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ANODIC FILMS ON BISMUTH

a thesis submitted to
the University of Auckland
for the degree of
Doctor of Philosophy

by

David Edward Williams

February 1974
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Abstract

This thesis deals with the nucleation, growth and defect structure of anodic oxide films formed on bismuth in aqueous electrolytes.

The early stages in the formation of continuous anodic layers of bismuth oxide were studied using the technique of cyclic voltammetry. During this period, the oxide, Bi$_2$O$_3$, covered the surface by a process of simultaneous thickening and spreading of patches. The study of oxide nucleation classified the metal surface into two different areas with different kinetics of oxide nucleation. The ratio of the two areas varied according to the history and original preparation of the surface. Film nucleation was also studied by the galvanostatic step and potentiostatic step methods. The rate of spreading of the oxide patches over the surface was shown to be controlled by the magnitude of the surface area still uncovered.

Film thickening was studied using both galvanostatic and cyclic voltammetric techniques. The high field growth law $i = \overline{A} \exp (\overline{B}E)$ where $i$ is the current density and $\overline{E}$ the field in the oxide layer, was found with parameters

$$\overline{A} = (1 \pm 0.5) \times 10^{-5} \text{ A cm}^{-2}$$
$$\overline{B} = (2.0 \pm 0.5) \times 10^{-6} \text{ cm V}^{-1}$$

This value of $\overline{B}$ gives an activation distance for high-field ion transport, $a^* = 0.2 \text{ nm}$, comparable to the radius of a lattice site. These parameters were determined for very
thin films in strongly alkaline electrolyte (pH 13; thickness <30 nm). At greater film thickness, cracking of the film gave a porous layer on top of a continuous barrier layer, and the apparent value of the parameter B increased to \(1.7 \times 10^{-5}\) cm V\(^{-1}\). All previous work on the bismuth anodic film thickening process has been affected to some extent by cracking of the film. In this work, cracking of the film was confirmed by microscopic observation, including scanning electron microscopy.

Dissolution of the film, giving breakdown of the oxide layer and pitting of the metal, was an important phenomenon. It became particularly significant for pH <8. The thickness attained by the anodic bismuth oxide layer was limited by this process to only 4 nm at pH 5, increasing to over 200 nm at pH 13.

The cathodic reduction of the oxide proceeded from the outer surface inwards, and a rough, porous metal surface resulted. A model involving electron injection from the metal into the oxide, diffusion of electrons through the film and their reaction at the outer surface has been proposed. Microscopic observation confirmed the porous nature of the electro-reduced surface.

The transient conductivity of the bismuth anodic film has been investigated, and the effects of standing at open-circuit in the electrolyte or of heating in air studied. The galvanostatic method was used. The observed effects
could be adequately explained as being due to the presence of a non-stoichiometric, n-type (excess metal) layer at the film-solution interface.

Cyclic voltammetry was used to investigate the possibility of nucleation of anodic bismuth oxo-halides from solutions containing halide ions. Solutions containing fluoride, chloride, bromide or iodide at pH 4-9, phosphate and phosphate with added methanol at pH 8.5 were used. Consideration of thermodynamic stability would indicate the formation of new phases, but results showed that, in the comparatively short time scale of the experiments, kinetic factors resulted in the formation of anodic Bi₂O₃, except when the solution contained iodide at low pH, when the oxo-iodide, BiOI, was probably formed.

Room lighting had no effect on the cyclic voltammetric or galvanostatic measurements. The transient response of anodic films on bismuth to an intense flash of white light was studied. In the case of a thick anodic oxide film (240 nm), the results were interpreted in terms of photo-excitation of the film, producing electron-hole pairs which were separated by the applied field. The recombination process was best described as rate-limiting thermal excitation of trapped electrons. The lifetime of an electron in the conduction band of anodic Bi₂O₃ was determined:

\[ \tau_c = 23 \text{ ms} \]
The photo-response of a very thin anodic oxide film (4 nm) involved internal photo-emission of electrons from the metal into the oxide. Formation of a positive space charge by the injection of extra cations from the metal into the film followed. The transient photo-potential (galvanostatic experiments) or photo-current (potentiostatic experiments) showed the decay of both excess electronic and ionic space charges. The density of electron traps in the anodic oxide film was determined as $N_T > 3 \times 10^{18}$ cm$^{-3}$.

When the anodic film was formed in a solution containing bromide or iodide at pH 5, an inversion of the sign of the primary photo-effect from that observed in the absence of additives (4 nm thick film) was seen, and interpreted in terms of the photo-excitation of halide ions incorporated in the film. The lifetime of a conduction electron in anodic BiOI was determined as $1.5 \pm 0.2$ ms, much less than in anodic Bi$_2$O$_3$ (23 ms).

In all the studies of the photo-effect, Gauss' theorem was used to relate the observed photo-potential (galvanostatic experiments) to the photo-induced charge separation. An approximate value of the conduction electron mobility in anodic Bi$_2$O$_3$ was thus obtained: $\mu = 5 \times 10^{-8}$ cm$^2$ V$^{-1}$ s$^{-1}$.

Parameters for the evolution of hydrogen on the bare bismuth metal surface, were obtained:
\[ b = 0.11 \text{ V}, \quad \log_{10}(i_o/\text{Acm}^{-2}) = -10.3 \]

and

\[ (\frac{\partial (\log_{10}i_o)}{\partial \text{pH}})_{\eta} = 0 \quad \text{where} \]

\[ \eta = E - 60 \text{ pH mV}. \]
List of Principal Symbols

\( \bar{A} \) parameters for high field growth law, \( i = \bar{A} \exp (B \bar{E}) \)

\( B \) capacitance per true unit area of electrode

\( C' \) capacitance per unit projected area of electrode

\( \bar{E} \) electric field

\( E \) electrode potential

\( \varepsilon \) permittivity

\( \varepsilon_0 \) permittivity of free space

\( e' \) conduction electron

\( |e| \) electronic charge

\( F \) Faraday

\( h \) oxide thickness

\( h \) Planck's constant

\( i \) current density per true unit area of electrode

\( i' \) current density per unit projected area of electrode

\( I \) current

\( k \) dielectric constant \((\varepsilon/\varepsilon_0)\)

\( K \) equilibrium constant

\( k \) rate constant

\( k \) Boltzmann's constant

\( L \) light intensity

\( p' \) positive hole

\( Q \) charge density per true unit area of electrode

\( Q' \) charge density per unit projected area of electrode
$R$  gas constant
$t$  time
$t'$  trapped electron
$T$  Kelvin temperature
$V_m$  molar volume
$\sigma$  roughness factor
$\lambda$  wavelength
$\phi$  galvani potential
$\eta$  overpotential
$\omega$  rotation rate
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CHAPTER 1
INTRODUCTION

1.1 Scope of this work

This thesis presents experimental work on the formation and properties of the anodic films obtained by polarizing bismuth metal in aqueous electrolytes.

Current ideas (1-3, 10-11) have been extended and applied to the data in an attempt to answer questions concerning the structure and mechanisms of nucleation and reduction of the film. The thickening of the films has been studied, and the applicability of various theories of high field ion transport assessed (1-9). A clear understanding of the limitations of the various experimental techniques and theoretical interpretations has been obtained.

Measurements of the transient photoconductivity of the films have been made in an attempt to further the understanding of their defect structure.

1.2 Aspects of Bismuth Chemistry

The systems studied in this thesis have involved bismuth and oxygen, with halogen added occasionally. Simplified Pourbaix diagrams for these systems are shown in fig. 1.1. In principle, anodic films of bismuth oxohalides could be formed by polarizing a bismuth electrode in a suitable solution containing halide ions.

The actual crystal structure of the bismuth anodic
Fig. 1.1  Simplified potential - pH diagrams for Bismuth 
electrochemical equilibria
films is unknown. Thus, some metals are said to form amorphous anodic oxides (1-3,12), whereas on others, the layers formed are crystalline (13).

Bismuth oxide itself exists in several crystalline modifications (14-18). If it is prepared by oxidation of thin layers of very finely divided bismuth then still more crystalline forms are observed (19), along with several structures with both bismuth and oxygen defects (20). Many non-stoichiometric mixed oxides are known (21, 22).

The halogen chemistry of bismuth is also complex. Besides the simple oxohalides, non-stoichiometric oxohalides are known (22, 23).

1.3 Previous Work on Bismuth Anodic Films

Early work (2, 24) showed that anodic polarization of bismuth in alkaline solutions gave an adherent, highly insulating film. Subsequent work (25-31,28) has been mainly concerned with the use of the galvanostatic method to study the kinetics of growth of this film. Fig. 1.2 gives a simplified summary of the situation. Physical properties of bulk and anodic Bi$_2$O$_3$ are given in table 1.1.

Masing and Young (25) investigated the transient and steady state kinetics of formation of anodic oxide films on electropolished single crystals of bismuth in 0.1M NaOH electrolyte. The dielectric properties were also studied.

No dependence of the kinetic parameters on the crystal face of the substrate was observed on single crystal specimens. However, different interference colours were occasionally seen
2 Bi + 3 H₂O → Bi₂O₃ + 6H⁺ + 6e⁻

Bi metal

Bi₂O₃ oxide film

H₂O solution

Interfacial Processes

Transport Processes

H₂O

2H⁺

(Anion)

(Cation vacancy)

(Anion vacancy)

 φ

Average electric field in film:

\[ E = \frac{\Delta \Phi}{h} \]

Current density:

\[ i = \bar{A} \exp(BE) \]

Fig. 1.2 Schematic Representation of Film Thickening Process.
on the different crystal faces of the polycrystalline specimens used in the study of dielectric properties.

They noted that dissolution of the film and the formation of micro-fissures were important phenomena. Thus, the total current density would be given by (31):

\[ A_i = a_{G}i_{G} + a_{S}i_{S} + a_{E}i_{E} \]  \hspace{1cm} (1.1)

where \( i \) is the applied, constant current density, \( i_{G} \) is the ionic current density, leading to film growth, \( i_{S} \) is the current carried by dissolution of the film, or of the metal, at cracks in the film, and \( i_{E} \) is the current carried by oxygen evolution at the metal, through cracks in the film. The factors \( a_{G} \), \( a_{S} \), \( a_{E} \) and \( A \) are areas.

Masing and Young were able to derive the ionic current density, \( i_{G} \), from the observed rate of increase of electrode potential, \( d\varepsilon/dt \), since they had obtained an independent estimate of the electric field. This was calculated from the electrode potential and the film thickness, determined by the optical interference method.

The behaviour of the bismuth anodic film was markedly different from that shown by the non-porous anodic films formed on Ta, for example. The activation distances found were much larger than expected on the basis of the simple Cabrera - Mott - Verwey theory of high field ion transport. The current - time transient observed after a step in potential during anodic film growth was qualitatively different to that observed in the case of Ta, fig. 1.3.
(a) Tracing of oscilloscope photograph showing current versus time following sudden change as potential reached 20 volt from formation at constant current density (2 ma cm⁻²) to formation at constant voltage (28 volt) for bismuth. Temperature 4°C.

(b) Similar but not identical experiment with tantalum. Initial formation at 4 ma cm⁻² to 90 volt. After 1 minute on open circuit, 100 volt was suddenly applied.

Fig. 1.3 Transient Conductivity of anodic bismuth oxide (a), compared with that of anodic tantalum oxide (b); L.Masing and L.Young; Can. J. Chem. 40(1962) 903
Table 1.1  **Physical Properties of Bulk and Anodic Bi₂O₃**

Density, \( \rho \)  
refractive index, \( n_D \)  and  
dielectric constant, \( \kappa = \varepsilon / \varepsilon_0 \)

<table>
<thead>
<tr>
<th>oxide</th>
<th>( n_D )</th>
<th>( \rho / g \text{ cm}^{-3} )</th>
<th>( \kappa )</th>
<th>ref.</th>
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<tr>
<td>( \alpha-\text{Bi}_2\text{O}_3 ) (bulk)</td>
<td>2.45</td>
<td>9.33</td>
<td>18.2</td>
<td>14, 24, 99</td>
</tr>
<tr>
<td>anodic ( \text{Bi}_2\text{O}_3 )</td>
<td>2.45(^a)</td>
<td>8.8(^b)</td>
<td>48(^c)</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>31</td>
<td>24</td>
</tr>
</tbody>
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**Notes.**

a) Refractive index of bulk and anodic \( \text{Bi}_2\text{O}_3 \) assumed to be the same, in order to derive values for the other constants.

b) An upper limit. The apparently low value may reflect cracking or porous nature of the anodic film.

c) For measurement at 1 kHz. The apparent dielectric constant was a function of the measurement frequency; affected by cracking or porosity of film.
In other work (26-28), the effects of surface preparation and film dissolution on the results were especially marked. Thus, one can interpret that cracking of the film is greatly reduced when the original surface is very smooth (e.g. electropolished), and is increased by the presence of halide additives. A qualitatively similar effect of surface preparation on film properties has been observed in the study of tantalum anodic films (32-34). The Bi results have been previously interpreted (26-28) in terms of the Cabrera-Mott-Verwey theory with the simplifying assumption \( i = i_G \), leading to erroneous conclusions.

The study of open circuit potential transients was applied to Bi anodic films formed in carbonate or borate buffers by De Smet and Hopper (35), who noted similarities to the behaviour of other metals. The results could not be interpreted in terms of a simple high field conduction model. This is a general problem of the study of transients in anodic films (2, 5, 9). In the case of bismuth, it would be further complicated by the effects of cracking and dissolution of the film (eq. 1.1).

Passivation of bismuth by a dissolution-precipitation mechanism analogous to that found for Fe in \( H_2SO_4 \) solutions (36), has been observed in acidic electrolytes (31). Dissolution of the metal occurs, followed by deposition of a crystalline precipitate on the surface. This blocks off some of the surface, giving an increase of current density and corresponding increase of electrode potential. The process
continues until the potential reaches a critical value for the nucleation of a continuous film, underneath the crystalline deposit and covering the entire surface. The development of the mechanism in reference (31) is somewhat incorrect. There is a possibility that other results (26-28) may have a similar interpretation.

Bismuth anodic films, in common with all such layers, show electrical rectification. That is, the film is a strong insulator with the metal positive, but conducts current easily with the metal negative. In the case of bismuth, the reaction resulting is reduction of the film. With films formed on more reactive metals (e.g. Al, Ta, Ti), hydrogen evolution at the film-solution interface occurs.

The behaviour can be understood in terms of the nature of the contact at the film-solution and film-metal interfaces (37). The energy levels of electrons in the solution usually lie too low to allow electron emission into the film. However, if some easily oxidized species is present in solution, then such electron emission could occur. Thus, iodine is produced at sufficiently positive potentials if iodide is present in the solution (26, 34). On the other hand, electron injection from the metal into the film is facile.

Rectification by anodic films has been explored extensively using metal counter electrodes (3, 38 and refs therein). Information on the electronic structure of the films is obtained. No such work has been done on Bi anodic films, although attempts have been made to study their oxidation.
state by investigating their cathodic reduction (39).

The potential-time curves for cathodic reduction at constant current usually exhibit a number of arrests before reduction is complete and hydrogen evolution is observed on the bare metal. The assignment of such arrests to the reduction of layers of different oxidation state is rather arbitrary. They have also been ascribed to surface effects (40), and probably reflect a varying contact resistance between metal and oxide as the reduction proceeds, and a different physical form of successive oxide layers (see Chapter 2 and 4).

The possible formation of layers involving anions from the electrolyte (e.g. oxohalides (27, 28), oxocarbonate (35), sulphate (27, 28), oxalate (31) in the examples above) has not usually been considered. Some examples on this are known (41-43). In other cases, no incorporation of anions has been observed (41). No systematic discussion has been given.

1.4 Organization of this Thesis

This thesis is arranged in a number of sections in which different aspects of the formation of bismuth anodic films have been investigated.

Cyclic voltammetry of bismuth is presented in Chapter 2, and corresponding steady state kinetic work using the galvanostatic method in Chapter 3. Attention is focused on the nucleation and early stages of thickening of the film.
The results of microscopic examination of etched, oxidized and reduced surfaces are given in Chapter 4, and related to the results of the electrical measurements.

Chapter 5 contains a study of the galvanostatic transients during film growth, and of the effects of standing or heating on the galvanostatic recharging curves. Detailed consideration of various theories of high field ion transport in anodic films is given.

In Chapter 6 the growth law under potentiostatic conditions is presented and related to the galvanostatic results.

Chapter 7 extends the study to examine the effects of various solution additives.

The transient photoconductivity is studied in Chapter 8-10, and in Chapter 11, an attempt is made to draw general conclusions from the whole work.

Relevant experimental information and a review of pertinent literature is given in each chapter.
CHAPTER 2
CYCLIC VOLTAMMETRY OF THE BISMUTH ELECTRODE

2.1 Introduction

Cyclic voltammetry (44), or linear sweep voltammetry, is a technique in which the electrode potential is made to cycle as a triangular function of time. The resulting current-potential curve is recorded. It has recently become widely used in the study of passivation of electrodes (45, 46). The potential sweep rate is the main variable (47).

The results of the technique can be interpreted at three levels - qualitative consideration of the shape of the current-potential curve and its position on the potential axis, quantitative consideration of the position, and finally quantitative consideration of the shape of the curve. In principle, a detailed mechanistic interpretation of the processes of nucleation, thickening and reduction of the anodic layer can be obtained. In fact, at each succeeding level, the number of corrections which must be applied to the data increases (48) and the amount of reliable information decreases rapidly.

In this work, the state of the surface was found to be a key factor affecting the shape of the curves. The position of the curves on the potential axis varied with solution pH in parallel with the reversible potential of the Bi$_2$O$_3$/Bi couple. At lower pH, dissolution of the film became important, and further changes in curve shape were thus noted. Variation of the potential sweep rate led to some discussion of the process of thickening of the film but it was
not possible to give any mechanistic discussion of the process of spreading of the film to cover the surface.

2.2 Experimental

2.2.1 Instruments

A conventional 3-electrode potentiostatic circuit was used, with a controlled potential sweep, Fig. 2.1. A Chemical Electronics (C.E.) type TR70/2A potentiostat was programmed by a C.E. type RB1 waveform generator. Current-potential curves were traced on a Riken F32 X-Y recorder. Current was measured as the potential drop across a precision resistor inserted in series with the auxiliary electrode of the cell. The potential scale was derived from the output of the waveform generator. In an alternative arrangement, a Heath EUA-19-2 polarography module was used as the sweep generator and potentials measured directly from the reference electrode, using a Keithly electrometer type 610C as a buffer amplifier. The Heath system, with an added current amplifier, was also used as an alternative potentiostat.

Instrument calibration was checked regularly. The voltage standard was a Weston cell, comparison being made using a Leeds and Northrup type K2 potentiometer. A zener diode controlled electronic regulator, and a Radiometer PHM4 were used as secondary standards. Time measurements were made using either a crystal controlled clock or a simple counter driven from the power main. The performance of the whole system was checked using a dummy cell (simple network)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rise time</td>
<td>0.3 μs</td>
</tr>
<tr>
<td>Input impedance</td>
<td>10^9 Ω</td>
</tr>
<tr>
<td>Response time</td>
<td>1.5 s for full scale deflection</td>
</tr>
<tr>
<td>Ramp rate</td>
<td>Automatic reversing of ramp</td>
</tr>
</tbody>
</table>

(1) Rise time 0.3 μs; output 70 V or 2 A; control accuracy ±0.5 mV
(2) Input impedance 10^9 Ω
(3) Response time 1.5 s for full scale deflection
(4) Ramp rate automatic reversing of ramp
(5) Manual reversing of ramp
(6) Rise time 40 μs; output 5 V or 0.5 A; control accuracy ±1 mV
fig. 2.1 Potentiostat Circuit for Cyclic Voltammetry

$R_m$ is the measurement resistor. Phase shifts introduced by the $2\mu F$ capacitor in the XY recorder caused oscillation of the fast response potentiostat. The arrangement with the terminals of the recorder interchanged was very unstable. Any residual inductance in $R_m$, or the use of a value for $R_m$ which was too high or too low (usually $>10k\Omega$ or $<10\Omega$) also resulted in instability.
of resistors and capacitors). The measurement accuracy determined was ±1%.

It was found that the current measuring circuit could introduce a phase shift sufficient to cause high frequency oscillations of the C.E. potentiostat. At high amplitude these destroyed the function of the potentiostat. At low amplitude they caused a large error, up to 10%, in the current measurement.

High amplitude oscillations could be avoided by a particular method of connection of the XY recorder (fig. 2.1). Low amplitude oscillations could be avoided by the use of a very high quality non-inductive resistance for the current measurement.

2.2.2 Electrodes

Generally, rotating disc electrodes, belt-driven, were employed (fig. 2.2). Electrical contact with the electrode shaft was made by a copper foil bearing onto a brass collar, whose surface had been amalgamated (49). The electrode shaft, made of stainless steel, was also fitted with a magnet. An adjacent pick-up coil (fig. 2.2) fed a counter which displayed the rotation rate. This could be varied continuously from zero to about 50Hz, the motor being supplied from a Variac transformer, and generally could be maintained constant to within 10%.

The electrode shaft passed through a Quickfit ST4W stuffing box gland into the cell. Its upper end was machined to a point and rode in a socket in a PVC block.
Fig. 2.2 Top Assembly for rotating disc electrode
Several different electrode preparations were studied:

(a) A zone refined Bi rod, >99.9999% pure, set in a concentric perspex tube with epoxy adhesive. The stainless steel shaft glued into the other end of the tube (fig. 2.3). The exposed face of bismuth was polished flat with successively finer grades of emery paper and finally with filter paper. It was either etched in 70% HNO₃ or electropolished (25) before use. Perspex was not an ideal material for the electrode holder as it became crazed and brittle on exposure to strong alkali. Cracks developed which were plugged with epoxy adhesive. Results obtained using both glass (fig. 2.3) and perspex surrounds were identical, however.

(b) An electrodeposited surface. A bismuth electrode prepared as above was polarized cathodically in a solution 0.15M in Bi(III). This was obtained by dissolving analytical reagent grade Bi₂O₃ in 2.5M HClO₄ (also A.R. grade). A layer about 0.1 mm thick of fine crystals, each about 10μm across, was obtained. As expected, the roughness factor, σ, (section 2.2.6; fig. 2.7) of these electrodes was very large, σ = 10 ± 1.

(c) Electrodes cast from high purity bismuth pellets (>99.999%). Non-rotating electrodes were made by pressing the end of a glass tube onto an asbestos board, packing it with pellets and melting (26). The resulting rod was removed from the glass and set in another glass tube using epoxy adhesive. The electrodes were abraded and etched in 70% HNO₃ before use.
Specimens for scanning electron microscopy were made by melting bismuth in a crucible along with some boric acid. This prevented oxidation of the surface of the melt. A length of glass tube, sealed at the upper end, was then heated and inserted into the melt. As the glass cooled, Bi was drawn up into the tube. The resulting casts were cut into short lengths with a diamond saw. These were mounted in the chuck of an electric motor and polished against emery and filter paper.

One of these small specimens was annealed in a nitrogen atmosphere at 470K (0.84 $T_m$, where melting point $T_m = 544K$) for 3 hours.

The specimens were mounted in the perspex holder shown in fig. 2.3 for polarization. Each electrode was etched briefly in 70% HNO$_3$ beforehand.

(d) A hanging drop microelectrode. A thick-walled glass capillary tube, of 2 mm internal diameter, was drawn out into a tip and mounted vertically. A melt of pure bismuth, protected from air by boric oxide, was poured into the capillary. At the tip, sudden cooling to give a pendant drop occurred. Fig. 2.4 gives the dimensions. The metal surface was electropolished before polarization. After a number of repetitions of the electropolishing and polarization sequence, the drop thinned at the neck and fell off. The resulting shape is shown in fig. 2.4. For the final measurements, the tip was ground flat with emery paper, to give a disc 0.48 mm in diameter.
**Fig. 2.3 Electrode Assemblies**

(a) zone-refined rod in perspex
(b) zone-refined in glass
(c) holder for short lengths of rod cast in glass
Fig. 2.4 Cross-section of Bismuth Micro-electrodes

(a) pendant drop

(b) "spike"
2.2.3 Solutions

Solutions of Na$_2$B$_4$O$_7$, NaOH, and HClO$_4$ were prepared from A.R. chemicals. Unless otherwise stated, they were not pre-electrolysed.

Carbonate-free NaOH was prepared by dilution of a solution 50% by weight in sodium hydroxide (50). It was standardized against hydrochloric acid prepared by dilution from the constant boiling point material, and the pH calculated using activity coefficients given by Robinson and Stokes (51).

Water was twice-distilled, the second time under nitrogen from acidic Cr$_2$O$_3$ solution through a fractionating column. It was stored under N$_2$, out of contact with the laboratory air.

2.2.4 Apparatus

The electrolysis cell was a jacketed cylindrical pyrex vessel of 500 cm$^3$ capacity. The cell lid was attached to the body by a flange joint sealed with an O-ring cut from PTFE sheet, and carried 5 ground joints through which passed the working and auxiliary electrodes, nitrogen bubbler and outlet, and Luggin capillary. The Luggin capillary was filled with the initial electrolyte, if this was NaOH solution, or with 0.1M Na$_2$SO$_4$ solution if the initial electrolyte was 0.1M borax, or contained perchlorate. The reference electrode was a Radiometer saturated calomel electrode. Its potential was taken as 250mV in order to refer potentials to the hydrogen scale. All electrode potentials in this thesis refer to
the standard hydrogen electrode (NHE) as zero. Junction potentials are included in the measurement.

The auxiliary electrode was a loop of Pt wire 4 cm in diameter and parallel to the plane of the working electrode surface. It was mounted at the base of the cell and centred on the working electrode. This arrangement (52) gave a symmetrical electric field, and allowed a calculation of the resistance of the solution between the Luggin capillary tip and working electrode surface (52, 53). The distance between these two was measured with a travelling microscope.

All glassware was cleaned by soaking in 2M HNO₃ solution for at least 48 hours before use (90). It was stored either filled with nitric acid solution or with twice-distilled water, and thoroughly washed with twice-distilled water before use. The criterion of cleanliness was that a film of water should flow evenly over the surface, without breaking into lenses.

Nitrogen was purified by twice bubbling through a solution of vanadium(II) (89), and twice through distilled water at the same temperature as the cell.

2.2.5 **Integration of charts**

This was performed either with a planimeter or by photocopying and weighing first the copy of the whole chart and next the area required. The methods were checked by measurement of known areas. The error in any one determination was ±2%. When using the planimeter, the mean of at least three determinations was taken.
The relationship between charge passed and chart area is

\[ Q = \frac{1}{v} \int i \, dE \]  

\[ \text{.........} (2.1). \]

where \( v \) is the applied potential sweep rate, \( i \) the current density, \( E \) the electrode potential and \( Q \) the charge passed.

2.2.6 Roughness Factor

The apparent current density is

\[ i' = \frac{\text{observed current}}{\text{projected area}} = \frac{I}{A} \]

The true current density is \( i = i'/\sigma \) where \( \sigma = \frac{\text{true area}}{\text{projected area}} \) is the roughness factor.

The projected area, \( A \), was measured using a travelling microscope. In some cases, the roughness factor was estimated from the differential capacitance per unit projected area, \( C' \), measured (54) at a potential such that the electrode was film-free. A triangular voltage waveform of amplitude 64mV was applied to the working electrode and the resulting current analysed (fig. 2.5, 2.6). A dummy cell test, (fig. 2.5) indicated an accuracy of ±20% at worst. The capacitance per true unit area, \( C = C'/\sigma \) was obtained approximately by a repetitive procedure of galvanostatic oxidation followed by dissolution of the film in acid (35). The assumption that a surface with \( \sigma \approx 1 \) would eventually result by this smoothing process. A value of \( C = 18 \ \mu F \ cm^{-2} \) for 0.1M Na\(_2\)B\(_4\)O\(_7\) electrolyte, independent of potential was obtained, close to the differential capacitance of a mercury electrode in the absence of specific adsorption (20 \( \mu F \ cm^{-2} \)). Previous measurements, on mechanically polished surfaces, using the galvanostatic method (below), have given \( C' \approx 30 \ \mu F \ cm^{-2} \) (55,
Fig. 2.5 Measurement of Capacitance by Triangular Wave Potentiostatic Method (54) (Dummy Cell Test)

\[ I = \frac{VCR_f}{R_f R_\Omega} \left[ 1 + \frac{t}{CR_f} - \frac{R_\Omega}{R_f R_\Omega} + \left[ 1 - \frac{R_\Omega}{R_f + R_\Omega} \right] \exp \left[ -\frac{R_f + R_\Omega}{R_f R_{RC}} t \right] \right] \]

set \( R_\Omega = 25\Omega \) \( v = 10.3 \text{ Vs}^{-1} \) \( C = 20\mu\text{F} \)

\( R_f = (i) \) 1k\( \Omega \) \( (ii) \) 300\( \Omega \)

measured

\( (i) \) \( C = 20\mu\text{F} \)

\( (ii) \) \( C = 18\mu\text{F} \) \( R_f = 450\Omega \)
Fig. 2.6 Capacitance measurements on bismuth electrodes
borate buffer; \( v = 10.3 \text{ Vs}^{-1}; \) 25°C; projected area 1.2 cm²

(i) 400

\[
\begin{array}{c|c|c|c|c|c}
& I/\mu A & 0 & & & \\
0 & 4 & 8 & 12 & 16 & \\
\hline
-400 & & & & & \\
\end{array}
\]

t/\text{ms}

Film-free electrode prepared by repeated cycles of galvanostatic oxidation followed by dissolution in HClO₄

\( E = -450 \text{ mV}; \ C' = 18 \mu F \text{ cm}^{-2} \)

If the electrode surface is porous, say as a result of the reduction of an anodic film (section 2.4), further distortion of the curve results (62).

(ii)

\[
\begin{array}{c|c|c|c|c|c}
& I/\mu A & 0 & & & \\
0 & 4 & 6 & 10 & 14 & 18 & \\
\hline
-40 & & & & & \\
\end{array}
\]

t/\text{ms}

Film-coated electrode.

