0$) - 3.71</td>
<td>38.7</td>
<td>8.94</td>
<td>10.42</td>
</tr>
</tbody>
</table>
Fig. 5.13  Plot of the forward slope resistance $R_e$ for the transients depicted in Fig. 5.10 as a function of the charge, $Q_e$, passed at the beginning of the anodic wave in excess of that described by the linear extrapolation. Digital data, $\eta = 0$ at $E = -332$ mV, data are listed in Table 5.3.
where

\[ R_e = R_a + R_m^0 \]  \hspace{1cm} (5.33)

where \( R_m^0 \) is the resistance of the film in the absence of any passivation.

The values for \( R_e \) and the equation for the linear region calculated from the linear least squares fit to the data are listed in Table 5.3. The intercept of the extrapolated linear regions with the overpotential axis represent the overpotential required before film transmission is possible and is denoted by \( \eta_o \). The small current evident before the linear \( I \) vs \( \eta \) region for each sweep rate is not explained by the model. A tentative suggestion may be advanced by consideration of the charge, \( Q_t \) of this unaccounted for small current. Fig. 5.13 shows a plot of \( R_e \) vs \( Q_t \). A linear relationship is found that is suggestive that \( R_e \) may be dependent on this charge. Furthermore it may be hypothesised that the charge \( Q_t \) and current passed before the linear region represents a film thickening process. The kinetics of this feature have not been evaluated in the present work.

The current eventually deviates from the linear \( I \) vs \( \eta \) relationship and passes through a maximum as a result of precipitation of crystalline \( \text{PbSO}_4 \) on the conductive film. The resistance of the film in the absence of precipitation is given by

\[ R_m^0 = \frac{i_m}{(k_m A)} \]  \hspace{1cm} (5.34)
where

\[ l_m \] is the thickness of the film [cm] and

\[ \kappa_m \] is the conductivity of the film [S cm\(^{-1}\)].

When PbSO\(_4\) deposits on the film (or possibly even grows through the film) the film resistance becomes \( R_m \)

\[ R_m = \frac{l_m}{\kappa_m A (1 - \xi)} \quad (5.35) \]

the parameters \( l_m \) and \( \kappa_m \) need never be determined as equation (5.35) simplifies to

\[ R_m = \frac{R_m^o}{(1 - \xi)} \quad (5.36) \]

The solution resistance within the pores is negligible and is not included in this model. Thus the total resistance is denoted by

\[ R_c = R_s + \frac{R_m^o}{(1 - \xi)} \quad (5.37) \]

and the current is given by

\[ I = \frac{vt}{R_c} \quad (5.38) \]

where \( t \) is measured from the point \( \eta_f \).

\( R_c \) is determined experimentally and \( R_s \) can be estimated by the Newman equation (5.29) or by \( IR \) compensation and was found to be \( 0.6 \pm 0.1 \) \( \Omega \).

Alternatively, the plot of \( R_c \) vs \( Q_t \) shown in Fig. 5.13 can be interpreted
for the limiting case where no pre-slope current is found (at infinite sweep rate) to suggest that the intercept on the resistance axis represents the solution resistance. The intercept is found to be 4.0 Ω which is significantly larger than that predicted by the Newman equation and no ready explanation for this is advanced here.

The model is solved for $R_s = 0.6$ Ω. The values for $\xi$ are determined by an iterative approach to equations (5.37) and (5.38). $\xi$ is optimised by incremented from zero to unity until the theoretical current fits the experimental current. The optimised values for $\xi$ are depicted as a function of $\eta$ for each sweep rate in Fig. 5.14. The semi-log plots of $\xi$ and $(1 - \xi)$ vs $\eta$ are shown in Figs. 5.15 and 5.16 respectively.

5.4.4 Discussion.

The film transmission model presented in Section 5.4.3 provides an adequate description of the events after a linear $I$ vs $\eta$ slope is attained for each sweep rate. The resistance model is supported by the experimental results by the extrapolation of the linear regions to a constant overpotential, which in the present work is denoted $\eta_0$, the overpotential required for resistance control. The calculated values for $\xi$ vs $\eta$ show that the deposition is initially rapid with a slope of 0.07 mV⁻¹. The initial slope is independent of sweep rate. The coverage of the passivating layer rapidly increases until a value of 0.85 is attained after which the gradient decreases resulting in a slow passivation event. The semi-log plots of $\xi$ and $(1 - \xi)$ were prepared to determine if any simple rate law may be applied to the growth of the passivating layer. Fig. 5.15 shows that the semi-log plot of $\xi$ tends to accentuate the initial
Fig. 5.14  Plot of the optimised passivation coverage $\xi$ as a function of the overpotential for the multi-cycled electrode at each sweep rate. Digital data, $\eta = 0$ at $E = -332$ mV.
Fig. 5.15 Semi-log plot of the optimised passivating coverage $\xi$ as a function of the overpotential for the multi-cycled voltammograms. Digital data, $\eta = 0$ at $E = -332$ mV.
Fig. 5.16 Semi-log plot of \((1 - \xi)\) as a function of the overpotential for multi-cycled voltammograms. Digital data, \(\eta = 0\) at \(E = -332\) mV.
fast change in the coverage. However the semi-log plots of \((1 - \xi)\) show behaviour that is hyperbolic or quadratic in nature, the interpretation being hampered by the scattered results at large \(\eta\) due to the digitising error in the original current determination. Thus no simple rate law may be derived to allow predictive modelling.

### 5.5 Conclusions

The model for the potential step experiment adequately describes the transients for the time and potential ranges examined. The model is complicated with three parameters to be optimised, but the rate equations are not independent, all of the charge-transfer processes being controlled by the growth of the conductive multilayer. The optimised parameters are found to show reasonable dependence on potential. The film transmission constant, \(k_1\), and the multilayer growth constant, \(k_2\), follow logarithmic dependence with \(E_2\) while the charge follows linear dependence. The thickness of the multilayer varies linearly with potential which suggests that this feature is controlled by a constant electric field. The model consists of several previously described features, namely dissolution, nucleation and growth, and film transmission. The new feature is the combination of these processes for the lead anode and consideration of the edge profile effect.

The optimised parameters for the potential step model were adapted for the cyclic voltammetry experiment for cathodically pretreated electrodes. The model was successful in describing the forward slope of the A1 peak and even predicted details of the minute variation in the forward slope at different sweep rate. The model did not adequately
predict the anodic peak current and the subsequent passivation at high sweep rate, this being in a potential region where no direct measurement of the potential step parameters had taken place and the values were determined by extrapolation. The degree of approximation was however within an order of magnitude which is reasonable considering the logarithmic variation of the optimised parameters. At worst the prediction of the peak current by the model was only overestimated by 200%. At lower sweep rates the model was successful in approximating the peak current and predicting the passivation event. The model was also successful in predicting the position of the dissolution current component which has been previously observed by other authors.

The model for the multicycled cyclic voltammetry experiments provided an interpretation of the experimental transients that result in a conductive thin film model. The passivation is controlled by precipitation of PbSO₄ onto the film changing the resistance. The model determined the coverage of the passive layer as a function of overpotential, but kinetics were not established. Nevertheless the model showed that the initial passivation was rapid followed by a gradual completion of the passive film.

In summary all the models presented in this chapter have provided further insights into the mechanism of the lead anode and may thus be regarded as successful.
CHAPTER SIX

EFFECT OF CHLORIDE ADDITION ON THE LEAD ANODE.

6.1 Introduction.

Exclusion of chloride from the electrolyte in lead-acid batteries has been recognised as beneficial. Manufacturing standards are proscribed in which the chloride concentration is to be maintained below 7 ppm.83-86 The detrimental effects of chloride (and subsequently formed chlorate and perchlorate) are understood in the industry to be the effects on the positive plate: that of liberation of chlorine gas at high chloride concentrations, and corrosion of the battery plate grid elements at lower concentrations. Bode87 notes that the corrosive properties of the perchlorate anion are deliberately employed during formation of Planté plates to yield a higher roughness factor and hence a greater charge capacity. Hampson et al.46,88 have investigated the perchlorate assisted formation of lead battery plates. After formation the perchlorate electrolyte is required to be rigorously removed by washing, prior to assembling into the complete battery, to arrest further corrosion.87 Other anions which form soluble lead salts such as nitrates, fluorides, and acetates are known to act similarly.89 Kolikova et al.90 have found for porous plates that formation may be enhanced if the chloride concentration is limited to 25 ppm.
Extensive inspection of the literature failed to reveal any further reports in this area and no single electrode experiments for either the lead anode or the lead dioxide electrode appear to have been published. One worker however has reported the use of organic reagents to scavenge chloride from the battery electrolyte.\textsuperscript{91} It is apparent that there is very little information on the effect of chloride on the negative plate and thus the work presented in this chapter was designed to elucidate the behaviour of the Pb/PbSO\textsubscript{4} electrode when chloride is introduced.

Sections 6.2 and 6.3 report the results for cyclic voltammetry and potential step experiments respectively. The results are discussed in Section 6.6. The occurrence of platinum contamination of the working electrode is reported in Sections 6.4 and 6.5 and discussed in Section 6.7. Section 6.8 is the conclusion for this chapter.

The electrolyte was 4.65 mol L\textsuperscript{-1} H\textsubscript{2}SO\textsubscript{4} prepared by dilution of 98\% H\textsubscript{2}SO\textsubscript{4} with chloride solutions in Milli-Q water, of the appropriate concentration. The chloride concentration investigated was in the range 0.02 mol L\textsuperscript{-1} to 0.20 mol L\textsuperscript{-1}. A lead counter electrode was employed. The working electrodes were polished prior to commencement of the experiments at each chloride concentration so that any films present were removed.

6.2 Cyclic voltammetry experiments.

6.2.1 General form of the voltammograms in the presence of chloride.

The transients for multicycled cyclic voltammetry experiments recorded for a sweep rate of 20 mV s\textsuperscript{-1} for each chloride concentration
are displayed in Fig. 6.1. The anodic peak current varies with each concentration, but there is no systematic dependence at this sweep rate. Conversely the cathodic peak current clearly increases with chloride concentration. The shape of the cathodic wave is markedly affected by chloride. The voltammogram in the absence of chloride in Fig. 6.1, and in the results in Chapter 3, are typically broad in nature with a peak current approximately one third of that for the anodic wave. The presence of chloride accentuates the cathodic peak and the cathodic peak current increases until for the highest chloride concentration examined the cathodic wave resembles an image of the anodic wave with a centre of symmetry at the foot of the two waves. The cathodic wave is initiated at more anodic potentials with increasing chloride concentration. At the highest concentration the foot of the cathodic wave is found at a potential where an anodic current is observed on the previous forward scan.

6.2.2  *Sweep rate and chloride concentration dependence.*

The sweep rate dependence was investigated for each chloride concentration. Table 6.1 lists the anodic and cathodic charge, charge ratio, and anodic peak current for each sweep rate and chloride concentration. Fig. 6.2 depicts the sweep rate dependence for a chloride concentration of 0.14 mol L\(^{-1}\). The anodic peak increases with \(v\) in a similar manner to the case of no chloride addition (Section 3.5), but the cathodic peak is greater in the presence of chloride.

The anodic peak current is plotted as a function of the square-root of the sweep rate for each chloride concentration in Fig. 6.3. The curvilinear relationship for the chloride free experiments is similar to
Fig. 6.1  Cyclic voltammograms at a constant sweep rate for multicycled electrodes in varying concentrations for chloride in the electrolyte. $v = 20 \text{ mV s}^{-1}$, $E_c = -756 \text{ mV}$, $E_a = 244 \text{ mV}$, analogue data. The temperature and acid concentration are the same throughout this chapter, $T = 18^\circ \text{C}$, $[\text{H}_2\text{SO}_4] = 4.65 \text{ mol L}^{-1}$. 
Table 6.1  The anodic and cathodic charge, charge ratio, anodic peak current, and cathodic pre-peak peak potential for each sweep rate and chloride concentration for cyclic voltammetry experiments.

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<th>[Cl\textsuperscript{-}] /mol L\textsuperscript{-1}</th>
<th>(v) /mV s\textsuperscript{-1}</th>
<th>(q_{A1}) /mC cm\textsuperscript{-2}</th>
<th>(q_{C1}) /mC cm\textsuperscript{-2}</th>
<th>(q_{C1}/q_{A1})</th>
<th>(i_{A1}) /mA cm\textsuperscript{-2}</th>
<th>(E_{mp}) /mV</th>
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Table 6.1 (continued)

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<th>(i_{A1}) /mA cm(^{-2})</th>
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Fig. 6.2 Cyclic voltammograms for a multicyced electrode in a chloride electrolyte where the sweep rate is varied from 5 to 100 mV s\(^{-1}\). \(E_c = -756\) mV, \(E_a = 244\) mV, \([\text{Cl}^-]\) = 0.14 mol L\(^{-1}\), analogue data.
Fig. 6.3  Plot of the anodic peak current, $i_{a1}$, versus the square-root of the sweep rate for each chloride concentration.  

- $\blacklozenge$ 0.20 mol L$^{-1}$.
- $\times$ 0.14 mol L$^{-1}$.
- $\bigstar$ 0.10 mol L$^{-1}$.
- $\bigcirc$ 0.08 mol L$^{-1}$.
- $+$ 0.06 mol L$^{-1}$.
- $\triangle$ 0.04 mol L$^{-1}$.
- $\oplus$ 0.02 mol L$^{-1}$.
- $\square$ 0.00 mol L$^{-1}$. Data are listed in Table 6.1, analogue data.
Fig. 6.4  Plot of the anodic peak current, $i_{pA}$, versus chloride concentration for each sweep rate. □ 100 mV s$^{-1}$. ⊙ 50 mV s$^{-1}$. △ 20 mV s$^{-1}$. ◇ 10 mV s$^{-1}$. ★ 5 mV s$^{-1}$. Data are listed in Table 6.1, analogue data.
Fig. 6.5  Plot of the anodic charge, $q_{A1}$, versus sweep rate for each chloride concentration. ★ 0.20 mol L$^{-1}$, ★★ 0.14 mol L$^{-1}$, ◆ 0.10 mol L$^{-1}$, × 0.08 mol L$^{-1}$, + 0.06 mol L$^{-1}$, △ 0.04 mol L$^{-1}$, ○ 0.02 mol L$^{-1}$, □ 0.00 mol L$^{-1}$. Data are listed in Table 6.1, analogue data.
Fig. 6.6  Plot of the anodic charge, $q_{\text{Al}}$, versus chloride concentration for each sweep rate. $\star$ 100 mV s$^{-1}$, $\diamondsuit$ 50 mV s$^{-1}$, $\Delta$ 20 mV s$^{-1}$, $\bigcirc$ 10 mV s$^{-1}$, $\square$ 5 mV s$^{-1}$. Data are listed in Table 6.1, analogue data.
Fig. 6.7  Plot of the charge ratio, $q_{Cl}/q_{Na}$, versus sweep rate for each chloride concentration. ★ 0.20 mol L$^{-1}$, ★★ 0.14 mol L$^{-1}$, ★★ 0.10 mol L$^{-1}$, × 0.08 mol L$^{-1}$, + 0.06 mol L$^{-1}$, △ 0.04 mol L$^{-1}$, ◇ 0.02 mol L$^{-1}$, □ 0.00 mol L$^{-1}$. Data are listed in Table 6.1, analogue data.
that depicted in Fig. 3.9. At high sweep rates the anodic peak current steadily increases with [Cl\(^-\)], while at low sweep rates the variation follows no regular pattern, as can be seen in Fig. 6.1. This is more readily evident in Fig. 6.4 for the plot of the anodic peak current as a function of [Cl\(^-\)] for each sweep rate. Fig. 6.3 shows that for most of the concentration range the plot of \(i_{a1} vs \sqrt{v}\) is approximately linear whereas for 0.00 and 0.20 mol L\(^{-1}\) a curvilinear relationship is found.

