CHAPTER I

THEORIES OF ANODIC OXIDE FILMS ON VALVE METALS
All metals, in contact with oxygen at atmospheric pressure, are unstable at room temperature and, thermodynamically, should tend to form oxide. These reactions often fail to occur at an appreciable rate. The usual reason for the lack of reaction is that a complete film of insoluble or slowly soluble oxide is formed. This separates the reactants, and further reaction can only occur by diffusion or migration (field-assisted movement) of metal or oxygen ions through the film. If this oxide-coated metal is made the anode of an electrolytic cell (with a solution that does not dissolve the oxide), the applied current sets-up an electrostatic field in the oxide (or increases the field already present). This produces continued growth of the film by causing the metal or oxygen ions to be pulled through the film. The growth of the anodic films is, thus, essentially a problem of ionic conduction at high field strength complicated by the presence of two interfaces — metal/oxide and oxide/solution at which transfer process must occur. Other anodic processes, such as oxygen evolution etc., are almost entirely inhibited, even though there may be a potential difference of some hundreds of volts across the film, provided the metal surface is smooth, not contaminated with other metals and free from inclusions. The formation of the film is normally limited by a breakdown which occurs when
a certain range of thickness or potential is reached. It is characterized by 'sparking', oxygen evolution and the formation of a thick discoloured film. Over the range of potential in which the current is very small, the oxide acts as the dielectric of a capacitor. Applications of the formula for a parallel-plate capacitor should give an estimate of the thickness of the film, if there is no flaw/pore in the film.

The oxide on aluminium and similar reactive metals is not removed by reduction on cathodic polarization. This is probably because the same order of field strength would be required to reverse the film forming process as to make the ions move during formation of the film, and the easy flow of electronic current during cathodic polarization makes such high fields difficult to obtain.

**THEORY OF GROWTH KINETICS OF ANODIC OXIDE FILMS AND EQUATIONS FOR HIGH FIELD IONIC CONDUCTIVITY**

Before dealing specifically with the theories for anodic oxide growth, it is necessary to classify the two situations where ionic charge transport is possible. Considering a cation mobile system, where movement of these cations depends on the electric field strength across the oxide film, the two types are: (1) high-field conduction, where it is assumed that the electric field strength is high enough to prevent
movement of cations against the field direction; (ii) low-field conduction, where it can no longer be assumed that movement of cations against the field direction is negligible. In the following theories, it is assumed that high-field ionic conduction is operative, since the electric field strengths lie between $10^6$ and $10^7$ V/cm, these fields being regarded as sufficient to prevent ionic motion against the field direction.

Under high-field conditions, Guntherschulze and Betz\textsuperscript{1} showed that the relation

$$i = A \exp BE$$

represents the dependence of ionic current density $i$ on electric field strength $E$, at least to a first approximation. Here $A$ and $B$ are temperature dependent constants involving parameters of ionic transport. As in an electrochemical reaction, charge transfer is controlled by the step which has the highest potential energy w.r.t. the initial state, i.e., the rate determining step. Examination of the reaction environment metal/metal-oxide/electrolyte permits the following three rate-determining steps to be postulated:

- (i) ion transfer across the metal/metal-oxide interface;
- (ii) ion transfer across the oxide bulk;
- and (iii) ion transfer across the metal-oxide/elect-
rolyte interface producing a solvated ion. Theoretical justification of the exponential relationship proposed by Guntherschulze and Betz\(^1\) has been based upon a combination of (i) and (ii) as the rate determining step.

Cabrera and Mott\(^2\) discussed the growth of very thin films formed both by anodic and atmospheric oxidation, the electric field necessary being produced by the applied potential and adsorbed oxygen, respectively. Several basic assumptions made were: (a) the transfer of an ion across the metal/oxide interface is the rate determining step in oxide growth; (b) the transfer of an ion through the oxide bulk is fast due to lowering of diffusion barriers by applied electric field; and (c) the field is sufficiently high to ensure that negligible amounts of ions are moving against the electric field direction. These assumptions imply that the number of ions in transit through the film is very small, and hence space charge (accumulation of charged ions in an oxide film which can lead to a net lowering of the applied field) is negligible. With these assumptions, Cabrera and Mott proposed that the ionic current density \(i\) could be written as

\[
i = n \gamma q \exp \left\{ \left( \frac{\Phi - qB}{kT} \right) \right\} \ ... \ (2)
\]

where \(n\) is the surface density of mobile ions (ions
cm$^{-2}$) at the metal; $\nu$ is the vibrational frequency of a surface metal atom, i.e., the number of chances the atom may jump; the energy barrier at the metal/oxide interface if it has sufficient energy; $\phi$ is the height of the energy barrier over which the ion must pass in order to enter the oxide bulk, i.e., activation energy; $q$ is the charge on the mobile ion; 'b' is the activation or half-jump distance, i.e., distance from the positions of minimum to maximum potential energy; and $K$ and $T$ have their usual significance.

