

# ANODIC OXIDE FILMS ON ALUMINUM

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## I. Introduction and General Background

In this review the authors have attempted to present a coherent picture of the present state of knowledge of anodic oxide films on aluminum. For the sake of completeness, and to maintain a logical sequence, the classical work has been included so that it can be reviewed in the light of the present day experimental evidence. The over-all period under review will be from approximately 1930 to the present day.

Because of the high affinity of aluminum surfaces for oxygen, the metal is always covered with a highly resistant oxide film; the improvement of this natural oxide film to produce an anodic oxide film which is attractively finished, has excellent corrosion resistance, and possesses other commercially desirable qualities is the aim of the anodizing industry today.

The type of anodic oxide film that can be produced upon aluminum when aluminum is made the anode in an electrolytic cell depends upon several factors, the most important of which is the nature of the electrolyte. Electrolytes in which the formed oxide film is completely insoluble are those electrolytes which produce *barrier-type* films; examples of this type of electrolyte include neutral boric acid solution, ammonium borate or tartrate aqueous solutions (pH 5-7), ammonium tetraborate in ethylene glycol, and several organic electrolytes including citric, malic, and glycolic acids. The specifying of neutral or pH value 5-7 aqueous solutions, for some electrolytes, is important since it is considered<sup>1,2</sup> that, in strongly acidic solutions, these electrolytes do not form completely nonporous barrier type films. Electrolytes in which the anodically formed oxide film is slightly soluble are those electrolytes which produce *porous-type* films; examples of this type of electrolyte are numerous, the most commercially important being sulfuric, phosphoric, chromic, and oxalic acids at almost any concentration. It should be stressed here that the classification of oxide films from the solubility of the oxide in the electrolyte is an extremely naive concept, yet it will suffice for the present introduction.

These two types of films differ in the thickness of film that can be produced and in the thickness controlling parameters. Apart from the temperature of the electrolyte, barrier-type film thickness is controlled solely by the voltage applied, whereas porous-type film thickness depends upon the current density and time. The maximum film thickness attainable for barrier-type films is restricted to a voltage below the oxide breakdown voltage value,<sup>3</sup> *i.e.*, 500-700 V, which corresponds to 7000-10,000 Å. The thickness of porous films, being time dependent, can grow to many times higher than the upper limit placed upon barrier-type films. For porous films, apart from the current density and time, the electrolyte temperature is an important criterion in determining the film thickness. At low temperatures (0-5°) the porous film formed is thick, compact, and hard—this is called hard anodizing. At high temperatures (60-75°) the porous film is thin, soft, and non-

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(1) R. W. Franklin, Conference on Anodising Aluminium, Nottingham, 1961, Aluminium Development Association.

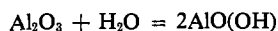
(2) M. A. Barrett, IVth Scandinavian Corrosion Congress, Helsinki, 1964, p 41 (Current Corrosion Research in Scandinavia).

(3) A. Charlesby, *Proc. Phys. Soc.*, B66, 317 (1953).

protective; under such conditions the process of electro polishing is achieved, *i.e.*, where the oxide film is dissolved by the electrolyte almost as soon as it is formed. From this temperature effect on the thickness of porous films, it is clear that the electrolyte plays an important part, not only in the formation of the porous films, but also in its subsequent existence.

The most important commercial use of the barrier-type films is in the field of dielectric capacitors and in the protection of vacuum-deposited aluminum; protection by porous films is not practical owing to the thin aluminum films used and the excessive amounts of aluminum consumed during porous oxide film formation. The porous-type films used commercially possess excellent corrosion and abrasion resistance and, owing to high porosity, form a good base for paints or dyes. Decorative anodizing is usually the dyeing, with the appropriate color, of the transparent colorless films formed by the sulfuric acid process; occasionally when the yellow color is required, oxalic acid films will be used, since they have a yellow coloration without subsequent dyeing. The chromic acid films are used only where the appearance is unimportant, since these films are usually gray and opaque in character.

The industrial uses of porous anodic oxide films are restricted to those films which are sealed. This process of sealing of the porous films involves immersing the films in hot water, usually purified water, or in aqueous solutions of certain salts above 90°. The process involves the closure of the porous structure to form a compact nonporous film, whose thickness is many orders higher than those attainable in barrier-type electrolytes. The chemical process, which is believed to be occurring, is the formation of boehmite by partial hydration of alumina.



During sealing in certain salts, *e.g.*, nickel acetate and potassium dichromate, sealing also produces the precipitation or incorporation of these salts within the sealed film. This will be covered more fully in a later section.

Although the barrier-type and the porous-type films are quite different in their over-all physical appearance and characteristics, they do, however, have one area of similarity. The porous films consist of a thick, porous outer layer of alumina overlying a thin, compact inner layer; the thickness of this thin inner layer is, as in the barrier-type films, controlled by the voltage that is applied across the electrolytic cell. Table I shows a summary of the two types of films that can be produced upon aluminum.

Recent developments in the field of metal protection, particularly in the field of refractory oxides, include the high-temperature oxidation utilizing the plasma jet from the field of magnetohydrodynamics. In this technique, various materials, between which reaction is sought, are fed into a suitable ionized atmosphere at a very high temperature, *e.g.*, 10,000°K. The resulting plasma, as this mixture of atoms, ions, and electrons is termed, can then be sprayed upon the surface one wishes to protect.

Plasma spraying is in extensive commercial use today; however, there are several disadvantages, *e.g.*, excessive and damaging heat evolution and the high cost of the necessary electrical power.

Table I

Classification of the Two Types of Anodic Oxide Film That Are Formed on Aluminum

	Barrier type	Porous type
Structure	Thin, compact, non-porous	Inner layer—thin, compact barrier-type Outer layer—thick and porous
Thickness	Voltage dependent to the extent of $14 \text{ \AA V}^{-1}$	Inner layer—voltage dependent, <i>e.g.</i> , sulfuric acid ( $10 \text{ \AA V}^{-1}$ ) Outer layer—voltage independent; current density, time and temperature dependent
Typical electrolytes	Solutions of boric acid-borax  Citric acid-citrate Ammonium tartrate <i>Barrier-type electrolytes</i>	Sulfuric, phosphoric, oxalic, and chromic acid aqueous solutions  <i>Pore-forming electrolytes</i>
Uses	Electrolytic capacitors	In the sealed condition can be used in any situation where excellent corrosion resistance is required. Prior to sealing, the adsorption of colored dyestuffs has wide application in decorative structures. Also provides an excellent base for paints and metal electrodeposits

## II. Anodic Oxide Film Composition

### A. GENERAL STRUCTURAL FEATURES

In an investigation of barrier-type oxide films, Verwey<sup>4-7</sup> found that the composition was crystalline  $\gamma'$ - $\text{Al}_2\text{O}_3$ , the distinction between crystalline  $\gamma$ - $\text{Al}_2\text{O}_3$  and crystalline  $\gamma'$ - $\text{Al}_2\text{O}_3$  being a different arrangement of cations in the structure, both having the same oxygen lattice.  $\gamma'$ - $\text{Al}_2\text{O}_3$  is regarded as an intermediate case between amorphous and  $\gamma$ -crystalline  $\text{Al}_2\text{O}_3$ . Harrington and Nelson<sup>8</sup> in an electron diffraction study of films formed in a wide variety of electrolytes found the composition of the films studied to be amorphous alumina of random structure. The structures tended to be less random when the films were formed at high temperatures. This was interpreted by Taylor, Tucker, and Edwards<sup>9</sup> as due to an increase in the crystalline proportion of the film, which was also favored by increasing film thickness, high formation voltages, dilute electrolytes, and ac current. This increase in the crystalline  $\gamma$ - $\text{Al}_2\text{O}_3$  proportion with increasing thickness was confirmed by Stirland and Bicknell<sup>10</sup> using a dissolution technique involving the measurement of the oxide solubility in a mixture of phosphoric

(4) E. J. W. Verwey, *Electroplating Metal Finishing*, 7, 274 (1954).

(5) E. J. W. Verwey, *J. Chem. Phys.*, 3, 592 (1935).

(6) E. J. W. Verwey, *Z. Krist.*, 91, 65 (1935).

(7) E. J. W. Verwey, *ibid.*, 91, 317 (1935).

(8) R. A. Harrington and H. R. Nelson, *Trans. Amer. Inst. Met. Eng.*, 137, 128 (1940).

(9) C. S. Taylor, C. M. Tucker, and J. D. Edwards, *Trans. Electrochem. Soc.*, 88, 325 (1945).

(10) D. J. Stirland and R. W. Bicknell, *J. Electrochem. Soc.*, 106, 481 (1959).

and chromic acids. Below 100-V formation voltage, barrier-type films were found to be amorphous. Above 100 V the film was again amorphous but crystalline  $\gamma\text{-Al}_2\text{O}_3$  was also detected.

Altenpohl,<sup>11</sup> in a study of barrier-type films, also using a dissolution technique, reported that the outer layer of such films was soluble and the inner layer insoluble; this inner layer was assumed to be crystalline  $\gamma\text{-Al}_2\text{O}_3$ , the proportion of which increased with increasing formation voltage. Stirland and Bicknell did not consider that the crystalline  $\gamma\text{-Al}_2\text{O}_3$  and the amorphous alumina existed in a layer-type structure, as suggested by Altenpohl, but favored a more random structure. Wilsdorf,<sup>12</sup> in an investigation of air-formed films, proposed a spatial arrangement similar to that shown by  $\text{As}_4\text{O}_6$  in order to account for the appearance of two diffuse electron diffraction rings due to small crystallites of  $\gamma\text{-Al}_2\text{O}_3$ . Kerr,<sup>13</sup> in general agreement with the work of Wilsdorf, also observed diffuse diffraction rings and proposed that these rings were due to crystallites of  $\gamma\text{-Al}_2\text{O}_3$  dispersed in amorphous alumina.

Franklin,<sup>1</sup> in an investigation of films prepared in boric acid-borax electrolyte, has reported the presence of at least three types of oxide: (1) a hydrated oxide at the oxide-electrolyte interface, (2) occurrence of irregular patches of crystalline  $\gamma\text{-Al}_2\text{O}_3$ , and (3) amorphous oxide constituting the majority of the film. The complexity of these films increases as the formation voltage increases; this again is probably due to an increase in film crystallinity. Trillat and Tertain,<sup>14</sup> investigating films formed in 20% aqueous solution of sulfuric acid, reported similar results: an outer layer consisting of a mixture of boehmite,  $\text{AlO}(\text{OH})$ , and crystalline  $\gamma\text{-Al}_2\text{O}_3$  and an inner layer of amorphous  $\text{Al}_2\text{O}_3$ , the presence of boehmite resulting from the incorporation of water, leading to a gradual formation of monohydrate from amorphous oxide. That the composition found by Trillat and Tertain for porous films resembles that found, for supposedly nonporous films, by Franklin, indicates that even in boric acid-borax electrolytes some degree of porous oxide film is formed. This is almost certainly true for the more acidic boric acid electrolytes, as Franklin has reported.

The existence of both amorphous and crystalline  $\gamma\text{-Al}_2\text{O}_3$  forms an integral part of the theory of anodic oxidation and the porous oxide film structure proposed by Murphy and Michelson,<sup>15</sup> both of which will be covered in a later section.

Some recent work by Dorsey,<sup>16-18</sup> using an ir reflectance technique, has indicated that the barrier-type layers formed in all electrolytes are in fact alumina trihydrates which appear to undergo structural changes when porous films are formed. The absorption band of the barrier film was reported as lying between 900- and 1000- $\text{cm}^{-1}$  wave numbers, and the position of this absorption band in films formed in boric acid was found to be unaffected by the length of the anodizing or formation time, thus implying that these films are truly nonporous. In pore-forming electrolytes, this absorption band shifted to higher frequencies as porous oxide growth proceeded. Dorsey proposed that in boric acid electrolytes

the barrier layer exists as a cyclic aluminic acid trihydrate, while in pore-forming electrolytes, in order to form pores, this cyclic form reverts to a decyclic form; i.e., an effective lowering of polymer weight occurs and hence the absorption band moves to higher frequencies. Dorsey thus considers that pore formation cannot occur without the initial formation of the decyclic alumina trihydrate. Kormany<sup>19</sup> has also reported the presence of alumina trihydrate in barrier layers, along with  $\gamma\text{-Al}_2\text{O}_3$ , aluminum hydroxide, and boehmite.

The conclusion that boric acid produces completely nonporous films is somewhat doubtful, since it relies on the fact that no change in the absorption band frequency of the barrier layer is observed with anodizing time; this in turn depends upon the sensitivity of this absorption band to the decyclization process. Although no indication is given by Dorsey as to how rapidly this absorption band frequency increases as the porous film is formed, it is noted that no absorption band attributed to porous layer is found for boric acid films. Porous layer, detected by the presence of its absorption band, was reported to occur in films prepared in ammonium tartrate and tartaric acid, which are two electrolytes often used to prepare what are supposedly barrier-type films. This absorption band was also found for films prepared in typical pore-forming electrolytes, e.g., sulfuric and phosphoric acids.

Although some of this work may appear contradictory, it may be concluded that in general nonporous films are regarded as amorphous, and porous films as crystalline, both being anhydrous; the work of Lichtenberger,<sup>20</sup> Thach Lan, Naudin, and Robbe-Bourget<sup>21</sup> and Pavelkina and Bogoyavlenskii<sup>22</sup> is also relevant in this respect. The work of Dorsey is an indication that the oxide films are not anhydrous, the presence of water being regarded by some workers<sup>23, 24</sup> as a necessity to exert a stabilizing effect on the spinel-type structure of alumina (similar to that reported<sup>25</sup> for  $\text{Fe}_2\text{O}_3$  where the  $\text{OH}^-$  ions replaced  $\text{O}^{2-}$  ions in the lattice).

## B. ANION INCORPORATION

The incorporation of anions into the oxide structure is closely associated with the degree of pore formation, being the greatest for pore-forming electrolytes, and the least for barrier-type electrolytes. Bernard and Randall<sup>26</sup> and Franklin<sup>1</sup> have reported the incorporation of 1% boron into films formed in ethylene glycol-ammonium pentaborate and boric acid-borax electrolyte, respectively. For pore-forming electrolytes, incorporation is generally high; up to 17% has been reported for films formed in sulfuric acid by Pullen,<sup>27</sup> Phillips,<sup>28</sup> and Mason.<sup>29</sup> Mason has also reported that the incorporation was the greater, the lower the anodizing temperature, and

(11) D. Altenpohl, *Conv. Record of I.R.E.*, 3, 35 (1954).

(12) H. G. F. Wilsdorf, *Nature*, 168, 600 (1951).

(13) I. S. Kerr, *Acta Cryst.*, 9, 879 (1956).

(14) J. J. Trillat and R. Tertain, *Rev. Aluminium*, 26, 315 (1949).

(15) J. F. Murphy and C. E. Michelson, ref 1, p 83.

(16) G. A. Dorsey, Jr., *J. Electrochem. Soc.*, 113, 169 (1966).

(17) G. A. Dorsey, Jr., *ibid.*, 113, 172 (1966).

(18) G. A. Dorsey, Jr., *ibid.*, 113, 284 (1966).

(19) I. T. Kormany, *Tavkozlesi Kut. Int. Kozlemen*, 9, 113 (1964); *Chem. Abstr.*, 64, 1619f (1966).

(20) E. Lichtenberger, *Zh. Prikl. Khim.*, 34, 1286 (1961).

(21) Thach Lan Tran, F. Naudin, and P. Robbe-Bourget, *J. Phys. (Paris)*, 25, 11 (1964).

(22) V. P. Pavelkina and A. F. Bogoyavlenskii, *Zh. Prikl. Khim.*, 37, 819 (1964).

(23) W. G. Burgers, A. Classen, and J. Zernicke, *Z. Phys.*, 74, 593 (1932).

(24) E. Lichtenberger, *Metalloberflaeche*, 15, 38 (1961).

(25) I. David and A. J. E. Welch, *Trans. Faraday Soc.*, 52, 1642 (1956).

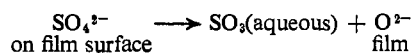
(26) W. J. Bernard and J. J. Randall, Jr., *J. Electrochem. Soc.*, 108, 822 (1961).

(27) N. D. Pullen, *J. Electrodepositors' Tech. Soc.*, 15, 69 (1939).

(28) H. W. Phillips, Symposium on Properties of Metallic Surfaces, Institute of Metals, Monograph 13, 1952.

(29) R. B. Mason, *J. Electrochem. Soc.*, 102, 671 (1955).

the higher the current density during film formation. Hoar<sup>30</sup> has proposed that this is due to the predominance of the following reaction as the temperature increases.



Randall, Bernard, and Wilkinson,<sup>31</sup> in an investigation of the formation of barrier-type films upon tantalum and niobium, have reported similar trends of anion incorporation as those reported by Mason. It was proposed that these were due to changes in the cation and anion movement during the growth of the film, the cation movement being the greater the lower the temperature and the higher the current density of formation. Since similar observations for the changes in anion incorporation with changing formation conditions are reported for both barrier-type and porous anodic oxide films, it is possible to suggest<sup>32</sup> that the porous layer in porous films is formed by conversion of the outermost section of the initially formed barrier, *i.e.*, that barrier layer formed by cation transport. A natural consequence of this proposal would be that, as the porous film growth proceeds, the anion distribution throughout the depth of the porous layer would be uniform. This has been found to be the case for the anodizing of an aluminum-magnesium alloy in sulfuric acid, by Wood, Marron, and Lambert,<sup>33</sup> using an electron-probe microanalysis technique. Assuming that electrolyte anions are immobile, porous films resulting from conversion of barrier layers formed only by anion motion, *i.e.*,  $\text{OH}^-$  or/and  $\text{O}^{2-}$ , would not contain incorporated electrolyte anions. Zirconium and hafnium are two metals which have been reported<sup>34</sup> to form barrier-type films by anion migration only; as to whether porous films upon these two metals would have zero electrolyte incorporation is, as yet, unknown.

Incorporation of electrolyte anions can occur by two methods, in either "bound" or "free" form. The "bound" form would result from the incorporation arising from the conversion of barrier to porous layer, and the "free" form from the accumulation of electrolyte anions within the pores. Ginsberg<sup>35</sup> has reported a total sulfur content corresponding to 13%  $\text{SO}_3$  which fell to 8%  $\text{SO}_3$  after prolonged washing, so the "bound" form contributes 8%  $\text{SO}_3$  and the "free" form 5% to the total anion incorporation.

Thach Lan,<sup>21</sup> using an ir technique, has reported that the sulfur is present as the anion, whereas Liechti and Treadwell<sup>36</sup> consider that the sulfur is present as a basic sulfate and that this sulfate is involved in a dissolution process in the pores. Liechti and Treadwell have also shown that the percentage of incorporation remains constant up to a porous film thickness of 6  $\mu$ . The incorporation then falls from 13 to 8%, expressed as  $\text{SO}_3$ , as the film continues to grow up to a thickness of 60  $\mu$ . Similar results have been reported by Brace and

Baker<sup>37</sup> and Bogoyavlenskii and Vedernikov.<sup>38</sup> The presence of an absorption band, attributed to the presence of the basic salt of the electrolyte anion, has been reported by Dorsey<sup>16</sup> for the anodizing of aluminum in sulfuric and phosphoric acids; this is in agreement with the proposal of Liechti and Treadwell.

For one metal, aluminum in this case, the incorporation of the electrolyte is closely related to the type of film that is produced upon the surface. The barrier-type films, which show little or no tendency to produce porous structures, incorporate very little electrolyte; porous films incorporate electrolyte anions to a much greater extent. For two pore-forming electrolytes, *e.g.*, sulfuric and phosphoric acids, it would not be unreasonable to expect that the levels of incorporation be comparable, provided (a) the cation mobilities involved in the growth of the initially formed barrier layers were similar, and (b) the mechanism of conversion of these barrier layers to the porous layers was also similar. As possible support for this, the values of 8%  $\text{SO}_3$ , reported by Ginsberg,<sup>35</sup> and 6%  $\text{PO}_4^{3-}$ , reported by Plumb,<sup>39</sup> are cited. Since incorporation appears closely related to porous structure, it is possible that it is also related to the amount of porous layer present upon a metal surface and any process which affects the porous layer also affects the level of incorporation. These proposals have been used by the authors in a study of the porous layer.<sup>40</sup>

### C. WATER CONTENT

Nonporous films are generally regarded as being anhydrous. However, as indicated previously, several workers have proposed that water is necessary to stabilize the spinel-type structure; *e.g.*, Lichtenberger<sup>24</sup> has indicated that 2.5% water present as boehmite is necessary.

In porous oxide films, formed in sulfuric and oxalic acids, Pullen<sup>27</sup> has reported 15% w/w water; Edwards and Keller<sup>41</sup> have found 1–6% in films formed in sulfuric acid, and Phillips<sup>28</sup> has detected a water content sufficient to produce  $2\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  for films formed in oxalic acid.

In general, the amount of water incorporated into anodic oxide films depends upon the conditions and treatment during formation. All the evidence available indicates that the water is not present in the "free" form, but occurs either as hydroxide or hydrated oxide or both.

## III. Barrier-Type Anodic Oxide Films

### A. FORMATION CHARACTERISTICS

Ideally, barrier films are nonporous thin oxide layers which conduct both electrons (electronic current) and ions (ionic current) at high electric field strength. The field strength is the voltage drop across the oxide film divided by its thickness; this voltage drop is not always equal to the applied voltage.

Below a minimum electric field strength ionic conduction is negligible, and electronic current becomes the predominant mode of charge transport; the magnitude of this electronic current, whether at a high or low electric field strength, is

(30) T. P. Hoar, "Modern Aspects of Electrochemistry, No. 2," Butterworth & Co., Ltd., London, 1959, p 309.

(31) J. J. Randall, Jr., W. J. Bernard, and R. R. Wilkinson, *Electrochim. Acta*, 10, 183 (1965).

(32) N. D. Tomashov and A. V. Byalobzhetskii, *Tr. Inst. Fiz. Khim., Akad. Nauk SSSR, Issledovan Korrozii Metal*, 4 (5), 114 (1955); *Chem. Abstr.*, 50, 11138i (1956).

(33) G. C. Wood, V. J. J. Marron, and B. W. Lambert, *Nature*, 199, 239 (1963).

(34) J. A. Davies, B. Domeij, J. P. S. Pringle, and F. Brown, *J. Electrochem. Soc.*, 112, 675 (1965).

(35) H. Ginsberg and K. Wefers, *Metall* (Berlin), 17, 202 (1963).

(36) F. Liechti and W. D. Treadwell, *Helv. Chem. Acta*, 30, 1204 (1947).

(37) A. W. Brace and H. Baker, *Trans. Inst. Metal Finishing*, 40, 31 (1963).

(38) A. F. Bogoyavlenskii and A. P. Vedernikov, *Zh. Prikl. Khim.*, 31, 310 (1958).

(39) R. C. Plumb, *J. Electrochem. Soc.*, 105, 498 (1958).

(40) J. W. Diggle, T. C. Downie, and C. W. Goulding, to be published.

(41) J. D. Edwards and F. Keller, *Trans. Electrochem. Soc.*, 79, 135 (1941).

governed by the electronic conductivity of the oxide film. Aluminum oxide films have a low electronic conductivity and a high ionic conductivity, and hence, at a high electric field strength, ionic conduction is the predominant mode of charge transport. If barrier films can be assumed to be completely nonporous, the films will continue to grow as long as ionic currents continue to flow, the ionic current being dependent on the electric field strength present across an oxide film, *i.e.*, the voltage drop across the film ( $V$ ) divided by its thickness ( $d$ ), the metal, and the metal oxide parameters, *e.g.*, the activation energy for ion motion. Therefore the extent of the ionic current at any one electric field strength will vary from metal to metal. The detectable movement of ions, *i.e.*, detectable in that an experimentally observable thickness change occurs, across an oxide film requires the presence of some certain electric field strength  $E'$ ; since the magnitude of the ionic current at any value of  $E$  depends upon the metal, this certain electric field would also be expected to vary from metal to metal.

The thickness of a barrier film is dependent upon  $V$  and is usually quoted in terms of the *anodizing ratio* (the number of ångströms of oxide formed per volt applied,  $\text{\AA V}^{-1}$ ); therefore with knowledge of the anodizing ratio and the volts applied, the oxide film thickness is simply but approximately calculated by  $(\text{\AA V}^{-1}) \times (\text{volts})$ . By inspection the anodizing ratio is seen to be equivalent to the reciprocal of the certain field strength (as defined above) required for ionic motion, and hence the anodizing ratio also varies from metal to metal. Tabulated in Table II<sup>42-49</sup> are a number of anodizing ratios for several metals. It should be realized that the value of the anodizing ratio depends upon the value of the certain electric field  $E'$ , *i.e.*, the value of the minimum ionic current, to which the films are formed.

In systems where porous-type films occur, *i.e.*, where the barrier-type oxide film is very sparingly soluble and where pore formation is favorable, the electric field strength does not decrease to the point at which the ionic current is low, since at this point experimentally detectable growth would effectively cease, and the film would not be of the porous type.  $V/d$  is greater than that value for a totally nonporous film, and therefore the anodizing ratio is lower than those values given in Table II.

Table III shows the  $\text{\AA V}^{-1}$  ratios which have been established<sup>50-52</sup> for some typical pore-forming electrolytes used in the anodizing of aluminum.

Since the formation of a porous anodic oxide film arises from some form of conversion of an initially formed barrier film, the mechanism of formation of the barrier film, *i.e.*, ionic charge transport, is of importance. The phenomena of ion transport through oxide films will now be reviewed with

Table II  
Anodizing Ratios<sup>a</sup>

Metal	Anodizing ratio ( $\text{\AA V}^{-1}$ ) and ref
Aluminum	13.0, <sup>42</sup> 13.5, <sup>42</sup> 13.7 <sup>43</sup>
Tantalum	16.0 <sup>44</sup>
Niobium	22.0 <sup>44</sup>
Zirconium	20.0, <sup>45</sup> 21.0, <sup>45</sup> 24.0, <sup>46</sup> 27.0 <sup>47</sup>
Tungsten	18.0 <sup>48</sup>
Silicon	3.8 <sup>49</sup>

<sup>a</sup> *I.e.*, the number of ångströms of oxide formed per volt applied for barrier-type film formation on several metals.