The anodic charge dependence on sweep rate for each chloride concentration is depicted in Fig. 6.5. The presence of chloride markedly alters the hyperbolic increase in anodic charge, as the sweep rate decreases, from that found for the chloride free case. The relationship is modified towards linearity. In general the anodic charge increases with chloride concentration. However at low sweep rates and low values for [Cl\(^-\)] this is not observed. This is more clearly depicted in Fig. 6.6 in the plot of the anodic charge vs [Cl\(^-\)] for each sweep rate. At the low sweep rate of 5 mV s\(^{-1}\) the charge initially decreases with [Cl\(^-\)] but passes through a minimum at 0.06 mol L\(^{-1}\) after which the charge increases. This behaviour is also evident for the sweep rates of 10 and 20 mV s\(^{-1}\) but the variation is not as pronounced as for 5 mV s\(^{-1}\). At sweep rates of 50 and 100 mV s\(^{-1}\) the charge initially increases with [Cl\(^-\)] but also passes through slight minima at 0.06 mol L\(^{-1}\), after which the charge resumes increasing. The charge ratio \(q_{cl}/q_{a1}\) is plotted as a function of sweep rate for each chloride concentration in Fig. 6.7. In general the charge ratio increases steadily with chloride concentration and decreases with sweep rate.

Similar voltammograms were obtained if the electrolyte was prepared
using Na⁺ or H⁺ as counter ions for chloride instead of K⁺, indicating that the effects are due only to the presence of chloride.

Extreme cathodic pretreatment ($E_{\text{ct}} = -1756$ mV) results in no change to the voltammograms unlike the behaviour described in Chapter 3.

6.2.3 Cathodic pre-peak

A new feature, observed in the presence of chloride is a pre-peak at the foot of the cathodic wave (Fig. 6.1 and 6.2). The pre-peak is better resolved at low sweep rates than at high sweep rates, where only a shoulder to the main cathodic wave is found. The pre-peak peak potential, $E_{\text{mp}}$, is generally found at more anodic potentials at higher sweep rates (see Table 6.1). Fig. 6.8 displays the variation of $E_{\text{mp}}$ with chloride concentration for each sweep rate. At lower concentrations the pre-peak is not always resolved. The pre-peak potential is dependent on sweep rate at low chloride concentrations but the dependence decreases as the chloride concentration increases. The charge associated with the pre-peak is estimated to be $500 \pm 200 \, \mu\text{C cm}^{-2}$ for all sweep rates and chloride concentrations.

6.3 Potential step experiments.

The potential step program used was the same as described in Section 4.2. A typical set of potential step transients for chloride in H₂SO₄ are depicted in Fig. 6.9. For the most part the transients are very similar to those shown in Fig. 4.5 for no chloride addition. However a new feature is evident at low stepping potentials, in that an initial decrease in current is found prior to the linearly increasing nucleation and growth.
Fig. 6.8  Plot of the potential, $E_{mp}$, of the reduction pre-peak peak versus chloride concentration for each sweep rate. ♦ 100 mV s$^{-1}$, ○ 50 mV s$^{-1}$, △ 20 mV s$^{-1}$, ⊙ 10 mV s$^{-1}$, □ 5 mV s$^{-1}$. Data are listed in Table 6.1, analogue data.
contribution. The decreasing transient is found at all chloride concentrations explored and is resolved for stepping potentials more cathodic than -286 mV. Fig. 6.10 shows an expanded view for the transients at low values of \( E_2 \). The charge of the decreasing portion, in excess of the current described by extrapolation of the linear region, is found to be \( 60 \pm 15 \mu \text{C cm}^{-2} \).

The variation in the potential transients as the chloride concentration is changed is similar to the variation displayed in Chapter 4 for potential step experiments performed on electrodes polished at different times (Fig. 4.3), but with no added chloride. Hence it can be concluded that there is no significant variation of the transient with chloride concentration.

### 6.4 Platinum contamination.

The data presented in the previous two sections was obtained whilst using pure lead counter electrodes. Some earlier experiments during the course of this work in chloride/H\(_2\)SO\(_4\) electrolyte with platinum counter electrodes yielded interesting results. The cyclic voltammograms displayed in Fig. 6.11 are those for an experiment immediately after the electrode was introduced to the electrolyte and at various times later. The voltammograms progressively change with time. The cathodic current due to hydrogen evolution steadily increases with time and distorts the anodic and cathodic waves. After 24 hr a voltammogram due only to hydrogen evolution is evident with no current contribution from the lead reactions. This change in behaviour is independent of whether the electrode was electrochemically cycled or left at open circuit over the time of the
Fig. 6.9 Plot of current-time transients after stepping to $E_2$, for different values of $E_2$ for an electrode within the same polishing period. $E_{pc} = -756$ mV, $E_1 = -456$ mV, [Cl$^-]$ = 0.04 mol L$^{-1}$, digitised data.
Fig. 6.10  Plot of current-time transients taken from Fig. 6.9 for the three most cathodic stepping potentials showing the initially falling transient at short times. $E_{pc} = -756 \text{ mV}$, $E_1 = -456 \text{ mV}$, $[\text{Cl}^-] = 0.04 \text{ mol L}^{-1}$, digitised data.
Fig. 6.11 Cyclic voltammograms recorded at different times for a Pb electrode in a chloride/H₂SO₄ electrolyte with a platinum counter electrode. a) first cycle, b) 1 hour later, c) 2 hours later, d) 24 hours later. The electrode was held at open circuit between the cycles shown. Continuous cycling resulted in closely similar results. $v = 20 \text{ mV s}^{-1}$, $E_c = -756 \text{ mV}$, $E_a = 244 \text{ mV}$, $[\text{Cl}^-] = 0.10 \text{ mol L}^{-1}$, analogue data.
Fig. 6.12 Cyclic voltammograms of various electrodes between the solvent potential limits in chloride/H$_2$SO$_4$ electrolyte with a platinum counter electrode. a) first cycle for a lead electrode. b) lead electrode after 24 hours. c) platinum sheet working electrode. $v = 20$ mV s$^{-1}$. $E_c = -756$ mV, $E_a = 2744$ mV, [Cl$^-$] = 0.10 mol L$^{-1}$. Digitised data.
experiment. The effect was postulated to be a consequence of dissolution of platinum from the counter electrode resulting in soluble platinum chloro complexes such as \( \text{PtCl}_4^{2-} \) and \( \text{PtCl}_6^{2-} \) and subsequent deposition of platinum on the lead electrode. This was confirmed by several means: replacement of the Pt counter electrode with Pb sheet resulted in no change in the hydrogen evolution, use of a Pb counter electrode and deliberate addition of \( \text{K}_2\text{PtCl}_4 \) solutions to the electrolyte instantly yielded voltammograms identical to those in Fig. 6.11, and surface analysis of a Pb electrode (Section 6.5) that exhibited the modified behaviour after immersion in a chloride/\( \text{H}_2\text{SO}_4 \) electrolyte with a Pt counter electrode. Fig. 6.12 shows cyclic voltammograms for a freshly polished lead electrode in the chloride/\( \text{H}_2\text{SO}_4 \) electrolyte, an aged lead electrode, and a platinum sheet electrode in the same solution. The aged lead and platinum electrodes display identical waveforms which are due only to \( \text{H}_2 \) and \( \text{O}_2 \) evolution.

6.5 Surface analysis of the platinum deposition on a lead electrode.

6.5.1 Introduction

The surface analysis technique used was X-ray Photoelectron Spectroscopy (XPS) obtained with a Kratos XSAM 800 spectrometer. A brief sputtering with argon ions was necessary to remove the inevitable oxide and hydrocarbon layer, there being no platinum signals prior to the sputtering event. Peak integration of the Pb and Pt signals indicate that the atomic abundance of the platinum in the volume from which photoelectrons were detected is 7%. 
Fig. 6.13  Binding energy spectrum for the 24 hour aged Pb electrode from the experiment given in Fig. 6.12, determined by X-ray Photoelectron Spectroscopy. Peaks due to sulphur 2p, lead 4f, and platinum 4f orbitals are found. Integration of the Pb 4f and Pt 4f peaks indicate that the atomic abundance of Pt in the analysed volume is 7%. Kratos XSAM 800 spectrometer.
Fig. 6.14  High resolution binding energy spectrum (noisy curve) and the gaussian fit to the data (smooth curves) for the 24 hour aged Pb electrode from the experiment given in Fig. 6.12, determined by X-ray Photoelectron Spectroscopy. The position of the Pt 4f peaks are corrected by subtraction of 1.48 eV because the hydrocarbon C 1s peak (used as a standard) was observed to be displaced by 1.48 eV due to surface charging. The position of the Pt 4f peaks indicate that the Pt is metallic.
6.5.2 Qualitative interpretation of the XPS spectrum.

The XPS binding energy spectrum in Fig. 6.13 shows that platinum is found on the electrode surface. The Pb 4f and Pt 4f peaks are identified in the spectrum. Fig. 6.14 showing the high resolution spectrum in the Pt 4F energy region confirms the presence of Pt; the peaks of the spin orbit doublet occur at 72.7 (4f7/2) and 76.0 eV (4f5/2). These are corrected by subtracting 1.48 eV because the hydrocarbon C 1s peak (used as a standard) was observed to be displaced by 1.48 eV due to minor surface charging. The binding energies are for 71.2 eV for Pt 4f7/2, and 74.5 eV for Pt 4f5/2. These are in excellent agreement with the values for Pt metal listed in Carlson's tables.97

6.5.3 Quantitative interpretation of the XPS spectrum.

Integration of the Pt 4f peaks and comparison with the Pb 4f peaks shows that, for the surface volume from which photoelectrons escaped and were subsequently measured, that the atomic fraction of Pt is 7%. For approximate binding energies of 73 eV and 141 eV, for Pt and Pb respectively, the mean free path or escape depth for the photoelectrons is of the order of 0.5 nm.97 For a 99% confidence interval an escape depth of 2 nm may be selected. The number of Pb atoms in a 2 nm layer per unit area, \( N_{\text{Pb}} \), is found to be 6.59 x 10^{15} \text{ cm}^{-2} using

\[
N_{\text{Pb}} = \frac{N_A \rho l_u}{M} \quad (6.3)
\]
where

\[ N_A \text{ is Avogadro's number [mol}^{-1}]. \]

\[ \rho \text{ is the Pb density [g cm}^{-3}]. \]

\[ l_a \text{ is the analysed depth [cm]}. \]

If it is assumed that the lattice spacing for the platinum metal deposit is the same for bulk lead metal then the number of Pt atoms in the analysed volume is 7% of the above value, that is \( 4.61 \times 10^{14} \text{ cm}^{-2} \). The number of Pb atoms at the surface, \( N_{\text{Pb}} \), is found to be \( 1.01 \times 10^{15} \text{ cm}^{-2} \) using

\[ N_{\text{Pb}} = q_m N_A / 2F \quad (6.4) \]

where \( q_m \) is the charge for oxidation of a monolayer of Pb atoms, \( q_m \) being \( 325 \mu \text{C cm}^{-2} \). Thus if all the Pt atoms are accumulated at the surface (which is likely as Pt diffusion through the lattice would be slow at room temperature) then the Pt is equivalent to 0.5 monolayers. The above calculation does not take into account any surface roughness effects increasing the surface area or shadowing the detection of the photoelectrons.

6.6 Summary and interpretation of the effect of chloride additions.

6.6.1 Introduction

The voltammograms depicted in Figs. 6.1 and 6.2 show clearly that the behaviour of the lead anode is considerably modified by addition of chloride to the electrolyte. The changes occur both to the anodic and cathodic waves. The changes to the anodic wave are illustrated by the
plots of the anodic peak current in Figs. 6.3 and 6.4 and the anodic charge in Figs. 6.5 and 6.6.

The potential step transients shown in Figs. 6.9 and 6.10 are modified only by the addition of a small falling current at short times in the presence of Cl⁻.

6.6.2 Sweep rate and chloride concentration dependence in cyclic voltammetry experiments

The dependence of \( i_{a1} \) on \( \nu^{1/2} \) shown in Fig. 6.3 shows that the presence of chloride alters the relationship from that found in the absence of chloride (Fig. 3.9). This is especially so at high sweep rates where the peak current increases with [Cl⁻]. For most of the values for [Cl⁻] an approximately linear dependence is found whereas in the absence of chloride a curvilinear dependence is observed.

The anodic charge dependence on sweep rate and [Cl⁻] is also affected. In chloride-free electrolyte a hyperbolic dependence of \( q_{a1} \) on sweep rate with a marked increase in charge as \( \nu \) decreases is found. In chloride containing electrolyte a more linear dependence is found. As a result extrapolation to zero sweep rate in Fig. 6.5 yields clear intercepts with the charge axis indicating that a limiting charge may be possible for chloride electrolytes. Extrapolation to zero sweep rates for chloride free experiments tends to indicate an infinite discharge capacity. An alternative interpretation can be made that voltammograms for the chloride cases do follow a hyperbolic sweep rate dependence but that the vertical asymptote is approached at lower sweep rates than that explored. The chloride concentration of 0.06 mol L⁻¹ appears to result in anodic waves that do
not follow the trend dictated by other concentrations. Repetition of the experiments yielded the same results. In general the anodic peak current and consequently the anodic charge are less for this concentration than that expected for the sequence of experiments. This is most clearly shown in Fig. 6.6 in the plot of $q_{A1}$ vs $[\text{Cl}^-]$ for each sweep rate. A discontinuity is observed for the anodic charge at each sweep rate for 0.06 mol L$^{-1}$. This figure shows that the anodic charge does not follow a simple increase with increasing $[\text{Cl}^-]$ and decreasing sweep rate. Apart from the deviation for 0.06 mol L$^{-1}$ at high sweep rates the anodic charge increases with $[\text{Cl}^-]$. However at low sweep rates $q_{A1}$ decreases with $[\text{Cl}^-]$ at low concentrations and only after passing through a minimum at 0.06 mol L$^{-1}$ does the charge increase. Similarly to the behaviour for the anodic peak current there is no proposed explanation.

