Introduction

Anodic oxide films on valve metals form an important ingredient of modern technology. These play an active role in industrial processes related to electronic devices, fuel cells, batteries, rectifiers and in capacitor technology as dielectric and insulating materials. These are useful in themselves as protective and decorative coatings. Anodic film constitute a special class of reaction films which are grown in electrolytic solutions. Formation from solution permits more freedom in the choice of the conditions of a growth of reaction film than does formation in gases especially, with regard to the driving force for the reaction. For example, the driving force can be kept constant by holding the potential constant or the driving force can be
continuously varied to keep the same rate by passing constant current through the cell. We shall deal, in particular, with oxide films produced galvanostatically on valve metals.

All the systems can be divided into two categories, one comprising the systems that behave in a manner characteristics of valve metals, the other, those that do not. The same metal can behave under one set of conditions of electrolyte composition, etc., as valve metal and under other conditions as a nonvalve metal, so that above divisions are ones in which systems, not metals, are placed.

The two principal characteristics of valve-metal anodic oxidation behaviour are the following:

1. The requirement of a very high overfield (overpotential divided by film thickness) for film formation, that is, of the order of \(10^6\) V/cm or larger.

2. The formation of an oxide film of essentially fixed stoichiometry, to the exclusion of other processes, such as metal dissolution and oxygen evolution. The metals that come the closest to exhibiting this behaviour are tantalum, niobium and aluminium in some electrolytes, with a large number of metals, semiconductors and alloys approaching the behaviour of these metals under certain conditions. The name valve-electrode (ventilelektrode) dates from the early researches in the field but is not altogether satisfactory,
since it stresses the rectifying action of the oxide coated electrode (forward direction: cathodic) rather than the more fundamentally characteristic property of the group, which is the tendency to form a protective high-resistance oxide film on anodic polarization to the exclusion of all other electrode processes. Thermodynamically speaking all these metals are reactive in the natural environment - air and water. Exposed to dry, pure and cool air, some metals quickly develop an oxide film which soon ceases to thicken. This happens because the oxide formed acts as a barrier between the metal and atmospheric oxygen. Further reaction can occur either by diffusion or migration (field-assisted movement) of ions through the oxide film. If this oxide coated metal made anode of an electrolytic cell, the applied external force sets up an electrostatic field or increases the field already present in it and this results a continuous growth of oxide film. In general, the transport of metal (and charge) upto the metal/oxide interface and of oxidizing agent (and charge)upto the film environment interface will no more be rate controlling, once the metal surface is covered with a film. The growth of the anodic oxide film is, essentially a problem of ionic conduction at high field strengths, 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 defined by sparking, maximum voltage, audible cracking and the voltage at which a deflection from linearity arises in the voltage versus time curve, oxygen evolution and the formation of thick discoloured film. Over the range of potential in which the current is very small, the oxide acts as the dielectric of a capacitor. Application of the formula for a parallel-plate capacitor should give an estimate of the thickness of film, if there is no flaw or pore in the film. There are, in fact, three basic methods of film preparation: evaporation, thermal oxidation and electrochemical method. In our case, the electrochemical method of production of film is used. The choice of substrate has been limited by thermal and electrical consideration yet, inspite of this, the choice of conditions to prepare dielectric films of requisite character is quite wide.

Theories 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: (i) 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 $10^6$ to $10^7$ V/cm, these fields being regarded as sufficient to prevent ionic motion against the field direction.

Guntherschulze and Betz\textsuperscript{2} have shown that under high field condition, relation
\[ i = A \exp(BE) \quad \text{..... (1)} \]
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/electrolyte interface producing a solvated ion.
Theoretical justification of the exponential relationship proposed by Guntherschulze and Betz\(^2\) has been based upon a combination of (i) and (ii) as the rate-determining step.

Cabrera and Mott\(^3\) 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 the 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

\[
i = n \nu q \exp\left(-\frac{(\phi - qbE)}{kT}\right) \quad ....(2)\]

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, $k$ is the Boltzmann constant and $T$ is absolute temperature.

