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# ANODIC OXIDE FILMS

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## I. INTRODUCTION

Oxide films on metals are widely used in the national economy, in various electrochemical devices, in condensers, in rectifiers, in chemical sources of current, and also for protecting metals against corrosion.

The metal–oxide–electrolyte system exhibits an appreciable capacity and can rectify alternating current over a wide range of potentials. Therefore such a system finds a wide use in electrical devices.

Oxide films also have independent importance in studying electrochemical reactions on metals, since under specific conditions it is necessary to take into account that all metals are covered with oxide films.

There is now considerable material on the experimental and theoretical problems of anodic oxide films, which it is difficult to generalise in a single review. Hence the present article will consider only certain questions concerning mechanism in the formation of anodic oxide films and of their properties.

This review considers the kinetic mechanisms of the growth of oxide films during anodic oxidation and also certain properties of films on valve metals.

## II. GROWTH OF ANODIC FILMS

Anodic oxide films on metals or semiconductors are formed in a solution of electrolyte on applying a potential more positive than the equilibrium potential. Afterwards as the metal becomes covered by a thin continuous layer of oxide, which is insoluble in the electrolyte, an electrostatic field is established in the oxide. This field causes ions of metal or oxygen to move through the oxide layer, which also leads to growth of the film. For the formation of each new layer of oxide an additional potential $dv$ is required, which is added to the existing potential in the film.

It is found experimentally that the quantity $dv/dx$ does not vary as the thickness increases, but for certain metals there is a departure in one direction or the other.

The growth of the film is greatly hindered by processes at the boundaries of the film with the metal and with the electrolyte[1-4].

The formation of centres of crystallisation and also the thickening of the films requires overpotentials of from 10 to 1000 mV. These are made up of; (1) the energy for the removal of a metal ion from the lattice to the metal–oxide boundary; (2) the kinetic energy of the metal ion through the film; (3) the energy for the exchange of charged particles between the electrode and the solution at the oxide–electrolyte boundary.

In their structure oxide films can be divided into porous and continuous (pore-free). The resistance of porous films is of the order of a few ohms, and their potentials at the time of growth are near to equilibrium, they are almost invariably crystalline, and their growth is essentially by diffusion of the ions through the oxides or through the electrolyte. Such films are formed on cadmium, zinc, and magnesium.

Vermilyea[5] considers that continuous films are formed during simultaneous oxidation of metal at all points of the surface.

Misch[6] thinks that the nature of the oxide film depends on the value of the ionic potential (the ionic charge divided by the radius), the lattice type of the metal and oxide, and also the bond energy. The adhesion of the oxide particles depends on the ionic nature of the oxide, the resistance to impregnation by water, and the extent to which the ratio of the molar volume of the oxide to the molar volume of the metal (the Pilling and Bedworth ratio) exceeds unity. Continuous growth of the film depends on the overall ionic current in the film, in which connection the following facts must be considered: (1) the overall electrical conductivity of the oxide, and (2) the transport numbers of the ions, electrons, and holes.

If the oxide is an electronic semiconductor, then all the current is used in the discharge and liberation of gaseous oxygen, the ionic current will be insignificant, and the thickness of the film will not increase — such a reaction takes place on titanium[7].

Another type of reaction is the processes taking place on tantalum[8], aluminium[9], zirconium, for which the effectiveness of the anodising of the pure metal is 100%. The

growth of such films begins with a monolayer and continues uniformly over the entire thickness approximately up to $10^{-4}$ cm; during this period the resistance of the film can reach a million ohms.

Such films can be crystalline, vitreous, or amorphous. They exhibit unipolar conductivity[10].

On certain metals, *e.g.*, aluminium, laminar oxide films are formed[11-16]: the layer close to the metal is continuous and that which is near to the solution is porous. As the thickness increases, conditions for the appearance of cracks are aggravated[17-21]: overheating in defect positions owing to the passage of a steady current through the film, transformation of the oxide from one modification to another, etc.

## III. NON-POROUS FILMS: EMPIRICAL RELATIONSHIP BETWEEN IONIC CURRENT, FIELD, AND TEMPERATURE

Fig. 1 gives the $i$ *vs.* $V$ relationship for valve metals coated with an oxide film, and shows that for a negative potential the current increases rapidly, the electrode process during this being accompanied by the liberation of hydrogen. In anodic polarisation the current is vanishingly small and rather irreproducible right up to that potential at which the ionic current exceeds the leakage current, which then rapidly increases with the potential. The passage of an anodic current is accompanied by the liberation of oxygen. This is linked with electronic conduction by the film.

The theoretical ionic current occurs at all potentials above the reversible oxygen electrode potential, and in practice it is insignificant in comparison with the leakage current in small fields.

As soon as the field potential is made sufficiently high for the appearance of an ionic current, the passage of the latter through the electrode causes growth of the film. This growth can be brought about in either potentiostatic or galvanostatic conditions.

When a direct current is passed through the film the formation of each new layer requires a field of potential $dv$ additional to that already existing in the film. The quantity $dv/dx$ is termed the differential field potential.

The relation between the growth rate of the potential and current density in such a case can be linked with the growth rate of the film, which is:

$$\frac{dD}{dt} = \frac{iM}{ZF\rho},$$

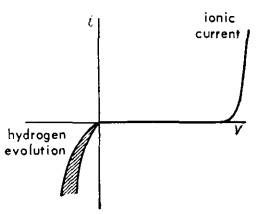



Fig. 1. Voltampere characteristics of an oxidised tantalum electrode.

where $i$ is the ionic current density, $F$ Faraday's number, $M$ the molecular weight of the oxide, $\rho$ the density of the oxide, $D$ the oxide thickness, and $t$ the time.