Comparing (2) with (1), it can be seen that

$$A = n \nu q \exp(-\phi/\kappa T)$$

&

$$B = \frac{q b}{\kappa T}$$

The constant $B$ also equals $d(\ln i)/dE$ which is, in effect, an inverse tafel slope. By equating the two expressions for constant $B$, the temperature dependence of the inverse tafel slope is obtained.

$$\frac{d \ln i}{dE} = \frac{qb}{\kappa T} \quad \cdots (3)$$

The theory due to Verwey$^3$ considered the energy barrier for ion movement through the oxide bulk, assumed to be in a state of electrical neutrality, as the rate-determining step. The equations for ionic current density are similar to those of Cabrera and Mott, the identification of the parameters being related now to
bulk oxide properties instead of metal/oxide interface properties. Hence the Cabrera and Mott and Verwey theories can be considered as limiting cases of one single barrier theory, Cabrera and Mott holding for thin films and Verwey for thick films where electrical neutrality exists in the bulk oxide. Verwey noted that the value of \( B \) in the empirical equation (1) for aluminium (\( \text{Al}^{3+} \)) gave an estimate of the activation distance \( 'b' \) using the relation \( \frac{dE}{d(\ln i)} = \frac{1}{B} = \frac{kT}{q_b} \), which was considered larger than expected on this basis. Verwey suggested that the discrepancy was due to imperfections in the oxygen lattice which made the ionic movement easier, but did not pursue the question in detail.

Ionic conductivity in crystalline lattice occurs through the movement of defects in the lattice, may be vacant anion or cation sites, interstitial anions or cations. The interstitial metal ions are supposed to be the mobile entity. It is also assumed that all interstitial ions are equivalently placed as regards the ease of movement. Since the present oxides are usually amorphous, this is only a first approximation. There must be a range of sites, jump distances and potential energy barriers. A further simplification in deriving the conventional equation for the ionic current is that no ion or vacancy is blocking the path of another.

The ions are supposed to be acquiring sufficient
energy from thermal agitation plus the applied field to jump the potential energy barrier and thus reach the next site. The potential energy/distance relation is assumed to be like that of Figure 1.

The interstitial ions are very crudely considered as vibrating in simple harmonic motion with a frequency. In the absence of a field, the proportion of ions which will possess at any given moment sufficient energy to jump the barrier is given by the kinetic theory as

\[ \exp\left(\frac{-\phi}{kT}\right) \]

where \( k \) is the Boltzmann's constant \( (k = 1.38044 \times 10^{-16} \text{ erg deg}^{-1}) \) and \( T \) is the absolute temperature. The field \( E \) is assumed to reduce the height of the barrier from \( \phi \) to \( \phi - q\beta E \) for ions moving with the field (where \( q \) is the charge on the ion and \( \beta \) is the distance from minimum to maximum potential barrier) and to increase the barrier for ions moving against the field from \( \phi \) to \( \phi + q\beta E \). For the sake of simplicity, it is assumed that the barrier is symmetrical for which \( \beta \) is half the separation of successive sites. \( \beta \) is known variously as the "activation distance" or the "half jump distance". It is assumed that a given ion has \( \gamma \) chances per second to jump the barrier if it has sufficient energy. Let the number of mobile ions per unit volume be \( n \). In general \( n \) is a function of position through the oxide. Each ion that moves carries a charge \( q \) through a distance \( 2\beta \). The observed current
Potential energy (P.E.) of mobile ions vs distance with and without an applied field.
is the difference between the forward current due to ions moving with the field and the backward current due to ions moving against the field. For the present purpose, we shall express the current as a flux of ions (i.e., in units \( q \ cm^{-2} \ sec^{-1} \)), thus omitting a factor \( q \).

