THE
POTENTIAL
OF THE
ALUMINIUM ELECTRODE

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The open-circuit electrode potential of aluminium cut under deoxygenated 1M KCl solution rises from a minimum potential of -1.65v 20µs after the metal is cut, to a steady potential of -0.9v after several minutes in solution. This behaviour has been investigated. Square-wave current methods were used to determine the change with time in the overvoltage parameters for cathodic, hydrogen ion discharge and for anodic, aluminium dissolution processes. The results indicate that the rise in open-circuit potential can be attributed to a decreasing anodic exchange current from 2.2 x 10^-2 amps/cm^2 at the bare metal surface to 1 x 10^-7 amps/cm^2 after some minutes in solution.

It is concluded that this effect is caused by the formation on the metal surface of a film which conducts electrons, but impedes the dissolution of aluminium. The suggestion is made that for aluminium, hydrogen ion may be discharged only from the film covered surface.

An explanation of the potential of -0.5v which has often been observed for aluminium in aerated chloride solution is offered.
2. INTRODUCTION

2.1 Historical Note

In the century following the first experiments in electrochemistry by Galvani in 1786, many basic fundamentals of electrochemistry were discovered by now famous scientists. However, investigation of the potential behaviour of polarised electrodes was not considered until 1904, when Tafel\(^1\) propounded an empirical relationship (equation (2.1)) between electrode potential and applied external current.

\[
V = a + b \ln i
\]  

(2.1)

The constants \(a\) and \(b\) characterise each electrode electrolyte system. Unfortunately the relationship between current and potential was incorrectly interpreted in terms of quasi equilibrium concepts and a thermodynamic terminology that persisted with some authors to the 1940's. Butler\(^2\) in 1924 first suggested a kinetic approach, but the essentially correct relationship between the current and overvoltage (that is the voltage between the measured potential and the reversible potential of the electrochemical process in the same electrolyte solution) was not given until 1930 (Erdéy-Cruz and Volmer\(^3\)). Further theoretical development by other authors, together with experimental verification\(^4,5\), has led to the general acceptance of the electrode kinetic theory as the explanation for the Tafel type behaviour of polarised electrodes. Equation (2.2) is the description of the overvoltage behaviour of the electrode in terms of the kinetic parameters \(\alpha\) and \(i_0\), which are termed, respectively, the overall transfer coefficient and the exchange current for the electrode reaction (see p.11).

\[
\eta = V - F = \frac{RT}{\alpha F} \ln \frac{i_0}{i}
\]  

(2.2)
The symbol $E$ is the reversible potential for the process and $\gamma$ is the overvoltage, $R$, $T$ and $F$ have their usual meaning. Equation (2.2) has the same form as the Tafel equation (2.1) as can be seen if $a$ and $b$ are given the following values.

\begin{align*}
a &= \frac{RT}{\alpha F} \ln i_0 + E \quad (2.3) \\
b &= -\frac{RT}{\alpha F} \quad (2.4)
\end{align*}

A plot of the Tafel lines, overvoltage versus log current density, from equation (2.2) is illustrated in fig. 2.1 for a reduction, that is, a cathodic process.

![Tafel lines diagram](image-url)

Fig. 2.1 An illustration of the Tafel lines for a cathodic process.

As the figure shows, $\alpha$ and $i_0$ for the electrode process determine respectively the slope and position of the Tafel line.

Graphical representation of electrode polarisation characteristics has been used, extensively in recent years, to interpret and predict the potential behaviour and susceptibility of metals to corrosion. In this thesis, the polarisation characteristics of aluminium have largely been interpreted using graphical methods similar to those described by
Stern and Geary. A brief resume of the pertinent theory from their papers is given below.

A N oncorroding Electrode System:

Consider a substance $Z$ in a solution containing its ions $Z^+$. In such a system at equilibrium, the rate of oxidation of $Z$ is equal to the rate of reduction of $Z^+$ ($Z^+ + e \rightarrow Z$). $i_{zo}$ is defined as the current in the forward (reduction) direction ($Z^+ + e \rightarrow Z$) and $i_{za}$ as the current in the reverse (oxidation) direction ($Z \rightarrow Z^+ + e$), the electrode equilibrium may be expressed in the form

$$i_{zo} = i_{za} = i_{oz} \quad (2.5)$$

When the reaction rate is controlled by a slow step requiring an activation energy, the dependence of current on overvoltage may be expressed as

$$i_{zo} = i_{oz} \exp \left( -\frac{\alpha \theta F}{RT} \right) \quad (2.6)$$

$$i_{za} = i_{oz} \exp \left( +\frac{\alpha \theta F}{RT} \right) \quad (2.7)$$

These relationships which are the inverse of equation (2.2) are plotted on fig. 2.2 by arbitrarily giving $2.3RT \alpha \theta F$ and $2.3RT \alpha \theta$ a value of 0.100 volts (v) and $i_{oz}$ a value of 1.0 μamps. When the electrode equilibrium is disturbed by an external current, the reaction rates change in accord with the curves in fig. 2.2, the external current used being a measure of the difference between the two rates. That is, for polarisation by an external cathodic current $i_{xc}$, we have

$$i_{zo} - i_{za} = i_{xc} \quad (2.8)$$

It is evident that at overvoltages greater than 100 mV, $i_{xc}$ approaches $i_{zo}$; that is, $i_{za}$ becomes negligible. It is important to realise the
Fig. 2.2 Relationship between overvoltage and current for the anodic and cathodic reactions of a single electrode system.

Only factors that can be measured directly are \( V \) and \( i_{x0} \). Using the same arbitrary values of the constants \( \frac{2.3RT}{\alpha F} \) and \( i_{oz} \) as indicated previously, and knowing the relationship between \( \eta \) and \( i_{oz} \), a plot of the variation of \( \eta \) with \( \log i_{x0} \) may be constructed. Such a plot, fig. 2.3, demonstrates that the linear Tafel behaviour applies only over a restricted current density range. This figure also shows the deviation from Tafel behaviour caused by concentration polarisation.
Overvolta.ge

"I

\[ f = -2 \cdot 3 \cdot \ln(x) \]

\[ \eta = \frac{2.3RT}{\alpha F} \ln\left(\frac{i_{xo}}{i_{oz}}\right) \]

\[ -2.3RT \alpha F = 0.100 \]

\[ i_{oz} = 1.0 \mu\text{amps/cm}^2 \]

Applied Cathodic Current Density \( i_{xo} \) (\( \mu\text{amps/cm}^2 \))

**Fig. 2.3** Relationship between overvoltage and applied cathodic current for a single electrode system with the effect of concentration polarisation.

Corroding Electrode System:

Two concurrent electrochemical reactions must now be considered:

(i) a reduction (cathodic) process \( Z^+ + e^- \rightarrow Z \)

(ii) an oxidation (anodic) process \( M \rightarrow M^+ + e^- \).

The only case discussed here is where the reverse reactions for both these processes may be considered negligible. Each of these processes has its own exchange current and Tafel slope, so that the steady state potential of the corroding metal is such that the total rate of oxidation equals the total rate of reduction. Thus, at the steady state corrosion potential or mixed potential, the currents from the cathodic and anodic processes are equal

\[ i_{zo} = i_{ma} \quad (2.10) \]
Fig. 2.4 illustrates the potential-current relationship for such a mixed electrode system. The metal oxidation system has been drawn assuming an $i_{om}$ of 0.1 amps, a $\frac{2.3RT}{\alpha F}$ value of 0.060v, and a reversible potential of -0.160v. The Tafel constants for the $Z$ reduction system are as previously described. Experimentally, however, the individual parameters $i_0$ and $\alpha$ cannot be measured within the mixed potential region because of the unknown magnitude of the internal or corrosion current.

![Diagram of potential-current relationship](image)

**Fig. 2.4 Relationship between potential and current for a mixed electrode system.**

The expected curve of the overvoltage as a function of applied cathodic current $i_{x0}$ for the system described above has been plotted on fig. 2.5. As shown by the figure, true Tafel behaviour for this corroding electrode system does not occur until polarising currents appreciably greater than the corrosion current are applied. The internal or local action current $i_{int}$ is represented in the figure by $i_{ma}$. 
2.2 Literature Survey

The highly electronegative reversible potential of aluminium -1.67 volts*, calculated from thermodynamic data by Latimer 7, suggests that like other highly electronegative metals such as sodium or calcium, aluminium should corrode rapidly and spontaneously in aqueous electrolyte solution. On the contrary the corrosion rate of aluminium in neutral solutions is generally negligible 8, except in aerated chloride solutions where Akimov and Glushova 9 have reported that the corrosion rate was as much as one thousand times greater than in sulphate solutions. The protection of aluminium metal against severe corrosion is generally credited to a thin 15-20Å, adherent, stable oxide film covering the surface. The high corrosion rates and low potentials observed in strongly alkaline solutions 10,11 and on amalgamated electrodes 12 have

*The Normal Hydrogen Scale has been used throughout this thesis.
been attributed to the disruption of this protective oxide film.

Open-circuit potential measurements made under specific conditions have been commonly used by previous authors for investigating the corrosion mechanism on aluminium. The aim of such work has been to identify the processes responsible for the observed electrode potentials. The aluminium electrode potential measured in aqueous solutions was more positive, usually by about a volt, than the reversible potential, and showed a remarkable degree of consistency between the measurements made by different authors for conditions of similar ion type, concentration and pH. For aluminium immersed in aerated normal chloride solutions, potentials close to -0.50v have been reported by several authors 13-16.

When oxygen was removed from the solution, French and Kahlenburg 13 reported that the aluminium electrode potential shifted "reversibly" to a more negative value. They interpreted this observation as supporting the idea that adsorbed oxygen, not an oxide film, was responsible for the more positive potential. Electrochemical reduction of aluminium oxide was improbable because of the stability of aluminium oxide and its fixed valency 17, but Hagyard and Santhiapillai 18 and Heine, Keir and Pryer 19 have shown that slow direct dissolution of aluminium oxide takes place in chloride solutions. Ergang, Masing and Mohling 14 have proposed a continuous film breakdown and formation mechanism to explain the observed potentials. Petrocchi 20 has advanced a mixed potential mechanism 22, involving cathodic hydrogen ion discharge and anodic aluminium dissolution, to explain his potential measurements.

However, the interpretation of these electrode potential measurements is open to question because of the ill-defined surface condition resulting from air oxidation of the electrodes prior to the experiments.
Ultra-violet reflectance studies by Hass\textsuperscript{23} and weight gain measurements by Trapnell\textsuperscript{24} and others\textsuperscript{25,26} have established that oxygen reacts quickly and spontaneously with freshly evaporated aluminium surfaces to form a 15-20\% oxide film. Because of the complexities involved in determining the reaction rates on oxide-covered electrodes, Hagyard and co-workers initiated a study of the electrode kinetics on unoxidised aluminium surfaces.

To carry out this investigation a promising new experimental technique was devised, whereby a polythene insulated aluminium rod was cut under solution in microseconds with a ruby. The potential of the cell, cut aluminium electrode 1N. calomel half-cell, was measured oscillographically through a high-impedance (5 x 10\textsuperscript{8} ohms) fast response (2\textmu s) cathode follower.

Williams and Hagyard\textsuperscript{21} give a detailed description of the electrode behaviour within 10 milliseconds (ms) of cutting the electrode, fig. 2.6. This measurement made by Williams is reprinted using the conventional co-ordinates, negative down.

![Fig. 2.6](image)

Fig. 2.6 Open-circuit potential versus time oscillographic trace for an electrode cut under 1N.KCl solution pH 5.2. C, peak potential; D-E mixed potential.
In photograph, fig. 2.1, A-B was the potential of the insulated aluminium electrode prior to cutting the electrode. At B the electrode was cut under solution, the electrode potential fell within microseconds to about -1.6v at C, from C the potential rose in 2-3ms to a plateau potential D-E at about -1.4v. The time and voltage scales for the measurement were taken from the 300 o/s sinusoidal trace, oscillating between zero and the potential of one Weston standard cell. The 20 microseconds (µs) fall in potential from A-B to -1.6v at C, was ascribed to anodic aluminium dissolution. The potential of -1.6v was more negative than any previously reported open-circuit aluminium electrode potentials in solutions of pH less than 12. The millisecond potential rise C-D was attributed to the establishment of the mixed potential D-E at -1.4v (solution pH 5.2) between the simultaneously occurring anodic and cathodic (hydrogen ion discharge) processes. Williams also found that the mixed potential decreased by between 0.12 to 0.05v per unit pH change in the range pH 2 to 5 but was unaffected by aluminium ion concentration.

Subsequently Earl\textsuperscript{27} has extensively investigated the kinetics of the anodic and cathodic processes occurring at the electrode within 5 ms of the cut. His kinetic parameters for aluminium dissolution measured within 0.1 ms of the cut were: \(\alpha = 0.10, i_o = 2.15 \times 10^{-2} \text{amps/cm}^2\), \(\text{Cdl} = 1.4 \mu\text{F/cm}\), and for hydrogen ion discharge measured 1 to 5 ms later \(\alpha = 0.225, i_o = 2.3 \times 10^{-6} \text{amps/cm}^2, \text{Cdl} = 7.6 \mu\text{F/cm}^2\). Earl attributed the positive transient in the 2 ms after the cut to a sudden change in the proportion of electrode area acting as anode and cathode. On this basis he found that the area changed from totally anodic in the microsecond region of rapidly falling potential B-C, fig. 2.6, to 200:1.
cathodic to anodic area ratio at the mixed potential D-E.

Criticism that the initial potential transient was a spurious signal generated by the fast cutting technique was dispelled by two experiments. First\(^2^9\), the potential of unoxidised aluminium electrodes formed by high vacuum evaporation was, at the instant of contact with solution, close to \(-1.65\)\,V. The potentials of these evaporated aluminium films all fell within the statistical limits of the minimum potentials measured on electrodes cut under solution. Second\(^3^0\), the well established cadmium reversible potential was attained by cadmium electrodes cut under solution in the same manner as that used by Williams\(^2^6\).

Williams\(^2^8\) made a few 15-second exploratory observations on electrodes cut under both air and hydrogen saturated electrolyte solutions. In air-saturated solutions, the potentials rose in a few seconds from the initial minimum potential of around \(-1.6\)\,V to an unsteady potential that fluctuated with small amplitude about \(-0.48\)\,V. Hagyard and Williams\(^2^1\) postulated that the slow potential rise was due to molecular oxygen, dissolved in solution, diffusing to and reacting with the electrode surface to form a mono-molecular oxide film layer. In hydrogen-saturated solutions pH 5.2, Williams reported that the potential was visually observed to remain constant and steady at about \(-1.2\)\,V from a few seconds after the cut to several minutes later. This potential was about 0.2\,V more negative than the previously reported potentials for air-oxidised electrodes in deoxygenated solutions\(^1^3,1^4\).
2.3 Scope of the Present Work

The present work continues that initiated by Williams and Earl by extending the investigations from milliseconds to seconds after the cut. Such an investigation was expected to assist in connecting the fundamental electrode processes with the electrochemical behaviour of aluminium under service conditions. Two questions arose from Williams' observations in hydrogen-saturated solutions pH 5.2:

What caused the potential rise from -1.4v 10 ms after the cut to -1.2v seconds later?

Why did the potential thereafter remain constant at -1.2v?

The explanations postulated by the author to account for this behaviour were a change of mechanism and/or area ratio for the electrode processes, or the onset of film formation. Factors favouring the latter explanation are the high heats of formation of aluminium oxide and hydroxide and the reactivity of the metal. Three possible film growth mechanisms were envisaged:

(i) direct chemical reaction between aluminium and water,

(ii) precipitation of hydroxide on to the electrode from the mixing of cathodic and anodic reaction products,

(iii) film formation by an electrochemical process.

The starting point of the present work was, therefore, to determine whether or not a film was formed on aluminium surfaces cut under deoxygenated solutions.

Open-circuit potential measurements alone, were considered inadequate for detecting the presence or growth of such a film because of the conceivably equal inhibiting effect of a film on both the anodic and cathodic processes. For this reason it was intended to use the
impressed square-wave current experimental techniques and the electrode kinetic analysis that have been successfully applied by Earl in studying the electrode processes occurring within 5 ms after the cut.

Because of the expected complexities, it was intended to limit the investigation to a study of the transient electrode phenomena occurring in the interval between 10 ms to 10 s after the cut, and to confine the measurements to hydrogen-saturated deoxygenated solutions. Deoxygenating the solutions eliminated the added complexities thought to be caused by molecular oxygen reacting with the electrode surface (p. 12).

2.4 Electrode Kinetics

Several authors have derived from the theory of absolute reaction rates the equations expressing the discharge rate of an ion at a static electrode for a single rate-determining step, equation (2.11). The rate of reaction

\[ A^+ + \text{n} \rightarrow B \]

is given by

\[ i = i_0 \left[ \exp \left( \frac{-nF\gamma}{RT} \right) - \exp \left( \frac{(1-\beta)nF\gamma}{RT} \right) \right] \]  (2.11)

The first term of this equation expresses the forward reaction rate and the second term the back reaction rate. \( i \) is the nett current density at the overpotential \( \gamma \). \( i_0 \) is the exchange current density for the process, the current density at zero overpotential. \( \beta \) has been defined by Bookris as that fraction of the potential difference between the solution and the metal electrode that assists the passage of the ions from solution to the transition state. \( n \) is the number of
electrons transferred in the rate-determining step; \( R, T \) and \( F \) have their usual meaning.

When \( \eta \) is greater than \(-100 \text{ mV}\) the rate of the reverse reaction becomes negligibly small by comparison with that of the forward reaction (see fig. 2.2) and equation (2.11) simplifies to

\[
i_c = \frac{i_{\infty}}{i_{\infty}} \exp \left[ \frac{-\alpha \phi F \eta}{RT} \right]
\]  
(2.12)

where \( \alpha \phi = \beta n \).

An equation for the rate of dissolution of ions from a metal, at potentials \( 100 \text{ mV} \) more positive than the reversible potential, can be obtained by similar reasoning.

\[
i = \frac{i_{\infty}}{i_{\infty}} \exp \left[ \frac{\alpha \phi F \eta}{RT} \right]
\]  
(2.13)

where \( \alpha \phi = (1-\beta)n \).

The parameter \( \alpha \) is generally used to report experimental kinetic data because the mechanism and rate-controlling step, and hence \( n \), is generally unknown. \( n \) can be evaluated independently of \( \beta \) at very small current densities and overvoltages where the kinetic equations linearize to

\[
i_0 = - \frac{n_i \gamma F \eta}{RT}.
\]

However, the aluminium electrode cannot be made to comply with these restrictions because of the significant internal corrosion current.

Delahay\(^{34}\) doubts whether the derivation of equations (2.12) and (2.13) from transition state theory for the reduction and oxidation at bare metal surfaces, is valid for film-covered electrodes because the film itself partially determines the kinetics of the electrode processes. However, expressions of the same form as equations (2.12) and (2.13) can be derived\(^{32}\) for the rate of any process controlled by a single activation energy barrier.
3. EXPERIMENTAL

3.1 Outline of the Experimental Work

The object of the experimental work was to interpret the potential rise observed in the period 5 ms to 10 s after the electrode was cut, in terms of the phenomena occurring at the aluminium electrode surface. Up to 0.02 ms after the cut the electrode process was substantially all anodic aluminium dissolution. From 0.02 ms onwards the electrode was at a mixed potential, that is the potential taken up by the electrode was such that the currents from the simultaneously occurring anodic and cathodic processes were equal. The observed potential rise was therefore due to either a decreasing rate of the anodic process or increasing cathodic rate. These rate changes were thought to be caused by one of the following mechanisms:

Anodic - decrease in the anodic overvoltage parameters
- increase in cathodic to anodic area ratio
- film formation

Cathodic - increase in the cathodic overvoltage parameters
- deposition of low hydrogen overvoltage impurities

Without data on the individual anodic and cathodic processes, interpretation of the aluminium electrode mixed potential behaviour was not possible.

Unambiguous data on each process were obtainable only outside the mixed potential region (see p. 6). For the anodic process this would have involved obtaining potential measurements close to the hydrogen reversible potential -0.2v (pH 3.2). Because of the resulting large polarisation and the complications from other processes (see section 9)
the data from measurements made at such potentials were considered to be inapplicable in explaining the phenomena at the mixed potential. Therefore information, useful in interpreting the anodic process, could be deduced only from measurements made within the complex mixed potential region. In the cathodic case, measurements could be made on the hydrogen ion discharge process outside the mixed potential region. Cathodic measurements could be made in solutions of zero aluminium ion concentration, at potentials much more negative than the aluminium reversible potential, where hydrogen discharge was the only possible electrochemical process.

Because of the relative simplicity in studying the hydrogen discharge process alone, the investigation was started by taking cathodic measurements using impressed square wave current techniques similar to those used by Earl 27. These cathodic measurements were expected to show the onset of film formation or any change in hydrogen ion discharge kinetics. It was also anticipated that the cathodic polarisation data so obtained would assist in interpreting the open-circuit mixed potential behaviour. To test whether oxide films could in fact be observed, the cathodic measurements were repeated on electrodes cut both under solution and in an oxygen or water vapour atmosphere with subsequent immersion in the electrolyte. The results and analyses of the cathodic measurements are discussed in detail in section 4.

From the overvoltage parameters determined from the cathodic measurements, the influence of the cathodic process at any potential within the mixed potential region could be calculated and the anodic polarisation deduced. This procedure enabled the anodic parameters
to be evaluated from the mixed potential response of the aluminium electrodes to small, low-frequency, impressed square-wave currents. To observe the effect of oxide films on the anodic process, similar measurements were made on electrodes pre-exposed to oxygen and water vapour. Section 6 covers this part of the investigation.

The best values of anodic and cathodic parameters so determined were then used in interpreting the open-circuit mixed potential behaviour of the electrodes cut under solution and electrodes pre-exposed to oxygen or water vapour, section 7. This whole procedure was far more complicated than it may appear to be from this brief description.

3.2 The Cell

The cell used for potential measurement on electrodes cut under solution has been described by Earl. A modified version of this cell, fig. 3.1, was used for pre-exposing the cut surface of the electrodes to gaseous atmospheres before their immersion in solutions.