Table III  
Anodizing Ratio, for the Barrier Layer Lying Adjacent to the Metal Surface, for Porous Films Formed on Aluminum in Four Commonly Used Electrolytes

Electrolyte concn (temp, °C)	Anodizing ratio ( $\text{\AA V}^{-1}$ )
15% sulfuric acid (10)	10.0
2% oxalic acid (24)	11.8
4% phosphoric acid (24)	11.9
3% chromic acid (38)	12.5

respect to the theories proposed, and these theories will be discussed in the light of present-day experimental evidence. In order that a complete comparison may be made, references to other metal-barrier-type oxide film systems are made.

## B. IONIC CHARGE TRANSPORT

Before dealing specifically with the theories for anodic oxide growth, it is necessary to classify the two situations where ionic charge transport is possible. Considering a cation mobile system, where movement of these cations depends on the electric field strength across the oxide film, the two types are: (1) high-field conduction, where it is assumed that the electric field strength is high enough to prevent movement of cations against the field direction; (2) low-field conduction, where it can no longer be assumed that movement of cations against the field direction is negligible. In the following theories it is assumed that high-field ionic conduction is operative, since the electric field strengths lie between  $10^6$  and  $10^7$  V/cm, these fields being regarded as sufficient to prevent ionic motion against the field direction.

Guntherschultze and Betz<sup>53-57</sup> have shown that under high-field conditions, the ionic current density ( $i_+$ ) and the electric field strength ( $E$ ) are related through the exponential law

$$i_+ = A_+ \exp(B_+ E) \quad (1)$$

where  $A_+$  and  $B_+$  are temperature-dependent constants involving parameters of ionic transport. In order to understand the processes that could lead to such an expression for the ionic current, an analogy can be drawn to a simple electrochemical reaction. As in an electrochemical reaction, charge

(42) G. Hass, *J. Opt. Soc. Amer.*, **39**, 532 (1949).

(43) M. A. Barrett and A. B. Winterbottom, "1st International Congress on Metal Corrosion, 1961," Butterworth & Co., Ltd., London, 1962, p 657.

(44) J. Klerer, *J. Electrochem. Soc.*, **112**, 896 (1965).

(45) A. Charlesby, *Acta Met.*, **1**, 340 (1953).

(46) G. C. Willis, Jr., G. B. Adams, and P. Van Rysselberghe, *Electrochim. Acta*, **9**, 93 (1964).

(47) R. D. Misch, *Acta Met.*, **5**, 179 (1957).

(48) H. J. Booss, *Metall* (Berlin), **18**, 466 (1964).

(49) P. F. Schmidt and W. Michel, *J. Electrochem. Soc.*, **104**, 230 (1957).

(50) M. S. Hunter and P. E. Fowle, *ibid.*, **101**, 481 (1954).

(51) M. S. Hunter and P. E. Fowle, *ibid.*, **101**, 514 (1954).

(52) F. Keller, M. S. Hunter, and D. L. Robinson, *ibid.*, **100**, 411 (1953).

(53) A. Guntherschultze and H. Betz, *Z. Phys.*, **68**, 145 (1931).

(54) A. Guntherschultze and H. Betz, *ibid.*, **71**, 106 (1931).

(55) A. Guntherschultze and H. Betz, *ibid.*, **73**, 508 (1932).

(56) A. Guntherschultze and H. Betz, *ibid.*, **91**, 70 (1934).

(57) A. Guntherschultze and H. Betz, *ibid.*, **92**, 367 (1934).

transport is controlled by the step which has the highest potential energy with respect to the initial state, *i.e.*, the rate-determining step. The other steps are taken to be fast and therefore non-rate determining. Examination of the "reaction" environment metal-metal oxide-electrolyte permits the following three possible rate-determining steps to be postulated: (a) ion transfer across the metal-metal oxide interface, (b) ion transfer through the oxide bulk, and (c) ion transfer across the metal oxide-electrolyte interface producing a solvated ion. As in any reaction these three possible rate-determining steps involve the surmounting of energy barriers, the step which has the greatest potential energy with respect to the initial state, under a given set of conditions, being the rate-determining process. Theoretical justification of the exponential relationship proposed by Guntherschultze and Betz has been based upon (a), (b), and a combination of (a) and (b) as the rate-determining step; these three theories are now briefly reviewed.

### 1. Cabrera-Mott Theory (Metal-Oxide Interface Control)

Mott<sup>58</sup> and Cabrera and Mott<sup>59</sup> 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 must be made. These are: (a) the transfer of an ion across the metal-oxide interface is the rate-determining step in oxide growth; (b) the transfer of an ion through the oxide bulk is fast due to lowering of diffusion barriers by the applied electric field; and (c) the field is sufficiently high to ensure that negligible amounts of ions are moving against the electric field direction.

The implication of these assumptions is that the number of ions in transit through the film is very small, and hence space charge is negligible. Space charge is the accumulation of charged ions in an oxide film which can lead to a net lowering of the applied field; a consequence of this is that the electric field strength becomes a function of oxide thickness in order to maintain a constant ionic current density.

With these assumptions Cabrera and Mott proposed that the ionic current density  $i_+$  could be written as

$$i_+ = nvq \exp[-(W - qaE)/kT] \quad (2)$$

where  $n$  is the surface density of mobile ions at the metal;  $v$  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;  $W$  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;  $a$  is the activation or half-jump distance, *i.e.*, distance from the positions of minimum to the maximum potential energy; and  $k$  and  $T$  have their usual significance.

Comparing with (1),  $i_+ = A_+ \exp(B_+E)$ , it can be seen that

$$A_+ = nvq \exp(-W/kT) \quad (3)$$

and

$$B_+ = qa/kT \quad (4)$$

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

$$\frac{d \ln i}{dE} = \frac{qa}{kT} \quad (5)$$

### 2. Verwey Theory (Bulk Oxide Control)

This theory due to Verwey<sup>60</sup> 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 the ionic current density are similar to those of Cabrera and Mott, the identification of the parameters being related now to bulk oxide properties instead of metal-oxide interface properties. Hence the Cabrera and Mott and Verwey theories can be considered as limiting cases of one single theory, Cabrera and Mott holding for thin films and Verwey for thick films where electrical neutrality exists in the bulk oxide.

In both these theories, eq 5 can show that the constant  $B_+$  should be dependent on temperature, *i.e.*,  $B_+ = qa/kT$ . The current dependence has been reported in some studies,<sup>61</sup> but in others  $B_+$  was found to be independent of temperature,<sup>62,63</sup> increasing with temperature,<sup>64</sup> and varying in some ill-defined manner with temperature.<sup>65</sup> The independence of  $B_+$  on temperature, although it has been related to a change in the activation distance as temperature increases,<sup>66,67</sup> could most probably have arisen because the determination was made over several values of the electric field strength.<sup>68</sup> If, as has been shown,<sup>68</sup> the  $\log i_+$  vs.  $E$  plots are slightly non-linear, then  $d(\ln i)/dE$  or  $B_+$  will be a function of  $E$ . Recently Dreiner<sup>69</sup> has also demonstrated the correct dependence of  $B_+$  on temperature, but, as he later pointed out,<sup>70</sup> the extrapolation of  $B_+$  to zero  $1/T$  did not pass through the origin. Consequently, it would appear that the exact dependence of  $B_+$  on temperature, on the basis of the expressions given to this point, has yet to be found. As is concluded later (section III.B.4), this is due to the inadequate description of the parameter  $B_+$ .

### 3. Dewald Theory (Dual-Barrier Control with Space Charge)

The possibility of an increase in the activation distance was discussed by Dewald<sup>71,72</sup> as resulting from a change in the rate-determining energy barrier from the metal-oxide interface to the oxide bulk. This, however, involves an assumption in that the potential energies of the two activated states involved are not too different. Dewald further considered that the near independence of  $B_+$  on temperature arose from

(60) E. J. W. Verwey, *Physica*, **2**, 1059 (1935).

(61) P. H. Draper and P. W. M. Jacobs, *Trans. Faraday Soc.*, **59**, 2888 (1963).

(62) D. A. Vermilyea, *Acta Met.*, **1**, 282 (1953).

(63) L. Young, *Trans. Faraday Soc.*, **50**, 159 (1954).

(64) A. L. Bacarella and A. L. Sutton, *Electrochem. Technol.*, **4**, 117 (1966).

(65) W. Muzushima, *J. Electrochem. Soc.*, **108**, 825 (1961).

(66) L. Young, *Trans. Faraday Soc.*, **52**, 510 (1956).

(67) L. Young, *ibid.*, **52**, 502 (1956).

(68) L. Young, *Proc. Roy. Soc.*, **A263**, 395 (1961).

(69) R. Dreiner, *J. Electrochem. Soc.*, **111**, 1350 (1964).

(70) L. Young and F. G. R. Zobel, *ibid.*, **113**, 277 (1966), note on p 278.

(71) J. F. Dewald, *Acta Met.*, **2**, 340 (1954).

(72) J. F. Dewald, *J. Electrochem. Soc.*, **102**, 1 (1955).

(58) N. F. Mott, *Trans. Faraday Soc.*, **43**, 429 (1947).

(59) N. Cabrera and N. F. Mott, *Rept. Progr. Phys.*, **12**, 163 (1948-49).

the neglect of a space charge generated in forming anodic oxide films.

If the electric field present at the metal-oxide interface is taken to be equal to that in the oxide bulk, the potential energy of the activated state at either position in the oxide depends upon the effective lowering of this energy by the ion moving with the field, which in turn depends upon the charge on the mobile ion and the activation distance at each barrier. Let this field equal  $E$ , and let the potential energy of the activated state at the metal-oxide interface and in the oxide bulk at zero field equal  $W$  and  $U$ , respectively.

Thus the effective lowering of each energy barrier is given by  $W - qaE$  and  $U - qa'E$ , where  $a$  and  $a'$  are the activation distances at each energy barrier, respectively, and  $q$  is the charge carried by the mobile ion. Hence, if  $W$  and  $U$  are similar and  $a$  and  $a'$  are not equal, then the effective field at each location will vary in a different manner with the field. Under such conditions a dual-barrier control mechanism could exist. It is clear that if  $U - qa'E > W - qaE$  an accumulation of charge will occur at the second barrier; i.e., a space charge will be set up. This treatment, Dewald proposed, can lead to the temperature independence of  $B_+$  noted experimentally, provided the values of the parameters are chosen carefully.

The average field  $\bar{E}$  according to the Dewald theory may be written as

$$\bar{E} = \left[ \frac{kT}{qa} \ln \frac{i_+}{nvq} + \frac{W}{qa} \right] + \frac{kT}{qa'} \left[ \left( 1 + \frac{1}{\delta} \right) \ln (1 + \delta) - 1 \right] \quad (6)$$

where  $\delta$  is a dimensionless quantity involving, among other parameters, the oxide film thickness, the potential energy  $U$  for diffusion through the oxide, the dielectric constant of the oxide, and the vibrational frequency of an ion in an interstitial position. Dewald<sup>72</sup> has indicated that when space charge is high, i.e.,  $\delta \gg 1$ , for a tenfold increase in oxide thickness, the electric field strength increases 7%. For intermediate space charge when  $\delta \approx 1$ , a 2% increase in the electric field strength would be theoretically expected, again for a tenfold increase in oxide thickness. Dewald has also indicated that under intermediate space charge influence, the plot of the electric field strength vs. log ionic current density would not be expected to be exactly linear.

The first term in eq 6 is identical with the Cabrera and Mott expression (eq 2), and the second is the term due to space charge; it is seen that when  $\delta \ll 1$ , eq 6 becomes equal to eq 2, i.e., zero space charge contribution.

#### 4. Experimental Evidence

The high-field conduction expression simplified to  $i_+ = A_+ \exp(B_+E)$  has been examined for a large number of metals; these include barrier films formed upon Al,<sup>8</sup> Ta,<sup>62</sup> Nb,<sup>66,67</sup> Zr,<sup>78</sup> W,<sup>74</sup> Si,<sup>49,70</sup> Ti,<sup>65</sup> and Fe.<sup>75</sup>

Johansen, Adams, and Van Rysselberghe<sup>76</sup> have examined Ta, Al, Zr, Nb, Hf, and Ti anodically oxidized at low current

densities in borate electrolytes; the films formed under these conditions were 20–100 Å thick, i.e., of such a thickness that the Cabrera and Mott theory would be expected to apply. Generally, it was found that all these metals obeyed the Cabrera and Mott theory in the thickness range indicated. For thick films on zirconium it has been found<sup>46</sup> that the Cabrera and Mott theory only appears valid above a certain current density; below this current density, the deviation from the Cabrera and Mott equation was tentatively suggested as being due to a variation in the number of active sites at the metal surface. The number of active sites was suggested to increase as the current density increased until, at some value of current density, the concentration of such sites reached a limiting saturation value. Therefore, since the number of active sites is essentially related to  $n$ , the number of ions at the metal surface, and hence to the preexponential factor  $A_+$ , the Cabrera and Mott theory may hold at current densities above this "limiting  $n$ " value. This was found to be the case. Further evidence as to the probability of a change in the preexponential  $A_+$  to a limiting value as the current density increases, i.e., as the electric field strength  $E$  across a fixed barrier-type film increases, has been reported by Vermilyea<sup>77</sup> for Ta<sub>2</sub>O<sub>5</sub> films.

Unlike the work with zirconium,<sup>46</sup> Vermilyea observed the value of  $A_+$  to decrease, because of, it was proposed, a decrease in the activation distance  $a$ . These two proposals outlined here concerning the value of  $A_+$  should not be taken as more than what they are intended to convey, i.e., the possibility that the parameter  $A_+$  may not be a constant.

In cases where the parameters of eq 2 were determined, it was found that  $E$  was in the range  $10^6$ – $10^7$  V cm<sup>-1</sup> (high fields) and  $B_+$  was about  $10^{-6}$ – $10^{-7}$  cm V<sup>-1</sup>. Assuming that the mobile cations carry their normal valency charge during ionic charge transport, the activation distances  $a$  were found to vary from  $2 \times 10^{-8}$  to  $5 \times 10^{-8}$  cm. These values for the activation distance (2–5 Å) are much larger than those expected from a consideration of the half-distance between equilibrium lattice positions, i.e., 1.5–2.0 Å.

Hence the simple Cabrera and Mott and Verwey expressions would appear to be initially inadequate on several points. These are: (1) the expected dependence of  $B_+$  with temperature is not found exactly; (2) the values of the activation distances calculated are larger than those theoretically expected when considering a crystalline lattice; and (3) Young<sup>68,70</sup> has demonstrated that the log ionic current density against the electric field strength plot is in fact slightly nonlinear.

As thin films grow thicker, transition from the Cabrera and Mott theory to Verwey theory should occur, and, if space charge is anything but minimal, to the Dewald theory. Several workers have reported results in agreement with the Dewald dual-barrier control model; such systems include tantalum<sup>61</sup> in 40% sulfuric acid with temperatures up to 150°, zirconium<sup>46</sup> in 0.25 *M* sodium sulfate, and niobium<sup>78</sup> in borate electrolyte.

Since the Dewald theory involves the generation of a space charge, then, if this space charge can be detected experimentally, the Dewald theory may be the correct model for the anodic oxide growth. Vermilyea,<sup>77,79,80</sup> in an investigation of barrier-type films on tantalum, has shown that, due to the low level of space charge probably, i.e., sufficient to

(73) G. B. Adams, T. S. Lee, S. M. Draganov, and P. Van Rysselberghe, *J. Electrochem. Soc.*, **105**, 660 (1958).

(74) H. W. Pitman and D. C. Hamby, P. B. Report No. 146, U. S. Department of Commerce, Office of Technical Services, Washington, D. C., 1959, p 794.

(75) K. J. Vetter, *Z. Elektrochem.*, **58**, 230 (1954).

(76) H. A. Johansen, G. B. Adams, and P. Van Rysselberghe, *J. Electrochem. Soc.*, **104**, 339 (1957).

(77) D. A. Vermilyea, *ibid.*, **102**, 655 (1955).

(78) G. B. Adams and T. Kao, *ibid.*, **107**, 640 (1960).

(79) D. A. Vermilyea, *Acta Met.*, **3**, 106 (1955).

(80) D. A. Vermilyea, *J. Electrochem. Soc.*, **104**, 140 (1957).



produce a 1% variation in the mean electric field strength across a film 5000 Å thick, the conclusive proof of such space charge may be difficult to obtain. Young<sup>66,67</sup> has reported some evidence, on the basis of capacitance changes, which may indicate the presence of space charge in Nb<sub>2</sub>O<sub>5</sub> films formed anodically.

The Dewald theory may account satisfactorily for some behavior, but it and the Cabrera-Mott and Verwey expressions have the major inadequacy in that they cannot adequately account for anodic transient behavior. When anodizing conditions are suddenly varied, whether it be an ionic current<sup>81</sup> or a voltage transient,<sup>82</sup> well-defined changes occur which cannot be accounted for on the basis of a simple, electrically uncompensated, single charge carrier (whether the carrier be cations, anions, or vacancies).

In electrically neutral oxide (far from the metal-oxide interface) with Frenkel disorder, the concentration of interstitial cations  $p$  equals the concentration of cation vacancies  $n$ . From transient behavior it could be concluded that the concentration of the interstitial cations varies sluggishly with the field, thereby producing the behavior observed. It can be shown, however, that by assuming, or inferring, that  $p = n$ , the time scale for the transients would be expected to be much shorter than experimentally observed. A similar situation exists in the phenomena associated with galvanostatic transients in metal electrodeposition. The so-called "rise time" was found to be much greater than that required for a charge-transfer-controlled reaction; this fact led to the proposal that the surface diffusion of adions was rate controlling.<sup>83</sup> It would appear that it is not sufficient to regard the oxide bulk merely as an electrically neutral medium, through which ions move when overcoming the appropriate energy barriers, to account for transient phenomena.

Vermilyea<sup>77</sup> has reported that the activation energy is not a linear function of the field present as proposed by Cabrera and Mott. Presenting the activation energy as  $(W - qaE)$ , this function, when plotted against the electric field strength  $E$ , undergoes a 2:1 slope change when the value of  $E$  approaches  $6 \times 10^6$  V cm<sup>-1</sup>. Vermilyea interpreted this as a change in the activation distance  $a$  from 4.8 to 2.4 Å at an electric field strength of  $6 \times 10^6$  V cm<sup>-1</sup>. Bean, Fisher, and Vermilyea,<sup>84</sup> with this experimental evidence, and the rejection of the space charge concept, used a model in which the cation forming an interstitial ion may jump initially either two or one lattice distances. In this treatment it was suggested that, assuming the cation vacancies produced by the formation of interstitial cations remain immobile, the interstitial ion formation and cation capture by cation vacancies allows a change in barrier height and activation distance as the field increases. From this theory transient phenomena could then be adequately explained on the basis of a sluggish variation in interstitial ion concentration with the electric field strength and time.

The observation by Young<sup>68</sup> that plots of the electric field strength against the log ionic current density were slightly nonlinear, led him to propose that the results could be ex-

plained by taking the activation distance as  $a = \alpha - \beta E$ , where  $\alpha$  and  $\beta$  are both positive constants. The complete equation now involves a quadratic function of the electric field strength  $E$ .

$$i_+ = n v q \exp[-(W - q\alpha E + q\beta E^2)/kT] \quad (7)$$

The theoretical justification for this quadratic function was proposed by Young<sup>65</sup> on the basis of developed condenser pressure. Pressure developed in the oxide film due to the electric field can be expressed as

$$P = E^2 \epsilon / 8\pi$$

where  $\epsilon$  is the dielectric constant (of the oxide) at zero electric field strength and where the electric field strength  $E$  is in esu's and  $P$  is in dynes cm<sup>-2</sup>. Assuming some value for the dielectric constant at zero field, the condenser pressure can be calculated at each electric field value. Young proposed that this developed pressure causes the potential energy of the activated state to increase due to a lattice shrinkage, and that this energy increase was sufficient to account for the nonlinearity of the electric field strength-log ionic current density plot. This was later rejected by Dignam<sup>86</sup> who proposed that the quadratic term arises from a more detailed consideration of the ion movement in high electric field. Recently, Ibl<sup>87</sup> has shown that by applying the transition-state theory to ionic conduction, assuming thermodynamic stability between normal and activated species, the equation proposed by Young<sup>68</sup>

$$i = A \exp[(\alpha - \beta E)E/kT] \quad (8)$$

can be derived. The significance of the term  $\beta$  was proposed to be the polarization of the dielectric medium, associated with the ionic species involved, most probably in the form of induced dipoles. An approximate calculation of the value of  $\beta$  was also reported by Ibl, the value obtained being twice the value of  $\beta$  obtained experimentally by Young. However, considering the assumptions involved in the theoretical calculation by Ibl, the agreement is quite reasonable. The assumption made by Ibl that cations only are mobile will not be correct for the value of  $\beta$  calculated for tantalum. Although this assumption may affect the value of  $\beta$ , it does not affect the conclusion that the ionic current can be found to be a quadratic function of the electric field strength  $E$  by the application of the simple transition-state theory.

All these theories reviewed so far imply the transport of ions through a crystalline lattice, although it was shown in section II.A that anodic oxide films have a high degree of amorphous nature. Hence the consideration of mobile interstitial ions is dependent upon the application of such terms as lattice and interstitial sites to an amorphous oxide. Winkel, Pistorius, and Van Geel<sup>88</sup> proposed that the migrating cation does not cross a regular periodic field as present in a crystalline lattice, but rather meets a Gaussian distribution of varying energy barrier heights and activation distances. Equations were obtained in which this activation distance increased as the electric field strength increased. Since this trend of activation distance with the electric field strength is opposite to that observed experimentally, Young<sup>68</sup> has indicated that

(81) D. A. Vermilyea, *J. Electrochem. Soc.*, **104**, 427 (1957).

(82) J. F. Dewald, *J. Phys. Chem. Solids*, **2**, 55 (1957).

(83) J. O'M. Bockris and A. Damjanovic, "Modern Aspects of Electrochemistry," No. 3, Butterworth & Co., Ltd., London, 1964, Chapter 4, p 224.

(84) C. P. Bean, J. C. Fisher, and D. A. Vermilyea, *Phys. Rev.*, **101**, 551 (1956).

(85) L. Young, *J. Electrochem. Soc.*, **110**, 589 (1963).

(86) M. J. Dignam, *Can. J. Chem.*, **42**, 1155 (1964).

(87) N. Ibl, *Electrochim. Acta*, **12**, 1043 (1967).

(88) P. Winkel, C. A. Pistorius, and W. Ch. Van Geel, *Philips Res. Rept.*, **13**, 277 (1958).



the application of a "queueing" mechanism, to predominantly noninterconnected pathways in amorphous solids, could produce a situation where the activation distance decreased with increasing electric field strength; however, the application of this mechanism to transient phenomena does not appear promising.

### 5. Ionic Mobility and Transport Number

Before proceeding further, the identity of the mobile ion involved in the conduction process must be established. In the previous theories the cation was assumed to be the only mobile species; although some evidence<sup>89-91</sup> exists to show that this is true, some recent evidence indicates that both the cation and an oxygen-bearing anion are mobile. Some of the earlier work on transport numbers could be criticized in that the boundary between the oxide formed by anion and cation migration was unclearly defined, and that some of the radioactive markers used may not have been truly immobile.

Davies, Domeij, Pringle, and Brown<sup>84</sup> have reported that by measuring the fractional burying of the isotope  $\text{Xe}^{125}$ , originally injected into the metal under study, the fraction of ionic charge carried by mobile anions can be obtained. This work has shown that oxide growth by solely cation movement does not occur for the metals Al, Nb, Ta, W, Zr, and Hf: both cations and anions being mobile for the first four metals and anion mobility being predominant for oxide growth on Zr and Hf. Other workers observing both cation and anion mobility include Klerer,<sup>44</sup> Cheseldine,<sup>92</sup> Randall, Bernard, and Wilkinson<sup>31</sup> and, by inference, from the work of Smyth, Shirn, and Tripp<sup>93</sup> and Francis.<sup>94</sup>

For aluminum it was reported<sup>84</sup> that, for the anodizing in sodium borate-ethylene glycol electrolyte, the fraction of the total charge carried by cations ( $t_m$ ) was  $0.58 \pm 0.04$ , whereas in aqueous ammonium citrate  $t_m$  varied from 0.37 to 0.72 as the experimental current density increased from 0.1 to 10  $\text{mA cm}^{-2}$ . This trend in increasing cation transport number with increasing formation current density is similar to that reported earlier in section II.B for the electrolyte anion incorporation into porous oxide films.

The determination of the transport numbers of the ions involved in oxide growth by a method involving the use of tracer atoms depends on the validity of the assumption that the tracer atoms, in this case  $\text{Xe}^{125}$ , in the metal are immobile. If the atoms of  $\text{Xe}^{125}$  were mobile, it could produce the results expected from a mechanism involving anion mobility. The immobility of  $\text{Xe}^{125}$  atoms during anodic oxidation has yet to be shown for growing oxides, although it has been established for nongrowing oxides.<sup>95</sup> Some indirect evidence of the mobility of  $\text{Xe}^{125}$  tracers could be inferred from a comparison of this  $\text{Xe}^{125}$  work with the results reported by Cheseldine<sup>92</sup> for  $\text{Ta}_2\text{O}_5$ , whose results are not based upon a similar assumption. The value obtained for  $t_m$  by the  $\text{Xe}^{125}$  tracer method was 0.30, which is lower than the result of 0.48 reported by Cheseldine. If the  $\text{Xe}^{125}$  atoms were mobile, even to the smallest extent, the result for  $t_m$  would be expected to be low.

Hence it would appear that conclusive evidence for  $\text{Xe}^{125}$  immobility in growing oxides is not completely established. From this evidence, it is clear that any theory which is proposed to account for oxide growth must involve both anion and cation motion, or be necessarily inexact.

Some recent work by Whitton,<sup>96</sup> on the cationic transport number  $t_m$  in the anodic film formation on tantalum and zirconium, has indicated that the radioactive inert gas markers used in this work, and that work previously discussed,<sup>84</sup> may be immobile during anodic film formation. Values reported by Whitton for  $t_m$  for tantalum and zirconium were in good agreement with those reported previously.<sup>84</sup> It was further reported that the migration of the oxygen-bearing species, at least in the case of crystalline oxide, occurs *via* defect lines in the lattice.

### 6. Some Basic Considerations

Up to the present the theories proposed have been Frenkel-type<sup>97</sup> equations where the mobile cation overcomes the energy barriers against migration by thermal excitation. Frenkel-type laws should lead to the linear relationship between log ionic current density and the electric field strength, but, as indicated by Young,<sup>68,70</sup> this is not always found. An equation of the form

$$i \propto i_0 \exp(W_0 - \alpha E + \beta E^2) \quad (9)$$

over a short range of electric field strengths, could be ascribed to a Schottky-type model of ion migration, in which ions are considered to move unhindered along widely spaced noninterconnected channels in the oxide, movement being hindered only when high oppositely charged centers exist, where the moving ion becomes trapped by Coulombic attraction. Although experimental evidence exists as to the applicability of the Schottky-type model to steady-state conditions, the explanation of transient phenomena has yet to be satisfactorily achieved.