The forward current is given by

\[
\dot{i}_{\text{f}} = \frac{2b n}{\exp \left\{ \frac{\phi - q b E}{k T} \right\}} \ldots (4)
\]

and the backward current by

\[
\dot{i}_{\text{b}} = 2b \left\{ n + 2b \left( \frac{\partial n}{\partial x} \right) \right\} \exp \left\{ \frac{\phi + q b E}{k T} \right\} \ldots (5)
\]

where \( x \) measures distance through the oxide. The term \( \left\{ n + 2b \left( \frac{\partial n}{\partial x} \right) \right\} \) represents the effect of the concentration gradient. The forward current may be considered to be due to ions on a plane where the concentration is \( n \). The backward current may be considered as due to ions on a plane \( 2b \) further on, where the concentration is \( n + 2b \left( \frac{\partial n}{\partial x} \right) \). For simplicity, we consider the jump as being made exactly in the direction of the field. If all the jumps were of the same length, then, in fact, the jumps quite close to the direction of the field would predominate, since for the values of \( \phi \) and \( E \) with which we are concerned, \( \exp \left\{ \frac{\phi - q b E \cos \theta}{k T} \right\} \) decreases very rapidly with decrease in \( \cos \theta \), where \( \theta \) = angle between jump direction and the field.

Now, to obtain measurable current, the field applied is so large that the backward current is negligible compared to the forward current, and the observed current is given directly by equation (4). This situation
is known as high field approximation and it is typical for the oxide films on most valve metals, so that equation (4) is a key equation in the theory of oxide growth and known as fundamental equation.

According to the Cabrera and Mott theory, the current over entrance barrier is given by the fundamental equation with the vital difference that the concentration of ions on the surface say \(N_s\) (ions \(\text{cm}^{-2}\)) replaces \(2bn\), where \(N_s\) is assumed to be constant, i.e., independent of \(E\) (compare equations (2) and (4)). This theory predicts a temperature dependent tafel slope—a result common to any theory based on current control by a single barrier where no limit is placed on the concentration of ions before the barrier. This theory was examined by a number of workers and reasonable values of \(A\) and \(B\) were obtained at any temperature; the value of \('b'\) deduced was rather high. Experiments of Vermilyea\(^7\), Young\(^8\), Bray et al\(^9\), Winkel et al\(^10\) have all led to the conclusion that within the experimental error, tafel slope is independent of temperature and thus showing disagreement with Cabrera-Mott theory. Soman et al\(^11\) studied the anodic film growth on aluminium in an electrolyte containing sodium carbonate–sodium borate in dioxane–water mixtures of varying composition and found the exponential correlation of Guntherschulze and Betz\(^1\) and Cabrera and Mott\(^2\) to be operative. It is possible that discrepancies lie in taking field \(E\)
same at the interface as in the bulk oxide and that the oxide is amorphous, not crystalline as is tacitly assumed. Also, this is not necessarily valid to assume that every ion which escapes from the metal is pulled right across the film.

Dewald\textsuperscript{12}, following some of the qualitative ideas put forward by Haring\textsuperscript{13}, discussed the possibility of an increase in the activation distance as resulting from a change in the rate-determining energy barrier from the metal/oxide interface to the oxide bulk. He considered the oxide as an ionic lattice of stoichiometric composition through which excess metal ions can move under the influence of field from an interstitial site to the next. This theory is able to account for all of Vermilyea's data and in particular, can predict a temperature independent tafel slope for a wide range of experimental data. It is assumed that when an ion traverses the film, it may very well experience de-activating collisions with the lattice and require reactivation before proceeding. As a first approximation, de-activation occurs immediately after each activation. It is shown by Dewald\textsuperscript{14} that the field $E$, as a function of $x$ in the oxide, is given by

$$E(x) = E_0 + \frac{1}{\beta} \ln (1 + \beta) n_0 x$$ \quad \ldots \quad (6)