The composite electrode, comprising a thin (0.02cm) flange turned from a ½" by ½" cylinder of aluminium screwed on to a 5/16" silver steel shaft, overcame the distortion problems experienced by Earl when using an all aluminium electrode. The cutting tool, a special wedge-shaped ruby (20° front rake and 5° back rake) mounted in a duralumin holder, was aligned with the electrode and fixed into the cell top. The portions of electrode and cutter protruding below the cell top were polythene-coated to electrically insulate (＞50 meg ohms) the uncut electrode surface from the solution as well as to stop contamination of the solution with corrosion products from the cutter. The 40 pF capacity
Fig. 3.1 Construction detail of cell and composite electrode.
of this 0.2 mm polythene coating was negligible compared with the electrode capacity of the cut metal surface. Bookris\(^{37}\) has suspected polythene of contaminating electrode surfaces, but the present work indicates that other factors had an over-riding influence on the potential behaviour of aluminium. The shortened glass boiling tube \(D\), with its end thinned over a small area to allow the electrode to be driven through, was pushed on to the spigot \(C\) to neatly encase the electrode-cutter assembly. The electrode, bearing in an earthed duralumin guide, was struck on the anvil \(G\) by either a falling weight or the swinging arm of a rat-trap device and driven on to and past the cutter through the glass cell and on into the solution.

The cell top used for the measurements on electrodes cut under solution was slightly different from the one shown in fig. 3.1. Gas inlet \(F\) and the glass cell surrounding the electrode and cutter were absent and spigot \(C\) was a push fit into the cell.

The glass tube of the hydrogen lead was connected at \(I\), and a \(1\text{N.}\) calomel half-cell at \(K\), the latter via a cellophane-sealed, glass tube salt bridge. The resistance of the electrolytic circuit was around 1000 ohms. The platinum loading electrode was sealed into the cell wall at \(K\).

The cell was not thermostated since temperature effects\(^{39}\), significant compared with the accuracy of potential measurement, were not expected from the variation in room temperature, 15–20\(^{\circ}\)C.
Sectioned Diagram of Rotating Electrode Cell

Fig. 3.2
Rotating Electrode System:

The need arose during the course of this work to study what effect stirring had on the potential behaviour of aluminium. These measurements were made in the apparatus shown in fig. 3.2, which was devised by the author for cutting a new surface on electrodes rotating under solution. Connected to the polythene cell base of this apparatus were the calomel half-cell, a gas inlet and a platinum loading electrode. The cutter, a ruby mounted in the end of a 5/16" steel rod, protruded from the cell wall and could be advanced towards the cell centre by a micrometer screw feed. The P.T.F.E. baffle, protruding from the cell wall, ensured that turbulent flow conditions were obtainable. The electrode consisted of an aluminium specimen clamped on to the reduced section of a 3/8" steel shaft which rotated in a P.T.F.E. bearing bushed into the polythene cell top. The electrode could be rotated at speeds up to 3600 r.p.m. by a pulley-belt system driven by an A.C. motor. The aluminium specimen was turned to a thin (0.2 mm) flange from which a parallel-sided offset section was cut (see diagram). With an aluminium specimen of this shape it was possible to obtain approximately reproducible current densities since successive measurements were made by turning a thin layer of metal off the outer edge of this offset section. The screw feed arrangement shown was used to slowly push the rotating electrode down past the cutter enabling about 0.002 inches to be turned off the edge of the protruding aluminium section. The earth connection to the electrode was a vertical copper wire dipping into a deep pool of mercury contained in the drilled out centre of the bolt screwed into the top of the steel shaft.
3.3 Measuring Circuit

A block diagram of the electrical circuit is shown in fig. 3.3. The calomel half-cell was connected by a low-capacity unscreened lead into a cathode follower whose input impedance was such that the current drawn from the measuring cell, aluminium electrode-calomel half-cell, was insignificant with respect to the local action or impressed current. For open-circuit and small (\(< 5 \times 10^{-4} \text{ amps/cm}^2\) impressed current density measurements, a $10^{14}$ ohm input impedance cathode follower was used. Measurements at higher current densities and high frequencies (500-5000 c/s) were made with a $5 \times 10^8$ ohm input impedance, 2$\mu$s second rise time cathode follower. The cathode follower circuits are given elsewhere $^{35,40}$.

Stray pick-up in the input circuit was effectively eliminated by shielding the cell and cathode follower in an earthed, sheet steel cabinet. The cathode follower output was fed into a type 535A H amplifier Tektronix oscilloscope and the oscillograph traces were photographed on Ilford HP3 film with an Asahi Pentax camera. The voltage scale was taken from the oscillographic traces of 1 and 2 Weston standard cells fed through the cathode follower and photographed prior to the experiment. The internally calibrated vertical graticule lines on the oscilloscope screen were used as the time-scale for the measurement.

The oscilloscope was triggered either externally just before cutting, or internally from the transient input signal generated at contact between electrode and solution.
Fig. 3.3a Layout of equipment for open-circuit measurements.

Fig. 3.3b Layout of equipment for impressed current measurements.

Fig. 3.4 Current impressor circuit.
3.4 Current Loading Equipment

An external current load, stable within the voltage range \(-4.5\) to \(+4.5\) volts, was applied to the cell, platinum electrode-electrolyte-aluminium electrode, from a simple transistorized, low-output impedance circuit, fig. 3.4. Anodic or cathodic direct current bias was applied by decreasing either resistance D or C respectively.

For static impressed loads, A and B were shorted. For square-wave current loads the electrically floating GRC pulse generator output was connected across terminals A and B. The rise time of the current impressing and measuring circuit, using the 2\(\mu\)sec. rise time cathode follower, was 20\(\mu\)sec.

The impressed current was photographed just before each experiment. The volt drop, induced by the impressed current passing through the standardized carbon resistance S, was recorded against the 1 and 2 standard cell potentials that were fed to the oscilloscope via the cathode follower. The value chosen for the resistance S was such that the volt drop across it fell conveniently within 2 standard cell voltages. The type of trace obtained in measuring the square-wave current is shown in fig. 3.5.

The GRC pulse generator and Tektronix oscilloscope were used only in the later stages of the work. These two pieces of equipment greatly improved the accuracy and ease with which potential time measurements could be made as well as making most of the previously required auxiliary electronic circuitry redundant\(^1\). Because of their comparative inaccuracy, only qualitative indications were taken from the large number of measurements made with the earlier equipment, which has been described by Wakelin\(^4\).
3.5 Materials

The electrodes were of the following analysis:

<table>
<thead>
<tr>
<th>Element</th>
<th>Analysis</th>
<th>Element</th>
<th>Analysis</th>
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<td>0.0014%</td>
<td>Ca</td>
<td>0.1 ppm</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;max&lt;/sub&gt;</td>
<td>0.003%</td>
<td>Cu</td>
<td>0.1 ppm</td>
</tr>
<tr>
<td>Cu&lt;sub&gt;max&lt;/sub&gt;</td>
<td>0.0025%</td>
<td>Mg</td>
<td>0.2 ppm</td>
</tr>
<tr>
<td>Mn</td>
<td>0.2 ppm</td>
<td>C</td>
<td>1</td>
</tr>
</tbody>
</table>

The aluminium used was supplied as \(\frac{1}{2}\)" diameter rods by the Aluminium Association, London, at 99.99% purity and by Light and Co. Ltd, England, at 99.999% purity. The purity difference was not detected in the potential behaviour.

Solutions were prepared from AR quality salts dissolved in deionized
water. Solution purification by pre-electrolysis to remove trace impurities was considered unnecessary since the deliberate addition of 1.3 ppm of Fe ions (5 times the maximum concentration of low hydrogen overvoltage impurities calculated from the AR analyses) did not significantly affect the cathodic polarisation. The solution pH was adjusted by the addition of 1N acid, the anion of which was common to the bulk electrolyte.

Hydrogen was supplied through an all glass line from a Milton Roy palladium tube hydrogen purifier. Oxygen was taken direct from a cylinder of the commercial gas. Practically all the experiments were carried out in 1N KCl solutions with the pH adjusted to 3.2 to avoid undue hydrolysis of the AlCl₃ formed at the anodes, since pH 3.2 was more acid than the pH of stoichiometric AlCl₃ between concentrations of 0.001 to 0.10 normal.

3.6 Experimental Procedure

The electrodes, fig. 3.1, 2, were prepared by turning the flange on the aluminium specimen with a sharp steel turning tool. Contamination of the turned surface with steel was not detrimental to the experiment since this surface was covered with an adherent layer of polythene, whereas the electrode surface was formed from the transverse cut made into the flange by the ruby. The electrodes were degreased by 20 minutes immersion in a stream of refluxing acetone vapour. The insulating polythene coating was applied by dipping the pre-heated (160°C) electrodes into powdered polythene and then fusing the layer by a further 5 minutes heating at the same temperature. The insulated electrode and outer were assembled in the cell as shown in fig. 3.1, 2. The solution 1N KCl, pH 3.2,
or less frequently 1N K₂SO₄; pH 3.2, was deoxygenated and hydrogen-saturated by hydrogen bubbling (3 or 4 bubbles per second) in the 30 minutes prior to the experiment. The equipment was set to the preselected requirements for the experiment and the measurement made. The detailed procedure for each of the several groups of experiments was, with minor modifications, essentially the same as that reported by Wakelin⁴¹. Features of the procedure unique to any one group of experiments are described in the discussion of the experimental results. At the conclusion of each experiment the cut was visually inspected and its area measured under a 10 times magnification, vernier scale, travelling microscope.

3.7 Concentration Polarisation

King⁴³ has calculated that for continuous hydrogen discharge from solutions of pH 3.0, stirred by gas bubbling, the electrode potential decreases by 0.4v at current densities greater than 10⁻³ amps/cm² due to the depletion of hydrogen ions at the electrode surface. Confirmation of this is suggested by the break at about 10⁻³ amps/cm² in the cathodic polarisation curve obtained by Goulding and Downie⁴⁹ on aluminium in solutions of pH 3.0. Calculations have shown that the transient potential decrease observed by the author on cathodically loaded aluminium electrodes cut under pH 3.2 solution can also be attributed to concentration polarisation. In the oscillographic trace shown, fig. 3.6, the current load on the electrode was 4 x 10⁻³ amps/cm². After the electrode was cut, the potential rose in microseconds from -4½v (the driving voltage of the current impressor) to the potential at
A after which the potential decreased until alkaline conditions were presumably reached at B.

In this work, concentration polarisation was avoided at current densities above $5 \times 10^{-4}$ amps/cm$^2$ by taking the potential measurements within 5 ms of applying the cathodic current load, that is before a significant depletion of hydrogen ions had occurred as indicated by the relatively constant potential in the 10 ms following the cut, fig. 3.6. Concentration polarisation was not expected at the non-externally loaded electrode since the internal current was estimated to be normally not greater than $2 \times 10^{-4}$ amps/cm$^2$, nor was concentration polarisation expected from external currents of $5 \times 10^{-4}$ amps/cm$^2$ or less. Stirring was the other method used to eliminate, or at least to reduce concentration polarisation at electrodes cut under solution, although most of the
information obtained from these measurements was not used in the analyses. The concentration polarisation for the rotating electrode apparatus already described (p. 22) was calculated to amount to no more than a pH difference of 0.25 between the bulk electrolyte and that adjacent to the electrode surface at 3600 r.p.m. and a cathodic current density of $10^{-3}$ amps/cm$^2$. This calculation was based on the correlation of Eisenberg, Tobias and Wilke$^{44}$. 
4. THE HYDROGEN DISCHARGE PROCESS

4.1 Hydrogen Overvoltage Parameters from Cathodic Measurements

Aim:

Described in this section are the measurements made with the object of establishing whether or not a change in the hydrogen discharge mechanism occurred in the first few seconds after the electrodes were cut. Earl\textsuperscript{27} has measured the hydrogen discharge overvoltage parameters on aluminium electrodes in the interval 1-5 milliseconds after the electrodes were cut under solution and obtained average values of $\alpha_H = 0.23$, $i_{oH} = 2.3 \times 10^{-6}$ amps/cm\textsuperscript{2}. In the present work the hydrogen overvoltage parameters were measured at 5 and 60 seconds after cutting the aluminium electrodes under solution.

Experimental Method:

These measurements were made using an impressed square-wave current technique, since this method enabled $\alpha$ to be evaluated unaffected by the surface roughness of the electrode. The experimental procedure was as follows. The electrode on open circuit was cut under solution and after 5s, the cathodic square-wave current of between $10^{-3}$ to $10^{-1}$ amps/cm\textsuperscript{2} was switched on momentarily. The abrupt change in electrode potential, caused by the sudden application of the current load, was used to trigger the oscilloscope for a 1 ms/cm single scan of the oscilloscope beam which was recorded photographically. 55s later the current was again switched on momentarily and another potential time trace recorded. Examples of these traces are shown in fig. 4.1.
Fig. 4.1a and b Cathodic square-wave current measurement

Trace 1 Current calibration

Trace 2 Open-circuit potential-time trace 0-10ms after cutting the electrode under 1M KCl pH 3.2

Trace 3 Potential time response of the aluminium electrode to a cathodic square-wave current of \(1.06 \times 10^{-2}\) to \(1.69 \times 10^{-2}\) amps/cm\(^2\)

Trace 4 Open-circuit potential 60s after cutting the electrode

Trace 5 Potential time response 60s after cutting the electrode
Method of Calculation:

The simple form (equation (4.1)) of the general kinetic equation (2.11) applied to these cathodic measurements made at potentials more negative than -1.7V, since the hydrogen overvoltage was more than 100 mV (see p.15).

\[ i = i_{dl} \exp \left( -\frac{\alpha_H F}{RT} (V - E_H) \right) \]  \hspace{1cm} (4.1)

Equations (4.2) and (4.3) which were deduced from equation (4.1) were used to evaluate \( \alpha_H \) and \( i_{dl} \) from the equilibrium potentials \( V_1 \), \( V_2 \) and overvoltages \( \gamma_1 \), \( \gamma_2 \) at two levels of current density \( i_1 \) and \( i_2 \). The values of these variables were measured from the recorded oscillographic potential-time traces, where \( V_1 \) and \( V_2 \) are the potentials of the flats or steady electrode potentials reached at each level of the impressed square wave current.

\[ \alpha_H = \frac{RT}{(V_2 - V_1)} \ln \frac{i_1}{i_2} \]  \hspace{1cm} (4.2)

\[ i_{dl} = \frac{\gamma_2 \ln i_1 - \gamma_1 \ln i_2}{V_2 - V_1} \]  \hspace{1cm} (4.3)

The actual calculations were done by an IBM 1620 computer, using a program written by Earl. This program calculated the 90% confidence limits on the average \( \alpha_H \) and \( i_{dl} \) for each group of experiments, as well as correcting the measured potentials for electrolyte ionic resistance. Since the major solution resistance was in the electrolyte close to the electrode, its affect was estimated by assuming the current conduction paths adjacent to the electrode, to be along the radii of the segment of a sphere (radius 2 mm, included angle equal to the ruby cutter angle). The correction required was less than 14 mV.
**Numerical Results:**

Table 4.1

Hydrogen Discharge Overvoltage Parameters for Aluminium Electrodes Cut under Solution.

Parameters evaluated from square-wave current measurements made at potentials more negative than -1.7 v.

<table>
<thead>
<tr>
<th>Electrode cut under solution. Measurement within 5ms of cutting.</th>
<th>Average Values</th>
<th>90% Confidence Limits</th>
<th>Solution</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha (A)</td>
<td>Current density (A/m^2)</td>
<td>Alpha (A)</td>
<td>Current density (A/m^2)</td>
<td>Electrolyte</td>
</tr>
<tr>
<td>0.23</td>
<td>2.3x10^-8</td>
<td>0.26</td>
<td>1.2x10^-9</td>
<td>1M KCl</td>
</tr>
<tr>
<td>0.17</td>
<td>1.7x10^-7</td>
<td>0.21</td>
<td>1.3x10^-8</td>
<td>1M KCl</td>
</tr>
<tr>
<td>0.16</td>
<td>3.1x10^-7</td>
<td>0.19</td>
<td>9.3x10^-6</td>
<td>1M K_2SO_4</td>
</tr>
<tr>
<td>0.16</td>
<td>1.7x10^-7</td>
<td>0.19</td>
<td>1.7x10^-8</td>
<td>1M KCl</td>
</tr>
<tr>
<td>0.15</td>
<td>2.1x10^-7</td>
<td>0.21</td>
<td>4.5x10^-9</td>
<td>1M K_2SO_4</td>
</tr>
</tbody>
</table>

*Measurement made by Earl using the same experimental technique.*
Errors:

The average values of $\alpha_H$ and $i_{dh}$, together with the 90% confidence limits on these parameters, are presented in table 4.1. To a large extent the wide spread in the 90% confidence limits on $\alpha_H$ and $i_{dh}$ was attributed to errors in measurement. The inaccuracy in measuring the waveform amplitude $V_2 - V_1$ from photographic enlargements of oscillographic potential-time traces (e.g. fig. 4.1) was estimated to be up to $\pm 15\%$. Consequently, $\alpha_H$ was subject to an error of similar magnitude (see equation (4.2)). The value of $i_{dh}$ was subject to both the error in measuring the voltage difference $V_1 - V_2$ (equation (4.3)) and the error in determining the current density term. In its turn, the current density not only involved the errors in the current and area measurement but also included the unknown surface roughness factor. The surface roughness was almost certain to have varied from one experiment to another, since the chisel action of the ruby cutting into the aluminium was unlikely to have produced a consistent surface finish. The inaccuracy in $i_{dh}$ may also be viewed as the result of the large extrapolation of the hydrogen discharge Tafel line from the cathodic region ($<-1.64\v$) to its intersection at $i_{dh}$ with the hydrogen reversible potential $-1.19\v$ (pH 3.2). Because the slope of this line was affected by the error in $\alpha_H$, the spread in the values of $i_{dh}$ and its 90% confidence limits were unavoidably large. (see fig. 4.2). These difficulties in obtaining accurate values of $i_o$ from potential measurements more negative than $-1.0\v$, are generally acknowledged. For example, on mercury, where the experimental difficulties are less, the confidence limits on some of the most accurate measurements of $i_{dh}$ spread over four decades.$^{45}$ Because of the relatively greater
Fig. 4.2 Tafel line for hydrogen discharge at aluminium electrodes from measurements made at potentials more negative than \(-1.7\)V, 5s after cutting the electrodes under solution.

\[ \alpha_H = 0.17, \quad i_{ch} = 1.7 \times 10^{-7} \text{ amps/cm}^2 \]

90\% confidence limits \(\alpha_H = 0.21\) and \(0.13, \quad i_{ch} = 1.3 \times 10^{-8}\) and \(2.1 \times 10^{-6}\) amps/cm\(^2\).

All measurements were made at about -2V.

Accuracy in \(\alpha_H\), it has been given more weight in reaching conclusions from the measured hydrogen discharge parameters.

Mathematical Significance of Results:

The results show that a small but detectable decrease in \(\alpha_H\) occurred between milliseconds \((\alpha_H = 0.23)\) and seconds after the electrodes were cut \((\alpha_H = 0.18\) at 5s, 0.16 at 60s). This small change in \(\alpha_H\) must, by the definition of \(\alpha = \beta n\), have been caused by either \(\beta\) or \(n\) changing. However, such a small change was unlikely to have been produced by a change in \(n\), the number of electrons in the rate determining step, since the most probable value of \(n\) was 1 or 2. While a small decrease in \(\beta\)
(the fraction of the applied voltage assisting the transfer of electrons in the rate determining step) due to some change occurring at the freshly-cut electrode surface does seem possible. For example, the formation of a film over the electrode surface was expected to impede the passage of electrons from the metal to the discharging hydrogen ions. The 90% confidence limits on $i_{CH}$ were too wide to detect any dependence of $i_{CH}$ on the time elapsed after cutting the electrodes under solution.

Electrochemical Implications of Results:

Had low hydrogen overvoltage impurities been depositing from solution or had the small concentration of this type of impurity already present in the metal been influencing the rate of hydrogen discharge, then the hydrogen overvoltage at the freshly-cut aluminium would have decreased between milliseconds and seconds after the cut. However, these possible effects were dismissed by the measurement of a slight but seemingly significant decrease in $\alpha_H$ with time after cutting the electrodes (table 4.1), since this decrease in $\alpha_H$ implied that as the freshly-cut aluminium surface aged from milliseconds to seconds, its hydrogen overvoltage increased. This observed increase in overvoltage therefore invalidated the argument of a decreasing hydrogen overvoltage with time after cutting the electrodes which was previously proposed (p. 16) to explain the observed rise in open-circuit potential following the cutting of the electrodes under solution.

An increase in hydrogen overvoltage was, however, expected if a film formed over the electrode surface. The film most likely to form was a thin amorphous aluminium oxide or hydroxide film of the type commonly held to be formed on aluminium. But such a film could not have had the
resistive properties of bulk alumina as it would have almost totally inhibited the electrode process as the calculations below show.

\[
\text{Bulk resistivity of alumina} = 10^{15} \text{ ohm cm}
\]

Assumed oxide film thickness = 10Å

Film resistance then \( = 10^{8} \text{ ohm cm}^2 \)

Therefore current at 2V \( = 2 \times 10^{-8} \text{ amps/cm}^2 \)

However, the electrical behaviour of a film of this thickness may well have been affected by the very high electric field stress of some \( 2 \times 10^6 \text{ volts/cm} \) that would be across it. This thin film may also have had the well-known, but not so well understood, rectifying property, common to anodically produced aluminium oxide films. This property allows electrons to be comparatively freely conducted through the film from the metal to solution but not from the solution to the metal.\(^4\)

Aluminium oxide films of this thickness might even have semi-conducting properties, although no reported evidence was found to support this idea.

To test whether the measured decrease in \( \alpha_H \) could be explained by the formation of a film of the order of 10Å and with a low electrical resistance, the contact resistance between mercury and an aluminium electrode that had been exposed to air for 15 minutes was measured. A resistance of 5 ohm cm\(^2\) was recorded which was more than 7 decades less than the resistance of \( 10^8 \text{ ohm cm}^2 \) calculated above for a 10Å oxide film assuming a resistivity of the oxide equal to that of bulk aluminium oxide. These measurements therefore proved that it is possible for thin aluminium films to conduct electrons. The effect of such a resistance in series with the electrode process on the evaluation of \( \alpha \) and \( i_0 \) from the potential flats of the electrode response is illustrated in fig. 4.3 and table 4.2.
Fig. 4.3 Effect of a resistance in series with the electrode process on the evaluation of $\alpha$ and $i_0$ from the potential at two levels of current density.