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

$$A = n v q \exp\left(\frac{-\eta}{kT}\right)$$

and

$$B = bq/kT$$

The constant $B$ also equals $d(lni)/dE$ which is, in fact, an inverse Tafel slope. By equating the two expressions for constant $B$, the temperature dependence of Tafel slope is given by

$$\frac{dE}{d(ln i)} = \frac{kT}{bq} \quad \ldots \ldots \quad (3)$$

The theory due to Verwey$^4$ 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-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. Anodic growth of Al, Ta, Pt and Fe has been examined and jump distances determined from Eq. (3),
which were considered larger than expected on this basis. Verwey suggested that the discrepancy was due to imperfections in the oxide 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\textsuperscript{5-7}, 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 case 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 and 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 Fig.1.

The interstitial ions are very crudely considered as vibrating in simple harmonic motion with a frequency $\nu$. In the absence of a field, the proportion of ions which will possess at any given moment sufficient energy to jump the
Fig. 1. Potential energy (PE) of mobile ions vs distance with and without an applied field.
barrier is given by the kinetic theory as \( e^{-\theta/kT} \) 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 \( \theta \) to \((\theta-qbE)\) for ions moving with the field (where \( q \) is the charge on the ion and 'b' is the distance from minimum to maximum potential barrier) and to increase the barrier for ions moving against the field from \( \theta \) to \((\theta+qbE)\). For the sake of simplicity, it is assumed that the barrier is symmetrical for which 'b' is half the separation of successive sites. 'b' is known variously as the activation distance or the half jump distance. It is assumed that a given ion has \( \psi \) chances per second to jump the barrier if it has sufficient energy. Let the number of mobile ions per unit volume to be \( n \). In general \( n \) is a function of position through the oxide. Each ion that moves carries a charge \( q \) through a distance \( 2b \). The observed current 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 unit \( q \text{ cm}^{-2} \text{ sec}^{-1} \)), thus omitting a factor \( q \), the forward current is

\[
\vec{i} = 2bn\psi \exp. - \left[ (\theta-qbE)/kT \right] \quad \ldots \ldots (4)
\]

and the backward current by

\[
\vec{i} = 2b\psi[n +2b(\partial n/\partial x)] \exp. -[(\theta+qbE)/kT] \ldots \ldots (5)
\]

where \( x \) measures distance through the oxide. The term \([n+2b(\partial n/\partial x)]\) represent the effect of 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 \( n + 2b (\partial n / \partial x) \). 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 \( \theta \) and \( E \) with which we are concerned, \( \exp(-[(\theta - q_b E \cos \theta)/kT]) \) decreases very rapidly with decrease in \( \cos \theta \), where \( \theta \) is the 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 Eq. (4). This situation is known as high field approximation and it is typical for the oxide films on most of the valve metals, so that Eq. (4) is a key equation in the theory of oxide growth and known as fundamental equation.

According to 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 \( \text{cm}^{-2} \)) replace \( 2bn \), where \( N_s \) is assumed to be constant, i.e., independent of \( E \) (compare Eq. (2) and Eq. (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. Experiment of Vermilyea\textsuperscript{8}, Young\textsuperscript{9}, Bray et al.\textsuperscript{10} and Winkel et al.\textsuperscript{11} have led to the conclusion that within the experimental error, Tafel slope is independent of temperature and thus showing disagreement with Cabrera and Mott theory.

A new theory of co-operative ion transport in anodic films on valve metals has been developed on the basis of a dielectric mosaic model by Dignam\textsuperscript{12}. The oxide, which is amorphous, is considered to be composed of very small crystallites or polymeric units. Ion transfer from the 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 event. The dependence of ion current on the effective field strength for steady state is given by

\[
i_s = i_0 \exp \left[ \phi - \frac{E \mu^*_s}{(1-E \mu^*_s)/C \phi} /kT \right] \quad \ldots \ldots \ldots \ldots (6)
\]

where $\mu^*_s = (1+ \delta \chi_s) \mu^*$.