If the differential field potential $E_d$ is constant, then the rate of increase of the potential is:

$$\frac{dv}{dt} = E_d \frac{dD}{dt} = iE_d \frac{M}{ZF\rho}. \quad (1)$$

For tantalum at room temperature, $dv/dt = 3$ V $s^{-1}$ for $i = 10^{-3}$ A $cm^{-2}$,[22] the field potential necessary for an ionic current of $10^{-8}$–$10^{-1}$ A $cm^{-2}$ to flow in the film being $10^6$–$10^7$ V $cm^{-1}$, or 0.01–0.1 V $Å^{-1}$. It is quite obvious that under such high electric field potentials Ohm's law is not obeyed.

The equation for the ionic current and electric field in arbitrary systems is in general well described by the relation:

$$i = 2A \operatorname{sh} BE. \quad (2)$$

For high potential gradients, Eqn. (2) transforms into the equation first given by Günther-Schulze and Betz[23]

$$i = A \exp BE, \quad (3)$$

where $A$ and $B$ are constants which depend linearly on temperature. Eqn. (3) satisfactorily describes the relation between $i$ and $E$ to a first approximation.

At low electric fields Eqn. (2) has the form:

$$i = 2ABE. \quad (4)$$

It is evident from Eqn. (3) that the slope $dE/d(\ln i)$, analogous to the Tafel slope, has a linear dependence on temperature. However, the experimental results show that, in certain cases, the temperature dependence is non-linear.

The equations mentioned do not reflect completely the film growth process, since they do not take into account phenomena at the metal–oxide and oxide–electrolyte boundaries.

To express more fully all the phenomena brought about by the field in the oxide film, it is convenient to introduce the concept of overpotential in the formation of oxide, which by analogy with the overpotential in hydrogen liberation, is determined in any electrode process as the difference between the potential drop at the oxide–solution boundary and the potential drop which there would be at the electrode if it were reversible for the given electrode reaction, or as the potential of the oxide electrode in relation to a reversible auxiliary electrode.

The connection between the oxide formation overpotential $\eta$ and the applied potential, *i.e.* the electric field potential $E$ in the body of oxide and at the metal–oxide and oxide–electrolyte boundaries can be represented as follows. Assuming that in the hypothetical reversible state the potential drops at the metal–oxide boundary, in the body of the oxide, and at the oxide–electrolyte boundary are respectively $\Phi_1^e$, $\Phi_2^e$, and $\Phi_3^e$; then the overpotential for oxide formation is expressed as the sum of the potential drops at the metal–oxide boundary $(\Phi_1 - \Phi_1^e)$, in the body of the oxide $(\Phi_2 - \Phi_2^e)$, and at the oxide–electrolyte boundary $(\Phi_3 - \Phi_3^e)$:

$$\eta = (\Phi_1 - \Phi_1^e) + (\Phi_2 - \Phi_2^e) + (\Phi_3 - \Phi_3^e), \quad (5)$$

where $\Phi_1$, $\Phi_2$, and $\Phi_3$ are the respective potential differences under the applied electric field.

As the quantities $(\Phi_1-\Phi_1^e)$ and $(\Phi_3-\Phi_3^e)$ are independent of the oxide thickness and depend only on the polarising current, the overpotential of the film growth process will be

$$\eta = \Phi_2 - \Phi_2^e \qquad (6)$$

and

$$E = \frac{\eta}{D},$$

applying the condition that, in the hypothetically reversible state, the field in the film is vanishingly small in comparison with that which brings about film growth.

## IV. THEORY OF THE GROWTH OF ANODIC FILMS

Contemporary theories of the growth of anodic oxide films are based on the celebrated theory of Mott and Cabrera[24] and Verwey[25], developed for the oxidation of metals in the gas phase.

Electrons can, with a certain probability, penetrate from the depth of the metal through the thin oxide film (10 Å) to the surface and ionise adsorbed oxygen atoms. This produces an electrical double layer with a certain potential difference, which at the film thickness mentioned gives a potential gradient of $10^7$ V cm$^{-1}$. The presence of such a field permits cations to diffuse throughout the film.

According to Mott and Cabrera, the volume charge is small in sufficiently thin films, therefore there are no appreciable changes in the field in the body of the film (the field is considered to be homogeneous in the film), and hence the ionic field current is determined by the energy for the escape of a metal ion at the metal–oxide boundary according to the equation:

$$i = n'\nu' \exp - \{(w' - q'a'E')/KT\}, \qquad (7)$$

where $\nu'$ = vibration frequency of the ion in the metal lattice, $w'$ = activation energy for the escape of an ion from the metal lattice, $q'$ = ionic charge, $a'$ = distance from maximum to minimum potential energy, $E'$ = field potential, $n'$ = surface concentration of the metal ions, $K$ = Boltzman's constant, $T$ = absolute temperature, and $i$ = ionic current density.

Mott assumed that the concentration of carriers in the body of the film was not constant but changed under the influence of the field until the current in the mass of the film:

$$i = 2a\nu n \exp\{(w - qaE)/KT\} \qquad (8)$$

became equal to the current through the oxide metal boundary, *cf.* Eqn. (7). At this point, the concentration of ions $n$ inside the oxide became equal to the surface concentration of metal ions. The slope $dE/d(\ln i) = kT/qa$ must be proportional to the temperature.