$\alpha$ and $i_0$ parameters for actual Tafel line.

- $i_R$: effect of resistance $R$ on the voltage measurement.
- $\alpha'$ and $i'_0$: apparent overvoltage parameters deduced from the measured potentials $V'_1$ and $V'_2$ at current densities $i_1$ and $i_2$. 

- Log Current Density
- Potential
The values of the apparent parameters $\alpha'$ and $i_0'$ in table 4.2 were calculated from equation (4.4) by assuming that $\alpha = 0.21$, $i_0 = 5.0 \times 10^{-8}$ amps/cm$^2$ at the bare metal surface and that the measured electrode potential $V'$ was equal to $V$, the voltage in the electrode process, plus $iR$, the voltage across the resistance.

$$1 = i_0' \exp \left[ -\frac{\alpha'F}{RT} (V - iR - E) \right]$$

(4.4)

Table 4.2
The Effect of a Resistance on the Determination of $\alpha$ and $i_0$.

<table>
<thead>
<tr>
<th>Resistance (ohm cm$^2$)</th>
<th>$\alpha'$</th>
<th>$i_0'$ (amps/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.21</td>
<td>5 x $10^{-8}$</td>
</tr>
<tr>
<td>0.2</td>
<td>0.20</td>
<td>9.4 x $10^{-8}$</td>
</tr>
<tr>
<td>0.5</td>
<td>0.164</td>
<td>2.2 x $10^{-7}$</td>
</tr>
<tr>
<td>1.0</td>
<td>0.165</td>
<td>6.9 x $10^{-7}$</td>
</tr>
<tr>
<td>2.0</td>
<td>0.136</td>
<td>3.8 x $10^{-6}$</td>
</tr>
<tr>
<td>3.0</td>
<td>0.115</td>
<td>1.3 x $10^{-5}$</td>
</tr>
<tr>
<td>4.0</td>
<td>0.100</td>
<td>3.2 x $10^{-5}$</td>
</tr>
</tbody>
</table>

It can be seen from table 4.2 that concurrent with an apparent decrease of $\alpha$, a resistance in series with the electrode process would also have caused the measured value of $i_0$ to appear larger, which agrees with the observed trend, table 4.1. A study of the values in table 4.2 indicates that the presence of an oxide film with resistance of about a few ohms cm$^2$ could well explain the observed apparent decrease in $\alpha H'$. 
4.2 Hydrogen Overvoltage Parameters for Electrodes Pre-exposed to Oxygen

Experimental Method:

To check on what effect an oxide film has on the value of the hydrogen discharge parameters, the square-wave current measurements at potentials more negative than -1.7v were repeated on aluminium electrodes deliberately pre-exposed to oxygen. In these experiments, the electrodes were put in an atmosphere of oxygen prior to their immersion in solution. The cell used is shown in fig. 3.1 (section 3.2) and fig. 3.4 shows the arrangement of the current impressing and potential measuring equipment, which was the same as that used to make the impressed cathodic square-wave current measurements just discussed. Before each experiment, oxygen was passed through the glass cell for 30 minutes, after which the electrode was put by pushing it past the cutter by hand. After the required period of exposure to oxygen, the electrode was driven through the glass cell into the solution. For measurements involving only milliseconds pre-exposure to oxygen, the electrode was driven by a falling weight in one movement, past the cutter, through the glass cell and on into the solution. The potential time trace of 10 ms duration was measured oscillographically from the instant of contact between the electrode and solution.

Numerical Results:

From these measurements on the hydrogen discharge process at aluminium electrodes pre-exposed to oxygen, the values of $\alpha_H$ and $i_{\text{th}}$ were evaluated by the same method as that outlined on p.33. These values are given in table 4.3.
Hydrogen Discharge Overvoltage Parameters for Aluminium Electrodes Pre-exposed to Oxygen and Water Vapour.

Parameters evaluated from square-wave current measurements made at potentials more negative than -1.7 V.

<table>
<thead>
<tr>
<th>Electrode pre-exposed to oxygen for 10 ms</th>
<th>Average Values</th>
<th>90% Confidence Limits</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha_H$</td>
<td>$i_{OH}$</td>
<td>$i_{OH}$</td>
</tr>
<tr>
<td></td>
<td>$\text{amps/cm}^2$</td>
<td>$\text{amps}$</td>
<td></td>
</tr>
<tr>
<td>Electrode pre-exposed to oxygen for 10 s</td>
<td>.17</td>
<td>$1.7 \times 10^{-7}$</td>
<td>.20</td>
</tr>
<tr>
<td></td>
<td>.15</td>
<td>$1.3 \times 10^{-6}$</td>
<td></td>
</tr>
<tr>
<td>Electrodes pre-exposed to oxygen for 15 minutes</td>
<td>.16</td>
<td>$2.4 \times 10^{-7}$</td>
<td>.23</td>
</tr>
<tr>
<td></td>
<td>.08</td>
<td>$2.0 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>Electrodes pre-exposed to water vapour for 10 ms</td>
<td>.13</td>
<td>$2.3 \times 10^{-6}$</td>
<td>.17</td>
</tr>
<tr>
<td></td>
<td>.10</td>
<td>$3.1 \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>*Electrodes pre-exposed to water vapour</td>
<td>.19</td>
<td>$4.0 \times 10^{-9}$</td>
<td>.13</td>
</tr>
<tr>
<td></td>
<td>.14</td>
<td>$3.0 \times 10^{-6}$</td>
<td></td>
</tr>
</tbody>
</table>

*Included in table 4.3 are the values of $\alpha_H$ and $i_{OH}$ calculated from three measurements made by Earl on electrodes pre-exposed to hydrogen plus water vapour. Earl used the same technique and equipment as described above.
Discussion:

While there may be some doubt about the possibility of an oxide film forming within a few milliseconds of the aluminium electrodes being cut in an oxygen atmosphere, there is no doubt that the electrodes were oxide-covered after 15 minutes exposure (p.10). The values of $\alpha_H$ and $i_{OH}$ for the electrodes after 15 minutes oxygen pre-exposure, were therefore definitely representative of the hydrogen discharge process on oxide-covered aluminium electrode. The best value of $\alpha_H$ and $i_{OH}$ determined from the measurements made milliseconds after the electrodes were cut under deoxygenated solution were $0.23$ and $2.3 \times 10^{-3}$; 5 s and 60 s later, $\alpha_H$ and $i_{OH}$ were about $0.17$ and $1.7 \times 10^{-7}$, respectively (see table 4.1). The average value for $\alpha_H$ and $i_{OH}$ given in table 4.3 for the electrodes pre-exposed to oxygen for seconds are 0.16 and $2.4 \times 10^{-7}$. This similarity in the hydrogen overvoltage characteristics between oxide-covered electrodes and electrodes seconds after being cut under solution strongly suggests that film formation could have caused the slight increase of hydrogen overvoltage in the interval 5 ms to 5 s after the electrodes were cut under solution. The same sort of argument indicates that a film could have formed on the electrodes pre-exposed to water vapour ($\alpha_H = 0.15$, $i_{OH} = 3.2 \times 10^{-7}$), although the number of measurements here is inadequate to be certain. If a film was on these electrodes pre-exposed to water vapour, then it suggests that water vapour and aluminium can react directly to form a film, since in a vapour atmosphere the absence of a liquid phase at the electrode surface makes an electrochemical reaction impossible.

The similarity between the values of $\alpha_H$ for the oxide-covered electrodes, and for the electrodes seconds after being cut under solution
was, however, not indisputable evidence for film formation because of the overlap of the 90% confidence limits. Because these values of $\alpha_H$ were determined from only the flats of the potential response curve, a more sensitive method for detecting the presence of a film was expected from a study of the shape of the potential waveform since a film over the electrode surface was expected to lead to a response curve, different in shape, from that of the simple electrode process at the bare metal surface. An analysis was therefore made of the shape of the cathodic response curves of both oxide-covered electrodes and electrodes cut under solution.

4.3 Analysis of the Cathodic Potential Response of Oxide-covered Electrodes to Impressed Square-wave Currents

Basis for Analysis:

The difference in shape between the potential response of an oxide-covered electrode and that for the aluminium electrode 1-5 ms after being cut under solution can be seen in fig. 4.4, where the response of both electrodes to the same impressed square-wave current of $9.05 \times 10^{-3}$ to $1.8 \times 10^{-2}$ amps/cm² are shown. The response curve (curve 4) for the oxide-covered electrode was redrawn from an oscillographic trace. The parameters $\alpha_H = 0.14, i_o = 1.5 \times 10^{-6}$ for this curve were evaluated as before from the steady potentials at the two levels of the impressed current. However, an experimental curve at exactly the same current density, measured on an electrode 1-5 ms after cutting under solution, was unobtainable because of the impossibility of forecasting the precise area of a cut and hence the current density.
Fig. 4.4 Measured and calculated cathodic potential response curves of the aluminium electrode to an impressed square-wave current of $9.05 \times 10^{-3}$ to $1.81 \times 10^{-2}$ amps/cm$^2$.

1. Calculated curve for the electrode 1-5 ms after being cut under solution $C=4.7 \mu F/cm^2$

2,3. Calculated response of model b, assuming $R=6$ and $9$ ohm cm, $C=4.7 \mu F/cm^2$

4. Measured resp. of oxide-covered electrode $\alpha_H=0.14$, $I_o=1.5 \times 10^{-6}$amp/cm$^2$, $C=4.7 \mu F/cm^2$
for the measurement. The response of the "film free" electrode to the same impressed square-wave current 1-5 ms after cutting (curve 1) was therefore calculated by substituting the best values of $\alpha_H$ and $i_{cH}$ available for the "film free" electrode ($\alpha_H = 0.23$, $i_{cH} = 2.3 \times 10^{-5}$) (see table 4.1), into the simple process model which has been found by Earl to be applicable to these conditions. The electrical circuit equivalent to this model consisted of the electrode process (equation (4.1)) paralleled by a capacity. It can be seen from curves 1 and 4 in fig. 4.4 that the potential response of the oxide-covered electrode was larger in amplitude and at a more negative mean potential.

In the present work, a study was made to evolve a model to represent the oxide-covered electrodes. Four equivalent circuits, figs 4.5, 6, 7, 9, of increasing complexity have been considered and the calculated potential response of these models compared with the measured response of the oxide-covered electrode. The two characteristics compared were the general shape and mean potential of the response curves. As a basis in calculating the response of these models the hydrogen overvoltage parameters for "film free" electrodes ($\alpha_H = 0.23$, $i_{cH} = 2.3 \times 10^{-5}$ amps/cm²) have been used on the assumption that the higher overvoltage measured on the oxide-covered electrodes could be attributed entirely to the potential drop across the oxide film.

Except for a few abnormal traces, to be explained later in this section, all the experimental waveforms recorded in the present work had an initial linear potential response. Had the aluminium electrode involved a two-stage electrode process, its initial response would have been S shaped; for this reason models involving two or more dependent stage processes were not considered. A predominant single-stage
electrode process was therefore implied from the initial linear response.

The voltage-time response to step current signals was calculated by numerically integrating the differential equations for each of the proposed circuits. These calculations were done on an I.B.M. 1620 digital computer using a program written by Earl. This versatile program could calculate the response of several single and two opposed single-stage models of the electrode processes, with or without the complication of film resistance.

Model a:

The first model considered was that of an electrode covered by a purely resistive oxide film, through which electrons were transmitted to the electrolyte-oxide interface where the electrode process and double layer were assumed to be occurring. The equivalent circuit for this is shown in fig. 4.5 where the box represents the electrode process, $R$ the resistance of the oxide film, and $C$ the solution double-layer capacity in parallel with the electrode process.

![Fig. 4.5 Circuit equivalent to model a](image)

The expression for the dynamic response of model a is given by equation (4.5), where the impressed current, $i$, is expressed in terms of current density and the resistance $R$ as ohm cm$^2$. 
\[
\frac{dV}{dt} = \frac{i_0}{C} \exp \left[ -\frac{\alpha F}{RT} (V - E) \right] + \frac{i}{C} 
\]  \hspace{1cm} (4.5)

\( i = f(t) \)

It can be seen from circuit a that the initial response of this model to a step current change would be an instantaneous jump in potential, equal to the change in voltage across the resistance \( R \). However, very few of the experimental potential waveforms showed such jumps and when they did appear there was always good reason for suspecting poor electrical contact between the electrode and electrolyte. Usually this was caused by a hydrogen bubble sticking to and blanketing off part of the electrode surface. Some trouble was also experienced during the insulating process (see section 3.6), with the tendency of molten polythene to work its way in between the aluminium specimen and the steel supporting shaft (see fig. 3.1) and thereby cause a bad electrical contact. Because of the absence of visible potential jumps in the normal traces, model a was rejected.

Model b:

The electrical circuit representing model b depicts an overall electrode capacity across the film and electrode process. Although a model corresponding to this circuit, fig. 4.6, was difficult to justify, its response was analysed as a first approximation to the more realistic model of separate capacities across the film and the electrode process.

Fig. 4.6 Circuit equivalent to model b
The dynamic equation for the response of model $b$ to a variable impressed current is given by

$$\frac{dV}{dt} = \frac{i}{C} \exp \left( -\frac{\alpha E}{RT} (V - E - i'R) \right) + \frac{i}{C} \quad (4.6)$$

In this equation $i'$ represents the current (expressed as current density) passing through the film of resistance $R$ ohms cm$^{-2}$. The electrode capacity $C$ was evaluated from the initial slope of the particular experimental traces being matched.

Plotted in fig. 4.4 are the curves computed for values of $R$ equal to 16 and 9 ohms cm$^{-2}$ and $C = 4.7\mu F/cm^2$ (curves 1, 2 and 3), together with the corresponding experimental curve for the oxide-covered electrode (curve 4). These curves show that the general shape of the calculated and experimental curves were distinctly different. Because of this distinct difference in shape, the oxide-covered electrode was considered not to be represented by electrical circuit $b$.

Model $c$:

Electrodes covered by a highly resistive oxide film of suitable dielectric properties are in many ways analogous to leaky capacitors. This suggested that in the model for the oxide-covered electrode, the oxide film should be represented as a parallel capacity-resistance stage, in series with the electrode process which was assumed to occur at the oxide-electrolyte interface. The equivalent circuit for this model is shown in fig. 4.7 where $R$ represents the oxide film resistance and $C_R$ its capacity.
Because an applied current $i$ would flow through each of the two independent stages in this series circuit, the total voltage is simply the sum of the volt-drop in each stage, that is

$$V_t = V_{Rt} + V_{Et}$$  \(4.7\)

The response of the resistive capacity stage is given by

$$i = C_R \frac{dV_R}{dt} + \frac{V_R}{R}$$  \(4.8\)

where $i = f(t)$

and in particular its response to a step current change is

$$V_R = R(i_2 - i_1)(1 - e^{-t/RC_R})$$  \(4.9\)

The response of the electrode process is given by

$$i = C \frac{dV_E}{dt} + i_0 \exp \left[ -\frac{\alpha F}{RT} (V_E - E) \right]$$  \(4.10\)

Hence the overall circuit response was obtained simply by summing the voltage response curves calculated for each stage.
By selecting suitable values for $C_R$ and $R$ in equations (4.8) and (4.10), a response curve having the same general shape and amplitude as the experimental curve was calculated for model $c$; however, the mean potential of this curve was incorrect (curve 2, fig. 4.8). Conversely, when a curve with the correct mean potential was calculated by using another value of $R$, the amplitude was then different (curve 3). Hence, for the particular values of the overvoltage parameters assumed for the electrode process (p. 46), model $c$ failed to simulate the response of the oxide-covered electrode. A complete match between the calculated and experimental curves might have been obtained by assuming other values for the overvoltage parameters. However, because such a procedure would not have led to a unique solution, further matching of curves by this method was not attempted. The analysis of model $c$ was therefore inconclusive.

Measurements Made with Small Impressed Cathodic Currents:

Some measurements, which are discussed in the following section (section 4.4), were made on the hydrogen overvoltage of oxide-covered aluminium electrodes using cathodic currents of about $2 \times 10^{-4}$ amps/cm$^2$. At these current densities the potential across the suspected resistance of the oxide film (about 5 ohm cm$^2$) would have been no more than 2 millivolts. With these measurements, therefore, the resistance of the oxide film could not have had a significant effect on the measurement of $\alpha_H^*$, yet $\alpha_H^*$ was still evaluated to be about 0.12, approximately the value determined from square-wave current measurements at current densities of between $10^{-3}$ to $10^{-1}$ amps/cm$^2$ (table 4.3). Hence, these measurements made with small impressed currents proved that the value of $\alpha_H^*$ for oxide-
Fig. 4.8 Measured and calculated potential response curves of the aluminium electrode to an impressed square-wave current of $9.05 \times 10^{-3}$ to $1.81 \times 10^{-2}$amps/cm$^2$.

1, 2, 3 Calculated response of model c, assuming $R = 0$, 5.2 and 13.2 ohm cm$^2$, $C = 4.7 \mu F/cm^2$.

4 Measured response of oxide-covered electrode $\alpha_H = 0.14$, $i_{ch} = 1.5 \times 10^{-6}$ amps/cm$^2$, $C = 4.7 \mu F/cm^2$. 

covered electrodes is about 0.13, and that the resistance of the oxide film had not had a marked effect on the measurement of $\alpha_H$ at higher current densities. Similar small impressed current density measurements on electrodes cut under solution confirmed that $\alpha_H$ does decrease from 0.23 milliseconds after cutting the electrode to 0.16 two seconds later.

Summary:

Impressed square-wave current measurements of between $10^{-3}$ to $10^{-1}$ amps/cm$^2$ were made on aluminium electrodes at potentials more negative than -1.7v. The flaps of the potential response curves obtained were used in determining the overvoltage parameters $\alpha_H$ and $i_{CH}$ for the hydrogen discharge process. For an assumed oxide-free surface, 1-5 ms after cutting the electrodes under solution, the values calculated for the parameters were $\alpha_H = 0.23$, $i_{CH} = 2.3 \times 10^{-3}$; for the electrode 60s after being cut under solution $\alpha_H = 0.16$, $i_{CH} = 1.7 \times 10^{-7}$ (table 4.1), and for an oxide-covered electrode $\alpha_H = 0.16$, $i_{CH} = 2.4 \times 10^{-7}$ (table 4.3). These figures suggested that the apparent change in the parameters occurring between milliseconds and seconds after cutting an electrode under solution was formation of a film over the electrode surface. It was then shown (table 4.2) that if a film with resistance 5 ohm cm$^2$ had been in series with the electrode process, incorrect potentials would have been measured and an apparently small value of $\alpha_H$ calculated. This hypothesis was strengthened when the resistance of an air-formed oxide film was measured and found to be about 5 ohm cm$^2$ (p. 36). To confirm the presence of a resistive film the shape of the potential response curves of the oxide-covered electrodes were examined and compared with the response curves of three possible models, all of which involved a resistance in series with
the electrode process. The curves for the models were computed, assuming that the parameters for the electrode process were the same as those for the "oxide-free" electrode. None of these models were found to represent the electrode. Positive evidence that the potential measurements were not affected significantly by the suspected resistance of the oxide film was obtained by using smaller impressed currents. These measurements showed conclusively that the value of $\alpha_H$ for oxide-covered aluminium is, as was found earlier, about 0.13. These measurements also showed that for electrodes out under solution, $\alpha_H$ does decrease between milliseconds and seconds after cutting the electrode.

Model d

Having established that the measurement of $\alpha_H$ and $i_{\text{off}}$ from the flats of the potential response curve had not been affected significantly by the resistance of the oxide film, a test was made to determine whether the potential response of the oxide-covered aluminium electrode could be matched when $R$, in equivalent circuits a, b, and c, was zero and the parameters for the electrode process were those evaluated from the flats of the experimental curve. When $R = 0$, these circuits all become the circuit equivalent to the simple process model. The test was therefore made by calculating the response of the simple process model to the same square-wave current as that used in the experiment. This calculated curve was then compared with the corresponding experimental curve.

The simple process model depicts a single-stage electrode process taking place at the electrode-electrolyte interface, together with an associated electrolyte double-layer capacity. The circuit equivalent to this model consists of the electrode process paralleled by a capacity, fig. 4.9.
Fig. 4.9 Circuit equivalent to model d

The dynamic equation for this model was given by

$$\frac{dV}{dt} = \frac{i_0}{C} \exp \left[ - \frac{\alpha F}{RT} (V - E) \right] - \frac{i}{C} \quad (4.11)$$

The results of the tests are shown in fig. 4.10, where the experimental and calculated waveforms are superimposed. The slight discrepancies between these curves mainly arose from the difficulty in accurately redrawing the experimental waveforms from the enlarged photographs of the oscillographic traces. A similar test was also made on the potential waveforms recorded seconds after cutting the electrodes under solution, fig. 4.10.

Conclusions:

The close similarity between these experimental and calculated waveforms has shown that, at potentials more negative than -1.7v, the discharge of hydrogen at the oxide-covered aluminium electrodes and at electrodes seconds after being cut under solution can be simulated by the simple process model, fig. 4.9. This model, with appropriate overvoltage parameters, was therefore representative of aluminium electrodes milli-seconds after cutting under solution and the electrode covered by an oxide film. These results imply that the hydrogen discharge process on oxide-
Electrode cut under solution. Measurement 1 minute after the cut.
\[ \alpha_H = 0.14, \quad i_{oh} = 1.25 \times 10^{-7} \]
\[ C = 6.59 \times 10^{-6} \]
\[ i_1 = 1.06 \times 10^{-2} \]
\[ i_2 = 1.89 \times 10^{-2} \]
\[ T = 65.5 \]

Electrode pre-exposed to oxygen for 15 minutes. Measurement 5 ms after contact with the solution.
\[ \alpha_H = 0.136, \quad i_{oh} = 1.01 \times 10^{-6} \]
\[ C = 3.72 \times 10^{-6} \]
\[ i_1 = 1.22 \times 10^{-2} \]
\[ i_2 = 1.94 \times 10^{-2} \]
\[ T = 56.3 \]

Electrode pre-exposed to oxygen for 15 minutes. Measurement 60s after contact with solution.
\[ \alpha_H = 0.125, \quad i_{oh} = 1.52 \times 10^{-9} \]
\[ C = 7.05 \times 10^{-6} \]
\[ i_1 = 2.96 \times 10^{-2} \]
\[ i_2 = 1.57 \times 10^{-2} \]
\[ T = 88.2 \]

Fig. 4.10 Measured and calculated potential response of the aluminium electrode to an impressed cathodic square-wave current. ———— experimental curve
-- -- -- calculated curve
covered aluminium electrodes follows a normal overvoltage type relationship, equation (4.1). The apparent common identity of the hydrogen discharge process on oxide-covered electrodes and on electrodes 5 and 60 seconds after being cut under solution (the same model and practically the same overvoltage parameters) strongly suggested that film formation was the probable explanation for the slight increase in hydrogen overvoltage, from milliseconds to seconds after cutting the electrodes under solution. Because these observed trends in hydrogen overvoltage were slight, more convincing evidence on the question of film formation was sought from a study of the anodic process.