Reproducibility of the cathodic wave in cyclic voltammetry was found to be poor in Chapter 3 (Fig. 3.2) and the parameter $q_{C1}$ was consequently not discussed. However from the voltammograms presented in Figs. 6.1 and 6.2 it is evident that the most significant effect of chloride occurs to the cathodic wave. The cathodic wave is found to accentuate with increasing $[\text{Cl}^-]$ and to result in a greater charge indicative of an increased deposition of solid Pb$^{2+}$ material on the electrode. This may be related to the model presented in the previous chapter in that the dissolution current, i.e. resulting in soluble Pb$^{2+}_{(aq)}$ that may diffuse irreversibly away from the electrode, is diminished. The parameter $q_{C1}$ is best shown in the plot of the ratio $q_{C1}/q_{A1}$ in Fig. 6.7 as a function of sweep rate for each chloride concentration. The cathodic charge is difficult to estimate and in the present work is calculated by the integral of the cathodic current on
the reverse scan to the lower potential limit $E_c$ less the integral of the cathodic current on the forward sweep from $E_c$ to the potential at which the anodic current is first observed, the latter integral being due only to $H_2$ evolution. This calculation assumes that the $H_2$ evolution charge for the forward sweep is identical to that for the prior cathodic sweep. Thus the cathodic charge is only an estimate. The charge ratio $q_{c1}/q_{a1}$ provides a measure of the charge reversibility of the electrode. In the chloride free case a hyperbolic dependence on $q_{c1}/q_{a1}$ vs $v$ is observed with the vertical asymptote on the charge ratio axis. Addition of $Cl^-$ to the electrolyte increases $q_{c1}/q_{a1}$ at all sweep rates but most markedly at higher sweep rates resulting in a more linear dependence on $v$. At low sweep rates the difficulties in estimating $q_{c1}$ result in charge ratios in excess of unity, suggesting that the hydrogen evolution reaction has not been completely accounted for. Thus the plot of $q_{c1}/q_{a1}$ may only be taken as an indication of the trends for increasing charge recycling with $[Cl^-]$ and low $v$ that total charge recycling is likely and that loss of soluble $Pb^{2+}$ away from the electrode is diminished. Barradas et al.\(^9^2\) have reported similar difficulties in estimating the cathodic charge for Pb in 1.0 mol L\(^{-1}\) HCl. Charge ratios were consistently recovered in excess of unity. These results were interpreted as being due to the parallel reaction

$$\text{Pb} + 2\text{H}^+ + 2\text{Cl}^- \rightarrow \text{PbCl}_2 + \text{H}_2$$

which may be plausible for freshly electro-crystallised Pb during the cathodic scan. This reaction does not result in any charge-transfer with the electrode, however the $Pb^{2+}$ species may be subsequently reduced as an
electrode process and thus the measured cathodic charge is increased.

6.6.3 *Cathodic pre-peak in cyclic voltammetry experiments.*

A new feature was found in the cyclic voltammograms in the presence of chloride. A pre-peak to the reduction wave is found that moves in position with sweep rate and [Cl\textsuperscript{-}] as is shown in Fig. 6.8. It is plausible to suggest that the pre-peak is the reduction wave for a new phase and an immediate candidate for this phase is PbCl\textsubscript{2}.

\[
PbCl_2 + 2e^- \rightarrow Pb + 2Cl^- 
\]

Barradas et al\textsuperscript{71,92,93} have found that the cathodic wave for PbCl\textsubscript{2} reduction is initiated at -256 mV, a position more anodic than that found for PbSO\textsubscript{4} reduction (-300 mV), and in good agreement with \(E_{mp}\). Thus an explanation for the anodically advancing foot of the cathodic wave in the present work may lie in the increasing parallel production of PbCl\textsubscript{2} during the anodic reaction. The pre-peak potential however moves to cathodic potential and appears to be approaching a stable value at -300 mV, this being the potential found for the first cathodic current in the absence of chloride. The charge for the pre-peak was estimated to be 500 ± 200 \(\mu\text{C} \text{cm}^{-2}\) a value consistent with the 325 \(\mu\text{C} \text{cm}^{-2}\) expected for a monolayer of PbSO\textsubscript{4}\textsuperscript{43} or PbCl\textsubscript{2}. The position of the peak suggests PbCl\textsubscript{2} is the phase being reduced. Therefore it is proposed that the pre-peak is a result of reduction of a monolayer of PbCl\textsubscript{2} formed as a consequence of the preceding anodic reaction. There is no accompanying anodic monolayer peak as any such peak would be expected to occur at a
potential more anodic than the reduction peak. This would place any
anodic monolayer peak in the middle of the anodic peak where it would
not be resolved against the large current.

6.6.4 \textit{Potential step transients.}

The new feature for the potential step transients is that of a falling
current transient at short times (Figs. 6.9 and 6.10). The potential step
model discussed in Chapter 5 deduced that the experimental transient was
a combination of three related charge-transfer processes: nucleation and
growth, dissolution, and film transmission (Section 5.2). The transients
displayed in Figs. 6.9 and 6.10 indicate the presence of a further charge-
transfer process at short times. Extrapolation of the linear part of the
transient for \( E_2 = -286 \) mV reveals the current transient due to the new
process, subsequent integration yields a charge of approximately
60 \( \mu \)C cm\(^{-2}\). Barradas \textit{et al}\textsuperscript{71,92} have reported transients with identical
features for Pb in HCl and NaCl electrolytes. They found that the falling
transient was only observed at low overpotentials, as is the case in the
present work. There was no discussion by Barradas \textit{et al}\textsuperscript{71,92} of the
falling transient portion. Examination of the figures in these publications
reveals that the charge of the falling portion in excess of the linear
region at short times is approximately 3 mC cm\(^{-2}\). The falling transient is
accentuated as the stepping potential becomes more anodic. The charge for
the falling transient in the present work is approximately 1/5 to 1/10 of
that expected for monolayer formation. Conversely the work by
Barradas \textit{et al}\textsuperscript{71,92} indicates a charge equivalent to eight monolayers.
Thus the resulting phase from the falling transient does not show rigid
monolayer behaviour. A mathematical expression may be proposed for the formation of this phase in which the charge-transfer rate, \( i_m \), is controlled by a Langmuir process where the rate of change of coverage of the growing phase is proportional to the area of the electrode uncovered by PbCl\(_2\) \(_{\text{mon}}\).

\[
i_m = i_m^0 \exp(-k_m t)
\]

(6.2)

where

- \( i_m^0 \) is the charge-transfer at \( t = 0 \) and
- \( k_m \) is the phase growth constant [s\(^{-1}\)].

The charge of the new phase is given by the ratio \( i_m^0/k_m \). This equation, in addition to the expressions for \( i_g, i_d, i_r \), derived in Chapter 5, provides an adequate description of the new current transient. The monolayer of PbCl\(_2\) should not impede dissolution of Pb\(^{2+}\)\(_{\text{aq}}\) or nucleation and growth of the PbSO\(_4\) multilayer.

Archdale and Harrison\(^{32}\) have reported potential step transients for pure H\(_2\)SO\(_4\) electrolyte similar to those described in the present work for chloride electrolytes. Interpretation of the figures in this article are not readily available as the current rather than the current density is quoted. The electrode working area is not mentioned. Archdale and Harrison\(^{32}\) are the only workers to have reported the initially falling transient in pure sulphuric acid electrolytes. Perhaps the working electrolyte employed in their study may have been contaminated with Cl\(^-\)? Further experiments in the present work showed initially falling transient at short times were still evident at 0.001 mol L\(^{-1}\) Cl\(^-\) for potential step experiments.
The potential step transients do not change significantly with \([\text{Cl}^-]\) and the only variability observed was of the same order as observed in Chapter 4 for electrodes polished at different times. Therefore it is construed that chloride does not change the nucleation and growth, dissolution, and film transmission processes and provides only the added feature of \(\text{PbCl}_2\) monolayer formation.

6.7 The influence of platinum deposits on the lead anode.

Contamination by platinum in the electrolyte has previously been mentioned as a possibility by Archdale and Harrison.\(^3\) These workers periodically employed frits to separate the platinum counter electrode from the lead working electrode to minimise any contamination and no cases of contamination were mentioned. The voltammograms depicted in Fig. 6.11 indicate that the transfer of Pt from the counter electrode is slow. That the rate of deposition is independent of whether the electrode is cycled or maintained at open circuit indicates that a redox pathway is operating at open circuit. Platinum will oxidise in acid via\(^9\)

\[
\begin{align*}
\text{Pt} &= \text{Pt}^{2+} + 2e^- & E^\circ &= 1.2 \text{ V} \\
\text{Pt} + 4\text{Cl}^- &= \text{PtCl}_4^{2-} + 2e^- & E^\circ &= 0.73 \text{ V} \\
\text{PtCl}_4^{2-} + 2\text{Cl}^- &= \text{PtCl}_6^{2-} + 2e^- & E^\circ &= 0.74 \text{ V} \\
\text{O}_2 + 4\text{H}^+ + 4e^- &= 2\text{H}_2\text{O} & E^\circ &= 1.229 \text{ V}
\end{align*}
\]

Thus trace oxygen in the electrolyte will tend to oxidise Pt metal to either the II or IV oxidation states in the presence of chloride. The rate
of oxidation of Pt in the presence of $\text{SO}_4^{2-}$ is negligible as the reaction is kinetically unfavourable through lack of a complexing anion. In water, solvolysis of $\text{PtCl}_4^{2-}$ occurs but the rate is slow.\(^{95}\)

\[
\begin{align*}
\text{PtCl}_4^{2-} + \text{H}_2\text{O} & \rightleftharpoons \text{PtCl}_3(\text{H}_2\text{O})^- + \text{Cl}^- & K_1 = 1.34 \times 10^{-2} \text{ mol L}^{-1} \\
\text{PtCl}_3(\text{H}_2\text{O})^- + \text{H}_2\text{O} & \rightleftharpoons \text{PtCl}_2(\text{H}_2\text{O})_2 + \text{Cl}^- & K_2 = 1.10 \times 10^{-3} \text{ mol L}^{-1}
\end{align*}
\]

The soluble platinum species is reduced on contact with Pb metal via the cementation reactions.\(^{94}\)

\[
\begin{align*}
\text{PtCl}_4^{2-} + 2e^- & = \text{Pt} + 4\text{Cl}^- & E^{\circ} = 0.73 \text{ V} \\
\text{Pb} & = \text{Pb}^{2+} + 2e^- & E^{\circ} = -0.126 \text{ V}
\end{align*}
\]

The voltammograms displayed in Fig. 6.12 show that the platinised lead electrode behaves identically to a pure platinum electrode with respect to the oxidation and reduction of water to $\text{O}_2$ and $\text{H}_2$. This indicates that a relatively small amount of Pt deposited on the surface (0.5 monolayers, Section 6.5.3) allows a Pb electrode to electrochemically mimic a Pt electrode. This finding may have important consequences for catalyst supports in industry. For example in stationary maintenance-free lead-acid batteries, $\text{H}_2$ and $\text{O}_2$ recombination is catalysed by the platinum group metals.\(^{98}\) The catalyst is loaded onto a high surface area support, palladium being most frequently used on carbon, alumina, or asbestos wool. A substantial amount of heat is evolved when $\text{H}_2$ and $\text{O}_2$ react on palladium and the ignition point for the gas mixture may be reached in extreme cases. The high price of palladium has prevented widespread
application of such catalysts, and maintenance-free batteries for vehicles rely on reaction of \( \text{O}_2 \) at the negative electrode and \( \text{H}_2 \) at the positive electrode according to

\[
\frac{1}{2} \text{O}_2 + \text{Pb} + \text{H}_2\text{SO}_4 \rightarrow \text{PbSO}_4 + \text{H}_2\text{O}
\]

and

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

It is known that oxygen is readily reduced on lead, finely divided lead being pyrophoric and susceptible to ignition in air at room temperature. \(^99\) Air oxidation of \( \text{Pb} \) contributes to the self-discharge of open-celled lead-acid batteries. \(^100\) Hydrogen is oxidised by \( \text{PbO}_2 \) at a very low rate. \(^100-102\) Hence if 0.5 monolayers of Pt on Pb is sufficient to mimic a Pt electrode for the formation of \( \text{O}_2 \) and \( \text{H}_2 \) then it should mimic the recombination reaction. The low solubility of hydrogen \(^103,104\) and oxygen \(^104\) in sulphuric acid and the small working area electrodes used in this study prevent elucidation of the recombination reaction at the present time.

6.8 Conclusions.

Addition of chloride to the acid electrolyte alters cyclic voltammograms significantly. Indications are found that the diffusion of soluble \( \text{Pb}^{2+} \) species away from the electrode is diminished with increasing [\( \text{Cl}^- \)]. Conversely the major features of the potential-step transients are not varied with chloride addition. In cyclic voltammetry a new feature is the reduction pre-peak due to the cathodic removal of \( \text{PbCl}_2 \) (mon). In potential step experiments a small falling transient component is observed
at low overpotentials, ascribed to the formation of the same monolayer of PbCl$_2$. The charges in both cases indicate the formation and reduction of a phase which is close to that for a monolayer. The potential position of the pre-peak in cyclic voltammetry shows that PbCl$_2$ is the monolayer. The formation of PbCl$_2$$_{(mon)}$ in potential step experiments is faster than formation of lead sulphate, which may be rationalised by chloride being a more effective complexing anion than sulphate.

None of these features suggest a detrimental effect on the negative plate of the lead-acid battery. Conversely beneficial effects may be noted: firstly the anodic charge capacity of the electrode is increased; and secondly the charge reversibility is improved, suggesting that more efficient charge/discharge cycles may be possible in the presence of chloride.

Platinum contamination is shown to have a significant effect on the lead anode. A fractional surface coverage of 0.5 by this metal inhibits all the lead reactions and the electrode displays behaviour identical to that for a pure Pt electrode.
CHAPTER SEVEN
THE ACTION OF METHYL ORANGE AND THE
MONO-DODECYL DERIVATIVE ON THE LEAD ANODE.

7.1 Introduction

7.1.1 Objective and strategy of this chapter.

The principal objective of this chapter was to investigate the effects of simple, monomeric, sulphonic acids on the lead anode as an attempt to model the behaviour for commercial ligno-sulphonate lead-acid battery expanders.

The approach has been the use of cyclic voltammetry and potential step techniques on small planar Pb electrodes and galvanostatic discharge of large porous negative battery plates.

Section 7.1 provides an introduction to the role of expanders in lead-acid batteries. Section 7.2 presents the results of the initial investigations on planar electrodes and identifies on sulphonic acid, methyl orange, as a potential expander. Subsequent testing of commercial battery plates is also reported. Modification of the structure of methyl orange was desired and Section 7.4 presents the results of the modified compound, lauryl orange, on planar electrodes and porous battery plates. Section 7.5 provides a conclusion to the electrochemical results.

The synthetic procedure employed to prepare the new derivative of
methyl orange is discussed in Section 7.6. The physical properties of the new compound are included in this section.

7.1.2 The role of additives in the negative plates of lead-acid batteries.

For many years lead-acid battery manufacturers have found it necessary to include additives in the manufacture of negative plates.\textsuperscript{1,2} In absence of the additives battery performance is found to be severely impaired at low temperatures and high rates of discharge. The useful lifetime of such batteries is also limited. The additives tend to alleviate these effects and are thus termed 'expanders'. Their effect depends on the ability to prevent sintering of sponge lead which leads to a coarsely crystalline structure.\textsuperscript{1} The current and capacity of a lead-acid battery is surface area dependent\textsuperscript{105} and any reduction in specific surface area (0.5 m\textsuperscript{2}/g for sponge lead\textsuperscript{106}) results in decreased performance.

In practice there are three main groups of additives:

\begin{enumerate}
\item Inorganic additives
\item Lampblack
\item Organic additives
\end{enumerate}

The additives are added in trace amounts to the paste used in plate preparation, typically less than 1\% of the weight of the dry mix. The probable co-operative behaviour between different additives result in difficulty in assigning effects to individual components.

Barium sulphate is used as an inorganic additive. It is generally assumed that BaSO\textsubscript{4} is favourable as a crystallisation seed for formation of lead sulphate on discharge as the two compounds are isomorphous.\textsuperscript{1} The
behaviour is independent of the method of addition as long as the particle sizes are small (less than 100 mesh). Both chemically precipitated BaSO₄ (blanc fixe) and the ground mineral (barite), free of iron and chloride compounds, are used commercially. Zachlin¹⁰⁷ studied the effect of BaSO₄ on battery plates and concluded that this additive was only essential for maintaining capacity during prolonged cycle life.

Lamblack or soot is an additive which has been used in the lead electrode for eight decades. Though this material is used in all commercial batteries, the function in porous electrodes is still unknown."¹⁰⁸ It is usually thought to improve the conductivity of the pasted electrode, and hence aid the formation of porous lead during the initial reduction. Zachlin¹⁰⁷ has observed improvement in cold starting and a decrease in the end-of-charge voltage. Standard specifications, such as that the lampblack should be tar-free and extraction with benzene should yield a colourless solution, are employed by manufacturers.