In conclusion here, and before moving to the work of Dignam, the following questions must be answered when considering eq 2

$$i_+ = nvq \exp[-(W - qaE)/kT]$$

(a) What value should be given to charge  $q$  of the mobile ion, *i.e.*, normal valency charge or less? (b) Which electric field strength model should be used, *i.e.*, Maxwell or Lorenz (the Maxwell field ( $E_m$ ) being the field either in a pencil-like cavity parallel to the applied field or in a flat cavity at right angles to the applied field, and the Lorenz field ( $E_L$ ) being the field that exists in a spherical cavity)? The two fields are related through eq 10, where  $\epsilon$  is the oxide dielectric constant. Evidence in

$$E_L = \frac{1}{3} (\epsilon + 2) E_m \quad (10)$$

favor of the use of the Lorenz field, instead of the usually used Maxwell field, has been reported by Maurer<sup>98</sup> and Bacarella and Sutton.<sup>84</sup>

In an investigation of the mobility of sodium ions in thin sheets of soda-lime glass, Maurer,<sup>98</sup> assuming the normal valency charge on sodium ions, reported values of 3-4 Å

(89) D. A. Vermilyea, *Acta Met.*, **2**, 482 (1954).

(90) J. E. Lewis and R. C. Plumb, *J. Electrochem. Soc.*, **105**, 496 (1958).

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as the distance between neighboring interstitial sites by using the Lorenz field value for  $E$ . If the external field, *i.e.*, Maxwell field, value was used, values in the region of 20 Å were obtained. The Lorenz field value, besides producing the most theoretically acceptable results, also produced the expected temperature independence of the distance between two neighboring interstitial sites, *i.e.*, twice the activation distance  $a$ . Barcarella and Sutton<sup>84</sup> have reported for oxide film growth upon zirconium in oxygenated 0.05 *M* sulfuric acid at 174–284° values for the activation distance of 1.5–1.6 Å, assuming both the Lorenz field value and that the mobile ion was  $Zr^{+}$ . The latter assumption is, however, in direct contradiction to the work of Davies, Domeij, Pringle, and Brown<sup>84</sup> who reported oxide growth upon zirconium to be almost 100% anion motion. Thus reinterpreting the work of Barcarella and Sutton, not as growth due to cations but growth due to anions, produces the possible univalent charge carrier as  $OH^{-}$ .

The applicability of the Lorenz field value in the calculation of the electronic polarizabilities of ions in crystals has been demonstrated by Tessman, Kahn, and Shockley.<sup>99</sup> The electronic polarizabilities of the alkali metal and the halide ions were calculated from the indices of refraction of the alkali halide crystals, the values calculated being in excellent agreement with the experimentally determined values.

Dignam,<sup>100</sup> in a recent discussion of the identity of  $q$  and  $E$ , has proposed that, assuming a lattice model through which ions move by diffusion under electrostatic potential and concentration gradients, when diffusion in the oxide bulk is rate controlling, the electric field  $E$  in the high field ionic conduction expression will be the external field, *i.e.*, the Maxwell field. The effective charge on the ion will, under the same conditions, be the valency charge. When ionic transport is controlled by some interface, *e.g.*, the metal-oxide interface, Dignam has indicated that the electric field  $E$  may be greater than the Maxwell field, *i.e.*, tending toward the Lorenz field value, and thus the effective lowering of the energy barrier  $qaE$  will not be given by the valency charge times the activation distance times the external (Maxwell) field.

The validity of these proposals concerned with oxide bulk diffusion control depends upon the applicability of the assumed lattice model to oxide films which are largely amorphous. Dignam<sup>100</sup> considers that such discrepancies, between his assumed lattice model and amorphous systems, will not effectively influence the conclusions about the identity of  $q$  and  $E$ .

### 7. *p-i-n Junction Theory of Anodic Oxide Films*

The presence of a *p-i-n* junction in anodic oxide films was proposed by Sasaki<sup>101</sup> for the Ta-Ta<sub>2</sub>O<sub>5</sub>-electrolyte system, and since the evidence upon which it was based applies to aluminum and other valve-type metals as well as to tantalum, the *p-i-n* junction could apply adequately well to the barrier-type films under discussion here. The evidence upon which the *p-i-n* junction is proposed includes the effect upon the metal-metal oxide system when subjected to ultraviolet radiation, the influence of applied voltage upon the capacitance of the system, the amorphous nature of the metal oxide, and the rectifying action of these systems. Sasaki demonstrated that

the property of rectification was due to the nature of the metal oxide itself and not, as previously believed,<sup>102</sup> to the contact between the metal oxide and the electrolyte.

The theory is that the oxide film, usually less than 1500 Å thick, consists of three different regions.

1. A region of oxide, lying adjacent to the metal surface, whose thickness is less than 50 Å and independent of applied voltage. Since metal ions have been assumed to be the mobile species (present evidence now shows that metallic ions are one of the mobile species), this layer of oxide will be a region of metal excess, *i.e.*, *n*-type semiconductor.

2. A central region of oxide whose thickness contributes the major part of thick films, and whose thickness is dependent upon the applied voltage. This oxide is taken to be nearly stoichiometric in nature.

3. An outer region of oxide, lying adjacent to the electrolyte, where anion excess stoichiometry is proposed. This anion-excess region, or *p*-type semiconductor, can be due either to a high concentration of adsorbed oxygen bearing species or to the fact that the oxygen-bearing species is a mobile charge carrier. Although both may in fact be operative, present-day evidence on ion mobilities during oxide anodic formation favors the latter explanation. The *p*-type layer is similar to the *n*-type layer with regard to its thickness and the voltage independence of this thickness.

Apart from this *p-i-n* junction theory due to Sasaki, many other proposals have been offered to account for the phenomenon of electrolyte rectification. Anderson<sup>103</sup> has reported that luminescence (related to rectification) is observed only for cation excess (*n*-type) semiconducting oxide films, *e.g.*, Zn, W, Al, Ta, and Mg; luminescence was not found for anion excess (*p*-type) oxides, *e.g.*, Cu, Ni, and Fe. Anderson considered that a Mott-Schottky theory could satisfactorily account for rectification. Haring<sup>104</sup> and Taylor and Haring<sup>105</sup> have suggested that an excess cation space charge region, close to the metal-oxide interface, could account for the flowing direction being with the metal cathodic, and the blocking direction being with the metal anodic. A similar explanation has been offered in several papers by Van Geel and co-workers.<sup>106–109</sup> Vermilyea<sup>110</sup> has suggested that a theory of rectification could be based upon the presence of weak spots in the oxide film, which produce a low resistance in the flowing direction, *i.e.*, cathodic direction. Weak spots or flaws have been reported in barrier-type oxide films produced upon tantalum<sup>111,112</sup> where the diameter of the flaw was approximately equal to the film thickness. The thickness of the oxide film at these flaws may be only half that over the non-flawed areas, and therefore these flaws may be points of preferential current flow under certain conditions. This type of flaw has been observed for oxide films upon niobium and zirconium as well as for tantalum, and may well be present in

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(111) D. A. Vermilyea, *J. Electrochem. Soc.*, **110**, 250 (1963).

(112) L. Young, *Trans. Faraday Soc.*, **55**, 842 (1959).

aluminum oxide films also.<sup>113</sup> The presence of voids or flaws has been reported by Stringer<sup>114</sup> for the high-temperature formation of Ta<sub>2</sub>O<sub>5</sub> films in low oxygen pressure atmospheres, which again demonstrates the similarity that exists between oxides formed by the anodic and by the high-temperature gaseous oxidation methods. The presence of flaws, which under certain conditions could lead to high local current densities, could be the precursor to pore formation. This will be examined further in section IV.B.

#### 8. "Polymeric Unit" Structure Theory

In several papers Dignam and colleagues<sup>86, 115, 116</sup> have verified the results of Young,<sup>88</sup> in that the simple exponential relationship between the ionic current density and the electric field strength should be replaced by

$$i_+ = \alpha' \exp \left[ \frac{q(\beta E - \gamma E^2)}{kT} \right] \quad (11)$$

where  $\alpha$ ,  $\beta$ , and  $\gamma$  are all positive constants. In the present context, it is emphasized that the constants  $\alpha$ ,  $\beta$ , and  $\gamma$  above have a different significance from that placed upon them in the work of Young.<sup>88</sup> Dignam<sup>115</sup> does not consider that this quadratic equation can be satisfactorily accounted for in terms of condenser pressure<sup>85</sup> and has proposed that the expression arises from a more detailed examination of the movement of a migrating ion. Dignam<sup>117, 118</sup> proposed also an entirely new concept for the conduction mechanism, which was more readily identifiable with amorphous oxides than were the earlier concepts. The proposal was that the oxide is composed of very small crystallites, or polymeric units, in a mosaic-type arrangement. An analogy could be drawn between this arrangement and the arrangement of the dipoles in a polarizable liquid. Ionic migration was seen to occur between one unit and the next unit, and by conduction within each individual unit. With reference to the analogous polarizable liquid, these two conduction modes can be viewed as being similar to the ionic and electronic polarizabilities of the dipolar liquid. As in polarized liquids, there are experimental conditions under which one type of conduction, *i.e.*, between or within units, can become predominant. This means that the conduction rate, *i.e.*, ionic current density, is controlled by the slow step in the over-all conduction process, whether it be between or within the polymeric units. Dignam has proposed that at high ionic current densities the slow step is the conduction between units, *i.e.*, the influence of the assumed cavity field upon the dielectric relaxation processes, while at low ionic current densities the slow step is the conduction within each unit. The agreement between the experimental facts and this theory has been reported as good for aluminum, tantalum, niobium, and bismuth with respect to the following points: (a) the observed transport number phenomena<sup>34</sup> can be adequately accounted for; (b) the experimental and theoretical correlation of the electric field dependence of the inverse Tafel slopes  $d(\log i_+)/dE$  was obtained; and (c) the form of the

transients observed can be accounted for on more than an empirical basis.<sup>119, 120</sup>

Dignam,<sup>121</sup> in a recent paper, has proposed a second physical model to account for the observed behavior during ionic conduction. In this model the anodic oxide film is regarded as having a vitreous structure (random three-dimensional network) in which defects are responsible for ionic transport. It is interesting that, with this model, a distinction between odd- and even-valent metal ion oxides might be expected. It is well known that the two even-valent metal ion oxides that have been most extensively studied, *e.g.*, ZrO<sub>2</sub> and HfO<sub>2</sub>, show considerable variation in behavior from that of Al<sub>2</sub>O<sub>3</sub> and Ta<sub>2</sub>O<sub>5</sub>; examples of this variation include the lack of transient phenomena<sup>81, 120</sup> with ZrO<sub>2</sub>, although this has been suggested as being due to a low current efficiency,<sup>122</sup> and the work of Davies and his colleagues<sup>34</sup> with regard to transport number phenomena.

In a recent paper, Dreiner,<sup>123</sup> effectively summing up the present situation as regards the single carrier theories presented for the ionic conduction in valve metal oxide systems, has indicated that it is difficult to decide exactly which law and theory provides the most effective model. Dreiner has reported that, for the three equations below, (1), (11), and (12), exact correlation with the single-carrier model is not obtained, each equation being adequate in some respects but not in others.

$$i_+ = A_+ \exp(qaE/kT) \quad \text{Frenkel law} \quad (1)$$

$$i_+ = \alpha' \exp[q(\beta - \gamma E)E/kT] \quad (11)$$

Frenkel law; Young (and Dignam) modified

$$i_+ = \alpha'' \exp(\Delta\sqrt{E}/kT) \quad \text{Schottky law} \quad (12)$$

In eq 12,  $\Delta$ , in common with  $A_+$ ,  $\alpha'$ ,  $\beta$ ,  $\gamma$ , and  $\alpha''$ , is given as a constant.

To end this discussion on ionic conduction mechanisms, it is worthwhile to consider a suggestion by Ord<sup>124</sup> that the discrepancy in the logarithm ionic current density–electric field strength relationship is due not to inadequacies in the equations but to effects produced within the film during a film thickness measurement, for example, the influence of the changing electric field strength on the refractive index of the oxide film whose thickness is being determined by ellipsometry. Since, for accurate measurements by ellipsometry, the refractive index of the oxide must be known, or at least be considered a constant, sufficient error may arise to produce nonlinear  $\log i_+$  vs.  $E$  plots.

#### 9. Kinetic Investigation Methods

During the preparation of barrier-type films, an examination of the changes in voltage and ionic current density with respect to anodizing time would usually show the behavior illustrated in Figure 1. This figure consists of two regions. One is region 1, in which a constant current density is maintained, where the voltage observed increases linearly with time. The maintenance

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(114) J. Stringer, *J. Less Common Metals*, **11**, 111 (1966).

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(116) M. J. Dignam and D. Goad, *J. Electrochem. Soc.*, **113**, 381 (1966).

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(118) M. J. Dignam, *ibid.*, **112**, 729 (1965).

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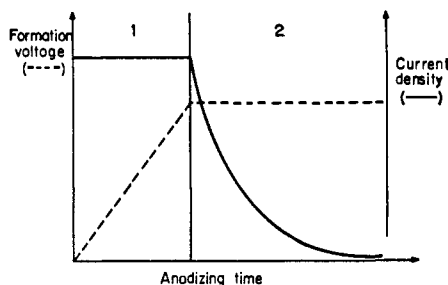
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(121) M. J. Dignam, Extended Abstracts, Dielectric and Insulation Division, Electrochemical Society Meeting, Dallas, Texas, Spring, 1967, Vol. I-2, p 33.

(122) L. Young, *Trans. Faraday Soc.*, **55**, 632 (1959).

(123) R. Dreiner, ref 121, p 43.

(124) J. L. Ord, ref 121, p 50.



**Figure 1.** Formation of a barrier-type anodic oxide film. In region 1 a constant current density is applied and the cell voltage is allowed to rise to the required value. When this required voltage is achieved it is maintained as a constant; consequently, the current density decreases, region 2.

of a constant current density requires a constant electric field strength across the barrier film; thus, as the film thickness increases, the voltage, or potential drop, across the film must also increase. This voltage increase is allowed to continue until the required voltage of formation is reached. Region 2, in which this formation voltage is maintained constant, now occurs, where, owing to further increases in the barrier film thickness, the current density decreases with time. Under constant voltage conditions, the decrease in the ionic current density with time is due to the continual thickening of the oxide film with a concurrent decrease in electric field strength. If the thickness of the oxide film can be determined, also as a function of time, values of the calculated electric field strength can then be correlated to the values of the ionic current density at any time during region 2. Hence the exponential dependence of ionic current density  $i_+$  on the electric field strength  $E$  can be examined as per eq 1, section III.A. It should be realized that such measurements outlined here are essentially non-steady-state measurements, and thus the results may differ from those obtained in the steady state.<sup>116</sup>

The accuracy of the calculated value of the electric field strength is clearly dependent upon the accuracy of the measurement of the constant voltage and the thickness determination; since voltages are usually measured and maintained more accurately than film thickness, it is primarily the accuracy of the thickness which determines the accuracy of the electric field strength. As changes in the electric field strength with respect to time calculated for region 2, Figure 1, may be quite small, a method of thickness determination accurate to  $\pm 1\%$  is desirable. The method used should preferably be rapid and nondestructive and ideally be an *in-situ* measurement. In section IV, methods available which fulfill some of these requirements are reviewed, along with other methods that have been used and reported in the literature.

A recent survey has been published by Gillespie<sup>125</sup> in which some 23 methods for thin-film thickness determinations are listed: some methods destructive, others nondestructive; some suitable, some unsuitable for the present type of investigation. However, with such a compilation, and knowing the accuracy and type of measurement required, one can determine which of the many methods available would be the most suitable for any system under examination.

## C. PHYSICAL AND STRUCTURAL PROPERTIES

### 1. Compact or Flawed Films?

This question is of fundamental significance to barrier-type films and, under certain circumstances, to porous films. In order to ascertain oxidation mechanisms and to identify the rate-controlling parameters, it is necessary to assume that any experimental results can be interpreted in terms of a compact and uniform oxide film. If the film were not uniform, *i.e.* if the film thickness varied from one point to another, then experimental results, *e.g.*, the change in the ionic current density with the electric field strength, cannot be unequivocally interpreted in terms of a conduction mechanism. To assume an oxide film as compact and uniform is to suggest that no point in the film transports charge preferentially over other points. Consequently, if an anodic oxide film is shown to be flawed in some way, due for instance to initial substrate surface roughness, then definite quantitative mechanistic interpretations are open to some ambiguity.

Flaws have been reported<sup>111</sup> to exist in oxide films formed upon tantalum, niobium, and zirconium, and Vermilyea has suggested there is no reason to suppose that they are absent in other anodic oxide films. Alwitt and Hills<sup>118</sup> have reported flaws in barrier-type oxide films formed on aluminum, and Young<sup>112</sup> and Alwitt<sup>126</sup> have suggested the presence of microfissures in  $\text{Nb}_2\text{O}_5$  and  $\text{Al}_2\text{O}_3$  films, respectively, to account for the frequency-dependent capacitance of such films.

It could be concluded here that the assumption of a structurally perfect oxide film is as uncertain as the assumption that this type of film is crystalline.

Apart from the presence of flaws, several other factors may influence the physical and structural properties of barrier-type oxide layers. These include the adsorption of water and anions and the presence of mechanical stress. The incorporation of water and anions was reviewed in section II. Whether the water is adsorbed or physically trapped is uncertain; perhaps adsorption will be more prevalent for barrier-type films and physical trapping, with consequent hydrated oxide formation, more prevalent for porous-type films. Low concentrations of adsorbed water on the surface of an insulator, or an *n*-type semiconductor, have been shown<sup>127, 128</sup> to produce increased electronic conductivity, while at high concentrations of surface adsorption, a protonic conductive network upon the surface of the film can result.<sup>15</sup>

### 2. The Presence of Stress

Stress, whether tensile or compressive, in anodic oxide films has been shown to be dependent on several factors. One is (a) the identity of the ionic species involved in the ionic charge transport process. If only anions are assumed<sup>84</sup> to be mobile, *e.g.*,  $\text{ZrO}_2$ , then because of the volume ratio of the oxide being greater than unity, compressive stresses arise within the oxide. Bradhurst and Leach<sup>129</sup> have calculated a stress of 36,000 kg  $\text{cm}^{-2}$  for  $\text{Al}_2\text{O}_3$  assuming 100% anion mobility. However, the magnitude of the compressive stress is always below this theoretical value.  $\text{ZrO}_2$ , which should show very high compressive stress, does generally exhibit compressive stress but

(125) D. J. Gillespie, "Measurement Techniques for Thin Films," The Electrochemical Society, Inc., New York, N. Y., 1967, p 102.

(126) R. S. Alwitt, *J. Electrochem. Soc.*, **114**, 843 (1967).

(127) H. Statz and G. A. De Mars, *Phys. Rev.*, **111**, 169 (1958).

(128) B. Rosenberg, "Physical Processes in Radiation Biology," Academic Press, New York, N. Y., 1964, p 111.

(129) D. H. Bradhurst and J. S. Ll. Leach, *J. Electrochem. Soc.*, **113** 1245 (1966).

in some instances exhibits tensile stress.<sup>130</sup> If the oxide is formed by cation mobility only, the film should form in a relatively stress-free condition. From the work of Davies, Domeij, Pringle, and Brown,<sup>84</sup> most metal oxides would be expected to possess small compressive stress since both the anion and cation contribute to ionic charge transport. Vermilyea<sup>130</sup> has reported that  $\text{Al}_2\text{O}_3$ ,  $\text{Ta}_2\text{O}_5$ , and  $\text{Nb}_2\text{O}_5$  show much lower compressive stress than  $\text{ZrO}_2$  while Bradhurst and Leach<sup>129</sup> have reported that the compressive stresses present in  $\text{Al}_2\text{O}_3$  films decrease as the cationic transport number increases; both experimental observations are in accord with transport number data.<sup>84</sup>

(b) The presence of an electric field across the oxide film produces a compressive stress;<sup>85</sup> the magnitude of the stress is proportional to the square of the electric field strength. When the electric field is removed, the oxide lattice relaxes and the compressive stress tends to decrease. Evidence of this effect has been reported by Bradhurst and Leach<sup>129</sup> for barrier-type films on aluminum, where the over-all stress, determined as tensile, becomes more compressive when an electric field is applied; when the electric field is removed, the stress increases in the tensile direction.

(c) The presence of a hydrated oxide, within a subsequently formed anodic oxide film, can produce an increase in the tensile stress observed for oxide films on aluminum. Vermilyea<sup>130</sup> has proposed that the tensile stress observed for films prepared in aqueous solution is dependent on the degree of physical trapping of water and on the extent of dehydration, which occurs concurrently by proton migration. Evidence that preformed layers of hydrated oxide are dehydrated by subsequent anodic oxidation has been available for many years<sup>131</sup> and has been reported by Schwabe,<sup>132</sup> Altenpohl,<sup>133</sup> and Alwitt.<sup>126</sup>

The resultant stress in any anodically formed oxide film is therefore seen to be a complex function of its formation mechanism, the presence or absence of an electric field, and the incorporation of water into the film during the preparation. The purity of the substrate metal, upon which the oxide is formed, has also been shown to influence the stress produced during anodic oxidation. Bubar and Vermilyea<sup>134</sup> have shown that  $\text{Ta}_2\text{O}_5$  produced upon vacuum-annealed tantalum is many orders more ductile than  $\text{Ta}_2\text{O}_5$  formed upon tantalum in the as-received condition. Bradhurst and Leach,<sup>135</sup> in agreement with Bubar and Vermilyea,<sup>134,136</sup> have reported that, compared to  $\text{Ta}_2\text{O}_5$ , thick alumina films, *i.e.*, 1000 Å, show little or no ductility and hence undergo only little deformation by stress before the oxide film separates from the substrate metal.

The presence of stress in anodic oxide films, when taken in conjunction with all the complicating phenomena mentioned earlier in this review, would appear to indicate that the "classical" picture of the oxide as a rigid, crystalline, unchanging body, through which only cations transport ionic charge, is untenable.

## D. MEASUREMENT OF THICKNESS

### 1. Application of Faraday's Laws

If, during electrolytic oxide formation, the amount of charge passed is noted, then, assuming Faraday's laws are applicable, one can calculate the amount of oxide laid down. In any determinations of this kind, several factors are of importance. (1) The current efficiency of the reaction occurring must be known, either to be 100%, *i.e.*, all the dissolving metal going toward oxide formation and no secondary reactions occurring, or to be known and constant throughout the duration of formation; (2) the molecular weight of the substance being formed must also be known, *i.e.*, the composition of the substance, whether pure or containing incorporated electrolyte ions; (3) the density of the formed film must also be known. In the case of the valve metal oxides the density is usually different from that of the bulk oxide, since one is amorphous and the other usually crystalline. The oxide density can usually be experimentally determined, for instance, using the method reported by Jepson.<sup>137</sup>

Allowing for all these possible inaccuracies, the volume of oxide laid down by the passage of charge  $Q$  can be written as

$$V = QM/xyF\rho \quad (13)$$

where  $M$  is the molecular weight of the oxide  $\text{A}_x\text{O}_y$ , which has density  $\rho$  and  $F$  is the Faraday.

The thickness of oxide is the volume of oxide laid down divided by the apparent area of specimen surface covered,  $A$ . Thus, from eq 13, the thickness is then given by

$$d = QM/xy\rho FA \quad (14)$$

This method for the calculation of film thickness is rarely used because of the disadvantages mentioned, although Bray, Jacobs, and Young<sup>138</sup> have used it to study the anodic oxidation kinetics of tantalum, and found results consistent with the Dewald dual-barrier theory. Bernard and Cook<sup>139</sup> have reported that for barrier-type oxide films produced on aluminum in ethylene glycol-ammonium pentaborate solution, the agreement between the film thickness determined by weight and by optical methods was satisfactory.

### 2. Optical Methods

Spectrophotometric and ellipsometric methods of examination are the most widely used techniques in the determination of oxide film thickness. These data are often the most accurate, provided that accurate information is available for the optical constants of the basis metal and the film substance. One particular advantage that these methods have over previous methods is that film thickness parameters can be determined *in situ*. Again, however, this method is applicable only to those systems where accurate optical data are available, and where the optical constants of the film-forming electrolyte differ appreciably from those of the film substance. For example, Young and Zobel<sup>70</sup> found that *in situ* measurements were impractical during the ellipsometric study of the anodization of silicon in N-methylacetamide where the refractive indices were 1.47 and 1.43 for anodic  $\text{SiO}_2$  and N-methylacetamide, respectively.

(137) W. B. Jepson, *J. Sci. Instr.*, **36**, 319 (1959).

(138) A. R. Bray, P. W. M. Jacobs, and L. Young, *Proc. Phys. Soc.*, **71**, 405 (1958).

(139) W. J. Bernard and J. W. Cook, *J. Electrochem. Soc.*, **106**, 643 (1959).

(130) D. A. Vermilyea, *J. Electrochem. Soc.*, **110**, 345 (1963).

(131) W. J. Muller and K. Konopicky, *Z. Physik. Chem.*, **A141**, 343 (1929).

(132) K. Schwabe, *J. Electrochem. Soc.*, **110**, 663 (1963).

(133) D. Altenpohl, *ibid.*, **108**, 628 (1961).

(134) S. F. Bubar and D. A. Vermilyea, *ibid.*, **113**, 892 (1966).

(135) D. H. Bradhurst and J. W. L. Leach, *Trans. Brit. Ceram. Soc.*, **62**, 793 (1963).

(136) S. F. Bubar and D. A. Vermilyea, *J. Electrochem. Soc.*, **114**, 882 (1967).

### a. Spectrophotometric Methods

Many valve metals, *e.g.*, Ta, Nb, and Zr, give oxide films exhibiting bright interference colors in the visible range due to light reflected and refracted from and into the oxide, respectively. The refracted light, on meeting the metal-oxide interface, is partially transmitted into the metal and absorbed and partially reflected. The reflected light, upon reaching the oxide-air interface again is partially reflected and partially transmitted out of the film. The result is a phase change between the reflected light and the emergent light after refraction, which often produces a visible interference color.