In the case of the anodic process, the easy passage of ions, either aluminium, hydroxyl or chloride, through an aluminium oxide film is unlikely, as evident by the rectifying properties of anodized aluminium, whereas for the cathodic process the high electronic conductivity was not unexpected (see p. 38). A film over the aluminium surface was therefore expected to cause a major change in the anodic overvoltage characteristics.

For the reasons mentioned before (p. 16), the anodic process could be investigated only within the mixed potential region, where five parameters $\alpha_a$, $i_{oa}$, $\alpha_H$, $i_{CH}$ and $C$ were needed to describe the potential behaviour of the electrode. At best, two of these parameters could be evaluated from potential measurements provided values for the other three parameters were available. The assumption was therefore made that $\alpha_H$ and $i_{CH}$, evaluated from measurements at potentials much more negative than the mixed potential, could be used to identify the hydrogen discharge process occurring at potentials close to the mixed potential. To ensure that reasonably correct values of $\alpha_H$ and $i_{CH}$ were used, further cathodic measurements were made to define $\alpha_H$ and $i_{CH}$ as functions of time elapsed after cutting the electrodes.
under solution.

4.4 The Hydrogen Overvoltage as a Function of Time

Change of $i_{OH}$ with Time:

The information available from this work on the variation of $i_{OH}$ with time was contradictory, presumably because of the inaccuracies involved in evaluating this parameter. The cathodic measurements (table 4.1) suggested that $i_{OH}$ increased, whereas the measurements made in the mixed potential region and discussed later in this section indicated that $i_{OH}$ decreased with time elapsed after cutting. For lack of more precise information on $i_{OH}$, further analysis was carried out assuming that $i_{OH}$ was substantially constant between 10 ms and 10 s after cutting the electrodes under solution.

Change of $\alpha_H$ with Time:

However, the cathodic measurements have established that $\alpha_H$ decreases with time after cutting the electrodes under solution. Some further experiments were made to determine this relationship. These measurements were made by applying small direct cathodic currents of the order of $2 \times 10^{-4}$ amps/cm$^2$ to the freshly-cut electrode and continuously recording its potential from the time of cutting the electrode under solution until 2 s later. From the traces obtained (see example fig. 4.11), the value of $\alpha_H$ could be determined at any time after the cut by substituting for $V_t$ the potential at time $t$, into equation (4.12).

$$\alpha_H = \frac{RT}{(V_t - E_H)^F} \ln \frac{i_{OH}}{i + i_a}$$  (4.12)
Fig. 4.11 Potential-time trace of an aluminium electrode from 0-2s after being cut under solution with a cathodic current loading of 3.2 x 10^{-4} amps/cm².
Solution 1N KCl, pH 3.2, H₂ saturated.

In equation (4.12), \( i_{\text{inj}} \) was assumed to be constant at \( 5 \times 10^{-7} \text{ amps/cm}^2 \), \( i \) was the impressed current, and \( i_a \) the internal anodic current estimated from anodic overvoltage data obtained in section 6. The internal current 0.2s after cutting the electrode was estimated to be about \( 10^{-5} \text{ amps/cm}^2 \), which was small compared with the impressed current of \( 2 \times 10^{-4} \text{ amps/cm}^2 \). From the values of \( \alpha_H \) and \( t \) obtained in this way, a functional relationship between \( \alpha_H \) and \( t \) was derived, which proved to be logarithmic (equation (4.13)).

\[
\alpha_H = 0.169 - 0.02 \log (t) \tag{4.13}
\]

\[10 \text{ ms} < t < 2 \text{ s}\]

Long-term Measurements:

The potential-time traces (e.g. fig. 4.11) indicated that the potential
was still decreasing 2s after the electrode was cut. For this reason, further measurements at the same current density were made on the same electrodes at later times after cutting the electrode. At specific times after the cut, the current was switched to the electrode for a few seconds and the electrode potential recorded oscillographically. Figs 4.12 and 13 are examples of the measurements made at 60s and 5 minutes after the electrodes were cut. Because the current density for the measurement on each electrode was the same, the change in cathodic overvoltage with time after the cut can be seen directly from the potential measurements made on any one electrode. The traces in figs 4.11-13 therefore show that a gradual increase in cathodic overvoltage occurred within the interval 0 to 5 minutes after cutting the electrodes under solution. At times greater than 5 minutes, the overvoltage was visually observed to remain constant, which suggests that the electrodes had reached a steady state condition. The range of hydrogen discharge parameters that could apply to this steady potential were $\alpha_H = 0.12$, $i_{CH} = 2 \times 10^{-3}$ amps/cm$^2$ to $\alpha_H = 0.085$, $i_{CH} = 1.0 \times 10^{-7}$ amps/cm$^2$. In the first case a low but possible value of $\alpha_H$ was assumed, and $i_{CH}$ calculated from the steady state potential, and in the second case a representative value of $i_{CH}$, determined from the cathodic measurements, was assumed and $\alpha_H$ calculated.

Oxide-covered Electrodes:

The analysis of the cathodic measurements (section 4.3) suggested that film formation might have been responsible for the increase in cathodic overvoltage with time after cutting the electrodes under solution. To test whether this was a plausible explanation for the decrease in $\alpha_H$
Oscillographic traces of the aluminium electrode potential with a cathodic current loading of $3.2 \times 10^{-4}$ amps/cm$^2$.

Fig. 4.12 and 4.13 respectively, 60s and 5 minutes after cutting the electrode under solution.

Solution 1N.KOH, pH 3.2, $H_2$ saturated.
deduced from the above measurements in the mixed potential region, these measurements were repeated on oxide-covered electrodes. The lack of adequate polarisation data to correct for differences in current density required that these measurements on the oxide-covered electrodes be made at the same current density as used for the measurements on the electrodes cut under solution. This requirement necessitated the use of the same electrode specimens for the measurement on the oxide-covered electrodes as that used for the measurements on the electrodes cut under solution (see p. 44).

The experimental procedure for these measurements in the mixed potential region was as follows.

First, the required potential measurements on the electrodes cut under solution were made. The electrode was then removed from the cell, washed with distilled water, dried and left exposed to the atmosphere for 5 minutes. After 5 minutes air-exposure the electrode was reassembled in the cell and the solution deoxygenated by hydrogen bubbling for 10 minutes, after which the electrode loaded with the same static cathodic current as used for the initial measurements, was plunged into the solution. An example of the oscillographic potential trace recorded from contact between the solution and the electrode, after being exposed to air, is shown in fig. 4.16. An oscillographic potential trace for the same electrode, 5 minutes after it was cut under solution, is shown in fig. 4.15. The similarity of potential, and hence cathodic overvoltage (see p. 60) between these measurements, clearly indicates that the cathodic potential behaviour of the aluminium electrodes cut under solution may be explained by a film forming over the cut surface. With these measurements at current densities of about 2 x 10^{-4} amperes/cm^2, the potential across the previously suspected
Oscillographic traces of the aluminium electrode potential with a cathodic current load of $3.2 \times 10^{-4}$ amps/cm$^2$.

Fig. 4.15  5 minutes after cutting the electrode under solution

Fig. 4.16  Same electrode after 5 minutes air-exposure

Solution 1N KCl, pH 3.2, H$_2$ saturated.
oxide film resistance of 5 ohm cm$^2$ (see p. 38) would not have been more than 1 or 2 mv. The measurements therefore show that aluminium electrodes covered by air-formed films do have high hydrogen overvoltages and small values for $\alpha_H$ of about 0.12.

4.5 The Anomalous Characteristic of Cathodically Polarised Aluminium Electrodes

Contrary to the expected negative polarisation, the aluminium electrode, when loaded from the instant of cutting with a small direct cathodic current, went initially to a potential more positive than that obtained from open-circuit measurements. An example of the potential behaviour of an aluminium electrode to a small direct cathodic current can be seen in fig. 4.17 (curve 1). Plotted on the same figure are the predicted response curve (curve 3) and the open-circuit measurement (curve 2). As the figure shows, the small cathodic current applied to the electrode was expected to drive the electrode potential to a value more negative than the open-circuit potential; in contrast, the potential measured 0.1s after the cut was some 200 mv more positive than the open-circuit potential. Curve 3 was calculated from cathodic data, which will be used in section 7 to reproduce the open-circuit potential behaviour of the aluminium electrodes (see section 7).

The interpretation of this anomalous potential behaviour in terms of the overvoltage relationships for the anodic and cathodic processes existing at the electrode is illustrated in the polarisation diagram. This diagram (fig. 4.18) has been drawn to represent the possible anodic and cathodic overvoltage relationships 0.1s after cutting the electrode under solution (see fig. 4.17).
Fig. 4.17 Potential-time behaviour of an aluminium electrode cut under a solution of 1N.KCl, pH 3.2, and H₂ saturated.

1. Experimental measurement, direct cathodic current loading of $3.17 \times 10^{-4}$ amps/cm².
2. Experimental measurement, open circuit.
3. Calculated curve for a direct cathodic current loading of $3.17 \times 10^{-4}$ amps/cm².

It will be shown in section 6 that a Tafel type relationship of the kind used in the diagram does describe the anodic process at potentials close to the open-circuit mixed potential.
Fig. 4.18 Representation of the Tafel lines existing at an aluminium electrode 0.1s after being cut under solution.

--- possible changes in the cathodic Tafel line

In the diagram, $V_2$ is the open-circuit mixed potential, $V_3$ represents the predicted potential, and $V_1$ the measured potential.

A possible explanation for this anomalous potential $V_1$ was that the anodic process was stifled in some way by the applied cathodic current. Such an event would have had the effect of reducing the total current at the cathode, thereby producing a more positive potential than $V_3$.

However, even when zero anodic process is assumed, the electrode potential should not have been more positive than $V_3'$. As the figure illustrates, the potential $V_1$ can be explained only if the cathodic overvoltage
parameters for the cathodically loaded electrode are assumed to be larger than those found to describe the open-circuit behaviour of freshly-cut aluminium. The difference in hydrogen overvoltage parameters required to account for this anomalous potential behaviour (a change of $i_{\text{OH}}$ from $10^{-7}$ to $5 \times 10^{-7}$ amps/cm$^2$ or $\alpha_H$ from 0.18 to 0.22) is small, although apparently quite critical. Why the application of such a small direct cathodic current should facilitate the discharge of hydrogen from newly-cut aluminium cannot, as yet, be adequately explained without further investigation.

Conclusion:

The measurements on the hydrogen discharge process at aluminium electrodes have shown that for electrodes cut under solution a small but measurable increase in hydrogen overvoltage occurs with time after cutting. This increase has been attributed to $\alpha_H$ decreasing, as a logarithmic function of time after cutting, from 0.23 milliseconds after the electrode is cut to 0.16 seconds later (equation (4.13)). It was found that this decrease in $\alpha_H$ may be ascribed to a film forming on the electrode surface as the hydrogen discharge at both initially oxide-free and oxide-covered electrodes attain the same overvoltage parameters after about 5 minutes in solution.

Although the overvoltage characteristics of the oxide-covered electrode can be described by an electrokinetic equation, there is some doubt as to whether the parameters have quite the same physical significance as those ascribed to the $\alpha$'s and $i_o$'s of bare metal electrodes. It is not improbable that the oxide film itself has a marked influence on the kinetics of the electrode process$^{34}$. The measurements indicate that the probable
value of $\psi_H^2 (\alpha = \beta n)$ for an oxide-covered aluminium electrode is 0.12 or 0.06, n generally being 1 or 2, whereas $\beta_H$ at bare metal surfaces often has a value close to 0.545. It could be that the very small value of $\beta$ for the aluminium electrodes is indicative of a film on the electrode surface, even from 1 or 2 milliseconds after cutting the electrode under solution.

The analysis of the potential response of the electrodes initially covered by an air-formed oxide film has clearly shown that the electronic resistance of the film must have been less than 0.1 ohm cm$^2$ for its resistance not to have had a significant effect on the potential measurements. Assuming this film has a thickness of $10^5\xi$, then its resistivity would be of the order of $10^6$ ohm cm or less, which is 10 decades smaller than the resistivity of bulk alumina. The electrical properties of these thin films are therefore quite different from those of the bulk material.

On the basis of the results obtained in this section, a value for $i_{OH} = 2 \times 10^{-7}$ will be used in the analysis of the anodic process, and $\alpha_H$ at any time after cutting the electrode will be calculated from the expression $\alpha_H = 0.169 - 0.02 \log (t)$.

Before the study of the anodic process was made, the capacity of the aluminium electrode was investigated as a possible means of detecting the formation and presence of a film. This was done because electrode capacities could be evaluated from potential measurements far more easily than the anodic parameters $\alpha_a$ and $i_{ca}$. These capacity measurements will now be discussed, followed by the discussion on the anodic process.
5. THE ELECTRODE CAPACITY MEASUREMENTS

5.1 Introduction

The electrical capacity normally associated with an electrode process is the double layer capacity, that is the capacity formed by the ordered arrangement of ions in the liquid layer adjacent to the electrode surface. Some authors have suggested that a film over the electrode surface could change the measured electrode capacity by altering the double layer structure. A change of electrode capacity could also be expected from a film which had dielectric properties, such that its capacity was of the same order or less than that of the double layer. By assuming in this case that the film could be approximated to a parallel plate capacitor, some authors have used the decrease in observed capacity of electrodes as a measure of the thickness of film on them. These considerations suggested that the presence of a film on the aluminium electrodes might be detected from capacity measurements.

5.2 The Electrode Capacity at Cathodic Potentials

Earl has reported that the average capacity, evaluated from cathodic square-wave current measurements taken within the interval 1-4 ms after cutting the aluminium electrodes under solution, was $7.6 \mu F/cm^2$. From the cathodic square-wave current measurements discussed in section 4.1, the author has determined the aluminium electrode capacity at 5s and 60s after the electrodes were cut under solution. As previously noted (p. 49), the electrode capacity in these measurements was inversely proportional to the tangent drawn to the potential response curve immediately following a
step change of current. The expression used for calculating the electrode capacities was deduced from the dynamic equation for the aluminium electrode under cathodic loading equation (4.11). At the steady potential just prior to the current change, the impressed current $i_1$ was equal to

$$i_1 = i_0 \exp \left[ - \frac{dF}{RT} (V - E_o) \right]$$

immediately after the current step from $i_1$ to $i_2$ and before the electrode potential had changed significantly

$$\frac{dV}{dt} = \frac{i_0}{C} \exp \left[ - \frac{dF}{RT} (V - E_o) \right] - \frac{1}{C}$$

substituting equation (5.1) in (5.2) gives

$$C = \frac{i_1 - i_2}{\frac{dV}{dt}}$$

This expression is identical to that derived by other authors $^{51,54}$ for evaluating the electrode capacity from step current measurements.

The average electrode capacities evaluated from five cathodic measurements on aluminium electrodes cut under solution are tabulated in table 5.1.

<table>
<thead>
<tr>
<th>Capacity $\mu$F/cm$^2$</th>
<th>Time</th>
<th>Solution</th>
<th>Electrolyte</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean min. max.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.6 1-4 ms</td>
<td>1N.KCl</td>
<td>3.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.5 4 19</td>
<td>5 s</td>
<td>1N.KCl</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>10.5 6 16</td>
<td>60 s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.9 8 16</td>
<td>5 s</td>
<td>1N.K$_2$SO$_4$</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>12.8 6 14</td>
<td>60 s</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Because the initial gradient in some of the potential-time traces was not clearly defined, the calculated values of the capacity were not always precise, with values falling in the range $4-19 \mu F/cm^2$. The results suggest a small increase of capacity in the few seconds after the cut, which is the opposite effect to that expected from film formation. The results also show that there was no noticeable change in capacity when $SO_4^{2-}$ ion was substituted for $Cl^-$ ion. The values of electrode capacity measured at potentials more negative than $-1.7 \text{v}$, table 5.1, were suspected of not being representative of the aluminium electrode in the mixed potential region ($-0.8$ to $-1.3 \text{v}$), as the electrode capacity for a number of metals is known to be dependent on the electrode potential. Although no such formation was available for aluminium, it was decided to repeat the capacity measurements in the mixed potential region.

5.3 Electrode Capacities from Sawtooth Potential Waveforms

Within the mixed potential region, the response of the electrode to a current change was found to be very slow. This slow response was associated with the small internal current at the electrode (estimated from hydrogen overvoltage data to be about $10^{-5}$ amps/cm$^2$). Because of these characteristics, potential waveforms, suitable for applying the above method of determining the electrode capacity, could not be obtained within the mixed potential region except by using small impressed currents and very low square-wave frequencies ($10^{-1}$ c/s). A superior and more versatile method was therefore devised. With this method, the frequency of the square-wave current was adjusted so that only the initial linear part of the potential response curves was recorded. The trace obtained
was a clearly defined sawtooth waveform, an example of which is shown in Fig. 5.1.

![Sawtooth potential waveform measured on an aluminium electrode impressed square-wave current, 1.76 x 10^-8 to -1.82 x 10^-3 amps/cm^2, frequency 500 c/s.]

**Fig. 5.1** Sawtooth potential waveform measured on an aluminium electrode impressed square-wave current, 1.76 x 10^-8 to -1.82 x 10^-3 amps/cm^2, frequency 500 c/s.

**Electrode Capacities from Sawtooth Potential Waveforms:**

In section 6 it will be shown that the dynamic response of the aluminium electrode in the mixed potential region may be represented by equation (5.4).

\[ C \frac{dV}{dt} = i_{oc} \exp\left[ -\frac{\alpha_c F}{RT} (V - E_c) \right] - i_{oa} \exp\left[ -\frac{\alpha_a F}{RT} (V - E_a) \right] + i \quad (5.4) \]

where the kinetics of the cathodic and anodic electrode processes are given respectively by the first and second terms on the right-hand side of the equation.

At time \( t^- \) just before the step current change, the electrode process may be described by equation (5.5).
\[ C \left( \frac{dV}{dt} \right)_t^- = i_\infty \exp \left[ -\frac{\alpha F}{RT} (V - E_o) \right] - i_\infty \exp \left[ \frac{\alpha F}{RT} (V - E_a) \right] + i_1 \]  (5.5)

where \( i_1 \) was the impressed current prior to the current change, and

\[ \left( \frac{dV}{dt} \right)_t^- \] the potential gradient. At time \( t^+ \), the instant after the step current change to \( i_2 \), the condition at the electrode is given by equation (5.6).

\[ C \left( \frac{dV}{dt} \right)_t^+ = i_\infty \exp \left[ -\frac{\alpha F}{RT} (V - E_o) \right] - i_\infty \exp \left[ \frac{\alpha F}{RT} (V - E_a) \right] + i_2 \]  (5.6)

As the electrode potential immediately after the current change is unaltered, the rates of the potential dependent electrode processes are unchanged. That is, the initial change in the impressed current goes entirely into charging or discharging the electrode capacity.

Eliminating the first and second terms in equations (5.6) and (5.5) gives

\[ C \left( \frac{dV}{dt} \right)_t^+ = C \left( \frac{dV}{dt} \right)_t^- - i_1 + i_2 \]  (5.7)

that is

\[ C = \frac{i_2 - i_1}{\left( \frac{dV}{dt} \right)_t^+ - \left( \frac{dV}{dt} \right)_t^-} \]  (5.8)

or, when tangent measurements are used,

\[ C = \frac{i_2 - i_1}{\tan \theta_t^+ - \tan \theta_t^-} \]  (5.9)

When the potential was steady prior to the step current change, \( \left( \frac{dV}{dt} \right)_t^- = 0 \), equation (5.8), simplifies to the previously derived expression, equation (5.3).

Fig. 5.2 illustrates how the measurements were made on the sawtooth waveforms.
Fig. 5.2 Data obtained from sawtooth potential waveforms for determining the electrode capacity.

For the aluminium electrode this type of waveform was always found to be symmetrical, that is

\[
\frac{dV}{dt}^- = -\frac{dV}{dt}^+
\]

from equation (5.8)

\[
C = \frac{(i_2 - i_1)}{2 \frac{dV}{dt}} 
\]

(5.10)

and from the diagram

\[
C = \frac{i_2 - i_1}{4HF} 
\]

(5.11)

where \( f \) was the frequency of the impressed square-wave current and \( H \) the height of the potential waveform. Hence only the amplitude of the sawtooth potential wave was needed to determine the electrode capacity. McMullen and Hackerman\(^5\) have also evaluated electrode capacities from sawtooth potential-time waveforms, but their analysis was based, incorrectly, on a series capacity-resistance equivalent circuit of the electrode process. Their analysis resulted in an expression of the same form as
equation (5.3) and not (5.8); consequently their capacity values were double the actual electrode capacities. McMullen and Hackerman's representation of the electrode by a capacity-resistance circuit was invalid because, contrary to actual electrode behaviour, this circuit does not conduct direct current. To obtain static conduction, the electrode capacity in the equivalent circuit must parallel the effective resistance of the electrode process.

In some measurements where the potential waveforms were curved (fig. 5.3), the capacity had to be determined from the slope of the potential-time curves immediately before and after the step current change.

![Fig. 5.3 Data obtained from a curved potential waveform for determining the electrode capacity.](image)

The method devised here for measuring electrode capacities from sawtooth potential waveforms may be profitably applied to other electrode systems. The method has several decided advantages. Because only the amplitude of the sawtooth waveform need be measured, the method is as accurate, if not more accurate, than most other methods. Interpretation of the potential measurement is not complicated by the faradaic processes as are measurements made by the A.C. bridge method.
By using a suitably biased square-wave current, the capacity can be measured at any desired potential quickly and conveniently before changes in electrolyte concentration can occur. Visual observation of the amplitude of the sawtooth waveform displayed on an oscilloscope screen may be used to follow the changes in capacity associated with film formation or breakdown at the electrode surface, see Fig. 5.4, the amplitude of the waveform being inversely proportional to the electrode capacity (equation (5.11)).