$i_0$, $\phi$, $\mu^*_s$ and $C$ and the four parameters to define the steady state behaviour. $i_0$ is the pre-exponential factor,
\( \Phi \) is an activation energy, \( \mu_s^* \) is an effective charge activation distance product and a parameter \( C \), to allow for 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\(^{13}\). For high ion current transient experiments, the present model of Dignam\(^{14,15}\) needs two additional parameter, 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

\[
\beta_s = \frac{\mu_s^*/kT}{[1 - (2\mu_s^* E/C\Phi)]} \quad \ldots \ldots (7)
\]

Both the field dependence and the anomalous temperature dependence of the Tafel slope for the steady state anodic oxidation of Ta, Nb and Al are accounted for quantitatively by the simple model of Dignam\(^{12}\), according to which the field-independent component of 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.
Haring\textsuperscript{16} put forward some qualitative ideas. These ideas were used by Dewald\textsuperscript{17} to discuss 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 requires reactivation before proceeding. As a first approximation, de-activation occurs immediately after each activation. Dewald\textsuperscript{18} has shown that the field ($E$), as a function of $x$ in the oxide, is given by

$$E(x) = E_o + \frac{1}{\beta} \ln \left(1 + \beta \gamma n_0 x\right) \quad \ldots \quad (8)$$

where $\beta = aq/kT$, $\gamma = 4 \pi q/\epsilon$, 'a' is bulk half-jump distance, 'b' is entrance half-jump distance, $\epsilon$ is the dielectric constant of the oxide, $n_0$ is the number of mobile ions cm$^{-3}$ at $x = 0$ and $E_o$ is the field due to surface charge. The second term in the Eq. (8) is the space-charge contribution. Space-charge term arises from the fact that the interstitial ions, in transit, are not compensated electrically under the 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 sight, one may conclude that if the activation energy for diffusive entrance into the film ($\vartheta$) 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, the activation energies for high field conduction are not $\vartheta$ and $U$ but ($\vartheta - bqE$) 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 $\vartheta$ is greater than $U$ and 'a' is 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 $\vartheta$ as the rate determining factor. The constant $E_0$ in Eq.(8) is given directly by Cabrera and Mott in the form

$$E_0 = kT/bq \ln \left( \frac{i_o}{N_s y_s} q \right) + \vartheta/bq \quad \ldots \ldots (9)$$

where $N_s$ is the number of ions cm$^{-2}$ of the metal surface, $y_s$ is their vibrational frequency normal to the barrier and $\vartheta$ is the potential barrier opposing entry into the oxide as the rate-determining step. The field $E$ due to Dewald is given by
\[ E = E_0 + \frac{1}{\beta} \left[ (1 + 1/\delta) \ln (1 + \delta) - 1 \right] \quad \ldots \ldots (10) \]

where \( \delta = p_v n_0 \Delta x \) and the Tafel slope by
\[ \gamma = kT/bq \left[ 1 + (a/b-1) \ln (1 + \delta)/\delta \right] \quad \ldots \ldots (11) \]

The second term in Eq.(10) is space-charge contribution to the average field. Dimensionless quantity \( \delta \) determines the importance of space charge. If \( \delta \ll 1 \), space charge is negligible and Tafel slope is given by \( kT/bq \); for very high value of \( \delta \), it is given by \( kT/aq \). \( \delta \) can not be calculated empirically and to find it, the experimental data must be fitted into Eq.(11), assuming reasonable values of 'a' and 'b'.

Dewald obtained from Vermilyea's data \( a = 3.1 \) \( \AA \), \( b = 2.3 \) \( \AA \) and \( W = 0.6 \) eV. Young obtained \( b = 3.1 \) \( \AA \) and \( W = 0.7 \) eV for Nb, assuming that \( \gamma = kT/bq \) at \( 0^\circ C \) and \( kT/aq \) at \( 90^\circ C \). Bray et al. made similar assumptions but used values of Tafel slope at \( -43^\circ C \) and \( +63^\circ C \) 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 tantalum. 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 compatible with the Dewald theory and has shown that is present in Nb$_2$O$_5$ film immediately after formation.

Bean, Fisher and Vermilyea 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. and Dewald 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

$$i = i_o \exp. \left[-\frac{(\varphi - qbE)}{kT}\right]$$

both $\varphi$ 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 $E$, $i$ and $T$ is given by Cabrera and Mott, Verwey and Bean et al. The difference lies in the interpretation of 'b'
Vermilyea's values showed a change in the activation energy at fields of $6 \times 10^6$ Vcm$^{-1}$. Bean et al. introduced a further complication into the theory, in that they suggested an abrupt change of jump distances at this field as shown in Fig.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. 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.