Verwey's theory, in contradiction to that of Mott, assumes that the ionic current in the film is determined by the movement of the ion through the bulk of the film, and the dependence of the ionic current on the electrical field is expressed by an analogous equation.

The use of the anodic method of oxidising metals – under more accurately defined conditions, permitted a more thorough investigation of the oxide film growth process.

Experimental results from studying the temperature dependence of anodic oxidation and a study of the transient processes showed that Eqn. (7) describes only the motion of individual ions in the film under conditions of an electric field of high potential and that the behaviour of the total ionic current in the film is more complex. It was found that the values of $a$ and $w$ in the kinetic equation for current are considerably greater than predicted by theory (*cf.* the Table). These two theories can be considered as boundary cases of a single theory.

Young[26] has given the fundamental electric field equation embracing these two cases as limits:

$$E(x) = E_0 + \frac{1}{\beta}\ln\{[n_0(n_0 - n)\exp(-\beta 4\pi qxn/\varepsilon)]n\}. \qquad (9)$$

Here $n$ = concentration of mobile ions in electrically neutral oxide, $n_0$ = concentration of mobile ions in the given field, $\epsilon$ = dielectric constant, $E$ = field potential in oxide, $x$ = = coordinate, $q$ = ionic charge, $a$ = distance from maximum to minimum potential energy, and $\beta = aq/KT$.

The quantities $E_0$ and $n_0$ in Eqn. (9) are the values of $E$ and $n$ at $x = 0$. In this case when $x$ is large, *i. e.* in thick films:

$$E(x) = E_0 + \frac{1}{\beta}\ln\frac{n_0}{n}. \qquad (10)$$

Substituting in this equation the values of $E$ and $n$ derived under the assumption that the rate of motion of an ion through the metal–oxide boundary is equal to rate of motion of an ion in the body of the film, we obtain the Verwey equation for ionic current:

$$E = \frac{1}{\beta}\left\{(\ln i/2a\nu p) + \frac{w}{KT}\right\}. \qquad (11)$$

From Eqn. (1) we see that the electrical field is determined by the bulk properties of the film. It can be shown that when $x$ is small Eqn. (9) transforms into Eqn. (7).

By determining the temperature dependence of the rate of growth of an anodic oxide film, Vermilyea found that between 0° and 80° the Tafel slope is independent of temperature.

Young[27] also confirmed this between 20° and 60° for films on niobium. The relation

$$\frac{dE}{d\ln i} = \frac{KT}{qa}$$

is valid between these temperature limits.

The experiments of Scholte and van Geel[28] and of Young[27,29] showed that the application of an electric field on an $Nb_2O_5$ film causes an increase in the concentration of mobile ions, and the space charge in the film attains an appreciable value, which depends on the current density. After switching off the forming potential a pseudo-equilibrium state is slowly established in the film – the distributed volume charge.

TABLE. $a$ and $w$ for ionic conductivity in a high field.

| Metal | Activation energy, $w$, eV | $a$, *cf.* Eqn. (7), $10^{-8}$ cm | Reference |
|---|---|---|---|
| Ta | 1.39 | 2.5 | 27 |
| Al | 1.55 | 2.5 | 48 |
| Zr | 1.34—1.84 | 2.3—3.7 | 1 |
| Zr | 1.04—1.19 | 2.8—4.4 | 83 |
| Nb | 0.71—0.76 | 3—4 | 33,84 |
| Nb | 1.19 | 2.4 | 85 |

By measuring the impedance of an oxidised niobium electrode immediately after breaking the external circuit, Young obtained curves for the increase of capacity with time for various space charges. The rise in capacity on the curves depended on the temperature but not on the ionic current density.

On the basis of these measurements and also of measurements of the impedance of a niobium pentoxide electrode as a function of frequency Young concluded that the resistance of the oxide changes exponentially with distance from the metal–oxide boundary to the oxide–electrolyte boundary, *i.e.* the field changes the concentration of mobile ions.

The percentage ratio of the change in reciprocal capacity for a given change in the logarithm of the frequency becomes independent of thickness. Hence the resistance of the layers of the film at the boundary with the metal and at the boundary with the solution must be considered independent of thickness (its total thickness), *i.e.* the degree of departure from stoichiometry under these conditions will be determined by the equilibrium at the metal–oxide and oxide–electrolyte boundaries.

The role of the space charge in the kinetics of the growth of the anodic film and the quantitative interpretation of the space charge were first given by Dewald[30,31] on the basis of a model of the oxide film developed by Haring[31] (*cf.* Fig. 2).

Fig. 2 shows that during escape from the metal to a distance $b$, a mobile ion must overcome a higher potential than during its further motion into the film, where the potential barrier equals $u$.

By considering the film as a lattice of stoichiometric composition through which metal ions move under the influence of the electric field, and taking into account the space charge, Dewald showed that the behaviour of such a system depends on a critical factor $\delta$ (a non-dimensional quantity), which is determined both by the lattice parameters of the oxide and by the experimental conditions:

$$\delta = \beta\gamma n_0 D = \left[\frac{4\pi q^2 (m_s \nu_s)^{a/b}}{K\nu}\right] \{\exp[(u - \varphi a/b)/KT]\} \frac{D}{T} i^{(1-a/b)}. \quad (12)$$

Here $u$ = activation energy for the motion of an ion between two position of equilibrium in the absence of an electric field, $2a$ = distance between the two equilibrium positions, $\nu$ = vibration frequency of an ion in an interstitial position, $\nu_S$ = vibration frequency of a metal atom at the surface, $n_0$ = concentration of the ions at $x = 0$, $\varphi$ = activation energy for the diffusion of an ion from the lattice into the film, $m_S$ = surface density of the metal ions, and $D$ = film thickness.