In the visible range of wavelengths, interference colors appear as yellow followed by red, violet, blue, and green, dependent upon oxide film thickness. The observed colors pass through several orders of interference as the film grows thicker, yellow through red, violet, blue, and green and yellow again, and so on. This will continue until the films become so thick that all the light refracted into the oxide is absorbed, *i.e.*, there is no emergent light, or the interference colors, being of ir wavelength, become invisible. Visible interference colors can be used to determine oxide film thickness by comparing the color observed with a set of carefully prepared color standards of known thickness (a thickness determination by other methods is required here). Such work has been reported<sup>46,62,77</sup> where this so-called step-gauge method was used. It is clear that one must ensure that the same order of interference is being observed. Hunter and Towner,<sup>140</sup> by using a method of observing the color under polarized light of grazing incidence with the aid of a polaroid filter, where the plane of polarization depended upon the order of interference, have reported that the yellow on the first interference order occurs at a film thickness of 500 Å and the second-order interference yellow at 1300 Å thickness.

The use and accuracy of step gauges will depend upon the rate of change of colors as the film thickness increases, being the most accurate measure of film thickness when the color changes most rapidly for small changes in film thickness. Vermilyea<sup>62</sup> has observed that from 500 to 900-Å films of Ta<sub>2</sub>O<sub>5</sub> the accuracy of a visual match was 30 Å, while in the range 350–450 Å the accuracy was 2 Å.

The observed visible interference color, instead of being compared with similarly prepared standards, can be compared with the well-known Rollet<sup>141</sup> tables of colors obtained from air films as seen by transmitted light. Some form of calibration curve is required here, relating the thickness of air films, divided by a mean value of the refractive index in the visible wavelengths, against some other measure of film thickness. This method has been applied by Kerr and Wilman<sup>142</sup> in the study of anodic oxide films on beryllium.

When light of wavelength  $\lambda$  at constant angle of incidence is projected onto a film-covered surface, the reflected light and the refracted light are out of phase with each other and produce interference bands. If the reflectivity of the surface is measured, minimum reflection will occur when the film thickness is proportional to  $\lambda/4n$ ,  $3\lambda/4n$ ,  $5\lambda/4n$ ,  $7\lambda/4n$ , etc., where  $n$  is the refractive index of the film at wavelength  $\lambda$ . With a film of constant thickness  $d$  examined with incident light of increasing wavelength, the minimum reflection will occur at wavelengths  $4nd$ ,  $4nd/3$ ,  $4nd/5$ ,  $4nd/7$ , etc.; therefore, plotting

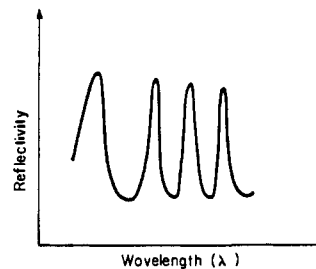


Figure 2. Reflectivity as a function of wavelength ( $\lambda$ ) of the incident light for an oxide film  $d$  cm thick having a refractive index  $n$ .

the reflectivity against the wavelength for films thick enough to give several orders of interference would ideally result in the diagram shown in Figure 2. When the film thickness is small, minimum reflection occurs at low wavelength (uv region), and hence interference colors are invisible. As the film thickness increases, the interference colors move into the visible range and the range of colors mentioned previously occurs. Finally, assuming nonabsorbing oxide, the interference colors again become invisible as the minimal reflection wavelengths move into the ir region.

At the minimum reflectivity the following equation holds

$$(d + D) = \frac{(2m - 1)\lambda}{4n \cos \phi} \quad (15)$$

where  $d$  is the film thickness,  $D = f(\lambda)/(2n \cos \phi) = \text{constant}$ ,  $m = 1, 2, 3, 4$  corresponding to the order of interference,  $\lambda$  is the wavelength of minimal reflection,  $n$  is the refractive index of film substance at wavelength  $\lambda$ , and  $\phi$  is the angle of refraction. If this determination of the wavelengths at which minimum reflectivity is observed is used in conjunction with another independent means of measuring film thickness, a graph of wavelength at minimum reflectivity *vs.* film thickness can be constructed and used to give direct absolute values of film thickness from optical measurements. This procedure was adopted by Young<sup>143</sup> in an investigation of Ta<sub>2</sub>O<sub>5</sub> films using formation-charge, capacitance, and interference measurements. The plot of film thickness against the wavelength  $\lambda$  for minimum reflection, using light of refraction angle  $11^\circ$ , is shown in Figure 3. This method has also been used in the study of oxide films on zirconium by Wilkins,<sup>144,145</sup> the accuracy of the film thickness determination being reported as  $\pm 3.5\%$  on the absolute thickness up to films  $3 \mu$  thick. This method has also been used in the investigation of the anodic oxidation of Nb,<sup>146</sup> Zr,<sup>63</sup> and U.<sup>147</sup> Booker and Benjamin,<sup>148</sup> using a twin beam interference technique for thick films, and a multiple beam technique for thin films, formed anodically on silicon, have reported an accuracy ranging from 1 to 5% for films up to 15,000 Å thick. These methods have also been used<sup>148,149</sup> to determine the refractive indices of oxide films of known thickness.

The extension of the interference method into the infrared

(140) M. S. Hunter and P. F. Towner, *J. Electrochem. Soc.*, **108**, 139 (1961).

(141) A. Rollet, *Sitzber. Akad. Wiss. Wien*, **77** (3), 229 (1878).

(142) I. S. Kerr and H. Wilman, *J. Inst. Metals*, **84**, 379 (1954).

(143) L. Young, *Proc. Roy. Soc.*, **A244**, 41 (1958).

(144) N. J. M. Wilkins, *J. Electrochem. Soc.*, **109**, 998 (1962).

(145) N. J. M. Wilkins, *Corrosion Sci.*, **5**, 3 (1965).

(146) L. Young, *Can. J. Chem.*, **38**, 1141 (1960).

(147) A. E. Stebbens and L. L. Shreir, *J. Electrochem. Soc.*, **108**, 30 (1961).

(148) G. B. Booker and C. E. Benjamin, *ibid.*, **109**, 1206 (1962).

(149) A. E. Stebbens and L. L. Shreir, *Nature*, **183**, 1113 (1959).

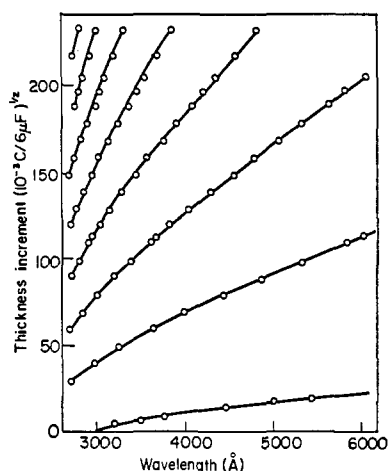


Figure 3. Oxide film thickness ( $d$ ) as a function of the wavelength ( $\lambda$ ) required for minimal reflection. Angle of incidence ( $\phi$ ) is taken as  $11^\circ$ .

region has been reported by Wilkins.<sup>150</sup> This has some advantages, particularly for thermal films, since, as the oxide film grows thicker, it may become too absorbing for measurement at visible wavelengths. The location of reflection minima is more accurately studied in the ir region.

#### b. Ellipsometric Methods

The use of polarized light as a light source in the determination of film thickness has become well established and has been widely used over the last few years. The original work on the mathematics of the optics involved, by Drude<sup>151, 152</sup> and by Tronstad,<sup>153</sup> gave complex mathematical expressions which, until quite recently, were used only with several simplifying approximations. However, now that computers are generally available, an exact interpretation of the experimental data is now possible,<sup>154</sup> provided the necessary optical constants for the system are available.

When polarized light is reflected, the two components, p-light, which is polarized in the plane of incidence, and s-light, which is polarized at right angles to the plane of incidence, suffer a change in amplitude and phase but to differing degrees. Hence reflection causes a *relative* shift in both phase and amplitude. These relative shifts depend upon the thickness, the absorption coefficient, and the refractive index of the forming film. The reflection coefficients, known as the Fresnel coefficients, for the two components of the polarized light are given by the following expressions

p component

$$r^p = \frac{n_2 \cos \phi_1 - n_1 \cos \phi_2}{n_1 \cos \phi_1 + n_2 \cos \phi_2} \quad (16)$$

s component

$$r^s = \frac{n_1 \cos \phi_1 - n_2 \cos \phi_2}{n_1 \cos \phi_1 + n_2 \cos \phi_2} \quad (17)$$

where  $n_1$  is the refractive index of the medium at the surface of the substrate,  $n_2$  is the refractive index of the substrate surface,  $\phi_1$  is the angle of incidence, and  $\phi_2$  is the angle of refraction.

The quantity measured by the ellipsometer is the ratio of reflection coefficients,  $\chi$

$$\chi = \frac{r^p}{r^s} = \tan \psi e^{i\Delta} \quad (18)$$

where  $\psi$  is relative amplitude shift,  $\Delta$  is relative phase shift, and  $i$  is the complex number  $\sqrt{-1}$ . The refractive index of the substrate surface can be calculated by using the expression<sup>154</sup>

$$n_2 = n_1 \tan \phi_1 \left[ 1 - \frac{4\chi \sin^2 \phi_1}{(\chi + 1)^2} \right]^{1/2} \quad (19)$$

If a film is now placed upon the substrate surface, the reflection properties of the substrate surface are changed and the Fresnel coefficients are now given by the exact Drude equations as

$$R^p = \frac{r_{12}^p + r_{23}^p \exp(D)}{1 + r_{12}^p r_{23}^p \exp(D)} \quad (20)$$

$$R^s = \frac{r_{12}^s + r_{23}^s \exp(D)}{1 + r_{12}^s r_{23}^s \exp(D)} \quad (21)$$

where

$$D = -4\pi i n_2 \cos \phi_2 d_2 / \lambda \quad (22)$$

$r_{12}$  is the Fresnel coefficient for the reflection between the medium and the film,  $r_{23}$  is the Fresnel coefficient for the reflection between the film and the substrate, and  $d_2$  is the film thickness.

The ratio of the Fresnel coefficients for an oxide-covered substrate is now given as

$$\rho = R^p/R^s = \tan \psi e^{i\Delta} \quad (23)$$

which is analogous to eq 18, which expresses the ratio of the reflection coefficients for the film-free substrate. Therefore, for a given angle of incidence  $\phi_1$ , film thickness  $d_2$ , and the refractive indices of medium, film, and substrate, the values of  $\psi$  and  $\Delta$  can be calculated. Theoretically, any of the previous parameters can be determined knowing all but the one required. In practice, the experimental values of  $\psi$  and  $\Delta$  are compared to theoretical evaluations of  $\psi$  and  $\Delta$ , assuming reasonable values for the optical constants.

Ellipsometric results and their interpretation are only relatively simple in the case of oxide films which are both homogeneous and nonabsorbing; *i.e.*, all the incident light is either reflected or refracted. In such cases, the plot of  $\Delta$  against  $\psi$  usually appears as a closed loop as the oxide thickness increases, the dimensions of the loop being dependent upon the refractive index assumed for the oxide with all other refractive indices being constant. For absorbing oxide films, the  $\Delta$  against  $\psi$  plots can have a variety of shapes, although in most cases a spiral results. Figures 4 and 5 illustrate the  $\Delta$ - $\psi$  behavior for nonabsorbing and absorbing oxide films; the arrows indicate the direction in which the oxide film thickness increases.

If p-light only is used, then the procedure for determining the film thickness is similar to that described in the earlier

(150) N. J. M. Wilkins, *Corrosion Sci.*, **4**, 17 (1964).

(151) P. Drude, *Ann. Physik*, **32**, 584 (1887).

(152) P. Drude, *ibid.*, **39**, 471 (1890).

(153) L. Tronstad, *Trans. Faraday Soc.*, **29**, 502 (1933).

(154) F. L. McCrackin and J. P. Colson, Ellipsometry Symposium, National Bureau of Standards, Miscellaneous Publication 256, U. S. Government Printing Office, Washington, D. C., 1963, p 61.



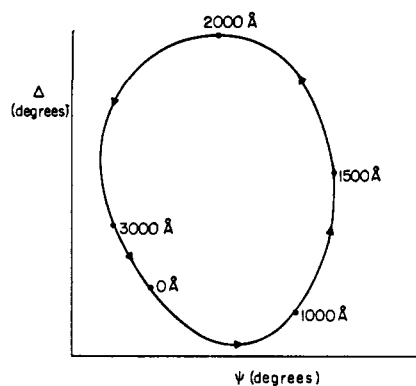


Figure 4.  $\Delta$ - $\psi$  relationship for a transparent, nonabsorbing oxide film; calculated assuming the following parameters:  $\phi_1 = 70^\circ$ ,  $\lambda = 5460 \text{ \AA}$ , and the refractive indices of the metal substrate, the oxide film, and the medium being 1.79–1.831, 1.50, and 1.33, respectively.

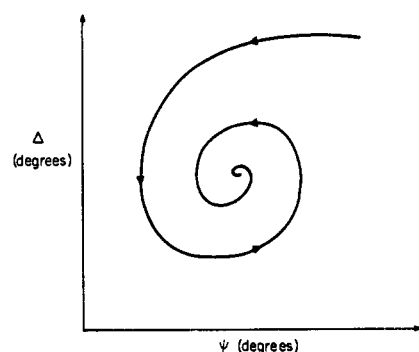


Figure 5. A typical  $\Delta$ - $\psi$  relationship for a transparent, absorbing oxide film.

spectrophotometric section. Masing, Orme, and Young<sup>155</sup> have shown that if the intensity of reflected p-light is measured as a function of the angle of incidence for increasing thickness of  $\text{Ta}_2\text{O}_5$  films, the refractive index can often be obtained. The reflectivity of p-light can be measured at almost any angle of incidence except one, that is at the Brewster angle where the reflectivity is zero. The Brewster angle  $\theta$  can be given by either  $\tan \theta = n$ , where  $n$  is the refractive index at the film-air interface, or by  $\tan \theta = n/n_1$ , where  $n_1$  is the refractive index of the medium in which the film is immersed.

The optical properties of tantalum and its anodic oxide film have also been investigated by Kumagi and Young<sup>156</sup> using polarized light with both p and s components present. The measurement of the relative phase and amplitude shifts have been studied during the film formation on aluminum in nonpore-forming electrolytes by Barrett and Winterbottom<sup>2, 48, 157</sup> who have reported an  $\text{\AA V}^{-1}$  ratio in close agreement with that reported by Hass.<sup>42</sup> This technique has also been used to study anodic behavior of titanium<sup>158</sup> in phosphoric and

sulfuric acids, formation of oxide films on iron,<sup>159, 160</sup> and the growth of oxide films on copper.<sup>161</sup>

In conclusion, although optical methods are, as a technique, capable of accuracies of  $\pm 1\%$ , it is well to consider the disadvantages inherent in these techniques. These include (a) the thickness obtained for a film is strictly an average value for the area under examination, (b) changes in the refractive index and/or the absorption coefficient of the film can occur if the film composition changes, and (c) the presence of an applied electric field strength may, as has been suggested,<sup>124</sup> influence the optical properties of the film. Referring now specifically to the ellipsometric technique, both (b) and (c) above will influence the values of  $\Delta$  and  $\psi$  obtained experimentally, which, if prior knowledge of (b) and (c) is unavailable, could be incorrectly interpreted in terms of a change in film thickness. Thus, inaccurate values for the electric field strength would result. Consequently, although optical methods are extensively and successfully applied to the study of oxide films, great care is necessary in order to avoid ambiguous interpretations.

### 3. Capacitance Method

If the oxide present on a metal is of a uniform thickness, the system metal-metal/oxide interface-oxide-oxide/electrolyte interface-electrolyte exists and can be likened to the system present in a parallel plate condenser. The capacitance  $C$  of such a condenser is given by

$$C = \epsilon A / 4\pi d \quad (24)$$

where  $\epsilon$  is the dielectric constant of the oxide medium,  $A$  is the surface area, and  $d$  is the dielectric medium thickness, with  $C$  being expressed in esu's. The applicability of capacitance measurements in the determination of the thickness of the oxide film present upon a substrate depends on several factors.

(a) The electrical double layer (edl) capacity  $C_{edl}$ , at the oxide interface with the electrolyte, must be high in comparison to that of the oxide. Two capacitances in series produce the resultant capacitance  $C_r$  expressed in

$$\frac{1}{C_r} = \frac{1}{C_{oxide}} + \frac{1}{C_{edl}} \quad (25)$$

When  $C_{edl} \gg C_{oxide}$  the measured resultant capacitance  $C_r$  approximates closely to the oxide capacitance, to within, usually,  $\pm 1\%$ .

(b) The type of oxide produced also affects the applicability of capacitance measurements. Lorking<sup>162</sup> has shown that where the film is coherent and impermeable the capacitance may be used to estimate film thickness; however, where the film has been rendered porous by corrosive solutions, the capacitance values do not indicate correct film thickness. When the oxide film is pore-free and devoid of any mechanical defects, etc., the capacitance measurements can give satisfactorily accurate results, with an error of less than 1%, and have the advantage of being rapid and nondestructive.

(c) If absolute values of the thickness are required, then an

(155) L. Masing, J. E. Orme, and L. Young, *J. Electrochem. Soc.*, **108**, 428 (1961).

(156) S. Kumagi and L. Young, *ibid.*, **111**, 1411 (1964).

(157) M. A. Barrett, ref 154, p 213.

(158) P. C. S. Hayfield, ref 43, p 663.

(159) C. E. Leberknight and B. Lustman, *J. Opt. Soc. Amer.*, **29**, 59 (1939).

(160) A. B. Winterbottom, *J. Iron Steel Inst.*, **165**, 9 (1950).

(161) E. W. Young, J. V. Cathcart, and A. T. Gwathmey, *Acta Met.*, **4**, 145 (1956).

(162) K. F. Lorking, *J. Appl. Chem.*, **10**, 449 (1960).

accurate value of the dielectric constant must be obtained, *i.e.*, by calibration with films of known thickness. Since capacitance is dependent upon the dielectric constant and the dielectric constant is often found to be a function of the frequency, the capacitance measurements are usually made at constant signal frequency.

(d) When measuring the capacitance of an oxide film whose capacitance does not differ greatly from that of the edl or when measuring edl capacitances, extreme care must be used so that the amplitude of the sinusoidal or square-wave signals do not influence the specimen electrode potential. The electrode potential will obviously influence the electrical double layer present and hence the value of  $C_{edl}$ . This has been demonstrated by McMullen and Hackerman<sup>163</sup> for Cu, Pt, and Ag in 1 *N* sodium sulfate. However, provided that  $C_{edl} \gg C_{oxide}$ , the influence of electrode potential on the measured capacitance will be negligible.

Many methods have been used for the measurement of capacitance, including the dc transient method, *i.e.*, the response of the system to a perturbation, and ac techniques. The former technique involves the application of, for example, a constant dc current suddenly to the electrode, and recording the resulting potential change with respect to time—the charging-curve technique. Using the simplified equation relating capacitance to current, time, and voltage,  $C = i/(dV/dt)$  where  $i$  is the constant applied dc current and where  $dV/dt$  is the rate of change of time with potential, the capacitance can then be calculated. Brodd and Hackerman<sup>164</sup> have reported the use of the measurement of capacitance, from charging curves, to determine the true surface area of solid metal electrodes. This method is based upon the assumption that the capacitance per unit area of the metal-solution interface is similar to that of mercury at the same potential relative to the zero point of charge. Having obtained a value for the capacitance, to obtain the true surface area, this capacitance is divided by the value of the capacitance for the mercury-identical solution interface at the equivalent potential relative to the zero point of charge. A roughness factor for the electrode can then be determined by the relationship

$$\text{roughness factor} = \frac{\text{true surface area}}{\text{apparent surface area}}$$

The assumption concerning the comparison of two capacitance values obtained at the same potential relative to the zero point of charge is true only in the absence of (i) specific adsorption of ions at the metal-solution interface, (ii) an oxide film, and (iii) the passage of faradaic current. Brodd and Hackerman<sup>164</sup> have indicated that this method of determining the true surface area of an electrode was satisfactory for Pt, Ni, and Cu but unsatisfactory for Al, Ta, Cr, Fe, and Pb; for Al and Ta this was due to oxide films; for Cr it was suggested that the porous nature of chromium plate produced surfaces which were unavailable to the edl; and for Fe and Pb specific adsorption of ions was suggested.

Bridge techniques have been used extensively since the accurate work reviewed by Grahame,<sup>165</sup> in which a Wheatstone bridge circuit is used with ac signals of less than 1-mV amplitude, the balance across the bridge being obtained by

the detection of the minimum noise level with earphones. Wood, Cole, and Hoar<sup>166</sup> developed a bridge consisting of an unknown impedance (the cell containing the test electrode and secondary electrode of high capacitance, for example, platinized platinum) and a balancing impedance, using an amplifier and oscilloscope as the bridge balance detector. The accuracy of any bridge technique depends on several factors, among which are (1) the efficiency of the grounding and the shielding of the apparatus and cables used, and (2) the ac or square-wave input voltage amplitude and frequency. Wood, Cole, and Hoar reported an accuracy of 5% using ac input voltages of 1–100 mV in the frequency range 10–500 Hz, while an accuracy within 5% can be obtained by using a very small ac input signal voltage amplitude.

The type of signal used, whether sine or square wave, determines the extent to which bridge balance is obtained. If sine waves are applied across the arms of the bridge, any combination of resistances and capacitances can be exactly balanced by one resistance and one capacitance, the values of which being dependent on the sine wave signal frequency. However, if square waves are used, which contain components of all frequencies, every element of a multiple impedance must be balanced. Thus when bridge balance is obtained, the electrical condition of each impedance network must be identical; this is a condition which does not apply to sine wave signals. The precise conditions necessary to attain accurate results depend very much upon the metal and conditions present, and also upon the sensitivity and grounding of the bridge circuitry.

The third method of capacitance measurement included here involves the use of electric analog circuits, of which many have been used. The two simplest are the series and parallel circuits illustrated in Figure 6 where  $R_s$ ,  $R_p$ , and  $R$  represent

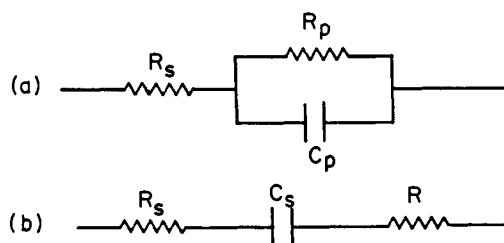


Figure 6. Two simple electrical analog circuits used to represent the electrical characteristics of a metal-oxide-solution system: (a) is the parallel and (b) the series analog.

noninductive resistance boxes and  $C_p$  and  $C_s$  are decade condenser boxes. Many more complex analogs have been demonstrated, notably by Hoar and Wood<sup>167</sup> in the study of the sealing process for porous anodic oxide films on aluminum.

The simple parallel resistance-capacitance network has been demonstrated by McMullen and Hackerman,<sup>163</sup> in which a square-wave current function was applied to the electrode and the network simultaneously. The response curve from the test electrode was compared to the response curve obtained from the electric analog circuit, the two curves being equated by selecting the correct values of  $R_s$ ,  $C_s$ , and  $R_p$ . The use of a value for  $R_s$ , other than zero, indicates that ohmic drop is

(163) J. J. McMullen and N. Hackerman, *J. Electrochem. Soc.*, **106**, 345 (1959).

(164) R. Brodd and N. Hackerman, *ibid.*, **104**, 704 (1957).

(165) D. C. Grahame, *Chem. Rev.*, **41**, 44 (1947).

(166) G. C. Wood, M. Cole, and T. P. Hoar, *Electrochim. Acta*, **3**, 179 (1960).

(167) T. P. Hoar and G. C. Wood, ref 1, p 186

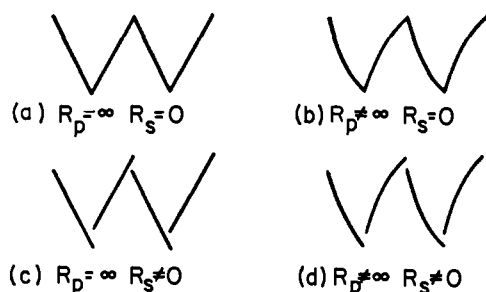
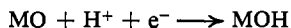


Figure 7. The responses of a parallel analog of known capacitance  $C_p$  as a function of the polarizability of the electrode. The responses are those from a low-frequency square-wave signal application. Responses (a) and (c) are those of an ideally polarizable electrode, while (b) and (d) are those from a nonideally polarizable electrode.

present between the electrodes; the presence of  $R_s$  can be most easily detected by the observation of the off-set charging curve obtained from a square-wave input signal (Figures 7c and d). The charging curves usually observed fall into four classes; these are shown in Figure 7. The use of the analog or comparison circuit method has also been used by Leach and Isaacs<sup>168-171</sup> in the study of capacitance, as a function of electrode potential, of the metals Al, Ta, Zr, Ti, Nb, U, V, Pb, and Sn. As observed by Brodd and Hackerman,<sup>164</sup> the metals Al and Ta show low capacities due to the presence of an oxide film; Zr also belongs to this class. Ti, Nb, U, and V all show very high capacities, many times larger than those expected from a pure electrical double layer capacitance. Isaacs and Leach<sup>171</sup> have proposed that these abnormal capacitance values are due to a contribution, to the measured capacity, of a faradaic reaction. The reaction was proposed to be the formation of lower valent cations, for example



The observation of very high capacitance values has also been reported by Vermilyea<sup>172</sup> during forward (cathodic) polarization of  $\text{Nb}_2\text{O}_5$  films. This work of Vermilyea and that of Isaacs and Leach<sup>171</sup> have shown that the capacitance of  $\text{Nb}_2\text{O}_5$  (and oxides upon Ti, V, and U) is greater on the reverse (anodic) polarization following a forward (cathodic) polarization. However, it is of interest to note that this difference either decreases substantially or is absent when the metal is in the abraded condition,<sup>171</sup> i.e., very thin oxide film present. If the proposal of Isaacs and Leach were correct, then a relationship between the capacitance increase during forward polarization and the electronic current density should exist. The work of Vermilyea<sup>172, 173</sup> has shown that such a relationship is not found experimentally. The evidence, therefore, would appear to favor the proposal due to Vermilyea,<sup>172</sup> which attributes the large capacitance values observed to the formation of a proton space charge within the oxide film present upon the metal surface. A quantitative theory was proposed, and the experimental evidence was considered to be in reasonable agreement with the theory.