where $\beta = \frac{a e}{k T}, = 4 \pi a / \varepsilon$, $\varepsilon$ is the dielectric constant of the oxide, $n_0$, the number of mobile ions
per cm$^3$ at $x = 0$, and $E_0$, the field due to surface charge. The second term in equation (6) is the space charge contribution. Space charge term arises from the fact that the interstitial ions, in transit, are not compensated electrically under conditions of high field formation. In an unbiased condition, electrons are present to neutralize excess charge of interstitial ions, but at high fields these would be removed from the film. At first glance, one might conclude that if the activation energy for diffusive entrance into the film ($\phi$) is larger than the activation energy for diffusion through the film ($U$), then the rate determining process would always be across the interface. Such a conclusion might be valid for the low field case but it is not necessarily valid for the high field case. In the first place, activation energies for high field conduction are not $\phi$ and $U$ but ($\phi - bqE$) and ($U - aqE$). Thus if 'b' is greater than 'a', one might expect that at sufficiently high fields, the entrance barrier would be reduced enough to be less than the barriers inside the film, even though the entrance barrier were higher than the film barrier in the absence of the field. Even if $\phi$ were greater than $U$ and 'a', greater than 'b', entrance into the film would not necessarily be the rate limiting process, for by allowing the film thickness to increase without limit under constant field, the
increasing large number of small barriers would eventually predominate over the single high entrance barrier $\phi$ as the rate determining factor. The constant $E_0$ in equation (6) is given directly by Cabrera and Mott in the form

$$E_0 = kT/bq \ln(i_0/N_s) + \phi/bq \quad \ldots (7)$$

The field $E$ due to Dewald is given by

$$E = E_0 + 1/p \left\{ (1 + 1/S) \ln(1 + S) - 1 \right\} \quad \ldots (8)$$

where $S = \beta \gamma n_0 \Delta x$ and the tafel slope by

$$\gamma = kT/aq \left\{ 1 + (a/b - 1) \ln(1 + S)/S \right\} \quad \ldots (9)$$

The second term in equation (8) is space charge contribution to the average field. Dimensionless quantity $S$ determines the importance of space charge. If $S \ll 1$, space charge is negligible and tafel slope is given by $kT/bq$; for very high values of $S$, it is given by $kT/aq$. $S$ cannot be calculated empirically and to find it, the experimental data must be fitted into equation (9), assuming reasonable values of $'a'$ and $'b'$.

Dewald$^{14}$ obtained from Vermilyea$^7$ data $a = 3.1$ Å, $b = 2.3$ Å and $W = 0.6$ ev. Young obtained $b = 3.1$ Å and $W = 0.7$ ev for Nb, assuming $\gamma = kT/bq$ at $0^\circ$ and $kT/aq$ at $90^\circ$. Bray et al$^{9}$ made similar assumptions but used values of tafel slope at $-43^\circ$ and $+63^\circ$ in a mixture of picric acid + acetone to define the low
temperature limit (i.e., to obtain $b'$) and found $a = 3.6 \AA$, $b = 2.4 \AA$ and $W = 0.36$ ev for Ta. The values of jump distances $a$ and $b$ seem to be rather high. They have also proved the invalidity of Vermilyea's rejection of the existence of any substantial space charge (and hence Dewald's theory) because his measurements showed no dependence of field $E$ on thickness.

Dewald has since demonstrated that his original theory is incompatible with the transient overshoot in voltage found abruptly increasing the current and indeed is explicable only by a model in which carriers of opposite signs participate in the rate controlling mechanism. Young, however, considers that the presence of a small space charge is not incompatible with the Dewald theory and has shown that it is present in Nb$_2$O$_5$ film immediately after formation.

Bean et al assumed that the vacant cation sites are immobile but the interstitial ions are mobile. This is rather an artificial assumption; since the field is strong enough to pull the ions from lattice positions into interstitial positions, one might expect that it would be strong enough to move a lattice ion into an adjacent empty site. It is also a concept applying in the finest place to a crystalline lattice. Its application to an amorphous oxide depends on the
justification of the persistence of distinction between lattice and interstitial sites in the amorphous oxide. Bean et al.\textsuperscript{15} and Dewald\textsuperscript{12} tacitly assumed that the oxide is always electrically neutral at all times. The essential result, as far as steady state kinetics are concerned, is that in the empirical equation

$$i = i_0 \exp \left\{ \frac{(\phi - q\mathbb{E})}{kT} \right\}$$

both \(\phi\) and \(b\) are the means of the parameters referring respectively to the movement of interstitial ions and movement of lattice ions into interstitial positions. The same form of equation for steady state relation between \(E\), \(i\) & \(T\) is given by Cabrera and Mott\textsuperscript{2}, Verwey\textsuperscript{3} and Bean et al.\textsuperscript{15}. The difference lies in the interpretation of \(b\) and \(\phi\).