When $\delta$ is small, corresponding to a small space charge, the film growth kinetics are determined by phenomena at the metal–oxide boundary. When $\delta$ is large, ~10 at a film thickness of 1000 Å, the rate of formation of the oxide is almost completely determined by the bulk of the film. Under a high electric field electrons are removed from the film and the interstitial motion of the ions is not electrically compensated, as a result which a space charge is set up.

For the mean electric field potentials Dewald obtained the equation:

$$\bar{E} = E_0 + \frac{1}{\beta}\left\{\left(1 + \frac{1}{\delta}\right)\ln(1-\delta) - 1\right\}, \quad (13)$$

from which it is evident, that at any point of the film the field is determined by two quantities: the surface charge $E_0$, due to the motion of the ions, and a quantity related to the space charge.

Eqn. (13) gives quite a simple relationship for $\delta \gg 1$ and $\delta \ll 1$, but is rather complex when $\delta$ is close to unity.

The interpretation of parameter $\delta$ also permitted the suggestion that the Tafel slope at certain current densities, oxide film thicknesses, and ratios of parameters $a/a'$ and $w/w'$, can be independent of temperature. The theory was confirmed by the experiments of Vermilyea[21] and Young[33].

Dewald's theory was an advance towards determining the combination of complex processes taking place during the anodic oxidation of metals and their interrelation.

The phenomena observable during the film growth process which are not covered by Dewald's theory include transient processes. The so-called transient processes reflect the non-steady behaviour of the film between two stationary conditions corresponding to two different values of the field potential. The transient processes were investigated suddenly changing the electric field in the film[34], which brings about two successive processes — an initial instantaneous, and then a slow, change in current.

When the current was increased instantaneously[35,36] the initial rise in potential shifted to a lower stationary potential corresponding to a new current (*cf.* Fig. 3). The value of the excess field was independent of the initial current density in the range $2 \times 10^{-6}$ to $4 \times 10^{-4}$ A cm$^{-2}$, of thickness, and of temperature, and depended only on the ratio of the final and initial current densities and on the method of interrupting the current.

The second method of studying the processes taking place in the transient state consists of the application of an alternating potential of low amplitude in addition to the constant forming potential[35].

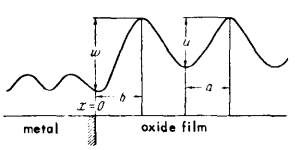



Fig.2. Potential curve for a metal ion in a high electric field. $x$ denotes the equilibrium position of the ion at the surface of the metal.

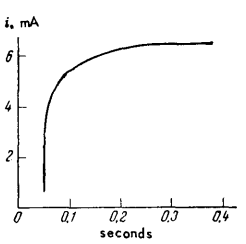



Fig.3. Transient state of the ionic current in a $Ta_2O_5$ film at the moment of change of an electric field from 0.057 to 0.062 V Å$^{-1}$ at 81°.

The activation energies and the distances between the two equilibrium positions in the transient state, calculated by the two types of experiment, were anomalously high, 0.7–1.4 eV for $w$ and 2.4–2.8 Å for $a$.

Unlike Verilyea and van Geel[37], who explained the anomalously high values of $a$ and $w$ by relaxation phenomena in the structure of the film, Young and Dewald consider the existence of the transient states in a film during a sudden change in applied potential to be the result of a change in the concentration of mobile carriers in the film.

These experimental results on transient processes show that in a sufficiently high field the rate of transfer of the ions through the film is determined not only by the applied potential but also by the carrier concentration gradient, and therefore cannot be described by any of the equations proposed earlier.

The experimental results on transient processes in the film were explained in theory proposed by Bean *et al.*[38] and simultaneously by Dewald[36], Young[26,39], and Winkel *et al.*[35]

From experimental results on ionic conductivity of oxides in high electric fields, Maurer[40] suggested a relation between the concentration of the moving ions in the oxide and the magnitude of the field. For a crystalline oxide the increase in ionic conductivity under the influence of the high-potential field is analogous to the formation of Frenkel defects. The possibility of formation of ionic conductivity in this way in electric fields with potentials of $6 \times 10^6$ V cm$^{-1}$ was confirmed experimentally by Tompkins and Jacobs[41].

Bean *et al.*, and later Dewald, used this theory to explain experimental results on transient processes in oxide films.

The theory was based on the assumption that ions are mobile and that holes are immobile, which is improbable under the conditions of electric fields of such high intensity. The concentration of mobile ions, $n$, was taken to be dependent on the field, but the oxide was assumed to be neutral. The rate of formation of Frenkel defects is given by the equation:

$$(N_0 - m)\,\nu_1 \exp\{-(w_1 - qa_1E)/KT\}, \qquad (14)$$

where $N_0$ = concentration of metal ions in the lattice, $m$ = = concentration of Frenkel defects, and $a$ = one-half the distance between neighbouring positions of equilibrium of the ion. All parameters with subscript 1 relate to the escape of ions from the metallic lattice.