\( E = +250 \text{ mV}; \ C' = 2.3 \mu F \text{ cm}^{-2}; \ R_f = 2.4 \times 10^4 \Omega \)
56), independent of electrolyte and potential. A value of ε about 2 is, indeed, commonly assumed for surfaces prepared in this way.

The electrode capacitance, C', was also occasionally obtained from the voltage transient following a current step, in a galvanostatic technique (fig. 2.7):

$$i' = C' \frac{dE}{dt}\bigg|_{t=0} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2.2).$$

At t=0, the step in potential observed allowed a calculation of the solution resistance, $$R_\Omega$$, between Luggin capillary tip and electrode surface, to check on the use of Newman's formulae (52, 53).

$$\Delta E_\Omega = \Delta I.R_\Omega \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2.3).$$

The calculated resistance (52, 53) was within 20% of that obtained from eq. 2.3. In general, the capacitance obtained by this method agreed with that obtained by the triangular wave potentiostatic method above. Recording instruments used were an SE3006 uv recorder with pre-amplifier, and a Tektronix 549 storage oscilloscope with differential input. A 2 cm² Pt foil was the reference electrode for the galvanostatic method.

The plateau current, $$i_G$$, (section 2.3), measured at a given sweep rate, could be used to compare the surface area of different electrodes, since it was independent of the surface state and solution composition (pH > 8.5; section 2.14) and unaffected by uncompensated solution resistance (section 2.5).

---

(a) A fast response (better than 0.01 s) chart galvanometer, which writes with uv light on sensitized paper; span 114 cm
(b) Input impedance 10⁶ Ω; sensitivity 10 to 100 mV per cm of scale
(c) Input impedance 10⁶ Ω; sensitivity 10 μV per 10 V cm⁻¹; band width DC to 500 kHz
Fig. 2.7 Capacitance measurement by galvanostatic method

Electrodeposited surface, pH 12.9; 25°C.

(a) program

(b) schematic result
(see fig. 3.9)

(c) slope gives $C' = 180 \pm 20 \mu F$ so $\sigma = 10 \pm 1$. (eq. 2.2).

\[
\left(\frac{dE}{dt}\right)_{t=0} / \text{Vs}^{-1}
\]

\[
\begin{array}{c|c|c|c|c|c}
0 & 0.1 & 0.2 & 0.3 & 0.4 & 0.5 \\
1.0 & & & & & \\
2.0 & & & & & \\
\end{array}
\]

$i'/\text{mA cm}^{-2}$
In this thesis, quantities have been expressed per unit of true area unless distinguished by a prime (eg. i'), used to denote quantities per unit projected area.

RESULTS AND DISCUSSION

2.3 General Features

Fig. 2.8 illustrates the general features of the process. In the region AB, one to three, usually two, peaks were observed, depending on the nature of the surface, (section 2.8). These are characteristic of the processes of nucleation of an anodic film and its spreading to cover the surface (section 2.9).

\[
2\text{Bi}_\text{(m)} + 3\text{H}_2\text{O} + \text{Bi}_2\text{O}_3\text{(s)} + 6\text{H}^+\text{(aq)} + 6\text{e}^-\text{(m)} \rightarrow \text{..... (2.4).}
\]

In the region BC, the current was approximately constant, indicating thickening of the film with a constant electric field (independent of thickness; section 2.14). The reversible potential for reaction (2.4);

\[
E_R = 371 - 60\text{pH mV} \quad \text{................. (2.5).}
\]

lay between the potentials $E_{AN}$ and $E_{CN}$ (fig. 2.8) characterizing the onset of an appreciable net rate of oxidation or reduction.

The shape in the region EF was variable, and can be interpreted satisfactorily in terms of the effect of porosity of the surface on the electric potential at the surface, and in terms of the reduction of any loose, crystalline material (sections 2.5 and 2.6). The cathodic current seen in FG is due to evolution of hydrogen on the bare metal surface (section 2.5).
Nomenclature

\( E_{AN} \) : anode nucleation potential
\( E_{CN} \) : cathode nucleation potential
\( E_{CP} \) : cathode peak potential

\( i_{AP} \) : anode peak current density
\( i_{CP} \) : cathode peak current density
\( i_G \) : plateau current density

Fig. 2.8 Cyclic voltammetry of Bismuth in alkali

pH = 12.6; \( v = 0.11 \text{Vs}^{-1} \);
\( \omega = 10 \text{Hz}; 25^\circ \text{C electrodeposited surface (b).} \)

arrows show direction of potential sweep.
In solutions with pH <8.5, a sudden rise in current was seen in the region BC. The formation of fluffy crystalline deposits on the electrode indicated that this was a dissolution reaction, followed by precipitation of Bi(OH)$_3$ or Bi$_2$O$_3$ (section 2.6).

Processes which involve the formation and reduction of an adherent film (A-E, fig. 2.8) showed a characteristic increase in current with increasing potential sweep rate, (tables 2.1 and 2.2). The other processes, dissolution and hydrogen evolution, for which the steady state hypothesis of constant concentration of intermediate holds, did not show this dependence. They may show instead a dependence on rotation rate. The processes of nucleation, thickening and reduction of a bismuth anodic oxide film were independent of rotation rate (table 2.3), showing that a process of direct nucleation of a film onto the surface (10), and not one of dissolution-precipitation (46, 82) was being observed.

There was no effect of room lighting on the curves.

2.4 Surface Roughening

Continued cycling caused an increase in the true surface area (increase in roughness factor, $\sigma$), measured as an increase in the capacitance (Ref 46; table 2.4). A corresponding increase in the observed current occurred. The true current density was unaffected (table 2.4).

The surface area would be increased because Bi$_2$O$_3$ occupies a 25% greater volume than the Bi metal from which it is formed. Reduction would thus lead to a porous surface layer of Bi metal, seen clearly in electron micrographs (Chapter 4). The effect would be most marked on the first few cycles.
### Table 2.1 Variation of Anodic current with Potential Sweep Rate

Electrodeposited surface; $\sigma = 10$; pH = 12.6; 25°C

<table>
<thead>
<tr>
<th>$10^2 \nu$ /Vs$^{-1}$</th>
<th>10.5</th>
<th>8.4</th>
<th>6.3</th>
<th>4.2</th>
<th>3.6</th>
<th>2.9</th>
<th>2.2</th>
<th>1.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i_{AP}$/mAcm$^{-2}$</td>
<td>0.49</td>
<td>0.42</td>
<td>0.32</td>
<td>0.20</td>
<td>0.24</td>
<td>0.21</td>
<td>0.16</td>
<td>0.12</td>
</tr>
<tr>
<td>$i_{G}$/mAcm$^{-2}$</td>
<td>0.50</td>
<td>0.43</td>
<td>0.31</td>
<td>0.20</td>
<td>0.23</td>
<td>0.20</td>
<td>0.17</td>
<td>0.13</td>
</tr>
</tbody>
</table>

The results are influenced by small variations in the surface area. Uncompensated solution resistance of 12Ω, and overlapping of peaks and plateau, means that no mechanistic interpretations of these results can be made.

### Table 2.2 Variation of Cathodic peak current with Potential sweep rate

Electrodeposited surface, $\sigma = 10$; pH = 12.6; 25°C

The cathodic peak current increases with increasing charge to be reduced. The results have been interpolated to a preceding anodic charge of 3.0 mC cm$^{-2}$.

<table>
<thead>
<tr>
<th>$10^2 \nu$ /Vs$^{-1}$</th>
<th>36</th>
<th>29</th>
<th>22</th>
<th>18</th>
<th>14</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i_{CP}$/mAcm$^{-2}$</td>
<td>3.3</td>
<td>2.7</td>
<td>2.4</td>
<td>2.2</td>
<td>1.9</td>
<td>1.7</td>
</tr>
</tbody>
</table>

As above, uncompensated solution resistance means that no mechanistic interpretation of these results can be made.

### Table 2.3 Effect of rotation rate

Electrodeposited surface, $\sigma = 10$; pH = 12.6; 25°C; $\nu = 0.11$ Vs$^{-1}$

<table>
<thead>
<tr>
<th>$\omega$/Hz</th>
<th>0</th>
<th>10</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i_{AP}$/mAcm$^{-2}$</td>
<td>0.50 ± 0.02</td>
<td>0.49 ± 0.02</td>
<td>0.50</td>
</tr>
<tr>
<td>$i_{G}$/mAcm$^{-2}$</td>
<td>0.47 ± 0.01</td>
<td>0.44 ± 0.01</td>
<td>0.46</td>
</tr>
<tr>
<td>$i_{CP}$/mAcm$^{-2}$</td>
<td>2.1 ± 0.1*</td>
<td>2.1 ± 0.1*</td>
<td>2.3*</td>
</tr>
</tbody>
</table>

* All measurements had $Q_A = 5$ mC cm$^{-2}$. 
Extended hydrogen evolution may also cause surface roughening (57). The effect on cyclic voltammetry shown in tables 2.4 and 2.5 is most likely due to such a process. Black metallic powder was observed spalling off the electrode at very high current density (order of 1 A cm\(^{-2}\)), so surface roughening by prolonged cathodization at lower current density seems very likely.

Other hypotheses have been proposed to explain similar effects. Thus, discharge of alkali metal to form an intermetallic compound has been postulated (56) to account for an increase in capacitance of a Bi electrode on prolonged cathodization in alkali. Ammar and Khalil (27) prepared bismuth electrodes for galvanostatic oxidation by evolving hydrogen from the surface for varying lengths of time. Although they interpreted the resulting change in shape of the anodic oxidation curve in terms of the formation of Bi\(_2\)H\(_6\), this species has not been found elsewhere with more than a transient existence (59–61). A simpler, and quite adequate interpretation is in terms of roughening of the electrode, giving an apparent current density greater than the true one.

2.5 Effect of Uncompensated Solution Resistance (Ohmic Drop)

The potential change in the solution between electrode surface and Luggin capillary tip means that neither the true electrode potential \(E_{\text{TRUE}}\), nor the true potential sweep rate, \(v_{\text{TRUE}}\), are the same as the values applied to the cell, \(E\) and \(v\):
Table 2.4  Electrode Roughening by Repeated Cycling

Zone-refined Bi, previously etched in conc HNO₃; 0.1 M Na₂B₄O₇; 25°C; ν = 0.10 Vs⁻¹

Capacitance measured by triangular wave potentiostatic method (section 2.2.6; ref. 54) at E = -250mV; C = 18 μF cm⁻²
Anodic charge of 9 mC cm⁻² passed in each cycle.

<table>
<thead>
<tr>
<th>no. of cycles</th>
<th>C' /μF cm⁻²</th>
<th>σ</th>
<th>i'_G /mA cm⁻²</th>
<th>i_G /mA cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>31</td>
<td>1.7</td>
<td>2.4</td>
<td>1.4</td>
</tr>
<tr>
<td>10</td>
<td>50</td>
<td>2.8</td>
<td>2.7</td>
<td>1.0</td>
</tr>
<tr>
<td>20</td>
<td>56</td>
<td>3.1</td>
<td>2.8</td>
<td>0.9</td>
</tr>
<tr>
<td>30</td>
<td>56</td>
<td>3.1</td>
<td>3.2</td>
<td>1.0</td>
</tr>
<tr>
<td>a</td>
<td>68</td>
<td>3.9</td>
<td>5.2</td>
<td>1.3</td>
</tr>
</tbody>
</table>

a  after H₂ evolution at approx. 3 mA cm⁻² for 30 minutes.

Table 2.5  Electrode Roughening by Hydrogen Evolution

Hydrogen evolved for t hrs at approx. 1 mA cm⁻²
Electrodeposited surface; pH = 12.6; 25°C; ν = 0.11 Vs⁻¹

<table>
<thead>
<tr>
<th>t/hr</th>
<th>i'_G /mA cm⁻²</th>
<th>2i'_{AP} /mA cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.6</td>
<td>6.6</td>
</tr>
<tr>
<td>2</td>
<td>6.0</td>
<td>8.0</td>
</tr>
<tr>
<td>5</td>
<td>9.0</td>
<td>12.0</td>
</tr>
</tbody>
</table>

First peak disappears gradually, due to effect of distributed solution resistance over an increasingly porous surface (section 2.5).
\[ E_{\text{TRUE}} = E - I R_\Omega \quad \cdots \quad (2.6) \]
\[ V_{\text{TRUE}} = V - R_\Omega \, dI/dt \quad \cdots \quad (2.7) \]

The effect on cyclic voltammetry is to flatten and extend the peaks observed (44, 48, 81), especially at higher sweep rates, for which the current is greater. In particular, the two anodic peaks usually observed in this work could merge as a result. Thus, although in theory the variation of peak current and potential with sweep rate can be used to discuss the mechanism of nucleation and spreading of a film (45, 47), in practice this cannot always be done. In this work, overlapping of the anodic peaks and plateau (growth current) caused even more obscurity. The nucleation potentials, defined in section 2.3, are, however, little affected (verified using the model curves in ref. 48), and the plateau current, \( i_G \), is unchanged since \( dI/dt = 0 \) there.

In the case of the cathodic peak, some idea of the true peak shape may be obtained by plotting an integrated form, \( \theta = Q(E)/Q_T \) as a function of \( (E - E_{CP}) \); where \( Q_T \) is the total peak charge and \( Q(E) \) is the charge passed between the start of the peak and potential \( E \) (fig.2.9). Simple theory (47) indicates that such curves should be independent of the sweep rate in the absence of ohmic drop (cf the method of ref. 81). Here, the total charge \( Q_T \) is an independent variable. The effects of ohmic drop become more significant as \( Q_T \) and hence the peak current increases. As a
Fig. 2.9  Integrated form of Cathodic Peak
pH 12.6; 0.36 Vs⁻¹; 25°C
fraction of total charge, \( \theta = Q(E)/Q_T \), against potential referred to peak, \((E-E_{CP})\).

inset  empirical extrapolation procedure to zero ohmic drop
result, the curve loses its symmetry about the peak, which
is seen to occur at $\theta = 0.45 \pm 0.05$ in the limit of $Q_T \to 0$.
Even this simple conclusion eliminates some mechanisms (45).

After a number of cycles, the electrode surface
became somewhat porous, and could also develop pits (sections
2.4, 2.6). The ohmic drop can then be divided into two parts;
a general part, the same over the whole surface, and a
distributed part, different for different parts of the surface
and depending on parameters describing the area and tortuo-
sity of the pores.

The effect of a distributed ohmic drop on the measure-
ment of electrode capacitance has been discussed recently
(62). Its effect on cyclic voltammograms was to further
broaden the peaks. The appearance of spurious "shoulders"
on the cathodic peak can also be attributed to this. In
principle, a pore distribution for the surface could be
derived (62).

2.6 Current Efficiency

The current efficiency is defined as the ratio of
the charge contained in the cathodic peak, $Q_{CP}$ (fig. 2.11),
to the total anodic charge, $Q_A$.

In very alkaline electrolytes, dissolution of the
film was unimportant on the time scale of these experiments,
about 20 s (section 3.4), and the current efficiency was close
to one (line (a) in fig. 2.10).
Fig. 2.10 Current Efficiency for Formation of an Adherent Film.

Anodic charge, $Q_A$ against charge in corresponding cathodic peak, $Q_{CP}$.

Line (a): pH 13.4; 0.16 Vs$^{-1}$
  current efficiency, $Q_C/Q_A = 0.95$

Line (b): pH = 8.87; 0.08 Vs$^{-1}$
  current efficiency below break = 0.77
When pH < 9, \( Q_A \) tended to exceed \( Q_{CP} \) (line (b) in fig. 2.10), the difference representing the amount of \( \text{Bi}_2\text{O}_3 \) dissolved. The cyclic voltammograms showed a cathodic tail following the peak (fig. 2.11) and much of the difference in charge was contained in this. When the anode potential became greater than some critical value, \( E_{CRIT} \), a rapid rise in the current was observed (fig. 2.11). As the anode reversal potential was increased through this critical value, the charge contained in the cathodic peak became almost constant but the charge in the tail continued to increase (fig. 2.11).

The rapid rise in current was due to the formation of pits through the anodic film and the dissolution of the metal from these pits. Precipitation of a crystalline product onto the surface resulted in the characteristic "swirl" pattern with a rotating disc electrode (fig. 2.12). Reduction of this loosely adherent product occurred in the cathodic tail of the cyclic voltammogram. The higher reduction overvoltage would be because of a poor electrical connection between the crystalline deposit and underlying film. The powdery mass of bismuth metal resulting was easily rubbed off the electrode surface, and gave it a black appearance.

The breakdown overvoltage, \( E_{CRIT} - E_R \), was irreproducible. Variation of the sweep rate, \( v \), and rotation rate, \( \omega \), had little effect. The breakdown overvoltage tended to increase with increasing \( v \) and \( \omega \). It was also markedly increased by increasing the ionic strength of the electrolyte. Since the current did not depend strongly on rotation
Fig. 2.11 Effect of Dissolution Process on Cathodic Curve

pH 8.87; 0.08 Vs\(^{-1}\); 25°C. Dotted line, obtained with a different electrode, shows an extreme example of a cathode tail.
Fig. 2.12 Pattern of crystalline deposit on bismuth electrode surface following dissolution.

Each trail terminates in a pit in the surface. The continuous film under the deposit showed as a golden colour (interference colour).

Zone-refined electrode, pre-etched in conc HNO₃, solution pH = 8.5, direction of rotation counter-clockwise.
rate, the Bi$_2$O$_3$ dissolution is surface controlled. The shape of the cathodic curve was influenced by rotation rate since this controlled the distribution of the deposit over the surface and also the amount of material lost from the surface.

Repetitive cycling in the dissolution region, that is without reduction of the film, eventually gave a current-potential curve with little hysteresis. The film had simply formed to a maximum thickness determined by the anodic limit of the sweep. Only the dissolution process was being observed.

Pitting and dissolution has been observed in more alkaline solutions, but at much higher overvoltages (section 3.3), consistent with the lower solubility of the film. Two factors seem important in its initiation and maintenance: heating of the film and adjacent solution (78, 80, 94) and a locally lower pH in the pits, due to the release of hydrogen ions by reaction 2.3. Heating of the solution would be most important in the case of a narrow pit with large internal surface area. The sweep rate, v, would be significant because it controls the current flowing, but also enters as a time factor. The rotation rate would be significant because it would affect heat transfer and H$^+$ diffusion. Heating of the solution would relate to the conductivity and hence the ionic strength of the solution.

2.7 Anode Nucleation Potential

The anodic nucleation potential, $E_{AN'}$, was defined in fig. 2.8. Its variation with solution pH parallels the
reversible potential of the Bi$_2$O$_3$/Bi couple (fig. 2.13). It also depends on the surface preparation, giving rise to the scatter of points in fig. 2.13. A systematic drift of the nucleation potential on continued cycling, such as is marked on fig. 2.13, was also accompanied by a drift of the current, indicating changing surface area.

2.8 Number of Anodic Peaks

The number of anodic peaks observed depended on the surface preparation. It correlated with the anodic overpotential, $\eta_{AN}$:

$$\eta_{AN} = E_{AN} - E_R$$

(2.8)

If $\eta$ was above a critical value, about +100 mV, only one anodic peak was observed. If $\eta$ was less than this value, two or more peaks were observed. In the majority of cases, $\eta$ was about +50 mV and two anodic peaks were observed. Experimental data is summarized in fig. 2.14. In the case of two anodic peaks, a nucleation overpotential for the second peak could be defined by extrapolating the tangent at the inflexion point to cut the potential axis. It had the same value as that observed in the case of only one anodic peak.

The effect is unlikely to be the adsorption of impurities from the solution as both classes of behaviour were observed with different electrodes in the same electrolyte. In the low overvoltage case, $\eta_{AN}$ was unaffected by pre-electrolysis of the solution sufficient to reduce the concentration of all electro active impurities by a factor of $10^2$. 
Fig. 2.13 Anodic Nucleation Potential; variation with solution pH

solid line is the reversible potential of the Bi$_2$O$_3$/Bi couple, eq. 2.5. dashed lines show the variation with continuous cycling which sometimes occurred.

symbols denote different electrode preparations

○ electrodeposited (a)          ● cast and annealed
● electrodeposited (b)          ▲ other cast electrodes
□ zone-refined (a)              ▲ zone-refined (b)
△ zone-refined (b)              ▼ zone-refined (c)
● zone-refined (d); upper point - prepared by film growth and dissolution
lower point - prepared by film growth to high potential and reduction.
electrode preparation pH

cast and annealed 13.2

cast 13±0.5

zone-refined (a) 9 → 13
(b) 9.2
(c) 12.9

electrodeposit (a) 13 → 7
(b) 12.5

microelectrodes

freshly polished 13

left standing in solution 13

number of anodic peaks one two three

Fig. 2.14 Correlation between number of peaks and anodic nucleation overvoltage
An interesting effect was observed with the micro-electrodes. These were prepared so as to have a highly strained surface. The freshly prepared electrodes all showed three sharp anodic peaks followed by a very large, broad peak (fig. 2.15). Standing in the solution for a period varying from 2 hrs for the drop electrode, to 12 hrs for the plane electrode, reduced the number of sharp peaks to two and removed the broad peak (fig. 2.15). Processes of film formation and dissolution would occur on standing the electrode in the solution (section 3.4). These would change the structure of the metal surface, seen as an increase in roughness (table 2.6). In the case of the freshly prepared micro-electrodes, one could interpret that once a continuous film had formed, a high density of surface defects led to much cracking of the film (32) with a consequent rise in current, and formation of a porous upper layer (section 4.5 and 4.6).

A similar result has been observed for the cyclic voltammetry of Tl in KCl solution (63). As in this case, larger Tl electrodes did not show the effect (64).

The larger plateau current density (section 2.14) observed for the micro-electrodes (fig. 2.15) is also consistent with cracking of the film.

2.9 **Charge in Anodic Peaks**

Some data concerning this is presented in table 2.6. No simple regularity in the ratio of the charge for the two peaks was observed. However, the total anodic peak charge
Fig. 2.15 Plane micro-electrode cyclic voltammetry.

pH 13.1; 0.077 Vs⁻¹; 25°C; gas stirring.

(a) freshly polished
(b) after overnight standing in the solution
was unaffected by the electrode preparation, \( Q_1 + Q_2 = 3 \pm 2 \text{ mC cm}^{-2} \) (definition of terms in table 2.6). It was also independent of the solution pH (table 2.7), and no statistically significant variation with applied sweep rate in the range 0.1 to 0.01 Vs\(^{-1}\) was observed.

The values of the film thickness, \( h \), formed by the total peak charge, \( Q_1 + Q_2 \), listed (table 2.6), have been calculated assuming the film material to be \( \alpha - \text{Bi}_2\text{O}_3 \):

\[
h = \frac{V_m Q}{6F}
\]

........................ (2.9)

where \( Q \) is the charge per unit surface area and \( V_m \) the molar volume of \( \alpha - \text{Bi}_2\text{O}_3 \), 53.2 cm\(^3\) mol\(^{-1}\).

Comparison with the parameters of various bismuth oxide crystal structures (table 2.8) showed that a layer rather more than one unit cell thick formed during the anodic peaks. However, values of \( h \) computed using \( Q_1 \) alone correspond approximately to one unit cell thickness. Certainly, \( h \) is much greater than that appropriate to a monomolecular layer (about 0.3 mm).

Anodic peaks are formed as a result of the process of spreading of oxide nuclei to cover the surface (47), and a simple model (section 2.12) interprets \( h \) as the thickness of the layer when coverage is just complete. The layer must also thicken as it spreads, to account for the values of \( h \) calculated above (table 2.6). The plateau current arises from the process of film thickening (section 2.14) so that the way the rise to the plateau (67) overlaps with the anodic peaks must also be taken to mean simultaneous
### Table 2.6 Charge in Anodic Peaks

Schematic diagram shows method for defining charges.

![Schematic diagram showing method for defining charges](image)

<table>
<thead>
<tr>
<th>pH</th>
<th>metal</th>
<th>(a) $\sigma$</th>
<th>$Q_1$/mC cm$^{-2}$</th>
<th>$Q_2$/mC cm$^{-2}$</th>
<th>$Q_1/Q_2$</th>
<th>$Q_1+Q_2$/mC cm$^{-2}$</th>
<th>h/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.4</td>
<td>electrodeposited(a)</td>
<td>10</td>
<td>0</td>
<td>0.90 ±0.1</td>
<td>0.</td>
<td>0.90±0.1</td>
<td>0.8</td>
</tr>
<tr>
<td>12.6</td>
<td>electrodeposited(b)</td>
<td>10</td>
<td>0.43</td>
<td>0.90</td>
<td>0.48±0.02</td>
<td>1.33 ± 0.1</td>
<td>1.2</td>
</tr>
<tr>
<td>12.9</td>
<td>zone-refined (c)</td>
<td>2.4</td>
<td>3.21</td>
<td>2.5</td>
<td>1.3</td>
<td>5.7</td>
<td>5.2</td>
</tr>
<tr>
<td>13.4</td>
<td>zone-refined (a),</td>
<td>1.4</td>
<td>2.7</td>
<td>2.0</td>
<td>1.3</td>
<td>4.7</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>after 200 cycles</td>
<td>5.1</td>
<td>0.31</td>
<td>2.6</td>
<td>0.12</td>
<td>2.9</td>
<td>2.7</td>
</tr>
<tr>
<td>13.2</td>
<td>cast (a)</td>
<td>1.5</td>
<td>0.83</td>
<td>2.2</td>
<td>0.38±0.1</td>
<td>3.0 ± 0.14</td>
<td>2.8</td>
</tr>
<tr>
<td>13.2</td>
<td>cast (b)</td>
<td>1.3</td>
<td>0.56</td>
<td>2.5</td>
<td>0.22</td>
<td>3.1</td>
<td>2.9</td>
</tr>
<tr>
<td>13.2</td>
<td>cast and</td>
<td>1.5</td>
<td>0</td>
<td>3.5</td>
<td>0</td>
<td>3.5</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>annealled</td>
<td>1.5</td>
<td>0.57</td>
<td>2.8</td>
<td>0.20</td>
<td>3.4</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>20 cycles later</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.1</td>
<td>micro-electrode,</td>
<td>7</td>
<td>0.45</td>
<td>1.6</td>
<td>0.27</td>
<td>2.1</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>after standing</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>micro-electrode,</td>
<td>3</td>
<td></td>
<td></td>
<td>3 peaks observed</td>
<td>2.2 total</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>freshly prepared</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Notes**

(a) Roughness factor, $\sigma$, estimated either directly from capacitance measurements or indirectly by comparison of the plateau current (section 2.2.6) of different electrodes.

(b) Subscript 1 denotes the first peak and 2 the second. Zero entry denotes one peak only.

(c) Error bound gives precision, determined by a number of measurements; accuracy depends on the accuracy of the value of $\sigma$ given—probably about ±20%.
Table 2.7  Total Anodic Peak Charge as a Function of Solution pH

<table>
<thead>
<tr>
<th>pH</th>
<th>12.9</th>
<th>12.9</th>
<th>8.7</th>
<th>5.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Q_1 + Q_2 / \text{mc cm}^{-2} )</td>
<td>5.7</td>
<td>4.7</td>
<td>3.1</td>
<td>4.8</td>
</tr>
<tr>
<td>h/nm</td>
<td>5.2</td>
<td>4.3</td>
<td>2.9</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Table 2.8  Bismuth Oxide Crystal Structures

<table>
<thead>
<tr>
<th>modification</th>
<th>( V_m / \text{cm}^3 \text{mol}^{-1} )</th>
<th>( a / \text{nm} )</th>
<th>( b / \text{nm} )</th>
<th>( c / \text{nm} )</th>
<th>molecules/unit cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )-monoclinic, ( \beta = 67.07^\circ )</td>
<td>53.2</td>
<td>0.584</td>
<td>0.816</td>
<td>0.749</td>
<td>4</td>
</tr>
<tr>
<td>( \beta = 90^\circ ) (alternative description)</td>
<td></td>
<td></td>
<td></td>
<td>1.381</td>
<td>8</td>
</tr>
<tr>
<td>( \beta )-tetragonal</td>
<td>54.8</td>
<td>1.093</td>
<td></td>
<td>0.562</td>
<td>8</td>
</tr>
<tr>
<td>( \gamma )-cubic</td>
<td>53.7</td>
<td>1.023</td>
<td></td>
<td></td>
<td>13</td>
</tr>
</tbody>
</table>
film spreading and thickening.

Multiple peaks could be interpreted as the nucleation and spreading of successive layers (65), the formation of layers beyond the first requiring ion transport through the oxide. In the case of multiple anodic peaks, the charge in each peak should be the same and should correspond to one monolayer. This simple relationship was not observed, but overlapping of the peaks and plateau would obscure it.

2.10 Variation of Cathode Reversal Potential

If the cathodic sweep was reversed before the film was completely reduced (fig. 2.16), the subsequent anodic curve was unchanged in shape, but the current was reduced, and the apparent anodic nucleation overvoltage increased slightly, by an amount depending on the amount of film remaining. This observation strongly supports the idea that the reduction reaction occurs at the film-solution interface (section 2.13), the reduced metal moving back through the film. Otherwise, on reversal of the sweep with film only partially reduced, the current would remain low until the field was sufficient for ionic migration, when it would gradually rise to its previous value, according to the formula presented by Bailey (67). The observation of peaks means the nucleation and spreading of oxide on metal. The newly reduced metal must therefore be on the outer surface of the film. Similar observations and conclusion have been made for the reduction of anodic thallium halides on Tl metal (64).
Fig. 2.16 Variation of Cathode Reversal Potential
zone-refined Bi; 0.1M Na₂B₄O₇ (pH 9.2) + 0.07 M KI, 0.1Vs⁻¹, 21°C
The presence of iodide does not affect the conclusions of sections 2.10 and 2.13 (see also Chapter 7).
The potential of reversal of the cathodic sweep was also altered in a range from a value corresponding to the completion of the cathodic peak to a value corresponding to a considerable rate of hydrogen evolution (fig. 2.17). The behaviour observed differed according to the number of anodic peaks.