Vermilyea's\textsuperscript{17} values showed a change in the activation energy at fields of \(6 \times 10^6 \text{ Vcm}^{-1}\). Bean et al.\textsuperscript{15} introduced a further complication into the theory in that they suggested an abrupt change of jump distances at this field as shown in Figure 2. The potential energy of an ion as it moves from a lattice position into successive interstitial positions was assumed to vary as shown above for zero applied field, a moderate electric field and a stronger field. The dip to the left at zero field represented the electrostatic attraction of the vacant cation site for the ion.
fig. 2: Potential energy vs distance for an ion leaving a lattice position for an interstitial position with zero, moderate and high applied field.
The attraction, thus suggested, gives a reduction in potential energy. Bean et al appeared to postulate that the formation of a Frenkel defect takes place in one jump over the highest barrier shown, since they considered that the figures quoted would demonstrate a change in 'a' from $\lambda_1 + \lambda_2 + \lambda_3$ to $\lambda_1$ as the field was increased and $a = (a_1 + a_2)/2$, where 'a_2' is the mean half separation of ions.

Recently, Young has published a theory which also assigns a range of values to the jump distances and energy barriers. He discusses numerous small influences of field strength on jump distances and also concludes from his own data that there is no evidence for the abrupt change in jump distances postulated by Bean et al. He also points out that at field strengths, high enough to remove lattice ions, it should also be possible to move an ion from one position to an adjacent empty one in the lattice. Young has treated the more general form of Dewald's theory of ions moving in a uniformly distributed negative space charge. If $q$ is the charge on the metal ion, $-pq$ is the space charge, where $p$ is the concentration of the mobile ions, then the Poisson equation is

$$\frac{\partial E}{\partial x} = 4\pi q (n - p)/\varepsilon \quad \ldots (10)$$

where $\varepsilon$ is the dielectric constant of the neutral oxide.
On applying steady state conditions and integrating as in Dewald's theory, he finds for the field

\[ E = E_0 + \frac{1}{\beta} \ln \left\{ \frac{(n_0 - (n_0 - p)) e^{-4\pi \varepsilon q \Delta x / \varepsilon}}{p} \right\} \ldots (11) \]

\(E_0\) and \(n_0\) are the values at the interface for the field and number of ions, and are given, as in Dewald's treatment by Mott's formula. When 'x' is large, the negative exponential can be neglected and so

\[ E = E_0 + \frac{1}{\beta} \ln \left( \frac{n_0}{p} \right) \]

and on substituting for \(E_0\),

\[ E = \frac{1}{\beta} \left[ \ln \left( \frac{1}{2a \sqrt{\varepsilon \alpha}} \right) + \frac{W}{kT} \right] \ldots (12) \]

Verwey, Bean et al and Dewald have assumed that the relationship holds at all x, but Young points out that the validity of the assumption is dependent on \(p/n_0\). The value of \(p\) controls the value of \(\varepsilon/4\pi q \Delta x\) which has the dimensions of length. For a value of 10 Å, \(p\) is \(\sim 10^{21}\) Ta ions cm\(^{-3}\), if \(a = 3\) Å. The total concentration of metal ions is \(\sim 10^{22}\) cm\(^{-3}\) and, therefore, one in ten is mobile. Bean et al\(^{15}\) have \(p\) varying exponentially with field and hence the assumption of no space charge will be in error at low fields. Unlike Dewald'd original model that the space charge can be positive or negative, Young has also treated the case of both ions being mobile and shown that negative space charge exists at the metal
Winkel et al. proposed a theoretical approach to the kinetics which set out to take account of the effects of the amorphosity of the oxide. The existence of a range of site parameters was introduced into the theory by writing (in their notation)

\[ i = 2p n \int_{0}^{\infty} a(q) \gamma(q) G(q) \exp \left\{ -\frac{q}{kT} \right\} \exp \left[ \frac{pE}{kT} \right] dq \cdots (13) \]

where \( q \) = depth of potential energy valleys, \( p \) = charge on the ion, \( a \) = activation distance, \( \gamma \) = frequency of vibration, \( G(q) \) = a distribution function such that \( \int G(q) dq \) is proportional to the number of valleys with \( q \) and \( q + dq \) and \( G(q) dq = 1 \) and \( E \), the field. It was concluded that the effective activation distance should increase with increasing field due to the increasing relative contribution of the sites with longer activation distance as the field increased. This conclusion seems wrong because it neglects the fact that the distribution function specifying the proportion of types of sites occupied will be a function of the field and, as observed earlier, where a given ion must traverse the different sites one after the other, the opposite field dependence of the activation distance is deduced.