As a rule the organic additives are derivatives of natural products such as lignin, ligno-sulphonic acids and humic acids in the form of salt solutions or solids. Lignins were only established to be necessary with the advent of polyvinylchloride plate separators.⁶ Prior to this thin wooden sheets had been employed and sufficient lignin and ligno-sulphonates leached into the electrolyte.

The basis for prevention of sintering process by lignins appears to be related to the lowering of the surface energy by adsorption of the additive.¹ The potential of zero charge for lead is \(-0.62\) V (vs SHE)⁷⁵ and lead is thus positively charged against the electrolyte at the equilibrium potential of the negative plate \((-0.35\) V vs SHE). High
molecular weight anions and negatively charged colloids are adsorbed under these conditions. Adsorption decreases the surface energy so that formation of coarser crystals becomes energetically less favourable in the presence of expanders, and the sponge lead will remain finely divided for a longer period.

Lignins are complex natural products that occur together with cellulose in trees, their exact structures being unknown. They are composed of three basic building blocks: coniferyl alcohol, sinapyl alcohol, and p-coumaryl alcohol.

The actual polymeric structures of the lignin contain a variety of types of linkages between the phenolic monomers to give rise to a poly-phenolic ether system. Sulphonation is found to occur on the aliphatic side chains. Fig. 7.1 illustrates a typical structure for softwood lignin.

Previous workers have investigated the effects of commercially employed ligno-sulphonates. Archdale and Harrison have proposed that the expander, when in sufficient quantities, completely covers the surface of the lead and all subsequent electrochemical events must ensue through this layer. Dissolving Pb$^{2+}$ ions from the metal face migrate through the ligno-sulphonate and a transport overvoltage is observed. The formation of PbSO$_4$ crystals proceeds on the
Fig. 7.1  Typical structure of a softwood lignin. The existence of the types of linkages illustrated have been established, but they are arranged in this partial structure in an arbitrary manner for illustrative purposes. Reproduced from reference 109.
adsorption layer rather than the lead surface as occurs in the absence of expander. The adhesion of PbSO₄ to the metal is weakened and the passivating charge increased. It is also proposed that the expander is adsorbed onto the growing PbSO₄ crystal with the polar components oriented towards the crystal. When two adjacent growing crystals make contact then a 'bilayer' of non-polar constituents results and it is suggested that transport of ions is still possible within the bilayer. This phenomenon is beneficial for battery discharge in that increased mobility of Pb²⁺ and SO₄²⁻ through the growing crystallites increases the capacity of the electrode. The open structure of the PbSO₄ layer also prevents a pH gradient from developing due to the semi-permeable membrane behaviour described by Pavlov and Popova. This effect accounts for the formation of PbO and basic lead sulphates on discharge in the absence of expanders. Pavlov et al have observed two types of structure in the porous active mass of lead in negative plates, a primary or skeleton structure and a secondary structure. The primary structure serves as a current collector and mechanical support for the secondary structure. Measurement of the energy parameters established that it was the secondary structure that predominates in the discharge-charge process. The primary structure only accounts for 10-15% of the active electrochemical capacity. The secondary structure is completely consumed upon discharge and thus is totally rebuilt on charging. In the absence of expanders, micrographs showed the presence of coral-like dendrites which replaced the secondary structure of small lead crystallites. Therefore it followed that the action of the expander is to suppress the growth of these dendrites. Pierson et al have also shown that the lignin
expanders are capable of altering the geometry of lead crystals formed on cycled porous plates.

The adsorption of the expander onto lead and PbSO₄ must be moderate so that instantaneous precipitation of a passivating Pb²⁺-expander complex or irreversible formation of such a complex does not occur. The expander must also not hinder the release of Pb²⁺ from PbSO₄ on subsequent re-charge.

Expanders can be seen as not altering the site of storage of discharged Pb in PbSO₄ crystals, but mediating the ion transport.

The 'ligands' present in the ligno sulphonates are the sulphonic acid residues. Previous workers [34,38,40-44,105,106,110-116] have examined the effect of the poorly characterised commercially employed expanders on planar electrodes. Exploration of the effect of simple, monomeric, well characterised organic sulphonic acids either for their intrinsic behaviour or as model compounds for ligno-sulphonates has not previously been reported. Extensive examination of the literature failed to yield any synthetic approach to battery expanders. Initial investigations of simple sulphonic acids was thus undertaken.

7.2 Initial Investigation

7.2.1 Introduction

The effects of the selected sulphonic acids were determined by cyclic voltammetry at room temperature. The lead working electrode was mechanically polished prior to the commencement of each experiment. The electrode was cycled between -750 mV and 244 mV at 20 mV s⁻¹ for
10 minutes to yield uniform voltammograms. Solutions of the sulphonic acids in sulphuric acid were added to the electrolyte to result in concentrations of 20 mg/100 mL or where the solubility is less than this, saturated solutions were prepared. A range of sulphonic acids were investigated, the higher molecular weight compounds were indicator dyes.

The compounds benzene sulphonlic, p-amino benzene sulphonlic, p-toluene sulphonlic and sulphamic acids have no influence on the voltammograms. The alkyl sulphonlic acids, methane sulphonlic and trichloromethane sulphonlic acid, result in a decrease of the anodic charge (10% decrease for methane sulphonlic and 30% for trichloromethane sulphonlic) with no shift in potential. Only two dyes were found to have any effect on the lead anode. Xylenol orange shifted the oxidation to more positive potentials (by 50 mV) and with repeated cycling diminished the charge capacity of the electrode to 20% of that in the absence of the dye, thus having extreme deleterious effects on the electrode. Methyl orange (Fig. 7.2) showed no immediate effect, but upon continued cycling the charge of the electrode increased by 50%. There was no change in the potential of the system and the forward slope of the anodic peak remained constant, while the peak moved to slightly more positive potentials. This indicates that a simple increase in surface area by roughening is not an adequate explanation, instead methyl orange appears to delay the precipitation event. This behaviour demonstrated that further examination was required.

7.2.2 Action of methyl orange on planar electrodes.

Cyclic voltammetry at lowered temperatures (-18°C) showed that
Fig. 7.2 Voltammograms at room temperature for different elapsed times after the introduction of methyl orange to the electrolyte: a) cycle before and immediately after addition, b) 45 minutes later, and c) 90 minutes after addition. $T = 22^\circ C$, $[\text{H}_2\text{SO}_4] = 4.65 \text{ mol L}^{-1}$, [methyl orange] = 20 mg/100 mL, $E_c = -756 \text{ mV}$, $E_a = 244 \text{ mV}$, $v = 20 \text{ mV s}^{-1}$, analogue data.
there was an immediate effect on addition of methyl orange in that the capacity of the electrode increased by 20% (Fig. 7.3). Further cycling did not change this capacity. This is in contrast to the behaviour found at room temperature (22°C) where no immediate effect is evident and the capacity increases only upon cycling. Potentiostatic transients at room temperature showed no change on addition of methyl orange and cycled electrodes with the increased capacity surprisingly demonstrated no change relative to the electrode without additive. This is unexpected for a proposed delay in precipitation. Despite these somewhat conflicting results it was considered necessary to observe the effect on a battery.

7.2.3 **Action of methyl orange on porous plates.**

Battery discharge tests were conducted at Lucas Industries NZ Ltd. A 6 volt, 2 ampere-hour battery was cycled to develop stable capacity and was characterised by observing the potential of a cell during a fast galvanostatic discharge at low temperature. Some of the electrolyte was removed from the monitored cell in the discharged battery and methyl orange was dissolved in it (0.1% solution) to give a deep red colour. The loaded electrolyte was placed back in the cell and the battery recharged. The potential of that cell was monitored as the battery was again discharged under galvanostatic conditions at the same temperature and current as before. The discharge was observed to occur at an overpotential 300 mV lower and discharged 1.2 times longer than in the absence of methyl orange. During recharge the red electrolyte became progressively more yellow in colour. The battery was subsequently
Fig. 7.3 Voltammograms at −18°C a) before and b) immediately after addition of methyl orange to the electrolyte. No variation after cycle b) is observed. [methyl orange] = 20 mg/100 mL. \( E_c = -756 \text{ mV}, \) \( E_a = 244 \text{ mV}, \) \( v = 20 \text{ mV s}^{-1}. \) Digital data.
discharged a second time and monitored. The overpotential was then found to be similar to the original experiment in the absence of methyl orange.

7.3 Discussion of the battery experiment with methyl orange additive.

The behaviour for the first discharge cycle with methyl orange is consistent with the negative plate having a significantly increased surface area and possibly a more open structure. In a real battery plate the overpotential is mostly due to transport and diffusional effects in the porous active mass.¹ The second methyl orange discharge cycle indicates that the effect is not present after the first cycle. This correlates with the presence of the methyl orange red colour lasting for only the first recharge. The change of colour is due to destruction of the methyl orange by the highly oxidising properties of the lead dioxide in the positive plate. This was confirmed by preparing methyl orange solutions in 35% H₂SO₄ which retained the red colour, but quickly became pale straw yellow on addition of PbO₂.

A permanent effect was judged to be possible if methyl orange could be prevented from coming in contact with the positive plate. This is not feasible by the use of separators in a battery. Consideration was given to the use of a compound which had similar structural elements to methyl orange, but was insoluble in 35% H₂SO₄. It being proposed that such a compound could be mixed into the negative plate paste or adsorbed onto a charged negative plate. A survey of the literature and suppliers catalogues shows the absence of such a compound. This is consistent with the use of methyl orange and related compounds as aqueous pH indicator dyes. Therefore synthesis of a suitable compound was undertaken.
Examination of the structure of methyl orange:

![Structure of Methyl Orange](image)

(7.1)

indicates that replacement of one or both of the methyl groups with a large or long chain alkyl group would presumably achieve diminished solubility while retaining the chemical properties of the aromatic moiety and sulphonic acid residues required for interaction with the surface of the negative plates. Consideration was also taken of the synthetic route employed in the manufacture of methyl orange; the reaction of dimethyl aniline with diazotised sulphanilic acid.119

\[
\begin{align*}
\text{NH}_3^+ & \xrightarrow{i) \text{Na}_2\text{CO}_3} \text{NaN}^+ \\
\text{SO}_3^- & \xrightarrow{\text{ii) NaNO}_2, \text{aq. HCl}} \text{N}^+ \text{N}^- \\
& \xrightarrow{\text{AcOH}} (\text{CH}_2)\text{N}^+ \text{N}^- \text{SO}_3^- \\
\end{align*}
\]

(7.2)

Thus replacement of dimethyl aniline with an N-alkylated aniline would achieve the desired result. N-alkyl anilines are readily prepared by reaction of aniline with an alkyl bromide using standard techniques. The ratios of the mono and dialkyl products depend on the solvent, the ratio of the starting materials, and the rate of alkylation of aniline versus the monoalkylated aniline. Cost was taken into account with the choice of
alkyl bromide and it was decided that lauryl bromide (dodecyl bromide) was sufficiently inexpensive while having an adequate alkyl chain length to render the end product insoluble. The resulting new compound, p-dodecylaminoazobenzene-p'-sulphonic acid was prepared by established procedures and the synthetic technique is detailed in Section 7.6. It will be referred to as lauryl orange for brevity in the discussion below.

7.4 The Electrochemical behaviour of p-dodecylaminoazobenzene-p'-sulphonic acid (lauryl orange) at the lead anode.

7.4.1 Action of lauryl orange on cyclic voltammetry.

The new compound was adsorbed onto multicycled lead electrodes by removing the electrode from the H₂SO₄ electrolyte at a cathodic potential, rinsing with ethanol and diethylether, and then immersion into a saturated solution of the dye in dichloromethane for a 30 second period. The electrode was then rinsed with fresh dichloromethane so that only the adsorbed dye persisted. Fig. 7.4 displays a series of voltammograms at varying sweep rates at room temperature for an electrode immediately after adsorption of lauryl orange. The forward slopes are coincident and the peak current at each sweep rate is less than that for electrodes without lauryl orange, as described in Chapter 3 (Fig. 3.5). The electrode does not exhibit complete passivation immediately after the anodic peak and a slowly decreasing current flows until a sharp decrease is evident at higher anodic potentials. The cathodic wave does not resolve into a peak. Fig. 7.5 depicts voltammograms recorded at a sweep rate of 20 mV s⁻¹ at room temperature immediately after adsorption, and two and twelve hours
Fig. 7.4  Sweep rate dependence at 22°C immediately after lauryl orange is adsorbed on the electrode. $E_c = -756$ mV, $E_a = 244$ mV, digital data.
Fig. 7.5  Time dependence at room temperature after lauryl orange is adsorbed on the electrode: a) immediately after adsorption, b) 2 hours later, and c) 12 hours after adsorption. \( T = 22^\circ \text{C} \), \( E_c = -756 \text{ mV} \), \( E_a = 244 \text{ mV} \), \( v = 20 \text{ mV s}^{-1} \), digital data.
later. The voltammogram at two hours follows a coincident forward slope to the initial voltammogram but does not resolve into a clear peak. A plateau current is attained and passivation occurs at high anodic potentials. The twelve hour voltammogram shows a markedly increased peak current and steeper forward slope than for the previous two waves. The passivation is delayed even further. The cathodic wave does not resolve into a peak. Capacitance measurements indicate no variation in the surface area of the electrode throughout this time.

The results are invariant of whether the electrode is electrochemically cycled or maintained at open circuit potential between voltammograms.

The dependence of the anodic peak current on the square root of the sweep rate is displayed in Fig. 7.6. Initially a dependence similar to that reported in Chapter 3 is evident (Fig. 3.9), but at two and twelve hours elapsed time this parameter shows diminished dependence on \( \nu \).

The cyclic voltammograms recorded at low temperature (\(-18^\circ C\)) for each sweep rate are shown in Fig. 7.7. The forward slopes are similar but are shifted to slightly more anodic potentials with decreasing sweep rate. A slight discontinuity is evident for each sweep rate at \(-250\) mV. The cathodic wave resolves a cathodic peak at this temperature. Fig. 7.8 displays the voltammograms at 20 mV s\(^{-1}\) at successive times for low temperatures. The anodic wave progressively diminishes with time over the period examined. Capacitance measurements indicate no change in surface area.

The anodic peak current and anodic charge values for both room and low temperature experiments are listed in Table 7.1.
Fig. 7.6 Plot of the anodic peak current as a function of $v^{1/2}$ at 22°C for cyclic voltammograms at different times after adsorption of lauryl orange. □ immediately after adsorption, △ 2 hours later, and ○ 12 hours after adsorption. Data are listed in Table 7.1.
Fig. 7.7  Sweep rate dependence at -18°C immediately after lauryl orange is adsorbed on the electrode. $E_c = -756$ mV, $E_s = 244$ mV, digital data.
Fig. 7.8  Time dependence at −18°C after lauryl orange is adsorbed on the electrode: a) immediately after adsorption, b) 2 hours later, and c) 12 hours after adsorption. $E_c = -756 \text{ mV}$, $E_a = 244 \text{ mV}$, $\nu = 20 \text{ mV s}^{-1}$. Digital data.
Table 7.1 Table of anodic peak current and anodic charge for both room and low temperature cyclic voltammetry experiments on electrodes with adsorbed lauryl orange.