Thus, when only one anodic peak was observed, variation of the cathode reversal potential in this range had no effect. However, for surfaces for which two anodic peaks were normally observed, reversal of the potential sweep before any hydrogen evolution occurred resulted in the gradual disappearance of the first anodic peak. The current at the second peak gradually increased and there was an increase in the anodic nucleation overvoltage. The effect was reversible and the cathodic nucleation overvoltage (section 2.11) unchanged. Discussion is given in section 2.12.

2.11 Cathodic Nucleation Potential

The cathodic nucleation potential was defined in section 2.3, and the cathodic nucleation overvoltage, a negative quantity, is defined as

\[ \eta_{CN} = E_{CN} - E_R \]  \[ (2.10) \]

It varied with the amount of charge passed during the preceding anodic sweep (fig. 2.18), the solution pH and, to a minor degree, the surface preparation (fig. 2.19).

The effect of surface preparation was noticeable in the reduction of a film which would only partially have covered the surface. In such a case, most preparations
Fig. 2.17  Effect of Previous H₂ Evolution on Anodic Nucleation
(a) original trace; sweep reversed at (a)
(b) gradual disappearance of first peak; sweep reversed at (b)
(c) gradual return to original trace; sweep reversed again at (a)
Fig. 2.18 Variation of cathode nucleation overvoltage, $\eta_{CN}$, with charge to be reduced, $Q_A$.

pH 13
- micro-electrode
- electrodeposit (a)

$Q_A$/mC cm$^{-2}$

$-\eta_{CN}$/mV
Fig. 2.19  Cathode nucleation overvoltage showing effect of solution pH and surface preparation at low coverage of oxide

- micro-electrode
- electrodeposit (a)
- electrodeposit (b) (range of sweep rate)
showed an underpotential for cathodic reduction (fig. 2.19). Those that showed only one anodic peak did not show this effect. Interaction between the metal and oxide surfaces may give rise to a reversible potential for formation of a very thin film different to that for formation of a bulk phase (91). Further discussion of the effect of surface preparation is given in section 2.13.

In those experiments in which a shift of the anode nucleation potential was observed on continued cycling, a corresponding change in the cathode nucleation potential was also observed. A variation of cathode nucleation potential with charge to be reduced has also been observed for the reduction of silver oxides on Ag (46), but not for reduction of thallium halides on Tl (64) or of copper oxides on Cu (66).

2.12 Mechanism for Effect of Surface Preparation on Anodic Peaks

The surfaces studied can be divided into two classes, according to the value of the anodic nucleation overvoltage. The simplest mechanism consistent with the data (section 2.9) involves a distribution of areas on the surface with different nucleation overvoltage, the distribution varying according to the history and original preparation of the surface (63). Two different types of area, with distinctly different nucleation overvoltage, are indicated, their ratio being given by the ratio of the charge in the two anodic peaks (table 2.6). Their sum would, of course, be constant (table 2.6).
The effect of variation of the cathode reversal potential in the region following the cathode peak (section 2.10) could perhaps be attributed to the chemisorption of a layer of oxygen atoms from dissolved oxygen, or oxide ions from water (68), removed by hydrogen evolution, on the more "active" of these areas. The nucleation of a film would be affected, but the amount of charge involved could be undetectably small.

Two different types of surface area have been detected by microscopy (Chapter 4). A tentative correlation could be made.

Nucleation phenomena are very sensitive to the state of the surface (1). Factors which may be important are the density of defects in the metal surface, the particle size or micro-roughness of the surface, and the presence of adsorbed layers. Of the preparations used, the microelectrodes were expected to have the highest surface defect density and the annealed electrode the least, in qualitative agreement with the anodic behaviour.

2.13 **Mechanism of Cathodic Reduction**

The overall reaction is:

\[ \text{Bi}_2\text{O}_3(s) + 3\text{H}_2\text{O(aq)} + 6e^-_\text{(m)} \rightarrow 2\text{Bi}_\text{(m)} + 6\text{OH}^- \quad \ldots \quad (2.11) \]

I should like to propose a model for it involving reduction of metal ions at the film-solution interface (fig. 2.20), the reduced layer of metal moving back through the film (section 2.10; fig. 3.2). Easy injection of electrons into the film over a low energy barrier at the metal-film in-
Fig. 2.20 Schematic diagrams for two mechanisms of Cathodic Reduction.

(a) electron migration in film; formation of new metal at solution interface.

(b) ion migration in film; formation of new metal at metal interface.
face could occur (38). These electrons may diffuse through the film, by "hopping" from one trap to another (38, 69). When an electron becomes trapped at the film solution interface, it may cause a reduction reaction, releasing hydroxyl ions into the solution, eq 2.12.

$$e_{(m)}^- + t'_\text{surface} \quad \cdots \cdots \cdots \quad (2.12a)$$

$$O_\text{O}^- + H_2O_{(aq)} + 2t'_\text{surface} + 2OH^-_{aq} + F_1 \quad \cdots \quad (2.12b)$$

where $O_\text{O}^-$ is an oxide ion in its lattice site, $t'$ denotes a trapped electron (at some lattice discontinuity) and the neutral $F_1$ centre is two electrons trapped in an anion vacancy. The reduced bismuth metal would thus first appear in isolated nuclei at the surface ($F_1$ centres). This idea is related to the theory of photolytic decomposition of ionic solids (70) and is the same as that proposed to describe the rectification behaviour of $Ta_2O_5$ films (38). In that case, the reaction at the film-solution interface is hydrogen evolution.

There are two important processes in this model: diffusion of electrons to the interface, assisted by the applied field (eq 2.12(a)), and aggregation of trapped electrons at the surface (71), involving diffusion along the surface perpendicular to the applied field to produce bulk bismuth metal from the nuclei (eq. 2.13).

$$2Bi_{Bi} + 3F_1 + 2Bi_{(m)} \quad \cdots \cdots \cdots \quad (2.13)$$

in which $Bi_{Bi}$ denotes an oxide lattice cation and $Bi_{(m)}$ a new speck of bismuth metal. The metal formed would be porous, occupying less volume than the original oxide, hence allowing the solution access to the oxide underneath and reduction to continue.
This model predicts an immediate change to a dark grey colour at the start of the reduction of thick films showing interference colours, as observed (fig. 3.2).

Localized regions of high conductivity in the oxide could occur, depending on the surface preparation (33, 34, 72). A variation of \( \eta_{CN} \) with surface preparation, could result. In all cases \( \eta_{CN} \) would describe a threshold electric field for an appreciable diffusion rate of electrons and so would vary with the film thickness. The electron conductivity of the film would depend on its morphology. Some evidence has been adduced (section 2.14) for a change in film morphology to a more porous state with decreasing solution pH. The pH dependence of \( \eta_{CN} \) is consistent with this. Differences between different metals would reflect the differences in oxide electron conductivity and height of potential barrier at metal-film interface. These factors would also be involved in experiments on the re-anodization of partially reduced surfaces (section 2.10).

A model involving reduction along preferred channels in a dendrite fashion (64, 73, 74) is a natural extension from the above discussion.

The idea of electron conduction through the film and reaction at the film-solution interface was supported by measurements made in solutions containing \( I_3^- \). A current due to reduction of \( I_3^- \) was observed on an electrode covered by a continuous film.

Another mechanism (46, 66, 75, 98, fig. 2.20) for cathodic reduction formulates this as the reverse of the anodic
process i.e. solid state diffusion of cations to the metal-film interface, and of anions to the film-solution interface, reduction of metal ions occurring at the metal-film interface. Ions would have to diffuse across the entire thickness of the film, so that the nucleation overvoltage, describing a threshold electric field, would vary with the film thickness. This model does not explain why current flow should be much easier in the cathodic than in the anodic direction (see also Chapter 1 and 3) nor is it in agreement with the results of experiments involving re-anodization of partially reduced surfaces (section 2.10). It predicts a progression of colours, reverse of that seen during film formation, in the reduction of thick films showing interference colours and this was not observed (fig. 3.2).

The only direct demonstration of the second mechanism, of solid state ion diffusion, has been a study in which the formation of Ag at the Pt was observed in the reduction of an Ag₂O pellet contacting a Pt grid on one face and an electrolyte on the other (98). However, the solution permeated into the pellet so that the oxide-solution interface could, in fact, have been found quite close to the Pt electrode. This result does not therefore, distinguish between the two models.

2.14 Plateau Current

This section is concerned with the dependence of the plateau current, \( i_G \), on the potential sweep rate, \( v \).

There are two possible interpretations of such a plateau current. One (76), in terms of dissolution of a layer of constant thickness, has been excluded by the measurements of current efficiency (section 2.6). The other is in terms of
thickening of the layer, involving some transport process driven by the electric field in the layer (fig. 1.2).

The system is considered to be in a kinetic steady state, of constant current and constant electric field, both uniform throughout the layer. The experiment is in fact analogous to the galvanostatic experiment, in which a constant current is applied and the resulting rate of potential increase determined.

By studying the dependence of the plateau current on the sweep rate, information on the relationship between current and electric field in the stage of growth immediately following complete coverage of the surface by the film was obtained. The variation with solution pH was also studied.

2.14.1 pH variation

The electrodeposited surface (a) was used. The initial solution, pH = 13.4, contained Na$_2$B$_4$O$_7$ and NaOH. The pH was altered by the addition of 1 M HClO$_4$ solution. The electrode was never removed from the solution.

The variation of apparent plateau current density with pH at various sweep rates is shown in fig. 2.21.

Some of this variation would be due to a steady change of the electrode surface area with continued cycling. However, since the average slope, $\frac{di}{dpH}$ (fig. 2.21) seems to be a function of the sweep rate, this change of electrode surface area is probably not the only factor contributing to the current variation.
Fig. 2.21 Variation of plateau current, $i'_G$, with solution pH, at various sweep rates, v.

$i'_G$/mA cm$^{-2}$

$v$/mV s$^{-1}$

pH
2.14.2 Sweep rate variation

The empirical high field growth law,

\[ i = \bar{A} \exp (B \bar{E}) \].............. (2.14)

where \( \bar{E} \) is the electric field in the layer,

\[ \bar{E} = \frac{6F}{V_m} \cdot \frac{V}{I} \].............. (2.15)

implies a linear plot of \( \log i \) against \( \frac{V}{I} \);

\[ \log i = \log \bar{A} + \frac{B}{2.3} \cdot \frac{6F}{V_m} \cdot (\frac{V}{I}) \].............. (2.16)

An assumption is that the layer thickens uniformly. The potential changes across metal-film and film-solution interfaces are constant, since the system is in a steady state.

Ohm's law,

\[ i = \alpha \bar{E} \].............. (2.17)

implies a linear plot of \( i \) against \( \sqrt{V} \)

\[ i = \left( \frac{6F\alpha}{V_m} \cdot V \right)^{\frac{1}{2}} \].............. (2.18)

The high field growth law has been derived (1, 2, 80) in terms of the alteration by the applied field of the energy barrier to ion transport. Eq. 2.17 with \( \alpha = 2\bar{A}B \) arises as an approximation at low field, when the rates of migration of ions with and against the field become comparable.

Figs 2.22 and 2.23 show the data plotted according to eq's 2.16 and 2.18. Equation 2.18 applies to the data for pH 7.47, except at very low sweep rates. Equation 2.16 applies to the data at higher pH.
Fig. 2.22 Plateau current as a function of sweep rate
Test of exponential growth law (eq. 2.14 and 2.16)
Fig. 2.23 Plateau current as a function of sweep rate

test of linear law (eq. 2.17 and 2.18)

\[ i_G / \text{mA cm}^{-2} \]

\[ (v/\text{mV s}^{-1})^{1/2} \]
2.14.3 Parameters of the growth laws

From fig. 2.21a and eq 2.16 the parameters of eq 2.16 are obtained as (solution pH > 8.5):

\[ B = (1.4 \pm 0.3) \times 10^{-6} \text{ V}^{-1} \text{ cm} \]
\[ \overline{A} = (7.0 \pm 1.5) \times 10^{-6} \text{ A cm}^{-2} \]

Here, the roughness factor, \( \sigma \), has been taken as 10 ± 2. The precision of the data of fig. 2.21(b) is poor, probably because of small variations in the surface area. The parameters are

\[ B = 2.3 \times 10^{-6} \text{ V}^{-1} \text{ cm} \]
\[ \overline{A} = 2.2 \times 10^{-7} \text{ A cm}^{-2} \]

In this case, an alternative method of obtaining \( B \) is a linear plot of \( i \) against \( v \) (fig. 2.24), since, from eq. 2.16,

\[ \frac{\text{di}}{\text{dv}} = \frac{\beta}{1 + \frac{3v}{1}} = \beta \quad \text{when} \quad i \gg \beta v \quad \ldots \ldots \ldots \ldots (2.19) \]

where

\[ \beta = \frac{6FB}{2.3V_m} \]

Fig. 2.24 gives \( B = 1 \times 10^{-6} \text{ V}^{-1} \text{ cm} \).

The estimates of \( \overline{A} \) and \( B \) are in reasonable agreement, considering that \( \overline{A} \) was obtained by a long extrapolation. They also compare well with values obtained using the galvanostatic method and a zone-refined electrode (Chapter 3). The best estimate of \( B \) from the above numbers is \( B = (1.5 \pm 0.5) \times 10^{-6} \text{ V}^{-1} \text{ cm} \).

Other work, using the galvanostatic method on much thicker films (25) gives a rather higher value for the parameter
Fig. 2.24 Linear plot of plateau current against sweep rate for evaluation of B parameter of high field growth law (eq. 2.19).
B and hence rather lower values for the field strength at a given current density. Comparison and discussion will be given in Chapters 3 and 4.

From fig. 2.23 and eq. 2.18 the parameter of equation 2.17 is obtained as

\[ \alpha \sim 10^{-10} \text{ A V}^{-1} \text{ cm}^{-1} \quad (pH = 7.47) \]

The roughness factor was assumed to be 10 but is likely to be rather less.

The value of the product 2\(\bar{A}B\) above and from Chapter 3, is

\[ \log (2\bar{A}B/\text{AV}^{-1} \text{ cm}^{-1}) \sim -11 \pm 1 \]

similar in magnitude to that obtained for \(\alpha\).

2.14.4 Discussion

Perhaps, at lower pH, the film forms in a different way to that at high pH, such that the parameter B is rather smaller, giving rise to the linear approximation (low field) of the film growth theory. A model (78) which is consistent with the data involves the initial formation of a continuous layer similar to that formed at high pH. A second layer, with lower B value, would form on top of this. The second layer may be somewhat porous, thickening by ionic migration in the pores. This model would predict an initial curved section followed by a linear section in a plot of \(i\) against \(V^{1/2}\) (79). Absorption of protons into the \(\text{Bi}_2\text{O}_3\) lattice (102, 103, Chapter 5) could also have the same effect, of increased conductivity in an upper layer.
The isoelectric pH of Bi$_2$O$_3$ has been determined as 7.6 (Chapter 7). The change in sign of the surface charge of the oxide may relate to the change in film morphology proposed.

A distinction between the Cabrera-Mott and Verwey models for film thickening (2, 80) could be made. In the high-field limit, both approximate to eq. 2.14 but in the limit of low electric field, the Verwey model (rate-limiting ion migration through the film) gives eq. 2.17 whereas the Cabrera-Mott model (rate-limiting ion injection into the film) gives:

\[ i = \alpha_s E^2 \]  \hspace{1cm} (2.20)

implying linear plot of \( i \) against (\( V/i^2 \)):

\[ i = 6F \frac{\alpha_s}{V_m} (\frac{V}{i^2}) \]  \hspace{1cm} (2.21).

Eq. 2.21 did not fit the results of this work. I applied it to cyclic voltammetric data for the anodization of Cu (66) and obtained a good fit. This gives further experimental support for the Cabrera-Mott model, previously used to explain a cubic growth law under potentiostatic conditions for this system (66).

2.15 Hydrogen Evolution

Some data is collected in fig. 2.25. The points have been corrected for the displacement of the potential scale caused by ohmic drop (eq. 2.6).

Tafel's law applies:

\[ \eta = b \log_{10} \left( \frac{i}{i_0} \right) = E + 0.060 \text{ pH V} \]  \hspace{1cm} (2.22)

with \( b = 0.11 \text{ V, log}_{10} \left( \frac{i_0}{A \text{ cm}^{-2}} \right) = -10.3, \frac{\partial \log_{10} i_0}{\partial \text{pH}} \frac{i_0}{\eta} = 0 \).
Fig. 2.25  Tafel plot for hydrogen evolution reaction on Bismuth

$\omega = 11 \text{ Hz}$
where \( \eta \) is the overvoltage for the hydrogen evolution reaction. Deviation from this law is observed at very high pH.

The hydrogen evolution current changed upon continued cycling of the electrode potential. The change mainly reflected a change in electrode surface area. Some hysteresis was also observed.

A previous study of hydrogen evolution on bismuth in strong alkali solution showed low reproducibility (56). The values given above are almost identical with those determined for hydrogen evolution on bismuth in strong acid solution (56), once correction has been made for the electrode roughness factor:

\[
b = 0.11 \text{ mV}; \quad \log_{10}(i_0/A \text{ cm}^{-2}) = -9.6.
\]

The results are consistent with a rate determining proton discharge mechanism (85):

\[
\text{(discharge step)} \quad M(e^-) + H^+ \rightarrow MH \quad \text{r.d.s.} \quad (2.23)
\]

\[
\text{(desorption step)} \quad MH + H_2O + M(e^-) \rightarrow H_2 + + 2M + OH^- \quad \text{fast} \quad (2.24(a))
\]

\[
\text{or} \quad 2MH \rightarrow 2M + H_2 \quad \text{fast} \quad (2.24(b))
\]

(where M denotes a surface metal atom) but not with the equivalent mechanism involving discharge of a water molecule.

The data was compared with a theory (84, 85) relating exchange current density, discharge mechanism and Pauling bond dissociation energy for the MH bond, \( D_{MH} \) (83). The value of
$D_{\text{BiH}}$ was interpolated from a plot against the electronic work function for a number of metals (84); $D_{\text{BiH}} = 67 \text{ Kcal mol}^{-1}$; and the result placed on a plot of $\log i_0$ against $D_{\text{MH}}$ for a number of metals (84, 85). This procedure classified Bi in the group of metals for which the proton discharge step (eq. 2.23), rather than the desorption step (eq. 2.24) is rate determining, in agreement with the conclusion derived from the measurement of the Tafel slope and the pH dependence of exchange current density, above.

2.16 Summary

(a) The early stages in the formation of continuous anodic oxide layers on bismuth have been studied. During this period the oxide, $\text{Bi}_2\text{O}_3$, covered the surface by a process of simultaneous thickening and spreading of patches of oxide.

(b) The electrode surface could be divided into two different areas of different anodic nucleation overvoltage (about 100 mV). The ratio of the two areas varied according to the history and original preparation of the surface.

(c) The cathodic reduction of the oxide proceeded from the outer surface inwards, and a rough, porous surface resulted. A model involving electron injection from the metal into the film, diffusion of electrons through the film and their reaction at the outer surface has been proposed.
(d) The rate of thickening of the oxide layer followed the exponential law of high-field ion conduction in the solid state, when pH > 8.

(e) The morphology of the continuous layer depended upon the pH of the electrolyte used. The isoelectric pH of the oxide (IEP 7.6) may be significant to a discussion of this phenomenon.

(f) Some dissolution of the oxide, with the formation of pits in the metal, occurred at lower pH (<9).

(g) Parameters for the evolution of hydrogen on bismuth in alkaline solutions have been obtained and compared with a correlation due to Conway & Bockris (84). Hydrogen evolution caused further surface roughening.
CHAPTER 3
GALVANOSTATIC STUDY OF ANODIC
BISMUTH OXIDE FORMATION

3.1 Introduction
The galvanostatic technique involves the application of a constant current to the electrode, and analysis of the potential-time trace resulting. The first part of this curve gives information about the nucleation of an oxide layer and its spreading to cover the surface (1, 92, 93). The later part gives information about the thickening process, as in previous work on bismuth anodic films (25-31). The result is similar to an integral form of the cyclic voltammogram (Chapter 2) and is more amenable to quantitative treatment. Cyclic voltammetry, however, gives a much clearer qualitative picture of the electrode phenomena.

The work presented in this chapter emphasizes the nucleation and spreading of the oxide layer and its growth while still only a few monolayers thick. The growth parameters for these thin layers were quite different to those for thicker layers (25). The growth parameters for thicker layers were re-determined using a transient technique (application of a current step during the film growth) and results in agreement with previous work (25) obtained.

3.2 Experimental
Instruments and technique were generally as described in section 2.2. The galvanostatic circuit is detailed in fig. 3.1. Capacitance measurements (section 2.2.6) were used to determine roughness factors.
Fig. 3.1 Galvanostatic circuit

Stability of the potentiostat required \( R_m \approx R_s \). Both were high quality non-inductive resistances. The reference voltage, \( V_s \), was set up on the potentiostat and pulse generator; the constant current in the circuit was: \( I = \frac{V_s}{R_s} \).
The programme used for nucleation studies was:

Anodic

\[ I_2 \]

Form film

Cathodic

\[ I_1 \]

\[ I_0 \]

\[ \text{H}_2 \text{ evolution} \]

Thus, the nucleation parameters obtained relate to an electroreduced surface.

For the study of transients during film growth, the steady current \( I_0 \) was made anodic and the double step, to \( I_1 \) and \( I_2 \), again imposed above it.

The input current of the oscilloscope or uv recorder flowing through \( R_s \) (fig. 3.1) would cause an error in the measured potential (88). This set an upper limit on the magnitude of \( R_s \). The response time of the uv recorder was checked by applying a potential step between the bismuth and SCE and recording the potential change at the Pt reference. The response time was less than 0.01s.

Results and Discussion

3.3 General Features

Some qualitative observations of the phenomena are described in fig. 3.2 and some typical potential time traces for different potential ranges are given in fig. 3.3. At higher potentials and high pH, random fluctuations, due to cracking of
of the film, giving oxygen evolution at high potential and metal dissolution, were observed. This potential region had the unusual property that the potential rose gradually on stirring and fell gradually, to a fraction of its previous value, when stirring ceased. At lower pH, less than about 9, and lower current density, less than about 1 mA cm$^{-2}$, such fluctuations and rotation rate dependence were not observed. The potential simply attained a constant value, equal to that shown by cyclic voltammetry (section 2.6) for film breakdown at the given current. The film breakdown occurred at a thickness greater than about 30 nm at pH 13, decreasing to 5 nm at pH less than 7.

Since a higher potential means a higher electrode resistance, the rotation rate effect above could be due to heating of the oxide and adjacent solution, reduced by stirring (section 2.6; ref. 94).

At lower potentials, where film breakdown was not observed, the curves were unaffected by the stirring rate but the nature of the surface was important. Usually the potential-time curves bent downwards, as a prelude to film breakdown. If, however, the surface was originally porous (e.g. electroreduced, or roughened by hydrogen evolution; section 2.4, ref. 27) a prior upward curve was observed. This was satisfactorily described in terms of "filling in" of the porous surface by the anodic film with a consequent decrease in electrode-solution interfacial area and increase
in the true current density (sections 2.2.6 and 2.4).

(a) Anodize in 0.1M NaOH. Tufts of white solid (Bi(OH))₃ or Bi₂O₃, covering pits observed.

Interference colour (1, 2, 24), running through the spectrum from violet to red on continued anodization, observed on the remainder of the surface. Gas bubbles form at some points at higher potentials (about 10 V).

(b) Current reversed and film reduced. The reverse colour sequence to (a) was not observed, but the surface went dark grey immediately and did not change colour thereafter, i.e. the film was reduced from the outer face inwards (section 2.13).

(c) Part of the surface anodized in 1 M HClO₄. This part changed to a silver grey colour. If the anodic film from (a) was dissolved in HClO₄, the reverse colour sequence was observed.

(d) Whole surface re-anodized in NaOH. Colours observed on bottom (etched) part but not on top (electroreduced) part. The explanation is that the electroreduced surface is very rough and porous.

Fig. 3.2 Qualitative Observations on Bismuth Anodising
Fig. 3.3 Anodic $\text{Bi}_2\text{O}_3$ Formation (galvanostatic)

pH 13; 25°C.

Bottom curve is a magnification of the initial section of the first.
The very first part of the potential-time curve had two transition periods ($\tau_1$ and $\tau_2$ in fig. 3.3) of approximately constant potential, followed by a linear rise of potential with time. Significant information concerning film nucleation and thickening can be obtained from this first section of the whole curve. Important parameters, whose variation with current density was studied, are the transition times, $\tau_1$ and $\tau_2$, the overvoltage, $\eta$ (eq. 2.8) during the transition period, and the slope, $v$, during the final linear rise.

During cathodic reduction the potential remained virtually constant, and much lower than that attained during anodic oxidation (26).

3.4 Current Efficiency

In experiments at low current density, the rate of dissolution of the oxide film in the electrolyte, at potentials well below that giving film breakdown, was significant even at pH 13 because of the long time span of the experiments.

The rate of the dissolution process in NaOH solution at pH 13 was obtained by anodizing for various times and then reducing the layer formed, the difference between anodic and cathodic charge giving the amount dissolved (fig. 3.4). This gave the dissolution rate as $(3\pm1) \times 10^{-11}$ mol. s$^{-1}$ cm$^{-2}$.

An independent measurement, of the rate of dissolution of the layer formed by reaction with dissolved oxygen, was made by electrolysing a clean solution of pH 13 with Pt electrodes, dipping in a piece of clean bismuth during the
Fig. 3.4 Current Efficiency

Difference, \( \delta Q \), between anodic and subsequent cathodic charge against total time for which film was present on electrode.

pH 12.9; 25°C; current 25\( \mu \)A cm\(^{-2} \).
electrolysis, then determining the amount of Bi deposited on the Pt cathode by anodic stripping voltammetry (44), to obtain the amount dissolved from the isolated piece of metal. This gave a dissolution rate of $(6 \pm 2) \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$, in agreement with the previous estimate.

The above numbers are a factor of $10^{20}$ times larger than the diffusion controlled rate calculated using the solubility product of $\text{Bi}_2\text{O}_3$ and the dissociation constants of Bi(III) species known in acid solution (95). The nature of the Bi(III) species in solution at pH 13 is not understood.

3.5 Transition Time

The definition used for the transition times was given in fig. 3.3. More potential-time traces are given in fig. 3.5.

The transition time $\tau_1$ was not significantly affected by rotation rate or light level (table 3.1) confirming the result obtained by cyclic voltammetry. Table 3.2 and figs 3.6 and 3.7 show the variation with applied current density. The charges $i\tau_1$ and $i\tau_2$ showed a linear correlation with $\log i$ (ref. 92, figs 3.6 and 3.7) although the scatter of points in fig. 3.6 at low current density is large. One might expect the correlation to fail at higher current, the charges $i\tau_1$ and $i\tau_2$ tending to some minimum limiting value.

The transition periods, in the galvanostatic experiment, and the anodic peaks, in the cyclic voltammetric exper-
Fig. 3.5  Early stage of anodic Bi$_2$O$_3$ formation (galvanostatic)

pH 12.9;  25°C.

$E$  
(vs. Pt)

0.2V↑

0  4  8  12  16  t/s

from bottom, $i$/mA cm$^{-2}$ = 0.29, 0.36 (repeated), 0.46, 0.57, 0.69, 0.79.

$E$  
(vs. Pt)

0.2V↑

0  0.2  0.4  0.6  0.8  t/s

from bottom, $i$/mA cm$^{-2}$ = 0.36, 0.9, 1.4, 2.0, 2.5, 3.1, 3.6, 4.6.
Fig. 3.6 Variation of charge in first transition period, $i \tau_1$, with applied current density, $i$.

$\text{pH 13; 25}^\circ\text{C.}$

limiting value?
Fig. 3.7 Variation of charge to second transition, $i_T$, with applied current density, $i$. PH 13, 25°C. limiting value?
iment, arise as a result of the process of lateral spreading of oxide islands, to cover the surface (47, 92). Indeed, for most of the range studied, the transition time data could be adequately represented as

\[ i_{T_1} = 1 \pm 0.5 \text{ mC cm}^{-2} \text{ and } i_{T_2} = 2 \pm 1 \text{ mC cm}^{-2}, \]

the same as the charge in the first anodic peak, and the total anodic peak charge observed in cyclic voltammetry, respectively (section 2.9).

A variation of transition time with current density is equivalent to a variation of peak charge with sweep rate in cyclic voltammetry. This was not observed (section 2.9) because measurements could not be made with sufficient precision over a wide enough range of sweep rate. Cyclic voltammetry of various surface preparations (section 2.9) has shown that the observation of \( i_{T_2} \) twice \( i_{T_1} \) above is coincidental.

The relationship between the galvanostatic and potentiostatic (Chapter 6) experiments should be emphasized. Thus, during a transition period, the electrode potential is almost constant (fig. 3.5), so that the observed potentiostatic law for the charge passed during the spreading process (Chapter 6) gives:

\[ i_{T_1} = q_1 \log \tau_1 \]

\[ \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (3.1) \]

where \( q_1 \) is a proportionality constant.
Table 3.1  Variation of Transition Time with Rotation Rate and Light Intensity

Base metal zone-refined; 73µA cm\(^{-2}\); 25.0ºC; pH 12.9 - 0.10 M NaOH, carbonate-free and pre-electrolysed; rotation rate \(\omega\) and relative light intensity \(L^{(a)}\).