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.
Fig. 2. Potential energy vs distance for an ion leaving a lattice position for an interstitial position with zero, moderate and high applied field.
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 also treated the more general form of Dewald's theory of ions moving in an 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's equation is

$$\frac{\partial E}{\partial x} = \frac{4\pi q}{\epsilon} \frac{(n - p)}{\epsilon} \quad \text{...(12)}$$

where $\epsilon$ 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

$$E = E_0 + \frac{1}{\rho} \left[ n_0 - \left( n_0 - p \right) e^{-\frac{4pqx}{\epsilon}} \right] \quad \text{...(13)}$$

$E_0$ 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

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

and on substituting for $E_0$,

$$E = \frac{1}{\rho} \left[ \ln \left( i/2a \right) + W/kT \right] \quad \text{...(14)}$$

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 $\varepsilon/4\pi \beta q$ which has the dimensions of length. For a value of $10^8$, $p$ is $10^{21}$ Ta ions cm$^{-3}$. If $a = 3 \Omega$, the total concentration of metal is $10^{22}$ cm$^{-3}$ and, therefore, one in ten is mobile. Bean et al.\textsuperscript{19} have $p$ varying exponentially with field and hence the assumption of no space charge will in error at low fields. Unlike Dewald's 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 interface.

Winkel et al.\textsuperscript{11} 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)

$$i = 2pn \int_{0}^{\infty} a(q)\psi(q) G(q) \exp \left[ -(q/kT) \right] \exp \left[ a(q)pE/kT \right] dq \quad \quad \quad \quad (15)$$

where $q$ is depth of potential energy valleys, $p$ is charge on the ion,'$a'$ is an activation distance, $\psi$ is frequency of vibration, $G(q)$ is a distribution function such that $G(q) dq$ is proportional to the number of valleys with $q$ between $q$ and $(q + dq)$ and $G(q) dq = 1$ and $E$ is the field. It was concluded that the effective activation distance should
increase with increasing field due to 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.

Data\textsuperscript{23-30} 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 co-operative phenomenon associated with ion migration through the film. Although the possibility of such phenomena have been mentioned by Young\textsuperscript{31}, no attempt has been made previously to allow quantitatively for them. According to high field Frenkel defect theory, transient conduction phenomenon arise as a result of a slow readjustment of the concentration of ionic carriers, being essentially independent of field strength and current density.

Fromhold\textsuperscript{32} gave a new model for the kinetics of growth of anodic films in high space-charge limit. He utilized a high field equation closely analogous to the one employed by Dewald.
\[ J_0 = \left( \frac{D}{2a} \right) C(x) \exp \left[ \frac{(Z \varepsilon E(x) a)}{kT} \right] \] (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 diffusion ionic species at position \( x \) in the oxide, \( E(x) \) is the macroscopic electric field at position \( x \), \( D \) is the diffusion coefficient, \( 2a \) is the hopping distance between potential minima within the oxide for the diffusing species, \( Z \) is the charge per particle of the diffusing ionic species, and \( kT \) is the thermal energy at temperature \( T \) involving the Boltzmann constant \( k \). Eq.(16) can easily be traced to the macroscopic hopping model. 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 latter can be entirely neglected. The essential point involves the ratio of the electrostatic energy difference \( (Z \varepsilon E(x) a) \) between a potential energy minimum and the adjacent potential energy barrier maximum to the thermal energy \( kT \). A sufficient condition for the validity of Eq.(16) is

\[ \frac{|Z \varepsilon E(x)|}{a/kT} \gg 1 \]

but as a practical matter, Eq.(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 homogenous field limit.

All the theories of ionic conduction along with 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 niobium 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. Hence, Chapter II and III cover a wide range of temperature and aqueous electrolytes and the data for oxide film growth in aqueous electrolyte on niobium have been discussed in the light of various theories reported in these Chapters.
Electrical Breakdown:

The anodic formation of barrier (nonporous) films on the so-called valve metals (Al, Ta, Nb, Zr etc.) can be carried on until the voltage attains a breakdown level designated as breakdown or sparking voltage ($U_B$). The phenomenon of sparking is still not well understood, despite its importance for electrolytic capacitors and anodization in general, since the breakdowns terminate the normal oxide growth process. The presence of electrolytic contact makes the breakdown features very peculiar and quite different from those of dry dielectrics, including metal/anodic film/metal system.