<table>
<thead>
<tr>
<th>t (hour)</th>
<th>v (mV s⁻¹)</th>
<th>(i_{A1}) (mA cm⁻²)</th>
<th>(q_{A1}) (mC cm⁻²)</th>
<th>(i_{A1}) (mA cm⁻²)</th>
<th>(q_{A1}) (mC cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>200</td>
<td>6.38</td>
<td>0.78</td>
<td>0.678</td>
<td>0.183</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>5.51</td>
<td>1.31</td>
<td>0.548</td>
<td>0.251</td>
</tr>
<tr>
<td>0</td>
<td>50</td>
<td>4.46</td>
<td>2.05</td>
<td>0.472</td>
<td>0.893</td>
</tr>
<tr>
<td>0</td>
<td>20</td>
<td>3.18</td>
<td>3.63</td>
<td>0.396</td>
<td>0.925</td>
</tr>
<tr>
<td>0</td>
<td>10</td>
<td>2.10</td>
<td>5.23</td>
<td>0.362</td>
<td>1.64</td>
</tr>
<tr>
<td>2</td>
<td>200</td>
<td>2.92</td>
<td>1.00</td>
<td>0.389</td>
<td>0.130</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>2.59</td>
<td>1.63</td>
<td>0.288</td>
<td>0.167</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>2.36</td>
<td>2.99</td>
<td>0.292</td>
<td>0.383</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>1.96</td>
<td>5.93</td>
<td>0.285</td>
<td>0.786</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>1.66</td>
<td>9.50</td>
<td>0.268</td>
<td>1.47</td>
</tr>
<tr>
<td>12</td>
<td>200</td>
<td>9.17</td>
<td>1.45</td>
<td>0.164</td>
<td>0.041</td>
</tr>
<tr>
<td>12</td>
<td>100</td>
<td>10.38</td>
<td>2.74</td>
<td>0.140</td>
<td>0.048</td>
</tr>
<tr>
<td>12</td>
<td>50</td>
<td>10.20</td>
<td>5.03</td>
<td>0.146</td>
<td>0.080</td>
</tr>
<tr>
<td>12</td>
<td>20</td>
<td>9.48</td>
<td>11.1</td>
<td>0.170</td>
<td>0.186</td>
</tr>
<tr>
<td>12</td>
<td>10</td>
<td>9.30</td>
<td>17.7</td>
<td>0.251</td>
<td>0.848</td>
</tr>
</tbody>
</table>
7.4.2 Action of lauryl orange on potential step experiments.

The new compound was adsorbed onto electrodes in the same manner as described in the previous section.

Fig. 7.9 displays the potential step transients for stepping potentials in the range −306 mV to −236 mV at room temperature. Falling transients are observed immediately after dye adsorption. An initially rapid decreasing portion is found at short times at large values for $E_2$. The transients do not cross over each other, so the current at any time for any potential is greater than that for lower (more negative) potentials.

The dependence on elapsed time after dye adsorption for potential step experiments is shown in Fig. 7.10. Falling transients are observed. The initial current increases with elapsed time. The behaviour is independent of whether the electrode is electrochemically cycled or maintained at open circuit. The low temperature potential step transients immediately after dye adsorption are shown in Fig. 7.11. The transients are similar to those for room temperature experiments. The current at any time is larger for a more anodic stepping potential. Variation in the transients with elapsed time shows a slight decrease (Fig. 7.12).

7.4.3 Preparation of battery plates with lauryl orange.

The action of p-dodecylaminoazobenzene-p'-sulphonic acid was investigated on porous lead plates at Lucas Industries NZ Ltd. All battery discharge tests were performed at this site. The leady oxide used to prepare the plates was manufactured by the Barton pot thermal process, the free lead content was determined to be 22%. The action of the dye on porous negative plates was determined by two methods: adsorption onto the
Fig. 7.9  Potential step transients at 22°C immediately after adsorption of lauryl orange on the electrode for stepping potentials, $E_2$, between $-306$ mV and $-236$ mV. Transients at lower values for $E_2$ are contained at all times within those for higher stepping potentials. $E_{pc} = -756$ mV, $E_1 = -456$ mV, digital data.
Fig. 7.10 Time dependence at 22°C for potential step transients after lauryl orange is adsorbed on the electrode: a) immediately after adsorption, b) 2 hours later, and c) 12 hours after adsorption. $E_{pc} = -756$ mV, $E_1 = -456$ mV. Digital data.
Fig. 7.11  Potential step transients at -18°C immediately after adsorption of lauryl orange on the electrode for stepping potentials, $E_2$, between -306 mV and -236 mV. Transients at lower values for $E_2$ are contained at all times within those for higher stepping potentials. $E_{pc} = -756$ mV, $E_1 = -456$ mV, digital data.
Fig. 7.12 Time dependence at -18°C for potential step transients after lauryl orange is adsorbed on the electrode: a) immediately after adsorption, b) 2 hours later, and c) 12 hours after adsorption, $E_{pc} = -756$ mV, $E_1 = -456$ mV, digital data.
ledy oxide prior to paste preparation, and adsorption onto fully charged negative plates. Bode,¹ Pavlov,² and Brown¹²⁰ adequately review the processes known to occur during paste preparation, curing and forming.

Lauryl orange was adsorbed onto leady oxide by stirring 100 g of the oxide with 100 mL dichloromethane solutions of the appropriate concentration. It was noted that the intense red colour in solution was instantly lost upon addition of the leady oxide to the solvent, indicating the ready adsorption of the dye onto the substrate. At dye concentrations greater than 10 mg/100 g leady oxide, the brown oxide particles were found to be in suspension in the solvent. The solvent was removed by rotary evaporation in a 20°C water bath. Loaded oxide samples were stored in a desiccator under dry nitrogen before use. Lead grids (3% antimony) were cut from a standard cast grid (115 mm x 120 mm) so that a small plate (50 mm x 120 mm) could be fabricated. A standard recipe was followed for preparation of the paste:

80.0 g leady oxide with adsorbed lauryl orange
0.238 g BaSO₄
0.160 g Carbon-black
6.20 mL 1400 g L⁻¹ H₂SO₄ (7.11 mol L⁻¹)

Prior to addition of the acid the dry ingredients were mixed thoroughly and slurried with distilled water. After the acid addition further water was added to afford the appropriate consistency. The paste was prepared in a plastic 200 mL beaker and a stainless steel rod was used for stirring. The acid addition was executed slowly over 15 min to maintain the temperature below 60°C. The grids were pasted against newsprint grade paper backing by applying the paste to the grid with a wiping diagonal
motion of the spatula. The pasted plates were then rolled with a cylindrical weight between two sheets of paper to give a smooth finish. The plates were cured in an oven at 80°C and 100% humidity.

The free lead metal concentration was measured after 24 hours and found not to have decreased from the original 22%. A further curing time of 24 hours was completed yielding the same result. Strongly oxidising conditions were then imposed by soaking the plates in 1100 g L⁻¹ H₂SO₄ and drying for 12 hours at room temperature. Subsequent free lead determination persistently returned a value of 22%.

The plates were assembled into individual cells for forming and subsequent testing. Each cell consisted of the small hand-made negative plate sandwiched between two full size commercially prepared positive plates (115 x 120 mm), commercial separators were employed. Thus the test cells were negative limited in capacity. The cells were formed in 1100 g L⁻¹ H₂SO₄ at a current of 1 A for 12 hours. After the formation the cells were placed in 1260 g L⁻¹ H₂SO₄ as the discharge electrolyte. The cells were then discharged by shorting so that a subsequent charge cycle could be applied.

Plates were prepared in the absence of adsorbed dye, similarly to the procedure described above. These plates yielded free lead concentrations below 5%. The plates were fully charged and rinsed with water, ethanol, and diethylether and then soaked in different concentrations of the dye in dichloromethane. The red solution became progressively colourless indicating the adsorption of lauryl orange onto the plate material.

Tables 7.2 lists the amount of dye adsorbed onto the leady oxide, the
amount of water for initial slurring of the dry mix, the extra water required to provide paste plasticity, and the mass of the cured paste. Table 7.3 lists the amount of dye adsorbed onto the post forming adsorbed plates.

7.4.4 Galvanostatic discharge of negative porous plates.

The room-temperature/low-rate discharge capacity of the leady oxide adsorbed plates was determined by a two current step process. The cells were individually discharged, initially at \( I_1 = 1 \text{ A} \) for 30 min and then \( I_2 = 2 \text{ A} \) until a negative plate potential of 0.9 V versus a cadmium reference electrode was achieved. The time required for this potential to be reached was recorded. The low-temperature/high-rate discharge characteristics were determined by recharging the cells at room temperature and placing the test cells in a refrigerator until the electrolyte and plates had cooled to \(-18^\circ\text{C}\). The cells were individually discharged at a current of 18.5 A and the time taken for discharge to 0.9 V (Cd) recorded (see Fig. 7.13). The post-forming dye adsorbed plates were discharged at low temperature only, using an identical method to that described above. The room-temperature discharge transients are similar in shape to those shown in Fig. 7.13 for a low-temperature discharge, except the discharge time is longer (Tables 7.3 and 7.4). Table 7.4 lists the results for the leady oxide adsorbed plates, the results are reported as time for the discharge to be completed and this time is ratioed to the mass of the cured paste for each plate, this being the value more readily compared between individual plates. Table 7.3 lists the discharge time and ratioed discharge time for the post forming adsorbed plates.
Table 7.2  List of paste weight and lauryl orange concentrations for plates prepared by adsorption onto the leady oxide. The dye concentration in column 2 is the mass of lauryl orange (mg) per 100 g of leady oxide. A surfactant Nital-X was added to facilitate wetting of the progressively more hydrophobic oxide with increasing dye concentration.

<table>
<thead>
<tr>
<th>plate number</th>
<th>dye conc. / (mg/100 g)</th>
<th>initial water / mL</th>
<th>extra water / mL</th>
<th>paste mass / g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>10.5</td>
<td>0.8</td>
<td>30.73</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>7.8</td>
<td>0.2</td>
<td>29.19</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>7.2</td>
<td>0.4</td>
<td>29.27</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>7.2</td>
<td>0.8</td>
<td>38.38</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>8.5</td>
<td>1.7</td>
<td>30.46</td>
</tr>
<tr>
<td>6</td>
<td>20</td>
<td>9.0</td>
<td>3.2</td>
<td>26.70</td>
</tr>
<tr>
<td>7</td>
<td>50</td>
<td>10.0</td>
<td>2.7</td>
<td>21.08</td>
</tr>
<tr>
<td>8</td>
<td>100</td>
<td>10.0</td>
<td>4.0</td>
<td>23.60</td>
</tr>
</tbody>
</table>
Table 7.3  List of paste weight, mass of adsorbed lauryl orange and low temperature discharge time for plates with the dye adsorbed after forming. The plates were discharged at -18°C. The last column gives the ratio of discharge time to mass of paste.

<table>
<thead>
<tr>
<th>plate number</th>
<th>paste mass /g</th>
<th>dye mass /mg</th>
<th>discharge time /s</th>
<th>ratio /(s/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25.67</td>
<td>1.0</td>
<td>22.5</td>
<td>0.88</td>
</tr>
<tr>
<td>2</td>
<td>20.51</td>
<td>2.0</td>
<td>34.5</td>
<td>1.68</td>
</tr>
<tr>
<td>3</td>
<td>20.32</td>
<td>5.0</td>
<td>33.0</td>
<td>1.62</td>
</tr>
<tr>
<td>4</td>
<td>24.37</td>
<td>10</td>
<td>36.0</td>
<td>1.48</td>
</tr>
<tr>
<td>5</td>
<td>25.90</td>
<td>25</td>
<td>51.0</td>
<td>1.97</td>
</tr>
<tr>
<td>6</td>
<td>20.20</td>
<td>0</td>
<td>63.0</td>
<td>3.12</td>
</tr>
<tr>
<td>7</td>
<td>24.89</td>
<td>0</td>
<td>42.0</td>
<td>1.69</td>
</tr>
</tbody>
</table>
Table 7.4 Table of discharge times for plates prepared with lauryl orange adsorbed on the leady oxide precursor.

<table>
<thead>
<tr>
<th>plate number</th>
<th>dye conc. / (mg/100 g)</th>
<th>t / min</th>
<th>t/(paste mass) / (min/g)</th>
<th>T = 22°C 30 min @ 1 A then 2 A</th>
<th>T = -18°C 18.5 A</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>64</td>
<td>2.08</td>
<td>70</td>
<td>2.28</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>35</td>
<td>1.24</td>
<td>86</td>
<td>3.05</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>&lt;30</td>
<td>&lt;1.02</td>
<td>50</td>
<td>1.71</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>102</td>
<td>2.66</td>
<td>54</td>
<td>1.41</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>102</td>
<td>3.35</td>
<td>52</td>
<td>1.71</td>
</tr>
<tr>
<td>6</td>
<td>20</td>
<td>70</td>
<td>2.62</td>
<td>40</td>
<td>1.50</td>
</tr>
<tr>
<td>7</td>
<td>50</td>
<td>65</td>
<td>3.08</td>
<td>38</td>
<td>1.80</td>
</tr>
<tr>
<td>8</td>
<td>100</td>
<td>&lt;30</td>
<td>&lt;1.27</td>
<td>46</td>
<td>1.95</td>
</tr>
</tbody>
</table>
Fig. 7.13  Potential-time transients for the galvanostatic discharge at $-18^\circ$C for a) negative plates prepared with lauryl orange adsorbed on the leady oxide precursor. [lauryl orange] = 10 mg/100 g leady oxide, and b) the discharge transient for a negative plate prepared in the absence of lauryl orange. The discharge time is measured until the negative plate potential reaches 0.9 V vs a cadmium reference electrode. $I = 18.5$ A, $T = -18^\circ$C, $[\text{H}_2\text{SO}_4] = 4.65$ mol L$^{-1}$.
7.4.5 Discussion.

The transients recorded for lauryl orange adsorbed on planar electrodes in both cyclic voltammetry and potential step experiments show that the new compound is modifying the behaviour of the lead anode. The influence of the new compound however can not be described as improving the characteristics of the lead anode. Figs. 7.4 and 7.5, and 7.7 and 7.8 show that the peak current is decreased by adsorption of lauryl orange when compared with the pure lead anode described in Chapter 3 (Fig. 3.5). The initial passivation event after the peak current is incomplete at room temperature. Complete passivation is only attained at higher anodic potentials. The large charge passed after the anodic peak does not increase the cathodic charge on subsequent cathodic scans and thus may represent a dissolution current resulting in diffusion of soluble \( \text{Pb}^{2+}_{\text{aq}} \) species away from the vicinity of the electrode.

A critical potential is evident at \(-250\, \text{mV}\) in Fig. 7.7 for low temperature cyclic voltammetry as a discontinuity in the anodic wave.

The voltammograms change with time both at room and low temperature. The change does not result in restoration of the voltammograms observed in the absence of adsorbed lauryl orange. This indicates that the dye is not desorbing but may be altering the morphology of the surface. Capacitance measurements show that a simple masking of the surface can not account for the decreasing charge of the voltammogram.

At low temperature the cathodic current on the cathodic scan is evident at high anodic potentials indicating that the anodic and cathodic reactions are not separated and operate simultaneously. Thus the anodic
charge represents only the integral of the net anodic current rather than the integral of the full anodic reaction.

Potential step transients both at room and low temperature show only decreasing transients. Thus nucleation and growth of a multilayer according to the model proposed in Chapter 5 is clearly suppressed. The initial current in the decaying transients is not easily determined at large anodic stepping potentials as this is dependent on the precision of the digitising event. Therefore this parameter is not tabulated.