<table>
<thead>
<tr>
<th>(\tau_1/\text{s})</th>
<th>24</th>
<th>25</th>
<th>25</th>
<th>24</th>
<th>16</th>
<th>18</th>
<th>13</th>
<th>14</th>
<th>14</th>
<th>15</th>
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<td>(\omega/\text{Hz})</td>
<td>3</td>
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<td>3</td>
<td>4.4</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>4</td>
<td>32</td>
</tr>
<tr>
<td>(\log L^{(a)})</td>
<td>1</td>
<td>-</td>
<td>3</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>-</td>
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</tr>
</tbody>
</table>

Note (a) blank entry denotes pitch darkness; for bright sunlight \(\log L \approx 5\).
Table 3.2  Variation of Transition Time with Applied Current Density

0.10 M NaOH, carbonate-free, pre-electrolysed; 25°C; base metal zone-refined.

<table>
<thead>
<tr>
<th>i (mA cm⁻²)</th>
<th>τ₁ (s)</th>
<th>τ₂ (s)</th>
<th>iτ₁ (mC cm⁻²)</th>
<th>iτ₂ (mC cm⁻²)</th>
<th>i(τ₂-τ₁) (mC cm⁻²)</th>
</tr>
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<tbody>
<tr>
<td>0.030</td>
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<td></td>
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<tr>
<td>0.056</td>
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<td>91</td>
<td>1.6</td>
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<td>7.4</td>
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<td>0.7</td>
</tr>
</tbody>
</table>

Each measurement of τ is an average of two determinations; reproducibility ±10%.
Equation 3.1 is almost equivalent to the empirical correlation of it with log i (figs 3.6, 3.7; ref. 92) and the data fits it quite well (fig. 3.8).

Both galvanostatic and voltammetric experiments show the effect of two areas on the surface of different nucleation overvoltage (section 2.12). Thus there are two anodic peaks in voltammetry (Chapter 2), and two transition periods in the galvanostatic experiment. The relationship of these observations to one another and to the potentiostatic experiment (Chapter 6) has been confirmed experimentally, above.

A model involving simultaneous thickening and lateral spreading of oxide islands on the surface accounts for the magnitude of the charge passed in the transition periods (see section 2.9) and also gives an adequate qualitative description of the variation of transition time with applied current, since if the current is smaller, it will take longer to pass a given amount of charge and hence allow more time for film thickening before the surface becomes completely coated. Since film thickening follows the Verwey high field growth law (sections 2.14 and 3.7), an approximately logarithmic relationship between thickness and time at constant potential, as in eq. 3.1, follows (104, 105, Chapter 6). The driving force for film thickening is the electric field.

$$\bar{E} = (E - E_R)/h \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (3.2)$$

in the nuclei, where h is their thickness.

The same interpretation can be applied to the results for galvanostatic formation of thallium halides on Tl (64)
Fig. 3.8 Variation of charge in first transition period, $i\tau_1$, with transition time, $\tau_1$.

pH 13; 25°C.
for which the transition charge \( \tau \) varies with \( \tau^{1/2} \), and the observed law for film thickening under potentiostatic conditions is a parabolic one, and to results for the nucleation of \( \text{Cu}_2\text{O} \) on copper \( (92, 66, 104) \).

The transition time is also affected by film dissolution, but, in the bismuth case, the calculated effect \( (97, \text{ section 3.4}) \) was very small, in the short interval of the transition time.

3.6 Nucleation

This section gives a study of the events immediately following the current application, i.e. at film coverage zero. A typical result is given in fig. 3.9.

An important qualitative observation is that no transient potential peak is observed. Instead, following the double layer charging, a fairly sharp decrease in the slope of the potential-time curve is seen, corresponding to the nucleation of an oxide phase on the surface - no step in the reduction curve was observed if the current was reversed before the break-point. The potential of film nucleation, \( E_{AN} \), was independent of the applied current density \( (\text{fig. 3.9}) \).

Any mechanism for the spreading of an oxide layer over the surface involves three fundamental steps - electrochemical reaction at the uncovered metal surface to form an adsorbed oxidised species, surface diffusion of this to the periphery of the spreading oxide patch and incorporation into the spreading patch. If the first step is rate controlling, then the rate is proportional to the uncovered area \( (45, 47) \);
Fig. 3.9 Film Nucleation (see sec. 3.2)

$i / \mu A \ cm^{-2} \ (a) \ (b) \ (c)$

<table>
<thead>
<tr>
<th></th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-150</td>
<td>0</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>-40</td>
<td>0</td>
<td>30</td>
<td></td>
</tr>
</tbody>
</table>

$pH \ 12.6; \ 25^\circ C$

$E/\text{mV}$

(vs Pt)

---

break when film nucleates

---

slope gives double layer capacitance

---

reduction

---
Vermilyea's model A (1)) but if the last step is rate controlling, then the rate is proportional to the length of the edge of the growing patch ((10, 92, 93); Vermilyea's model B(1)). A transient potential peak is predicted in this latter case but not in the former. Surface diffusion control relates to the average distance between a discharge site and the edge of a patch. No transient potential peak is predicted. Thus, in this case, electron transfer or surface diffusion, but not lattice incorporation, is the rate determining process.

Some insight into the nucleation mechanism is possible from a consideration of the pseudocapacitance, \( C_s \) (96), immediately following film nucleation (table 3.3).

\[
C_s = i(d\Delta/dt)^{-1}
\] ........................ (3.3)

Two simple mechanisms, both consistent with the qualitative considerations above, were assessed.

A Rate determining discharge reaction, all intermediates at low coverage:

\[
\text{Bi}(m) + \text{OH}^-_{(aq)} \underset{k}{\overset{+}{\rightarrow}} \text{Bi(OH)}_{\text{ads}} + e^- \] ................ (3.4A)

Subsequent reactions of electron transfer, surface diffusion and incorporation into the spreading patches of Bi\(_2\)O\(_3\) are assumed fast.

B Initial electron transfer at quasi-equilibrium, some subsequent reaction of electron transfer or surface diffusion being slow. Intermediates may attain high coverage.
Bi(m) + OH\(_{aq}\) \rightleftharpoons \frac{K}{\text{Bi(OH)}_{ads} + e^-} \quad \ldots \ldots \ (3.4B)

The fraction of the surface covered by Bi\(_2\)O\(_3\) is denoted \(\theta\) and the fraction of the free surface covered with intermediate (mechanism B) is denoted \(\bar{\theta}\),

\[
\bar{\theta} = K(\text{OH}^-) \exp \left(\frac{\beta F}{RT}\right) \quad \ldots \ldots \ldots \quad (3.5)
\]

The pseudocapacitance for mechanism A was calculated assuming spreading of the oxide patches to be the only process. Extrapolation to \(\theta = 0\) was assumed to remove the effect of thickening of the nuclei. Thus:

\[
i = 3Fk (\text{OH}^-)(1-\theta) \exp \left(\frac{\beta F}{RT}\right) \quad \ldots \ldots \ldots \quad (3.6)
\]

and

\[
i = \frac{6Fh}{V_m} \frac{d\theta}{dt} \quad \ldots \ldots \ldots \quad (3.7)
\]

where \(h\) is the thickness of the oxide nuclei and \(V_m\) is the molar volume of Bi\(_2\)O\(_3\), assumed to be the same for the nuclei and bulk material. Differentiation, with respect to time, of eq. 3.6 gives (i constant):

\[
\frac{d\theta}{dt} = (1-\theta) \frac{\beta F}{RT} \cdot \frac{d\theta}{dt} \quad \ldots \ldots \ldots \quad (3.8)
\]

which, with eq. 3.7 and 3.3 gives

\[
C_s = \frac{6Fh}{V_m} \cdot \frac{\beta F}{RT} (1-\theta) \quad \ldots \ldots \ldots \quad (3.9)
\]

Values of the factor \(h\beta\), the characteristic parameter of mechanism A, were calculated from the initial slope following nucleation (table 3.3).

\[
h\beta = \frac{C_s V_m RT}{6F^2} \quad (\theta \to 0) \quad \ldots \ldots \ldots \quad (3.10)
\]
Mechanism B differs from A in that the pseudocapacitance is determined by a quasi-reversible process of formation of an intermediate, rather than by the irreversible process of film spreading. For mechanism B (96),

\[ C_s = \frac{q_m F}{RT} \cdot \Xi (1 - \theta) \] ........................ (3.11)

where \( q_m \) is the charge required to form a monolayer of the intermediate, BiOH, estimated as approximately 0.1 mC cm\(^{-2}\). With this value of \( q_m \) and \( \theta \rightarrow 0 \), the value attained by \( \Xi \) at film nucleation, according to mechanism B, was calculated (table 3.3):

\[ \Xi = \frac{RTC_S}{q_m F} \] ........................ (3.12)

The values of \( h\beta \) indicated by mechanism A seem far too small (factor of 100), given that the height of a monolayer should be about 0.3 nm and \( \beta \) about 0.5. The values of \( \Xi \) given from mechanism B can be interpreted as a critical surface concentration of intermediate for film nucleation. Thus mechanism B is preferred. One might expect \( \Xi \) to vary with the surface preparation and to reflect the presence of adsorbed impurities. No other preparations were studied however.

Mechanism B gives a good qualitative description of the shape of the potential-time curve during the process of spreading of oxide patches to cover the surface (transition period). Thus, substitution of eq. 3.5 into 3.11 gives:

\[ C_s = \left( \frac{q_m FK(OH^-)}{RT} \right) (1 - \theta) \exp \left( \frac{FE}{RT} \right) \] ........................ (3.13)
Table 3.3  Nucleation of a Bi$_2$O$_3$ Anodic Film

0.047 M NaOH; pH 12.6; 25.0°C; Base metal electrodeposited. Galvanostatic step method. Capacitance calculated from double layer charging section (see fig.2.7 and 3.9) used to obtain true current density. Slope \((dE/dt)_{E=E_{AN}}\) immediately upon film nucleation (fig. 3.9) used to calculate the pseudo-capacity, \(C_s\), (eq. 3.3) and hence the parameters \(h\beta\) (eq. 3.10) and \(E\) (eq. 3.12).

<table>
<thead>
<tr>
<th>i (mA cm$^{-2}$)</th>
<th>(\frac{(dE/dt)}{E_{AN}})</th>
<th>(10^4 C_s) (Fcm$^{-2}$)</th>
<th>(h\beta) (pm)</th>
<th>(E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.023</td>
<td>0.255</td>
<td>0.90</td>
<td>2.1</td>
<td>0.023</td>
</tr>
<tr>
<td>0.029</td>
<td>0.30</td>
<td>0.97</td>
<td>2.3</td>
<td>0.025</td>
</tr>
<tr>
<td>0.038</td>
<td>0.52</td>
<td>0.73</td>
<td>1.7</td>
<td>0.019</td>
</tr>
<tr>
<td>0.043</td>
<td>0.40</td>
<td>1.1</td>
<td>2.5</td>
<td>0.029</td>
</tr>
<tr>
<td>0.052</td>
<td>0.92</td>
<td>0.55</td>
<td>1.3</td>
<td>0.014</td>
</tr>
<tr>
<td>0.090</td>
<td>2.18</td>
<td>0.41</td>
<td>1.0</td>
<td>0.011</td>
</tr>
<tr>
<td>0.097</td>
<td>1.99</td>
<td>0.49</td>
<td>1.1</td>
<td>0.013</td>
</tr>
</tbody>
</table>

Mean values: \(h\beta = 1.7\) pm; \(E = 0.019\)
Equation 3.13 states that when $\theta = 0$, as $E$ increases, $C_s$ also increases, i.e. the slope, $dE/dt$, of the potential-time trace decreases (eq. 3.3), as observed (fig. 3.9), however, as the film spreads to cover the surface, the factor $(1 - \theta)$ will eventually cause $C_s$ to decrease, i.e. the slope, $dE/dt$, to increase. Equation 3.13 predicts sigmoid potential-time curve during the transition periods, in qualitative agreement with experiment (figs 3.5, 3.9).

Mechanism A, on the other hand (eq. 3.9), predicts that $C_s$ should decrease uniformly with time. In order to make it conform to experimental data, one must allow extremely rapid thickening of the newly-formed oxide nuclei to occur. In that case, in equations 3.6 and 3.7, $i$ is no longer constant, differing from the total current by the current going into vertical growth of the nuclei. The slope, $dE/dt$, would then become zero when the rates of vertical growth and lateral spreading were equal.

The best description of the experimental potential-time trace comes from mechanism B: spreading of oxide islands over the surface controlled by a reaction on the uncovered area involving an initial very rapid electron transfer followed by some slow step. It is interesting that mechanisms for the anodic dissolution of bismuth in acid solutions involve similar models for the charge transfer reaction (52,88).

3.7 Film Thickening ($t > \tau_2$)

In fig. 3.10, the data for the thickening of the film, for $\tau_2 < t < 4\tau_2$, has been plotted according to the high field growth law, (eq. 2.14, 2.15 and 2.16). At low current
Fig. 3.10  Thickening of anodic film according to high-field growth law. \((\tau_2 < t < 4\tau_2)\)

Current density \(i\) related to rate of potential rise, \(v\). \((i_G\) from equation 3.14)

\(\text{pH 13}; \quad 25^\circ\text{C.}\)

\[
\begin{align*}
\text{i/mA cm}^{-2} \\
\text{slope gives } B &= 2.5 \times 10^{-6} \text{ cm V}^{-1} \\
\text{intercept gives } A &= 2 \times 10^{-5} \text{ A cm}^{-2} \\
(\text{v}/i_G)/\text{V} &\text{ cm}^{-2}
\end{align*}
\]
density, the growth current has been corrected for the effect of dissolution from the film-solution interface (section 3.4):

\[ i_G = i - i_s \]  \hspace{1cm} \text{(3.14)}

In table 3.4, the parameters derived for the thickening of these very thin films are compared with those from earlier work, and with those obtained, in this work, for thicker films (>30 nm) using a transient method (section 3.8). The values of \( \bar{A} \) show a large variation because of the extrapolation needed to obtain it. Of the values of \( B \), those obtained in this work for films of thickness less than 30 nm are the smallest (i.e. apparent field strength greatest). For thicker films, cracking of the layer would cause an increase in the apparent \( B \) value (see section 4.4.1). The possible formation of an almost continuous layer of crystalline material on top of the film in refs 28, 31 and 35 could be the reason for the \( B \) values quoted there being rather lower than those of ref. 25.

The simple theory of high field ion transport (1, 2, 80) interprets

\[ B = \frac{a^* z F}{RT} \]  \hspace{1cm} \text{(3.15)}

where \( a^* \) is the half-width of the barrier to ion movement, and \( z \) is the valency of the moving ion. Substituting \( B = 2 \times 10^{-6} \) cm \( V^{-1} \) and \( z = 3 \) gives \( a^* = 0.17 \) nm. This value is quite reasonable for ion transfer between adjacent sites and is rather smaller than values obtained by the steady state method for high field ion transport through other anodic oxides (2). Important assumptions (2) are that the valency of the moving ion in the transition state is the same as that of a free ion,
Table 3.4  Parameters for the High Field Growth Law 
(298 K)

\[ 2\text{Bi}_{(m)} + 3\text{H}_2\text{O} \rightarrow \text{Bi}_2\text{O}_3(s) + 6\text{H}^+ + 6\text{e}^- \]
\[ i = \bar{A} \exp \left(\frac{BE}{E}\right) \]

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>( A ) ( \text{cm}^{-2} )</th>
<th>( B ) ( \text{cm} \ V^{-1} )</th>
<th>Ref. and Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH, pH 12.9</td>
<td>( 2.0 \times 10^{-5} )</td>
<td>( 2.5 \times 10^{-6} )</td>
<td>This work, galvanostatic (h &lt;30nm)</td>
</tr>
<tr>
<td>NaOH, pH 9.5-13</td>
<td>( 7 \times 10^{-6} )</td>
<td>( 1.4 \times 10^{-6} )</td>
<td>This work, cyclic voltammetry (h &lt;30nm)</td>
</tr>
<tr>
<td>NaOH, pH 12.9</td>
<td></td>
<td>( 1.7 \times 10^{-5} )</td>
<td>This work, transient, (h &gt;30nm)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>The numbers following refer to films with h &gt;30 nm</td>
</tr>
<tr>
<td>NaOH, pH 12.9</td>
<td>( 2 \times 10^{-8} )</td>
<td>( 1.5 \times 10^{-5} )</td>
<td>25</td>
</tr>
<tr>
<td>NaOH, pH 12.9</td>
<td>( 10^{-6} )</td>
<td>( 3 \times 10^{-5} )</td>
<td>26 greatly affected by pitting</td>
</tr>
<tr>
<td>NaOH, pH 12.5</td>
<td>( 1.5 \times 10^{-5} )</td>
<td>( 3.7 \times 10^{-6} )</td>
<td>28 apparent B value at lower</td>
</tr>
<tr>
<td>Na(_2)CO(_3), pH 10.9</td>
<td>( 3.6 \times 10^{-6} )</td>
<td>( 5.2 \times 10^{-6} )</td>
<td>28 current (&lt;0.1mA cm(^{-2})) is</td>
</tr>
<tr>
<td>Na(_2)SO(_4), pH 7.0</td>
<td></td>
<td>( 2.1 \times 10^{-5} )</td>
<td>28 higher, due to breakdown of high field approximation</td>
</tr>
<tr>
<td>((\text{COOH})_2), pH 3</td>
<td>( 4 \times 10^{-6} )</td>
<td>( 5 \times 10^{-6} )</td>
<td>31</td>
</tr>
<tr>
<td>((\text{COOH})_2), pH 1</td>
<td>( 4 \times 10^{-8} )</td>
<td>( 7 \times 10^{-6} )</td>
<td>31 Following induction period</td>
</tr>
<tr>
<td>Na(_2)B(_4)O(_7), pH 9.2</td>
<td></td>
<td>( 7 \times 10^{-6} )</td>
<td>35</td>
</tr>
</tbody>
</table>
and that the field acting upon it is the same as the externally applied electric field.

The significant finding here is that the anomalously large values of $a^*$ (up to 2 nm) indicated by previous work (25-31) are not found if the film growth is studied at a sufficiently short time following its nucleation. The difference has been explained in terms of cracking of the film as it thickens (section 4.4.1).

3.8 Growth of Thicker Films – Transient Method

The $B$ parameter for the growth of a thicker film was obtained by the application of a current step during film growth (fig. 3.11). The potential overshoot is discussed in Chapter 5. Extrapolation of the new steady state potential to the onset of the step, as shown (fig. 3.11) gave the change in potential for a given change in current at constant film thickness, plotted in fig. 3.12. The slope of this plot is, according to the high field growth law,

$$\left( \frac{\partial \log i}{\partial E} \right)_{h} = \frac{B}{2.3h} \quad \ldots \ldots \ldots \ldots \ldots (3.16)$$

The thickness $h$, of the layer, obtained from the total charge passed, increased from 40 to 70 nm during the series of measurements, so eq. 3.16 should not apply exactly. However, the plot of $\Delta \log i$ against $\Delta E$ (fig. 3.12) is indeed linear.

Substitution of the slope of fig. 3.13, 1.5 $V^{-1}$, and an average thickness $h = 50$ nm into eq. 3.17, gives $B = 1.7 \times 10^{-5}$ cm $V^{-1}$, in agreement with the steady state value of
Fig. 3.11 Galvanostatic Step Experiment, during film growth

h = 50 nm; pH 12.9; 25°C.
Fig. 3.12 Change in steady-state potential, $E$, for a step change in current density, $i$. 

\[ \Delta(\log i) \]

\[ \Delta E/V \]
Masing and Young (25). A marked decrease in the slope of the steady state potential-time curve, recorded simultaneously, was indeed noted when h reached 30 nm.

This value of B gives a value of \( a^* = 1.4 \text{ nm} \) (eq. 3.15), much longer than the expected half-jump distance (about 0.2 nm) and greater than values found for the thickening of other anodic films (about 0.5 nm).

3.9 Summary

(a) Spreading of bismuth oxide anodic films to cover the surface proceeds at a rate determined by the magnitude of the area still uncovered, with rate determining step subsequent to the first electron transfer.

(b) Simultaneous thickening of the oxide patches occurs throughout the lateral spreading process.

(c) Film growth immediately following the complete coverage of the surface is described by the simple high field ion transport theory, with a half-jump distance \( a^* = 0.17 \text{ nm} \). Cracking of the film at thicknesses greater than about 30 nm leads to measurement of a half-jump distance which is apparently anomalously large (direct observation of film cracking, and theory for the effect on \( a^* \) is in Chapter 4).
CHAPTER 4
STUDY OF FILM STRUCTURE AND METAL SURFACE
BY MICROSCOPIC AND OTHER METHODS

4.1 Introduction

Microscopy was undertaken to study the morphology of the anodic layer during growth and to confirm the porous nature of the electroreduced surface. Capacitance and dissolution rate measurements also aimed at studying the film structure.

Three stages of growth were observed: the formation of a featureless, continuous layer, cracking of this to form a porous but adherent over-layer and finally localized film breakdown with pitting of the surface.

A study of the etching of the surface with various reagents failed to identify one which left it completely free of oxidation product. A classification of the surface into two different types of area, each polycrystalline, was made, however. The ratio of the two areas varied widely from one sample to another. The appearance of the electroreduced surface at low magnification gave a similar classification.

The results correlated with conclusions from voltammetric and galvanostatic experiments concerning the nature of the film and the properties of the metal surface.

4.2 Experimental

Scanning electron microscopy, with no additional surface preparation, was performed (JEOL, type JSMU3) with
the sample oriented at 45° to the incident electron beam. The height of surface features could thus be estimated as approximately equal to the length of the shadow they cast.

A projection microscope ("Projectina") with vertical illumination top-lighting was used for optical microscopy (86). An effective alternative to the camera attachment supplied was a standard accessory by which the microscope eyepiece could be replaced by the back of an ordinary 35 mm single lens reflex camera, the image formed by the objective lens being focused directly onto the film.

Table 4.1 describes the various surface treatments examined.

4.3 Results and Discussion

4.3.1 Anodized surface (figs 4.1, 4.2, 4.3)

Fig. 4.1 shows the formation of a very thin continuous layer, visible as a yellowish colour over the surface. The surface features seen reflect the structure of the underlying metal; thus the height of the ridges is 50 - 100 nm and the apparent height of the domains, from the shadows at their edges, appears to be about 200 nm. Both numbers are an order of magnitude greater than the film thickness. The domains appear to be divided by fairly deep surface cracks, but it proved very difficult to confirm the existence of these domains by etching (section 4.3.2).
Fig. 4.1  Anodically oxidized surface,
          h ≈ 20 nm
          scanning e-m

Fig. 4.2  Anodically oxidized surface,
          h ≈ 200 nm
          scanning e-m
fig. 4.1(a)

fig. 4.1(b)

fig. 4.2(a)

fig. 4.2(b)
In the next stage of growth (fig. 4.2), optical microscopy showed the domains as different colours, indicating that each had grown to a different thickness. Scanning e-m (fig. 4.2) showed localized cracking of the film, probably caused by local heating and stress, and prelude to the formation of a porous overlayer (87).

Following continued growth after localized film breakdown, the surface showed, under the microscope, a uniform colour.

Tiny lumps of oxide, precipitated at the mouth of pits were seen (fig. 4.3). These became visible to the naked eye after the passage of a much larger anodic charge (fig. 3.2). The oxide layer had a three-fold structure (fig. 4.3). The uppermost part was a system of flat platelets, interlocking to some extent and covering about 30% of the surface. Below this, there was a layer about 500 nm thick, in the form of elongated ridges, covering everywhere except along the top edge of a step in the metal, about 95% of the surface. The bottommost layer, probably also about 500 nm thick, appeared to be continuous and featureless.

Fig. 4.4 shows a model consistent with these observations. A continuous barrier layer is overlain by a cracked and porous layer. On top are plaques of precipitated material formed by localized film breakdown and subsequent healing, and lumps of material formed by active dissolution from pits.
Fig. 4.3

(a) anodically oxidized surface following film breakdown, 
$h \approx 1000$ nm. 
scanning e-m.

(b) voltage-time trace for the production of the surface of (a).
Fig. 4.3(a) 20μm

Fig. 4.3(b)

\[ i = 7 \text{ mA cm}^{-2} \]
Fig. 4.4  Model for Bismuth Anodic Oxide Film
Table 4.1  

**Surface Treatments**

Anodically oxidized (section 4.3.1) at current density $i$ to overvoltage $\eta$, in NaOH solution; pH = 12.9. Charge passed = $Q_A$, approximate layer thickness (eq. 2.9) = $h$.

<table>
<thead>
<tr>
<th>$i$/mA</th>
<th>$\eta$/V</th>
<th>$Q_A$/mC cm$^{-2}$</th>
<th>$h$/nm</th>
<th>fig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>25</td>
<td>20</td>
<td>4.1</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>200</td>
<td>200</td>
<td>4.2</td>
</tr>
<tr>
<td>7</td>
<td>14</td>
<td>1000*</td>
<td>1000*</td>
<td>4.3</td>
</tr>
</tbody>
</table>

* film breakdown occurred;

electroreduced (section 4.3.2) Film of thickness originally $h$ reduced at current $i'$ per unit projected area.

<table>
<thead>
<tr>
<th>$h$</th>
<th>$i'$</th>
<th>roughness factor (sec 2.4)</th>
<th>final</th>
<th>fig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>350 ± 50 nm</td>
<td>2.5mA cm$^{-2}$</td>
<td>1.8</td>
<td>7.6</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Etched (section 4.3.3)

<table>
<thead>
<tr>
<th>reagent</th>
<th>surface appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>conc. HNO$_3$</td>
<td>partly covered with a red-brown film; fig. 4.6</td>
</tr>
<tr>
<td>2 M aq HNO$_3$</td>
<td>as above. Uncoated areas much more facetted, however, after prolonged etching. Fig. 4.7</td>
</tr>
<tr>
<td>2 M aq HClO$_4$ + 0.02 M H$_2$O$_3$</td>
<td>granular grey-black coating over entire surface. However, boundaries outlining tiny irregular domains could be seen. Fig. 4.8.</td>
</tr>
<tr>
<td>aq I$_2$/KI/HCl solutions containing: ethanol, 100 vol; conc HNO$_3$, 2 or 5 vol; conc HCl; up to 30 vol</td>
<td></td>
</tr>
</tbody>
</table>
4.3.2 Electroreduced Surface (fig. 4.5)

The appearance of the surface at low magnification (fig. 4.5) allowed a classification into two different areas - "rough" grains and "smooth" grains. The rough grains covered about 30% of the total surface. At high magnification (fig. 4.6), both looked the same, and the porous nature of the surface was plain.

The pattern of parallel ridges on the rough grains had a different direction for each grain, and was also visible in scratches on the smooth grains. The rough areas probably resulted from the reduction of a cracked overlayer as, initially, this formed only over some of the surface grains of the metal. A similar pattern has been observed in the electron conductivity of anodic Ta$_2$O$_5$ (33) and is said to reflect cracking of the film (72).

4.3.3 Etched Surfaces (figs 4.6, 4.7 and 4.8)

A brief summary of the reagents and results is given in table 4.1. The brown coating formed over part of the surface upon etching with acidic aqueous solutions of oxidizing agents (figs 4.6, 4.7) was probably a non-stoichiometric bismuth oxide. It was visible on the surface during the etching as an area of different reflectivity. Gas bubbles were not evolved from it and it could not be removed by long standing in conc HClO$_4$ or HCl or by boiling in conc HCl. Boiling in 3M HClO$_4$ turned the surface first red and then black. The transformed coating could then be rubbed off.
Fig. 4.5  
(a) Electroreduced surface scanning e-m.  
(b) voltage-time trace for reduction.
The location on the surface of any given sample covered by the brown oxide was not changed by changing the composition or stirring of the etchant, but the ratio of coated to uncoated area varied widely between samples. Thus, the surface could be classified into two areas of different properties according as to whether or not a coating formed during etching.

Etching of the electroreduced surface (4.3.2) with these reagents indicated a correspondence, on the basis of number and general shape, between the "rough" areas and those which were subsequently left uncoated by the etchant (fig. 4.7).

The non-aqueous etches (fig. 4.8) left the entire surface covered with oxidation product, but domains of similar size to those in figs 4.1 and 4.2 were visible in the surface after brief etching (less than 1 minute). The results with these, and with the dilute aqueous acid reagents (fig. 4.7) emphasized that each of the large grains visible in the surface of the bismuth metal (fig. 2.12) was in fact poly-crystalline.

The classification of the surface into two areas of different electrochemical potential seems indicated. The reason for this is uncertain. It may reflect the density of surface defects. A similar classification has been made according to the anodic nucleation potential (section 2.12). No close correlation between the relative areas of the two classes of surface above and the relative charge in the two
Surface of figs 4.1 - 3 etched with conc HNO₃. Areas covered with brown coating look smooth under the scanning e-m at low magnification. At high magnification, both areas look the same.
Fig. 4.7  
(a) Surface of fig. 4.5 etched with HClO$_4$/H$_2$O$_2$.

(b) Surface of fig. 4.5 etched with 2M HNO$_3$ (uncoated grain) optical microscopy.
Fig. 4.8 Surface of figs 4.1 - 3 etched with conc HNO₃ (5 volumes) with conc HCl, (30 volumes) in ethanol (100 volumes) optical microscopy.

100μm
anodic peaks (section 2.9) could be established, however.

4.4 Correspondence to Electrical Measurements

4.4.1 Film Thickening

Although no difference has been found in the kinetics of film growth on different crystal faces of single crystal specimens (25), the film forms to different thicknesses on the different faces of polycrystalline specimens (section 4.3.1; ref. 25). The cracking of some faces of a polycrystalline surface before others (fig. 4.2) would give such an effect.

The results presented in section 2.14 and 3.7 refer to thickening of the film before the onset of cracking, at \( h \sim 30 \text{ nm} \). The results of earlier work (25) and of section 3.8 refer to the thickening of a barrier layer overlain by a cracked and porous layer (fig. 4.4). In this case, suppose that \( h_1, \Delta E_1, h_2, \Delta E_2 \) are the thicknesses and potential change in the continuous and cracked layers respectively:

\[
\text{Thickness measurement by the optical method or by measurement of charge would give the sum, } h_1 + h_2. \text{ Thus, the apparent electric field is } E_{\text{apparent}} = \frac{\Delta E_1 + \Delta E_2}{h_1 + h_2} \quad \ldots (4.1)
\]

The system is in a kinetic steady state, so that the current density is

\[
i = \bar{A} \exp \left( B \frac{\Delta E_1}{h_1} \right) \quad \ldots (4.2)
\]
where \( \bar{A} \) and \( B \) are the parameters (sections 2.14 and 3.7) for the thickening of the barrier layer.