5.4 The Electrode Capacity at the Mixed Potential

These capacity measurements at the open-circuit mixed potential were made using an impressed current that oscillated by equal amounts from positive to negative, such that the nett current impressed per cycle was zero. This waveform will be referred to as a balanced square wave. The frequencies of the square-wave currents used were between 500 and 5000 c/s. The experimental procedure was similar to that used for the cathodic measurements (see section 4.1) in that the electrodes were first cut under solution on open circuit, then at 5s, 12s and 60s after the cut the load was applied momentarily and the measurements made.

Results:

The results of the mixed potential capacity measurements on electrodes cut under solution are summarized in Table 5.2. About four measurements were made at each condition.
Fig. 5.4 Observed change in electrode capacity with time. Measurement on an aluminium electrode pre-exposed to oxygen for 15 minutes. Square-wave current $1.29 \times 10^{-3}$ to $-1.06 \times 10^{-3}$ amperes/cm², frequency 500 c/s. Solution 1N $K_2SO_4$, pH 3.2, air-saturated.

a. Oscillographic trace at contact between electrode and solution.
b. Oscillographic trace 5s later.
TABLE 5.2

Aluminium electrode capacities measured at the mixed potential of electrodes cut under solution. Capacities determined from sawtooth potential waveforms.

<table>
<thead>
<tr>
<th>Capacity $\mu F/cm^2$</th>
<th>Solution</th>
<th>Electrolyte</th>
<th>pH</th>
<th>Saturating gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean</td>
<td>min.</td>
<td>max.</td>
<td>Time</td>
<td>Electrolyte</td>
</tr>
<tr>
<td>8.6</td>
<td>6</td>
<td>10</td>
<td>5s</td>
<td>1N. KCl</td>
</tr>
<tr>
<td>9.2</td>
<td>8</td>
<td>10</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>10.6</td>
<td>7</td>
<td>13</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>5.5</td>
<td>4</td>
<td>7</td>
<td>5</td>
<td>1N. K$_2$SO$_4$</td>
</tr>
<tr>
<td>9.2</td>
<td>7</td>
<td>16</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>10.3</td>
<td>4</td>
<td>18</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>13.9</td>
<td>7</td>
<td>20</td>
<td>5</td>
<td>1N. KCl</td>
</tr>
<tr>
<td>14.9</td>
<td>7</td>
<td>21</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>16.4</td>
<td>7</td>
<td>29</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>7.3</td>
<td>5</td>
<td>9</td>
<td>5</td>
<td>1N. K$_2$SO$_4$</td>
</tr>
<tr>
<td>6.8</td>
<td>6</td>
<td>9</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>7.8</td>
<td>6</td>
<td>9</td>
<td>60</td>
<td></td>
</tr>
</tbody>
</table>

No attempt was made to apply any statistical test or confidence limits to these measurements because of the small number in each group and the spread of values 4-20 $\mu F/cm^2$. Despite these limitations, the results appeared to show that for the experimental conditions the aluminium electrode capacity was influenced by neither the anion in solution nor whether the solution was oxygenated or deoxygenated. Also, there was no difference between anodic or cathodic polarisation of the electrode, as the capacity derived from the potential waveforms was essentially the same, whether the current step had been in the positive or negative direction. Overall, the values of capacity measured at the mixed
potential (-0.8 to -1.3v) were apparently the same as those measured at potentials more negative than -1.7v (table 5.1). Also there was no marked difference between the electrode capacity measured milliseconds after cutting the electrode under solution and those measured seconds later. The similarity between these capacity measurements could mean that (i) a film does not form on the electrodes cut under solution, or (ii) all the capacity measurements were made with a film covering the electrode surface, including the measurements made within milliseconds of cutting the electrode, or (iii) the presence of a film over the electrode surface does not affect the capacity of the electrode. With only one exception, the mean values of the capacity increase with time in solution, which is the opposite trend to that expected from the growth of a film. To clarify this information, measurements were made to determine the capacity of oxide-covered electrodes.

5.5 The Electrode Capacity of Oxide-covered Electrodes

The measurements on oxide-covered electrodes were made using the same method and apparatus for pre-exposing the electrodes to oxygen as was used in the cathodic overvoltage measurements on pre-oxygen exposed electrodes (section 4.2). Like the capacity measurements made within the mixed potential region, the capacity of the oxide-covered electrodes were evaluated from sawtooth potential waveforms obtained from impressing square-wave currents of 500-5000 c/s.

The results of the capacity measurements on oxide-covered electrodes are presented in table 5.3. Three or more measurements were made for each condition. Two examples of the traces from which these capacities
were evaluated are given in fig. 5.4.

**TABLE 5.3**

Capacity measurements on oxide-covered aluminium electrodes.
Capacity determined from sawtooth or curved potential waveforms.

<table>
<thead>
<tr>
<th>Pre-treatment of the electrode surface</th>
<th>Capacity $\mu F/cm^2$</th>
<th>Time Electrolyte pH Saturating gas</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mean</td>
<td>min</td>
</tr>
<tr>
<td>Mixed Potential Measurements</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen exposed</td>
<td>5.9</td>
<td>2</td>
</tr>
<tr>
<td>15 minutes</td>
<td>5.7</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>7.4</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>6.2</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>8.0</td>
<td>6</td>
</tr>
<tr>
<td>Oxygen exposed</td>
<td>4.6</td>
<td>3</td>
</tr>
<tr>
<td>15s</td>
<td>10.1</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>10.5</td>
<td>9</td>
</tr>
<tr>
<td>Oxygen exposed</td>
<td>2.4</td>
<td>1</td>
</tr>
<tr>
<td>10 ms</td>
<td>4.2</td>
<td>2</td>
</tr>
<tr>
<td>Oxygen plus water vapour exposed 15 s</td>
<td>4.3</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>5.7</td>
<td>4</td>
</tr>
<tr>
<td>Oxygen plus water vapour exposed 8 ms</td>
<td>3.2</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>5.2</td>
<td>3</td>
</tr>
</tbody>
</table>

Cathodic Measurements

| Oxygen exposed 15 min.                  | 4.2  | 3   | 6   | 5ms    | 1N.KCl | 3.2 | air  |
| Oxygen plus water vapour exposed 7 ms  | 4.4  | 3   | 7   | 5ms    | 1N.KCl | 3.2 | air  |
| *Oxygen exposed 15 min.                | 5.9  | 5   | 9   | 5ms    | 1N.KCl | 3.2 | air  |
| *Oxygen exposed 10 s                    | 7.0  | 6   | 8   | 5ms    | 1N.KCl | 3.2 | air  |

*These capacities were evaluated from the initial potential gradient of the cathodic measurements used in obtaining the hydrogen overvoltage parameters on oxide-covered electrodes (section 4.2).
The results of the capacity measurements on the electrodes pre-exposed to oxygen indicate that the electrode capacity was apparently independent of the presence or absence of molecular oxygen dissolved in solution or whether the anion was sulphate or chloride. As for the electrodes cut under solution, the mean values for the electrode capacity of oxide-covered electrodes all increased with the time the electrode was in solution. In this case such a behaviour might have been caused by thinning or hydration of the oxide film. Comparing the values of capacity given in tables 5.1-3, it appears that, overall, the capacity of the electrodes pre-exposed to oxygen (about 3-7\(\mu F/cm^2\)) are slightly smaller than the capacity of the electrodes cut under solution (about 8-12\(\mu F/cm^2\)).

Because of the general similarity in the aluminium electrode capacity for all the conditions tested, the formation of a film on the aluminium electrode freshly cut under solution was not detectable. None of the three possible explanations proposed to account for the results of the electrode capacity measurements (see p. 79) seem to be consistent with both the observed increase in electrode capacity with the time the electrodes were in solution and the slightly smaller value for the capacity of the electrodes deliberately pre-oxidised before the experiment.
6. THE ANODIC PROCESS

6.1 Expanding Potential Waveform Phenomenon

The Expanding Potential Waves:

Referring back to the original problem of interpreting the rise in open-circuit potential in the interval 10 ms to 10 s after the electrodes were cut under solution, the analysis of the cathodic measurements (section 4.1) has shown conclusively that this potential rise can in no way be attributable to the hydrogen discharge process. The small measured increase in hydrogen overvoltage with time could only have influenced the open-circuit mixed potential by a small amount and towards a more negative potential. The rise in open-circuit potential with time after cutting the electrodes under solution, must therefore have been due to a large reduction in the current from the anodic process. The same general conclusion was reached by Earl in explaining the potential rise in the first few milliseconds after the cut. Earl interpreted the decrease in current carried by the anodic process as being at least partly caused by a several hundred-fold decrease in the proportion of electrode surface acting anodically, or by a correspondingly large decrease in the exchange current \( i_{oa} \) for the anodic process.

These two explanations for the decrease in anodic current with time have been considered in this thesis as possible explanations for the rise in open-circuit potential in the interval 10 ms to 10 s after cutting. Mathematically, however, these two explanations are equivalent since

\[
\frac{i_{oa} A'}{i_{oa} A} = \frac{i_{oa} A}{i_{oa} A'} \quad (6.1)
\]

where the constant \( i_{oa} \) represents the value of \( i_{oa} \) evaluated within 20 μs.
of cutting the electrode when its surface is totally anodic and $A'$, the proportion of the area acting anodically, is a function of the time after cutting. Conversely, on the right-hand side of equation (6.1) $i_{oa}'$ is the time-dependent variable and the constant $A$ represents the total electrode area. Therefore, for convenience it has been assumed in the rest of the text that $i_{oa}$ is changing and not the proportion of electrode area acting anodically.

In the present work, a study was made of the anodic process to determine the cause of the decrease in anodic current between 10 ms and 10 s after cutting the electrodes. This study was complicated by the necessity of having to make these potential measurements in the mixed potential region, whereas those made by Earl on the anodic process occurring within 20 $\mu$s of cutting the electrodes were not subject to this complication being wholly anodic. Even within the mixed potential region, the range of potentials over which measurements could be taken was restricted. At potentials 200 to 300 mV positive of the open-circuit mixed potential, a radical change in the anodic dissolution mechanism was observed (see section 9). As it was not the object of this work to investigate the changed dissolution mechanism, the measurements described in this section were made within 200 mV of the open-circuit potential. By using balanced impressed square-wave currents, with amplitudes within the limits $\pm 10^{-4}$ amps/cm$^2$, it was possible to obtain a large amount of polarisation data from within this voltage range. A balanced square wave was used (see p.76) to avoid biasing the mean of the potential response away from the open-circuit mixed potential. It was found that for these experiments made with small impressed currents, a comparatively long time was required to charge the electrode.
capacity to the equilibrium electrode potential. Therefore, to obtain potential waveforms suitable for analysis, low-frequency square waves had to be used (2.5-10 c/s). The current was applied to the electrode from the instant of cutting it under solution, which was possible because the influence of concentration polarisation was considered negligible at these small current densities.

The measurements made using this technique showed a surprisingly large change in the amplitude and shape of the potential response between milliseconds and seconds after the electrodes were cut. This change in waveform may be seen from the oscillographic trace, fig. 6.1.

![Fig. 6.1 Potential-time trace of an aluminium electrode cut under H₂ saturated 1N.KCl pH 3.2 solution and loaded from the instant of cutting with a balanced square-wave current of 6.15 x 10⁻⁵ amps/cm², frequency 10 c/s.](image)

For this measurement a balanced square-wave current (current density 6.15 x 10⁻⁵ amps/cm², frequency 10 c/s) was applied to the electrode and a moving film camera used to photograph the electrode potential displayed on the oscilloscope screen.
Proposed Explanation:

The explanation proposed to explain these effects is that either $\alpha_a$ and/or $i_{oa}$ was decreasing with time after the cut. How the amplitude of the potential waveform could have been increased by either of these parameters decreasing with time is illustrated in the polarisation diagram (fig. 6.2).

Fig. 6.2 Illustration of the influence of $\alpha_a$ and $i_{oa}$ on the amplitude and mean potential of the electrode response to an impressed square-wave current.
For the purpose of this illustration, the cathodic polarization parameters have been assumed to be independent of time, as the reasoning is not affected by the slight increase in hydrogen overvoltage with time measured in section 4.1. It has also been assumed that the internal current is zero.

In the figure, the Tafel line for the cathodic process is represented by the line R-S, the anodic Tafel line, at time $t_1$ after the electrode was cut under solution by L-M, and the balanced impressed square-wave current by the line I-J. From fig. 6.2, it can be seen that at time $t_1$ after the cut, the amplitude of the electrode potential response to the step current change would be from $V_1$ to $V_2$. The explanation proposed assumes that a few seconds later at $t_2$ the anodic overvoltage is greater which is shown in the diagram by a shift in the line L-M to either G-F or L-N, with G-F representing a decrease in $i_{\alpha a}$ alone or L-N a decrease in $\alpha_a$. As the figure shows, this increase in anodic overvoltage would cause the voltage amplitude to be much larger ($V_1$ to $V_3$) at $t_2$ seconds after the cut. Curves 1 and 2 show the possible potential waves corresponding to time $t_1$ and $t_2$ after the cut. Not only is the increase in amplitude in general agreement with that observed experimentally, but the tendency for the mean potential expansion to move in the positive direction from $P_1$ to $P_2$ also follows the trend of the experimental waves. The object of the following work was therefore to examine the shape, maximum, minimum, and mean potential of the expanding square waves to determine what changes with time were occurring to the overvoltage parameters and whether such changes could explain the observed phenomenon. By examining the shape of the curve, it was expected to obtain not only information on the electrode process but also data on possible effects caused by resistance.
and/or capacity. For this purpose further measurements were made on electrodes cut under solution and loaded with a balanced square-wave current.

Experimental:

The equipment and procedure used for making these measurements were similar to that discussed in section 3.2-6. As before, the electrodes were cut under solution by the ruby cutter. From the time of cutting the electrode a low-frequency 2.5-10 c/s balanced square-wave current was impressed on it. The impressed current for these measurements was so small (± 5 x 10⁻⁷ amps) that it was necessary to use the high-impedance cathode follower, the output of which was fed to the oscilloscope and photographed.

Rather than taking a continuous record of these expanding potential waves, like the oscilloscope trace in fig. 6.1, a method was developed for sampling the potential response by repetitively triggering the oscilloscope with the same square-wave voltage pulse as that fed to the current impresser (see fig. 3.4). To prevent feedback to the electrically floating pulse generator via the electrode and oscilloscope, the oscilloscope triggering mechanism was connected through a capacity to the pulse generator.

By this sampling method a set of synchronous potential waveforms, of the electrode potential response at every third cycle of the impressed square-wave current, could be recorded on a single photograph. An example of this kind of measurement is shown in fig. 6.3. In this photograph, as in all these measurements, the first potential waveform is the most negative trace; thereafter, the traces for successive
measurements move progressively more positive in the anodic or positive half-cycle.

Fig. 6.3 A set of oscillographic potential-time traces of an aluminium electrode cut under solution. Impressed square-wave current \pm 7.8 \times 10^{-5} \text{amps/cm}^2, \text{frequency} 5 \text{c/s}.

6.2 Analysis of the Expanding Potential Waves

Several methods for the elucidation of electrode kinetics from square-wave current measurements have been reported, but because of certain limiting assumptions, fully discussed by Earl\textsuperscript{27}, these methods are not applicable to the measurements made on aluminium. Even the methods used by Earl for examining single electrode processes on aluminium were not applicable to the expanding potential waves discussed in this section because, in this case, two electrode processes were involved, both of which apparently varied with time. A technique was therefore
developed by the author for interpreting these expanding potential waves in terms of the four overvoltage parameters \( i_{ca}, \alpha_a, i_{cc}, \alpha_c \), and the electrode capacity \( C \). Resistance was excluded at this stage.

The Two-electrode Process Model:

The model assumed for the aluminium electrode in the mixed potential region, consisted of a parallel arrangement of two opposed single-stage electrode processes and a capacity to represent the anodic and cathodic electrode reactions and associated electrode capacity. The electrical circuit equivalent to this model is given in fig. 6.4, where the boxes A and H represent the anodic and cathodic electrode processes, and C the electrode capacity.

![Fig. 6.4 The circuit equivalent to electrode with simultaneously occurring anodic and cathodic electrode processes.](image)

The cathodic process for these measurements was hydrogen evolution since in the deoxygenated 1N.KCl and 1N.K₂SO₄ solutions used, hydrogen ion was the only species present that was reducible at the mixed potential
(approximately -1.0 v). The anodic process was the dissolution of aluminium by some mechanism yet to be determined.

Development of the Method of Analysis:

The polarisations of both electrode processes were assumed to be described by the overvoltage relationships, equations (6.2) and (6.3), for the cathodic and anodic processes respectively.

\[i_o = i_{oo} \exp \left[ -\frac{\alpha_o F}{RT} (V - E_o) \right]\]  
\[i_a = i_{oa} \exp \left[ \frac{\alpha_a F}{RT} (V - E_a) \right]\]  

Throughout this work the anodic exchange current has been based on the measured electrode area and an aluminium reversible potential of -1.67 v, there being considerable doubt as to the actual reversible potential of aluminium milliseconds after it has been cut under solution.

The total current flow at the aluminium electrode in the mixed potential region is given by equation (6.4).

\[i = i_a - i_o + i_{cap}\]  

(6.4)

The dynamic response of the two process models, equation (6.5) was obtained by substituting for \(i_{oa}\), \(i_{oo}\) and \(i_{cap}\) in equation (6.4).

\[i = i_{oa} \exp \left[ \frac{\alpha_o F}{RT} (V-E_a) \right] - i_{oo} \exp \left[ -\frac{\alpha_o F}{RT} (V-E_o) \right] + C \frac{dV}{dt}\]  

(6.5)

Equation (6.6) describes the steady state condition of the electrode.

\[i = i_{oa} \exp \left[ \frac{\alpha_a F}{RT} (V-E_a) \right] - i_{oo} \exp \left[ -\frac{\alpha_a F}{RT} (V-E_o) \right]\]  

(6.6)

Of these two equations, equation (6.5) was the more useful because it enabled information on the kinetics of the electrode processes to be deduced from not only the flats and mean potential of the potential
waveform, but also from the shape. With this model (fig. 6.4) the capacity $C$ and the four overvoltage parameters $\alpha_0\, i_{oo}, \alpha_a\, i_{oa}$, were required to define the potential response curve. The electrode capacity $C$ was determined from the initial gradient of the potential waveform as fully explained in section 5.3. The method proposed for obtaining values of $\alpha_0\, i_{oo}, \alpha_a\, i_{oa}$ was to substitute into equation (6.5) experimental values for $C \frac{dV}{dt}$, $V$ and $i$, then solve the resulting equations for the parameters. However, discrete values for the four overvoltage parameters were unobtainable analytically because only two simultaneous equations could be formed from the non-linear equation (6.5). At best, equation (6.5) could be solved for two parameters, by the method of simultaneous equations, provided predetermined values were available for the other two parameters which, for accuracy, were required to be one parameter for each process. As a unique analytical solution was impossible, a trial and error procedure was developed to find the four overvoltage parameters that would best describe each waveform in a set, like that shown in fig. 6.3.

The following description is an outline of this trial and error procedure for analysing a potential waveform recorded at time $t$ seconds after the cut. A trial value for $\alpha_a$ was first selected and a value for $i_{oo}$ was chosen from the results of the square-wave current measurements made on the hydrogen discharge process at potentials more negative than the reversible aluminium potential. The values for $V$ and $C \frac{dV}{dt}$, were measured at two points on the wave cycle being analysed. The current density $i$ at each level of impressed square-wave current was calculated from the measurements of the current and electrode area. With these values of the variables, two simultaneous equations were formed from equation (6.5) and solved for $\alpha_H$ and $i_{oa}$. Using the four overvoltage
parameters determined in this way from two points on the experimental potential wave cycle, the response of the assumed two process model to the same step change in current density was calculated. This response curve was then superimposed on, and its shape compared with, the experimental curve. Another trial value of $\alpha_a$ was then carefully selected to reduce the discrepancies between the experimental and calculated curve. The whole procedure was repeated until a satisfactory match between the calculated and experimental curve was obtained. By applying this method to other experimental curves from the same set, e.g. fig. 6.3, it was possible to obtain an estimate of the changes occurring to the overvoltage parameters with time after cutting the electrode under solution.