It has been suggested that breakdowns are triggered by conduction through electrolyte filled fissures and flaws of oxide. This explains the dependence of breakdown voltage ($U_B$) upon the resistivity of electrolyte ($\rho$), but it remains incomprehensible, why $U_B$ does not depend on the history of film formation, on the presence of foregoing breakdowns and on the topography of the electrode surface since all these factors should affect the type and the number of flaws and fissures.

The idea, that breakdowns are controlled by electrochemical reactions at electrolyte/oxide interface, is confirmed by dependence of $U_B$ upon nature of the anodized metal, as well as on the composition and the resistivity of the electrolyte and breakdown depends on the solid state properties of the oxide. This suggests the usual
avalanche breakdown in the bulk of the anodic film, the initial electron being injected into the film from the electrolyte. Ikonopisov put forward a model which is based on this conception. According to him, during anodization, the electrolytic contact not only provides ions for the oxidation, but also injects electrons into conduction band of the oxide. The high field strength in it can accelerate these electrons to an energy $\mathcal{E}_m$ which is sufficient to free other (secondary) electrons by impact ionization, so that an avalanche multiplication occurs. The general equation for breakdown voltage is given by

$$U_B = \frac{\mathcal{E}_m}{r e \left[ \ln j_B - \ln j_e(0) \right]} \quad \ldots (17)$$

Where $r$ is the recombination constant and given by

$$r = \frac{a_r}{a_r + 1} < 1$$

and $x_r \propto a_r D$ where $D$ is the thickness of oxide film, $x_r$ is recombination length, $a_r$ is proportionality constant, $U_B$ is breakdown voltage, $\mathcal{E}_m$ is the difference between the mean energy of electron when it is able to ionize and the mean energy of the electrons emerging from the ionization event, $j_e(0)$ is the primary electronic current density, injected at the electrolyte/oxide - interface (at $x = 0$) and $j_B$ is the electronic current density at a thickness $x = D_B$. Ikonopisov's model explains quantitatively the dependence of $U_B$ on electrolyte resistivity, as well as its independence
of current density. This model also explains the independence of $U_B$ of the anode surface topography.

The mechanism of avalanche breakdown proposed by Ikonopisov is shown in Fig. 3. In this model, an electronic current $j_o$ is supposed to be injected from the electrolyte to the oxide conduction band by a Schottky mechanism. Other injection mechanisms, such as the Fowler–Nordheim tunneling, have been suggested, for example by Kadary and Klein \(^{51}\), the injected electrons are accelerated towards the anode by a strong field of anodization, causing an avalanche breakdown when a certain critical electron current is reached.

In a simple avalanche model of breakdown during anodic oxidation, it is assumed that the electronic current density, $j_o$, injected to the conduction band of the oxide from the electrolyte/oxide interface, increases exponentially according to an avalanche process \(^{50}\). Therefore, the electronic current density at the anode, $j_e$, should be given by: $j_e = j_o e^{\alpha d}$, where $\alpha$ is impact ionization coefficient and $d$ is the distance travelled by the primary electrons on their way to the anode. As a first approximation, $d$ is assumed equal to the thickness of oxide film.

In anodization experiments at constant current density, $j_t$, the oxide thickness increases linearly with the voltage ($d = aV$). As a consequence, the differential equation regulating the growth of potential with time is given by
Fig. 3. Schematic representation of the band structure and avalanche breakdown mechanism during anodization.
\[
\frac{dV}{dt} = K j_i 
\]  

(18)

where \( j_i \) is the ionic current density of anodization and \( K \) is the unitary anodization rate, given by

\[
K = \frac{ME}{10F}
\]

where \( M \) is the molecular weight of the oxide, \( F \) the Faraday constant, \( p \) the oxide density and \( E \) the electric field during anodization. Taking into account the presence of avalanche electronic current \( j_e \) during the anodization, the ionic current will be: \( j_i = j_t - j_e \), so that

\[
\frac{dV}{dt} = K(j_t - j_e) = K(j_t - j_o e^{\alpha d}) = K(j_t - j_o e^{\alpha' V}) \quad \ldots (19)
\]

where \( \alpha' = \alpha a \)