A reasonable approximation for eq. (4.1), in terms of the 2-layer model, is \( h_2 \gg h_1 \) but \( \Delta E_2 \ll \Delta E_1 \). This model states that the thickness determination gives \( h_1 + h_2 \) but the potential measurement gives \( \Delta E_1 \) only. That is:

\[
\bar{E}_{\text{apparent}} = \frac{\Delta E_1}{h_2}
\]

(4.3)

and the current density, from (4.2) is

\[
i = A \exp (B_{\text{apparent}} \cdot \bar{E}_{\text{apparent}})
\]

(4.4)

where \( B_{\text{apparent}} = (h_2/h_1) \cdot B \)

(4.5)

Eq. 4.5 shows the relationship between the results of sections 2.14 and 3.7 (measurement of \( B \) for continuous layer) and those of ref. 25 and section 3.8 (measurement of \( B \) for 2-layer system). The apparent electric field for thickening of a 2-layer system would be much less than that appropriate to thickening of a continuous barrier layer. It may also decrease slowly with increasing total thickness. Substitution of experimental values gives \( h_2/h_1 \sim 10 \), which does seem rather large. The model is undoubtedly over-simplified.

4.4.2 Cathodic reduction

The potential-time trace (fig. 4.5) for the production of the electroreduced surface studied here showed three sections: two arrests and a gradual drift to the hydrogen evolution potential. The deposited material could also be divided into three classes: that on the "smooth" grains,
that on the "rough" grains, and some loose material, rubbed off, formed from reduction of the product precipitated at pits. It seems reasonable to identify these three classes with the three regions of the E-t curve. The reduction overvoltage would be different for each class because of the variation of electronic resistance with morphology (section 2.13).

4.5 Morphology by Capacitance Measurement

Cracking of the anodic film would give a value for the apparent dielectric constant of the film much greater than that of the bulk material, as is observed in the case for thick films on bismuth (table 1.1).

Capacitance measurements were made, at 1 kHz using an A.C. bridge (Radiometer CMBlc), on the plane microelectrode (section 2.2.2) with a film formed by cyclic voltammetry. The results (fig. 4.9) indicated a dielectric constant of 100,

\[ k = C V_m Q_A/6F \varepsilon_0 \]

(4.6)

where \( k \) is the dielectric constant, and \( \varepsilon_0 \) the permittivity of free space, \( 8.85 \times 10^{-14} \) F cm\(^{-1}\).

The dielectric constant of bulk \( \alpha-\text{Bi}_2\text{O}_3 \) is 18.2 (table 1.1), so the result indicates a cracked and porous film on the micro-electrode, even at very low thicknesses. This had been anticipated by cyclic voltammetry (section 2.8).

Capacitance measurements, by the triangular wave potentiostatic method (section 2.2.6), on films formed by cyclic voltammetry in borate buffer or borate/acetate buffer pH 5-9, showed a dielectric constant of 50. Cracking of the
Fig. 4.9 Capacitance of Oxide Film formed on plane micro-electrode

pH = 13; slope gives $\mathcal{E} = 90 \times 10^{-11}$ F m$^{-1}$

ie $\kappa = 100$ (eq. 4.6)
thin films, or penetration of protons into the anodic film (102), at low pH, had been deduced previously (section 2.14). The same result was obtained for a thick (300 nm) film formed at constant current in NaOH, pH 13. However, no capacitance measurements were made on the thin, non-porous barrier layers formed in NaOH solution (section 2.14; 3.6). They would be expected to show a dielectric constant similar to that of the bulk material.

4.6 Morphology by Measurement of Dissolution Rate

The dissolution rate of anodic Ta$_2$O$_5$ has been used extensively to study the film composition (43, 100). Such measurements are potentially useful for the study of the defect structure of films (101).

The dissolution rate of anodic bismuth oxide films grown on the plane microelectrode (section 2.2.2), was obtained in 0.01M HClO$_4$/1.0M NaClO$_4$ solution by the measurement of capacitance. This was done either with the A.C. bridge or with the automatic system shown in fig. 4.11. Results (figs 4.10 and 4.11) showed a rapid rate of dissolution for about 0.9 of the total film thickness, and a markedly slower rate for the remaining part. This could be interpreted as the rapid dissolution of a thick porous layer followed by the slower dissolution of a continuous barrier layer (i.e. an experimental determination of the ratio $h_2/h_1$ in section 4.4.1). The dissolution rate of films formed on a zone-refined electrode (section 2.2.2) in the same solution
(at t = 0), \((1/C) - (1/C_{dl}) = 300 \ \mu F^{-1}\)
Fig. 4.11 Current Pulse Measurement of Dissolution Rate of Film in Acid

A time switch, closed for 0.03s every 1.00s, applies a current of 1mA cm$^2$ to the electrode. A charging current flows which divides between the recorder and bismuth electrode. As the capacitance of the Bi increases with the film dissolving, the current pulse flowing into the recorder input declines.

![Electrical circuit diagram with labels: P/Stat, W.E, R.E, A.E, Bi, Pt, S.E.3006 oscillograph and pre-amplifier, time-switch.]

Typical result. Original film thickness about 250 nm, dissolving in 0.01M HClO$_4$/1.0M NaClO$_4$. 
was much slower. This could be interpreted as less cracking of the film, a result also indicated by cyclic voltammetry (sections 2.8 and 2.14).

4.7 Summary
(a) The formation of a 2-layer film structure following cracking of an initial barrier layer has been demonstrated by microscopic observations.
(b) The porous nature of the electroreduced surface has been confirmed.
(c) A tentative classification of the surface into two areas of different electrochemical potential has been made.
(d) The relationship of the film structure to the results of electrical measurements has been emphasized. Apparently disparate results for the growth parameters have been reconciled.
(e) The study of film morphology using capacitance and dissolution rate was attempted. Preliminary results were in agreement with (a) above.
CHAPTER 5
TRANSIENT CONDUCTIVITY OF THE
ANODIC OXIDE FILM

5.1 Introduction

The problem concerns the transient conductivity of the anodic film in response to a change in the applied electric field. If a current step is applied during film growth, then a transient potential peak, relaxing to the new steady state, is observed (figs 3.11 and 5.1; ref. 5, 35, 114, 115).

A particular case that is of special interest (9) is the transient current which follows the re-application of the electric field following a period at zero net field. A variation of this involves removing the electrode from the solution and heating it before re-applying the field. In this work the converse method-control of the current and measurement of the potential-was used. Re-application of the current following open-circuit standing or heating of the electrode showed a transition period, of fairly low, constant potential followed by a rapid rise to the value attained before the current interruption.

Interpretation of the transients is important to models for the high field ion conduction process (5-9). The Cabrera-Mott-Verwey model does not give qualitatively the form of the transients observed. An assessment of other models (9) is included in this chapter, and another possible mechanism for the transients, based on an electron space charge in the oxide film (38, 116) described. Emphasis is placed on obtaining a satisfactory qualitative description
of the observed phenomena.

5.2 Experimental

Materials and methods were those described in sections 2.2 and 3.2. Electrodes used were of zone-refined metal or were short lengths of a rod cast in glass and mounted in a screw-in holder (fig. 2.3), as for microscopy (section 2.2.2).

All experiments used NaOH solution, pre-electrolysed and carbonate-free, pH 12.9, as the electrolyte. Oscilloscope traces were photographed (Tektronix C27 Polaroid Camera) and enlarged for measurement. The temperature was 25°C.

5.3 Results

5.3.1 Potential Overshoot Following Current Step During Film Growth

When a current step was applied during anodic bismuth oxide growth a potential overshoot was observed for an upward current step and an undershoot for a downward step, followed by a relaxation to the steady state potential (fig. 5.1). The ratio \( P = (\text{final current})/(\text{initial current}) \) was varied over a range from 0.1 to 5 (table 5.1), values of \( P \) less than one denoting a downward step.

The charge passed to the transient maximum \( Q_p \), was independent of the initial and final currents of the step (table 5.1); \( Q_p = 4 \pm 1 \, \mu \text{C cm}^{-2} \), similar to the values observed for anodic Ta\(_2\)O\(_5\) (5), Al\(_2\)O\(_3\) (114) and Fe\(_2\)O\(_3\) (115).
Fig. 5.1 Potential overshoot at a current step during film growth

(a) experimental curve, $h = 50$ nm; definition of excess potential change. pH 12.9; 25°C.

(b) schematic decomposition into a rising and a falling part (enlargement of the step region).
The excess field, $\delta \bar{E}_p$, is defined as the difference between the field at the transient maximum, $\bar{E}_p$ and the steady state field at the same current density, $\bar{E}_\infty$

$$\delta \bar{E}_p = \bar{E}_p - \bar{E}_\infty$$ .................. (5.1)

$$= \delta E_p / h$$ .................. (5.2)

where the excess potential, $\delta E_p$, is defined in fig. 5.1

Equation 5.2 is a statement of the assumption (5-9) that the interfacial potentials remain unchanged during the transient, being a function of the applied current density only, so that the transient is a variation of the potential across the film; $h$ is the film thickness, considered constant over the short time interval of the transient.

Following Dewald (5), $\delta E_p$ was studied as a function of the initial current density and of the ratio $P$ (table 5.1). It was not significantly affected by the value of the initial current density for any given value of $P$ (table 5.1, fig. 5.2) and was directly proportional to $\log P$, regardless of the actual values of the initial and final currents (fig. 5.2).

$$\delta E_p = 0.12 \log P \ V$$ .................. (5.3)

These relationships have been observed previously in the case of anodic oxide films on Ta (5), Al (114) and Fe (115).

Equation 5.3 can be compared with the data of Masing and Young (25) for anodic $\text{Bi}_2\text{O}_3$, who, by a potentiostatic technique, determined

$$\partial (\bar{E}_p) / \partial (\ln P) \sim 2 \times 10^5 \ V \ cm^{-1}$$
Fig. 5.2 Variation of Potential Overshoot, $\Delta E_p$ with Current ratio, $P$,

pH 13; 25°C; 50 nm thick oxide film
Table 5.1 Parameters describing Potential Transients Following Current Step

\[ P = \frac{i_f}{i_i} = \text{(final current density)}/\text{(initial current density)} \]

\( Q_p \) - charge to maximum

\( \delta E_p \) - difference between maximum and new steady state potential (fig. 5.1). Negative value denotes an undershoot.

\( k_1 \) - rate constant for decay from maximum

\( k_2 \) - rate constant for rise to maximum

film thickness - 50 nm (see section 3.8)

electrolyte - NaOH, pH 12.9

<table>
<thead>
<tr>
<th>( i_i ) mA cm(^{-2} )</th>
<th>( i_f ) mA cm(^{-2} )</th>
<th>( P )</th>
<th>( Q_p ) ( \mu \text{C cm}^{-2} )</th>
<th>( \delta E_p ) mV</th>
<th>( k_1 ) s(^{-1} )</th>
<th>( k_2 ) s(^{-1} )</th>
<th>( k_2/k_1 )</th>
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<td>4.9</td>
<td>28±5</td>
<td>12</td>
<td>85</td>
<td>7.1</td>
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<td>85±7</td>
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<tr>
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<td>3.6</td>
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<tr>
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<td>2.0</td>
<td>3.5</td>
<td>35</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.23</td>
<td>0.45</td>
<td>2.0</td>
<td>3.3</td>
<td>45</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
where $\Delta E_p$ is the difference in field between the initial steady state and the transient maximum.

By combining eq. 5.1, 5.2, 5.3 and 3.16 and using $h = 50$ nm, the result of this work (see also section 3.8) can be given as $\partial (\Delta E_p)/\partial (\ln P) = 0.68 \times 10^5$ V cm$^{-1}$ which is different from the previous result (25), due to the difference of technique (117). In both Masing and Young's work and in section 3.8 here, the assumption that the interfacial potentials change little following a current step has been made.

A satisfactory empirical description of the shape of the transient was obtained by treating the observed curve as the sum of a rising and a falling exponential (fig. 5.1 and 5.3). Thus, using the notation of fig. 5.1,

$$\Delta E = \Delta E_1 + \Delta E_2 \quad \ldots \ldots \quad (5.4)$$

so

$$\Delta E - \Delta E_\infty = (\Delta E_1 + \Delta E_2) - (\Delta E_{1,\infty} + \Delta E_{2,\infty}) \quad \ldots \ldots \quad (5.5)$$

After the peak has been passed, $\Delta E_2 \approx \Delta E_{2,\infty}$ because the rate of the rise was much greater than the decay rate as seen by inspection of the curves, i.e. the shape of the curve following the peak gives the slow decay process alone. The plots in fig. 5.3 illustrate the exponential decay law

$$\Delta E - \Delta E_\infty = \Delta E_{1} - \Delta E_{1,\infty} = (\Delta E_{1,0} - \Delta E_{1,\infty}) \exp (-k_1 t) \quad \ldots \ldots \quad (5.6)$$

The parameter $\Delta E_\infty$ was determined graphically. Values of the rate constant $k_1$ are given in table 5.1.
A single exponential decay has been observed for the transients in the case of passive iron (115). In the case of anodic Al₂O₃ (114) and Ta₂O₅ (5, 114), the transient was the sum of two exponentials. This would account for the qualitative difference between transients in anodic Bi₂O₃ and Ta₂O₅ observed by Masing and Young (25, fig.1.3).

The equation for the rising curve was obtained by combining the experimental data with the value of $\Delta E_1$ given by eq. 5.6, extrapolated to short times (before the peak was reached). From eq. 5.5,

$$
\Delta E_2 - \Delta E_{2,\infty} = (\Delta E - \Delta E_{\infty}) - (\Delta E_1 - \Delta E_{1,\infty}) \quad \ldots \ldots \ldots \quad (5.7)
$$

where the first term, $(\Delta E - \Delta E_{\infty})$, was determined from the experimental curve, and the second $(\Delta E_1 - \Delta E_{1,\infty})$, by extrapolation of the decay curve. An exponential equation for the rising function was also observed, fig. 5.3:

$$
\Delta E_{2,\infty} - \Delta E_2 = (\Delta E_{2,\infty} - \Delta E_{2,0}) \exp (-k_2 t) \quad \ldots \ldots \ldots \quad (5.8)
$$

Values of $k_2$ are given in table 5.1. An initial very rapid change (within 5 ms), where eq. 5.8 did not hold, was observed (fig. 5.3).

The data in table 5.1 show that the current density prior to the step was not a significant variable. The rate constants depended only on the final current, a correlation between $i_f$ and log k (k stands for either $k_1$ or $k_2$) being observed (fig. 5.4). An interesting point here is that the ratio $k_2/k_1$ (table 5.1) was independent of the current; i.e. (fig. 5.4)
Fig. 5.3 Expression of the potential transient as the sum of two exponentials

(see equations 5.4 to 5.8)

\[ i_f = 0.45 \text{ mA cm}^{-2}; \quad P = 0.25 \]

pH 13; 25°C; 50 nm thick oxide film
Fig. 5.4 Rate Constants for the decay, $k_1$, and rise, $k_2$, of the potential transient, against final current density, $i_f$ (galvanostatic step experiment).

$pH$ 13; $25^\circ C$; 50 nm thick oxide film
\[ \frac{\partial \log k_1}{\partial i_f} = \frac{\partial \log k_2}{\partial i_f} = (4.9 \pm 0.3) \times 10^3 \text{ A}^{-1} \text{ cm}^2 \]

implying some common factor for the two processes.

In contrast, a linear correlation between \( i_f \) and \( k_1 \) has been observed in other cases - \( \text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3 \) and \( \text{Ta}_2\text{O}_5 \) (5, 114, 115). However, data taken over a much wider current range in the case of \( \text{Ta} \) (118) can be interpreted as showing a breakdown in this linear relation. In this work, a linear relation between \( i_f \) and \( k \) described the data only for \( i_f < 0.2 \text{ mA cm}^{-2} \).

5.3.2 Galvanostatic Re-Charging Following a Period in the Solution at Open Circuit

A film was grown to a known thickness, the current switched off for some time and then re-applied. The potential transient resulting was recorded. Some typical results are shown in figs 5.5, 5.6 and 5.7.

The observed transient differed from the overshoot type previously discussed. After a sufficient interval at zero current, a transition period was observed during which the potential remained low and constant. The charge in the transition period varied with the time of open-circuit standing in the solution (fig. 5.6), increasing to a maximum value between 10 and 30 mC cm\(^{-2}\) after about 1000 s. Following this, the potential rose fairly rapidly to the value it had before the current was interrupted (fig. 5.5). The process by which the potential attains its original value will be referred to as "re-charging".

If the current was interrupted when the electrode potential reached its steady, breakdown value (section 3.3),
Fig. 5.5 Interruption of current during film growth

pH 13; 25°C; i = 1mA cm⁻²; micro-electrode
Fig. 5.6  Galvanostatic recharging

(a) original growth curve, \( i = 10 \text{ mA cm}^{-2} \), pH 13, 25°C;
(b) recharging transient, for various times at open circuit;
(c) continued thickening following the recharging process in (b).
then, upon re-application of the current, breakdown did not again occur until some higher potential, dependent on the time interval of current interruption, was reached (fig. 5.6). Clearly, some structural change, possibly the healing of pits and cracks by a dissolution-precipitation process, occurs in the film on standing at open circuit.

The transient was qualitatively different from that expected following observations with Ta or Al anodes (9, 119). The current variation for these systems on re-application of a constant potential following an open circuit period is shown in fig. 5.8. The corresponding galvanostatic experiment would show an overshoot type transient sketched on fig. 5.8. In fact, in the case of anodic Bi$_2$O$_3$, only the first part of the above transient was seen. No overshoot was observed, even at very short times upon re-application of a current following a period at open circuit (fig. 5.6 and 5.7). This disappearance of the overshoot has also been observed in the case of passive iron (115).

5.3.3 Application of Current Steps During Galvanostatic Recharging

The relationship between the galvanostatic recharging process (section 5.3.2) and the potential overshoot following a current step (section 5.3.1) was explored. The program chosen, applied at intervals during the recharging is shown below

![Diagram of current step](image)

(i mA cm$^{-2}$

$\Delta t$ (varied in the range 30 to 300 ms)
Fig. 5.7 Potential variation immediately on re-applica-
tion of current
\[ i \sim 2 \text{mA cm}^{-2}; \ h \sim 150 \text{ nm}; \ \text{pH} \ 12.9; \ 25^\circ \text{C} \]

Fig. 5.8 Expected form of galvanostatic recharging
transient following the experimental pot-
tentiostatic transient for Ta_{2}O_{5} (6,9,119)
Of interest was the potential variation following the increase of current to 4 mA cm\(^{-2}\). Important variables were the time interval \(\Delta t\), the length of time, \(t_o\), the electrode had spent at zero current before recharging, and the particular time during the recharging process that the pulse was applied (fig. 5.9).

A typical result is shown in fig. 5.9. A potential overshoot only developed as the recharging process proceeded. The two phenomena were apparently intimately connected. If \(\Delta t\) was made sufficiently long, no overshoot was observed at any stage during re-charging. The necessary value of \(\Delta t\) increased as \(t_o\) decreased.

A similar program to that above has been used during galvanostatic film growth on passive iron to show the disappearance of an overshoot as \(\Delta t\) increased. A relationship to the decay of electrode potential during \(\Delta t\) was demonstrated.

5.3.4 Effect of Heating of the Anodic Film

Bismuth electrodes carrying an anodic oxide film (-200nm) were heated in air at 420K for various periods. The subsequent recharging process was studied.

The result (fig. 5.10) was similar to that obtained by leaving the electrode in the solution at open-circuit for a long time. A well-defined transition period, of constant potential, requiring about 20 mC cm\(^{-2}\) - about 10% of the total charge required to reduce the film subsequently was observed. Five minutes in the oven was sufficient to obtain the maximum effect.
Fig. 5.9 Relationship between recharging process and potential overshoot following a current step (pH 13; 25°C)

Top transient, bottom recharging curve, $i = 2\text{mA cm}^{-2}$ current pulse sequence (section 5.3.3) $2+0+4+2\text{mA cm}^{-2}$ applied at 1 to 4.
Fig. 5.10 Recharging of heated film
pH 13; \( i = 2.2 \text{ mA cm}^{-2} \); film previously heated in air at 150°C for 15 min.
In one case after recharging, the B parameter (sections 2.14 and 3.7) for high field growth was determined by applying a succession of current steps, as in section 3.8. The capacitance was also measured before and after recharging, in order to obtain the apparent dielectric constant, \( k \) (A.C. bridge at 1 kHz; section 4.5). The film thickness was determined from the charge required subsequently to reduce the film. Hence:

\[
B = 2 \times 10^{-6} \text{ V}^{-1} \text{ cm}
\]

\[
k = 75 \pm 20 \text{ (uncertainty in electrode area)}
\]

The value of B is comparable with that obtained for very thin films, before the onset of cracking (table 3.4; sections 3.7 and 4.4). Presumably the heat treatment sealed the film. A somewhat similar procedure (a period in boiling water) is used to seal the pores in anodic \( \text{Al}_2\text{O}_3 \) (2).

Given the value of B and the interpretation above, the value of \( k \) is much larger than expected (value 18 as for bulk \( \text{Bi}_2\text{O}_3 \) - section 4.5). One possible reason for this (section 5.5) is the existence of an electronic space charge (non-stoichiometry) in the film.

5.4 Models for the Transient Behaviour of Anodic Films

Bartlett et al (115, 120, 121) have described the derivation of two empirical parameters which reflect the electric field and density of charge carriers in an anodic film during a transient. They have shown that these change during a transient and also undergo slow variations dependent on the history of the sample. De Smet and Hopper (35) have demonstrated the application of Bartlett's empirical equation to the case of anodic \( \text{Bi}_2\text{O}_3 \), and discussed qualitat-
ively its relation to the potential overshoot described in section 5.3.1.

Models for the transients can be divided into two classes – those that focus on variation in the density of charge carriers and those that focus on variation in the actual electric field causing ionic migration.

The Cabrera-Mott-Verwey model (80, 106), generalized by Dewald (4), is not consistent with any of the transient measurements, (2, 5, 35). In it, the anodic film is regarded simply as a medium through which ions move from the metal-oxide interface to the oxide-electrolyte interface, and, in consideration of space-charge effects, is assumed to be stoichiometric and therefore always electrically neutral. In the galvanostatic step experiment, a smoothly increasing potential variation – i.e. no overshoot – is predicted (2, 5). The failure of this model to account for the overshoot type transient observed has led to a closer examination of the relationship between the anodic oxide structure and the conduction process.

5.4.1 **High Field Frenkel Defect Model** (Dewald, ref. 5)

This model states that, under the influence of the applied field, ions leave their lattice sites and move through the oxide. This field-assisted defect generation can be summarized as:

\[ \Delta + \frac{k_1}{(Bi \text{ lattice site})} \xrightarrow{k_2} \frac{1}{(Bi \text{ lattice site})} \xrightarrow{\frac{k_3}{(Bi \text{ interstitial cation})}} \xrightarrow{\frac{k_4}{(Bi \text{ interstitial cation})}} \xrightarrow{\frac{k_5}{(Bi \text{ vacancy})}} \]

\[ \text{interstitial cation on lattice site} \text{ Bi}^{3+} \text{ vacancy} \]

(5.9)
(The . ' symbol'ism represents the charge on a species in
the lattice; . = one positive and ' = one negative).

The interstitial cations are mobile and in the steady state, the rates of generation and capture are equal. Following a current step, however, it takes some time for the mobile ion concentration to adjust to its new steady-state value. In a galvanostatic step experiment a potential overshoot arises because \( k_2 >> k_1 \) in eq. 5.9. These are identified with the rate constants for the rise and decay of the transient found in section 5.3.1, and the theory does give them as approximately proportional to the applied current density.

In a first-order approximation, the linear relation of fig. 5.2 is predicted, and the slope of that plot is interpreted by Dewald's theory (5) as:

\[
\frac{\theta(\delta E)}{\partial (\log P)} = \frac{2.3}{a^*} \frac{RT}{zF} \left( \frac{\lambda^* - a^*}{\lambda^* + a^*} \right) \quad \ldots \ldots \ldots \ldots (5.10)
\]

where \( a^* \) is the activation distance for ion migration through the film and \( \lambda^* \) is the activation distance for production of an ion-vacancy pair; \( z \) is the charge on the moving ion.

Also, in the steady-state growth law,

\[
i = \bar{A} \exp (B E),
\]

the parameter \( B \) is interpreted as

\[
B = (\lambda^* + a^*) \frac{ZF}{2RT} \quad \ldots \ldots \ldots \ldots (5.11)
\]

Using the experimental data,
\[ \frac{\partial (\delta E_p)}{\partial (\log P)} = 120 \text{ mV (fig. 5.2)}, \ B = 1.7 \times 10^{-5} \text{ cm V}^{-1} \text{ (section 3.8)}, \ h = 50 \text{ nm and } z = 3, \text{ substitution in eqs. 5.2, 5.10 and 5.11 gives } \lambda^* = 1.3 \text{ nm and } a^* = 1.1 \text{ nm. These seem anomalously large.} \]

However, the model can give a reasonable description of the magnitude of the overshoot observed if one attributes the effect to a barrier layer comprising only a fraction of the total film thickness, as in section 4.4.1. Thus, setting \( h = 5 \text{ nm (section 4.4.1) and } B = 2.5 \times 10^{-6} \text{ cm V}^{-1} \text{ (section 3.7) gives } \lambda^* = 0.15 \text{ nm and } a^* = 0.12 \text{ nm. These are quite reasonable values.} \]

The high field Frenkel defect model has been criticized as not correctly describing the effects of the history of the film - standing and heating (9, 119). The disappearance of the potential overshoot following a period at zero current might be interpreted as due to a decrease in the number of sites available for forming ion-vacancy pairs. However, the form of the recharging curve expected is an initial high potential with a steady decline to the final value. This was not observed. Hence the model fails to explain these observations.

5.4.2 **Channel Model** (Young; ref. 2, 7, 9,)

In some ways, this is a modification of the high field Frenkel defect model. It can be represented schematically as:
It bears an obvious relationship to the development of pits through the film. It has been applied to the overshoot and recharging process in an empirical way. It does not describe the form of the recharging curve observed with Bi, since it predicts a regular decrease of $E$ with time.

5.4.3 Dielectric Polarisation Model (Dignam, ref.6,114,118,119)

This model proposes a variation of the electric field during the transient, in contrast to the above models. It postulates a non-homogeneous film, and two variants, corresponding to control of the current by transport through the bulk of the film, or at the interfaces, have been given. They can be represented schematically as:
In the bulk-control case, the rate is controlled by the field in the "voids", and in the interface-control case by the field in the hydrous layer. This field is greater than the actual field in the oxide (measured by the measured potential) by an amount depending on the surface charge density (the polarization, $P$) of the oxide (122):

$$E_{\text{effective}} = E + \frac{P}{\varepsilon_o} \quad \quad \quad (5.12)$$

Dignam postulates that part of the polarization of the oxide by the applied field is thermally activated and therefore takes some time. He also postulates a special additional polarization dependent on ion transport. Ion migration through the oxide is supposed to create structural defects which result in an additional surface charge on the oxide.

Empirical equations are used to describe the polarization components. The molecular basis for the postulates
above is vague and a large number of adjustable parameters are involved. A good description of the transient phenomena (in the cases of Al and Ta) has been obtained.

In applying the theory to the Bi case described here, one must postulate that the ion-transport coupled polarization component disappears on standing or heating, in order to account for the lack of an overshoot-type transient in galvanostatic re-charging, and that this polarization component gradually re-appears during the recharging process. The molecular basis for these new postulates is by no means clear.

5.5 A New Model

The models above describe the film as a stoichio-
metric oxide and attribute the transients to structural changes associated with ion transport. In this section, emphasis is placed on another possible process, namely thermionic emission of electrons from the metal into traps in the adjacent oxide. This would be significant if the potential barrier at the metal-film interface was less than about kT = 0.03 eV at room temperature, and seems reasonable in view of the discussion of cathodic reduction in section 2.13. An estimate of the barrier height would be the value of the voltammetric cathodic nucleation overvoltage (eq. 2.10) at very low film thickness. A value of nearly zero is indicated (fig. 2.19). Electron tunnelling between the metal and traps in the oxide is another possibility (116).
Thermionic electron emission would give rise to a space charge in the oxide near the metal surface. The steady-state electron distribution would depend on the field in the oxide, but would not change instantly with a change in field because a change in the distribution would involve thermal activation of trapped electrons.

The presence of a negative space charge due to electrons would give a non-uniform electric field in the layer, leading to a net accumulation of mobile ions in the film, sufficient to cancel the electron space charge. The model of an electronic space charge with extra interstitial ions is equivalent to a non-stoichiometric (excess metal) n-type semiconductor layer at the metal-oxide interface.

The model can be represented schematically as:

![Diagram](image)

The potential change across the oxide, \( \Delta \phi \), can be calculated approximately using Gauss' theorem:

\[
\Delta \phi = (Q_m + Q_e + \sigma) \cdot \frac{h}{\varepsilon}
\]

(5.13)

The interpretation of the overshoot transient following a current step during from growth comes directly from eq. 5.13 (cf. section 5.3.1):
An overshoot arises because the relaxation time of the electron space charge is much less than that of the ionic space charge. The rate constants observed (section 5.3.1) are related to the mobility of the species.

The model is identical with that used in Chapter 9 to describe the potential transients under galvanostatic conditions following photo-emission of electrons from the metal into the film. The method used in Chapter 9 could be used here to derive the form of the overshoot transient. The qualitative description above is sufficient for the purposes of this chapter, however.