By assuming that the rate of recombination (capture of an ion by a hole) is $im\sigma$, a differential equation for the concentration of the holes was obtained:

$$\frac{\partial m}{\partial t} = (N_0 - m)\,\nu_1 \exp - \{(w_1 - qa_1E)/KT\} - im\sigma. \qquad (15)$$

By putting $m = n$, we obtain:

$$i = 2a_2 m\nu_2 \exp - \{(w_2 - qa_2E)/KT\}. \qquad (16)$$

Here the parameters with subscript 2 relate to interstitial movement. In the stationary state:

$$\frac{\partial m}{\partial t} = 0, \qquad (17)$$

then at $N_0 \gg m$, Eqns. (15) and (16) are transformed into:

$$m = \left(\frac{\nu N_0}{2\sigma a_2\nu_2}\right)^{1/2} \exp - \frac{w_1 - w_2}{2KT} \exp \frac{q(a_1 - a_2)}{2KT}; \qquad (18)$$

hence the rate of anodic oxidation is:

$$i = 2a_2\nu_2 \left(\frac{\nu_1 N_0}{2\sigma a_2\nu_2}\right)^{1/2} \exp - \frac{w_1 - w_2}{2KT} \exp q\frac{a_2 + a_1}{2KT}. \qquad (19)$$

Eqn. (18) agrees in external form with Mott's equation for ionic current. The only difference is in the treatment of the quantities $a$ and $w$. The authors consider $a$ to be a continuous function of the field potential. The equation for the field potential shows the effect on the rate not only of ionic motion, but also that it brings about other changes in the film and these secondary changes affect the ionic current.

Such secondary changes can be of two types. The first is that the field changes the concentration of the moving ions by creating Frenkel defects — the values of $a$ and $w$ then become greater.

The second change[34,42] is that there is an alteration in the local ionic configuration of the film, *i. e.* its parameters and the activation energy of the escape and interstitial motion of ions are changed. This explanation was confirmed experimentally by Verkerk *et al.*[43]

Young[44,45] studied the transient processes in the oxidation of a tantalum electrode. He observed that during a sudden increase in the potential of the field applied to an electrode with a low initial concentration of Frenkel defects, there is an increase in the ionic current, initially slow and then rapid. This contradicted the statement that † = 0, *i. e.*, that the current is maximal at $t = 0$.

Young concluded from these results that Frenkel defects arise as a result of a cascade process, which drive ions out of the lattice of the oxide into the interstices, and not as a result of the interconnected action of field and thermal diffusion in the oxide.

## V. PROPERTIES OF NON-POROUS OXIDE FILMS

The properties of pore-free anodic films of the $Ta_2O_5$ and $ZrO_2$ type depend significantly on whether or not they are in contact with the electrolyte. The applied potential in the metal–oxide–metal system is a measure of the difference in chemical potentials along this system, *i. e.* in the direction of the field, and the driving force of the current is the equalisation of the Fermi levels. In the metal–oxide–electrolyte system, owing to the electrochemical reaction at the oxide–electrolyte boundary the applied potential includes the overpotential of the liberation of hydrogen in cathodic polarisation, or of oxygen in anodic, depending on the direction of the current. For this reason the voltage–current characteristics of the dry and moist systems can be compared only with the proviso that the electrochemical reaction at the oxide–electrolyte boundary is taken into account.

Young considers that in the region of near-stationary potentials one of the reactions:

$$OH^- = O^{2-} \text{ (in the oxide)} + H^+,$$

$$5OH^- + 2Ta^{5+} \text{ (in the oxide)} = Ta_2O_5 + 5H^+,$$

takes place, according to which stoichiometry breaks down in the outer layer of the oxide due to the introduction of oxygen.

† Symbol(s) missing from Russian text (Ed. of Translation).

The electrical conductivity of oxide films in anodic polarisation depends on the magnitude of the applied potential[40,46]. At small potentials the conductivity is electronic and the dependence of the current on potential obeys Ohm's law. When sufficiently high electric fields are applied the conductivity is ionic and it obeys other relationships[47,48].

## 1. Electronic Conductivity

The electronic component of the anodic current in so-called barrier films, *i. e.* in films with unipolar conductivity, falls with increase in the applied potential less rapidly than the ionic component[49]. This circumstance allows them to be separated and studied independently. The electronic conductivity of thin oxide films was studied by Charlesby[48,50], by Vermilyea[51], and by other investigators, who established that the dependence of electronic current on field potential is expressed by a hyperbolic sine relation. Frenkel's theory[52] was used to explain the experimental results in terms of the electronic current mechanism.

Vermilyea advanced the following mechanism for electronic conductivity: in the film there is a potential barrier of breadth $2a$ and height $u$ through which the electrons must pass. The presence of an electric field decreases the barrier and increases the probability of the motion of the electrons in the field direction.

Vermilyea showed that, at a potential below the formation potential the electronic current which flows through the film is a function of the potential gradient in the film.

$$i = 2A\exp\left(-\frac{u}{KT}\right)\mathrm{sh}\left(\frac{eaE}{KT}\right), \qquad (20)$$

where $A$ is a constant, $i$ the electronic current density, and $E$ the field.

The field changes the lattice parameters, allowing the electrons to pass through a symmetrical potential barrier of height $u$ and breadth $2a$.

Vermilyea started from the semiconductor nature of the oxide film and considered electrical conductivity to be the result of increased electron emission in the conductivity zone under the influence of the electric field. He showed that when there was a field of $5 \times 10^6$ V cm$^{-1}$ in the film the probability of the motion of electrons by a tunnel mechanism was 100 times greater than by thermal excitation.