The pasted plate discharge results are equally discouraging for the utility of the synthetic expander. In room temperature discharge experiments for plates prepared from leady oxide with adsorbed dye no clear trend of discharge capacity with adsorbed lauryl orange is evident (Table 7.4). The ratio of the discharge time to paste mass is consistently lower for the lauryl orange plates than for the plate prepared in the absence of the dye. This indicates the discharge is hindered by the dye. Low temperature results for these plates show diminished discharge time to paste mass ratios, and hence capacity, at all concentrations.

It is noted that with dye adsorbed on leady oxide that the dry leady oxide became progressively more hydrophobic with increasing dye concentration (Table 7.2). This may be seen in the increased water volume required for initial slurrying and paste consistency. This necessitated the addition of a detergent 'Nital-X' to allow slurry formation. This observation is consistent with the proposition that expanders adsorb onto Pb compounds with the polar end orientated towards the centre of the particle. In this case the orientation results in the long hydrophobic alkane chain being presented to the solvent. This hypothesis is further
confirmed by the persistence of free lead during prolonged plate curing. This fact shows that lauryl orange has adsorbed onto the free lead particles and effectively sheathed the metal surface from the effects of $\text{H}_2\text{SO}_4$ and $\text{O}_2$. This would appear to be in agreement with Sharpe\textsuperscript{112} and Yampol'skaya\textit{ et al.}\textsuperscript{121-123} who have reported a pronounced adsorption of commercial expanders on finely divided lead metal.

The post-forming adsorbed plates were loaded with smaller quantities of the dye but the compound is located rigidly on the surface of the formed plate rather than encapsulating free lead particles throughout the leady oxide precursor. Calculations based on the surface area of charged negative plates (0.5 m\textsuperscript{2}/g)\textsuperscript{106} and the charge associated with oxidation of a monolayer of lead (325 $\mu$C cm\textsuperscript{-2})\textsuperscript{43} were employed to estimate the number of equivalent monolayers of dye adsorbed on the surface of the negative plates. For 25 g of paste approximately 120 mg of dye is required for a monolayer coverage. Successively more concentrated dye solutions were sorbed onto negative plates until incomplete adsorption was evident by the colour of the solution. This occurred at a loading of 25 mg of dye, approximately one fifth of a monolayer. The discharge times at $-18^\circ\text{C}$ for all dye concentrations show diminished capacity compared with the blank plates.

7.5 Conclusions.

The present attempt to develop a negative plate expander failed to yield favourable results. The new compound, however, clearly shows the required ability to bind to lead metal as evidenced by the prevention of free lead oxidation during plate curing and in the modified behaviour of
planar lead electrodes. The aim of synthesising a new homologue of methyl
orange that is insoluble in aqueous solvents was successful. The synthesis
of the new dye is discussed along with the physical properties of the
compound in the following section.

7.6 Synthetic Procedure for lauryl orange.

7.6.1 Discussion.

Preparation of the substituted aniline precursor.

Alkylation of primary aromatic amines with alkyl halides is well
established but avoided as the extent of alkylation is difficult to control.
Thus mixtures of secondary, tertiary, and quaternary amine products are
often recovered, where only one of these is desired. The ratios of the
products depend on the solvent, the ratio of the starting materials, and
the relative rates of alkylation of alkylation of the primary, secondary,
and tertiary amines.

In the present work the mono-alkyl product was desired. Therefore
n-dodecyl bromide was treated with a three molar excess of aniline in
refluxing N,N-dimethylformamide in the presence of sodium hydrogen
carbonate giving N-dodecylaniline and N,N-didodecylaniline in yields of
70% and 6% respectively.

\[
\begin{align*}
\text{C}_{12}\text{H}_{25}\text{Br} + 3 \text{NH}_2 & \rightarrow \text{NaHCO}_3 \quad \text{DMF} \quad \text{reflux} \\
& \rightarrow \text{NH(C}_{12}\text{H}_{25}) + \text{N(C}_{12}\text{H}_{29})_2 \\
& \quad 70\% \quad 6\%
\end{align*}
\] (7.3)
The majority of the solvent was readily removed by rotary evaporation, and total removal was achieved by washing an ether solution of the resulting oil with water. Aniline however was not removed by this process and even washing with acidic aqueous solutions did not remove this compound as the water soluble hydrochloride salt. Vacuum distillation did not provide adequate separation of the three aromatic amines as they tended to co-distill. Thin layer chromatography determined that no solvent mixture would adequately separate all three compounds in one elution. However elution with ether separated aniline from the N-alkylated compounds and then elution with hexane separated these two compounds. Therefore an ether solution of the oil was passed through a short column of silica to remove aniline. The oily solid recovered on solvent removal was loaded onto a silica column at a loading of 1:60 and eluted with hexane. The two compounds eluted together and so chromatography on preparative layer plates (1 mm) was performed, eluting twice with hexane to give good separation of the N-alkylated amines.

Azo coupling between the aniline derivative and sulphanilic acid.

Azo coupling was achieved using the standard method as used for the preparation of methyl orange,119 (Scheme 7.1 in Section 7.2.3) with N-dodecylaniline replacing N,N'-dimethylaniline.

Slight modifications were employed, using extra glacial acetic acid to maintain solubility of the aniline derivative and isolation of the zwitterion rather than the anionic product.

Chromatography could not be readily used as the new compound adsorbs strongly to silica, alumina, and desiccating agents such as
magnesium sulphate. Thin layer chromatography and n.m.r. however showed the absence of the aniline precursor. Electron impact mass spectrometry did not reveal a molecular ion therefore Fast Atom Bombardment mass spectrometry was performed and yielded $M^+ + H$, $M^+ + 2H$, and $M^+ + 3H$.

7.6.2 Physical properties of lauryl orange.

The new compound, $p$-dodecylaminoazobenzene-$p$'-sulphonic acid, has a similar action as methyl orange as a pH indicator and has distinctive colours for the acid and base forms. The acidic form is a zwitterion and has a red hue, the basic form is anionic and is yellow in colour.

The site of protonation for the acid form of methyl orange has received much attention, with no definitive result available. Protonated $p$-aminoazobenzene compounds are found to have tautomeric structures:\textsuperscript{124-129}

\begin{align}
\begin{array}{c}
\begin{array}{c}
\text{H}^+
\end{array}
\end{array}
\end{align}

where $X$ is a substituent. The acid proton is found at the $\beta$-azo nitrogen or the amine nitrogen. Sawicki\textsuperscript{124-127} has estimated the position of the equilibrium, $K_T$, for a number of $p$-aminoazobenzene compounds using the ratio $C_e/A_e$, where $C_e$ and $A_e$ are the molar extinction coefficients in the
UV-visible region for the tautomeric forms C and A (7.4) respectively ($\lambda_{\text{max}} (A) = 320 \text{ nm, } \lambda_{\text{max}} (B) = 520 \text{ nm}$). Sawicki\textsuperscript{126} determined that the ratio $C_e/A_e$ was influenced by the substituent X (7.4) and in general as the electron-donor strength of the substituent increases from H to OMe the $C_e/A_e$ ratio decreases (2.57 for H, 1.00 for OMe), and as the withdrawing strength of X increases from H to NO$_2$, $C_e/A_e$ increases (8.7 for NO$_2$). The $C_e/A_e$ ratio decreases in the order -NHR > -NR$_2$ > -NH$_2$ for the amine substituents. Methyl orange was not determined in this study.

Yeh and Jaffe\textsuperscript{128} have commented that the ratio $C_e/A_e$ does provide a crude estimate of the tautomeric equilibrium (7.3) but only if the extinction coefficients are insensitive to the substituent effects which these workers considered unlikely.

Bershtein and Ginburg\textsuperscript{129} have reviewed further the tautomerism and have noted the absence of $\alpha$-azo nitrogen protonation. A value for the equilibrium for methyl orange is provided in this review ($K_T = 3.7$)\textsuperscript{130} indicating that protonation of the $\beta$-azo nitrogen predominates.

Machida et al\textsuperscript{131} measured the resonance raman spectra for methyl orange and the isotopically labelled D and $^{15}$N derivatives in dilute acid. These workers confirmed that the $\beta$-azo nitrogen was protonated but neglected to consider the tautomerism described in (7.4). Simultaneously these workers presented another report in a separate journal in which the resonance raman of methyl orange in 98\% H$_2$SO$_4$ was measured together with the D and $^{15}$N derivatives.\textsuperscript{132} In this paper the dicationic form of methyl orange was concluded to be
These workers incorrectly stated that the protonation of the α-azo nitrogen was in agreement with Sawicki.\textsuperscript{124-127} They did not state that the protonation of the α-azo nitrogen was inconsistent with their work in dilute acid.\textsuperscript{131} Therefore the results of Machida et al.\textsuperscript{131,132} may be regarded as erroneous and it may be assumed that methyl orange is predominantly in the C form (7.4) based on the measurement of \( K_r \) and the trend for \( C_e/A_e \) for electron withdrawing substituents observed by Sawicki.\textsuperscript{125}

\begin{equation}
\text{Me}_2\text{N}^+ \text{C}_6\text{H}_4\text{N}^+ \beta \text{N}_2\text{H}^- \text{C}_6\text{H}_4\text{SO}_3^- \quad (7.5)
\end{equation}

The acid form of lauryl orange is expected to follow the same site of protonation as methyl orange.

The acidic form could be expected to have conflicting solubility properties as a long alkyl residue is coupled to a cationic and anionic charge closely associated with the aryl ring system. In the extremely polar solvents dimethyl sulphoxide and dimethyl formamide the compound displays adequate solubility (ca. 40 mg/mL). The solubility in glacial acetic acid is moderate (ca. 5 mg/mL) while in the halocarbon and alcohol
solvents the solubility decreases (CH₂Cl₂: 1 mg/mL, CHCl₃: 0.5 mg/mL, MeOH and EtOH: 0.08 mg/mL). The acid form is insoluble in water, but a trace of base yields a yellow coloured solution of the anion. The compound is insoluble in hexane, acetone, ether, and 35% H₂SO₄, this last solvent being where insolubility was desired and designed for. The compound is soluble in conc. HCl, dilution with water to 5.1 mol L⁻¹ resulting in the separation of the compound from the aqueous phase. This increase in solubility is due to the formation of the dication, presumably by protonation of the amino nitrogen (7.4). There is no discussion in the literature of the pKa for the sulphonate group in methyl orange. Machida et al.¹³² indicate that the sulphonate is not protonated in 98% H₂SO₄. The new compound showed unchanged melting point and ¹H and ¹³C n.m.r. spectra after being maintained as a suspension in 35% H₂SO₄ for 30 days indicating the stability in this media.

In summary it is observed that the polar constituents of the molecule outweigh the non-polar components in the solubility. Preparation of the basic sodium salt (yellow) of lauryl orange was found to be difficult as this yields essentially a sulphonic acid detergent. Solutions of the acid form in organic solvents when shaken with aqueous base result in coagulated mixtures and suspensions that do not separate on washing with brine. The basic form can be made on silica by loading a column with a CH₂Cl₂ solution of the acid form and then eluting with tetrahydrofuran. The basic form gradually separates from the origin but can not be removed from the column. Consistent to this behaviour, CH₂Cl₂ solutions of the acid form tend to stain glassware leaving a red sheen that can not be removed with CH₂Cl₂, but may readily be removed by washing with MeOH.
to give a yellow solution of the basic form. Dilution of the acid form in EtOH converts the acid form to the base form, at concentrations less than ca. 40 mg/mL the base form predominates.

Aggregation occurs for both the zwitterion and the anionic forms. In the halocarbon and alcohol solvents, the rates of aggregation being MeOH, EtOH > CHCl₃ > CH₂Cl₂. This is a problem if solutions are required for n.m.r. spectroscopy. Aggregation is known to occur with methyl orange and the rate has been previously studied.¹³³⁻¹³⁵ The rate of aggregation for the present compound could well be expected to be faster, as the long alkyl chain would form bilayers in the zwitterion similar to that found for lipids, and the basic (anionic) form could well form micelle structures.¹³⁶

The UV-visible spectra of the compound in both the acid and base form were measured and compared with methyl orange. EtOH was employed as a solvent, dilution to the appropriate concentration converting the acid form to the base form as described above. The zwitterion is formed at the same concentration by addition of small quantities of conc. HCl. The spectra were measured on a Varian DMS100 UV-Visible Spectrophotometer using quartz 1.0 cm cells. The spectra were corrected for solvent absorption. The values for λₘₐₓ and log ε are listed in Table 7.5. The UV-visible maxima for methyl orange are identical to that reported previously.¹³⁷ It can be seen that there is no major difference between methyl orange and lauryl orange in the acid form apart from higher molar absorbivities for methyl orange. In the base form lauryl orange displays an absorbance at 248.8 nm that is not present for methyl orange.

The new compound is a pH indicator. The pKa is of interest, but
Table 7.5  Table of the UV-visible absorption maxima for lauryl orange and methyl orange in ethanol.

<table>
<thead>
<tr>
<th></th>
<th>acid</th>
<th>base</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$</td>
<td>log $\varepsilon$</td>
</tr>
<tr>
<td>$p$-dodecylaminoazo-</td>
<td>511.5</td>
<td>4.34</td>
</tr>
<tr>
<td>benzene-$p'$-sulphonic</td>
<td>321.9</td>
<td>3.62</td>
</tr>
<tr>
<td>acid (lauryl orange)</td>
<td>282.0</td>
<td>3.61</td>
</tr>
<tr>
<td></td>
<td>232.1</td>
<td>3.62</td>
</tr>
<tr>
<td>$p$-diaminoazobenzene-</td>
<td>519.2</td>
<td>4.60</td>
</tr>
<tr>
<td>$p'$-sulphonic acid</td>
<td>319.7</td>
<td>3.99</td>
</tr>
<tr>
<td>(methyl orange)</td>
<td>284.2</td>
<td>3.97</td>
</tr>
<tr>
<td></td>
<td>230.1</td>
<td>4.05</td>
</tr>
</tbody>
</table>
as the new compound is insoluble in water, this parameter can not be directly measured and must be inferred from other solvents. This is achieved by determining the position of the acid-base equilibrium of the compound at a given acid strength in EtOH and comparing this with the position of the equilibrium for methyl orange in the same solvent/acid mix. An ethanolic solution of lauryl orange had sufficient glacial acetic acid added until the colour of the system had partially changed from yellow to red (21.3 mL acetic acid to 100mL of EtOH). An identical solvent mixture was prepared for the solvent blank and for a solution of methyl orange. The spectra for methyl orange and lauryl orange were recorded and the relative amounts of the acid and base forms were calculated by curve fitting for the peaks at wavelengths greater than 400 nm.

The relationship:

$$\text{pH} = \text{pKa} + \log \frac{[\text{base}]}{[\text{acid}]}$$

(7.7)

is true for aqueous systems. In other solvents a correction may be applied:

$$\text{pH} = \text{pKa} + \log \frac{[\text{base}]}{[\text{acid}]} + \text{pK}_{\text{sol}}$$

(7.8)

indicating that the pKa in non-aqueous solvents differ to that in water by a constant, pK_{sol}, dependent on the solvent. In the present system there are two compounds in identical solvents and at the same hydrogen ion concentration, therefore:

$$\text{pKa}_1 + \log \frac{[\text{base}_1]}{[\text{acid}_1]} = \text{pKa}_2 + \log \frac{[\text{base}_2]}{[\text{acid}_2]}$$

(7.9)
where 1 and 2 denote methyl orange and lauryl orange. The pKa for methyl orange is known (pKa = 3.76)\textsuperscript{137,138} and the ratios of the acid and base forms for both compounds under these conditions was determined by UV-visible spectroscopy. It was found that the pKa for p-dodecylaminoazo-benzene-p'-sulphonic acid was 4.06. This value indicates that the acid form is more stabilised by the mono dodecyl group in lauryl orange than methyl orange is by two methyl groups. The previously determined values for pKa for the higher homologues of methyl orange in water are\textsuperscript{138}: methyl orange, 3.76; ethyl orange, 4.34; propyl orange, 3.95; butyl orange, 4.01; and hexyl orange, 3.71. There is no correlation of the length of alkyl chain with pKa for the series of dyes. The pKa determined for the new compound falls within the limits of the homologues.