According to the above model, standing at open-circuit, or heating, increases the electron space charge in the oxide by thermionic emission from the metal. Indeed, a darkening of the interference colour of a Bismuth anodic oxide film did occur on standing, consistent with this idea.
Upon its reapplication, the current would at first be almost entirely carried by electrons as the space charge in the film decayed. During this period the potential would be low and constant. It would rise only when the process of scavenging of surplus electrons from the film was nearly complete and the fraction of the current carried by ion transport started to increase. Overshoots upon the application of a current step would only be observed once the field was large enough for ionic migration.

The formation of an electronic space charge in an anodic oxide film upon standing at zero current has recently been demonstrated for films on Al and Zr (123) by the method of thermally stimulated currents. The existence of an electronic space charge would increase the apparent dielectric constant of the film (section 5.3.4).

The qualitative differences between anodic Bi$_2$O$_3$ and anodic Al$_2$O$_3$ and Ta$_2$O$_5$ behaviour noted earlier may arise from several factors:

(a) different barrier heights for thermionic emission;
(b) different ionic mobilities;
(c) mobility of both anions and cations in Al$_2$O$_3$ and Ta$_2$O$_5$ (3, 43) - but not in Bi$_2$O$_3$ - giving two decay constants for the ionic space charge.

5.6 Effect of Hydration of an Outer Surface Layer

Some of the effects noted in this chapter may arise from a proton space charge, or electrical double layer, in the outer part of the anodic oxide layer (102, 124).
Incorporation of protons would generate cation vacancies (103) and hence greatly alter the ionic conductance of the oxide. The recharging phenomena could involve proton migration.

5.7 Summary
(a) A short review of models of high field ion transport has been given.
(b) The transient conductivity of bismuth anodic oxide films has been investigated and related to the history of the film.
(c) A new model for the transients has been given. It involves an electronic space charge in the oxide, generated by thermionic emission from the metal.
CHAPTER 6
POTENTIOSTATIC TRANSIENT STUDY
OF ANODIC BISMUTH OXIDE NUCLEATION

6.1 Introduction

The potentiostatic transient method for the study of film nucleation was developed by Fleischmann and Thirsk (10, 111). Transient current peaks, due to the nucleation and spreading of successive layers were observed (e.g. \( \text{Hg}_2\text{Cl}_2 \) on \( \text{Hg} \); \( \text{TlCl} \) or \( \text{Tl/Hg} \) (111)). The results of double potential step measurements were used to determine whether the nuclei formed were two-or three-dimensional.

In the study of film thickening (66), the potentiostatic experiment is the equivalent to the study of oxide growth by reaction with gaseous oxygen, in which a constant potential is maintained across the film by reactions at the interfaces, (71, 106, 107, 108, 110).

In this work, a logarithmic relation of charge and time has been found for both the surface covering and subsequent thickening processes. This has been interpreted in terms of simultaneous thickening and lateral spreading of the oxide nuclei and a Verwey high field law for the thickening process, as described previously (Chapters 2 and 3).

The gas phase oxidation of bismuth obeys a parabolic law, oxide thickness being proportional to \( \sqrt{\text{time}} \) (109), and this has been previously explained in terms of Wagner's theory of oxidation (108, 109). The alternative interpretation (110), that the law arises as a low field approximation
to Mott's model (106), has been considered here, using the
growth parameters determined in Chapters 2 and 3 and found
equally valid.

6.2 Experimental

A conventional 3-electrode potentiostatic circuit
(fig. 2.1) was used. Current transients were recorded by a
uv chart voltmeter (SE3006 with SE4510 preamplifier) connect-
ed across the standard resistor (fig. 2.1).

The presence of an uncompensated solution resistance
between the Bi and reference electrodes meant that the true
electrode potential was not constant but changed by up to
100 mV during a current transient.

The solution was 0.047 M NaOH, pH 12.61, maintained
at 25°C, and the surface an electrodeposited preparation
with anodic nucleation overvoltage, determined by cyclic
voltammetry (section 2.7), $\eta_{AN} = 50$ mV.

The Bi electrode was maintained at an initial
potential of -750 mV (NHE), slightly negative of the cathodic
peak in cyclic voltammetry (fig. 2.8) and pulses to anodic
overvoltages, $\eta$ (eq. 2.8), in the range 100 to 800 mV applied,
without at any stage removing the electrode from the
solution.

6.3 Results

Typical current-time traces are shown in fig. 6.1.
No transient current peaks were observed, in contrast to
other work on electrocrystallization (10, 64, 65, 111).
The transient currents, and hence total charge, increased
with increasing step overvoltage.
Fig. 6.1  Anodic Bi$_2$O$_3$ nucleation.

Current as a function of time following a potential step.
Plots of the charge as a function of time

\[ Q - Q_0 = \int_{t_0}^{t} i \, dt \] ........................ (6.1)

are given in fig. 6.2. Here, \( t_0 \) is the time at which the current falls to within the range of measurement, and \( Q_0 \) is the unknown charge passed in the time interval \((0, t_0)\), time zero at the application of the potential step. The minimum value experimentally obtainable for \( t_0 \) was 0.05 to 0.1 s. The charge \( Q_0 \) for \( t_0 = 0.1 \) s was estimated as not greater than 0.4 mC cm\(^{-2}\) at the highest overvoltage employed.

Plots of \((Q-Q_0)\) against log \( t \) were linear (fig. 6.2), although the linear relation failed when \( Q \) was sufficiently small (<0.25 mC cm\(^{-2}\)). The effect of the ohmic drop between working and reference electrodes would be most important at small \( Q \) (when \( i \) is large) and would reduce the amount of charge passed in a given time interval. This would displace the time axis to longer time, and give the upward curve observed at short time.

At the three highest overvoltages (step overvoltage greater than 500 mV), a second linear region in the \((Q-Q_0)\) v. log \( t \) graph was observed, when the total charge, \( Q \), was greater than 2.0 ± 0.2 mC cm\(^{-2}\) (fig. 6.2). This is the same as the total charge contained in the two anodic peaks of cyclic voltammetry, 3 ± 2 mC cm\(^{-2}\) (section 2.9).

The slope, \( q \), of the two linear sections above (table 6.1), was a linear function of the step overvoltage, \( \eta \)
Fig. 6.2 Charge as a function of time (potentiostatic step experiment)

pH 12.6; 25°C
(fig. 6.3) and unaffected by the electrode rotation rate, \( \omega \), in the range 0 to 10Hz (fig. 6.3). Thus, from figs 6.2 and 6.3, the potentiostatic transients can be described by the experimental relationship

\[
Q - Q_o = q_o \eta \log \left( \frac{t}{t_o} \right)
\]

............... (6.2)

where

\[
q_o = \frac{q}{\eta} = 2.4 \times 10^{-3} \text{ C cm}^{-2} \text{ V}^{-1}; \quad Q < 2.0 \text{ mC cm}^{-2}
\]

\[
1.7 \times 10^{-3} \text{ C cm}^{-2} \text{ V}^{-1}; \quad Q > 2.0 \text{ mC cm}^{-2}
\]

Table 6.1  

| \( \omega \)/Hz | \( \eta/V \) | \( q/\text{mC cm}^{-2} \) | \( \text{Q<2mC cm}^{-2} \) | \( \text{Q>2mC cm}^{-2} \) |
|---------------|------------|-----------------|-----------------|
| 10            | 0.135      | 0.27            |                 |
| 10            | 0.235      | 0.71            |                 |
| 10            | 0.335      | 0.74            |                 |
| 10            | 0.435      | 0.87            |                 |
| 10            | 0.535      | 1.27            | 0.92            |
| 10            | 0.635      | 1.54            | 1.09            |
| 10            | 0.835      | 2.18            | 1.36            |
| 10            | 0.835      | 2.18            | 1.54            |
| 0             | 0.835      | 2.25            | 1.56            |
| 0             | 0.235      | 0.62            |                 |
Fig. 6.3  Slope of charge-time plots

q against $\eta_A$

pH 12.6; 25°C
6.4 Discussion

Two simple points can be emphasized. First, the absence of a current maximum means that lattice incorporation (65) - the process by which adsorbed intermediates on the surface become incorporated into the spreading patches of oxide - is not the slow step of the reaction, since this process is proportional in rate to the total perimeter of the oxide patches, which goes through a maximum as spreading proceeds. The same qualitative conclusion was reached previously by the galvanostatic method (section 3.6).

Second, the break in the charge-time curves (fig. 6.2) corresponds to the completion of coverage of the surface by the oxide, as shown by the correspondence between the charge to the break and the total charge contained in the anodic peaks of cyclic voltammetry (section 2.9).

The high-field growth law (eq. 2.14) can be written

\[
\frac{dQ}{dt} = \bar{A} \exp \left( \frac{6F\eta B}{V_m Q} \right) \quad \text{............... (6.3)}
\]

on the assumption that the electric field \((\eta/h)\) is zero when \(\eta=0\). Equation 6.3 can be integrated for constant \(\eta\) to give (104):

\[
\bar{A}t = V_m Q \exp \left( -\frac{6F\eta B}{V_m Q} \right) + 6F\eta B. E_i \left( \frac{6F\eta B}{V_m Q} \right) \quad \text{..... (6.4)}
\]

where the exponential integral

\[
E_i(x) = \int_x^\infty (e^{-x}/x) \ dx = \ln x + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \text{(etc.)} \quad \text{............... (6.5)}
\]

A very rough approximation to eq. 6.4, when \(V_m Q \ll 6FB\eta\), is (104, 105, 106, 112):

\[
6F\eta B \eta, \text{ is (104, 105, 106, 112):}
\]
\[ Q - Q_0 = \frac{2.3 \times 6FB}{V_m} \cdot \eta \log \left( \frac{t}{t_0} \right) \quad \ldots (6.6) \]

which is the same as the experimental equation 6.2 and should apply to the section where \( Q > 2mC \text{ cm}^{-2} \). Thickening of the completed layer is the process occurring in this section.

Comparison of eqs 6.2 and 6.6 gives

\[ q_0 = 2.3 \times 6FB/V_m \quad \ldots (6.7) \]

and substitution of the experimental value of \( q_0 \), and \( V_m = 53 \text{ cm}^3 \text{ mol}^{-1} (\alpha-\text{Bi}_2\text{O}_3) \), gives \( B = 6.5 \times 10^{-8} \text{ V}^{-1} \text{ cm} \), considerably different from the value obtained previously \( (2 \times 10^{-6} \text{ V}^{-1} \text{ cm, section 3.7}) \). This can be attributed to the approximate nature of eq. 6.6.

The first stage of the transient, \( Q < 2mC \text{ cm}^{-2} \), must involve simultaneous thickening and spreading of oxide patches, as previously described (section 2.9). Attempts to formulate this model in order to interpret eq. 6.2 for the first stage were unsuccessful.

6.5 Relation Between Solution Studies and Gas Phase Growth

According to Mott's theory (106, 107) for the growth of an oxide layer on a metal by reaction with oxygen gas at high temperature, thermionic emission of electrons from the metal, through the oxide to adsorbed oxygen atoms forms adsorbed oxide ions and establishes an electric field in the oxide layer which assists the thickening process:

\[ \frac{dh}{dt} = \frac{V_m A}{6F} \exp \left( \frac{Bn}{h} \right) \quad \ldots (6.8) \]
where $\bar{A}$ and $B$ are the same as the high-field growth law parameters for thickening of an oxide in solution and $\eta$ is the potential change established within the oxide.

The low-field approximation

$$\frac{dh}{dt} = 2V_m \bar{A}B\eta/6F_B$$  \hspace{1cm} (6.9)

can be integrated to give a parabolic growth law:

$$m^2 = K_p t = (4\rho^2V_m\bar{A}B\eta/6F) \cdot t$$  \hspace{1cm} (6.10)

where $m$ is the mass of oxide formed per unit area of substrate, and $\rho$ is its density ($m = \rho h$).

Oxidation of Bi at 520 K and 30 torr follows eq. 6.8 (Hapase, Tare and Biswas, ref. 109) with

$$K_p = 1.7 \times 10^{-13} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$$

It is of interest to compare this experimental value of $K_p$ with the value predicted by eq. 6.8.

The value $\log (2\bar{A}B/Ac^{-1}V^{-1}) = -11 \pm 1$ at 298 K (section 2.14.3), from the high-field growth law parameters for oxide formation from aqueous solution, was corrected to 520 K by ignoring the temperature dependence of $B$ and correcting $\bar{A} = \bar{A}_o \exp (-W/RT)$ using an activation energy of $W = 97 \text{ kJ mol}^{-1}$, for diffusion of Bi through Bi$_2$O$_3$ (109, 113). A value of $\log (2\bar{A}B) = -10 \pm 1$ at 520 K was obtained. Putting $\eta \sim 1 \text{ V}$ (106, 107) and $\rho \sim 10 \text{ g cm}^{-3}$ in eq. 6.8 gives

$$K_p = 2 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$$

in reasonable agreement with the experimental value.
The experimental value had previously been interpreted according to Wagner's model (108, 109, 110) in which diffusion in the oxide is assisted by an electric field set up by a concentration gradient of the more mobile charge carrier (gas phase oxidation - electrons or positive holes). The above calculation shows Mott's model to be equally valid and gives an interesting relationship of anodic to gas phase oxidation.
CHAPTER 7
EFFECT OF SOLUTION ADDITIVES ON
BISMUTH ANODIC FILM FORMATION

7.1 Introduction

In this chapter, the possibility of nucleation of phases other than Bi$_2$O$_3$ (e.g. oxo-halides in solutions containing halide ions (26)) was explored, using the technique of cyclic voltammetry.

Solutions containing fluoride, chloride, bromide or iodide at pH 4-9, phosphate and phosphate with added methanol at pH 8.5 were investigated. Consideration of thermodynamic stability would indicate the formation of new phases, but results showed that, in the comparatively short time scale of the experiments, kinetic factors resulted in the formation of anodic Bi$_2$O$_3$, except when the solution contained iodide at low pH, when the oxo-iodide was probably formed. The iso-electric pH of the anodic product has been proposed as a key kinetic factor.

Iodide at low concentration ($10^{-3}$M) inhibited the nucleation of anodic Bi$_2$O$_3$, regardless of the solution pH.

In other work on Bi, no significant effect on the kinetics of film growth of phosphate, tartrate, benzoate, carbonate, sulphate or oxalate in dilute aqueous solution has been found (table 3.4, ref. 27, 28, 31, 35, 125). Incorporation of solution anions into the bismuth anodic film to an extent sufficient to affect the kinetics of film growth has been found only for very concentrated electrolytes
(41). In this chapter, the rate of ion exchange at the film-solution interface has been identified as the key factor controlling the composition of the thickening layer.

The anodic layers of bismuth oxo-halides observed by Burstein (26) probably formed by a dissolution-precipitation mechanism following film breakdown. His graphs show a long transition period consistent with the gradual coverage of the surface by a precipitate.

Evolution of iodine from the film-covered bismuth electrode in electrolytes containing I\(^-\) is observed at potentials greater than about 5V. This probably occurs at cracks, where the film is thinner and thus subject to a higher electric field (1, 33, 34, 72).

7.2 Experimental

All the techniques used were described in section 2.2. For experiments in which the electrolyte contained iodide, the auxiliary electrode was a Pt foil enclosed in a glass tube terminated by a fritted disc. The auxiliary electrode compartment contained no iodide in the electrolyte.

The weakly acidic buffer solutions used contained NaClO\(_4\) (1M), Na OAc (0.1M) and Na\(_2\)B\(_4\)O\(_7\) (0.05M) with the pH adjusted by additions of HClO\(_4\) (1M). Iodide-containing solutions were given cathodic pre-electrolysis with N\(_2\) stirring, in a two compartment cell. Other halide-containing solutions were prepared by adding the appropriate solid to a pre-electrolysed buffer solution.
7.3 Results

7.3.1 Cyclic Voltammetry in Iodide-Containing Media

Addition of iodide at low concentration (10^{-3} M) caused the anodic peaks observed by cyclic voltammetry to broaden and split (fig. 7.1). The effect was seen even in strongly alkaline solution (pH 13) for which Bi_{2}O_{3} is favoured thermodynamically as the anodic product. In alkaline solutions, however, the anodic nucleation potential (section 2.3) was unaffected by additions of I^{-}, and thus the anodic product would be Bi_{2}O_{3}. The cathodic peak was not split, therefore the anodic film was homogeneous and uniform.

...can be attributed to specific adsorption of I^{-}, affecting the kinetics of nucleation and spreading of oxide patches over the surface. The metal surface has been divided previously (section 2.12), by the method of cyclic voltammetry, into two or more areas of different anodic nucleation overvoltage. The effect of iodide may well be different on these different areas.

Anodic nucleation potentials (section 2.3) measured at lower pH in solutions containing iodide are shown in fig. 7.2. At pH 9 there was no significant effect of iodide on the anode nucleation potential. At pH 7.5, there was a slight effect of concentrations greater than 10^{-3} M:

\[ \frac{\partial E_{AN}}{\partial (pI^{-})} \approx 20 \text{ mV} \]

This could be interpreted as the nucleation of BiOI as the anodic product.
Fig. 7.1 Effect of iodide on cyclic voltammetry of bismuth
(25°C, zone-refined electrode)

(a) pH 12.9  \( \text{[I}^-\] = 0.01\text{M}, v = 0.1\text{Vs}^{-1} \)
\[ \text{---} \text{[I}^-\] = 0, v = 0.04\text{Vs}^{-1} \]
(two independent experiments with electrodes having different surface area).

(b) pH 9.2  \( \text{[I}^-\] = 0.01\text{M}, v = 0.1\text{Vs}^{-1} \)
\[ \text{----} \text{[I}^-\] = 0, v = 0.1\text{Vs}^{-1} \]
(two experiments using the same electrode surface; effect of ohmic drop blurs the two peaks when \( \text{[I}^-\] = 0 \)).
Fig. 7.2  Anodic Nucleation Potentials in Media Containing

25°C.  lines show the equilibrium potentials;

PH 7.5

PH 9.2

Bi₂O₃  BiO

BiO

Bi

E/mV

2

2

3

0

0

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

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One might expect that, on account of the larger size of the iodide ion compared to the oxide ion, that the electronic conductivity of BiOI would be greater than that of Bi$_2$O$_3$. This should show up as an effect on the curve of cathodic nucleation potential against charge to be reduced (sections 2.11 and 2.13). However, at pH 7.5, no significant effect was observed. The conclusion is that, at this pH, the nucleation of BiOI is possible, but not certain.

7.3.2 Cyclic Voltammetry in the Presence of Other Additives

No significant effect of bromide, chloride or fluoride at concentrations up to 0.1M and pH greater than 5 was observed on the anodic nucleation potential. Bromide addition did cause some broadening of the anodic peaks, but much less marked than that observed with iodide additions. The presence of phosphate at pH 8.5 (0.1M Na$_2$HPO$_4$ in 1M NaClO$_4$), with up to 50% by volume of methanol added, also gave no significant change in the cyclic voltammograms.

Changes in the surface resulting from film breakdown and dissolution obscured any effects on film growth due to the variation of the solution composition. No such effects have been observed previously (27, 28, 125).

7.4 Ion-Exchange at the Solution Interface of the Anodic Film

Even though the phase nucleated on the electrode is Bi$_2$O$_3$, the occurrence of ion-exchange at the film-solution interface, between oxide ions of the lattice and anions of the solution, means that solution anions can be incorporated
into the thickening film. The extent of incorporation would depend on the relative rates of ion-exchange and film thickening.

Ion-exchange of $\text{Bi}_2\text{O}_3$ is known (126, 127) but the rate is low (e.g. time scale $\sim 10^3$ s for appreciable exchange with halides (127)). Thus the growth of a layer containing appreciable amounts of bismuth oxohalide would require a growth current density $\sim 1 \mu A \text{ cm}^{-2}$, much lower than any that have been used so far. If the film was allowed to stand in the solution, the thermodynamically stable phase would form eventually.

7.5 **Significance of the Iso-Electric pH (IEP)**

Consideration of the IEP was an attempt to answer the question why, in a medium in which some other phase was the equilibrium product, the initial anodic product was bismuth oxide.

The IEP of $\text{Bi}_2\text{O}_3$ (AR grade) was measured roughly by finding the pH at which the rate of settling of a suspension was greatest (128, 129). A value of $\text{IEP} = 7.6$ was determined using borate buffers, pH adjusted using $\text{HClO}_4$. The empirical correlation given by Parks (128) gave a value of $\text{IEP} = 7.3$ for $\text{Bi}_2\text{O}_3$.

No maximum settling rate was found for BiOI, in the range of pH 4 to 10. Application of Parks' correlation (128) to the bismuth oxohalides indicated that they all had an iso-electric pH in the range 9-10.
Thus, for all solutions pH < 10, the oxo-halides would have a positive surface charge, whereas the oxide would have a positive surface charge only for pH < 7.6. The nature of the charged surface is shown schematically as (129):

\[ \text{positive surface} \quad \text{iso-electric pH} \quad \text{negative surface} \]

\[ \begin{align*}
\text{positive surface} & \quad \text{iso-electric pH} & \quad \text{negative surface} \\
\text{Bi}^+ \text{OH}^+ & \quad \text{Bi}^+ \text{OH}^+ \text{H}_{\text{aq}}^+ & \quad \text{Bi}^- \text{O}^- + 2\text{H}_{\text{aq}}^+ \\
\text{positive surface} & \quad \text{iso-electric pH} & \quad \text{negative surface}
\end{align*} \]  
(7.1)

There may be some correspondence to the experimental conclusion that oxo-iodide could perhaps be nucleated on the surface at pH 7.5 but not at pH 9; that is, a phase with a negative surface charge can maybe nucleate and spread more easily than one with a positive surface charge. One might speculate that the different surfaces of eq. 7.1 have different kinetic properties.
CHAPTER 8
TRANSIENT PHOTO-CONDUCTIVITY
IN BISMUTH ANODIC OXIDE FILM

8.1 Introduction

In this chapter, a study of the response of anodic films on bismuth to an intense flash of white light, will be presented. The study concerned an oxide film 240 nm thick formed on a zone-refined bismuth electrode in an alkaline electrolyte, at pH 13.

Galvanostatic conditions were employed. The electrode was polarized throughout the measurements and the photo-induced potential change and subsequent relaxation were studied as a function of applied current density.

The results were interpreted in terms of photo-excitation in the bulk of the film, producing electron-hole pairs which were separated by the applied field. The recombination process was best described as rate-limiting thermal excitation of trapped electrons.

The photo-response of very thin films, involving processes at the metal-film interface, will be present in Chapter 9.

The behaviour of crystalline Bi₂O₃, and of thermally grown Bi₂O₃ layers, on exposure to uv light, have been explored briefly.

The photo-effect is characterized by the mobility and lifetime of the carriers and both are structure-sensitive properties (130-134). Thus a study of the photo-
effect in an anodic film might be expected to yield structural information complementary to that obtained by other measurements.

8.2 Previous Work

Effects due to bulk photo-excitation in insulating anodic layers have been studied in the case of oxides on Al (135), Ta (136-140), Ti (140-144), Nb (140, 145, 146), Zr (146, 147), W (138) and Bi (41).

The photo-currents observed in anodic layers of Bi$_2$O$_3$ (41) were very small ($10^{-8} - 10^{-6}$ A cm$^{-2}$), proportional to electric field strength and light intensity, and increased with increasing film thickness at constant field. The spectral sensitivity exhibited a peak at $\lambda_p = 400$ nm, with half-peak sensitivity at $\lambda_{1/2} = 450$ nm, corresponding to a band gap of 2.8 eV, the same as that for the bulk Bi$_2$O$_3$ (159). The incorporation of phosphate into the film from concentrated phosphate solution was detected by a shift of $\lambda_{1/2}$ to 500 nm. The data was rationalized on the assumption that photo-electrons were produced in direct proportion to the incident light intensity and followed a first order decay law.

Some secondary photo-effects, similar to photo-induced growth (138, 148, 149) have been observed in bismuth anodic film growth (35).

The trapping of photo-electrons in localized, metastable states is an important phenomenon. Anodic oxides
have a high density of such states. Their properties have also been studied by electron injection from a cathode (38, 140) and by internal photo-emission (140, 156, 157). Very high open-circuit photo-potentials may be generated across an anodic oxide layer (147), by internal photo-emission from the metal substrate and trapping of the emitted electrons in the oxide at low temperature.

8.3 Experimental

8.3.1 Electrical Measurements

The cell assembly, galvanostatic procedure and details of the electrode preparation (zone-refined Bi rod) were described in Chapters 2 and 3. The film was grown at a current density of 45 μA cm\(^{-2}\) and reached a steady state film thickness (section 8.4). For a photo-effect measurement, the current was reduced to the desired value. Immediately following a measurement it was returned to its initial value.

In the measurement of transient potential changes (Tektronix 549 storage oscilloscope fitted with a high gain differential amplifier at the input; section 3.2), the oscilloscope trace was triggered from the input signal itself, so that changes which occurred in the first fraction of a millisecond were not displayed, and the time scale was in error by some unknown, but small amount. Photo-potential versus time curves were traced directly from the screen of the storage oscilloscope.

The electrolyte (0.10M NaOH, carbonate-free and pre-
electrolysed - section 2.2) was stirred continuously by a stream of purified nitrogen gas.

The cell assembly was in a closed box, painted matt black inside, with the temperature maintained at 25 ± 1°C using a fan and 250W lamp with simmerstat control.

8.3.2 Light Source

A photographer's electronic flash unit rated at 80J (energy input to the light source), light output constant to ±2%, was used. It was mounted firmly against the bottom of the cell, approximately 10 cm distant from the electrode surface. At this distance, the beam was effectively collimated and was 10 cm in diameter. The plane of the electrode was at right angles to the direction of the light beam.

The spectrum of the flash was measured using a Hilger prism Raman spectrograph and recorded photographically, fig. 8.1. The intensity-time characteristic was measured using the assembly shown in fig. 8.2. The arrangement was set up in a dark-room, the camera shutter was opened and, while the disc was being rotated at high speed, the flash was fired. The resulting negative showed each hole as an arc, the density of which was measured as a function of angle of rotation. Angle of rotation was converted into elapsed time using the known rotation rate of the disc (stroboscopic measurement) and the density of the negative was converted into light intensity using the known characteristics of the film (150), allowance being made for the different velocities of each hole. The intensity-time characteristic determined in this way is given in fig. 8.3. The actual light intensity
Fig. 8.1 Microdensitometer tracing of spectrum of flash unit (Kodak 103ag plate).

Optical density, D versus wavelength, $\lambda$. 
Fig. 8.2 Experimental Arrangement for measuring intensity-time characteristic of photo-flash unit.
Fig. 8.3  Time Dependence of Light Intensity of Photo-Flash

Relative light intensity, $L_r$, is given by $kr$ where $I$ is the absolute intensity and $k$ is a constant.
on the electrode surface at the peak of the flash was
-1W cm^{-2}.

8.3.3 Film Thickness

The film thickness was determined by measurement of the electrode capacitance (section 2.2.6; ref. 54), eq. 8.1, and from the charge required to reduce the film after the measurements, eq. 8.1:

\[ h = \frac{\varepsilon \cdot Q_{V_m}}{C \cdot 6F} \]  

where \( C \) is the measured capacitance and \( Q \) the measured charge per unit true area of the film-covered electrode. The permittivity, \( \varepsilon \), was taken as \( 5 \times 10^{-12} \, F \, cm^{-1} \) (table 1.1, ref. 25).

The thickness was determined as 260 nm (capacitance) and 220 nm (charge) and taken as 240 ± 40 nm.

8.4 Dissolution of Film

In the experiments described here, a steady state of constant film thickness was attained. This was due partly to dissolution of the film (section 3.4) and partly to pitting. The anodic film was punctured by a small number of tiny holes beneath which the metal had corroded into deep pits (sections 3.3 and 4.3.1). The bottoms of the pits showed rough metal crystal faces (optical microscopy, 100X magnification), and appeared free of film. The remainder of the surface was covered with film and was very smooth. Some evolution of oxygen may also occur in the pits (27, 28).
Pitting is not expected to complicate the interpretation of the photo-effects, since the photo-effects are known to decrease with decreasing film thickness (41). I have assumed that the photo-effect in the anodic film is much greater than any photo-effect on the processes occurring at a pit (Chapter 9).

8.5 Results

8.5.1 Photo-potential Measurements on Bismuth Oxide Anodic Film

The potential variation immediately at the onset of the flash is shown in fig. 8.4. The potential of the metal fell abruptly, in time with the increasing light intensity from its steady-state (dark value), reaching a new steady value, much lower, before any significant decline in the flash intensity had occurred.

The return of the electrode potential to the steady-state (dark value) following the decay of the light intensity to zero is shown in fig. 8.5. The decay of the potential change induced by the light flash, shown in fig. 8.5, was much slower than its rise, shown in fig. 8.4. Furthermore, two decay processes were seen, one substantially faster than the other (fig. 8.5). The diagram below shows schematically the course of the whole transient and defines terms used in the discussion (values given in table 8.1):
Fig. 8.4 Initial Potential change on illumination of electrode

Fig. 8.5 Decay of photo-potential following light flash

Three separate determinations with different time scales.

for both: potential change, $\Delta E$, against time, $t$; $i = 45 \mu$A cm$^{-2}$; 240 nm oxide film; pH 13; 25$^\circ$C. Light intensity variation shown -----.
Both decay processes showed a first order law:

\[
\Delta E = \Delta E_p \exp(-k_1t), \quad t < 15 \text{ ms (fast process)} \\
= \Delta E_o \exp(-k_2t), \quad t > 15 \text{ ms (slow process)}
\]

\[\cdots \cdots \cdots (8.2)\]

The parameters of the slow decay process were studied as a function of the applied current density. Data is given in table 8.1. The intercept, \(\Delta E_o\) was directly proportional to the applied current density fig. 8.6, and thus (low field approximation for low current density) to the electric field in the layer. There is a non-zero intercept on this plot at \(i = 0\), corresponding to an open-circuit photopotential:

\[
\Delta E_o \ (i = 0) = -250 \text{ mV}
\]

This is of particular interest (section 8.6.2)

The rate constant \(k_2\) was independent of the applied current density and therefore of the electric field in the layer:

\[
k_2 = 14 \pm 2 \text{ s}^{-1}
\]
Fig. 8.6  Decay intercept, $\Delta E_o$ (eq. 8.2), of potential change in response to a flash of light against applied current density, $i$.