The three parameters \( K, j_o \) and \( \alpha' \) of Eq. (19) can be obtained through an accurate determination of the variation of the \( dV/dt \) values with the voltage in the range of voltages where no scintillation sparks appear. By operating in Eq.(19), one obtains

\[
\ln \left(1 - \frac{1}{KJ_t} \frac{dV}{dE}\right) = \ln \frac{j_o}{j_t} + \alpha' V = \ln \frac{j_e}{j_t} \quad \ldots (20)
\]
Therefore, a graphic representation of the values of

\[ \ln \left(1 - \frac{1}{K_j t} \frac{dV}{dt} \right) \]

as a function of anodization voltage, \( V \), must fit a straight line whose slope is \( \alpha' \) and the intersection with the ordinate axis is given by \( \ln(j_0/j_\tau) \). The first step in this calculation is to obtain the value of the constant \( K \). An approximate value of \( K \) can be obtained from the extrapolated value of \( dV/dt \) at \( V = 0 \), which from Eq. (19) and with the additional condition \( j_0 \ll j_\tau \), is given by

\[ K = \left[ (dV/dt)_{V = 0} \right]/j_\tau \]

Montero et al. \(^{52}\) have found that avalanche model is able to explain the main characteristics of anodization curves and breakdown on anodic tantalum oxide grown in phosphoric and oxalic acid electrolyte at different concentrations. The close correlation between \( j_0/j_1 \) and the mole concentration of incorporated phosphorous in the oxide firmly supports the hypothesis that the incorporated phosphate anions act as a source of primary electrons for the avalanche. The residual leakage current measurements as well as \( j-V \) characteristics seem to indicate that the primary electrons are released from the impurity centres in a Poole - Frenkel mechanism. The presence of phosphorous in the anodic oxide also gives rise to an increase of the anodization electric field needed to maintain a definite current density. According to their model the direct control of breakdown is mainly attributed to the electrolyte anions incorporated into the oxide and
to their ability to release electrons to the conduction band. This is in contradiction to the previous theories of the breakdown during anodization\textsuperscript{51,53} those speculate about the injecting properties of the electrolyte/oxide interface. Lately, the Ikonopisov model\textsuperscript{50} has been extended by Albella et al.\textsuperscript{54} to explain the curvature of the voltage curve as a function of time in anodization experiments of tantalum at a constant current density. Albella et al.\textsuperscript{55} have further studied the electrical breakdown during anodic growth of Ta\textsubscript{2}O\textsubscript{5} in H\textsubscript{3}PO\textsubscript{4} electrolyte with different current densities. They provided a strong evidence of avalanche breakdown model proposed by Ikonopisov\textsuperscript{50} and also explained scintillation process\textsuperscript{54}. On the origin of primary electrons causing the avalanche breakdown, they proposed that these electrons, instead of being injected through the electrolyte/oxide interface, are originated within the oxide itself by ionization of the electrolyte impurities incorporated into the oxide film during the anodization.

Post breakdown anodization of aluminium was also reported by Ikonopisov et al\textsuperscript{56}. Two type of breakdown was reported by Francesco Di Quarto et al.\textsuperscript{57} for zirconium metal. It has been shown that both mechanical and electrical breakdown can occur during the anodization process. Each type of breakdown occurs in a different way and depends on the anodization parameters.
The Chapter IV deals with the detailed investigations of breakdown phenomenon at different fields in aqueous electrolytes of different resistivities over a wide range of temperatures. Electronic conduction measurements through the $\text{Nb}_2\text{O}_5$ film as a function of temperature and applied field have also been done to examine the validity of Ikonopisov theory of breakdown quantitatively.

In Chapter V, the rectification behaviour and dc electronic conduction mechanism through Nb-$\text{Nb}_2\text{O}_5$ - metal devices have been discussed. We have shown that the phenomenon of electronic conduction can be accounted for in terms of Schottky mechanism.

The final Chapter in this thesis deals with certain other aspects of $\text{Nb}_2\text{O}_5$ films such as mobility of ions, current efficiency, dielectric measurements, effect of halide ions, heat treatment of $\text{Nb}_2\text{O}_5$ films and formation characteristics and breakdown phenomenon in the presence of UV radiations.
References

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