7.6.3 Nuclear Magnetic Resonance Spectroscopy.

Assignment of the n.m.r. signals for the zwitterion form of lauryl orange was achieved by comparison with the related compound methyl orange\textsuperscript{139}. The anionic form of the new compound was not examined due to the difficulties imposed by the detergent-like behaviour.

Exhaustive examination of the literature failed to locate published n.m.r. assignment for methyl orange. Thus the n.m.r. spectra for both anionic and zwitterion forms for this compound were measured and interpreted during the course of the present work and are presented here. The base form was the commercially available sodium salt and spectra were recorded in deuterated dimethylsulphoxide (DMSO-d6). The red acid form was prepared by acidification of DMSO-d6 solutions of the sodium salt with minute additions of concentrated hydrochloric acid. An X-H
correlation spectrum was determined for the base form. The structural assignment of methyl orange was facilitated by comparison with the reported $^{13}$C n.m.r. signals for N,N'-dimethylaniline, azobenzene, and sodium benzenesulphonate, and by consideration of the X-ray crystallographic structure of methyl orange.

The assigned signals according to the numbering scheme below are listed in Table 7.6 for the base form (7.1) and Table 7.7 for the acid form (7.6).

\[(7.10)\]

Spectroscopic assignment of lauryl orange was hindered by the presence of two tautomeric isomers in solution. This is evident in the splitting pattern of the aromatic $^1$H signals and the $^1$H signals for the alkyl methylene group bound to the amine nitrogen. The latter appearing as triplets at two different downfield shifts. The assignment was facilitated by addition of hydrochloric and trifluoroacetic acids to the n.m.r. solvent resulting in one tautomer predominating in each case. Dynamic effects in the $^{13}$C spectra result in signal averaging and thus only the downfield shifts are reported. The tautomeric isomers are denoted below.

\[(7.11)\]
Table 7.6  Table of n.m.r. signals for the anionic form of methyl orange in DMSO-d6.

<table>
<thead>
<tr>
<th>Position</th>
<th>$^{13}$C/ppm</th>
<th>$^1$H/ppm</th>
<th>Coupling</th>
</tr>
</thead>
<tbody>
<tr>
<td>la'</td>
<td>39.81</td>
<td>3.05</td>
<td></td>
</tr>
<tr>
<td>lb'</td>
<td>39.81</td>
<td>3.05</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>148.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>120.89*</td>
<td>7.71</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>126.25*</td>
<td>7.71</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>142.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>120.89*</td>
<td>7.71</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>126.25*</td>
<td>7.71</td>
<td></td>
</tr>
<tr>
<td>1''</td>
<td>152.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2''</td>
<td>124.51</td>
<td>7.79</td>
<td>$J_{2',3'} = 11$ Hz</td>
</tr>
<tr>
<td>3''</td>
<td>111.28</td>
<td>6.83</td>
<td>$J_{3',x'} = 11$ Hz</td>
</tr>
<tr>
<td>4''</td>
<td>151.83</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5''</td>
<td>111.28</td>
<td>6.83</td>
<td>$J_{5',8'} = 11$ Hz</td>
</tr>
<tr>
<td>6''</td>
<td>124.51</td>
<td>7.79</td>
<td>$J_{6',8'} = 11$ Hz</td>
</tr>
</tbody>
</table>

* interchangeable
Table 7.7  Table of n.m.r. signals for the zwitterion form of methyl orange in DMSO-d6.

<table>
<thead>
<tr>
<th>Position</th>
<th>$^{13}$C/ppm</th>
<th>$^1$H/ppm</th>
<th>Coupling</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a'</td>
<td>43 br</td>
<td>3.15</td>
<td></td>
</tr>
<tr>
<td>1b'</td>
<td>43 br</td>
<td>3.15</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>148.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>120.99</td>
<td>7.78</td>
<td>$J_{2,3} = 8.5$ Hz</td>
</tr>
<tr>
<td>3</td>
<td>126.44 br</td>
<td>7.72</td>
<td>$J_{3,2} = 8.5$ Hz</td>
</tr>
<tr>
<td>4</td>
<td>143.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>126.44 br</td>
<td>7.72</td>
<td>$J_{5,6} = 8.5$ Hz</td>
</tr>
<tr>
<td>6</td>
<td>120.99</td>
<td>7.78</td>
<td>$J_{6,5} = 8.5$ Hz</td>
</tr>
<tr>
<td>1''</td>
<td>152.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2''</td>
<td>128.84</td>
<td>7.95</td>
<td>$J_{2',3'} = 8.9$ Hz</td>
</tr>
<tr>
<td>3''</td>
<td>114.62 br</td>
<td>7.21</td>
<td>$J_{3',2'} = 8.9$ Hz</td>
</tr>
<tr>
<td>4''</td>
<td>152.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5''</td>
<td>114.62 br</td>
<td>7.21</td>
<td>$J_{5',6'} = 8.9$ Hz</td>
</tr>
<tr>
<td>6''</td>
<td>126.84</td>
<td>7.95</td>
<td>$J_{6',5'} = 8.9$ Hz</td>
</tr>
</tbody>
</table>
Table 7.8 Table of n.m.r. signals for tautomer 3a of lauryl orange in DMSO-d6 + CF₃COOH.

<table>
<thead>
<tr>
<th>Position</th>
<th>¹³C/ppm</th>
<th>¹⁹H/ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1'</td>
<td>49.66</td>
<td>3.20</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>7.35</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>7.45</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>7.45</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>7.35</td>
</tr>
<tr>
<td>1''</td>
<td></td>
<td>7.70</td>
</tr>
<tr>
<td>2''</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3''</td>
<td></td>
<td>6.69</td>
</tr>
<tr>
<td>4''</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5''</td>
<td></td>
<td>6.69</td>
</tr>
<tr>
<td>6''</td>
<td></td>
<td>7.70</td>
</tr>
</tbody>
</table>
Table 7.9 Table of n.m.r. signals for tautomer 3b of lauryl orange in DMSO-d6 + HCl.

<table>
<thead>
<tr>
<th>Position</th>
<th>$^{13}$C/ppm</th>
<th>$^1$H/ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1'</td>
<td>51.08</td>
<td>3.18</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>7.44</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>7.50</td>
</tr>
<tr>
<td>4</td>
<td></td>
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<td>7.50</td>
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<tr>
<td>6</td>
<td></td>
<td>7.44</td>
</tr>
<tr>
<td>1''</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2''</td>
<td></td>
<td>7.58</td>
</tr>
<tr>
<td>3''</td>
<td></td>
<td>7.58</td>
</tr>
<tr>
<td>4''</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5''</td>
<td></td>
<td>7.58</td>
</tr>
<tr>
<td>6''</td>
<td></td>
<td>7.58</td>
</tr>
</tbody>
</table>
The assigned n.m.r. signals for the aromatic constituents of 3a and 3b are listed in Tables 7.8 and 7.9 respectively (see Section 7.6.4 for a complete list of n.m.r. signals).

7.6.4 Experimental.

Melting points were determined on Reichert Kofer block and were uncorrected.

All $^1$H n.m.r. spectra were measured at 400.13 MHz and all $^{13}$C n.m.r. spectra were measured at 100.62 MHz on a Bruker AM400 instrument operating at 9.2 Tesla. The n.m.r. data is expressed as parts per million downfield shift from trimethylsilane as the internal reference. The $^1$H n.m.r. data is quoted as position ($\delta$), multiplicity (s = singlet, d = doublet, t = triplet, quint = quintet, m = multiplet, br = broad), coupling constant ($J$, Hz) and assignment. The $^{13}$C n.m.r. data is quoted as position ($\delta$) and assignment (quaternary nuclei as determined by DEPT analyses without further assignment are indicated).

Ultra-violet spectra were determined using 1.0 cm cells on a Varian DMS 100 spectrometer.

Low resolution electron impact mass spectra were determined on a VG 705E mass spectrometer using an ionising potential of 70 eV at a nominal resolution of 1000. High resolution spectra were obtained at a nominal resolution of 5000. Fast Atom Bombardment mass spectra were determined at a nominal resolution of 800 by argon bombardment of the sample suspended in a glycerol matrix.

Silica gel for column chromatography was Kieselgel S (Riedel-de Haën). Analytical thin layer chromatography (t.l.c.) was conducted on
0.2 mm plates of Merck aluminium backed silica gel, and the
cromatograms were developed with anisaldehyde or visualised under ultra-
violet light. Preparative thin layer chromatography (p.l.c.) was carried out
on 1 mm thick plates of Kieselgel PF254 + 366 (Merck).

Ether refers to diethylether. Hexane refers to the commercial
hydrocarbon solvent, b.p. 66-70°.

The numbering of the prepared new compounds are given below.

\[ \text{R} = \text{H (1) or C}_{11} \text{H}_{25} (2) \]

\[ \text{N-dodecylaniline (1) and } \text{N,N'}-\text{didodecylaniline (2).} \]

Dodecyl bromide (20 g, 0.08 mol), aniline (20 g, 0.21 mol) and sodium
bicarbonate (30 g, 357 mmol) were refluxed in dimethyl formamide (100 mL)
for 36 hrs after which time t.l.c. showed the absence of dodecyl bromide.
The dark reaction mixture was filtered and the solvent was removed under
reduced pressure. The resulting oil was dissolved in ether and washed with
water. The crude product was filtered through a short silica column to
remove aniline. Rotary evaporation yielded an oily solid (4.3 g). A portion
(2.04 g) was chromatographed (p.l.c.) on silica and elution with hexane gave two bands. The first band gave N-dodeylaniline (1) (1.61 g, 70%) which crystallised from ether/hexane as needles, m.p. 26-27° (Found M+ 261.2474, C18H31N requires 261.2457).

δH (CDCl3) 0.89, t. (H 12)_3; 1.25, br. s. (H 3')_2 - (H 11')_2; 1.56, dt, J2,1: 7.1 Hz, J2,3: 6.9 Hz, (H 2')_2: 3.04, t, J1,2: 7.1 Hz, (H 1')_2: 3.50, br. s, NH: 6.54, dd, J2,3 = J6,5 8.1 Hz, J2,4 = J6,4 1.0 Hz. H 2 and H 6.

δc (CDCl3) 14.16, C 12'; 22.75, C 11'; 27.24, C 10'; 29.43 - 29.75. multiple CH₂ signals; 31.99, C 2'; 43.98, C 1'; 112.64, C 2; 129.18, C 3, C 5; 148.54, C 1.

m/z 261 (M+, 18%). 106 (M+ - C11H23, 100%).

The second band gave N,N'-didodecyraniline (2) (0.25 g, 6%) as an oil, m.p. 5° (Found M+ 429.4319, C30H55N requires 429.4335).

δH (CDCl3) 0.88, t. (H 12')_3; 1.28, br. s. (H 3')_2 - (H 11')_2; 1.56, dt, J2,1: 7.7 Hz, J2,3: 6.9 Hz, (H 2')_2; 3.23, t, J1,2: 7.7 Hz, (H 1')_2; 6.60, m, H 1, H 4, H 6; 7.17, dd, H 3, H 5.

δc (CDCl3) 14.15, C 12'; 22.74, C 11'; 27.25 - 29.73, multiple CH₂ signals; 31.98, C 2'; 51.08, C 1'; 111.68, C 2, C 6; 115.08, C 4; 129.17, C 3, C 5; 148.17, C 1.

m/z 429 (M+, 9%). 274 (M+ - C11H23, 100%), 120 (274 - C11H22, 30%).

p-dodecylaminoazobenzene-p'-sulphonic acid (3).

Sulphanilic acid dihydrate (0.40 g, 1.9 mmol) was neutralised in a solution of anhydrous sodium carbonate (0.10 g, 0.95 mmol) in warm (< 50°C) water (4 mL). The solution was then cooled to ca. 15° and a solution of sodium nitrite (0.14 g, 2.1 mmol) in water (0.4 mL) was added.
The mixture was poured with stirring into conc. HCl (0.4 mL) and crushed ice (2.5 g) and was stirred for 20 min after which time a suspension of pale yellow diazobenzene sulphonate crystals had formed. N-dodecylaniline (0.50 g, 1.9 mmol) was dissolved in glacial acetic acid (5 mL) and added with stirring to the suspension of diazobenzene sulphonate. Sufficient glacial acetic acid (10 mL) was added to redissolve precipitated N-dodecylaniline. After 15 min the mixture became blood red in colour and a red solid formed. The mixture was extracted with chloroform. Removal of the solvents under reduced pressure gave p-dodecylaminoazobenzene-p'-sulphonic acid (3) (0.68 g, 80%) as a waxy solid, m.p. 87-89°, m/z (FAB) 448 (M⁺ + 3H, 2.0%), 447 (M⁺ + 2H, 1.7%), 446 (M⁺ + H, 2.3%). N.m.r. indicated the presence of two tautomers: (3a) and (3b) (see Section 7.6.3, (7.11)). The relative ratio of each conformer was found to vary, dependent on the solvent used. The data reported are for the prevalent conformer in each case.

\[ DMSO + CF₃COOH \text{ (3a):} \]

\[
\begin{align*}
\delta_H & \quad 0.83, \text{ t, (H 12)}_3; \\
& \quad 1.20, \text{ br s, 18H, (H 11)}_2 - (H 3)_2; \\
& \quad 3.20, \text{ t, (H 1)}_2; \\
& \quad 6.69, \text{ d, H 3"}, \text{ H 5"}; \\
& \quad 7.45, \text{ m, H 3}, \text{ H 5}; \\
& \quad 7.70, \text{ m, H 2"}, \text{ H 6"}. \\
\delta_C & \quad 11.35, \text{ C 12}; \\
& \quad 22.06, \text{ C 11}; \\
& \quad 25.87, \text{ C 10}; \\
& \quad 28.43 - 28.97, \text{ multiple CH₂ signals}; \\
& \quad 31.26, \text{ C 2"}; \\
& \quad 49.66, \text{ C 1"}; \\
& \quad 120.94, \text{ CH}; \\
& \quad 121.59, \text{ CH}; \\
& \quad 125.42, \text{ CH}; \\
& \quad 126.46, \text{ CH}; \\
& \quad 126.93, \text{ CH}; \\
& \quad 129.69, \text{ CH}. \\
\]

\[ DMSO + HCl, \text{ (3b):} \]

\[
\begin{align*}
\delta_H & \quad 0.80, \text{ t, (H 12)}_3; \\
& \quad 1.19, \text{ br s, 18H, (H 11)}_2 - (H 3)_2; \\
& \quad 3.18, \text{ t, (H 1)}_2; \\
& \quad 7.44, \text{ d, H 2}, \text{ H 6}; \\
& \quad 7.50, \text{ d, H 3}, \text{ H 5}; \\
& \quad 7.58, \text{ d, H 2"}, \text{ H 3"}, \\
& \quad H 5", \text{ H 6"}. \\
\]

\[ \delta_c \ 14.12, \ C \ 12'; \ 15.88, \ C \ 11'; \ 22.24, \ C \ 10'; \ 25.25 - 29.15, \ \text{multiple CH}_2 \text{ signals}; \ 31.44, \ C \ 2'; \ 51.08, \ C \ 1'; \ 123.45, \ CH; \ 129.15, \ CH; \ 129.97, \ CH; \ 136.39, \ CH. \]

iii) DMSO: 50/50 mixture (3a) and (3b):

\[ \delta_h \ 0.83, \ t, \ 3b-(H 12)_{3}, \ 3a-(H 12)_{3}; \ 1.2, \ \text{br s}, \ 36H, \ 3b-(H 11')_{2}-(H 3')_{2}, \ 3a-[(H 11')_{2}-(H 3')_{2}]; \ 1.56, \ \text{dt}, \ 3b-(H 2)_{2}, \ 3a-(H 2')_{2}; \ 3.11, \ t, \ 3b-(H 1)_{2}; \ 3.23, \ t, \ 3a-(H 1)_{2}; \ 6.68, \ d, \ 3a-H \ 3'', \ 3a-H \ 5''; \ 7.30, \ m, \ 3b-H \ 2, \ 
3b-H \ 6, \ 3a-H \ 2, \ 3a-H \ 6; \ 7.45, \ d \ d, \ 3b-H \ 3, \ 3b-H \ 5, \ 3a-H \ 3, \ 3a-H \ 5; \ 7.70, \ m, \ 3b-H \ 2'', \ 3b-H \ 3'', \ 3b-H \ 5'', \ 3b-H \ 6'', \ 3a-H \ 2'', \ 3a-H \ 6''. \]

\[ \delta_c \ 13.93, \ 3b-C \ 12', \ 3a-C \ 12'; \ 22.10, \ 3b-C \ 11', \ 3a-C \ 11'; \ 25.89, \ 
3b-C \ 10', \ 3a-C \ 10'; \ 28.48 - 29.02, \ \text{multiple CH}_2 \text{ signals}; \ 42.55, \ 3b-C \ 2', \ 3a-C \ 2'; \ 49.45, \ 3b-C \ 1', \ 3a-C \ 1'; \ 111.66, \ CH; \ 121.02, \ CH; \ 125.41, \ CH; \ 126.49, \ 
CH; \ 129.78, \ CH; \ 142.62, \ 3b-C \ 4, \ 3b-C \ 4; \ 148.44, \ 3b-C \ 1, \ 
3a-C \ 1; \ 152.08, \ 3b-C \ 4'', \ 3a-C \ 4''; \ 152.41, \ 3b-C \ 1'', \ 3a-C \ 1''. \]
8.1 Introduction