Equations for Evaluating $i_{oa}$ and $\alpha_o$:

The equations from which $i_{oa}$ and $\alpha_o$ were calculated, were derived from equation (6.5). This derivation was simplified by first shifting the reference potential for each process; the anodic process from $E_a$ to the minimum point $V_1$ on the potential wave being analysed and the cathodic process from $E_c$ to the maximum point $V_2$ (see fig. 6.4, p. 224). That is:

$$i = i_{oo} k_a \exp \left[ \frac{\alpha_a^F}{RT} (V - V_1) \right] - i_{oo} k_c \exp \left[ - \frac{\alpha_c^F}{RT} (V - V_2) \right] + C \frac{dV}{dt} \quad (6.7)$$

where constant $k_a = \exp \left[ \frac{\alpha_a^F}{RT} (V_1 - E_a) \right] \quad (6.8)$

and constant $k_c = \exp \left[ - \frac{\alpha_c^F}{RT} (V_2 - E_c) \right] \quad (6.9)$

when $V = V_1$

$$i_1 = i_{oo} k_a - i_{oo} k_c \exp \left[ - \frac{\alpha_o^F}{RT} (V_1 - V_2) \right] + C \frac{dV}{dt} \quad (6.10)$$
when $V = V_2$

$$i_2 = i_{oa} \frac{k_a}{k_0} \exp \left[ \frac{\alpha F \Delta V}{RT} (V_2 - V_1) \right] - i_{oc} \frac{k_0}{k_a} + C \left( \frac{dV}{dt} \right)_2$$  \hspace{1cm} (6.11)

Solving (6.10) and (6.11) for $\alpha_o$ and $i_{oa}$

$$i_{oa} = \frac{1}{k_0} \left[ \frac{i_2 - C \left( \frac{dV}{dt} \right)_2 - (i_1 - C \left( \frac{dV}{dt} \right)_1) \exp \left( \frac{\alpha F \Delta V}{RT} \right)}{\exp \left( \frac{\alpha F \Delta V}{RT} \right) - \exp \left( \frac{\alpha F \Delta V}{RT} \right)} \right]$$  \hspace{1cm} (6.12)

$$\alpha_o = \frac{RT}{F \Delta V} \ln \left[ \frac{1}{i_{oa} k_0} \left[ (i_2 - C \left( \frac{dV}{dt} \right)_2) \exp \left( \frac{\alpha F \Delta V}{RT} \right) + i_1 - C \left( \frac{dV}{dt} \right)_1 \right] + \exp \left( \frac{\alpha F \Delta V}{RT} \right) \right]$$  \hspace{1cm} (6.13)

where $\Delta V = V_2 - V_1$

Equations (6.12) and (6.13) were the equations used in the analytical procedure to evaluate $i_{oa}$ and $\alpha_o$. For potential waveforms that reach a steady potential in one half cycle of the impressed square-wave current, a simplified form of equations (6.12) and (6.13) could be used (equations (6.14 and 15)).

$$i_{oa} = \frac{1}{k_a} \left[ \frac{i_2 - i_1 \exp \left( \frac{\alpha F \Delta V}{RT} \right)}{\exp \left( \frac{\alpha F \Delta V}{RT} \right) - \exp \left( \frac{\alpha F \Delta V}{RT} \right)} \right]$$  \hspace{1cm} (6.14)

$$\alpha_o = \frac{RT}{F \Delta V} \ln \left[ \frac{1}{i_{oa} k_0} (i_2 \exp \left( \frac{\alpha F \Delta V}{RT} \right) + i_1) + \exp \left( \frac{\alpha F \Delta V}{RT} \right) \right]$$  \hspace{1cm} (6.15)

Fig. 6.4 shows how the data was measured from the wave cycle being analysed.
It can be seen from equations (6.12,13) that the calculations of $i_{oa}$ and $\alpha_o$ were most accurate when the experimental data was taken at the maximum and minimum potentials $V_2$ and $V_1$, where the capacity currents $C(\frac{dV}{dt})_1$ and $C(\frac{dV}{dt})_2$ were minimal. A small value for current going to charging the electrode capacity was desirable because of the inaccuracies in evaluating this term from the slope of the potential waveform. The optimum shape of the potential waveform for evaluating $i_{oa}$ and $\alpha_o$ is one that reaches a steady potential within a half cycle of the impressed square-wave current (equations (6.14,15)).

This method of analysis is also applicable to other metals that normally have a mixed open-circuit potential, the value of which is determined by the kinetics of the anodic and cathodic processes. The method is particularly useful for metal like aluminium, where one of these electrode processes can only be investigated at potentials close to the mixed potential.
Results:

The value for $i_{\text{CH}} = 2 \times 10^{-7}$ amps/cm$^2$, selected from the summary of the cathodic measurements, table 4.1, was chosen for the analysis of all the potential waveforms in this section. The initial trial values of $\alpha_a$ were 0.05, 0.1, 0.2, and 0.5. Later curves were analysed only for trial values of $\alpha_a$ equal to 0.1 and 0.2 as these values seemed to give satisfactory results for all the traces analysed. Using the chosen values of $\alpha_a$ and $i_{\text{CH}}$ and the values of $V$ and $C(\frac{\partial V}{\partial t})$ measured from the curve being analysed, equations (6.12) and (6.13) were solved for $i_{oa}$ and $\alpha_H$. These calculations were done on an IBM 1620 computer using a program written by the author to solve equation (6.12) and (6.13) (appendix 12.1). For the trace shown in fig. 6.6, the possible values of $i_{oa}$ and $\alpha_H$ were calculated for the assumed parameters $\alpha_a$ and $i_{\text{CH}}$. These calculated and assumed values of the parameters are given in table 6.1.

<table>
<thead>
<tr>
<th>$\alpha_a$ selected</th>
<th>$i_{\text{CH}}$ assumed</th>
<th>$\alpha_H$ calculated</th>
<th>$i_{oa}$ calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>$2 \times 10^{-7}$</td>
<td>0.166</td>
<td>$3.32 \times 10^{-5}$</td>
</tr>
<tr>
<td>0.1</td>
<td>$2 \times 10^{-7}$</td>
<td>0.162</td>
<td>$7.09 \times 10^{-6}$</td>
</tr>
<tr>
<td>0.2</td>
<td>$2 \times 10^{-7}$</td>
<td>0.162</td>
<td>$3.33 \times 10^{-7}$</td>
</tr>
<tr>
<td>0.5</td>
<td>$2 \times 10^{-7}$</td>
<td>0.155</td>
<td>$3.76 \times 10^{-11}$</td>
</tr>
</tbody>
</table>
Using each set of the four overvoltage parameters given in Table 6.1, a calculation was made of the potential response of the assumed two process model to the same step change in current as that applied to the electrode. These curves were calculated by numerically integrating equation (6.5) using the computer program written by Earl (see p. 33).

Before the digital computer was applied to this work, a determined effort was made to simulate the assumed model on a faster calculating TR-48 analogue computer. The analogue computer, however, proved to be unsatisfactory for these calculations because the required degree of accuracy and stability was unobtainable, although better results may have been obtained with this method had log function generators been available to handle the exponential functions.

The potential response curves, calculated by the digital computer for the trial values of $\alpha = 0.05, 0.1, 0.2$ and 0.5, can be seen in fig. 6.6 where they are superimposed on the experimental waveform being analysed. When comparing the closeness of match between the calculated and experimental curves, some discrepancy must be allowed for the inaccuracy in redrawing the experimental curves from the enlarged prints of the oscilloscope traces. The points for the experimental curve were taken from the middle of the oscillographic trace which, at moderate enlargements, was 1/16" to 3/16" thick. From such broad traces as these, some inaccuracy in the redrawing process was unavoidable. Also, where two or more traces came close together, they blurred into a wide trace from which the individual traces could not always be clearly distinguished. For the computed curves, a small change in the value of $C$ used in the integration of equation (6.5), had a very marked effect on the shape of the calculated curve. In view of these factors, the match obtained
between the experimental curves and those calculated for $\alpha_a = 0.1$ and 0.2 was considered very satisfactory. However, the close match for both curves also implied that $\alpha_a$ could be determined only to within an accuracy of $\pm 0.05$ by this analytical procedure. Other computed curves to match other traces measured at different times after the cut on the same electrode may be seen in fig. 6.5,7. Also shown in fig. 6.8,9 are the computed and experimental traces for an oxide-covered electrode, at the time of contact with solution and after 5 minutes immersion.

The values of $i_{oa}$ and $\alpha_H$, determined from the curves shown in fig. 6.5,6,9, are more precise than those determined from the traces shown in fig. 6.7,8 since in the latter case only part of the applied current was going through the electrode process at the minimum and maximum potentials (see p. 94). The rest of the applied current was going into charging the electrode capacity. It has been calculated that in the worst case, at the minimum potential of the negative half cycle, fig. 6.8, only 20% of the applied current was going through the electrode process. Better values of $i_{oa}$ and $\alpha_H$ could have been obtained from measurements made using smaller impressed currents and lower square-wave frequencies, but this was not possible with the equipment used since the smallest controllable current and square-wave frequency were already in use to make the measurements on the oxide-covered electrodes. Further refinement of the equipment was considered unnecessary because even with the most favourable shape of waveform $\alpha_a$ could not be determined to better than $\pm 0.05$ with the analytical method.

The values of the four overvoltage parameters $i_{oa}$, $\alpha_a$, $i_{oh}$ that were chosen to give the best fit with the experimental curves are tabulated in table 6.2.
Fig. 6.5 Potential response of the aluminium electrode to a balanced square-wave current (5 c/s, $1.29 \times 10^{-4}$ to $-1.24 \times 10^{-4}$ amps/cm$^2$) 1.5 seconds after being cut under H$_2$ saturated 1N.KCl solution, pH 3.2.
Fig. 6.6 Potential response of the aluminium electrode to a balanced impressed square-wave current ($5c/s, 1.29 \times 10^{-4}$ to $-1.2 \times 10^{-4}$ amps/cm$^2$) 5.5 seconds after being cut under $H_2$ saturated 1N.KCl solution, pH 3.2.
Fig. 6.7 Potential response of the aluminium electrode to a balanced square-wave current (5 c/s, 1.29 x 10^{-4} to -1.24 x 10^{-4} amps/cm²) 30 seconds after being cut under H₂ saturated 1N KCl solution, pH 3.2.
Fig. 6.8 Potential response of the aluminium electrode to a balanced square-wave current (1.25 c/s, 9.94x10⁻⁶ to -7.67x10⁻⁶). Electrode pre-exposed to oxygen for 15 minutes. Measurement at contact with the solution. Solution H₂ saturated 1N.KCl, pH 3.2.
Fig. 6.9 Potential response of the aluminium electrode to a balanced square-wave current (1.25c/s, 9.94 x 10⁻⁵ to -7.67 x 10⁻⁶). Electrode pre-exposed to oxygen for 15 minutes. Measurement 15 minutes after contact with solution. Solution H₂ saturated 1N.KCl, pH 3.2.
Table 6.2

Values of $\alpha_a$, $i_{oa}$, $\alpha_H$, $i_{dH}$ chosen to give the best fit with experimental curves, fig. 6.5-9.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$a$</th>
<th>$i_{oa}$</th>
<th>$H$</th>
<th>$i_{dH}$ (assumed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5s after cutting under solution</td>
<td>0.1</td>
<td>1.52x10^{-5}</td>
<td>0.175</td>
<td>2.0x10^{-7}</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>1.09x10^{-6}</td>
<td>0.169</td>
<td>2.0x10^{-7}</td>
</tr>
<tr>
<td>5.5s after cutting under solution</td>
<td>0.1</td>
<td>7.1x10^{-6}</td>
<td>0.162</td>
<td>2.0x10^{-7}</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>3.3x10^{-7}</td>
<td>0.155</td>
<td>2.0x10^{-7}</td>
</tr>
<tr>
<td>30s after cutting under solution</td>
<td>0.1</td>
<td>2.6x10^{-6}</td>
<td>0.149</td>
<td>2.0x10^{-7}</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>6.0x10^{-8}</td>
<td>0.145</td>
<td>2.0x10^{-7}</td>
</tr>
<tr>
<td>Pre-exposed to oxygen for 10min. Measurement at contact with the solution</td>
<td>0.1</td>
<td>1.1x10^{-7}</td>
<td>0.09</td>
<td>2.0x10^{-7}</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>1.8x10^{-9}</td>
<td>0.07</td>
<td>2.0x10^{-7}</td>
</tr>
<tr>
<td>Pre-exposed to oxygen for 10min. Measurement 5 min. after contact with the solution</td>
<td>0.1</td>
<td>3.3x10^{-7}</td>
<td>0.132</td>
<td>2.0x10^{-7}</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>8.3x10^{-9}</td>
<td>0.121</td>
<td>2.0x10^{-7}</td>
</tr>
<tr>
<td>*Measurements made within 20µs of cutting the electrode under soln Measurements made 1-4ms later</td>
<td>0.10</td>
<td>2.15x10^{-2}</td>
<td>0.23</td>
<td>2.3x10^{-8}</td>
</tr>
</tbody>
</table>

*Values obtained from Earl.27.
Interpretation of Results:

The reasonably good match obtained between the calculated and experimental curves, figs 6.5-9, showed that the assumed two process model does correctly simulate the potential behaviour of the electrodes and that the assumption made for the analytical procedure was reasonable. The effects of resistance were therefore assumed to be zero. The identical range in the values of $\alpha_a$ given in table 6.2 for aluminium under the five conditions considered implies that to within the accuracy of the method, $\alpha_a$ was unaffected by the presence of an oxide film over the electrode surface or to the time elapsed after cutting the electrodes under solution. The value of $\alpha_a$ deduced from these measurements $\alpha_a = 0.1$ to 0.2 compares with the value of 0.1 determined by Earl\textsuperscript{27}, from measurements made within 20 $\mu$s of cutting the electrode under solution, but his best value for $i_{oa} = 2.15 \times 10^{-2}$ amps/cm$^2$ was several orders of magnitude larger than any value for $i_{oa}$ determined in this work.

One noticeable trend in the parameters recorded in table 6.2 for the electrode cut under solution was that in accordance with the increase in amplitude (see figs 6.5-7) $i_{oa}$ and $\alpha_a$ both decreased with time after cutting. Between 1.5 s and 30 s after cutting, $i_{oa}$ apparently decreased from $1.5 \times 10^{-5}$ to $3 \times 10^{-6}$ ($\alpha_a = 0.1$) or $1 \times 10^{-5}$ to $6 \times 10^{-8}$ ($\alpha_a = 0.2$).

For the oxide-covered electrode, the shape and amplitude were also observed to change with time of immersion (figs. 6.9,10), but in this case the amplitude decreased with time which was apparently caused by a small but evidently significant change in $i_{oa}$ from $1.1 \times 10^{-7}$ to $3.4 \times 10^{-7}$ ($\alpha_a = 0.1$) or $1.8 \times 10^{-9}$ to $8.3 \times 10^{-9}$ ($\alpha_a = 0.2$). This increase in $i_{oa}$ may have been caused by the air-formed oxide film hydrating or being broken down by chloride ion.
The Anodic Overvoltage Parameter $i_{oa}$ as a Function of Time

Mathematical Relationships:

The values of the overvoltage parameters evaluated from the measured potential response indicate that $\alpha_a$ was constant within the limits $\pm 0.05$ and that $i_{oa}$ and $\alpha_H$ decreased with time, after cutting the electrodes under solution, towards the values of $i_{oa}$ and $\alpha_H$ measured on the oxide-covered electrode. From the plots of $\log i_{oa}$ and $\alpha_H$ against the logarithm of time after cutting (lines A, B and C, fig. 6.10, 11), it can be seen that the rates of decrease of $\log i_{oa}$ and $\alpha_H$ were logarithmic with time after cutting the electrodes under solution. The relationship deduced from fig. 6.10 for $\log i_{oa}$, given values of $\alpha_a = 0.2$, $i_{OH} = 2 \times 10^{-7}$, was

$$\log i_{oa} = -5.8 - 0.95 \log(t)$$

and for $\alpha_a = 0.1$, $i_{OH} = 2 \times 10^{-7}$

$$\log i_{oa} = -4.7 - 0.58 \log(t) \quad \alpha_a = 0.1$$

The relationship for $\alpha_H$ obtained from fig. 6.11, given $\alpha_a = 0.1$, $i_{OH} = 2 \times 10^{-7}$, was

$$\alpha_H = 0.178 - 0.02 \log(t)$$

This last relationship for $\alpha_H$ agrees very well with that determined from the square-wave current measurements made at potentials less than $-1.7V$ (equation (6.19))

$$\alpha_H = 0.169 - 0.02 \log(t) \quad i_{oa} = 5 \times 10^{-7}$$

The close agreement between these equations is strong support for the method used to obtain $\alpha_H$ from square-wave current measurements at the mixed potential.
Fig. 6.10 Change in $i_{oa}$ with time. A, B electrodes out under solution. A', B' electrodes pre-exposed to oxygen.

Fig. 6.11 Change in $\alpha_H$ with time. C electrode out under solution. C' electrode pre-exposed to oxygen.
Also drawn on figs. 6.10, 11 are the lines $A'$, $B'$, $C'$, which represent the increase in $i_{\text{oa}}$ and $\alpha_{\parallel}$ with time of immersion for the electrodes initially covered by an air-formed oxide film. The lines in the diagram indicate that for corresponding values of $\alpha_a$, $A$, $B$, $G$ and $A'$, $B'$, $C'$ converge and would intersect at about 5-10 minutes after contact between electrode and solution. Where the lines intersect it is assumed that the surface of the electrodes reach a steady state condition.

This estimate of 5-10 minutes in solution before the electrode surfaces reaches a steady state condition agrees with the 5 minutes deduced from the measurements made on the electrodes cut under solution with small direct cathodic currents (section 4.4). These measurements on the cathodic process also showed that in the steady state the hydrogen overvoltage at the electrodes cut under solution was approximately the same as that at electrodes initially covered by an air-formed oxide film, although the value for $\alpha_H$ ($\alpha_H = 0.085$) was less than the value of $\alpha_H$ ($\alpha_H = 0.14$) obtained from the measurements discussed in this section.

Conclusions:

The value of $\alpha_a$ for anodic dissolution of aluminium is within the range 0.1 to 0.2, independent of time after cutting the electrodes under solution or by pre-exposing the electrodes to oxygen prior to their immersion in the solution.

A large decrease in the value of $i_{\text{oa}}$ occurs between measurements made microseconds ($2.2 \times 10^{-7}$) and minutes ($1 \times 10^{-7}$) after cutting the electrode under solution. The value of $i_{\text{oa}}$, measured on electrodes pre-exposed to oxygen, increases with time in solution towards the same value as that measured on the electrode cut under solution.
It has been concluded from these results that the surfaces of both the initially bare and the initially oxide-covered electrode tend with time in solution towards the same condition. The very much larger change in the value of $i_{\text{oa}}$ for the electrode cut under solution is considered to indicate the formation under solution of a film on the newly cut aluminium surface. The alternative interpretation to a decrease in $i_{\text{oa}}$, that of a changing area ratio (p. 82), will be discussed later in section 8. The results obtained in this section suggest that the following values for $\alpha_a$, $i_{\text{oa}}$, $\alpha_H$, $i_{\text{off}}$ should be used to interpret the rise in open-circuit potential of the aluminium electrodes cut under solution.

$$\alpha_a = 0.1$$
$$\log i_{\text{oa}} = -4.7 - 0.58 \log (t)$$
$$\alpha_H = 0.169 - 0.02 \log (t)$$
$$i_{\text{off}} = 2 \times 10^{-7}$$
7. OPEN-CIRCUIT MEASUREMENTS ON THE ALUMINIUM ELECTRODE

7.1 Electrodes Cut Under Solution

Aims:

Prior to this work, the measurement of the open-circuit potential of the aluminium electrode cut under deoxygenated solutions, has been confined to the interval 0-10 ms after the electrodes were cut. Williams has made some visual observations over longer periods (see p. 12). However, for the reasons given in p. 13, the steady potentials observed by Williams seconds after cutting the electrodes, could not be adequately explained without first interpreting the transient potential behaviour occurring between 10 ms and seconds after cutting the aluminium electrodes under solution. This section of the work was therefore aimed at measuring and interpreting the open-circuit potential behaviour in the interval 10 ms to 10 s after cutting the electrodes under solution.

Experimental Method:

The experimental equipment used to make these open-circuit potential measurements was simply the cell, calomel half-cell, cathode follower and oscilloscope (see fig. 3.3). The high impedance cathode follower was used for the measurements of more than a few milliseconds duration (see p. 23). The problem arose in these measurements that detailed information on the change in open-circuit potential, occurring in the three-decade period 10 ms to 10 s after cutting the electrodes, was not obtainable from a single oscillographic trace. Such information was, however, obtained by combining measurements made with sweep rates of the oscilloscope beam from 1 ms/cm to 1 s/cm.
Fig. 7.1 Open-circuit potential of the aluminium electrode from 0-10 ms after being cut under solution.
Solution 1N.NaCl, pH 3.2, H₂ saturated.

Fig. 7.2 Open-circuit potential of the aluminium electrode from 0-10 ms after being cut under solution.
Solution 1N.K₂SO₄, pH 3.2, H₂ saturated.
Fig. 7.3 Open-circuit potential of the aluminium electrode from 0-100 ms after being cut under solution. Solution 1N.KCl, pH 3.2, H₂ saturated.

Fig. 7.4 Open-circuit potential of the aluminium electrode from 0-100 ms after being cut under solution. Solution 1N.K₂SO₄, pH 3.2, H₂ saturated.
Shown in fig. 7.1,3 are examples of two of the open-circuit potential measurements recorded from the instant the electrodes were cut to respectively 10 ms and 100 ms later. These measurements were made in hydrogen-saturated deoxygenated 1M KCl solutions pH 3.2. Similar 10 ms and 100 ms measurements, made in deoxygenated 1M K₂SO₄ solution pH 3.2, can be seen in fig. 7.2,4. Inspection of such traces as these, showed that the rate of potential rise between A, 0.05 ms after the electrodes were cut, and B 5 ms later, was noticeably slower in chloride solutions than in sulphate. In the measurements of 100 ms duration, the potential traces in chloride solution were, if anything, slightly more positive than those in sulphate. Other measurements of 10 ms and 100 ms duration, made in oxygen-saturated chloride and sulphate solutions, showed that the presence of molecular oxygen in solution had no noticeable effect on these potential measurements.

Interpretation of the Results:

Earl²⁷ has ascribed the slower rate of open-circuit potential rise, observed within the interval 0.1-5 ms after cutting the electrodes under chloride solutions, to the specific adsorption of chloride ion on to the freshly-cut aluminium surface. The adsorption of chloride ion was assumed to inhibit the discharge of hydrogen from the aluminium electrode. Earl has also clearly demonstrated that the rate of potential rise between 0.1 to 5 ms after the electrodes were cut, was independent of the anodic process, being determined entirely by the electrode capacity and overvoltage parameters for the hydrogen discharge process.

From fig. 7.1,3 it can be seen that the rise in potential, following
the cut, was a nonlinear function of the time after cutting the aluminium electrodes. To facilitate the study of this nonlinear potential-time behaviour from 0.1 ms to 10 s after the electrodes were cut, the potential-time measurements were replotted against a logarithmic time scale, fig. 7.6. The data for this figure was taken from the oscillographic traces shown in fig. 7.1,2,5. Fig. 7.5 is an example of the oscillographic trace, measured in the interval 0-2 s after cutting the electrodes under 1N KCl solution pH 3.2.

Fig. 7.5 Aluminium electrode open-circuit potential from 0-2 s after being cut under solution.
Solution 1N KCl, pH 3.2, H₂ saturated.
Fig. 7.6 Open-circuit potential versus log time after cutting aluminium electrodes under $H_2$ saturated solution, pH 3.2.
It can be seen from this plot of potential versus log-time, shown in fig. 7.6, that a distinct change of slope occurs at 0.5 ms in sulphate, and 1.0 ms in chloride, after cutting the electrodes under solution. This change of slope suggests that a complete change in the mechanism of one or both electrode processes occurs at 0.5 ms or 1 ms after cutting the electrodes, and implied that a different phenomenon was probably occurring in the interval 10 ms to 10 s after the cut, to that investigated by Earl, in the interval 0.1 to 5 ms after cutting the electrodes.