The capacitance method to determine film thickness has

been and is being used extensively, but the system under examination must, as has been indicated, be carefully examined to determine the suitability of this method. In some instances the capacitance values produce inadequate results and hence would appear to be inapplicable, for example, the thickness of films formed in nonpore-forming electrolytes upon tantalum where the growth is photoinduced by a suitable wavelength ultraviolet light.<sup>174</sup>

As far as aluminum is concerned, the charging curve method, although inapplicable in the determination of true surface areas and roughness factors due to the presence of an oxide film, may still be used to determine oxide film thickness, provided an accurate slope  $dt/dV$  can be obtained.<sup>164</sup> The method used by McMullen and Hackerman<sup>168</sup> has shown that oxide-coated aluminum, under the experimental conditions used, has a capacitance of  $3 \mu\text{F cm}^{-2}$  which, taking a value of 8 for the dielectric constant, corresponds to a film thickness of  $20 \text{ \AA}$ . Turpin and Testerman<sup>175</sup> have reported a value of  $4 \mu\text{F cm}^{-2}$  for untreated, presumably oxide-covered, aluminum which was, as expected, independent of the electrode potential. When the aluminum was pretreated in 10% trisodium phosphate to remove the oxide coating, the capacitance was found to be dependent on the initial preparation, in this case, sanding. For rough sanding followed by pretreatment to remove the oxide coating, the capacitance was  $20 \mu\text{F cm}^{-2}$ ; when smooth sanded and pretreated, the capacitance was  $13\text{--}15 \mu\text{F cm}^{-2}$ . Both values exhibited the expected potential dependence since, under such conditions, the electrical double layer capacitance now contributes a significant proportion to the measured resultant capacitance. However, in most cases of oxide-coated electrodes, where the oxide thickness is greater than  $10 \text{ \AA}$ , the oxide capacitance is smaller than that of the electrical double layer, so the measured capacitance would be primarily that of the oxide layer.

In those capacitance measurements based upon relaxation techniques,<sup>176-181</sup> i.e., those methods where either potential or current excursions are observed following galvanostatic or potentiostatic perturbations, respectively,<sup>182</sup> it is usually assumed that any current involved is due to capacitance charging only. For example, in the measurement of  $C_{\text{edl}}$  in the presence of a faradaic reaction, the potential changes following a galvanostatic current application are due to two causes: (1) electrical double layer charging, and (2) the charge involved in the faradaic process. Since it cannot be assumed that the current involved produces electrical double layer charging only, the value of  $C_{\text{edl}}$  expressed as  $i/(dt/dV)$  will be in error. Several methods have been proposed to overcome this problem, including the use of a square-wave perturbation and making compensations for the faradaic current<sup>183</sup> and the

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(174) A. R. Bray, P. W. M. Jacobs, and L. Young, *J. Nucl. Mater.*, **1**, 356 (1959).

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(178) M. Proskurnin and A. Frumkin, *ibid.*, **31**, 110 (1935).

(179) J. S. Riney, G. M. Schmidt, and H. Hackerman, *Rev. Sci. Instrum.*, **32**, 588 (1961).

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(181) L. Ramaley and C. G. Enke, *J. Electrochem. Soc.*, **112**, 943 (1965).

(182) W. H. Reinmuth, *Anal. Chem.*, **36**, 211R (1964).

(183) G. D. Robbins and C. G. Enke, *J. Electroanal. Chem.*, **12**, 102 (1966).

application of the double perturbation or pulse method.<sup>184, 185</sup> The latter is often used to determine transient behavior of faradaic processes without electrical double layer complications.

The semiautomatic measurement of capacitance has been reported by Breiter,<sup>186</sup> Kowalski and Srzednicki,<sup>187</sup> and Valeriotte and Barradas.<sup>188</sup>

#### 4. Cathodic Reduction Methods

In this method, the oxide-coated metal is subjected to a constant cathodic current density reduction in a suitable electrolyte, the electrode potential of the metal electrode being observed with respect to time, and the rate of change of potential related to the progress of cathodic reduction. For example, Hancock and Mayne<sup>189</sup> examined the cathodic reduction of air-formed oxide films upon iron and obtained an electrode potential against time plot similar to that shown in Figure 8. The first arrest in the electrode potential marks the completion of the cathodic reduction of the oxide film, and the second arrest indicates the occurrence of hydrogen evolution. If the time required to reach the first electrode potential arrest is known, the amount of charge required to reduce the oxide film can be calculated.

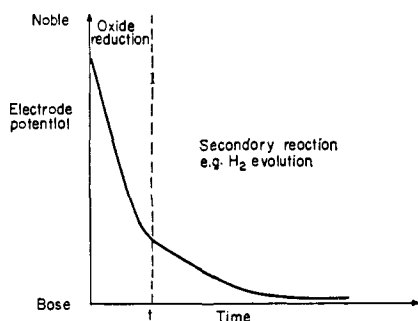


Figure 8. A typical electrode potential *vs.* time curve for the cathodic reduction of an oxide film. The time *t* (in seconds) times the cathodic current density is the number of coulombs per square centimeter required to reduce the oxide film.

At this point it is necessary to assume or determine (a) that the total charge, determined in the cathodic reaction, was used in oxide film reduction and not in other cathodic reactions, *e.g.*, reduction of oxygen in aerated solution; (b) that all the oxide has been reduced, *e.g.*, some oxides are not cathodically reducible (Buob, Beck, and Cohen<sup>190</sup> have shown that magnetite films produced on iron at 250° cannot be cathodically reduced); and (c) that the electrolyte does not attack and dissolve the oxide film before or during the reduction process. Hancock and Mayne have reported that 0.1 and 0.2 *N* ammonium chloride will rapidly dissolve the oxide

film  $\gamma\text{-Fe}_2\text{O}_3$  and attack the metal, and therefore would produce erroneous results.

The assumption concerning oxygen reduction, during cathodic reduction of oxide films, can be made if the deaeration of the electrolyte used is sufficient. The efficiency of such deaeration can only be determined by experiment, being the point where further deaeration does not lower the charge required for oxide reduction. Deaeration is also often useful in reducing the amount of dissolving power the electrolyte has for the film. Efficient deaeration, either by alternate freezing and thawing *in vacuo* or by boiling the electrolyte under reduced pressure, considerably reduces the solvent action of sodium hydroxide and potassium chloride for  $\gamma\text{-Fe}_2\text{O}_3$  films.<sup>189</sup> Provided that the current density is applied to the specimen as soon as it touches the electrolyte surface, and assuming that the rate of reduction is much greater than the electrolyte solvent action, the charge required can be determined with a considerable degree of accuracy. Hancock and Mayne<sup>189</sup> reported the thickness of the air-formed film on pickled iron to be  $40 \pm 2 \text{ \AA}$  over the current density range 20–80  $\mu\text{A cm}^{-2}$ , thereby demonstrating the reproducible nature of the cathodic reduction and its independence of the current density used. If it can be assumed that the cathodic reduction reaction is  $\gamma\text{-Fe}_2\text{O}_3$ , forming iron ions in solution, the amount of metal in solution can be determined and so provide a check on the film thickness.

Because of the many precautions necessary to obtain good results, much of the earlier work with this electrometric method produced results inferior to those of other methods. The initial electrometric method, used by Miley<sup>191</sup> and Miley and Evans,<sup>192</sup> consisted of determining the number of coulombs required to reduce the iron oxide film immersed in ammonium chloride in an open beaker. The thickness of 170–210  $\text{\AA}$  obtained in this study can be compared with those of 30–80  $\text{\AA}$  obtained by gravimetric<sup>193</sup> and optical<sup>160</sup> methods for similar substrates. However, with adequate consideration of the problems involved, this method can give satisfactory results.

Buob, Beck, and Cohen<sup>190</sup> have demonstrated that an accurate measure of thickness can be obtained by this method even for two-layer oxide-scale on iron,  $\gamma\text{-Fe}_2\text{O}_3$ , and  $\text{Fe}_3\text{O}_4$ . Apart from the use of this technique in the field of oxide films, Hoar and Stockbridge<sup>194</sup> have demonstrated the determination of the sulfide content of cuprous sulfide films on copper to be accurate up to 15  $\mu\text{g cm}^{-2}$  sulfide content. Between 15 and 50  $\mu\text{g cm}^{-2}$  this method underestimates the true result, but adequate separation of the potential arrests for the reduction of the oxide, sulfide, and hydrogen is, however, maintained. Above 50  $\mu\text{g cm}^{-2}$  this separation is no longer clear; hence at this level of sulfide content the method is not quantitative. Rao and Udupa<sup>195</sup> have used this electrometric method to determine the oxygen content in lead dioxide; the results obtained compare favorably with those obtained by the more usual iodimetric method. In common with Hancock and Mayne,<sup>189</sup> Rao and Udupa<sup>195</sup> have shown that the current density used for the reduction had little influence upon the

(184) H. Gerischer and M. Krause, *Z. Phys. Chem.* (Frankfurt am Main), **10**, 264 (1959).

(185) H. Matsuda and P. Delahay, *J. Amer. Chem. Soc.*, **81**, 5077 (1959).

(186) M. W. Breiter, *J. Electrochem. Soc.*, **112**, 845 (1965).

(187) Z. Kowalski and J. Srzednicki, *J. Electroanal. Chem.*, **8**, 399 (1964).

(188) E. M. L. Valeriotte and R. G. Barradas, *ibid.*, **12**, 67 (1966).

(189) P. Hancock and J. E. O. Mayne, *J. Chem. Soc.*, 4167 (1958).

(190) K. H. Buob, A. F. Beck, and M. Cohen, *J. Electrochem. Soc.*, **105**, 74 (1958).

(191) H. A. Miley, *Iron Steel Inst.* (London), *Carnegie Schol. Mem.*, **25**, 197 (1936).

(192) H. A. Miley and U. R. Evans, *Nature*, **139**, 283 (1937).

(193) E. A. Gulbrandsen, *Trans. Electrochem. Soc.*, **82**, 375 (1942).

(194) T. P. Hoar and C. D. Stockbridge, *Electrochim. Acta*, **3**, 94 (1960).

(195) P. V. V. Rao and H. V. K. Udupa, *ibid.*, **7**, 651 (1965).

accuracy of the method. The particle size of the lead dioxide was, however, shown to be important, and it was concluded that the lead dioxide must be in a finely divided form, *i.e.*, possess the highest effective surface area, to obtain adequate separation between the oxide reduction and the hydrogen evolution.

The type of oxide film present upon a metallic surface can sometimes be partially elucidated by this cathodic reduction method. Caplan, Harvey, and Cohen<sup>196</sup> have shown that, as the chromium content of an iron-chrome alloy increases, the cathodic reduction curve shows a minimum electrode potential prior to H<sub>2</sub> evolution. This anomalous behavior, it was suggested, was due to the nonstoichiometry of the oxide Cr<sub>2</sub>O<sub>3</sub>, in which Cr<sup>6+</sup> ions are being reduced to Cr<sup>3+</sup>.

### 5. Miscellaneous Methods

Hunter and Fowle<sup>50</sup> have determined barrier layer thickness values by a method in which the minimum voltage required to cause further growth is taken as an estimate of its thickness. This method is based upon the fact that a minimum electric field strength is required to promote ionic conduction across an assumedly fixed, but unknown, barrier film thickness.

A barrier-type film, the thickness of which is required, is immersed in an anodizing electrolyte having a known negligible dissolving action; a slowly increasing voltage is then applied across the film. Assuming  $V/d = E$ , where  $V$  is the voltage being applied,  $d$  is the unknown barrier layer thickness, and  $E$  is the electric field strength, the value of  $V$  required to produce the minimum electric field strength for ionic conduction is then used to calculate  $d$ . When this minimum electric field strength is achieved, at a known value of  $V$ , the current will increase sharply, indicating the passage of ionic current. The passage of ionic current will produce further growth which could be reflected in an increase in the measured capacitance of the barrier layer.

This basic technique was applied by Hunter and Fowle<sup>50</sup> to determine the barrier layer thickness underlying the porous layer in porous anodic oxide films on aluminum. The pre-formed porous oxide film was immersed in 3% w/v ammonium tartrate and a steadily increasing voltage was applied. The voltage value at which the current increased sharply was noted. It should be stressed here that this technique indicates the thickness of the thin barrier film lying adjacent to the metal, and not the total film thickness. The relationship between the current and the applied voltage in the tartrate electrolyte could be represented as the curve shown in Figure 9.

The value of the barrier layer thickness  $d$  can be calculated by either (a) assuming the value for the anodizing constant in 3% w/v aqueous ammonium tartrate as  $14 \text{ Å V}^{-1}$ , or (b) by knowledge of the minimum field strength  $E$  required for ionic conduction. Method a was used by Hunter and Fowle. The assumption of  $14 \text{ Å V}^{-1}$ , without experimental verification, is somewhat suspect in view of the slight dissolving or solvent power that aqueous ammonium tartrate seems to possess. The greatest discrepancy, however, does not lie in this direction, but in the assumption, made by Hunter and Fowle, that the total voltage  $V$  applied equals that voltage which appears across the barrier layer. In other words, is the equation  $V = Ed$  correct? Considering the parallel plate condenser, eq 24,

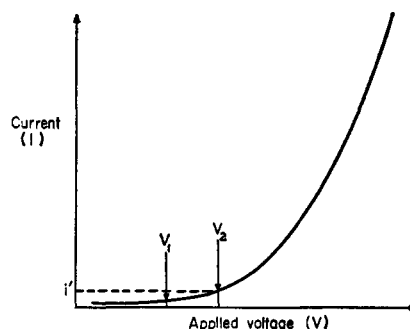


Figure 9. Determination of the barrier film thickness by the experimental observation of the minimum voltage required to produce the flow of ionic current.  $V_1$  is representative of the voltage required to cause the first increase, while  $V_2$  is that voltage required to exceed some minimum current density  $i'$ .

and assuming that  $V = Ed$  is valid, substituting for  $d$  in eq 24 produces eq 26, which relates  $V$ ,  $E$ , and  $C$ .

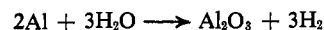
$$V = E \frac{\epsilon A}{4\pi C} \quad (26)$$

Therefore, the determination of  $1/C$  at various values of applied voltage should show a linear relationship passing through the origin, providing the total voltage applied is involved in voltage drop across the barrier film. McMullen and Pryor<sup>197</sup> have reported that the plot of the reciprocal capacitance against the anodizing voltage is linear in the range of 5–72 V for anodizing in 3% aqueous ammonium tartrate (pH 7.0). However, the intercept was found to be not zero, but approximately  $-2.0 \text{ V}$ .

The voltages that are applied during anodizing across the aluminum anode and a platinum cathode should be corrected for potential drop due to external and/or solution resistance, cathode overpotential, and reaction voltage to obtain the actual potential drop, assumed as an activation potential, across the oxide film. Vermilyea<sup>198</sup> has reported that

$$V_{\text{true}} = V_{\text{applied}} - (\eta_0 + \sigma iR) + V_{\text{reaction}} \quad (27)$$

where  $\eta_0$  is the cathode overpotential, which is some function of  $i$ ,  $\sigma$  the specimen surface area,  $i$  the current density, and  $R$  the total ohmic resistance of the solution and any external series resistance.  $V_{\text{reaction}}$  is the reaction voltage for the formation of oxide, which, assuming the reaction to be<sup>199</sup>



has been equated to  $1.5 \text{ V}$  from thermodynamic data.<sup>200</sup> Therefore

$$V_{\text{applied}} \neq Ed \text{ but } V_{\text{true}} = Ed$$

$$V_{\text{applied}} = Ed + (\eta_0 + \sigma iR) - V_{\text{reaction}} \quad (28)$$

$$V_{\text{applied}} = E \frac{\epsilon A}{4\pi C} + (\eta_0 + \sigma iR) - V_{\text{reaction}} \quad (29)$$

A plot of applied voltage against reciprocal capacitance, according to eq 29, might not now be expected to pass through

(197) J. J. McMullen and M. J. Pryor, ref 43, p 52.

(198) D. A. Vermilyea, *J. Electrochem. Soc.*, 101, 389 (1954).

(199) T. P. Hoar and J. Yahalom, *ibid.*, 110, 614 (1963).

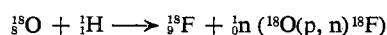
(200) W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1959.

(196) D. Caplan, A. Harvey, and M. Cohen, *J. Electrochem. Soc.*, 108, 134 (1961).

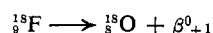
the origin, and this agrees with the intercept of approximately  $-2.0$  V reported by McMullen and Pryor<sup>197</sup> and also by Vermilyea<sup>201</sup> for the anodic oxidation of tantalum. Therefore the assumption that the total applied voltage is involved in voltage drop across the oxide film would appear incorrect.

However, Hunter and Fowle<sup>50</sup> have reported an accuracy of approximately  $3 \text{ \AA}$  in their determination of barrier film thickness, providing a correction is applied to allow for the expected electronic current level of  $100 \text{ \mu A}$ . This means that the voltage value,  $V_2$ , required to increase the current in excess of  $100 \text{ \mu A}$  ( $i'$  in Figure 9) is used in the calculation, and not the voltage,  $V_1$ , required to cause the first increase in current, say from  $10 \text{ \mu A}$ . This is illustrated in Figure 9. This accuracy of  $3 \text{ \AA}$  reported by Hunter and Fowle may have been due to the fact that the error incurred in assuming that  $V_{\text{applied}} = V_{\text{true}}$  is counteracted by the allowance of a higher current, *i.e.*, a higher voltage, at which the value of the barrier layer thickness is calculated, *i.e.*, voltage  $V_2$  in Figure 9. It can be shown that the error between voltages  $V_2$  and  $V_1$  in Figure 9 from the Hunter and Fowle work is 9–10%, which agrees well with the calculated difference between  $V_{\text{applied}}$  and  $V_{\text{true}}$  ( $V_{\text{true}}$  is greater than  $V_{\text{applied}}$  because  $(\eta_0 + \sigma iR) - V_{\text{reaction}}$  is negative).

Another method for assessing the thickness of barrier-type films was developed by Thompson<sup>202</sup> using a proton activation technique. Proton activation of the naturally occurring  $^{18}\text{O}$ , incorporated into tantalum oxide films, proceeds according to the reaction



The isotope  $^{18}_8\text{F}$  then decays with positron emission and has a half-life of 1.8 hr.



The extent of positron emission is taken as a measure of the  $^{18}\text{O}$  initially present in the film, *i.e.*, oxide film thickness.

The procedure used was to produce tantalum oxide films anodically in an aqueous 1% sodium sulfate solution, with thicknesses varying from 500 to 2000  $\text{\AA}$ . These films were then subjected to proton activation, by 4.0 MeV protons in a cyclotron for 10 min, and the emitted radiation was measured using a scintillation method. Thompson<sup>202</sup> found that the  $\gamma$ -ray spectrum exhibited a maximum radiation at 0.511 MeV, and it was this peak that was used as a measure of positron emission. The plot of radiation counts per minute at 0.511 MeV against the theoretical film thickness was reported to be linear above 500  $\text{\AA}$  thickness. The accuracy was reported as  $\pm 10\%$ , although it was considered that this could be improved considerably with closer voltage control. The range of oxide film thickness which could be determined by using 4.0 MeV protons was quoted as 1 to  $10^5 \text{ \AA}$ , the determination of 1  $\text{\AA}$  requiring stringent experimental precautions, and  $10^5 \text{ \AA}$  being the range of 4.0 MeV protons.

Perhaps the largest single disadvantage of this method is the interference that can occur from other elements present; for example, Cu, Ni, Zn, and Ti all interfere. The interference from titanium can, however, be eliminated by using proton energies less than 3.8 MeV.<sup>202</sup>

The application of the measurement of the oxide film breakdown voltage has also been used as a measure of film thickness. The application of this method is limited since dif-

ferences occur, not only as the thickness of the oxide changes, but also between coatings produced by different methods and operating conditions. Compton and Mendizza<sup>203</sup> have reported an accuracy of  $\pm 10\%$  with anodic oxide coatings formed on aluminum under direct current. The procedure used was to press a chromium-plated steel ball of  $1/8$ -in. diameter against the oxide film with a load of 1000 or 2000 g. Alternating current was then applied and the voltage increased slowly until breakdown occurred, at which point a sudden decrease in the voltage was observed. In the British Standard<sup>204</sup> electrical breakdown test, a polished  $1/16$ -in. radius spherical head is placed upon the anodic film surface in a dry condition, and a load of 50–75 g applied. The ac voltage is increased at a rate not exceeding 25 V/sec until either the specified voltage required to match the specification is reached or electrical breakdown occurs. In the latter case, the film is considered to be inferior and is rejected.

Pullen<sup>27</sup> has shown that the electrical breakdown voltage increased linearly in the range 5–20  $\mu$  film thickness and that the breakdown voltage for alumina increases approximately 30 V for every micron increase in thickness above 5  $\mu$ .

The purity of the aluminum used also affects the breakdown voltage recorded. For example, Campbell<sup>205</sup> has shown that the presence of copper, as the intermetallic compound  $\text{CuAl}_2$ , is sufficient to decrease the breakdown voltage for 100- $\mu$  coating on pure aluminum from 10,000 to 500 V. Brace and Pocock,<sup>206</sup> in an investigation into the testing of anodic oxide coatings, have also found that the breakdown voltages were affected by aluminum purity and alloying constituents.

This method is therefore rarely used because of the several drawbacks mentioned, and since the experimental technique must be carefully calibrated under the exact operating conditions used. For instance, calibration of breakdown voltages against the thickness of oxide formed in borate electrolytes of constant composition at  $25^\circ$  should only be used to determine the thickness of films prepared in an identical manner. The accuracy, reported by Compton and Mendizza,<sup>203</sup> of  $\pm 10\%$  would clearly be unsatisfactory for the determination of electric field strengths in kinetic studies of anodic oxidation.

In general, the film thickness in kinetic studies of anodic oxidation processes are determined by optical methods since they can be made *in situ*, and are nondestructive and accurate to  $\pm 1\%$ . The other methods are useful where nondestructive methods are not of advantage and where great accuracy is not required.

## IV. Porous-Type Anodic Oxide Films

### A. GENERAL PHENOMENOLOGICAL OBSERVATIONS

Before reviewing the detailed structures and the pore-formation theories that have been put forward, some general observations are presented concerning this type of film in order to indicate the difficulties in studying such films.

(203) K. G. Compton and A. Mendizza, *Proc. Amer. Soc. Testing Mater.*, 40, 978 (1940).

(204) British Standard 1615, British Standards Institution, London, 1961.

(205) J. C. Campbell, ref 1, p 137.

(206) A. W. Brace and K. Pocock, *Trans. Inst. Metal Finishing*, 35, 277 (1958).

(201) D. A. Vermilyea, *J. Electrochem. Soc.*, 103, 690 (1956).

(202) B. A. Thompson, *Anal. Chem.*, 33, 583 (1961).

### 1. The Consequence of the So-Called "Anodizing Ratio"

It has been shown<sup>50</sup> that, apart from some initial transient behavior, the thickness of the thin barrier layer, lying adjacent to the metal surface and beneath the porous structure, remains at a constant value during porous oxide film formation. The thickness of this thin barrier film is dependent on the anodizing voltage applied, expressed in terms of anodizing ratio ( $\text{\AA V}^{-1}$ ). This  $\text{\AA V}^{-1}$  ratio for aluminum, which has been reported<sup>50</sup> to be a constant over the electrolyte temperature range 80–160°F, is dependent upon the electrolyte used in the film formation much more markedly than in the case of non-porous films. This marked dependence (illustrated in Table III) is to be expected if the electrolyte plays an integral part in the porous oxide formation, as indeed it does.

The influence of the electrolyte concentration upon the  $\text{\AA V}^{-1}$  ratio provides further evidence as to the importance of the electrolyte in porous oxide formation. It has been shown<sup>50</sup> that in very dilute sulfuric acid electrolyte the  $\text{\AA V}^{-1}$  ratio tends toward  $14 \text{\AA V}^{-1}$ , i.e., to a value indicative of very little porous oxide formation (cf. barrier film  $\text{\AA V}^{-1}$  ratio). As the electrolyte concentration increases to 40% w/w, the  $\text{\AA V}^{-1}$  ratio decreases to  $8 \text{\AA V}^{-1}$  where it remains constant up to 60% sulfuric acid. As the sulfuric acid concentration is increased to 75% w/w, the ratio increases to  $9.5 \text{\AA V}^{-1}$ , and finally as the concentration approaches 90% the ratio decreases rapidly to  $1 \text{\AA V}^{-1}$ . Hunter and Fowle<sup>50</sup> have shown further that the correlation of this behavior with the bulk properties of sulfuric acid, i.e., its dissolving or solvent power with respect to temperature, is only possible over a very limited range of concentration. Therefore it would appear that whatever the mechanism of porous oxide formation, the function of the electrolyte is complex.

However, irrespective of the function played by the electrolyte, it is necessary to examine the implications of the reported constant barrier layer thickness maintained during porous oxide growth. Since the thickness of the porous film increases with time and current density, the independence of the barrier film thickness on the anodizing time suggests that one of the following two processes follows the establishment of this constant barrier film thickness: (a) either the migrating cations emerging at the barrier layer–electrolyte interface form, with  $\text{O}^{2-}$  or  $\text{OH}^-$ , porous oxide directly; or (b) the migrating cations and/or anions form barrier layer oxide at the oxide–electrolyte and/or the metal–oxide interfaces, respectively, and this barrier layer oxide is then converted into porous layer, by some means or other, at a rate equal to the rate of formation of barrier layer, thereby maintaining the effective barrier layer thickness a constant.

In the absence of a conversion process, whatever its nature, if (a) were correct, this would, if anions were mobile to any extent, produce a barrier layer whose thickness was continually increasing with time. Since this is not observed experimentally, and since it has been demonstrated<sup>84</sup> that even in porous film formation anions are a mobile species, (a) is clearly untenable and can be rejected. Therefore it can be tentatively concluded that (b) is the more feasible process. However, this now introduces the difficulty of describing the nature of the barrier layer oxide to porous layer oxide conversion process.

Morphological changes in depositing material are a common occurrence in electrochemistry,<sup>207</sup> but in the present case the

situation is complexed by the appearance of what is reported<sup>52, 208, 209</sup> to be a uniform geometric distribution of pores throughout the second morphological form, the porous oxide. Hunter and Fowle<sup>51</sup> have suggested that this conversion process is of a purely chemical nature, involving acidic electrolyte conditions at the pore bases, i.e., the conversion sites, far removed from those existing in the bulk of electrolyte. This will be dealt with more fully later in the pore-formation theories section.