The aim of this investigation was to use the two transient techniques, potential sweep and potential step, to elucidate the kinetics of the lead anode in aqueous sulphuric acid. The previous models for this reaction have been significantly altered by the work presented in this thesis. The sections that follow in this chapter summarise the findings of the experimental chapters in this thesis, and discuss the new concepts that have been used to interpret the kinetics. Cross-referencing to relevant figures and sub-sections is provided.

8.2 Potential sweep experiments.

The techniques used in Chapter 3 were the potential sweep methods: cyclic voltammetry and potential-ramp/hold.

i) Initial investigations showed an anodic peak, followed by complete passivation. The first cycle gave higher anodic current than all subsequent cycles, for a freshly polished electrode (Section 3.2, Fig. 3.1). It was deduced that a surface film was formed in the first cycle and remained present in subsequent cycles, hence lower current.

ii) Cathodic potential treatment of multicycled electrodes and
subsequent cycling resulted in voltammograms similar to that found for the first cycle (Section 3.4, Fig. 3.3). Thus the cathodic pre-treatment removes the surface film and larger currents are seen.

(iii) The sweep rate dependence was found to be significantly different for multicycled and cathodically pre-treated electrodes (Section 3.5, Figs. 3.5-3.9, Tables 3.1 and 3.2).

(iv) Both potential-ramp/hold and pseudo-capacitance and faradaic resistance measurements (Section 3.6 and Figs. 3.10 and 3.11, and Section 3.7 and Figs. 3.12 and 3.13 and Tables 3.3 and 3.4 respectively) indicated that multicycled and cathodically pre-treated electrodes are controlled by different mechanisms, because of the presence, or absence respectively, of a surface film.

(v) The temperature dependence of multicycled electrodes was demonstrated (Section 3.8, Figs. 3.14-3.20, Table 3.5). In general the anodic charge and peak current were found to diminish at progressively lower temperatures.

(vi) The behavioural differences between multicycled and cathodically pre-treated electrodes were interpreted to be due to fundamental mechanistic differences (Section 3.11, Fig. 3.21). It was construed that multicycled electrodes are controlled by a thin resistive film and subsequent modification of the resistance occurs by precipitation of microcrystalline PbSO$_4$. Conversely, cathodically pre-treated electrodes initially are film-free and the transient reflects the development of the film under control by two-dimensional growth laws (evident by the growth transients in Fig. 3.11). It was found that a significant proportion of the charge passed, during both resistance control or two-dimensional growth
control, represents the formation of a soluble Pb²⁺ species that may diffuse irreversibly away from the electrode.

8.3 Potential step transients.

i) Potential-step transients were found to be only poorly reproducible between different polishing intervals of the electrode (Section 4.3, Fig. 4.3). This is in contrast to the good reproducibility found for cyclic voltammetry (Section 3.3, Fig. 3.2). Potential-step transients within the same polishing interval were found to have good reproducibility (Section 4.3, Fig. 4.2). It is clear that nucleation is involved, since small differences in surface preparation would affect the number and appearance rate of nuclei.

ii) Unlike cyclic voltammetry, potential-step transients displayed insignificant variation with the cathodic pre-treatment (Section 4.4, Fig. 4.4). In all cases there was an initial current, deduced to be dissolution from the bare surface, and an increasing current to a peak followed by a decay, due to growth of a surface film and passivation of the electrode by microcrystalline PbSO₄ respectively.

iii) The dependence of the form of the transient on anodic stepping potential was explored (Section 4.5, Figs. 4.5-4.7, Table 4.1). The initial current and rate of increase of the initial current were found to increase with stepping potential, indicative of the increase in dissolution and growth of the surface film. The passivation rate was also increased.

iv) The temperature dependence of potential-step transients was examined (Section 4.6, Figs. 4.8-4.11, Table 4.2). In general the features of dissolution and surface film growth are diminished, and the passivation
rate increased, at lower temperatures.

v) Previous attempts at interpreting the mechanism that controls the transients were discussed and found to be inadequate (Section 4.8). However, most previous interpretations have concluded that the transients represent growth of a solid phase on the electrode surface, though whether the charge-transfer should be controlled by a two- or three-dimensional growth law was not agreed upon.

vi) The potential-step transients were found to be similar to the potential-ramp/potential-hold transients (Section 4.9) described in Chapter 3 (Section 3.6, Fig. 3.11) for cathodically pre-treated electrodes.

8.4 Quantitative kinetic model.

A mathematical model was developed to account for the transients reported in Chapters 3 and 4.

8.4.1 Formulation of the potential-step transients.

A mechanism was developed for the anodic reaction consisting of five processes, of which three contribute directly to the charge-transfer (Section 5.2.1, Fig. 5.1)

i) A multilayer grows under control by two-dimensional kinetics giving rise to a growth current.

ii) Dissolution from the bare surface results in soluble Pb$^{2+}$ species that diffuse away from the electrode and gives rise to a dissolution current. This reaction is progressively stifled by the increasing coverage of the multilayer.
iii) The multilayer is postulated to be thin, conductive, and non-stoichiometric. Pb\(^{2+}\) ions migrate through the film to the film/electrolyte interface under the influence of the electric field. The migration of the ions gives rise to a transmission current. The non-stoichiometry may correspond to a composition \((\text{Pb}^{2+})_{1-x/2}(\text{SO}_4^{2-})_{1-x}(\text{HSO}_4^-)_{x}\), for example, with cation vacancies compensated by the charge of protons on some of the sulphate ions. Pb\(^{2+}\) would migrate through \(V_{\text{Pb}^{2+}}\) vacancy motion. The film transmission is progressively stifled by the precipitation of insulating microcrystalline PbSO\(_4\) onto the multilayer.

The mathematical expressions for each of these steps are derived and the parameters optimised so that the theoretical transient simulates the experimental transients (Figs. 5.2-5.4). The optimised parameters are found to vary in a plausible manner with stepping potential (Fig. 5.5, Table 5.1). In particular, the charge of the multilayer varies linearly with stepping potential indicating that the multilayer maintains a constant electric field. The thickness of the multilayer lies in the range of 60 monolayer equivalents in the potential region examined.

8.4.2 Mechanism of the cyclic voltammograms controlled by film growth.

The model was extended to predict the cyclic voltammograms measured for two-dimensional control (Section 5.3). The optimised parameters determined by the potential-step model were extrapolated into potential regions not examined by potential-step experiments so that the voltammograms could be synthesised. The model adequately describes the initial part of the voltammograms (Fig. 5.6 and 5.7) but fails to describe
precisely the anodic peak current (Fig. 5.8, Table 5.2). However, the anodic peak occurs in a potential region where the parameters are derived by extrapolation, and at worst the peak current only overestimates the experimental transient by 70%.

The dissolution component transient is shown to be in good agreement with the position for the reduction wave due to soluble Pb\(^2+\) determined by other authors using ring-disc electrodes (Section 5.3.4, Fig. 5.9).

8.4.3 Mechanism for the resistance controlled voltammograms.

A model was developed for the cyclic voltammograms controlled by a surface film resistance (Section 5.4). A model is based on transmission through a resistive film and subsequent change of the resistance by precipitation of PbSO\(_4\) onto the film provides an explanation for the experimental voltammograms. The film resistance in the absence of any passivation effects was determined by extrapolation of regions of the voltammograms. A constant overpotential for resistance control is observed (Fig. 5.12, Table 5.3). The film resistance was found to correlate with the small charge passed prior to resistance control (Fig. 5.13, Table 5.3). This charge may represent a film building or thickening process. The coverage of the passivation layer was determined for a series of voltammograms and no simple rate law could be elucidated.

8.4.4 Comment on the model.

The model provides a significant improvement to the previous level of understanding. Few models for the lead anode have been quantitatively
discussed to the extent as achieved in Chapter 5. The new feature introduced in this thesis is the conductive surface film.

8.5 Effect of chloride.

The effects of chloride addition to the electrolyte on the lead anode are determined in Chapter 6 using both cyclic sweep and potential-step methods. In the past an understanding has developed in the battery industry that chloride is detrimental to the positive plate (though very little information is available in the literature). There have been no previous studies reported on the effect of chloride on the lead anode (negative plate in a battery) and thus the present work represents a significant advance in this area.

i) In general, the charge for both anodic and cathodic reactions is enhanced by the addition of chloride in cyclic voltammetry experiments (Sections 6.2.1 and 6.2.2, Figs. 6.1-6.6, Table 6.1). The ratio of the cathodic to anodic charge (representing the coulomic efficiency of the electrode) was found to increase with chloride concentration (Fig. 6.7). The increased cathodic charge was suggested to be due to the simultaneous parallel oxidation of freshly formed Pb crystals by H⁺, enhanced by the influence of the complexing anion, chloride. The resultant Pb²⁺ is subsequently electrodically reduced thus increasing the recorded charge (Section 6.6.2).

ii) A new feature was found as a pre-peak to the reduction of PbSO₄ (Section 6.2.3, Fig. 6.1 and 6.2). The position of the pre-peak was observed to vary with both sweep rate and chloride concentration
Integration of the pre-peak indicates that the charge is close to that for a monolayer.

iii) The gross features of potential-step transients were found to be independent of chloride concentration. A new feature was evident at short times as a falling component to the transient (Figs. 6.9 and 6.10). Integration of this new component indicates a charge of the order of monolayer formation.

iv) The pre-peak to the cathodic wave in cyclic voltammetry and the falling transient at short times in potential-step transients were concluded to be due to reduction and formation of a monolayer of PbCl₂ since the potentials are close to that for Pb/PbCl₂ (Section 6.6.3).

v) In summary, the experiments showed no detrimental effects of chloride on the lead anode. On the contrary, beneficial effects such as increased charge capacity and enhanced discharge/charge efficiency have been found. Features such as long term corrosion of lead metal have not been investigated and may result in undesired effects.

8.6 Platinum deposition on the lead anode.

i) Platinum was found to dissolve from the counter electrode and to plate-out on the working electrode (Sections 6.4 and 6.5). The process is slow and independent of whether the electrode is electrochemically cycled or left at open-circuit, indicating that a simple redox reaction is operating. With time, the lead electrode electrochemically resembles a platinum metal electrode, with charge-transfer due only to hydrogen and oxygen gas evolution (Figs. 6.11 and 6.12).

ii) Surface analysis of the contaminated lead electrode by X-ray
Photoelectron Spectroscopy (Section 6.5) confirmed the presence of platinum on the electrode (Section 6.5.2, Fig. 6.13). Analysis identified the platinum as platinum metal (Fig. 6.14) and showed that the equivalent surface coverage of platinum on the lead electrode was about 0.5 monolayers (Section 6.5.3).

8.7 The role of organic sulphonate additives.

The effects of simple sulphonic acids on the lead anode were investigated in Chapter 7.

i) Initial investigations at room-temperature illustrated that methyl orange enhanced the anodic and cathodic charge of an electrode undergoing continuous cyclic voltammetry (Section 7.2.2, Fig. 7.2). Low-temperature experiments showed only a slight increase in anodic charge (Fig. 7.3) and potential-step experiments exhibited no modification both at room and low-temperature.

ii) Galvanostatic discharge experiments on small batteries in the presence of methyl orange at low-temperature indicated that the discharge capacity was increased and the overpotential required to maintain the discharge rate was less than in the absence of the compound (Section 7.2.3). The effect was limited to one discharge cycle as was the characteristic red colour of methyl orange in solution. The methyl orange was destroyed by the highly oxidising positive plate active mass (PbO₂), and this was confirmed by addition of PbO₂ to acid solutions of the dye.

iii) The effect of methyl orange was considered to be of interest and a permanent effect was judged possible if a suitable compound was obtained or prepared that was similar in nature to methyl orange but
insoluble in the electrolyte (Section 7.2.4). No suitable compound was available and thus a new compound was designed and successfully prepared with a C\textsubscript{12} carbon chain replacing the N-methyl group of methyl orange. (Section 7.6).

\textit{iv)} The new compound, lauryl orange, inhibited the anodic reaction on planar lead anodes (Section 7.4) in both cyclic voltammetry (Figs. 7.4-7.8, Table 7.1) and in potential-step experiments (Figs. 7.9-7.12). In general the anodic charge was diminished in cyclic voltammetry and multilayer growth was stifled in the potential step transients.

\textit{v)} Negative battery plates were prepared (Section 7.4.3) with lauryl orange either adsorbed on the leady oxide precursor (Section 7.4.4, Fig. 7.13, Table 7.2 and 7.4) or on fully charged negative plates (Table 7.3). In general the battery plates displayed diminished charge capacity.

\textit{vi)} Lauryl orange did, however, show the required ability to adsorb onto lead metal as evidenced by the planar electrode results (Sections 7.4.1 and 7.4.2) and by loss of the characteristic colour in dichloromethane solutions when added to leady oxide (Section 7.4.3).

8.8 Conclusions.

Previous models for the lead anode could not account for the quantitative results. It was found essential to include the new concept of a conductive film. The film is a major finding in this area as previously other workers have only considered formulation of insulating, crystalline PbSO\textsubscript{4}. The new phase was not identified but the electrochemical behaviour
is characterised. A possible composition for the new phase is amorphous 

$$(\text{Pb}^{2+})_{1-x/2} (\text{SO}_4^{2-})_{1-x} (\text{HSO}_4^-)_x$$

where Pb$^{2+}$ ions migrate through $V_{\text{Pb}^+}$ vacancy sites.
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