The conductivity in the film

$$\sigma = A\exp\left(-\frac{\epsilon_0 - |V_0|}{2KT}\right) = \sigma\exp\left\{\left[\frac{q^3E}{\epsilon}\right]^{1/2}/KT\right\} \qquad (21)$$

on applying the field is increased owing to the Schottky effect. Here $E$ = electric field, $\epsilon_0$ = breadth of forbidden gap, $\epsilon_0|V_0|$ = breadth of forbidden gap on applying the field, $q$ = charge on the electron, and $\epsilon$ = dielectric constant of the oxide. According to this equation, there is a linear relationship between $\ln i$ and $E^{1/2}$, as Charlsby showed[48].

Vermilyea calculated that $10^6$ traps arise per 1 cm$^3$ in $ZrO_2$, *i. e.* a number quite small in comparison with the other semiconductors ($10^{14}$–$10^{20}$) and by this explained the low conductivity in oxides.

The electronic conductivity in an oxide film is evidently not homogeneous throughout its entire thickness.

Scholte and van Geel[28] concluded, from a.c. measurements of the resistance of an oxide film, that its resistance consists of several resistances connected in series, the resistance of each element depending on distance. According to this model, the film consists of a part with moderate resistance and another part whose resistance is appreciably greater and is a function of distance (*cf.* Fig. 4). The changes in resistance of the oxide with distance were also explained in terms of variation in the composition of the oxide with distance by other investigators[53–55].

Since the distribution of the electronic current in the film has not been studied accurately, only the lower limit of conductivity can be determined.

Vermilyea calculated that for $Nb_2O_5$ films of thickness 2000 Å, the total current at a potential of 100 V is $10^{-8}$ A cm$^{-2}$, hence the resistance of the oxide film should be $10^{15}$ Ω cm.

## 2. Rectification

Oxide films on niobium, bismuth, antimony, zirconium, and other valve metals have the property of unipolar conductivity[56]. They conduct electricity in one direction only. Walter[57] reported the ability of zirconium to rectify alternating current. Carmody[58] compared the coefficients of rectification by oxide films on zirconium and tantalum in dilute sulphuric acid and also studied the use of zirconium in electrolytic condensers.

$Ta_2O_5$ films sharply change their electrical conductivity on being immersed in electrolyte solution; the current which passes through even quite a small area ($10^{-2}$ cm$^2$) can change by $10^4$ times when the sign of the polarisation is changed.

Taylor and Haring[59] observed the evolution of hydrogen and deposition of copper on a tantalum electrode covered with an oxide film.

If instead of the electrolyte, a layer of metal is evaporated on to an $Al_2O_3$ oxide film, then the metal–oxide–metal system initially appears to be short-circuited, but on increasing the potential the circuit is broken by vaporisation of metal situated inside the pores and its penetration into the conducting side of the film. After disconnection such a system is an insulator at all potentials[60].

Although the property of the metal–oxide–electrolyte system to stop the current in the anodic direction was discovered long ago, this phenomenon has not yet been explained properly. Although the mechanism of current rectification by porous films has recently been clarified[61–63], in the

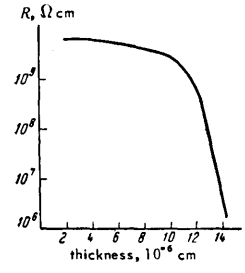



Fig. 4. Change in the resistivity of the film with its thickness.

case of continuous films there are very many experimental results which cannot be explained by any of the existing theories.

The large number of theories of the nature of unipolar conductivity of oxide films can be divided into two groups.

The first group consists of the theories based on the assumption that structural defects are present in the film — cracks which are filled with electrolyte and the latter for various reasons (concentration polarisation, Faraday rectification) exhibit conductivity only in the cathodic direction. This group includes the electroosmotic theory developed in 1930.[61] An indispensable condition of this theory is the existence of pores through the oxide film. On applying a potential to the $Al-Al_2O_3$–electrolyte system, the electrolyte in the pores of the oxide is subjected to the action of two forces: that of the electrostatic attraction of the condenser plate striving to draw electrolyte into the pores up to contact with the second plate, and that of an electroosmotic force, which can act either to assist or inhibit conduction, depending on the electrolyte and oxide combination. During anodic connection, the electroosmotic force opposes the electrostatic one and drives out the electrolyte from the pores of the film, converting it into an insulator. In the cathodic direction, these forces act in the same direction. This theory was confirmed by Zakgeim's experiments[62], which showed that the rectification coefficient of the $Al-Al_2O_3$–electrolyte system increases with the valency of the cation in the electrolyte.

The second group of theories connects unipolar conductivity with the semiconductive nature of the film. In this group two boundary tendencies can be distinguished. One consists in unipolar conductivity being determined by the existence of $p-n$ transition in the film and the oxide–electrolyte boundary takes no part in cathodic conductivity[64]. The other[65,66] considers, on the contrary, that cathodic conductivity is the consequence of electrochemical reaction at the oxide–electrolyte boundary, producing a change in the stoichiometric composition of the film and hence the emergence of conductivity.

Günther-Schulze[67] considered, in his various works, that unipolar conductivity is determined by the asymmetrical properties of the discharge through gaseous traps in the film. Subsequent experimental results obtained by him and his coworkers introduced a change in the original theory: in the cathodic direction oxygen leaves the oxide lattice, converting it into a semiconductor with an excess of metal. In this case a very high oxygen mobility is assumed. van Geel[68,69] considers that unipolar conductivity in the oxide film is determined by the presence of a $p-n$ transition.