Recent data concerning the anodic oxidation of the valve metals have revealed serious limitations in all previous quantitative theories dealing with the growth mechanism of these oxides. The fault of previous
theories lies in their failure to allow for cooperative phenomenon associated with ion migration through the film. Although the possibility of such phenomena has been mentioned by Young, no attempt has been made previously to allow quantitatively for them. According to high field Frenkel defect theory, transient conduction phenomenon arises as a result of slow readjustment of the concentration of ionic carriers, being essentially independent of field strength and current density.

A new theory of cooperative ion transport in anodic films on valve metals has been developed on the basis of a dielectric mosaic model. The oxide, which is amorphous, is considered to be composed of very small crystallites or polymeric units. Ion transfer from one such unit to another is strongly influenced by the distribution of ions within these units since the field assisting the transfer will be a function of the polarization of dielectric oxide medium. Transient ionic conduction phenomenon and amorphous charging currents arise as a result of the slow adjustment of the polarization of the medium to new conditions. Two mechanisms for the rate of change of the polarization are employed, one involving thermally activated ion migration and the other being associated with the large energies dissipated during an ion transfer
The dependence of ion current on effective field strength for steady state is given by

\[ i_s = i_0 \exp\{-\phi - E\mu^*_s (1 - E\mu^*_s/C\phi)\} / kT \] \[ \cdots \ (14) \]

where \( \mu^*_s = (1 + 5^2) \mu^*_s; i_0, \phi, \mu^*_s \), and \( C \), the four parameters to define the steady state behaviour. \( i_0 \) is the pre-exponential factor, \( \phi \), an activation energy, \( \mu^*_s \), an effective charge activation distance product and a parameter \( C \), to allow for the non-linear dependence of the net activation energy on field strength.

A precisely analogous set of parameters are required for high field Frenkel defect theory \(^{29}\). For high ion current transient experiments, the present model of Dignam \(^{30, 31}\) needs two additional parameters, i.e., another effective charge activation distance product and a constant \( B \) related to cross-sectional area of a polymeric unit. The reciprocal of tafel slope for steady state would, thus, be given by

\[ B_s = \mu^*_s / kT \left\{ 1 - (2\mu^*_s E/C\phi) \right\} \] \[ \cdots \ (15) \]

Both the field dependence and the anomalous temperature dependence of the tafel slope for steady state anodic oxidation of Ta, Nb and Al are accounted for quantitatively by the simple model of Dignam \(^{28}\), according to which the field-independent component of the potential energy function for displacement of a mobile charged species is assumed to resemble a Morse
function. Accordingly, the steady state anodic oxidation data for these metals are represented, within experimental error, by only three empirical constants—the pre-exponential factor, the activation energy and the Morse function distance parameter. If, in place of Morse function, a parabolic or cosine potential energy function is assumed, less satisfactory agreement with the data is obtained.

Recently, Fromhold$^{32}$ gave a new model for the kinetics of growth of anodic films in high space charge limit. He utilized a very high field equation closely analogous to the one employed by Dewald$^{12}$.

\[ J_0 = \frac{D}{2a} C(x) \exp \left\{ \frac{ZeE(x)}{aKT} \right\} \ldots (16) \]

where \( J_0 \) is the steady state particle current through the existing anodic oxide film, \( C(x) \) is the bulk defect concentration of the uncompensated charged diffusing ionic species at position \( x \) in the oxide, \( E(x) \) is the macroscopic electric field at position \( x \), \( D \) is the diffusion coefficient, \( 2a \), the hopping distance between potential minima within the oxide for the diffusing species, \( Ze \), the charge per particle of the diffusing ionic species, and \( KT \), the thermal energy at temperature \( T \) involving the Boltzmann constant \( k \). Equation (16) can easily be traced to the microscopic hopping model$^{33}$. The assumption made is that the electric field is so large that the forward hopping current so greatly
exceeds the reverse hopping current that the later can be entirely neglected. The essential point involves the ratio of the electrostatic energy difference $(Ze E(x))$ between a potential energy minimum and the adjacent potential energy barrier maximum to the thermal energy $kT$. A sufficient condition for the validity of equation (16) is

$$\left| Ze \frac{E(x)}{kT} \right| \gg 1$$

but as a practical matter, equation (16) can, generally, be utilized whenever the ratio exceeds 2 or 3.