Before further attempts are made to identify this conversion process, the influence of the anodizing electrolyte temperature upon the porous film formation rate will be considered. As the electrolyte temperature increases, the current density produced at any constant applied voltage increases rapidly; the relationship between the two appears to be exponential. Since the porous film formation rate should increase with an increase in current density, thicker films should be found at higher temperatures. That this is not so has been shown by Spooner<sup>210</sup> and has been well known for many years. This temperature effect, which, at low temperatures (0–5°) produces the type of porous film referred to as a "hard" oxide coating and at high temperatures (70–80°) produces conditions near to those present in electropolishing, is due to an external surface dissolution process by the electrolyte—in the present context, 15% w/v sulfuric acid.

To summarize the situation with respect to temperature, as the electrolyte temperature increases the current density, based upon the electrode geometric area, at any constant voltage increases. This current density increase is not reflected in an increased film thickness since there is a complex dissolution process at the porous layer outer surface. From the results of Hunter and Fowle,<sup>51</sup> it can be seen that an increase in temperature from 43.3 to 71.1° produces a fourfold increase in the current density. How does this current density increase arise, considering that the barrier layer thickness has been reported<sup>50</sup> as being approximately constant up to at least 60°? Analysis of the situation shows that, at the electric field strengths involved in this process, a very small increase in  $E$  can influence  $i_+$  greatly. It can be shown that it requires only a 6–7% increase in  $E$  to effect a fourfold increase in  $i_+$ . A 6–7% increase in  $E$  requires either a commensurate increase in the potential drop across the film or a decrease in the barrier layer thickness. It should be mentioned here that any thickness measurement, which is either not accurate to 6–7% or gives only an average value of the thickness, will not be adequate to decide which of these two possible reasons is correct. The present authors suggest that, although evidence has been reported in favor of a constant barrier layer thickness up to 60°, the small variation required in the thickness may fall below the experimental accuracy of the method of thickness determination used by Hunter and Fowle (see section II.C.5).

In conclusion it could be said that the so-called "anodizing ratio" is a misnomer, in that it applies only at one electric field strength value; e.g.,  $10 \text{\AA V}^{-1}$  applies only at fields to  $10^7 \text{ V cm}^{-1}$  and at no other. For those instances where the exact barrier film thickness is not required, it is, at least, an adequate measurement of the thickness. However, in those

(208) C. J. L. Booker, J. L. Wood, and A. Walsh, *Nature*, 176, 222 (1955).

(209) C. J. L. Booker, J. L. Wood, and A. Walsh, *Brit. J. Appl. Phys.*, 8, 347 (1957).

(210) R. C. Spooner, *J. Electrochem. Soc.*, 102, 156 (1955).

(207) K. Huber, *J. Electrochem. Soc.*, 62, 675 (1958).



cases where accurate values are important, e.g., in kinetic studies, it will obviously be inadequate.

With respect to the conversion process of barrier layer to porous layer, the possibility of a small decrease in the barrier layer thickness as the electrolyte temperature increases, with the concurrent increase in porous layer formation rate, makes the purely chemical conversion process even more difficult to accept. At the present time, however, it is difficult to conceive the exact nature of this conversion process, although the authors do consider that the process may be a field-assisted process in some way, as suggested originally by Hoar and Mott.<sup>211</sup>

## 2. The Coating Ratio and the Outer Porous Oxide Surface Dissolution Process

The coulombic efficiency for the formation of porous oxide films on aluminum in sulfuric acid has been determined by many workers.<sup>210, 212, 213</sup> This efficiency can be expressed in terms of a coating ratio which is given by

$$\frac{\text{weight of oxide formed}}{\text{weight of aluminum consumed}}$$

and is determined as follows. The aluminum electrode to be used is carefully weighed just prior to oxide formation; let this weight be  $W_1$ . The oxide formation is then carried out for the required time under carefully controlled known conditions, and the electrode is then reweighed: weight  $W_2$ . The electrode with its oxide film is then immersed in a solvent which dissolves only the oxide film, i.e., phosphochromic acid. Following oxide removal, the electrode is then reweighed: weight  $W_3$ . The usual practice in the oxide removal stage is to immerse the electrode in the phosphochromic acid and reweigh until a constant final electrode weight is obtained. The coating ratio is then calculated from the weighings. Thus

$$\text{coating ratio} = \frac{W_2 - W_3}{W_1 - W_3}$$

If the coulombic efficiency of aluminum conversion to alumina were 100% (as has been shown<sup>214</sup>), then the coating ratio would be 1.89 (2.20 if 14%  $\text{SO}_3$  were incorporated into the oxide film). Experimental observations indicate that the values measured are always less than these values and decrease as the electrolyte temperature and concentration increase. For example, with 12 A ft<sup>-2</sup> in 25% sulfuric acid at 120°F the anodic oxide formed upon aluminum dissolves almost as fast as it is formed. These are conditions approximating to electropolishing, where the coating ratio is <0.3.

The possible reasons for this behavior are the following. (a) Not all the aluminum consumed goes toward oxide formation. Some aluminum may go directly into solution without recourse to oxide formation. (b) Aluminum may be dissolving with the known "negative difference effect"<sup>215, 216</sup> which has been attributed to a low apparent valency state. (c) Although

the conversion of aluminum to oxide may be 100% efficient, the observed coating ratios are low, owing to outer surface dissolution of the porous film formed.

Dealing firstly with (c) and rewriting the coating ratio as

$$\frac{(\text{wt of oxide formed}) + (\text{wt of oxide lost due to dissolution})}{\text{wt of Al consumed}}$$

or as

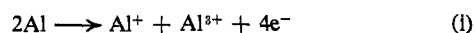
$$\frac{\text{wt of oxide formed}}{(\text{wt of Al consumed}) - \left( \frac{\text{wt of Al found in solution}}{\text{due to oxide dissolution}} \right)}$$

would, these authors suggest, produce coating ratios up to theoretical expectations. The experimentally observed porous film thickness ( $D$ ), under conditions where an outer surface oxide dissolution process was present, may be written as

$$D = D_0 - k f(c, T) t$$

where  $D_0$  is the theoretical porous film thickness obtained by calculation,  $k$  is the outer surface dissolution rate constant which is some direct function of electrolyte concentration  $c$  and temperature  $T$ , and  $t$  is the anodizing time. It can be seen that, if  $D_0$  is taken as a constant in a series of experiments, i.e., films formed under constant current density for a constant time interval, then any increase in temperature  $T$ , or concentration  $c$ , will increase the second term and hence reduce the observed oxide thickness,  $D$ . Similarly, if the dissolution rate constant is held constant, i.e., anodizing at constant electrolyte concentration and temperature, then an increase in  $D_0$  will produce an increase in the observed oxide thickness,  $D$ . Hence, the coating ratio will increase with increasing formation current density as observed, since the increased formation rate is not accompanied by an increased outer surface dissolution rate. It can also be seen that, except perhaps at very low temperatures where  $k$  may be small compared to  $D_0$ , the experimental porous oxide film thickness  $D$  will always be less than the theoretical value  $D_0$ . This has been partially confirmed by Wood, Marron, and Lambert<sup>33</sup> who reported that the thickness of porous films, produced on an Al-Mg alloy from sulfuric acid at 30°, is one-third thinner than theoretically expected. A similar conclusion has been made by the present authors<sup>217</sup> from the work of Nagayama and Tamura.<sup>218</sup>

Referring now to reason (a) as to why low coating ratios are experimentally observed, it would be difficult to distinguish between that aluminum going directly into solution without recourse to oxide, and that aluminum in solution resulting from outer oxide surface dissolution. However, it is difficult to envisage why the ratio of aluminum going directly into solution to the aluminum going toward oxide formation should be such a strong function of temperature, as it necessarily must be to obtain thinner films at higher temperatures. This difficulty is also incurred if one considers the possibility of formation of the univalent  $\text{Al}^+$  ion. This can be seen clearly from the following reactions. Consider



Neglecting, for the present discussion, the fact that reaction

(217) J. W. Diggle, T. C. Downie, and C. W. Goulding, *J. Electroanal. Chem.*, **18**, 192 (1968).

(218) M. Nagayama and K. Tamura, *Electrochim. Acta*, **12**, 1097 (1967).

(211) T. P. Hoar and N. F. Mott, *J. Phys. Chem. Solids*, **9**, 97 (1959).

(212) R. B. Mason and P. E. Fowle, *J. Electrochem. Soc.*, **101**, 53 (1954).

(213) R. B. Mason and C. J. Slunder, *Ind. Eng. Chem.*, **39**, 1602 (1947).

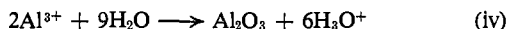
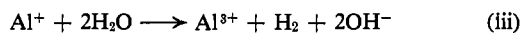
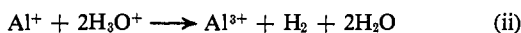
(214) M. Tosterud and R. B. Mason, *J. Electrochem. Soc.*, **90**, 221 (1946).

(215) M. Straumanis and Y. N. Wang, *ibid.*, **102**, 304 (1955).

(216) E. Rajola and A. W. Davidson, *J. Amer. Chem. Soc.*, **78**, 556 (1956).

i is unlikely to occur as written, this equation gives aluminum dissolving anodically with an apparent valency of 2, *i.e.*, the activities of  $\text{Al}^+$  and  $\text{Al}^{3+}$  are equal. If the activity of  $\text{Al}^{3+} >$  activity of  $\text{Al}^+$ , the apparent valency will lie between 2 and 3.

Reaction i could then be followed by reactions ii or iii and iv.



The only way one can account for the low coating ratios (completely ignoring outer oxide surface processes) is to propose that the  $\text{Al}^{3+}$ , produced in reaction ii or iii, diffuses rapidly into the solution bulk without recourse to oxide formation, the  $\text{Al}^{3+}$  produced by reaction i being the only oxide producing species *via* reaction iv. Reaction iii pertains strictly to magnesium; an analogy is assumed.<sup>219, 220</sup>

Since coating ratios are known to decrease rapidly with temperature, and assuming all the above reactions to be correct, the only way one can explain this is to suggest that the ratio  $\text{Al}^+/\text{Al}^{3+}$  in reaction i increases with temperature, *i.e.*, the apparent valency of anodically dissolving aluminum in sulfuric acid should tend to unity as the temperature increases. As far as the authors are aware, the apparent valency of aluminum dissolving anodically in sulfuric acid has not been reported. The anodic dissolution of aluminum in a magnesium perchlorate-water-alcohol mixture has been reported by Garreau and Epelboin,<sup>221</sup> who have shown that the limiting value of the mean valency for dissolving aluminum is unity; therefore, the primary stage in aluminum dissolution may be  $\text{Al}^+$  formation as per reaction i. However, to account for the low coating ratios at high temperatures, it is still necessary to assume the  $\text{Al}^{3+}$  produced from  $\text{Al}^+$  by chemical reaction diffuses away rapidly into solution without oxide formation.

The temperature coefficient of the apparent valency has been studied<sup>222</sup> for the anodic dissolution of cadmium. A small temperature dependence was observed—apparent valency decreasing as temperature increases—but was not of the magnitude required by aluminum dissolving in sulfuric acid, *i.e.*, tending from 3 to 1 as the temperature increased. Cadmium and aluminum, although both exhibiting low apparent valencies when dissolving, may not be analogous from a mechanism standpoint, since anodic disintegration was proposed<sup>223</sup> to account for the low apparent valency in the case of cadmium, and therefore absence of the required temperature dependence in the case of cadmium may not be too meaningful.

At the present time, although the formation of  $\text{Al}^+$  may be involved in primary dissolution reactions, it is considered by the authors that the outer surface dissolution of the forming porous oxide film is the more probable explanation of the low coating ratios.

In conclusion, the phenomena of the formation of porous layers and the concurrent dissolution processes can be sum-

marized as follows. (a) Ionic migration, initially to form a barrier layer which, in the complete absence of electrolyte solvent power, will remain as barrier layer. (b) In electrolytes with solvent power, a conversion process becomes operative when the barrier layer reaches a certain thickness. This barrier layer to porous layer conversion is believed to be a field-assisted electrochemical process. (c) The porous layer thickness due to the conversion process in (b) becomes a function of current density, time, electrolyte temperature, and, to a limited extent, the electrolyte concentration. (d) Outer surface dissolution by the bulk electrolyte, which is seen as a purely chemical process, results in porous films which are experimentally thinner than those expected from the amount of charge passed calculations. This process is strongly temperature dependent in the range 5–70° and weakly dependent upon the electrolyte concentration.

Having dealt with some general phenomena, the details of structure and formation theories of porous films will now be reviewed.

## B. STRUCTURE

It has been known<sup>224</sup> from as early as 1932 that the anodic oxide film on aluminum consists of two regions: an outer region of thick porous-type oxide and a thin, compact inner region lying adjacent to the metal.

From the many electronoptical investigations,<sup>52, 208, 209, 225, 226</sup> both by the replicating and the direct transmission technique, and from some gas adsorption studies,<sup>227, 228</sup> the structure of the porous anodic oxide film would appear to be essentially that reported by Keller, Hunter, and Robinson.<sup>52</sup> The technique used by Keller, Hunter, and Robinson was as follows. The aluminum, after a suitable surface pretreatment, was immersed in the anodizing electrolyte and a constant voltage was applied. The time of formation was unspecified in the original paper, but has been reported<sup>229</sup> to have been 5 min. Following formation of the film, the specimen film was then either examined by transmission electron microscopy, from which pore densities were determined, or the oxide film was stripped off in phosphochromic acid (time again unspecified; see ref 113,126) to reveal the metal-oxide interface structure. The metal surface so revealed was seen to be covered with a large number of hemispherical depressions, whose number per square centimeter corresponded to the pore density found by direct transmission. On the basis of such information, and of the influence of the formation voltage, a model was proposed for the porous oxide film; Figure 10 illustrates this structure for a film prepared in 4% phosphoric acid at 120 V.

The essential points of this structure are that each pore whose cross section was suggested (not proven) to be star shaped, lies in the center of a hexagonal-shaped oxide cell whose width is *C*. The pore diameter was reported as being independent of the anodizing voltage and the time of film formation, and to be dependent only on the electrolyte used (Table IV). The oxide cell width *C* is dependent on the an-

(219) H. H. Uhlig and R. Krutenat, *J. Electrochem. Soc.*, **111**, 1303 (1964).

(220) R. Krutenat and H. H. Uhlig, *Electrochim. Acta*, **11**, 469 (1966).

(221) M. Garreau and I. Epelboin, *J. Chim. Phys.*, **63**, 1515 (1966).

(222) J. W. Johnson, E. Deng, S. C. Lai, and W. J. James, *J. Electrochem. Soc.*, **114**, 424 (1967).

(223) M. E. Straumanis and K. Poush, *ibid.*, **112**, 1185 (1965).

(224) S. Setoh and A. Miyata, *Sci. Pap. Inst. Phys. Chem. Res. (Tokyo)*, **19**, 237 (1932).

(225) H. Grubitsch, W. Geymeyer, and E. Buvik, *Aluminium*, **37**, 569 (1961).

(226) M. Paganelli, *Aluminio*, **27**, 3 (1958).

(227) R. L. Burwell, P. A. Smudski, and T. P. May, *J. Amer. Chem. Soc.*, **69**, 1525 (1947).

(228) G. Paolini, M. Masaero, F. Sacchi, and M. Paganelli, *J. Electrochem. Soc.*, **112**, 32 (1965).

(229) R. W. Franklin and D. J. Stirland, *ibid.*, **110**, 262 (1963).

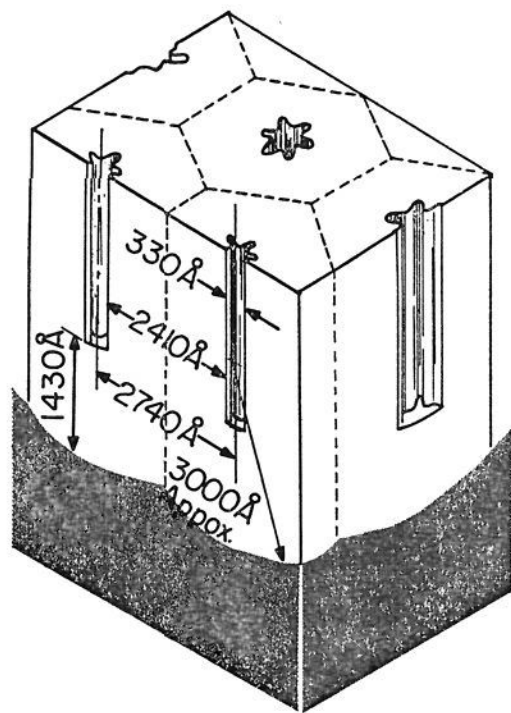


Figure 10. Cylindrical pore model proposed by Keller, Hunter, and Robinson<sup>52</sup> for a porous film prepared in 4% phosphoric acid at 120 V and 24°.

Table IV

The Pore Diameter, Given as Being Independent of the Formation Voltage, of Porous Films Formed in Four Commonly Used Electrolytes<sup>a</sup>

Electrolyte concentration (temp, °C)	Pore diameter, Å
4% phosphoric acid (24)	330
3% chromic acid (38)	240
2% oxalic acid (24)	170
15% sulfuric acid (10)	120

<sup>a</sup> Values are those reported by Keller, Hunter, and Robinson.<sup>52</sup>

odizing voltage since, as was the case for the barrier layer thickness (see Table III), the pore wall thickness has a certain Å V<sup>-1</sup> anodizing ratio; Table V shows this pore wall thickness anodizing ratio for the four most commonly used pore-form-

Table V

The Pore Wall Thickness Anodizing Ratio for Porous Films Formed in Some Typical Pore-Forming Electrolytes<sup>a</sup>

Electrolyte concentration (temp, °C)	Pore wall thickness, Å V <sup>-1</sup>
4% phosphoric acid (24)	11.0
3% chromic acid (38)	10.9
2% oxalic acid (24)	9.7
15% sulfuric acid (10)	8.0

<sup>a</sup> Reported by Keller, Hunter, and Robinson.<sup>52</sup>

ing electrolytes. As the anodizing voltage increases, the width *C* of the oxide cell increases also and so consequently the number of pores per unit area should decrease. Table VI shows the pore density as a function of anodizing voltage for 15% sulfuric acid at 10°.<sup>52</sup>

Table VI

Pore Density as a Function of the Applied Anodizing Voltage for Films Formed in 15% Sulfuric Acid at 10°

Anodizing voltage, V	Pore density × 10 <sup>9</sup> cm <sup>-2</sup>
15	83
20	56
30	30

An important property of a porous film is its pore volume, which is defined as the percentage or fractional volume of the film occupied by pores. If the pores are considered as perfect cylinders,<sup>52</sup> then the pore volume should be independent of the porous film thickness, current density, electrolyte concentration, and anodizing temperature. Evidence has been reported to indicate that the pore volume is in fact a function of all four of these parameters.<sup>32, 228, 230</sup> Therefore the treatment of the pores as perfect cylinders would appear to be incorrect. The evidence reported by Mason,<sup>230</sup> with regard to pore volume as a function of the anodizing temperature, for films prepared in 15% sulfuric acid, would appear, however, to be slightly ambiguous. The anodizing process used was a constant current density formation, and, presumably, as the electrolyte temperature increased, the voltage required to maintain this constant current density decreased. Since the decrease in the formation voltage will produce an increase in the film pore volume, the increase in the pore volume due to an electrolyte temperature increase cannot be considered conclusive.

Some recent work by Wood, O'Sullivan, and Vaszko<sup>231</sup> has shown that the geometrical pore model of Keller, Hunter, and Robinson is essentially correct. By a sectioning technique, vertical to the aluminum surface, the pores, the barrier layer, and the scallops, above which the pores are located, can all be clearly seen. The dimensions of the porous film prepared in 4% phosphoric acid at 25° (77°F) are somewhat different, particularly with respect to the pore diameter. For example, according to Table IV, the pore diameter by Keller, Hunter, and Robinson,<sup>52</sup> although an extrapolated value, is seen as 330 Å; Wood, O'Sullivan, and Vaszko<sup>231</sup> have reported values ranging from 700 to 800 Å. This pore diameter is larger than that reported for an electropolished film formed in H<sub>3</sub>PO<sub>4</sub>-butyl alcohol mixture at 60° (see Table IX). This is perhaps somewhat unusual considering the stronger dissolution processes operative in an electropolishing bath.

The barrier layer Å V<sup>-1</sup> ratio was reported<sup>231</sup> as being 10.1 Å V<sup>-1</sup>, somewhat less than the value reported<sup>52</sup> in Table III. The pore wall thickness was assumed<sup>231</sup> to be equal to the barrier layer thickness at one voltage, an assumption not verified by Table V. Despite the reported variations in the film dimensions, this work does provide excellent evidence for the model of Keller, Hunter, and Robinson.<sup>52</sup>

Consideration of the outer surface dissolution processes can lead to the proposal of nonuniform pore geometry as the outer surface is approached; evidence for such nonuniformity has been reported.<sup>231</sup> The true pore geometry has been proposed<sup>228</sup> to be that of a truncated cone whose basal diameter is

(230) R. B. Mason, *Metal Finishing*, 8, 55 (1957).  
(231) G. C. Wood, J. P. O'Sullivan, and B. Vaszko, *J. Electrochem. Soc.*, 115, 618 (1968).

that reported by Keller, Hunter, and Robinson,<sup>52</sup> and whose mouth diameter depends on the current density and the anodizing time, *i.e.*, upon the film thickness. Table VII illustrates these proposals in the case of 20% sulfuric acid anodizing. The degree of slant of the pore walls can be indicated by considering that the pore diameter changes from 120 to 159 Å through a porous film thickness of 9  $\mu$ , *i.e.*, very slight slant.

Table VII

Tabulation of Available Data<sup>228</sup> Showing How the Pore Mouth Diameter Increases as the Formation Current Density and the Anodizing Time Increases

Current density, mA cm <sup>-2</sup>	Anodizing time, min	Pore base diameter, Å	Pore mouth diameter, Å
10	30	120	159
15	30	120	182
15	60	120	246
25	30	120	208

From Table VII it is seen that the anodizing time increases from 30 to 60 min, at a current density of 15 mA cm<sup>-2</sup>; the pore mouth diameter increases from 182 to 246 Å, *i.e.*, the pore mouth diameter approaches the value of the oxide cell width reported<sup>228</sup> as 316 Å. If the anodizing were to proceed beyond 60 min, the pore mouth diameter may approach this figure of 316 Å until finally the pore mouth diameter equals the oxide cell width. This then defines the maximum thickness to which the porous film can grow; the use of anodizing times in excess of this point will not produce a thicker film, but may even produce a decrease in film thickness due to the outer surface dissolution processes. Some evidence in favor of this maximum anodic film thickness concept can be obtained from the work of Liechti and Treadwell<sup>86</sup> in which the anodic film thickness and the change in the total specimen thickness were determined for sulfuric acid and oxalic acid anodizing. Figure 11 represents graphically the results obtained. Curve i represents a theoretically determined formation rate, at a current density of 10 mA cm<sup>-2</sup>, of 0.33  $\mu$  min<sup>-1</sup>. Curve ii represents the oxide film thickness against anodizing time for a stirred solution of 0.16 M (oxalic acid, formation conditions:  $i = 10$  mA cm<sup>-2</sup>,  $V = 120$  V). Curve iii represents the oxide film thickness-anodizing time relationship for a stirred solution of 10% sulfuric acid (formation conditions:  $i = 10$  mA cm<sup>-2</sup>, temperature 18–20°, and a formation voltage of approximately 15 V). Curve iv is the change in the total specimen thickness with respect to anodizing time for 10% sulfuric acid; *i.e.*, curves iii and iv are related.

It is seen from Figure 11 that the oxide film thickness is always less than the theoretical value whether the electrolyte be oxalic or sulfuric acid. After 5 hr, where the oxide film is 70  $\mu$  thick, the film in sulfuric acid is seen to have attained a maximum thickness. Curve iv is seen to have an inflection point at 4 hr, beyond which the thickness of the specimen decreases rapidly owing to metal loss without a commensurate increase in the oxide film thickness. If the descending section of curve iv were due to direct metal loss to solution without oxide formation, it can be shown that the slope of the descent should be approximately 0.33  $\mu$  min<sup>-1</sup>. If metal loss occurs *via* oxide film formation and equal subsequent loss by dissolution, the slope should also have a value approaching 0.33  $\mu$  min<sup>-1</sup>. The slope from Figure 11 is found to be 0.29  $\mu$  min<sup>-1</sup>,

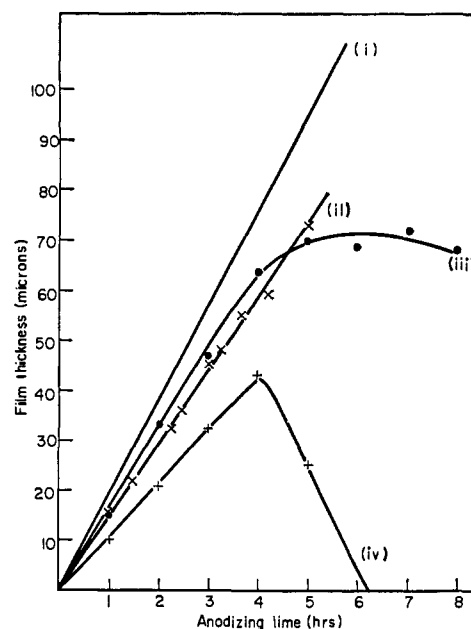


Figure 11. Porous film thickness as a function of the anodizing time at a current density of 10 mA cm<sup>-2</sup>. Curve i is the theoretical rate of formation, equal to 0.33  $\mu$  min<sup>-1</sup>; (ii) is the experimental plot for 0.16 M oxalic acid; (iii) is the experimental plot for 10% sulfuric acid; and (iv) is the change in the total specimen thickness for the anodizing process represented by curve iii.

and therefore either of the above arguments could be correct. The latter is favored by the present authors as the more probable.

Oxalic acid, although apparently similar to sulfuric acid with respect to dissolution power (Figure 11, curves ii and iii), is unlike sulfuric acid with respect to the maximum attainable film thickness. This may be due simply to the much greater oxide cell size in the case of oxalic acid. Table VIII illustrates this difference.

Table VIII

Tabulation of the Pore Diameter, Oxide Cell Size, and the Maximum Oxide Thickness for Anodizing in Two Pore-Forming Electrolytes under the Conditions Specified

Liechti and Treadwell <sup>27</sup> anodizing conditions	Pore diameter, Å <sup>232</sup>	Oxide cell size, Å <sup>232</sup>	Maximum oxide thickness, $\mu$
15% sulfuric acid at 15 V	120	360	70
0.16 M oxalic acid at 120 V	170	2500	Estimated by the present authors as 1000

Similar work has been reported by Golubev and Ignatov,<sup>233</sup> in which it was shown that anodic films formed either on pure aluminum or its alloys exhibited a much lower maximum thickness in the case of 20% sulfuric acid than for a solution of 20% sulfuric acid containing 1% oxalic acid. The maximum

(232) It is assumed that the anodizing ratios presented in the literature<sup>92</sup> apply to these anodizing conditions.