Taylor and Haring[59] also explain their experimental results on a solid electrolytic condenser by the presence of a $p-n$ transition in the oxide.

Dekker and van Geel[70] used a bridge to compensate for the capacitative current in investigating unipolar conductivity of $Al_2O_3$ films. With the aid of a cathode oscillograph they thus succeeded in separating the conductivity current from the total current during the polarisation of the specimen by an alternating potential. The cathodic current on the film at the given potential was greater in that quarter-cycle where the cathodic potential is decreasing than in the quarter-cycle in which it is increasing. This gave hysteresis on the current *vs.* potential curve (*cf.* Fig. 5). These experiments did not permit unambiguous conclusions to be drawn about the reason for unipolar conductivity.

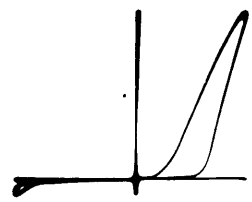


Fig.5. Voltampere characteristics of an oxide film for a sinusoidal potential at a frequency of 200 c $s^{-1}$.

Parallel change of the capacity and resistance in the compensating circuit in these measurements did not correspond to the equivalent circuit of the test system and, moreover, in this change the active and reactive constituents of the impedence have a complex relation to the potential.

van Geel and Bouma[71] used an improved method for similar measurements. They found that the hysteresis loop increases with time during polarisation by an alternating current and decreases with increase in frequency. The effect is considered to be the consequence of reversible change in the stoichiometric composition of the oxide.

van Geel and Pistorius [? Bouma (Ed. of Translation)][72] found that the longer the period of preliminary anodic polarisation the less the cathodic current. It was found that a sixfold increase in the thickness of the film requires the potential to be increased by only 30% in order to obtain the same current. On the basis of this it was concluded that the $i$ *vs.* $v$ relationship for cathodic current is a function of thickness.

van Geel and coworkers[28,67,73,74] studied the $Al-Al_2O_3$–electrolyte, $Ta-Ta_2O_5$–electrolyte, and $Zr-ZrO_2$–electrolyte systems under various conditions. It was found that at high current density the cathodic polarisation produces good conductivity in both directions but the conductivity of the oxides in the anodic direction decreases with time.

It was also shown that the production of conductivity in the cathodic direction in the oxide film depends on time and that in zirconium, for example, similar excitation requires an appreciable time. The authors assumed that rectification is determined by a $p-n$ transition at the boundary of the two layers of the film: the layer adjoining the solution (of $p$ type) and with the remaining part of the film ($n$ type).

Sasaki[64] considers that rectification is determined by the presence of a $p-i-n$ transition in the film.

From experiments with a mercury probe, Vermilyea[75] established that the oxide film has separate portions, area $\sim 10^{-2}$ $cm^2$, with conductivity a hundred times greater than the conductivity of the main surface of the oxide. A current of $10^{-9}$ A passes through such a place of reduced resistance in both directions up to considerable potentials. Evolution of hydrogen bubbles is observed at these places during cathodic polarisation.

Vermilyea also showed that the anodic leakage current (electronic constituent of the formation current), like the cathodic current during cathodic polarisation, increases with the film thickness at a fixed oxygen overpotential. He assumes that the conductivity of the film in the cathodic

direction can be the consequence of dislocations originally present in the metal lattice and then in the oxide – sections of low conductivity on which he observed evolution of hydrogen.

In measuring the impedance of oxidised zirconium and niobium electrodes, Young[29,46] found that at a given potential, $\tan\theta$ (the tangent of the dielectric loss angle) increases with the thickness, and for a fixed thickness the leakage current increases with decrease in frequency. At the first moment of cathodic polarisation the film resistance increases, but then falls, which the author explained by penetration of $H^+$ at the dislocations. The leakage current fell with time at constant potential.

Young[76] obtained results on the cathodic liberation of hydrogen at the surface of oxides prepared by various methods; these results were also interpreted by the presence of cracks, mechanical defects in the film, through which hydrogen can reach the metal.

By cracks Young implies also imperfections in the structure of the oxide film[77] which bring about packing stresses in its construction, due to non-uniform oxidation of the metal. The non-uniform oxidation of the metal is facilitated by the presence of various impurities and lattice defects. Imperfections in the periodic structure of the oxide lattice can appear as cracks or in other forms.

Young assumes that cracks or, more probably, dislocations are those portions which have good conductivity in the cathodic direction and less in the anodic direction. As acceptors, protons create conductivity in the film under the condition that defects (cracks) exist in it. However, Young does not exclude the possibility that, in the absence of cracks, the film does not lose its property of unipolar conductivity.

Fig. 6 shows the frequency dependence of capacity for films of various thickness. Young explained the observed departure from a rectilinear dependence by the existence in the film of cracks, whose dimensions must increase with thickness. In cathodic polarisation, hydrogen ions, being small, penetrate these cracks and are discharged there as $H_2$. In this, part of the hydrogen is liberated at the surface of the oxide. However, the author does not exclude the discharge of hydrogen also being localised and in the case of distortion of the film, with its subsequent conversion into an $n$-type semiconductor. If the film contains.... [line omitted from Russian text (Ed. of Translation)] normal semiconductor similar to zinc oxide or germanium (*cf.*

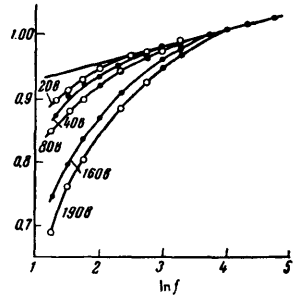



Fig. 6. Dependence of capacity on frequency for films of various thicknesses.