Fromhold examined the predictions of the model analytically and numerically. The results illustrate that space charge effects do not disappear and do not saturate with increasing electric field value. On the contrary, the space charge retardation is even more pronounced in the realm of very high electric fields, large applied voltages, and very thick anodic films. For the case of growth under constant current conditions in the presence of space charge, a given growth rate was found to require a significantly larger voltage than would be predicted in the usually considered homogeneous field limit.

The ionic conduction phenomena of anodic oxide growth on metals is, essentially, a process consisting of three stages—(i) metal/metal oxide interface; (ii) bulk oxide; and (iii) oxide/electrolyte interface.
Theoretical justification of the exponential relationship proposed by Guntherschulze and Betz has been based upon a combination of (i) and (ii) as the rate-determining step. Cabrera and Mott theory emphasises the importance of first stage and has been derived assuming only the metal ion to be mobile. This theory and that due to Verwey can be treated as limiting cases of one single theory, Cabrera and Mott holding for thin films and Verwey for thick films where electrical neutrality exists in the bulk oxide.

However, the simple Cabrera and Mott and Verwey expressions would appear to be initially inadequate on several points. These are (1) the expected dependence of \( B \) with temperature has not been found exactly, (2) the values of the activation distances calculated are larger than those theoretically expected when considering a crystalline lattice and (3) Young has demonstrated that log ionic current density against the electric field strength plot is, in fact, slightly non-linear. Dewald introduced the idea of space charge emphasizing oxide bulk control. His theory was capable of explaining temperature-independent tafel slope values. Generally, it has been found that almost all the 'valve' metals obeyed the Cabrera and Mott theory in the lower thickness ranges. As thin films grow thicker, transition from the Cabrera and Mott theory to Verwey theory should occur, and, if space charge is anything but minimal, to the Dewald theory. The Dewald theory may account satisfactorily for some behaviour, but
it and Cabrera and Mott and Verwey expressions have the major inadequacy in that they cannot suitably account for anodic transient behaviour. When anodizing conditions are suddenly varied, whether it be ionic current$^{22}$ or a voltage transient$^{14}$, well-defined changes occur which cannot be accounted for on the basis of a simple, electrically uncompensated, single charge carrier (whether the carrier be cations, anions, or vacancies). Propounding a theory of ionic growth mechanism, Winkel et al$^{10}$ took account of the effects of amorphosity of the anodic oxide. In his theory, Young$^{18}$ treated the case of both ions being mobile and showed, unlike Dewald's original model, that the space charge could be positive or negative and that negative space charge existed at the metal/oxide interface. In his equation derived on empirical basis, Young$^{34}$ justified the quadratic term inclusion on the basis of an increase in the activation energy with increasing condenser pressure. As the condenser pressure is proportional to $E^2$, this explanation predicts a quadratic term of the correct sign. The main defect of all these theories is their failure to give an account of cooperative ion migration through the film. Dignam$^{28}$ incorporated this idea in his theory based on a dielectric mosaic model. He rejected the idea of Young$^{34}$ and proposed that the quadratic term arises from a more detailed consideration of the ion movement in high electric field. Ibl$^{35}$ arrived
at the same equation proposed by Young\textsuperscript{34} by applying the transition state theory to ionic conduction, assuming thermodynamic stability between normal and activated species. Very recently, Fromhold\textsuperscript{32} developed a theory to examine whether the space charge retardation effects of film growth rate at intermediate field strengths would persist and to what extent at higher electric fields.

All the theories of ionic conduction alongwith their present status are discussed in this chapter to provide a ready reference to the literature. It can be observed that a critical investigation of these theories for data on anodic film growth on valve metals in suitable electrolytes is required to examine their validity over a wider range of temperature. Majority of the studies have been done for limited lower ranges of temperature and in aqueous electrolytes. Hence, Chapters II, III and IV cover a wide range of temperature and electrolytes, and the data for oxide film growth in aqueous and non-aqueous electrolytes have been discussed in the light of various theories reported in this chapter. The metal used is superpurity aluminium. Aluminium has been extensively used in the recent years due to its economic and technical importance. Most of these studies have been performed on alloys or on relatively impure metal. However, the presence of impurities in the metal highly influenced the reactions taking place on metal surface\textsuperscript{36}. Hence, in order to study quantitatively the mechanism of ionic conduction and properties of anodic films on aluminium, it was considered desirable to take superpurity aluminium for our investigations.
REFERENCES

18. L. Young, ibid., 111, 1289 (1964).