(233) A. I. Golubev and N. N. Ignatov, *Protect. Metals*, 4, 396 (1965); *Zashchita Metal.*, 4, 445 (1965).

anodic film thickness for the sulfuric–oxalic acid electrolyte was reported to decrease rapidly as the anodizing temperature increased from 15 to 35°; the maximum thickness at 35° for this electrolyte was approximately equal to that for 20% sulfuric acid at 20°. This behavior of the sulfuric–oxalic acid mixture may be due partly to a reduced degree of dissolution at the outer oxide surface,<sup>212,224</sup> and to an increase in the oxide cell size. However, without definite evidence for this increase in the oxide cell size, this can only be regarded as speculative.

In summarizing, it may be said that the dissolution processes at the outer oxide surface govern, to a greater or lesser extent, not only the final film thickness, *i.e.*, the coating ratio, but also the pore mouth diameter, the pore volume, and the maximum film thickness attainable during any anodic oxidation. Evidence has been reported<sup>235,236</sup> to show that the pore diameter is a function of the sulfuric acid electrolyte concentration, which provides another indication as to the importance of electrolyte in defining the dimensions of the porous film.

Franklin and Stirland<sup>229</sup> have reported, from a study of the optical anisotropy of these types of films, that the pore axis is not vertically inclined to the metal surface, as assumed in the models previously outlined, the angle subtended to the metal surface being either greater or less than 90°. The degree of axis slant is dependent on the substrate grain orientation, being a constant over one particular orientation.

Apart from the structure proposed by Keller, Hunter, and Robinson,<sup>52</sup> several other studies have been reported, the results of which have been suggested to reveal a basic inconsistency in the cylindrical pore model.

Csokán<sup>237–239</sup> in an investigation of hard anodic oxide films on aluminum, *i.e.*, those films formed at low temperatures (0–5°) and usually in dilute sulfuric acid, has reported that the pore structure is not as regular as was previously believed. The structure that was observed experimentally was one in which the pore distribution was irregular and where the pores themselves were twisted and bent or otherwise distorted. The occurrence of a high density of pore openings at the surface appeared to produce a fibrous structure, whose size, shape, and orientation varied considerably. This type of arrangement produced what appeared to be, under polarized light, a laminated structure lying parallel to the aluminum surface. The aluminum subgrain structure was suggested to influence, at least partially, the orientation of the groups of pore channels. That pore colonies can occur at some preferred sites has also been suggested by Renshaw.<sup>240</sup>

The porous structure, instead of being represented as an array of regularly distributed, densely packed oxide cells, has been suggested<sup>35,241</sup> to be a fibrous structure, the hollow fibers standing vertically to the aluminum surface. The alumina was reported as being amorphous and to contain significant quantities of the hydroxide and the electrolyte anion. Similar to the proposal<sup>10,242</sup> that the material comprising the center of

an oxide cell is more soluble than the material at the outer boundaries of the cell, the outer wall of the fiber was said to be amorphous alumina and the inner wall aluminum hydroxide containing the electrolyte anion.

Basically, the models proposed by Csokán<sup>238</sup> and by Ginsberg and Wefers<sup>35</sup> are similar in that a fibrous structure is proposed, which can be either regular<sup>35</sup> or irregular.<sup>238</sup> Apart from being fibrous, Csokán suggests a laminar-type structure which is not inferred by Ginsberg and Wefers. Reference will be made again to this laminar oxide structure when the Murphy and Michelson<sup>15</sup> model for these porous anodic films is discussed.

Since it has been said that the electrolyte used in the anodizing process governs, to some extent, not only the type of film but also the dimensions of the film structure, it is perhaps then not surprising that the structure proposed by Keller, Hunter, and Robinson<sup>52</sup> for films formed near room temperature is different, in structural detail, from that reported by Csokán at 0–5°. For these low-temperature films it might be predicted that the pore mouth diameter and the oxide cell size will be smaller; *i.e.*, the pore density for a film growing at an equivalent rate to that at room temperature will be much greater. The maximum film thickness will be greater, and the film will be mechanically harder and more abrasion-resistant owing to a general tightening-up of the porous structure.

If anodic oxide films were to be formed in 10–20% sulfuric acid at 60–70°, it is possible, on the basis of increased electrolyte dissolution activity, to suggest what one might expect to find in a structural investigation. Firstly, the pore mouth diameter should have a value which approaches the width of the oxide cell. Secondly, the porous layer thickness should be many orders thinner than that formed under comparable conditions at room temperature. Thirdly, the barrier film thickness should be slightly thinner than that obtained at room temperature under comparable voltage conditions—thinner because of the much higher current densities and hence the higher electric field strengths. A decrease of 6–7% was estimated earlier in section IV.A for a fourfold current density increase. The structure reported by Holló<sup>243,244</sup> for electropolished aluminum surfaces reveals at least some of these characteristics. The electropolishing procedure used in this work<sup>243</sup> was to take an 80–20 mixture of phosphoric acid and butyl alcohol, at a temperature of 60–65°, with voltages ranging from 10 to 40 V; these conditions produced current densities of 30–50 mA cm<sup>-2</sup>. Figure 12 shows the essential features of the structure proposed by Holló for an electropolished aluminum surface formed at 30–35 V. The present authors, using the data of Holló, have estimated that such a film, formed at 30 V, should have a theoretical alumina formation rate (assuming 100% current efficiency and 100% conversion of aluminum to alumina) of approximately 9000 Å min<sup>-1</sup> for a reported<sup>243</sup> period of 10–15 min. The porous layer thickness shown in Figure 12 is seen to be considerably less than this theoretical figure. Calculation shows that this represents a dissolution of the formed film of 98–99% at this temperature of 60–65°. (This can be compared to the figure of 33% at 30° for sulfuric acid films.<sup>33</sup>)

Table IX shows a comparison of the film parameters for a 30-V 4% H<sub>3</sub>PO<sub>4</sub> film and an electropolished structure also

(234) P. N. Petrov, *Zh. Prikl. Khim.*, **39**, 589 (1966).

(235) C. N. Ts'ao, *Chung Kuo K'o Hsueh Yuan Ying Yung Hua Hsueh Yen Chiu So Chi K'an*, **5**, 6 (1962); *Chem. Abstr.*, **64**, 1621a (1966).

(236) C. N. Lee, S. J. Lee, and H. J. Kim, *Kungnip Kongop Yonguso Pogo*, **15**, 121 (1965); *Chem. Abstr.*, **67**, 28646x (1967).

(237) P. Csokán and M. Gy. Holló, *Werkstoffe Korrosion*, **12**, 288 (1961).

(238) P. Csokán, *Electroplating Metal Finishing*, **15**, 75 (1962).

(239) P. Csokán, *Trans. Inst. Metal Finishing*, **41**, 51 (1964).

(240) T. A. Renshaw, *J. Electrochem. Soc.*, **108**, 185 (1961).

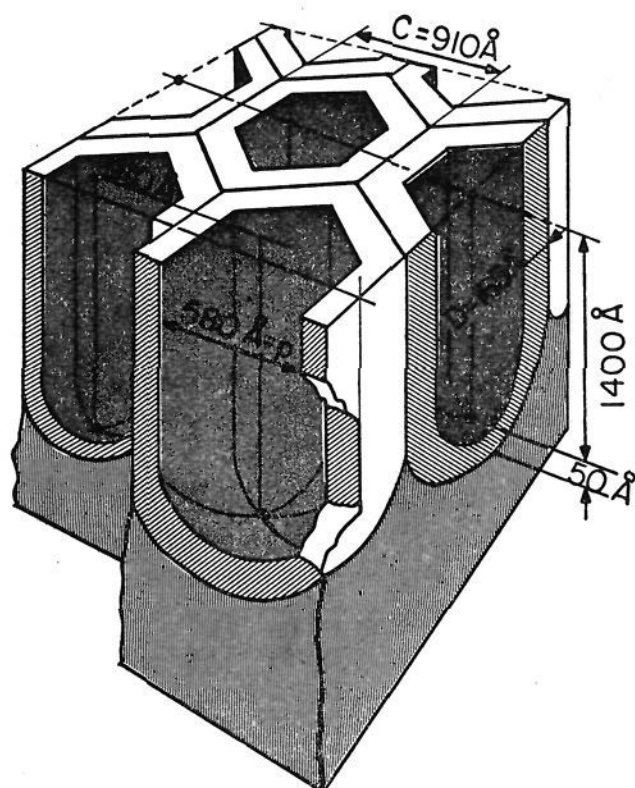
(241) H. Ginsberg and K. Wefers, *Metall* (Berlin), **16**, 173 (1962).

(242) R. W. Franklin, *Nature*, **180**, 1470 (1957).

(243) M. Gy. Holló, *Acta Met.*, **8**, 265 (1960).

(244) M. Gy. Holló, *Rev. Met.*, **57**, 23 (1960).





**Figure 12.** Idealized cellular structure proposed by Holló for the oxide film formed upon aluminum (99.99% purity) by electropolishing in a phosphoric acid-butyl alcohol mixture at 30 V.

formed at 30 V (Figure 12). From this table the pores per square centimeter and the oxide cell size for the two films are in good agreement, but the barrier layer is much thinner in the case of the electropolished surface structure. The pore

Table IX

Comparison of the Dimensions of a Porous Film Formed in 4%  $H_3PO_4$  and an Electropolished Film Structure Formed on Aluminum in Phosphoric Acid-Butyl Alcohol Mixture

Anodic film parameter	30-V 4% $H_3PO_4$ film, 24° <sup>a</sup>	30-V electro- polished film, $H_3PO_4$ -butyl alcohol, 60-65° <sup>b</sup>
Pore diameter (Å)	330	580
Oxide cell size (Å)	990	910
Barrier layer thickness (Å)	360	50
Pores per sq cm	$7-8 \times 10^9$	$7-8 \times 10^9$

<sup>a</sup> Keller, Hunter, and Robinson, ref 52. <sup>b</sup> Holló, ref 243, 244.

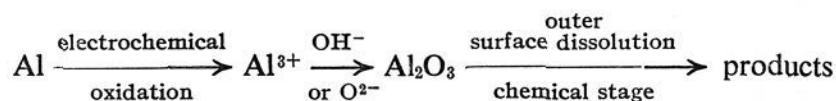
diameter at the higher temperature is much larger than that at the lower temperature, and this is what would be expected considering the evidence presented for the pore mouth diameter being dependent on the temperature of film formation. In Figure 12 the pores are shown to be parallel sided, but since the pore diameters were obtained<sup>243</sup> from direct transmission electron micrographs, the diameter of the pores in Figure 12 strictly refers to the pore mouth diameter, and therefore the pore itself may have a truncated cone shape.

The value of 50 Å reported for the barrier layer thickness (Figure 12) at an applied voltage between 30 and 35 V, as compared to that for a film formed in 4%  $H_3PO_4$ , would suggest either (a) a very low anodizing ratio, *i.e.*, between 1 and 2 Å V<sup>-1</sup>, or (b) that the potential drop across the barrier layer is considerably less than 30-35 V; assuming a 10 Å V<sup>-1</sup> anodizing ratio, a 50-Å film would require only 5 V potential

drop. Since the pores per square centimeter, the value of which is inversely proportional to the formation voltage, of the two films are in good agreement (Table IX), (b) would appear to be unlikely. With regard to (a), evidence has been presented<sup>51</sup> to show that the anodizing ratio of 90% w/w sulfuric acid is <1 Å V, and, since 80% v/v (90% w/w) phosphoric acid is used in the electropolishing solution, a similar anodizing ratio may not be considered unusual in the present case. Evidence for this is, however, lacking, as is an understanding as to why the anodizing ratio should rapidly decrease to <1 Å V for 90% w/w sulfuric acid.<sup>51</sup>

Although the agreement between the pores per square centimeter and the oxide cell size for the anodic film and the electropolished structure (Table IX) are in good agreement at 30 V, agreement is not so good at other voltages. This is due to the fact that the oxide cell size, for an anodic film, has been reported<sup>52</sup> as being a linear function of the formation voltage, while for the electropolished structures in the work of Holló a parabolic relationship was found. The intersection of these two relationships occurs at 30 V for a substrate 99.99% pure. This parabolic relationship between oxide cell, pore diameter, and pore wall thickness appears to depend upon the purity of metal and on whether the pure metal or alloy is used as the substrate. Extrapolation of the parabolic curve to zero voltage gave an intercept whose value was determined both by the substrate and the electrolyte; in the case of pure aluminum, the intercept value of the pore diameter approximated to that reported for a 4% phosphoric acid film.<sup>52</sup> An interpretation was offered by Holló<sup>243, 244</sup> for the formation of these electropolished structures which involved the opposing interactions of the oxidation and dissolution rates, each rate being dependent on substrate grain orientation to some extent.

Although it is often implied that electropolished surfaces, involving oxide formation, are distinct from anodic oxide films, the present authors have included the electropolished structures formed on aluminum since it is considered that such structures can arise naturally from anodic oxide films, providing adequate consideration is given to the outer porous surface dissolution processes. A recent study of electropolished and anodized aluminum surfaces<sup>245</sup> has concluded that the two surfaces differ only in the type of control in operation. Anodic oxidation is under the chemical stage control (electrochemical formation rate fast), while electropolishing is under electrochemical oxidation control (chemical stage now being the fast stage). To make this a little clearer, the following may be written.



anodic oxidation: electrochemical oxidation fast  
chemical dissolution stage slow  
electropolishing: electrochemical oxidation slow  
chemical dissolution stage fast

Before moving to the final model for the porous anodic oxide structure, an important experimental fact will be considered. This is during a porous anodic oxide formation; *e.g.*, in 15% w/w sulfuric acid, in which a formation voltage change is made, the oxide cell base pattern, revealed upon oxide stripping, is that characteristic of the second voltage (in a multi-change process, the cell base characteristics are those of the

(245) S. Ya. Grilikhes and N. P. Fedot'ev, *Zh. Prikl. Khim.*, **40**, 841 (1967).

final voltage). Interpretation of this in terms of the cylindrical pore model<sup>52</sup> requires that, for a voltage decrease, new pores should be formed, while for a voltage increase some pores should cease to function. It should be noted, however, that changes in the porous film dimensions away from the barrier layer interface cannot be inferred from this evidence, but only that changes occur at the interface between the porous and the barrier layers.

Murphy and Michelson,<sup>15</sup> with knowledge of the experimental fact above,<sup>246</sup> and a suggestion that the pores are actually formed during the preparation of the film for electron-optical investigation (this latter suggestion is, however, largely nullified, since a great amount of evidence has been obtained by direct transmission,<sup>52, 228, 247</sup> sectioning,<sup>208, 209, 226, 281</sup> and by other methods<sup>227</sup>), have proposed a structure which has been described as a triple layer or a colloidal gel model. The suggested composition of these three layers is as follows. (1) An inner, relatively compact, anhydrous form of alumina. Most probably this is of nonuniform composition, with small submicro crystallites joined by regions in which the oxide structure is not so uniform and where hydration can occur. (2) An intermediate transition region, where the conversion of the inner anhydrous region to an outer region of high hydration is seen. The hydration, present in this region, is intermediate between that of the inner and outer regions. The structure can be regarded again as submicro crystallites surrounded by regions of moderately hydrated material; it is through these regions of hydrated oxide that electrolytic conduction is assumed to occur. (3) An outer region consisting mainly of hydrated oxide, where the extent of hydration and oxide density varies. It was suggested<sup>15</sup> that it is this region, of high hydration extent and where the minimum number of submicro crystallites, exists, that possesses the precursors of the pores which are observed upon electronoptical examination.

The electric field strength present during anodizing was assumed<sup>15, 211</sup> to be sufficient to draw  $\text{OH}^-$  and water molecules in the direction of the barrier layer; the  $\text{OH}^-$  ions and the water molecules in the barrier layer-porous layer interface were suggested to cause a modification of the preformed barrier layer into a more hydrous oxide in localized regions, thereby tending to decrease the effective barrier layer thickness. At the same time, the field in this interface is such as to cause migration of protons away from the barrier layer. This results in a tendency to deprotonate or dehydrate the oxide in that region. The opposing actions of these two processes were suggested<sup>15</sup> to explain the observed dependence of the barrier film thickness on the applied formation voltage.

This structure is of the laminar type as suggested earlier by Csokán<sup>238</sup> for the hard anodic oxide film, but, unlike the Csokán model, pores were not thought to penetrate the outer sections completely to the inner layer. The pores were suggested<sup>15</sup> to penetrate only a short distance through the outer layers, in which case the pores form a much less significant part in this theory than they do in the Keller, Hunter, and Robinson model.<sup>52</sup>

Apart from structural differences, the Keller, Hunter, and Robinson<sup>52</sup> and the Murphy and Michelson models differ also with regard to the mechanism by which anions reach the

barrier layer (or inner layer (1)). In the former model, the anions are considered to diffuse by mass transport down the pore length to the barrier layer surface; in the latter model, the anions are considered to move through the oxide phase on a hydrogen-bonded network in which the anion progresses by moving from one lattice unit to the next, making and breaking hydrogen bonds as it proceeds.<sup>15</sup>

A somewhat similar model has been suggested by Bogoyavlenskii<sup>248</sup> in which the film was seen as micelles of  $\text{Al}(\text{OH})_3$  gel-like material oriented vertically to the aluminum surface by action of the electric field. The micelles, or nonons as Bogoyavlenskii terms them, are supposedly separated by pores through which further material required for continued growth is transported. These micellular interspaces reach from the outer surface of the nonons to the metal surface; the continuity of the barrier layer, which is observed experimentally, was considered to be due to the filling of the pore ends by nonons when the current was removed. This latter proposal is, however, unacceptable, since current-voltage<sup>50, 51</sup> and capacitance behavior<sup>199</sup> both indicate the presence of a compact oxide layer adjacent to the aluminum throughout the porous film formation process.

Shreider,<sup>249</sup> accepting the presence of pores at the centers of oxide cells, as proposed by Keller, Hunter, and Robinson,<sup>52</sup> has also suggested that the film is composed of a gel-like  $\text{Al}(\text{OH})_3$ ; apart from the difference in composition of the film, the model proposed by Shreider is essentially that outlined earlier.<sup>52</sup>

Although the Murphy and Michelson and Bogoyavlenskii models offer some new concepts in the structure of porous films, both are still lacking with regard to experimental verification. For example, formation of colloidal  $\text{Al}(\text{OH})_3$  is considered unlikely in highly acidic solutions, and as yet no direct evidence for the gel structure has been reported, whereas the cylindrical pore model, although realized as being ideal, has experimental verification from direct microscopical techniques. There are, however, many questions that must be answered before any model can be accepted with any degree of certainty.

One of these questions is the voltage of formation increase and decrease experiments mentioned earlier in this section. The requirement here is simply that the pore base characteristics must be a function of the voltage of formation—according to the cylindrical pore model the cell wall thickness must also change as the voltage changes; however, these changes are secondary to those at the pore base, since an increase in the cell size as the voltage increases requires the cell wall thickness to increase if the pore diameter remains appreciably constant. Evidence has been presented<sup>250</sup> to show that for porous films (prepared on aluminum in a chromate-borate electrolyte) which have undergone a three-step voltage increase during formation, the number of pores per square centimeter at the film surface is many times the number of oxide cells found at the metal surface when the oxide film is stripped off. A structure of the porous film after a threefold voltage increase was proposed and an ideal structure is shown in Figure 13 (dissolution which would lead to some distortion is ignored). Evidence to support such a structure includes the opacity

(246) It is interesting to note that this experimental evidence has been taken as strong evidence against the cylindrical pore model.<sup>52</sup> See ref 15 and 239 and a later discussion in this section.

(247) J. D. Edwards and F. Keller, *Trans. Amer. Inst. Mining Met. Engrs., Inst. Metals Div.*, 156, 288 (1944).

(248) A. F. Bogoyavlenskii, *Anodic Protection of Metals*, Paper Presented at the First Interuniversity Conference, Moscow, 1964.

(249) A. V. Shreider, *J. Appl. Chem. USSR*, 39, 2533 (1966).

(250) M. P. Gracheva, A. I. Golubev, and A. M. Ginberg, *Protect. Metals*, 1, 370 (1965); *Zashchita Metal.*, 1, 420 (1965).



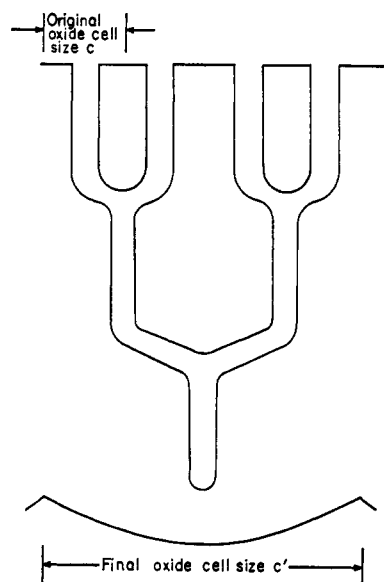


Figure 13. Structure proposed for a porous film formed in a chromate-borate electrolyte during a three-step voltage increase formation process. In this present example the number of pores is seen to be four times the number of the oxide cells at the metal surface.

of such films compared to the one-constant-voltage anodized films, and the fact that the transition times required for "steady-state" current density attainment increased from voltage 1 to voltage 3.<sup>250</sup> Wood, O'Sullivan, and Vaszko<sup>251</sup> have, by the use of micrographs, provided some degree of further proof.

If the model shown in Figure 13, proposed for a porous film having undergone a voltage increase during formation, is correct, then a voltage decrease structure should then be the reverse of Figure 13, *i.e.*, the number of oxide cells should be many times the number of pores. Some evidence is available<sup>251</sup> to show that this is essentially correct, although further work will be necessary to establish to what extent Figure 13 reflects the true situation.

Although these changes in the metal-oxide interface structure, with changes in formation voltage, would account for the final voltage value defining the oxide cell size found on stripping the oxide film, it is necessary to examine the theoretical implications of what has been suggested. Evidence is available to suggest that the pores of a porous film appear to occur at some points which are defined by the characteristics of the substrate, *e.g.*, the defects present at the substrate surface,<sup>248,244</sup> subgrain boundaries,<sup>259</sup> and preferred orientations.<sup>240</sup> It is not clear whether these authors consider the pore to occur above this characteristic, the oxide cell being then defined as the area around the pore, or whether the oxide cell structure is established around the characteristic, thus giving the barrier layer a cellular structure even without pores.<sup>10,242,251</sup> the pores then following the establishment of this cell structure, the degree of pore formation being dependent on the electrolyte, and other circumstances. In either case, the occurrence of the structure shown in Figure 13 requires that these characteristics of the substrate surface be distributed in an orderly manner,<sup>252</sup> and their readiness to

act as pore centers increases as the voltage of formation increases.

The importance of the metal substrate dislocation density has been reported<sup>88,253,254</sup> in the field of metal dissolution and deposition, the identification of the rate-controlling step being related to the dislocation density. If such a relationship were determined for oxide nucleation, and if each dislocation were the site for an oxide cell, then as the anodic formation voltage increases, the number of oxide cells may decrease. This is, however, speculative, but it would account for the appearance of oxide cells in both porous and barrier-type oxide layers and confirm the statement that the oxide cell is defined before the pore is formed. Some indication as to whether the dislocation density of the substrate does control the oxide cell density could be obtained from a study of the film structure for films on annealed and for varying degrees of cold-worked aluminum.

### C. PORE FORMATION THEORIES

Since the first observations, over 30 years ago, of the porous nature of alumina films produced in certain electrolytes, several theories have been proposed to account for the pore formation using what evidence there was available at that time. These early theories include those due to Setoh and Miyata<sup>224,255</sup> involving nascent oxygen, Wernick<sup>256</sup> involving peptization of an  $\text{Al}(\text{OH})_3$  gel, Baumann's<sup>257</sup> oxide kernel theory, and Akahori<sup>258</sup> involving both vaporization of the electrolyte and melting of the aluminum. These theories will not be discussed further since they have been reviewed adequately elsewhere.<sup>259</sup>

Further evidence that the electrolyte plays an important part in the formation of porous films, perhaps by some dissolution process, has been reported by Barrett,<sup>2</sup> Hunter and Towner,<sup>140</sup> and Dunn<sup>260</sup> for the formation of oxide films in electrolytes which would, under normal conditions, produce barrier-type films. Hunter and Towner, anodizing aluminum in 3% aqueous ammonium tartrate (pH 5.6), reported that maintaining a constant voltage over a long period produces a porous film, whereas maintaining the constant voltage only long enough for the barrier-type film to reach complete formation, the film was completely nonporous. Dunn,<sup>260</sup> working with aluminum in similar electrolytes, has shown that rapid film formation results in entirely nonporous films, while slow formation produces porous films. In both cases, it is clear that when a preformed barrier-type film is held at a constant voltage, in an appropriate electrolyte, for a period well in excess of its formation time, a porous film results from a slow dissolution process involving the electrolyte. It would be of interest here to know whether the lowering or the complete removal of the voltage following the formation of the barrier-type film, and allowing the film to dissolve in the electrolyte, would still produce the porous film. Work along these lines has been reported by Renshaw,<sup>240</sup> in which barrier-type films were prepared upon aluminum,

(251) M. A. Chernykh, *Sb. Nauchn. Rabot Aspirantov, Voronezhsk. Gos. Univ.*, 2, 41 (1965); *Chem. Abstr.*, 68, 7142k (1968).

(252) B. Nost, G. Sorensen, and E. Nes, *J. Crystal Growth*, 1, 149 (1967).

(253) M. Fleischmann and H. R. Thirsk, *Advan. Electrochem. Electrochem. Eng.*, 3, 123 (1963).

(254) A. Damjanovic and J. O'M. Bockris, *J. Electrochem. Soc.*, 110, 1035 (1963).

(255) S. Setoh and A. Miyata, *Bull. Inst. Phys. Chem. Res. (Tokyo)*, 11, 317 (1932).

(256) S. Wernick, *J. Electrodepositors' Tech. Soc.*, 9, 153 (1934).

(257) W. Baumann, *Z. Phys.*, 111, 708 (1939).

(258) H. Akahori, *J. Electronmicroscopy (Japan)*, 10, 175 (1961).