The measurements on the anodic and cathodic processes discussed in sections 4 and 6, indicate that the rise in open-circuit potential from 10 ms to 10 s after cutting was caused by decrease in $i_{oa}$ with time. It was also shown in these sections that the potential rise could not have been caused by the changes occurring to the hydrogen discharge process. As a test to confirm that the rise in open-circuit potential between 10 ms and 10 s after the cut may be attributed to the decrease in $i_{oa}$ with time, the open-circuit potential-time characteristics were reproduced by calculation. These calculations were made by substituting into the model representing the aluminium electrode in the mixed potential region (fig. 6.4), the time-dependent relationships for $i_{oa}$ and $\alpha_H$ and the values of $i_{dh}$ and $\alpha_a$ (which were determined in section 6). Equation (7.1) is the dynamic equation for this model on open circuit

$$0 \frac{dV}{dt} = i_{oa} \exp \left[ \frac{\alpha_a F}{RT} (V-E_a) \right] - i_{oo} \exp \left[ - \frac{\alpha_a F}{RT} (V-E_o) \right] \quad (7.1)$$

The potential-time curve for this model was computed by numerically integrating equation (7.1), using a computer program written by Earl (p. 7) and modified by the author to handle $i_{oa}$ and $\alpha_H$ as time-dependent variables.
The value of the electrode capacity $C$, was not important, as it was found that the shape of the computed open-circuit response was practically independent of the value of $C$. The calculations were made using the following values for the parameters.

$$\alpha_a = 0.1$$
$$\alpha_H = 0.169 - 0.02 \log(t)$$
$$\log i_{ca} = -4.7 - 0.58 \log(t)$$
$$i_o = 2 \times 10^{-7} \text{amps/cm}^2$$
$$C = 8 \mu\text{F/cm}^2$$

The curve computed using these parameters was of a widely different shape from that measured experimentally. However, after several trial and error recalculations using other values for the constants in the expression for $i_{ca}$, and the same values for the other parameters, a reasonably good match with the experimental curve was obtained (fig. 7.7).

The expression finally used for $i_{ca}$ was

$$\log i_{ca} = -5.18 - 0.57 \log(t)$$

(7.2)

---

Fig. 7.7 Open-circuit potential of the aluminium electrode from 0-2s after being cut under solution T.892.

1 Experimental curve
2 Calculated curve $\alpha_a = 0.1, i_o = -5.18 - 0.57 \log(t), i_{oH} = 0.169 - 0.02 \log(t), i_{oH} = 2 \times 10^{-7}$

$C = 8 \mu\text{F/cm}^2$
By reproducing in this way the open-circuit potential behaviour of the electrodes, it has been clearly shown that the cause of the potential rise within the interval 20 ms to 2 s after cutting the electrodes can, as the anodic measurements suggested, be interpreted as a decrease in $i_{oa}$ with time. It was also shown by these calculations that within this potential region the electrode potential is dependent on the value of the overvoltage parameters for both electrode processes, but not on the electrode capacity; whereas Earl has found that in the interval 0.1 ms to 5 ms the potential was independent of the anodic process (see p. 112). From 10 s after cutting the electrode under solution, the potential has been observed to remain substantially constant (p. 121). Such a potential behaviour is forecast by the time-dependent relationships deduced for $i_{oa}$ and $\phi_H$. These relationships imply that 10 s after cutting the electrode, the increase in anodic overvoltage with time is approximately equal to that of the cathodic process.

Comparing equation (7.2) for the decrease of $i_{oa}$ with time, with that deduced from square-wave current measurements, equation (7.1), it would appear that the value of $i_{oa}$ calculated from both expressions would be incompatible. However, the values of $i_{oa}$ calculated from both expressions at discrete times within the interval 10 ms to 10 s are not very different, and certainly lie within the two decades that is often accepted as the limits on $i_{oa}$.

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>$i_{oa}$ from equation (7.2)</th>
<th>$i_{oa}$ from equation (7.1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>$3.6 \times 10^{-4}$</td>
<td>$2.9 \times 10^{-4}$</td>
</tr>
<tr>
<td>0.10</td>
<td>$4.9 \times 10^{-5}$</td>
<td>$7.6 \times 10^{-5}$</td>
</tr>
<tr>
<td>1.0</td>
<td>$6.6 \times 10^{-6}$</td>
<td>$2.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>10.0</td>
<td>$8.9 \times 10^{-7}$</td>
<td>$5.2 \times 10^{-6}$</td>
</tr>
</tbody>
</table>
The similarity in the values for $i_{\text{oa}}$ obtained from these two relationships supports the method used in section 6 to obtain the anodic overvoltage parameters. The evidence produced in section 6 strongly suggested that the reason for the decrease in $i_{\text{oa}}$ with time is the formation of a film over the electrode surface. This implies that the fundamental cause for the rise in open-circuit potential of the electrode cut under solution is the formation of a film at the electrode surface.

Open-circuit Potential Behaviour of Aluminium Electrodes in Aerated Solutions:

As mentioned on p. 112, the presence of molecular oxygen in solution appeared to have had no effect on the open-circuit aluminium electrode potential within the first 0.1 s after cutting the electrodes. However, Williams and Nagy noted that after several seconds in oxygen or air-saturated chloride solution, the electrode potential was -0.5 v compared with -1.2 v in deoxygenated solutions pH 5.2. In this work a few measurements were made to study what effect the presence of molecular oxygen in solution had on the open-circuit aluminium potential in the interval 0.1 s to 10 s after the electrodes were cut. For this purpose, measurements of 10 s duration were made in both oxygen-saturated and deoxygenated, hydrogen-saturated chloride solutions. Examples of the oscillographic traces obtained from electrodes in both solutions are shown in fig. 7.8,9. These traces have been reproduced on the same graph in fig. 7.10. This figure shows that from 0.1 s after cutting the electrode, the potential measured in the oxygen-saturated solution rose above that in deoxygenated solution and continued to rise steadily until at about 3 s after the electrode was cut, the potential became unstable at approximately -0.7 v.
Fig. 7.8 Open-circuit potential of the aluminium electrode from 0-10s after being cut under solution. Solution 1N.KCl, pH 3.2, H₂ saturated.

Fig. 7.9 Open-circuit potential of the aluminium electrode from 0-10s after being cut under solution. Solution 1N.KCl, pH 3.2, O₂ saturated.
Fig. 7.10 Open-circuit potential versus time trace for aluminium.
A Cut under 1N KCl, pH 3.2, H₂ saturated
B Cut under 1N KCl, pH 3.2, O₂ saturated
Thirty seconds later the mean of the fluctuating potential was visually observed to be \(-0.5\) \(\text{v}\). By comparison, the electrode potential in the deoxygenated solution rose smoothly to a constant \(-0.9\) \(\text{v}\), visually observed 30s after the electrode was cut. Hagyard and others using microsized electrodes, have investigated this unsteady aluminium potential in air-saturated chloride solution. The author's comments on the characteristics of the open-circuit potential rise in oxygen-saturated solutions and the potential of \(-0.5\) \(\text{v}\) are given in section 9.

7.2 Electrodes Pre-exposed to Oxygen

The potential that has often been reported for oxide-covered aluminium electrodes in chloride solutions is \(-0.5\) \(\text{v}\). The mixed potential calculated for the oxide-covered electrode from the anodic and cathodic overvoltage parameters, determined in sections 4.2 and 6.2, indicate that this electrode should have an open-circuit potential of about \(-0.9\) \(\text{v}\). To test this predicted value of potential, measurements of the open-circuit potential were made on electrodes pre-exposed to oxygen for seconds before immersion in hydrogen-saturated 1N.KOH or 1N.K2SO4 solutions, pH 3.2.

Experimental Method:

For the open-circuit measurements on electrodes pre-exposed to oxygen, the arrangement of the electrical equipment was the same as that for the measurements just discussed in section 7.1. The cell, with glass chamber for pre-exposing the electrodes, was assembled as shown in fig. 3.1. The procedure for making these measurements was very similar to that outlined in section 4.2.
Fig. 7.11 Open-circuit potential, measured at contact between the solution and an aluminium electrode pre-exposed to oxygen for 10 ms.
Solution \(1\text{N.K}_2\text{SO}_4\), pH 3.2, air saturated.

Fig. 7.12 Open-circuit potential, measured at contact between the solution and an aluminium electrode pre-exposed to oxygen for 10s.
Solution \(1\text{N.KCl}\), pH 3.2, air saturated.
Results and Discussion:

The oscillographic traces, fig. 7.11,12, are examples of the measurements made on electrodes pre-exposed to oxygen for 10 ms and 10 s. These two measurements, like all the open-circuit measurements on the pre-exposed electrodes, were recorded from the instant electrical contact was made with the solution. The most noticeable difference between these traces for electrodes pre-exposed to oxygen, and those recorded on electrodes cut under solution, was the complete absence of the 2-3 ms negative potential transient that is characteristic of the open-circuit measurements on electrodes cut under solution, fig. 7.1,2. At the instant of contact with the solution, the potential of the oxide-covered electrodes fell almost immediately to a value that remained fairly steady in the following 20 ms. For the electrodes pre-exposed to wet or dry oxygen for 5-10 ms (fig. 7.11), this steady potential lay between -1.15 to -1.35v, which is within the same potential range as that recorded 10-100 ms after cutting the electrode under solution. For the electrodes pre-exposed to oxygen for 10 s (fig. 7.12), the steady potential at contact with the solution was -0.8 to -0.9v which was close to the constant potential reached 30s after cutting the electrodes under solution, p.121. These measurements on the electrodes pre-exposed to oxygen clearly show that the potential was dependent on the time of oxygen pre-exposure. The disparity between the open-circuit potential measurements on the aluminium electrodes after different pre-treatments of the electrode surface can probably best be seen from fig. 7.13, where the different oscilloscope traces have been superimposed.
Fig. 7.13 Open-circuit aluminium electrode potentials after various surface pretreatments.

A  Cut under solution 10 msec trace  
B  Cut under solution 10 second trace  
C  10 msec pre-exposure to dry hydrogen  
D  10 msec pre-exposure to hydrogen plus water vapour  
E  10 msec pre-exposure to oxygen  
F  15 seconds pre-exposure to hydrogen plus water vapour  
G  10 seconds pre-exposure to oxygen plus water vapour
A suspected reason for the absence of the 2-3 ms negative potential transient in the potential measurements on the oxide-covered electrodes, was slow wetting of the electrode surface, as the wetting rate of these electrodes as they entered the solution was much less than that for the electrodes cut under solution. However, this suspicion was dismissed when negative potential transients to -1.62v were recorded on electrodes pre-exposed in the same way to dry hydrogen for milliseconds, fig. 7.14.

![Graph](image)

Fig. 7.14 Open-circuit potential measured at contact between the solution and an aluminium electrode pre-exposed to hydrogen for 10 ms.
Solution 1N.KCl, pH 3.2, air saturated.

The potential of the electrodes after milliseconds (-1.15v to -1.35v) and seconds (-0.8v to -0.9v) pre-exposure to oxygen, indicates that the total internal current at these electrodes was very much less than that for the "oxide-free" electrode, 0.1 ms (-1.65v) after being cut under solution. Calculations based on the values for the anodic and cathodic overvoltage parameters obtained in sections 4.1,2 and 6.2 show that the internal current was 50 to 100 times less for the electrodes pre-exposed
to oxygen for milliseconds, and 2000 times less after pre-exposing the electrode to oxygen for several seconds. The reason for this much reduced internal current is, as table 6.2 suggests, attributable to \( i_{\text{oa}} \) being several orders smaller for the electrodes pre-exposed to oxygen. It may therefore be concluded that pre-exposing aluminium to oxygen greatly inhibits the anodic process. The significant decrease in anodic current after only 5 milliseconds exposure to oxygen clearly shows that oxygen, either by adsorption or reaction, can rapidly alter the electrochemical activity of aluminium. In fact, the method used in this work for pre-exposing the freshly-cut aluminium to oxygen for milliseconds, could possibly be developed into a technique for studying the kinetics of the oxidation of aluminium at atmospheric pressure.

In this work, the oxide film formed during 10s exposure of the freshly-cut aluminium to oxygen was expected to be similar to the 10Å thick oxide layer normally found on aluminium. The figures for the internal current, given above, suggest that the electrodes pre-exposed to oxygen for only 5-10 ms were covered by a thinner and/or less inhibiting film. It may even be that the potential of these electrodes (approximately -1.2v) is that of an aluminium electrode covered by a monomolecular film of absorbed or reacted oxygen.

The potential measured on the electrodes after being exposed to oxygen for seconds are in close agreement with the potential of -0.9v forecast (see p.121). This agreement between the experimental and calculated potential indicates that the methods used in sections 4 and 6 to determine the parameters for the oxide-covered electrode were reasonably well founded.
7.3 **Electrodes Pre-exposed to Hydrogen plus Water Vapour**

These open-circuit potential measurements on the electrodes pre-exposed to water vapour were made to confirm the notion suggested by the cathodic measurements (section 4.1) that freshly-cut aluminium does react non-electrochemically with water. Information was also expected from these measurements on the rate of reaction between aluminium and water.

**Experimental:**

The equipment and procedure used for these measurements was exactly the same as that for the open-circuit measurements on pre-oxygen exposed electrodes, except that hydrogen plus water vapour instead of oxygen was flushed through the glass chamber for 30 minutes prior to cutting the electrodes. The water vapour atmosphere for these measurements was generated by bubbling purified hydrogen, the inert carrier gas, through a NaCl solution just before it entered the glass cell. The function of the KCl bubbler was to prevent moisture forming in the glass cell by keeping the partial pressure of water vapour in the system below saturation.

Most of the potential measurements made on the electrodes pre-exposed to water vapour were marred by make-and-break electrical contact between the electrode and solution. This defect in the oscillographic traces was attributed to splashing from the shock entry of the electrode into the solution. Better results were later obtained by allowing the electrodes to travel further into the solution. Despite these defects in the oscilloscope traces, enough information was gained from the measurements on electrodes pre-exposed to water vapour to show that after 5-10 ms exposure, the potential at contact with the solution was -1.45 to
Fig. 7.15  Open-circuit potential, measured at contact between the solution and an aluminium electrode pre-exposed to hydrogen plus water vapour for 10 ms. Solution 1N KCl, pH 3.2, air saturated.

Fig. 7.16  Open-circuit potential, measured at contact between the solution and an aluminium electrode pre-exposed to hydrogen plus water vapour for 15 s. Solution 1N KCl, pH 3.2, air saturated.
-1.55v, and was followed by a 2-3 ms potential rise to -1.3v, fig. 7.15. The electrodes pre-exposed to water vapour for 15s, immediately attained a steady potential of -1.2 to -1.3v at contact with the solution, fig. 7.16.

However, the validity of these measurements is doubtful because oxygen was suspected to contaminating the water vapour. A defective seal between the glass cell and the polythene spigot of the cell top could have allowed atmospheric oxygen into the water vapour atmosphere contained in the glass cell. Some valid conclusion can, however, be deduced from the potential level of these measurements since the effect of oxygen could only have been to make the electrode potential more positive. The small initial negative transient in the oscillographic traces for the electrodes pre-exposed to water vapour for 5-10 ms distinguishes these measurements from the measurements on pre-oxygen exposed electrodes, see fig. 7.11. The potentials measured after several seconds pre-exposure to water vapour were 0.3 to 0.4v more negative than the potential of the electrode pre-exposed to oxygen for seconds. These differences in electrode potential between the pre-water vapour and pre-oxygen exposed electrodes imply that either the reaction rate between aluminium and water vapour was very much slower than that with oxygen, or that film produced from the reaction with water vapour was less inhibiting to the electrode processes.

The other point deduced from these measurements was that the potential of the electrodes pre-exposed to water vapour for a given time was much more negative than that for the electrodes cut under solution and left exposed to the solution for the same interval of time. For instance, the potential of the electrodes after 15s pre-exposure to water vapour
was about -1.2v, compared with a potential of -1.0v 10s after cutting an electrode under solution (see traces B and F, fig. 7.10). Calculations based on the cathodic overvoltage parameters indicate that the corrosion current at -1.2v was 3 times that at -1.0v. This smaller current at the electrodes after cutting under solution suggests that a more complex inhibiting reaction occurs in solution than the chemical reaction between water and aluminium; the only reaction that could have occurred at the electrodes cut in the water vapour atmosphere.

Electrochemical formation of a film was also considered. However, calculations based on the sum of the internal corrosion current from the time the aluminium electrodes were cut under solution, showed that only 3% of a monomolecular oxide coverage could possibly have formed in the 20 milliseconds following the cutting of the electrodes and only a 9% coverage was possible 2s later.

The properties of the film assumed for this calculation were Al₂O₃ of density 4 g/cm³ and unit cell dimension 7.84Å. These calculations completely eliminate the possibility of the measured potential behaviour of aluminium electrodes being explained by the electrochemical formation of a film, since the amount of film formed could not possibly have accounted for the measured decrease in the internal current at the aluminium electrodes. These calculations also showed that a film covering most of the electrode surface could not possibly have been formed by the precipitation of anodic and cathodic reaction products.
Discussion:

Earl has shown that for aluminium electrodes cut under solution the open-circuit peak potential of -1.65v cannot be explained unless there is: (i) a change either in anodic parameter, $i_{oa}$, or area function with time (time constant* for the change 0.2 ms or less), and (ii) a 20μs delay before the start up of the cathodic hydrogen discharge process. Some of the evidence on which he based his conclusions is presented in fig. 7.17. In this figure, curve (a) is a typical open-circuit curve obtained experimentally. The remaining curves show the result of (b), $i_{oa}$ changing more slowly (T.C. = 2 ms) but still starting to do so after 20 s delay, (c) starting the change in area ratio from time zero (i.e. no delay), but with T.C. = 0.2 ms, (d) starting the change in $i_{oa}$ from time zero with $T = 2$ ms. Whether $i_{oa}$ changed after 20μs delay either instantaneously, or smoothly with T.C. 0.2 ms, apparently made no significant difference to the resulting curve.

Consider now the measurements on the open-circuit potential behaviour of aluminium electrodes after their pre-exposure to oxygen or water vapour (see section 7.2 and 3, fig. 7.13). Within microseconds of contact with the solution the potential of the electrodes pre-exposed to water vapour fell to about -1.5v and then rose in the next 2-3 ms to about -1.3v (curve D, fig. 7.13). The similarity between the potential behaviour of this electrode and that of the electrode cut under solution (curve a, fig. 7.17) suggests that the same conditions (viz. 20μs delay, T.C. < 0.2ms) apply to this electrode as for the electrode cut under solution. It would seem that what takes place in milliseconds in the vapour phase is accomplished in microseconds in the liquid phase, and that adsorption of

*Time constant T.C., defined as time taken for 63.2% of the final effect of a step change in input to be attained.
water on to the bare aluminium surface does not significantly affect its electrochemical behaviour.

For the electrodes pre-exposed to oxygen for milliseconds, the potential at contact with solution fell within microseconds to a steady potential of about -1.25v (trace E, fig. 7.13). The absence of a negative transient to a peak in these measurements indicates that there is no delay in start up of the hydrogen discharge process on aluminium covered by an adsorbed or reacted layer of oxygen (curves a and c, fig. 7.17).
From these observations there is a strong implication that the formation of a film is necessary before hydrogen ion can discharge from aluminium electrodes.

A tentative description may now be made of the possible phenomena occurring at the aluminium electrode freshly cut under deoxygenated 1M KCl solution. The fall in potential from an initial zero volts to about -1.65v, measured 20$\mu$s after cutting the electrodes, represents ionisation of the new aluminium surface unaccompanied by any appreciable hydrogen ion discharge. After 20$\mu$s the new surface of aluminium starts to react non-electrochemically with water to form presumably a monomolecular oxide or hydroxide film which covers most of the surface in about 200$\mu$s. The formation of this film has the effect of reducing the current from the anodic dissolution process either by reducing the area of bare metal or by impeding the transfer of aluminium ions through it to the solution.

As the film forms, hydrogen ions start to discharge from its surface and a mixed electrode system is established with a mixed potential of -1.3v, reached 2-3 ms later. The rise in open-circuit potential after 3 ms is due to a further reduction in current from the anodic process apparently caused by the film thickening. The electrode attains a steady potential of -0.9v some minutes after the electrode is cut, when the changes in the film become very much slower. This potential is the same as that for aluminium, covered by an air-formed oxide film, in oxygen-free electrolyte solutions.
8. CONCLUSIONS

Summary of Results:

1. The cathodic overvoltage parameter $\alpha_H$ for the discharge of hydrogen on aluminium decreased from a value of 0.23 measured milliseconds after the electrodes were cut under solution, to about 0.16 several seconds later. The relationship which describes this decrease in $\alpha_H$ in this time interval is

$$\alpha_H = 0.169 - 0.02 \log(t)$$

The value of $\alpha_H$ for an aluminium electrode pre-exposed to oxygen for 15 minutes was about 0.09 at contact with the solution, increasing approximately 0.12 after 5 to 10 minutes.

2. The value of the cathodic hydrogen overvoltage parameter $i_{0H}$ (about $2 \times 10^{-7}$ amps/cm$^2$) was substantially independent of the time in solution after cutting the electrodes and also unaffected by pre-exposure of the electrodes to oxygen prior to their immersion in solution.

3. The approximate value of the anodic overvoltage parameter for aluminium dissolution $\alpha_a$ was estimated at 0.45 $\pm$ 0.05 from mixed potential measurements. This value was not altered by the time of contact between electrode and solution or even by pre-exposing the electrodes to oxygen.

4. A large decrease in the value of the anodic overvoltage parameter $i_{0a}$ was observed with time elapsed after cutting the aluminium electrodes under solution. The value of $i_{0a}$ was measured to be $2.2 \times 10^{-2}$ amps/cm$^2$ microseconds after cutting the electrode, and $1 \times 10^{-7}$ amps/cm$^2$ some minutes later. Between 10 ms and 10 s the decrease in the value of $i_{0a}$ has been described by an equation of the form
\[ \log i_{oa} = -5.0 - 0.6 \log (t) \]

For the electrodes pre-exposed to oxygen for 15 minutes before being immersed in solution, \( i_{oa} \) was very small initially \((1 \times 10^{-8})\), but increased with time in solution towards the same value as that for the electrode cut under, and left in, solution for 5 minutes.