Dewald's work[78]). This does not persist on thin films, where the space charge region is restricted to the thickness of the film.

Young[44,45] assumes that the application of the electric field causes a change in the electronic structure of the film. This change is characterised by two successive processes: (1) disruption of the cathodic resistance is very rapid due to the delay of the conductivity in the cracks, and (2) changes in the stochiometry which change the film into a conductor.

He considers that for the anodic direction the film should be considered free from space charge and carriers. The field at the oxide–electrolyte boundary necessary for the injection of electrons from the solution into the film must be continuous through the whole film, since the overpotential of oxygen at the oxide–electrolyte boundary is distributed between two layers: in the outer layer of the oxide film and in the double layer at the oxide–electrolyte boundary.

Schmidt[65] investigated the behaviour of an oxidised tantalum electrode and $n$-type silicon in anhydrous solutions of $NH_4NO_3$ in liquid ammonia and of $RuI_2$ in liquid $SO_2$. In the first solution, which contained protons, rectification took place, but in the second where protons are absent there was no rectification. This suggested that during the period of cathodic polarisation protons enter the oxide and during the period of anodic polarisation they leave it. The protons in the oxide create donor centres which determine the conductivity of the oxide.

Investigation of cathodic currents on oxidised electrodes[66,79] showed that the magnitude of the cathodic current for a given potential depends on the size of the cation in the electrolyte. Evidently the electric field of the ion creates a potential barrier at the oxide–electrolyte barrier.

Smith[80,81] concluded, from a study of the $i$ *vs.* $v$ relation for oxide electrodes, that the oxide film is an insulator at whose boundary with the electrolyte there is injection of carriers during both cathodic and anodic polarisation, due to the electrode process producing the current. The difference in the magnitude of the currents in the cathodic and anodic directions was related to the electronic structure and the ratio of the activation energies of these processes.

Odynets[63], in studying the same system, concluded that the oxide film on aluminium does not exhibit unipolar conductivity when out of electrolyte. The valve action of the $Al–Al_2O_3$–electrolyte system was attributed to a change in the rate of the electrochemical reaction taking place on the surface of the oxidised electrode during a change in the polarity.

It is evident from the experimental works on the question of the rectifying action of anodic oxide films which have been mentioned that this question is still a subject of discussion, owing to the considerable complexity of the metal–oxide–electrolyte system. The main source of the complexity is that the resistance of the body of the film in the field direction responsible for its growth is not uniform but is determined by the space charge distributed exponentially in it.

When new layers of oxide are being built up a change in the oxide modification can occur. The presence of electric fields of high potential which bring about the growth of the film can simultaneously cause structural defects. Such defects can arise from internal stresses in the film

or can be formed by the transmission of dislocations present in the metal lattice[82].

In constructing theories of the rectifying action of compact oxide films foreign scientists have used several terms: *cracks, fissure, weak spots,* and *imperfections* which imply the incompleteness of the compact structure of the film, which is responsible for the rectifying action.

This requires discussion in greater detail. The incompleteness of the compact structure of the film must be described independently of how the various authors define it. Such imperfections can be of two types: in the presence of the first we have the division of the film into two phases between which there is a third, for example, the molecules of ions of the electrolyte. In such a case the picture is one of separate centres, spots of other substances, which for various reasons can bring about conductivity in the cathodic direction and stop the current in the anodic direction.

Dislocations, *i.e.* those breaks in the periodic lattice of the oxide which lead to the appearance of acceptor or donor levels[83-85], belong to the second type of imperfections in the compact structure of the film. Such imperfections affect the electrical properties of semiconductors, since they cause the scattering of current carriers and can act as centres for the recombination and regeneration of carriers.

Dislocations can be formed by the thermal effects of the electric fields, the effect of the medium in which one crystal or another is located, etc.

It is quite probable that during the growth of the film, as its thickness increases[2] the internal stresses in a high electric field increase and imperfections of the second type are produced, which can be the cause of imperfections of the first type.

The phenomena at the metal–oxide boundary and especially at the oxide–electrolyte boundary, for example, the distribution of potential in the fixed part of the double layer at this boundary, the influence of the electrochemical reaction — all this complicates the system considerably.

All that has been written above shows the difficulty involved in the study of the rules which govern the process of film growth now under discussion and the kinetic phenomena which take place either in the film itself or at its boundaries with the metal and the electrolyte. In many instances several phenomena simultaneously affect the course of the process taking place at the boundaries and those in the body of the film.

In the development of theories to describe the current laws it is necessary to consider the relations effective at the two boundaries of the film, its semiconductive nature, and in several instances also the mechanical fractures in the structure.

All this indicates that there are still several fundamental relationships in the film which have not been revealed.


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# CHEMICAL EFFECTS OF NUCLEAR TRANSFORMATIONS IN SOLIDS (CHEMICAL CONSEQUENCES OF NUCLEAR RECOIL)

A. N. Murin, R. V. Bogdanov, and S. M. Tomilov

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## I. INTRODUCTION

Many features of the chemical processes accompanying nuclear transformations are still obscure, and far from adequately interpreted in the literature. The ever increasing number of new facts, and the difficulty of interpreting the results, which characterise studies of this type, by pointing to the weakness and contradictions of the conventional inorganic chemistry of, apparently, even the most thoroughly investigated elements, such as manganese, chromium, phosphorus, bromine, iodine, etc., stimulate new work in different branches of chemistry. Among the