240 nm oxide film; pH 13; 25°C.

Fig. 8.7  Photo-voltage, $V$, developed by the cell
SCE//0.1M NaOH/Bi$_2$O$_3$/Bi, Pt.
The photo-excitation process (section 8.6.1) gives electrons in the conduction band and positive holes in the valence band of the anodic oxide. The open-circuit photopotential indicates an internal field in the oxide with no applied current (section 8.6.2). The decay process involves recombination of electrons and positive holes (133). Some of the conduction electrons may become trapped in localized, metastable states before re-combining with the positive holes. Thus, after the flash goes off, the decay process proceeds in two stages (134) - recombination of electrons still in the conduction band, a rapid process, and thermal activation to the conduction band and subsequent recombination of trapped electrons, a slow process (section 8.6.3).

Thus, the lifetime in the conduction band of the photo-electrons, $\tau_c$, is obtainable directly from the experimental data (133, 134):

$$\tau_c = \frac{1}{k_1} = 23 \pm 5 \text{ ms}$$

The rate constants for the decay observed here are much larger than those observed in bulk $\text{Bi}_2\text{O}_3$ containing a slight excess of Bi ($k_1 \approx 0.03\text{s}^{-1}$ (158)). The anodic oxide must have a much higher density of recombination centres than the bulk material.

8.5.2 Photo-effects on Crystalline $\text{Bi}_2\text{O}_3$

Crystalline $\text{Bi}_2\text{O}_3$ (B.D.H. Laboratory Reagent) darkened on irradiation with uv light of predominantly 250 nm wavelength, from a 15W, low-pressure, mercury arc. The process was accelerated by covering the powder with aqueous 0.1M NaOH solution. After 2 hour exposure, the surface of the oxide was a uniform grey colour. Microscopic examination
Table 8.1 Parameters for decay of photo-potential

film thickness: 240 nm; 0.10M NaOH; 25°C.

<table>
<thead>
<tr>
<th>i/μA cm⁻²</th>
<th>E₁/V</th>
<th>ΔE_p/V</th>
<th>ΔE_o/V</th>
<th>k₁/s⁻¹</th>
<th>k₂/s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>12.1</td>
<td>-10</td>
<td>5.7</td>
<td>44</td>
<td>15*</td>
</tr>
<tr>
<td>18</td>
<td>4.75</td>
<td></td>
<td>2.6</td>
<td></td>
<td>13</td>
</tr>
<tr>
<td>9.1</td>
<td>2.55</td>
<td></td>
<td>1.4</td>
<td></td>
<td>13</td>
</tr>
<tr>
<td>4.5</td>
<td>1.50</td>
<td></td>
<td>0.80</td>
<td></td>
<td>13*</td>
</tr>
</tbody>
</table>

* mean of 4 determinations at the given current, reproducibility ±10%.

(100X) showed the crystals apparently unchanged in size or shape.

The effects can be interpreted as:

Photo-generation of positive holes and electrons

\[ hν \rightarrow p' + e' \]  .............. (8.3)

Reduction of bismuth ions in the lattice

\[ Bi_{Bi} + 3e' \rightarrow Bi_{Bi}^{'''} \]  .............. (8.4)

Oxidation of aqueous OH⁻ by positive holes at the oxide surface

\[ 4OH^-_{(aq)} + 4p' \rightarrow O_2_{(aq)} + 2H_2O_{(l)} \]  .............. (8.5)
8.5.3 Photo-potential of Thermally Prepared Bi$_2$O$_3$ films

A bismuth oxide electrode was made by melting bismuth metal (B.D.H, granulated) in a crucible in air, inserting a Pt connecting wire and cooling. The air-formed oxide layer on the surface showed a yellow colour, indicating a thickness \( \sim 100 \) nm (25).

The crucible was filled with 0.1M NaOH solution and the potential of the (Pt) Bi/Bi$_2$O$_3$ electrode measured with respect to a saturated calomel electrode, both in the dark and under illumination with uv light from the 15W mercury lamp. Measurement was made with a Keithley 610C electrometer driving a Heath EUW20A recorder. Results are in fig. 8.7 and table 8.2.

A photo-potential, \( \Delta E_p \), of \(-3\)mV was observed on initial illumination. The photo-potential steadily declined, over about 100s (table 8.2), to a final value of \(-1\)mV. No corresponding overshoot was observed when the light was switched off.

<table>
<thead>
<tr>
<th>Table 8.2</th>
<th>Photo-potential of (Pt)Bi/Bi$_2$O$_3$ electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta E_p /\text{mV} )</td>
<td>light on</td>
</tr>
<tr>
<td>light off</td>
<td>2.0</td>
</tr>
<tr>
<td>illumination time/s</td>
<td>2</td>
</tr>
</tbody>
</table>
The photo-potential has the same negative sign as that observed with the anodic film (section 8.5.1) but a much smaller magnitude. The difference is most likely due to a different light intensity rather than any intrinsic difference in the film properties in the two cases.

8.6 Interpretation of Photo-Effect in Bismuth Oxide anodic films

There are three steps involved in the interpretation:
(a) photo-excitation of the film to produce free carriers and their separation by the applied field; (b) trapping of the photo-generated carriers in metastable states; and (c) the subsequent recombination process.

8.6.1 Photo-excitation process

Simple considerations (130) lead one to expect that light of a suitable wavelength will excite electrons from the valence band to the conduction band of an insulator. If the insulator, in this case an anodic film, is subjected to an electric field, then the photo-electrons and positive holes produced will be separated by the field, giving rise to a current charge under potentiostatic conditions or a potential change under galvanostatic conditions.

The carriers generated by the light will move so as to cancel the applied field. Thus in a galvanostatic experiment, the electrode potential will fall, as observed. If the rate of photo-excitation of the carriers is much greater than their rate of recombination, then the field in the oxide layer will fall almost to zero. This is also observed, during the 'on' period of the flash (table 8.1, fig. 8.4).
The details of the excitation mechanism may be more complex. For example, light may produce excitons in the film (151), which diffuse through the film and release electrons into the conduction band from a grain boundary or lattice defect, or by a redox reaction at the film-solution interface. Alternatively, an electron may tunnel directly from an exciton to a trap never becoming free.

Internal photo-emission of electrons from the metal into the oxide (Chapter 9) would result in a flow of negative charge towards the solution and this would drive the metal positive with respect to the reference electrode. But a positive photo-potential is not observed, and hence photo-emission is ruled out as the dominant process.

8.6.2 Open-Circuit Photo-potential

A negative open-circuit photo-potential is observed. This means that the electrons and positive holes generated by the light become separated even in the absence of an applied electric field, the electrons moving towards the metal or the positive holes towards the solution. The purpose of this section is to discuss the mechanism (table 8.3) for this phenomenon.

The simplest mechanism for generation of a negative open-circuit photo-potential involves removal of the positive holes by reaction at the film-solution interface (33, 70):

\[
4\text{OH}^-_{(aq)} + 4p^+ + \text{O}_2(aq) + 2\text{H}_2\text{O}(l) \quad \cdots \cdots (8.5)
\]
leaving the electrons free to migrate to the metal or become trapped in the oxide (eq. 8.4). The magnitude of the photo-potential depends on the mean free path of the photo-electrons (130). This scheme has already been used to describe the effect of uv light on crystalline Bi$_2$O$_3$, and is equivalent to the contact potential theory (table 8.3). The reaction of solution species with photo-generated holes in an insulating anodic oxide layer (Ta$_2$O$_5$) has previously been demonstrated directly (33).

The sign of the photo-potential has been used to distinguish the conductivity type of anodic films (66, 154) (n-type, conduction by electrons; p-type, conduction by positive holes). This distinction is useful for films which are semiconductors (e.g. Cu$_2$O) but is confusing for films which are insulators (e.g. Bi$_2$O$_3$). The significant parameter is the mean free path, $l_e$, of photo-electrons, before their capture by deep traps, from which thermal activation to the conduction band is unlikely. If $l_e$ is sufficiently short, the photo-electrons are effectively immobile and the film will behave as a p-type conductor.

Of the other theories shown in table 8.3, only the p-i-n junction theory will be considered. Evidence which has been adduced in favour of the p-i-n junction theory includes the effect of etching of the oxide layer on the photo-potential developed by the system Nb/anodic Nb$_2$O$_5$, 200 nm thick/electrolyte solution (145). The photo-potential decreased as the outer layers of oxide were removed, disappearing entirely when the thickness had been reduced by 20 nm. This was taken to be the thickness of p-type, oxide-
rich layer at the film-solution interface. Removing this removed the source of the gradient (electric field) responsible for separating the photo-generated carriers to give the observed photo-potential. Huber (141) has demonstrated directly the existence of a p-type conducting layer at the oxide-solution interface of an anodic TiO₂ film. Capacitance measurements (143) have also been used to support this conclusion. Such a layer would only exist if there was some oxide ion migration during film growth.

All three mechanisms for the open-circuit photo-potential probably operate, to different extents depending on the nature of the material being irradiated. Thus, the photo-potentials observed by Williams (70) at electrodes of binary semiconductors were of similar magnitude to those observed across insulating anodic films (135-146). However, the carrier mobility in the semiconductors, \(10^{-8} - 10^{-3} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}\) (155), is much greater than that in insulating anodic films (e.g. Ta₂O₅: \(10^{-16} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}\) (38)). Thus, since the mean free path of carriers would be much less, the quantum yield of separated carriers would have to be much greater in the latter case than in the former, to give a similar photo-potential at similar light intensity. The dominant mechanism of carrier separation is therefore unlikely to be the same in the two cases. The simple mechanism (eq. 8.5) has been used here to describe the open-circuit photo-voltage in the case of anodic Bi₂O₃. In fact, the interpretation must remain uncertain.
<table>
<thead>
<tr>
<th>Theory</th>
<th>Ref.</th>
<th>Origin of photo-potential</th>
<th>Sign of photo-potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Internal Field in Oxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Contact potential difference</td>
<td>70, 139, 135</td>
<td>Different work functions at metal-film and film-solution interfaces. Field set up by charge transfer across interfaces.</td>
<td>Depends on work function ions</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. p-i-n junction</td>
<td>141-145</td>
<td>Non-stoichiometric regions at metal-film (n-type) and film-solution (p-type) interfaces. Stoichiometric (i-type) in centre. Field set up by gradient of composition.</td>
<td>Negative</td>
</tr>
<tr>
<td>B. Concentration gradient</td>
<td>152, 153</td>
<td>Diffusion potential. Gradient depends on the ratio of light intensity in film $\frac{I_1}{I_2}$ and diffusion potential of $e'$ and $p'$ generated. Since $e'$ and $p'$ have different mobility, $\mu$, and mean free path, $l$, (130, 131, 133), a diffusion potential results.</td>
<td>Depends on $\frac{I_1}{I_2}$ &gt; 1, positive if $&lt; 1$.</td>
</tr>
</tbody>
</table>

Table 8.3 Theories for Open-circuit Photo-potential
8.6.3 Decay of Photo-generated Carriers

In this section, the slow decay process, recombination of trapped electrons, will be discussed. Gauss' theorem will be used to relate the observed photo-potential to the photo-induced charge separation in the film.

Suppose trapped electrons are denoted $t'$, conduction electrons $e'$ and holes $p'$, then the recombination of trapped electrons can be expressed as

$$
t' + \frac{k_6}{k_{-6}} e' \quad \cdots (8.6)
$$

$$
e' + p' + \frac{k_7}{k_{-7}} (e' \cdot p')^* \quad \cdots (8.7)
$$

$$(e' \cdot p')^* + \text{ground state} \quad \cdots (8.8)
$$

Here, $k_6$ represents the thermal excitation of a trapped electron into the conduction band

$$
k_6 = A_6 \exp \left(-\frac{W}{kT}\right) \quad \cdots (8.9)
$$

where $W$ is the trap depth.

The constant $k_{-6}$ represents the process of "retrapping" (131, 133, 134) and involves a diffusion step, to another trap. The process (8.7) represents recombination of an electron and a hole into an exciton which may subsequently decay to the ground state. The forward step ($k_7$) involves diffusion in the conduction band.

Let $v$ denote reaction rate, then the simplest decay
law (133) corresponds to the forward process (8.6) being rate determining:

\[ v = v_1 = -\frac{d(t')}{dt} = k_6(t') \]

or

\[ (t') = (t'_0) \exp (-k_6 t) \quad \cdots \cdots \cdots \quad (8.10) \]

where \((t')\) is the concentration of electrons in traps at time \(t\) and \((t'_0)\) is the value at \(t = 0\), taken as being equal to the trap density, \(N_T\).

Equation 8.10 can be related to the experimental data using Gauss' theorem.

Bulk photo-excitation of the oxide produces carriers which are separated a mean distance \(x\) by the applied field \(E_o\). As a result, the field is reduced to \(E_1\) in the middle of the film. The effective surface charge density, \(q_e\) generated by the light pulse, is an average of the distribution of photo-generated carriers.

\[ q_e = |e| (t') \Delta h / 2 \quad \cdots \cdots \cdots \quad (8.11) \]

where \(e\) is the electronic charge.
Gauss’ law is an electrostatic description and so is limited to a discussion of the effect due to stationary, i.e. trapped carriers.

\[ \overline{E}_1 = \overline{E}_0 - q_e/\varepsilon \]  \hspace{1cm} (8.12)

so \[ \Delta \phi - \Delta \phi_0 = \Delta E = -q_e x/\varepsilon \]  \hspace{1cm} (8.13)

In obtaining equation 13, constancy of the interfacial potentials during the transient has been assumed.

An approximate equation for \( x \), the distance the carriers are separated by the applied field, is

\[ x = \frac{\mu \overline{E}_0}{\tau_C} \]  \hspace{1cm} (8.14)

where \( \mu \) is the electron mobility in the conduction band of the oxide; \( x \) is considered constant throughout the decay.

From equations 8.10, 8.11, 8.13 and 8.14 the potential variation due to the recombination of trapped electrons can be obtained:

\[ -\Delta E = \frac{q_e x}{\varepsilon} = |e| (t') h x/2\varepsilon \]

\[ = (|e| N_T \mu \tau_C h \overline{E}_0/2\varepsilon) \exp (-k_6 t) \]  \hspace{1cm} (8.15)

Equation 8.15 gives a consistent description of the slow decay process, since \( k_6 \) is independent of the applied field. According to this model, the rate constant reflects an average trap depth, \( W \) (eq. 8.9). The rate constant is rather greater than that observed for the photo-potential decay of anodic \( \text{Ta}_2\text{O}_5 \) (137) or \( \text{ZrO}_2 \) (146) (both about 0.1 s\(^{-1}\)) implying shallower traps in anodic \( \text{Bi}_2\text{O}_3 \). The cation valence may be the key factor.
It is apparent that any version of the mechanism that did not have the first step rate controlling would give field-dependent rate constants, through the factors $k_{-6}$ and $k_7$.

A number of other mechanisms were tested and found to be inadequate. Among them were rapid decay of electrons by migration to the metal followed by slow decay of holes by migration to the solution and reaction there, and the converse, slow migration of electrons and rapid migration of holes. Both would give a different form for the transient.

Since, at low current, the linear approximation, eq. 2.17, for the field-current relationship holds, equation 8.15 predicts the observed linear relationship of $\Delta E_o$ on $i$:

$$\Delta E_o = -(N_T \mu \tau_C |e| h/4\overline{AB}\epsilon) \cdot i$$  \hspace{1cm} (8.16)

As shown in section 8.6.2, the intercept in fig. 8.6 is due to an additional open-circuit field, not included in eq. 2.17.

An attempt was made to obtain numerical estimates of the parameters $N_T$ and $\mu(\tau_C$ has already been given - section 8.5.1). From eq. 8.16 and fig. 8.6,

$$N_T \mu \tau_C |e| h/4\overline{AB}\epsilon = 1.2 \times 10^5 \text{ V A}^{-1} \text{ cm}^2$$  \hspace{1cm} (8.17)

Substituting of $\epsilon = 5 \times 10^{-12} \text{ F cm}^{-1}$ (25), $\overline{AB} = 5 \times 10^{-11} \text{ A V}^{-1} \text{ cm}^{-1}$ (section 3.7), $h = 2.4 \times 10^{-5} \text{ cm}$ and $|e| = 1.6 \times 10^{-19} \text{ C}$ into (8.17) gives:
\[ N_T \mu \tau_C = 3 \times 10^7 \text{ cm}^{-1} \text{ cm} \cdot \text{s}^{-1} \] \hspace{1cm} (8.18)

Since the quantity \( \tau_C \) is related theoretically to the quantities \( \mu \) and \( N_T \) (170), and has also been obtained independently (section 8.5.1), enough information has, in principle, been obtained to evaluate \( N_T \) and \( \mu \) for the bismuth anodic film. However, both the approach leading to eq. 8.18 and the theoretical relation between \( \mu \), \( \tau_C \) and \( N_T \):

\[ N_T \sim (\mu \tau_C \cdot kT/|e|) \] \hspace{1cm} (8.19)

were too approximate to yield a realistic result.

8.7 Summary

(a) A study of the photo-potential and subsequent relaxation induced in a 250 nm anodic film of Bi₂O₃ by an intense flash of white light has been presented.

(b) The results were interpreted in terms of photo-excitation in the bulk of the film, producing electron-hole pairs which were separated by the applied field.

(c) By using Gauss' theorem, the observed photo-potential can be simply related to the photo-induced charge separation in the film.

(d) The recombination process was described as rate-limiting thermal excitation of trapped electrons.

(e) A negative open-circuit photo-potential was observed. This was related to the reaction
of photo-generated holes at the film-solution interface. A summary of the various models that have been given for the open-circuit photo-potential has been included.
CHAPTER 9
THE PHOTO-EFFECT IN VERY THIN
ANODIC OXIDE FILMS ON BISMUTH

9.1 **Introduction**

The photo-effect in thick anodic oxide layers on bismuth has been presented in Chapter 8, and the results interpreted in terms of photo-excitation of electrons in the oxide. In this chapter, results on the photo-effect on bismuth electrodes with a very thin anodic oxide layer (4 nm thick) will be presented. New effects, which can be interpreted in terms of internal photo-emission (75, 156, 157, 160-162) of electrons from the metal into the oxide, have been observed. The relaxation of the electrode following an intense flash of white light was studied, and interpreted in terms of the formation and decay of electronic and ionic space charges in the film.

9.2 **Experimental**

Experimental procedure was as described in sections 2.2, 3.2 and 8.3. Two different metal preparations were used: zone-refined (A) and cast (B). The electrodes were prepared by electropolishing (25) and were polarized continuously throughout the measurements. The electrolyte was an aqueous acetate/borate/perchlorate buffer (section 7.2) of pH 5.0 and ionic strength 1.0M, prepared using A.R. chemicals and doubly-distilled water, and pre-electrolysed (section 2.2) with N₂ stirring.
As described in section 2.6, continuous polarization of a bismuth electrode in a weakly acidic solution gives a film of constant thickness, as a result of the effects of film dissolution and breakdown. Film thicknesses were determined from measurements of the capacitance (section 2.2.6 and 8.3) at a potential such that no current was flowing, and from the charge required to form the film to its limiting, steady-state thickness, determined by cyclic voltammetry (eq. 2.9). The values of film thickness derived by the above two methods agreed to within 10%. The steady state thickness was $h = 4.0 \pm 0.5$ nm and the roughness factors (section 2.2.6) of the electrodes were 1.85 for the zone-refined (A) and 1.47 for the cast (B) electrodes.

For these experiments, the energy input to the flash tube was doubled to 160J, doubling the light output from the level used in Chapter 8. The temperature was $25^\circ$C (air bath, section 8.3). Oscilloscope traces were photographed and measured with a travelling microscope.

9.3 Results

9.3.1 Photo-Effect at Film-Free Electrode

The photo-current at constant potential was investigated using 0.10M $\text{HClO}_4$/1.0M $\text{NaClO}_4$ as the electrolyte. In this electrolyte the metal is film-free at all potentials (52, 55). No photo-current was detected over a potential range of $+0.45$ (rapid anodic dissolution) to $-1.05V$ NHE (rapid $\text{H}_2$ evolution). Saturation of the electrolyte with
$N_2O$ had no effect, neither did the amalgamation of the surface with mercury. Saturated bismuth amalgam is 98% mercury.

The detection limit of the measurement system was limited by circuit noise to $10^{-5}$ A cm$^{-2}$. Photo-currents of up to $10^{-3}$ A cm$^{-2}$ have been reported for flash-irradiated mercury electrodes (163), but with the use of a more intense light source with a strong uv component.

It is notable that the photo-currents at the film-free electrode were far lower than those at the oxide-coated electrode (section 9.3.4). This effect has been observed before (75, 164) and is discussed in section 9.4.1.

### 9.3.2 Pitting of Electrode

The anodic film was punctured by a small number of tiny holes beneath which the metal had corroded into deep pits. The bottoms of the pits showed rough metal crystal faces and appeared free of film. The film-covered surface was very smooth.

In the steady state, some fraction of the current would be flowing through pits. Disturbance of the steady state may result in a redistribution of the current which could complicate the results.

A direct photo-effect at the pits would be unimportant, as shown above (9.3.1).

### 9.3.3 Photo-Effect at Film-Coated Electrode under Galvanostatic Conditions

The initial photo-potential observed was positive with respect to the reference electrode (fig. 9.1), opposite
to the result of Chapter 8. The difference must lie in the much lower film thickness in this experiment, 4 nm compared with 240 nm for the film studied in Chapter 8.

The subsequent development of the photo-potential transient depended on the applied current, i.e. on the electric field in the layer. At higher current density, the photo-potential decayed through zero, showing a minimum (negative) value before returning finally to zero. However, if the applied current was sufficiently small, negative photo-potentials were not observed at any stage of the transient (fig. 9.1). The co-ordinates of the maximum and minimum of the photo-potential transient are given in table 9.1. The magnitude of the initial maximum photo-potential decreased and the magnitude of the subsequent minimum increased with increasing applied current (table 9.1, fig. 9.1).

It is apparent (fig. 9.1) that the decay of the photo-potential from the initial maximum, at the higher currents, followed the decay of the light intensity from the flash. At lower currents, the decay was slower. The rate of relaxation from the minimum value also correlated with the applied current, being greater for larger current.

There was an effect of the electrode preparation. The magnitude of the minimum photo-potential was much less for electrode A than for electrode B at similar applied current (table 9.1). The steady state, dark current-potential relation was the same for the two preparations (table 9.1).
Fig. 9.1 Photo-Potential at Constant applied current

Bi$_2$O$_3$ film, 4 nm thick; pH 5.0; 25°C.

<table>
<thead>
<tr>
<th>$i/\mu A \text{ cm}^{-2}$</th>
<th>4.5</th>
<th>45</th>
<th>110</th>
<th>210</th>
</tr>
</thead>
</table>

electrode preparation | A   | A   | B   | B   |

--- light intensity,
(arbitrary units)
### Table 9.1 Turning Points of Galvanostatic photo-potential transients

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$i/\mu\text{Acm}^{-2}$</th>
<th>$E$/mV</th>
<th>$\Delta E$/mV</th>
<th>$t$/ms</th>
<th>$\Delta i$/mV</th>
<th>$t$/ms</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>230</td>
<td>350</td>
<td>8</td>
<td>0.5</td>
<td>-2.2</td>
<td>9.0</td>
</tr>
<tr>
<td>A</td>
<td>45</td>
<td>300</td>
<td>22</td>
<td>0.4</td>
<td>-1.1</td>
<td>80</td>
</tr>
<tr>
<td>A</td>
<td>4.5</td>
<td>230</td>
<td>41</td>
<td>1.0</td>
<td>not observed</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>210</td>
<td>360</td>
<td>10</td>
<td>0.3</td>
<td>-20</td>
<td>7.0</td>
</tr>
<tr>
<td>B</td>
<td>110</td>
<td>330</td>
<td>22</td>
<td>0.3</td>
<td>-16</td>
<td>16</td>
</tr>
<tr>
<td>B</td>
<td>21</td>
<td>280</td>
<td>50</td>
<td>0.4</td>
<td>not observed</td>
<td>-</td>
</tr>
</tbody>
</table>

i : applied current  
$E$ : steady state dark potential  
$\Delta E$ : photo-potential

### Table 9.2 Turning Points of Potentiostatic Photo-current transients

<table>
<thead>
<tr>
<th>Metal</th>
<th>$E$/mV</th>
<th>$i/\mu\text{Acm}^{-2}$</th>
<th>$\Delta i/\mu\text{Acm}^{-2}$</th>
<th>$t$/ms</th>
<th>$\Delta i/\mu\text{Acm}^{-2}$</th>
<th>$t$/ms</th>
<th>$\Delta i/\mu\text{Acm}^{-2}$</th>
<th>$t$/ms</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>250</td>
<td>8.3</td>
<td>-1600</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>350</td>
<td>90</td>
<td>-1300</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>360</td>
<td>320</td>
<td>-640</td>
<td>0.2</td>
<td>430</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>250</td>
<td>7.1</td>
<td>-380</td>
<td>0.22</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>300</td>
<td>37</td>
<td>-150</td>
<td>0.18</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>350</td>
<td>170</td>
<td>-</td>
<td>77</td>
<td>0.05</td>
<td>-11</td>
<td>0.43</td>
<td>9</td>
</tr>
</tbody>
</table>

$E$ : applied potential  
i : steady-state dark current  
$\Delta i$ : photo-current
9.3.4 Photo-effect at Film-coated Electrode under Potentiostatic Conditions

In this experiment, as a result of the processes of film and metal dissolution (pitting), an anodic dark current flowed continuously. The change in current on application of a light pulse was recorded (fig. 9.2).

At lower potentials, the initial current change was negative (a cathodic photo-current) and far larger in magnitude than the dark current. At higher potentials, the initial current change became positive (an anodic photo-current).

The subsequent development of the transient depended on the applied potential. When the photo-current was initially negative, it decayed through zero, at a much faster rate than the decay of the light pulse, and showed a maximum (anodic) value before decaying slowly to zero again (fig. 9.3). When the photo-current was initially positive, it oscillated through zero, showing a minimum (cathodic) value, and back again to another maximum (anodic) value before decaying finally to zero (fig. 9.2). There was an appreciable light intensity for the whole time of these oscillations, except for the final slow decay. The co-ordinates of the maxima and minima are presented in table 9.2.

There was an effect of surface preparation. Electrode A showed much lower photo-currents than electrode B, throughout the course of the transient (table 9.2).

A similar change with increasing electrode potential, from cathodic to anodic photo-currents, has been observed for oxide-coated silver electrodes (75). Cathodic photo-
Fig. 9.2  Photo-current at constant potential
Bi$_2$O$_3$ film, 4 nm thick; 25°C; pH 5.0; electrode A.

Fig. 9.3  Decay of photo-current at longer time
Bi$_2$O$_3$ film, 4 nm thick; pH 5.0; 25°C; electrode B;
$E = 360$ mV
currents at low potentials and anodic photo-currents at high potentials have also been observed in thick anodic films on Ta (135, 137), but it is believed that a different mechanism operates here (section 9.4). Rotenberg (164), in a study of the photo-current observed during cyclic voltammetry of lead in iodide solutions, observed a similar change in the sign of the photo-current, but the situation was complicated by the presence of I⁻ in solution (Chapter 10).

9.3.5 Comparison of Photo-potential Transients (Galvanostatic case) with Potential Transients following Short Current Pulses

In a galvanostatic experiment, the total current density

\[ i = i_{el.} + i_{ion} + i_{cap}. \]  \hspace{1cm} (9.1)

is constant. Here, \( i_{el.} \) is the electronic current, stimulated by the light flash, \( i_{ion} \) is ionic current (film growth and dissolution, metal dissolution in pits) and \( i_{cap.} \) is the capacitance charging current, which goes to charge up the ionic double layer capacitance at the film-solution interface.

In a photo-effect experiment, an electronic current pulse is balanced by an equal and opposite pulse of ionic and capacitance current. A pulse of ionic and capacitance current, in the absence of electronic current, can be produced, in the dark, by applying a brief, controlled current pulse to the electrode. Comparison of the result of such an experiment with the result of the photo-effect experiment
should therefore be interesting.

Anodic current densities of 23, 92 or 230 \( \mu A \ cm^{-2} \) were applied to the electrode and single anodic current pulses of 690, 2300 or 6900 \( \mu A \ cm^{-2} \) for 0.1 or 0.3 ms superimposed. The relaxation of electrode potential was observed. The electrode potential rose rapidly during the pulse and, after the pulse, fell steadily to its original value. The potential did not obtain values less than the steady-state value at any stage during the transient, in contrast to the photo-potential transient.

In fig. 9.4, the initial course of the photo-potential transient, following the positive peak, has been plotted for comparison with the potential transient following an anodic current pulse. The two experiments gives similar results in this short time domain, before the photo-potential change takes on negative values.

The change in sign of the photo-potential, from positive to negative, during the course of the transient, is thus identified as a unique effect dependent on the pulse of electronic current produced by the light flash.

9.4 Discussion

9.4.1 Proposed Model for the Photo-Effects in Thin Anodic Films

The primary photo-event must cause electrons to move away from the metal towards the solution, giving a positive photo-potential in galvanostatic experiments and a cathodic photo-current in potentiostatic experiments. The results
Fig. 9.4 Comparison of photo-potential transient with potential transient following a current pulse (in the dark)

Electrode potential change, $\Delta E$, against time, t. pH 5; 25°C; 4 nm thick film.