5. Aluminium has an electrode capacity of between \(4-10 \mu F/cm^2\) for a wide range of conditions.

Conclusions:

1. These variations in overvoltage parameters can be used to explain the rise in open-circuit aluminium electrode potential from 20 ms to 2 s after cutting the metal under solution.

2. The overvoltage parameters of the initially bare and the initially oxide-covered aluminium electrodes, tend to converge towards the same values with time in solution. This suggests that the state of the surface at these electrodes, after a few minutes contact with the solution, is intermediate between that of the bare metal and an air-formed oxide film. However, the much greater change in the overvoltage parameters for the electrodes cut under solution strongly points to the formation of a film on these electrodes, although thinning or hydration of the air-formed oxide film may occur.

3. Calculations have shown that the electrochemical process considered here could not have formed this film on the initially bare metal surface.

4. The film has electron conducting properties.

5. The film impedes the dissolution of aluminium. The decrease in \( i_{oa} \)
with time after cutting the aluminium electrode under solution may be attributable to the film acting as a barrier to the transfer of aluminium from the metal to the solution.

6. The discharge of hydrogen on aluminium appears to occur only on the film-covered surface. This seems a probable explanation for the fact that $i_{\text{OH}}$ which is normally sensitive to the condition at the electrode surface, has apparently the same value whether measured milliseconds or minutes after the electrode is cut under solution or even on an air-oxidised aluminium surface.

It is concluded that a film with electron but not ion-conducting properties forms non-electrochemically on aluminium surfaces freshly cut under solution. The rise in open-circuit mixed potential between 10 ms and 10 s after cutting a new aluminium surface under solution is attributed to the much larger inhibiting effect that this film has on the anodic dissolution of aluminium compared with that on the cathodic hydrogen ion discharge process.

The question of whether the observed decrease in current from the anodic process is due to a decrease of $i_{\text{pa}}$ with time, or to a reduction in the proportion of electrode area acting anodically, has not been resolved by this work. However, the measurements on the aluminium electrodes covered by an air-formed oxide film suggest that it is more reasonable to assume a decrease in $i_{\text{pa}}$ with time.
The Constant Potential Phenomenon of Anodically Loaded Aluminium Electrodes in Chloride Solution

A number of experiments were made to confirm the author's suspicion that, at anodic current densities higher than those previously used in this work, the anodic polarisation of aluminium was influenced by the anion in solution. The results of these experiments led to some interesting and illuminating conclusions on why aluminium has a potential of -0.5v in aerated solutions (see section 2.2).

Experimental Method

The experiments were made by measuring the electrode potentials for a range of static anodic currents impressed on to the electrodes. From a plot of these potential measurements against the logarithm of the current densities at the electrode, it was possible to observe the anodic polarisation characteristics of the aluminium electrode. For convenience, the experiments were confined to measurements made in chloride, bromide and sulphate solutions, as these ions were thought to typify the ions in solutions of which anodically loaded aluminium is active or passive.

The arrangement of the equipment used for these measurements can be seen in fig. 9.1. The direct current for the measurement was applied from the current impresser (fig. 3.5), through a Kipp Microva ammeter to the platinum electrode-electrolyte-aluminium electrode cell. The potential of the cell, aluminium electrode-calomel half-cell, was measured with the high-impedance cathode follower (p. 23), the output of which was read from a Kipp Microva voltmeter.
Calibration of this measuring circuit was by switching a Weston standard cell to the input of the cathode follower before and after each experiment. The cell for the spinning electrode apparatus, fig. 3.2, was used for these measurements, although most of the measurements were made with the electrode stationary.

The aluminium electrode was cut under solution by the procedure described in section 3.2. A series of current-potential measurements was started 2-3 minutes later, when the open-circuit potential had reached a steady value. These measurements were made by applying an impressed direct current to the electrode in step increments, and recording the electrode potential at each level of current. The readings were taken at about 2 minutes after each current change which, except for the measurements in sulphate solutions, was the time required for the electrode potential to reach a steady value. In sulphate solutions, the electrode potential was still drifting by 2-3 millivolts per minute when the reading was taken. The total time for each experiment was about 30 minutes.
Fig. 9.2 Anodic polarisation of aluminium.

A 1M. KSO4, pH 3.0, H2 saturated
B 1M. KCl, pH 3.2, H2 saturated
C 1M. KBr, pH 3.2, H2 saturated
D 1M. KCl pH 3.2, O2 saturated
E 1M. KCl pH 3.2, H2 saturated
F Cathodic reduction of hydrogen ion on aluminium in 1M. KCl.

Potential -0.6 ~ -0.8 ~ -1.0 ~ -1.2 ~ -1.4 ~ -1.6 ~ -1.8 ~ -2.0
Log Current Density

IC = 2 x 10^-7 amps/cm^2.
The Experimental Results:

In fig. 9.2 are shown the anodic polarisation curves plotted from the measurements made in hydrogen-saturated solutions of normal KCl, K₂SO₄, KBr, and the curve obtained in oxygen-saturated 1N. KCl. The solution pH for these four experiments was 3.2. These measurements show conclusively that, at current densities greater than 5 x 10⁻⁴ amps/cm², the anodic polarisation of aluminium was dependent on whether the anion in solution was Cl⁻, Br⁻, or SO₄²⁻. Curve A, for the electrode in sulphate solution, shows the onset of passivation as indicated by the large potential change for a small increase of current, at current densities of about 10⁻³ amps/cm². Curves B and C, obtained in chloride and bromide solutions, are quite different in that they show no sign of passivation as the electrode was at an almost constant potential from 10⁻⁴ to 10⁻¹ amps/cm². A similar potential behaviour of the aluminium electrodes in chloride solutions has been reported by Ergang, Masing, Mohling¹⁴, but their measurements did not extend beyond current densities of 10⁻⁴ amps/cm².

Zirconium⁵⁵ and magnesium⁵⁶ are reported to have similar constant potential characteristics in chloride and bromide solutions. Other measurements by the author have shown that for aluminium the potential of the linear section of the curve, measured in 1N. KCl solution, was the same whether the measurements were made with the impressed current initially zero and increased to the maximum, or initially at the maximum and decreased to zero. This linear section was also found to be unaffected by solution pH within the range 2 to 11, change of electrolyte cation from K to Sr, whether the solution was oxygenated or deoxygenated, stirred (Ref No. 7200) or unstirred or, finally, whether the electrode was cut under solution or pre-exposed to air for minutes prior to the experiment.
However, the position of the curve was affected by the concentration of chloride, the linear section being 0.043v more positive in 0.4N.KCl solution.

Calculation has shown that any slight rise in potential at current densities greater than $5 \times 10^{-2}$ amsp/cm$^2$ can be attributed to the electrical resistance in the electrolyte adjacent to the electrode. At the higher anodic current densities in chloride solutions, a copious gaseous discharge from the aluminium electrode surface was visually observed. Inspection of the electrode surface at the completion of each experiment showed that, in general, the electrode surface was rough, but that the metal had dissolved from the whole surface. However, for the measurements in solutions of high pH or solutions containing a mixture of chloride and sulphate ions, the surfaces of the electrodes were pitted with a few deep pits.

The Anodic Polarisation Curve in Aerated Chloride Solutions:

Curve D, shown in fig. 9.2 for the potential characteristics of the aluminium electrode in oxygen-saturated 1N.KCl solution, indicates that the electrode potential was substantially constant at about -0.5v over the current density range $10^{-6}$ to $10^{-1}$ amps/cm$^2$. At current densities below $10^{-4}$ amps/cm$^2$, this potential was distinctly more positive than the potential measured in deoxygenated solutions (curve B). A tentative explanation for this distinction between curves D and B is given in section 9.2, following.

The open-circuit potential of -0.5v measured in this work for the aluminium electrode in oxygenated chloride solution agrees with the potential recorded by most other observers (see p. 9). Previous
observers\textsuperscript{13,14,21} have, however, associated the potential of -0.5v only with the presence of molecular oxygen in solution, whereas this work shows that a potential of -0.5v can also be induced by an anodic current load of $10^{-4}$ amps/cm\textsuperscript{2} or greater, even in the absence of molecular oxygen. This suggests that the potential of -0.5v recorded in oxygenated chloride solutions is associated in some way with the unusual anodic polarisation characteristics of aluminium in chloride solutions.

9.2 Molecular Oxygen Reduction on Oxide-covered Aluminium

Oxygen Reduction:

When attempting to explain the potential of -0.5v for the aluminium electrode in aerated normal chloride solution, other authors have seemingly ignored the possibility of the reduction of molecular oxygen as being the major cathodic process, although there is some evidence to suggest that this process is catalysed by metal oxides\textsuperscript{60}. Hakerman et al\textsuperscript{57,58} have reported polarisation curves for the reduction of molecular oxygen on oxide-covered titanium and zirconium electrodes. Their polarisation curves showed that the limiting current for the diffusion of molecular oxygen from the bulk solution to the electrode surface was $10^{-4}$ amps/cm\textsuperscript{2} at -1.0v. This experimental value for the limiting diffusion current of molecular oxygen in solution agrees closely with that calculated by King\textsuperscript{59}, $1.5 \times 10^{-4}$ amps/cm\textsuperscript{2}, for solutions stirred by gas bubbling.

Similar polarisation curves for the cathodic reduction of molecular oxygen at aluminium electrodes in chloride solutions could not be obtained because of the unusual constant potential behaviour of the aluminium
electrode in this solution (see curve D, fig. 9.2). This behaviour made it impossible to polarise the electrode either more positive or more negative of -0.5v. An experiment was therefore made to determine whether molecular oxygen could also be reduced at an oxide-covered aluminium surface. For this test, a rod of 99.999% aluminium, which had been exposed to the atmosphere for several weeks, was immersed and left in a 1N.KCl or 1N.K2SO₄ solution of pH 3.2, contained in an open test tube. Several hours later the specimen was removed and the solution tested for the presence of hydrogen peroxide by the Kingsell's iodide method. The detection of hydrogen peroxide in this solution was indisputable evidence for the reduction of molecular oxygen at oxide-covered aluminium, since under the condition of the experiment, the peroxide could have come only from molecular oxygen being reduced at the aluminium electrode.

An indication as to the polarisation characteristics of this process at the aluminium electrode was obtained from measurements made in stirred and unstirred aerated 1N.K₂SO₄ solution. In the unstirred solution, the open-circuit potential was -0.48v; stirring the solution by rotating the electrode at 3600 rpm (Re No. 7600) shifted the potential to about -0.28v. Had the anodic process been affected by the stirring, a negative shift in potential would have been recorded. The stirring must, therefore, have caused a higher internal cathodic current. However, for this to have happened the current from the cathodic process must have been limited by diffusion of the active species through the electrolyte, which strongly suggests that the reduction of molecular oxygen, being the major cathodic process, was limited by the diffusion of dissolved oxygen through the electrolyte. Although there is no data available on the kinetics for
oxygen reduction at aluminium electrodes, a reaction rate significantly higher than the rate of oxygen diffusion is not improbable because of the large overvoltage (about \(-1.3\, \text{V}\)) for this reaction at \(-0.3\, \text{V}\) to \(-0.5\, \text{V}\). As the current from diffusion limited electrode processes are independent of the electrode, the above considerations suggest that the polarisation curve for the reduction of oxygen at aluminium electrodes would, if it could be measured, be similar to the limiting diffusion curve measured on zirconium electrodes.

**Oxygen Reduction as the Cathodic Process at Aluminium Electrodes:**

In fig. 9.2, the polarisation curve for the reduction of molecular oxygen at a zirconium electrode (curve E) is superimposed on the anodic polarisation curves for aluminium. Hakerman et al.\(^5\) claim that the steep slope of this curve at potentials more negative than \(-0.3\, \text{V}\) is the limiting current for the diffusion of molecular oxygen, and they claim that the change of slope at about \(-1.0\, \text{V}\) indicates the onset of hydrogen ion discharge as the major cathodic process. If curve E also represents the limiting diffusion current of aluminium electrodes, then the open-circuit mixed potential of this electrode in aerated chloride solution is given by the intersection of curve E with the anodic polarisation curve (curve B). That is where the total current from the anodic and cathodic processes are equal. As the diagram shows, the point of intersection occurs within the constant \(-0.5\, \text{V}\) region of curve B, which explains why \(-0.5\, \text{V}\) is always measured for the open-circuit potential for the aluminium electrode in aerated chloride solutions (curve D). The graph also shows why a potential of \(-0.5\, \text{V}\) is recorded regardless of the precision of measurement, the effect of a large measuring current being merely to move the point of
intersection to a higher current density at the same electrode potential (see fig. 9.2).

The Negative Potential Shift:

The observation has been made by several authors that the potential of an aluminium, immersed in an aerated solution, gradually shifts to a more negative potential when the solution is purged of oxygen (see p. 9). The following explanation for this potential behaviour has been deduced from the polarisation data given in fig. 9.2. The potential of -0.5v for aluminium in an aerated chloride solution is, as explained above, a mixed potential between the cathodic reduction of molecular oxygen and the anodic process. This condition is shown by point 1 in fig. 9.2.

Now, removing molecular oxygen from the solution merely eliminates oxygen reduction as the major cathodic process. The potential of the electrode is, therefore, induced to change to a more negative mixed potential with hydrogen discharge as the cathodic process. That is, the potential shifts from -0.5v at 1, to -1.0v at 2, the point of intersection of the anodic polarisation curve B, with the hydrogen discharge polarisation curve F. The curves in fig. 9.2 indicate that a similar potential behaviour is to be expected when sulphate solutions are deoxygenated. Such a behaviour has been observed. Ergang et al.\(^\text{14}\) have suggested that the observed potential behaviour was caused by breakdown of the oxide film, but it is highly improbable that oxide film breakdown would have occurred in sulphate solution.

Conclusions:

The measurements discussed in this section substantiate the conclusion
already reached that oxide-covered aluminium electrodes are at a mixed potential, the value of which is determined by equal currents from the anodic and cathodic processes. In chloride and bromide electrolytes, the anodic polarisation of aluminium is characterised by a constant potential in the current density range from $10^{-4}$ to at least $10^{-1}$ amperes/cm². It has been suggested and supported by strong evidence that the major cathodic process occurring at an oxide-covered aluminium electrode in an aerated electrolyte solution is the reduction of the molecular oxygen dissolved in solution. Indications are that, for aluminium electrodes in such solutions, the oxygen reduction current is limited by the rate of arrival of oxygen at the aluminium surface. The potential of aluminium in aerated chloride solution is, therefore, established by the limiting diffusion current for oxygen ($10^{-4}$ amperes/cm²), polarising the anodic process into its constant potential region, which for chloride solutions occurs at -0.5v. This explanation therefore explains why a potential of about -0.5 has been generally reported as the potential of the aluminium electrode in aerated chloride solutions. The removal of oxygen from solution simply eliminates the reduction of molecular oxygen as the major cathodic process, and causes the aluminium electrode to take up a mixed potential with the cathodic hydrogen discharge process at a more negative potential.
10. **SYMBOLS**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>electrode capacity</td>
<td>farads/cm²</td>
</tr>
<tr>
<td>E</td>
<td>reversible potential of the electrode with respect to the same reference electrode as V</td>
<td>volts</td>
</tr>
<tr>
<td>F</td>
<td>Faraday</td>
<td>coulombs/mole</td>
</tr>
<tr>
<td>H</td>
<td>amplitude of sawtooth waveform</td>
<td>volts</td>
</tr>
<tr>
<td>R</td>
<td>universal gas constant</td>
<td>joules/°K</td>
</tr>
<tr>
<td>R</td>
<td>resistance</td>
<td>ohm cm²</td>
</tr>
<tr>
<td>T</td>
<td>absolute temperature</td>
<td>°K</td>
</tr>
<tr>
<td>V</td>
<td>potential of the electrode with respect to a reference electrode</td>
<td>volts</td>
</tr>
<tr>
<td>V₁</td>
<td>electrode potential at the minimum point on the potential waveform</td>
<td>volts</td>
</tr>
<tr>
<td>V₂</td>
<td>electrode potential at the maximum point on the potential waveform</td>
<td>volts</td>
</tr>
<tr>
<td>ΔV</td>
<td>V₂ - V₁</td>
<td>volts</td>
</tr>
<tr>
<td>kₐ</td>
<td>( \exp \frac{\alpha F}{RT} (V₁ - E_a) )</td>
<td></td>
</tr>
<tr>
<td>kₒ</td>
<td>( \exp - \frac{\alpha F}{RT} (V₂ - E₀) )</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>slope of Tafel line</td>
<td></td>
</tr>
<tr>
<td>f</td>
<td>frequency of square-wave current</td>
<td>cycles/second</td>
</tr>
<tr>
<td>iₒ</td>
<td>exchange current density</td>
<td>amps/cm²</td>
</tr>
<tr>
<td>i</td>
<td>impressed current density: anodic if positive cathodic if negative</td>
<td>amps/cm²</td>
</tr>
<tr>
<td>i₁, i₂</td>
<td>impressed current densities corresponding to the flats on the square-wave current</td>
<td>amps/cm²</td>
</tr>
</tbody>
</table>
\( i_{\text{cap}} \) capacitive current density \((\text{amps/cm}^2)\)

\( n \) number of electrons transferred in the rate-controlling process

\( t \) time elapsed after contact between electrode and electrolyte \((\text{seconds})\)

\( \alpha \) overall transfer coefficient

\( \beta \) electron transfer coefficient \(0 < \beta < 1\)

\( \eta \) overvoltage \(= V - E\) \((\text{volts})\)

\( \theta \) angle of tangent drawn to the initial slope of the potential response curve \((\text{degrees})\)

Subscripts

a anodic

b cathodic

H hydrogen ion discharge

\( t \) time after contact between electrode and electrolyte

\( t^+ \) instant before a step change in current

\( t^- \) instant after a step change in current

R resistance

E electrode process
11. REFERENCES


36. Earl W.B., Private communications.
59. King C.V., ibid., 102, 693 (1955).
12.1 IBM 1620 Computer Program for Obtaining Estimates of $i_{oa}$ and $\alpha$

This program calculated $i_{oa}$, $k_a$, and $\alpha$ from equations (6.12) and (6.13) and the electrode capacity from either equation (5.9) or (5.11). The electrode capacity is first computed from the slope of the potential waveform at the minimum and maximum potentials. This value of capacity, together with trial estimates of $\alpha_a$ and $i_{oo}$, are then used in the calculations of $i_{ca}$, $k_a$, and $\alpha$. Significance of the program variables is given below, and the program listing follows. Operating and input specification details are available from the complete write-up in the Department of Chemical Engineering, University of Canterbury.

$W$ and $E$  length and breadth of electrode

$F$  length of flat on tip of chisel electrode-cutter

$\text{ANG}$  angle of cutter

$\text{AREA}$  area of electrode

$R$  current calibrating resistor

$T$  time scale

$V$  voltage scale

$\text{CA}, \text{CB}$  current density for respective flats

$\text{CC}, \text{AC}$  electrode capacity at minimum and maximum potential

$\text{VA}, \text{VB}$  minimum and maximum potential on electrode potential waveform

$\text{VRA}, \text{VRB}$  reversible potential of cathodic and anodic process on the same voltage scale as VA and VB

$A, B$  $\alpha_a, \alpha$, overall transfer coefficient for respective cathodic and anodic processes

$\text{CAR}$  $i_{oo}$ exchange current for cathodic process
measurements from photographic traces

CR,B,A for area calculation

P,S,U,W capacity from angle measurements

H,D,T,V capacity from sawtooth potential waveform

VR voltage scale

VT time scale

The remaining variables in this program are used internally and may not have any physical significance.
READ21, W, E, F, ANG, R, CR, B, A
PRINT21
Z=3.1416/180.
AREA=W*(F+(E-F)/SIN(ANG*Z/2.))*1.0E-6
READ31 VR, TR, T, V, H, D, P, S, U, W, L
PRINT31
CA=1.018*(CR+A)/(CR*R*AREA)
CB=1.018*(CR+B)/(CR*R*AREA)
IF (SENSE SWITCH 1) 22, 24
22 G=T*VR/ (TR*V)
IF (L-1)=26 23, 26
23 CC=(CA-CB)*D*G*.5/H
AC=CC
GO TO 24
26 CC=(CA-CB)*G/(SIN(P*Z)/COS(P*Z)-SIN(W*Z)/COS(W*Z))
AC=(CB-CA)*G/(SIN(S*Z)/COS(S*Z)-SIN(U*Z)/COS(U*Z))
PRINT25 CA, CB, CC, AC
IF (SENSE SWITCH 2) 27, 29
27 CA=CA-G*CC*SIN(U*Z)/COS(U*Z)
CB=-CB-G*AC*SIN(W*Z)/COS(W*Z)
CALL PIP(CA, CB)
GO TO 29
31 FORMAT(10H)
21 FORMAT(10H)
28 FORMAT(3X18HIMPRESSED)
25 FORMAT(4E10.3)
END
SUBROUTINE PIP(CA, CB)
READ 10, CAR, VA, VB, VRA, VRB, A, B
PRINT11 CA, CB, CAR, VA, VB, VRA, VRB
T=39.4349*(VA-VB)
PRINT13
2 E=(CA-CB*EXP(-T*B))/((EXP(T*A)-EXP(-T*B))
F=(CB-CA*EXP(-T*A))/((EXP(T*B)-EXP(-T*A))
G=EXP(LOG(E)-A*(VRA-VA)*39.4349)
H=EXP(LOG(F)+B*(VRB-VB)*39.4349)
IF (SENSE SWITCH 3) 3, 4
3 AA=LOG(CAR/E)/(39.4349*(VA-VRA))
IF (AA-A-.002)5 4, 6
5 IF (AA-A+.002)6, 4, 4
6 A=AA-(AA-A)/2.
GO TO 2
4 PRINT12. A, B, G, H
RETURN
10 FORMAT(E7,3,6F5.3)
11 FORMAT(E9,2,2XE9.2,2XE9.2,2XF6.3,2XF6.3,2XF6.3,2XF6.3)
13 FORMAT(4X5HALPHA 12X7HCURRENT)
12 FORMAT(2F7.3,2XE10.3,2XE10.3)
END