- photo-effect experiment, electrode B, 23$\mu$A cm$^{-2}$
- photo-effect experiment, electrode A, 45$\mu$A cm$^{-2}$
- current pulse experiment, electrode B, 23$\mu$A cm$^{-2}$; current pulse to 690 A cm$^{-2}$ for 0.3 ms applied at $t = 0$. 
can be explained simply in terms of internal photo-emission of electrons from the metal into the oxide (75, 156, 157, 160-162, 165). This process is opposed by the applied electric field, and as this is increased, the range of the photo-electrons will be reduced. Thus, an electronic space charge would form in the oxide layer (165). Photo-emission of electrons right through the oxide to reduce water at the film-solution interface would not have occurred at the light wavelengths and electrode potentials used to study the photo-effect on the anodic oxide (166).

The reason that a large photo-effect was observed at an oxide-coated electrode, whereas a negligible effect was observed at a bare metal electrode (section 9.3.1) is that electrons emitted into the oxide become trapped, preventing their immediate recapture by the metal.

Under the conditions of these experiments there was also a flux of ions in the film. Formation of an electronic space charge in the film would increase the electric field and hence the rate of injection of positive ions across the metal-film interface (sections 9.4.2 and 9.4.3). Formation of an ionic space charge in the film, sufficient to cancel the photo-generated electron space charge, would result. This secondary process (sections 9.4.2 and 9.4.3) would give negative photo-potential or anodic photo-current following the initial change, and the final transient behaviour would reflect the decay of this ionic space charge.
A difference between the two types of metal surface used (electrodes A and B) is consistent with this model, since the zone-refined bismuth (electrode A) and the cast bismuth (electrode B) could be expected to have slightly different work functions for electron emission into the oxide film.

The sign and magnitude of the photo-current in thick anodic films has been described by previous workers in terms of the superposition of an applied field onto an internal field (135-143; section 8.6.2). When the metal is made positive, the two fields are oppositely directed, so that at low applied voltages there is a net negative field in the oxide layer. Such a mechanism is not applicable here, as one of the experimental constraints is that an anodic dark current flows continuously. The new features arise because the anodic film is very thin, so that photo-excitation of the film material is only a small effect (41) compared with direct photo-emission from the metal phase.

9.4.2 Formation and Decay of Space Charge under Galvanostatic Conditions

In a galvanostatic experiment, the current which goes to build up the ionic and electronic space charges (section 9.4.1) is compensated by a current which goes to charge the interfacial capacitance (eq. 9.1), thereby changing the observed electrode potential. The situation can be considered in two stages: (a) a transport of charge at constant potential due to the photo-effect and (b) an equal and opposite transport of charge due to the charging current. The potential changes are caused by this latter process.
While the space-charge currents are very small, and undetectable for longer than 1 ms after the initiation of the flash (potentiostatic experiments), the potential changes resulting can be detected up to several hundred milliseconds after the flash (galvanostatic experiments). The reason is that the capacitance of the metal-film solution system is quite small (~10 \( \mu \)F cm\(^{-2} \)) so that small charge fluctuations give large potential fluctuations.

The following diagrams describe the sequence of events according to the model proposed here. Gauss' theorem is used to give a simple analysis. Space charges are considered as charge densities located in the oxide on a plane parallel to the metal-oxide interface (cf. Chapter 8).

(a) **before flash**

\[
\begin{align*}
\text{metal} & \quad \text{film} & \quad \text{solution} \\
\phi & \quad + & \quad + & \quad h & \quad - \\
\Delta \phi_{\text{o}} & \quad + & \quad \bar{E}_{\text{o}} & \quad -1 & \quad \Delta \phi_{\text{i}} \\
+q_{\text{o}} & \quad + & \quad -q_{\text{o}} \\

\bar{E}_{\text{o}} = q_{\text{o}}/\varepsilon & \quad \text{........................... (9.2)} \\
\text{and } \Delta \phi_{\text{o}} = q_{\text{o}}h/\varepsilon + \Sigma \Delta \phi_{\text{i}} & \quad \text{........................... (9.3)}
\end{align*}
\]

(b) **During flash**

Photo-emission of electrons from the metal to form a space charge \(-q_{\text{e}}\) at a distance \(x_{e}\) from the metal-oxide
interface occurs.

Here, \( \frac{1}{E_1} = \frac{E_o}{\varepsilon} + \frac{q_e}{\varepsilon} \) ........................ (9.4)

and \( \Delta \phi_1 = \Delta \phi_0 + q_e x_e / \varepsilon \) ........................ (9.5)

The interfacial potentials \( \Sigma \Delta \phi_1 \) are assumed unchanged, and hence the observed photo-potential will be:

\[ \Delta \phi = \Delta \phi_1 - \Delta \phi_0 = q_e x_e / \varepsilon \] ........................ (9.6)

The interfacial potentials \( \Sigma \Delta \phi_1 \) are assumed unchanged, and hence the observed photo-potential will be:

\[ \Delta \phi = \Delta \phi_1 - \Delta \phi_0 = q_e x_e / \varepsilon \] ........................ (9.6)

corresponding to the observed maximum photo-potential.

(c) \textbf{After flash; formation of positive, ionic space charge}

The higher field \( \frac{1}{E_1} \) causes the production of extra cations from the metal, which form a positive space charge density \( q_p \) at \( x_p \).
Here, $2E_1 = \overline{E}_o + q_e/\varepsilon - q_p/\varepsilon$ ........................ (9.7)

$2E_2 = \overline{E}_o + q_e/\varepsilon$ ........................ (9.8)

and $\Delta \phi_2 = \Delta \phi_0 + q_e x_e/\varepsilon - q_p x_p/\varepsilon$ ........................ (9.9)

Equation 9.9 shows that the photo-potential will fall due to the ionic space charge (last term in eq. 9.9). When $q_p x_p = q_e x_e$, the photo-potential passes through zero.

(d) **Decay of electron charge, leaving ion charge**

The electron space charge would decay by the thermal activation of trapped electrons into the conduction band of the oxide, and their migration back to the metal. The rate of this process could depend on the field in the oxide layer. The positive space charge would be left behind.
Here, $3E_1^o = E_0^o - q_p/\varepsilon$  

and $\Delta \phi_3 = \Delta \phi_0 - q_p x_p/\varepsilon$  

Hence a negative photo-potential will be observed

$$\Delta E = \Delta \phi_3 - \Delta \phi_0 = -q_p x_p/\varepsilon$$

corresponding to the observed minimum photo-potential.

The final decay is the slow decrease of $q_p$ and increase of $x_p$ as the excess cationic charges pass through the oxide film.

The experimental photo-potential versus time curve can be correlated with the above simple model, thus

$q_e x_e > q_p x_p$

rise of ion charge and decay of electron charge

$q_e x_e = q_p x_p$

decay of ion charge

$q_e x_e < q_p x_p$
The initial rise corresponds to the formation of the electronic space charge. The subsequent fall corresponds to the rise of the ion charge and the decay of the electron charge, and the negative region to the decay of the ion charge.

The charge \( q_e \) is a function of the light intensity and the distance \( x_e \) is an inverse function of the applied current density (or electric field). Thus higher light intensity and lower electric field should increase the maximum photo-potential. The rate of formation of the positive space charge and the rates of decay of both ionic and electronic charges would increase with increasing field, so that the magnitude of the minimum should increase, and the decay times should be shorter.

At sufficiently low field, the decay time of the ionic and electronic charges could be equal so that a negative photo-potential would not be observed. These ideas are consistent with experiment (fig. 9.1 and table 9.1).

9.4.3 Comparison of Galvanostatic Photo-Effect Experiment with Current Pulse Experiment

The current components due to the decay of space charges are the feature of the photo-effect experiment which is absent in the current pulse experiment (section 9.3.5). The following diagram gives another way (idealized) of looking at the problem which emphasizes this point.
The potential of the metal with respect to the reference electrode varies in accordance with the variation in charging current.

9.4.4 Formation and Decay of Space Charge under Potentiostatic Conditions

The formation of an electronic space charge in the oxide by photo-emission from the metal is a transfer of positive charge towards the metal and is therefore a cathodic photo-current. The subsequent decay of electronic and ionic space charges is a transfer of positive charge away from the metal and thus gives an anodic photo-current.
According to the model, the general form of the photo-current transient is therefore:

![Diagram showing light intensity, formation of positive space charge and decay of electron and ion charges over time.]

The lower the potential, the greater the primary photo-current, since photo-emission is opposed by the applied field. This is in agreement with experiment (fig. 9.2). However, the complex transient at high electrode potential is difficult to explain with this simple model. At higher field, the magnitude of the photo-emission current may be reduced to a value comparable to the current resulting from bulk photo-excitation of the oxide. Since the light intensity was appreciable throughout the transient, the transient probably reflects an interaction of the two effects above, as bulk photo-excitation would tend to reduce the local electric field at the metal-film interface, allowing photo-emission to occur subsequently.

The primary cathodic photo-current observed is a net transfer of electrons from the metal into the oxide, i.e.
into trapping states in the oxide. The number of electrons transferred can be obtained from the total cathodic photocurrent, and would give a lower limit to the density of traps in the oxide. From fig. 9.2, at \( E = 250 \text{ mV} \), the lowest potential used, the total cathodic photocurrent transferred from the metal into the oxide was 0.2 \( \mu \text{C cm}^{-2} \). Using \( h = 4 \text{ nm} \), and \( 1.6 \times 10^{-19} \text{C per electron} \), one obtains the number of electrons transferred as \( 3 \times 10^{18} \text{ cm}^{-3} \) of oxide. That is, the trap density in the oxide is

\[
N_T > 3 \times 10^{18} \text{ cm}^{-3}
\]

This is a large number, comparable in magnitude to the trap density observed in anodic \( \text{Ta}_2\text{O}_5 \) (about \( 10^{18} \text{ cm}^{-3} \) (38)). The molar volume of \( \alpha-\text{Bi}_2\text{O}_3 \), 53 \( \text{cm}^3 \text{ mol}^{-1} \), can be used to calculate that the oxide has about \( 10^{22} \) molecule \text{cm}^{-3}. The above value of the trap density therefore corresponds to a mole fraction of lattice defects of about \( 3 \times 10^{-4} \).

An estimate of the electron mobility, \( \mu \), in the anodic oxide can be obtained by combining this value of \( N_T \) with the conduction band lifetime \( \tau_c = 2 \times 10^{-2} \text{ s} \) (section 8.5.1) and the relation

\[
N_T \mu \tau_c = 3 \times 10^7 \text{ cm}^{-1} \text{ V}^{-1}
\]

found in Chapter 8. The result:

\[
\mu = 5 \times 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}
\]

is very low value for the mobility, consistent with a conduction process in which an electron 'hops' between localized states (168).
9.5  Summary

(a) Transient potential changes under galvanostatic conditions and current changes under potentiostatic conditions following flash illumination of a bismuth anode carrying a 4 nm thick oxide film have been studied.

(b) A model involving internal photo-emission of electrons from the metal into the oxide, with the subsequent formation of a positive space charge in the film by movement of cations from the metal was in qualitative agreement with the results.

(c) Gauss' theorem has been used to relate the transient potential or current changes to the formation and decay of the space charges.

(d) The following parameters for the bismuth anodic film have been obtained by combining numerical results from this chapter and from Chapter 8.

- Trap density, \( N_T > 3 \times 10^{18} \text{ cm}^{-3} \)
- Electron mobility, \( \mu = 5 \times 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \)
- Lifetime of a conduction electron, \( \tau_c = 2 \times 10^{-2} \text{ s} \)
CHAPTER 10
EFFECT OF HALIDES ON TRANSIENT PHOTO-
CONDUCTIVITY IN VERY THIN BISMUTH ANODIC FILMS

10.1 Introduction
In Chapter 7, the cyclic voltammetry of bismuth in weakly acidic buffer solutions with halide additives was presented, and the possibility of incorporation of halide ions into the anodic film discussed. In this chapter, the transient photo-conductivity of the films formed in such solutions will be presented.

An aqueous acetate/borate/perchlorate buffer of ionic strength 1.0M and pH 5, containing iodide, bromide or chloride at a concentration of 0.01M was used. Both galvanostatic and potentiostatic conditions were employed. A change in the sign of the photo-effect from that observed in the absence of additives (Chapter 9) was observed with iodide or bromide but not with chloride additive, and was explained in terms of the photo-excitation of halide ions incorporated in the anodic film.

10.2 Experimental
The methods used were described in Chapter 9. Both zone-refined (A) and cast (B) electrodes were used. A two-compartment cell was employed for experiments with iodide present, as described in Chapter 7. Pre-electrolysis with nitrogen stirring in a two compartment cell ensured the absence of iodine from iodide-containing electrolytes (Chapter 7).
Film thicknesses were obtained by measurement of capacitance and formation charge, as previously described (Chapters 8 and 9). The value of the dielectric constant of anodic Bi₂O₃ was used in the computation of film thickness from capacitance. The thickness was determined as 5 ± 1 nm in all cases.

The electrode was polarized throughout the measurements. Ion-exchange at the film-solution interface would therefore give a layer of bismuth oxohalide at the film-solution interface (Chapter 7). In the case of iodide-containing electrolytes, the anodic film was probably BiO\textsubscript{I} (Chapter 7).

Light intensity was altered by changing the energy input to the flash tube. In the following \( \frac{1}{2} \) denotes 80J and 1 denotes 160J input to the flash tube.

10.3 Results

10.3.1 Photo-Effect in the Presence of Chloride, under Galvanostatic Conditions

Photo-potential transients observed on photo-excitation of a bismuth electrode anodized in a solution containing chloride at pH 5 are shown in fig. 10.1. They are qualitatively similar to those observed in the absence of halide (Chapter 9). The photo-potential was positive at first, went through zero to a minimum (negative) value and then relaxed very slowly to zero. The coordinates of the minimum and maximum photo-potential are recorded in table 10.1.
Fig. 10.1  Photo-potential of very thin bismuth anodic film in presence of chloride (galvanostatic conditions)

pH 5; (Cl\textsuperscript{-}) = 0.01M; 25\textdegree C; 5 nm thick film; electrode B; L = 1.

time variation of light intensity shown -------
(arbitrary units)
The magnitude of the minimum and maximum photopotential was smaller than the corresponding value in the absence of halide (table 9.1). However, the rate of the various decay processes was similar in the two cases.

10.3.2 Photo-Effect in the Presence of Bromide, under Galvanostatic Conditions

The photo-effect in the presence of bromide was more complicated (fig. 10.2). At low applied current, (<45 \( \mu A \ cm^{-2} \)), the photo-potential was positive at first, changing sign later, as before (Chapter 9). However, at higher applied current (450 \( \mu A \ cm^{-2} \)), the initial photo-potential was negative, in contrast to the behaviour exhibited in the absence of halide (Chapter 9), and decayed steadily to zero. The decay process showed an initial rapid rate equal to the decay rate of light intensity (fig. 10.2), and a final, much slower rate. The coordinates of the turning points of the transients are collected in table 10.1.

10.3.3 Photo-Effect in the Presence of Iodide, under Galvanostatic Conditions

In the presence of iodide, the photo-potential was negative throughout the course of the transient for the range of applied current used (4.5 to 45 \( \mu A \ cm^{-2} \)), and much larger in magnitude than that observed in the previous cases (no additive, chloride or bromide), fig. 10.3. The behaviour is similar to that observed in Chapter 8, for the photo-effect in thick anodic oxide layers.
Fig. 10.2 Photo-potential of very thin bismuth anodic film in the presence of bromide (galvanostatic condition)

pH 5; (Br\(^-\)) = 0.01M; 25\(^\circ\)C. 5 nm thick film;
electrode A. \( L = 1 \) and its time variation is shown as

\[
\Delta E / \text{mV}
\]

\[
\begin{align*}
\text{t/\text{ms}} & \quad 0 & \quad 2 & \quad 4 & \quad 6 & \quad 8 & \quad 10 & \quad 20 & \quad 30 \\
\Delta E / \text{mV} & \quad -12 & \quad -8 & \quad -4 & \quad 0 & \quad 4 & \quad 8 & \quad 12 \\
\end{align*}
\]

\[
4.5 \mu A \text{ cm}^{-2}
\]

\[
45 \mu A \text{ cm}^{-2}
\]

\[
450 \mu A \text{ cm}^{-2}
\]
Fig. 10.3 Photo-potential of very thin bismuth anodic film in the presence of iodide (Galvanostatic conditions)

pH 5; (I⁻) = 0.01M; Electrode A; 25°C; 5 nm thick film.

photo-potential was negative for the whole course of the transient. Time variation of light intensity (arbitrary units) shown -------.
Table 10.1 Coordinates of turning points of photo-potential transients at constant applied current, in the presence of halides

pH 5; 25°C; film thickness 5 nm.

<table>
<thead>
<tr>
<th>Add</th>
<th>electrode</th>
<th>L</th>
<th>i (µA/cm²)</th>
<th>ΔE (mV)</th>
<th>E∞ (mV)</th>
<th>ΔE/mV maximum</th>
<th>t/µs</th>
<th>ΔE/mV minimum</th>
<th>t/µs</th>
</tr>
</thead>
<tbody>
<tr>
<td>I⁻</td>
<td>A</td>
<td>½</td>
<td>45</td>
<td>338</td>
<td>-54</td>
<td>1.3</td>
<td></td>
<td>-65</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>0.01M</td>
<td>1</td>
<td>36</td>
<td>331</td>
<td>-24</td>
<td>1.2</td>
<td></td>
<td>-33</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>½</td>
<td>1</td>
<td>36</td>
<td>331</td>
<td>-33</td>
<td>1.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>½</td>
<td>1</td>
<td>36</td>
<td>313</td>
<td>-21</td>
<td>1.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>½</td>
<td>1</td>
<td>36</td>
<td>313</td>
<td>no maximum; photo-potential always negative</td>
<td>-23</td>
<td>1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>½</td>
<td>1</td>
<td>4.5</td>
<td>287</td>
<td>-11.5</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>½</td>
<td>1</td>
<td>4.5</td>
<td>287</td>
<td>-14.0</td>
<td>1.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br⁻</td>
<td>A</td>
<td>½</td>
<td>450</td>
<td>360</td>
<td>-4.7</td>
<td>0.5</td>
<td></td>
<td>-10.0</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>0.01M</td>
<td>1</td>
<td>450</td>
<td>360</td>
<td>-10.0</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>primary photo-potential negative</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>primary photo-potential positive</td>
<td>1</td>
<td>45</td>
<td>254</td>
<td></td>
<td>maximum present but not measured</td>
<td>-5.3</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>4.5</td>
<td>240</td>
<td>13</td>
<td>0.4</td>
<td>not measured</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl⁻</td>
<td>B</td>
<td>1</td>
<td>210</td>
<td>360</td>
<td>6.4</td>
<td>0.3</td>
<td>-12.4</td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.01M</td>
<td>1</td>
<td>110</td>
<td>344</td>
<td>10.2</td>
<td>0.4</td>
<td>-6.8</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>21</td>
<td>302</td>
<td>21</td>
<td>0.4</td>
<td>-5.3</td>
<td>90</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: L refers to the distance from the light source.
An exponential decay of the photo-potential was observed, but the rate constant depended upon the applied current, being higher at higher current, in contrast to the behaviour seen in Chapter 8.

The photo-potential was increased by increasing the intensity of the flash. The coordinates of the minimum of the transient are in table 10.1.

10.3.4 Photo-Effect in the Presence of Iodide, under Potentiostatic Conditions

A typical result is shown in fig. 10.4. The photo-current was large and always anodic (E in the range +290 to +350 mV), in contrast to the effect observed in the absence of halide (Chapter 9). It showed two components - a peak and a slowly relaxing tail. The current during the peak followed the light intensity and the tail showed an exponential decay, fig. 10.4:

\[
\Delta i = \Delta i_0 \exp\left(-t/\tau\right)
\]

(10.1)

The decay time constant, \(\tau\), was independent of the applied potential (table 10.2):

\[\tau = 1.5 \pm 0.2 \text{ ms}\]

The peak photo-current increased with increasing applied potential. The time at which the rapid decay of the peak changed into the slower decay of the tail (break-point) was independent of applied potential, and probably simply related to the decay of light intensity. Data is given in table 10.2.
Fig. 10.4 Photo-current at constant potential; iodide-containing electrolyte

\[ E = 315 \text{ mV}; \quad \text{pH 5}; \quad 25^\circ \text{C}; \quad \text{electrode A.} \]

\[ (I^-) = 0.01 \text{M} \]

------------- light intensity (arbitrary units)

\[ \Delta i/\text{mA cm}^{-2} \quad \text{time constant, } \tau = 1.7 \text{ ms} \]

\[ t/\text{ms} \]
Table 10.2 Characteristics of Photo-Current Transients under Potentiostatic Conditions (Iodide Addition) (see fig.10.4)

(I\(^-\)) = 0.01M; pH = 5.0; 25\(^\circ\)C; 5 nm thick film

\(E\) = applied potential; \(i_\infty\) = steady-state (dark) current

<table>
<thead>
<tr>
<th>(E) (mV)</th>
<th>(i_\infty) ((\mu)Acm(^{-2}))</th>
<th>peak coordinates</th>
<th>breakpoint coord.</th>
<th>tail parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>59</td>
<td>710</td>
<td>0.44</td>
<td>190</td>
</tr>
<tr>
<td>330</td>
<td>36</td>
<td>520</td>
<td>0.61</td>
<td>130</td>
</tr>
<tr>
<td>315</td>
<td>20</td>
<td>400</td>
<td>0.58</td>
<td>100</td>
</tr>
<tr>
<td>300</td>
<td>10</td>
<td>310</td>
<td>0.62</td>
<td>86</td>
</tr>
<tr>
<td>290</td>
<td>6.8</td>
<td>230</td>
<td>0.69</td>
<td>91</td>
</tr>
</tbody>
</table>

10.4 Mechanism of the Thin-film Photo-Effect in the Presence of Halides

In Chapter 7, the possibility of nucleation of anodic BiOI in acidic solutions containing \(I^-\) was discussed, eq.10.2:

\[\text{Bi}^{(m)} + \text{H}_2\text{O} + I^- (\text{aq}) \rightarrow \text{BiOI} (s) + 2\text{H}^+ (\text{aq}) + 3\text{e}^- (\text{m}) \]  \hspace{1cm} (10.2)

In solutions of other halide ions, the incorporation of halide as an impurity anion in anodic \(\text{Bi}_2\text{O}_3\) was proposed, eq. 10.3:

\[\text{Bi}_2\text{O}_3 (s) + 3\text{H}^+ (\text{aq}) + 6X^- (\text{aq}) \rightarrow 2(\text{Bi} | \Box\text{Bi}) + 2\Box\text{Bi}'''' + 6(X | \Box\text{O})^\cdot + 3\text{OH}^- (\text{aq}) \]  \hspace{1cm} (10.3)

where \(X\) denotes halide, \(\Box\text{Bi}\) a bismuth lattice site and \(\Box\text{O}\) an oxygen lattice in anodic \(\text{Bi}_2\text{O}_3\). Equation 10.3 shows how 6\(X^-\) take up positions in the lattice normally occupied by \(\text{O}^{2-}\).
The new photo-effect observed in this chapter was an initial negative photo-potential (galvanostatic conditions) upon flash illumination of a very thin film (5 nm) polarized in iodide-containing solution or in bromide-containing solution at higher current density (i.e., higher electric field). It could occur as a result of the interaction of light with halide ions in the anodic film. Equation 10.4 shows the photo-chemical reaction for BiOI.

\[(I | \square_1) + h\nu + (I | \square_1)' + e' \quad \cdots \cdots \quad (10.4)\]

Most of the electrons would promptly recombine (reverse of equation 10.4) but some would move towards the metal giving a negative photo-potential, opposite to the effect of photo-emission of electrons from the metal discussed in Chapter 9. In the case of Br\(^-\) additions, where the Br\(^-\) ion is an impurity ion in the lattice, as shown in eq. 10.3, a similar photo-chemical reaction would occur, giving \((Br | \square_0)''\). In other words, the incorporation of halide ions into the anodic film would increase the amount of light absorbed in the film and so decrease the importance of internal photo-emission. The observed effect would show the combined result of photo-excitation in the film (eq. 10.4) and photo-emission from the metal, and would depend on the applied field, the nature of the halide ion and the amount of it incorporated in the film. Table 10.3 summarizes the interpretation.
Table 10.3  Mechanism of the thin-film Photo-effect in the Presence of Halides

<table>
<thead>
<tr>
<th>Halide</th>
<th>Dominant Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride</td>
<td>Internal photo-emission from metal</td>
</tr>
<tr>
<td>Bromide</td>
<td>Either internal photo-emission or photo-excitation in the film, depending on the applied field</td>
</tr>
<tr>
<td>Iodide</td>
<td>Photo-excitation in the film</td>
</tr>
</tbody>
</table>

10.5  Relaxation of Photo-Current in Potentiostatic Experiments

The movement of electrons towards the metal given by equation 10.4 would give an anodic photo-current at constant potential, as is observed in the presence of iodide (section 10.3.4). The current is actually caused by the movement of electrons in the conduction band of the oxide. Some of these conduction electrons move into the metal, others become trapped in the film. The observed transient results from the superposition of these two effects (130).

The parameter $\tau = 1.5 \pm 0.2$ ms in equation 10.1 is the time constant for the second process, trapping of electrons in the film, equation 10.5

$$e' \rightarrow t' \quad \cdots \quad (10.5)$$

with rate constant $1/\tau$. That is, $\tau$ is the average lifetime of a conduction electron in the anodic film (131). This
number is much less than the lifetime in anodic Bi$_2$O$_3$ determined in Chapter 8: $\tau_c = 23$ ms. This can be taken as evidence for a different structure for the anodic film formed in weakly acidic iodide solutions, in support of the conclusion of Chapter 7 that BiOI is formed (pH 5).

10.6 Relaxation of Photo-Potential in Galvanostatic Experiments

The relaxation of the photo-potential shown in figs 10.1, 10.2 and 10.3 was complex and much slower than the photo-current relaxation under potentiostatic conditions. The photo-current relaxation gives the decay of conduction electrons and the photo-potential relaxation gives the subsequent decay of the space charges formed in the film (trapped electrons and excess cations). Where internal photo-emission is the dominant process, the photo-potential relaxation under galvanostatic conditions has been shown to involve the formation and decay of a positive space charge set up by the injection of extra cations into the film (Chapter 9). Figs 10.1 and 10.2 (low i) show this effect. Where photo-excitation of the film, eq. 10.4 is the dominant process, the relaxation mechanism proposed is (169):

$t^' \rightarrow e^' \rightarrow \text{metal} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots
The mechanism differs from the recombination mechanism given in Chapter 8 in the step (10.5). Equation 10.5 is important because the film is very thin. Capture of electrons by the metal leaves a positive space charge behind, which relaxes in a complex manner dependent on the applied electric field (eq. 10.7). Figs. 10.2 (high i) and 10.3 show this effect. The photo-potential remains negative because equations 10.5 and 10.6 are both equivalent to a movement of positive charge away from the metal.

The recombination process (reverse of eq. 10.4):

\[ t' + e' \quad \text{............. (10.9)} \]
\[ e' + (\text{I} | \text{O}_1) - (\text{I} | \text{O}_1) \quad \text{............. (10.10)} \]

would give a decay constant independent of the applied field corresponding to the rate of equation 10.9 (see Chapter 8).

In potentiostatic experiments, the current flowing as a result of the decay of trapped electrons (equations 10.6 and 10.7) was too small to detect. However, the potential changes resulting in galvanostatic experiments were marked (see Chapter 9).

10.7 Summary
(a) The photo-effect on very thin (5 nm thick) bismuth anodic films formed in solutions of pH 5 containing halides has been investigated.
(b) The initial photo-effect had the same sign as in the absence of additives in the case of bromide at low field or chloride, and the opposite sign in the case of bromide at high field or iodide as the solution additive.

(c) The result has been explained in terms of the competing effects of internal photo-emission of electrons from the metal and of photo-excitation of halide ions incorporated into the anodic film.

(d) The lifetime of a conduction electron in the anodic film formed from iodide-containing electrolyte at pH 5 was 1.5 ms, much less than the lifetime in anodic Bi$_2$O$_3$ (23 ms, Chapter 8). In the former case, the anodic layer was probably BiOI.
CHAPTER 11

CONCLUSION

In this thesis, two important ideas of general significance have been developed and applied specifically to the case of bismuth anodic oxide films:

(a) Cathodic reduction of the anodic film occurs at the film-solution interface, the layer of metal formed spreading backwards through the film. The mechanism involves injection of electrons from the metal into the film (Chapter 2).

(b) The anodic film has an n-type, non-stoichiometric (excess metal) layer at the metal-film interface (Chapter 5). This layer gives the transient conductivity effects observed.

Other conclusions, specifically concerning the behaviour of bismuth anodic oxide films have been:

(c) The films crack as they thicken, affecting the kinetics of film growth (Chapters 3 and 4).

(d) In the early stage of formation of a bismuth anodic oxide film, the layer thickens at the same time as it spreads to cover the surface. The rate of spreading is proportional to the area not covered (Chapters 2 and 3).
Films containing halide ions can be formed at low pH (Chapters 7 and 10).

Film dissolution, breakdown and pitting limits the thickness to which a film can be grown. This is only 4 nm at pH 5, increasing to over 200 nm at pH 13 (Chapter 2).

The photo-effect on a 240 nm thick anodic film results from photo-excitation in the film. The photo-effect on a 4 nm thick anodic film results from internal photo-emission from the metal. An alternative interpretation, not previously considered, is that the n-type layer at the metal-film interface ((b) above) could be the source of the photo-electrons in this case. Incorporation of bromide or iodide into such very thin films (5 nm thick) can be detected by a change in the sign of the primary photo-effect. Some idea of the electronic properties of the films can be obtained, namely that they have a high density of electron traps and a low electron mobility, indicating that the material is somewhat amorphous.

Areas on the bismuth metal surface of different electrochemical potential were detected (Chapters 2 and 4).

The metal formed by cathodic reduction of an anodic film was very porous (Chapters 2 and 4).
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\[ \varepsilon = 18 \mu F \text{ cm}^{-2} \]

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