(259) S. Wernick and R. Pinner, "The Surface Treatment and Finishing of Aluminum," Robert Draper Ltd., Teddington, 1964, p 274.

(260) C. G. Dunn, ref 121, Abstract No. 44, p 54.

immersed in chromic acid, and a low voltage applied across the film. Renshaw observed the formation of a porous structure, as might be expected. However, since the time required for the appearance of the pore structure was only approximately 30 min, it was concluded that dissolution of the preformed barrier layer was not involved. This, the present authors consider, is based upon an assumption which may not be correct: it was assumed by Renshaw<sup>240</sup> that the rate of dissolution of the preformed barrier film in chromic acid upon "open circuit" was equal to that dissolution rate in the presence of an applied electric field. This assumption must be considered doubtful, since evidence does exist to show that the presence of an electric field does affect dissolution in some way.<sup>2, 199, 211, 231</sup>

In order to identify the nature of the process by which porous films are formed it is necessary to locate the exact point at which pore initiation occurs. Figure 14 shows the

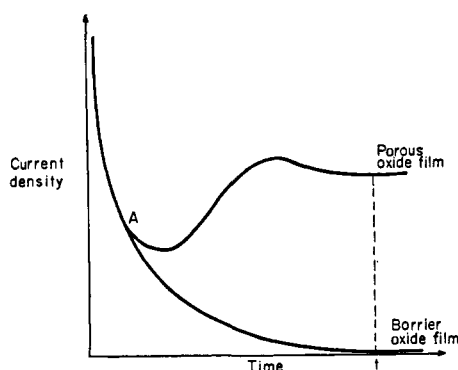


Figure 14. Current density-time transients for the formation of a barrier-type and a porous-type anodic film on aluminum. Point A represents the point at which divergence of the two curves occurs, and hence may be related to pore initiation phenomenon. Time  $t$  is typically 25 sec for a 15-V step application to aluminum in 15% sulfuric acid.<sup>50</sup>

current density-time transients observed for a constant voltage step preparation of a porous and a barrier-type film. Initially both transients are identical; as the initially formed barrier layer thickens, the electric field strength decreases and the current density ( $i$  in eq 1) decreases rapidly. At point A, the two curves now begin to diverge; the barrier film current density continues to decrease exponentially, while the porous film current density, after a short period of continuing decrease, begins to increase. The final current density for the two films differ widely. The barrier film current density is mainly electronic current, while the porous film current is almost completely ionic. (For porous films on other metals this may not be true, since the magnitude of ionic to electronic current depends, not only on the electric field strength, but also on their respective conductivities.)

Figure 14 then shows that pore initiation occurs at some point close to A, and also that this pore initiation process requires the thickness of the barrier layer formed up to this point to decrease. If this decrease or thinning of the barrier layer does not occur, it is difficult to account for the rise in the current density (although Hoar and Yahalom<sup>199</sup> have suggested that the barrier layer current does in fact continue to decrease exponentially, the increase in the current observed being attributed to a pore current; the origin of and the driving

force for such a current were not specified). Hunter and Fowle,<sup>50</sup> in an examination of this behavior during pore initiation, have demonstrated that changes, both increases and decreases, in the barrier layer thickness do occur before the final steady current density is attained. These results are shown in tabular form in Table X for a 15-V film prepared in 15% w/v sulfuric acid at 21°.

Table X

Changes in the Barrier Layer Thickness during the Initial Current-Time Transient Observed for the Anodization of Aluminum in Sulfuric Acid<sup>50</sup>

Time interval, sec	Barrier layer thickness
0-5	Increases to 190 Å
5-18	Decreases to 140 Å
18-24	Increases to 150 Å
24 onwards	Constant at 150 Å

The time scale and the current density changes involved in these current-time transients are dependent on the voltage applied and on the electrolyte,<sup>199</sup> the minimum current density occurring the earlier the higher the applied voltage and the more acidic the electrolyte. The value of the minimum current density is the larger, *i.e.*, the greater the electric field strength, the lower the pH, and the higher the temperature.

The transient shown in Figure 14 for the barrier film anodizing, when extended to long anodizing times, *i.e.*, 60 min, does in fact show a similar behavior to that of the porous film, although at a much lower current density.<sup>261</sup> In the case of the ammonium tartrate electrolyte, the current density minimum occurs the earlier the higher the pH of the tartrate solution.<sup>261</sup> Since the ammonium tartrate films have been shown to possess a cellular structure, the identification of a current minimum in the current-time transient, with either pore or oxide cell formation, would appear established; only the time scale differs from one electrolyte to another.

Having established where porous films are initiated, and having related such initiation with changes in the barrier layer thickness, it is now necessary to attempt to identify the role of anion in porous film formation. Why do porous films initiate more rapidly in sulfuric acid than in phosphoric acid<sup>262</sup> or in ammonium tartrate? Are the differences due solely to varying solubilities of alumina in the three electrolytes, or is the electrolyte anion involved directly in pore formation? Kissin<sup>264</sup> has suggested that preparation of porous films requires the anion to be either di- or trivalent. This, however, cannot be taken as a general rule, since excellent films of a porous nature

(261) K. Videm, paper presented at the 17th Meeting of C.I.T.C.E., Tokyo, 1966, personal communication, 1967.

(262) If the current-time transients over a time interval of 25 sec are observed for 15% w/v sulfuric and 15% w/v phosphoric acids, the following can be concluded: sulfuric acid shows a typical pore-forming current-time relationship (Figure 14), whereas phosphoric shows an almost ideal barrier-type film current-time relationship.<sup>263</sup> Phosphoric acid films are definitely of a porous nature, and so it is concluded that pore initiation occurs at some time in excess of 25 sec. A consequence of this is that the rate of porous film formation is greater for sulfuric than for phosphoric acid, as would be expected from the anodizing ratios in Table III, at one and the same voltage.

(263) J. R. House, personal communication, 1967.

(264) G. H. Kissin, "Anodized Aluminium," ASTM Special Technical Publication No. 388, 1965.

have been prepared in sulfamic acid,  $\text{NH}_2\text{SO}_3\text{H}$ ,<sup>265-267</sup> and the fact that phosphoric acid is present predominantly as  $\text{H}_2\text{PO}_4^-$ . Murphy<sup>268</sup> considers that both protons and anions are involved in the formation of porous films. That protons and  $\text{OH}^-$  ions are the controlling ions for alumina films has been demonstrated from electrokinetic<sup>269,270</sup> studies. Murphy<sup>268</sup> has also shown that the pore density decreases linearly with decreasing  $\text{pK}_a$  for the series of electrolytes 15% sulfuric acid, 2% oxalic acid, 3% chromic acid, and 4% phosphoric acid.

The electrolyte anions have been suggested to undergo discharge during oxide film formation;<sup>271</sup> these discharged anions were then suggested to replace oxygen atoms in the oxide lattice, thus lowering its specific resistance. It should be pointed out that these conclusions,<sup>271</sup> concerning a lowering of the oxide specific resistance  $R$ , were obtained from an expression based upon the assumption that the oxide film acts as an ohmic device, i.e.,  $V = Rdi_+$ , where  $V$  is the potential drop across an oxide film  $d$  cm thick and  $i_+$  is the ionic current density. It is well known that semiconducting oxides, e.g.,  $\text{Al}_2\text{O}_3$ ,  $\text{Ta}_2\text{O}_5$ , and  $\text{Nb}_2\text{O}_5$ , are nonohmic devices at all but very low fields, i.e., low current densities. Therefore,  $V$  being proportional to  $i_+$  will be valid only at low current densities, as is reported,<sup>271</sup> and conclusions concerning the value of  $R$  above must be regarded as being of uncertain significance at all but very low current densities. The entry of sulfate into an oxide lattice, as proposed above,<sup>271</sup> has been reported as being negligible<sup>272</sup> for the alumina lattice, as compared to that of the chloride ion whose effect upon the ionic ac resistance can be substantial. It is worthwhile to note that those ions known to penetrate the oxide lattice, e.g., halide ions, do not permit the formation of a stable oxide film as the anodic process,<sup>273</sup> and therefore lattice oxygen substitution would appear to be something to avoid.

Although the anions present in an electrolyte are of obvious importance in the formation of oxide films on clean metal surfaces in passivation, it is difficult to conceive what role they play in the formation of porous-type oxide films. There are several indications that the proton, or more correctly ( $\text{H}_3\text{O}^+$ ), may be the more important ion in porous film formation, e.g., the tendency for typically nonpore-forming electrolytes to form pores over a long anodizing period<sup>260</sup> (this is true particularly in the more acidic solutions) and the influence of pH on the current-time transients.<sup>199</sup> Brock and Wood,<sup>274</sup> in an investigation of the hydroxyl and proton mobilities during the anodic oxidation of aluminum in aqueous tartrate solutions of pH ranging from 5 to 9, have shown that the ac resistance of the outer layer of oxide film decreases as current decay (see Figure 14) proceeds. This decrease in ac resistance was related to the occurrence of pore formation, which occurs the earlier the lower the pH of the electrolyte. Hydration was suggested to

play a part in pore formation since no pore formation was observed in nonaqueous borate solutions (i.e., the ac resistance was independent of formation current density).

Franklin<sup>242</sup> suggested many years ago that there was no essential difference between porous films and barrier-type films; both possess a cellular structure, the degree of pore formation being dependent on the solubility of the oxide comprising the center of the oxide cell. The decreasing rate of pore formation under constant voltage conditions in the series 15% sulfuric acid (10°), 2% oxalic acid (24°), 4% phosphoric acid (24°), 3% chromic acid (38°), and 3% ammonium tartrate (25°), pH 7, is clearly seen to be in accord with increasing pH from sulfuric acid (pH <0.3) to ammonium tartrate.

The importance of pH, and the distinction that lies between aqueous and nonaqueous electrolytes, noted by Wood and Patrick,<sup>275</sup> may indicate the importance of the electrolyte dissociation constant in the initiation and growth of porous films. Although considerable progress has been made in the identification of those parameters apparently important in the initiation of porous films, little progress has been made toward the attainment of a suitable mechanism to explain the facts. Keller, Hunter, and Robinson<sup>52</sup> suggested, over 10 years ago, that pores were initiated at "weak" spots in the preformed barrier film. At such "weak" spots, where a high local current density exists, local heat is produced, and this heat then produces enhanced dissolution of the barrier film. Hence pores are initiated. Since the thickness of the barrier film at constant cell voltage remains essentially constant for anodizing times in excess of 25 sec (see Figure 14), i.e., apparently the barrier layer is dissolved (porous layer is produced) as fast as it is formed, Hunter and Fowle<sup>51</sup> proposed the high-temperature-high-concentration electrolyte pore base conditions mentioned earlier. Regardless of the model proposed, there is this basic question: Is dissolution, in the sense in which the word is normally used, of the preformed barrier layer involved? Is a conversion process, in which protons, hydration processes, and the electric field play a part, not more probable?

An electric field assisted process for the formation of porous films has been suggested by Hoar and Mott,<sup>211</sup> in which an  $\text{OH}^-$  ion, produced from alumina dissolution, migrates across the barrier layer to the metal-oxide interface. At this interface the  $\text{OH}^-$  combines with  $\text{Al}^{3+}$  to produce barrier layer oxide; the proton released in this combination then returns to the oxide-electrolyte interface. This suggestion, however, loses some significance in its explanation as to the formation of porous films, when it is remembered that the anion (either  $\text{O}^{2-}$  or  $\text{OH}^-$ ) mobility is independent of the type of film produced,<sup>34</sup> i.e., whether porous or barrier type. With regard to this theory of Hoar and Mott, it should be noted that it still depends to some extent on an unspecified dissolution process.

The influence of an applied electric field in the barrier layer to porous layer conversion process has been indicated in some recent work by Murphy and Michelson.<sup>15,276</sup> It was found that the time required for a 15-V porous anodic film to attain equilibrium conditions, i.e., with respect to current density and barrier layer thickness, upon reanodization at 10 V depended, in any one electrolyte, almost entirely on the mode of the

(265) A. La Vecchia, G. Piazzesi, and F. Siniscalco, *Electrochim. Metal.*, **2**, 71 (1967).

(266) A. La Vecchia, R. Piontelli, F. Siniscalco, and A. Varengo, *ibid.*, **2**, 84 (1967).

(267) A. F. Bogoyavlenskii and N. M. Vaevodina, *Zh. Prikl. Khim.*, **40**, 2068 (1967).

(268) J. F. Murphy, *Plating*, **54**, 1241 (1967).

(269) V. C. P. Morfopoulos and H. C. Parreira, *Corrosion Sci.*, **7**, 241 (1967).

(270) H. Yokata, *Denki-Kagaku*, **35**, 14 (1967).

(271) S. Tajima, N. Baba, and M. Shimura, *Electrochim. Acta*, **12**, 955 (1967).

(272) M. A. Heine, D. S. Keir, and J. J. Pryor, *J. Electrochem. Soc.*, **112**, 24 (1965).

(273) K. Lorking and J. E. O. Mayne, *J. Appl. Chem.*, **11**, 170 (1961).

(274) A. J. Brock and G. C. Wood, *Electrochim. Acta*, **4**, 395 (1967).

(275) G. C. Wood and G. W. Patrick, *Trans. Inst. Metal Finishing*, **45**, 174 (1967).

(276) C. E. Michelson, *J. Electrochem. Soc.*, **115**, 213 (1968).

voltage change. If the change from 15 to 90 V is achieved very quickly (*i.e.*, the electric field is decreased instantaneously), then the time required is of the order of minutes; however, if the voltage change is made slowly (*i.e.*, over a 15–30-sec period in which the electric field remains of ionic magnitude), equilibrium occurs concurrently with the end of voltage change. Simple chemical dissolution of the barrier layer was considered unlikely, since the time required to dissolve a 50-Å barrier-layer oxide and attain equilibrium conditions for the changes 15–10 and 14–9 V should be equal; experimentally this was not found. Owing to conflicting experimental evidence concerning the capacitance of the barrier layer undergoing this change, the present authors disagree with Murphy and Michelson<sup>15, 276</sup> as to the interpretations of these results. More evidence as to the nature of this phenomenon is required before a sound argument can be made in favor of either the Keller, Hunter, and Robinson,<sup>52</sup> the Murphy and Michelson,<sup>15</sup> or any other model for the porous anodic oxide film on aluminum.

The importance of the proton in the initiation process has been proposed by Hoar and Yahalom<sup>199</sup> as being due to proton entry into the preformed barrier layer, at preferred sites, at some low electric field strength. These preferred sites then become points of high local current density, with its ensuing high dissolution rate, and a pore is thus initiated. This theory of the role of the proton suffers, however, the same disadvantages as the Keller, Hunter, and Robinson<sup>52</sup> suggestion, in that "preferred sites" are not identified and their inverse dependence on the applied formation voltage, directly in one case<sup>52</sup> and indirectly in the other,<sup>199</sup> is assumed.

In conclusion it might be said that there is yet no fully acceptable pore formation theory available; recent evidence concerning the importance of protons, hydration processes, and the presence of an applied electric field would seem to indicate that the initiation and growth of a pore is something more than a purely chemical process.

## D. PROPERTIES OF POROUS ANODIC OXIDE FILMS

### 1. Sealing

The phenomenon of sealing has been well known for many years, and has been utilized throughout the anodizing industry to produce hard, corrosion-resistant coatings on aluminum. The excellent corrosion resistance of anodized aluminum is due partly to the thicker oxide coatings produced in electrolytes such as sulfuric acid, and to the ability of such films to be sealed in hot water or in aqueous organic and inorganic salt solutions. Without sealing, porous anodic oxide films possess poor corrosion resistance since the only impervious feature of such films is the thin barrier layer lying adjacent to the metal.

During this sealing process, the high porosity that these films possess is drastically reduced and their ability to absorb or adsorb colored dyestuffs is almost completely lost. For many years the loss of dyeing ability, and the production of a thick impervious film with good corrosion resistance, was considered to be due to the hydration of the porous alumina, often assumed to be amorphous, to produce a crystalline hydrate  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , known as boehmite, which filled in the pore spaces. This view is still generally held today. Recently a new theory for sealing was proposed by Murphy<sup>288</sup> in which the sealing process was seen as an anion exchange between the absorbed incorporated electrolyte anions and the

sealing medium to produce an inert hydrated oxide skin over the internal pore surfaces. In order to decide which theory best explains the known experimental facts, a brief review of these facts is now presented.

That the phenomenon of sealing does not require the presence of the basis metal aluminum has been shown by Spooner<sup>277</sup> and McLennan<sup>278</sup> for porous oxide films, and by Hinde, Kellet, and Harris<sup>279</sup> for nonporous oxide films. Hart<sup>280</sup> has, however, reported that, for nonporous films, the presence of the basis metal is required to achieve sealing. The mechanism suggested by Hart was electrochemical in nature, involving ionic migration of  $\text{Al}^{3+}$  ions to the oxide-electrolyte interface where reaction with  $\text{OH}^-$  occurs.

Further studies<sup>281, 282</sup> of the hydration processes, involved in the sealing of nonporous films, have shown that as hydration proceeds the thickness of the preformed barrier-type film decreases as the barrier layer is hydrated from the electrolyte interface. When complete barrier-layer hydration has occurred, direction reaction of hot water with aluminum produces the same alumina hydrate as barrier oxide hydration, *i.e.*, boehmite or  $\alpha$ -alumina monohydrate. If these hydration processes were regarded as electrochemical in nature, involving mobile cations, then formation should occur on top of the barrier layer, the latter remaining intact. Since the barrier layer thickness decreases as hydration proceeds,<sup>281</sup> an electrochemical mechanism involving migrating  $\text{Al}^{3+}$  reacting at the oxide-electrolyte interface would appear unlikely.

Hydration of the barrier layer also occurs in the sealing of porous films, but only to a limited extent; hydration will occur only as long as water is able to diffuse down the pore length to the barrier layer. If pore mouth blockage by some material does occur during sealing, as has been suggested,<sup>167, 283–285</sup> then hydration of the barrier layer will proceed only as long as the pore mouth is open. The times involved in these two processes are in approximate agreement, thus providing further evidence against an electrochemical mechanism.

To summarize so far, sealing of porous oxide films is seen as a hydration process, hydration occurring both at the barrier layer surface and in the pores. These processes are regarded as chemical processes, proceeding with a decrease in free energy, and can proceed equally well in the absence, as in the presence, of the basis metal.

Wood and Marron,<sup>284, 285</sup> in a study of the sealing of porous films in hot water and in several salt solutions by the use of impedance measurements and the determination of anion concentration profiles through the oxide film using electron probe microanalysis, have shown the following.

(1) Indichromate-chromate sealing, the chromium content of sealed films is much greater than that chromium content that would result if the pores were simply filled with dichromate sealant. The chromium content of films immersed in dichro-

(277) R. C. Spooner, *Nature*, **178**, 1113 (1956).

(278) D. F. McLennan, *Corrosion*, **17**, 283 (1959).

(279) R. S. Hinde, E. A. Kellet, and P. H. Harris, *Nature*, **183**, 39 (1959).

(280) R. K. Hart, *Trans. Faraday Soc.*, **50**, 269 (1954).

(281) M. S. Hunter, P. F. Towner, and D. L. Robinson, *Tech. Proc. Amer. Electroplaters' Soc.*, **46**, 220 (1959).

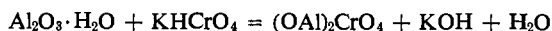
(282) W. J. Bernard and J. J. Randall, Jr., *J. Electrochem. Soc.*, **108**, 822 (1961).

(283) A. F. Bogoyavlenskii and V. T. Belov, *Zashchita Metal.*, **3**, 477 (1967).

(284) G. C. Wood and V. J. J. Marron, *Trans. Inst. Metal Finishing*, **45**, 17 (1967).

(285) G. C. Wood and V. J. J. Marron, *ibid.*, **45**, 107 (1967).

mate-chromate sealants at 20° also show higher values. It was concluded that chemical combination between the chromium-bearing species and the alumina occurs. Tomashov and Tyukina<sup>286, 287</sup> in some earlier work also suggested this chemical combination, and proposed that these chemical compounds were oxydichromate in acid solution and oxychromate at higher pH values. The important point is, however, that these compounds arise from reaction with boehmite, not with alumina, *e.g.*



(2) The chromium content for films sealed at 110° increases rapidly as the porous layer-electrolyte interface is approached. The degree of incorporation of chromium, at any point in the oxide film, at any sealing time in excess of 1 min, increases as the pH decreases.

This is in accord with the chromium incorporation being due to the above reaction. As the pH increases, the amount of boehmite formed in any one time interval increases. Thus, if the formation of oxychromate is slow, then at higher pH values the pores will be sealed before appreciable amounts of oxychromate can form. In acidic sealing solutions of dichromate, the formation of boehmite is reduced, and the formation of oxydichromate is favored. Hence, sealing takes a longer time to reach an effective level and the degree of chromium incorporation is high.

(3) The measured resistance and capacitance of porous films undergoing sealing, by ac impedance techniques, shows that when the resistance is taken as a guide to complete sealing (as is suggested), complete sealing throughout the pore length is rarely achieved. The measured resistance is still increasing after 1500 min in potassium chromate, pH 9.7 at 100°, while the measured capacitance remains approximately constant after 150 min, the chromium uptake also remaining constant after 1 min.

These observations were interpreted as being due to a three-stage sealing process, the first stage being the pore mouth closure, with the second stage being continued boehmite, and possibly trihydrate formation, from the initially formed gel-type substance which was responsible for pore blockage. The third stage is seen as the slow continual crystallization of the oxide throughout the film.

Although impedance measurements have shown that changes do occur during sealing at times beyond which sealing would normally be considered to be complete, these do not necessarily mean that long-term sealing would be advantageous. In actual fact it is very often harmful to the final film, in that the film ages much more rapidly than that film sealed for the normal time period. The phenomenon of ageing, which has been associated with the stress produced within the film during crystallization<sup>288, 289</sup> (the result of this stress is crazing of the film), has been found to be accelerated in those films which have been excessively sealed.

It has often been suggested<sup>167, 289-292</sup> that impedance measurements could be used as an "on-site" method for assessing

the effectiveness of sealing, replacing the usual destructive tests;<sup>293</sup> equipment for such tests is commercially available.<sup>292</sup> As Wood and Marron<sup>282</sup> have indicated, care must be taken when assessing sealing efficiency for different sealants, since the effective resistance will depend upon the conductivity of the pore blocking material.

The effectiveness of hot-water sealing has been extensively investigated by Spooner,<sup>294</sup> who has shown that the chemical resistance of 5% v/v sulfuric acid and the electrical resistivity both increase as the sealing water pH increases from 4 to 6; from pH 6 to 9, these properties of the sealed film are appreciably constant. That the pH range 4-8 is most satisfactory for hot-water sealing is also shown by the lack of "bleeding" of dyed films which are subsequently sealed in this pH range.<sup>293</sup>

By calculation, Spooner has shown that a sealing mechanism involving pore mouth blockage cannot be solely responsible for the increased chemical resistance observed since insufficient material, assuming it to be the monohydrate, is produced. These calculations by Spooner can be said to be in considerable error as regards the assumption that, of the total water in the sealed film, only 50% is chemically combined. If it can be assumed that, on heating, the water, which is physically adsorbed, is lost from the sealed film before the film temperature reaches 100°, then a value of approximately 90% chemically combined water can be obtained from Spooner's work. Further, assuming as Spooner does that only the outer 5-10% of the pore length is initially blocked, then it can be shown that for a 20-μ porous film, whose pore diameter is 180Å and which is sealed in hot water at 100°, pore blockage will be complete in 5 min. The density of alumina and of boehmite have been reported<sup>294</sup> as 3.2 and 3.0, respectively, and hence from a known weight of alumina an increase in volume of 25% would be expected as alumina undergoes hydration to form boehmite. However, if the boehmite formed is of a gel-like nature which contains excess water, this volume increase may reach 70-80%.

Spooner and Forsyth<sup>295, 296</sup> using an X-ray emission spectroscopic technique, in conjunction with progressive thinning of the oxide film, have shown that some process is involved which results in a more pronounced sealing at the surface than in the depth of the film. If this process is indeed pore sealing at the mouth, Hunter, Towner, and Robinson<sup>281</sup> have shown that to seal a pore of 168 Å diameter requires the hydration of only a 56-Å annulus. This conclusion was reached from a study of the hydration of a 560-Å thick, nonporous film, in which it was shown that when this film is completely hydrated, a 1400-Å thick monohydrate film had been formed. Since the sealing process, *i.e.*, the hydration process, in the case of nonporous films has been reported to be a nonelectrochemical process,<sup>270</sup> it may be valid to assume, as was done to achieve the above conclusion, that the volume increase resulting from hydration of nonporous and porous alumina is essentially the same.

The sealing of porous films, formed in sulfuric, oxalic, and phosphoric acids, in hot water shows that although films formed in sulfuric and oxalic acids are hydrated at approximately equal rates, films formed in phosphoric acid are hydrated less rapidly during sealing; *i.e.*, the sealing process is apparently retarded by the presence of phosphate ions.<sup>281, 297</sup>

(286) N. D. Tomashov and A. Tyukina, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 325 (1944).

(287) N. D. Tomashov and A. Tyukina, *J. Appl. Chem. USSR*, 18, 149 (1945).

(288) C. E. Michelson, *S.A.E. J.*, 73 (10), 60 (1965).

(289) T. P. Hoar and G. C. Wood, *Electrochim. Acta*, 7, 333 (1962).

(290) W. Leute and H. Birtel, *Aluminium*, 41, 52 (1965).

(291) H. Birtel and W. Leute, *ibid.*, 43, 93 (1967).

(292) G. E. Gardam, private communication, 1967.

(293) S. Wernick and R. Pinner, ref 259, p 497.

(294) R. C. Spooner, *Tech. Proc. Amer. Electroplaters' Soc.*, 44, 132 (1957).

(295) R. C. Spooner and W. J. Forsyth, *Plating*, 55, 336 (1968).

(296) R. C. Spooner and W. J. Forsyth, *ibid.*, 55, 341 (1968).

(297) C. J. Amore and J. F. Murphy, *Metal Finishing*, 63, 50 (1965).

The theory of sealing proposed by Murphy<sup>288</sup> suggests that hydroxyl ions penetrate the porous layer and replace the anions of the electrolyte in which the film was formed, *e.g.*, sulfate, oxalate, or phosphate. The result of this anion exchange is the formation of an inert oxide skin on the pore walls effectively blocking off the high surface area internal surfaces. A certain amount of evidence is available<sup>288, 298</sup> to suggest that, of three electrolyte anions mentioned, phosphate is the most strongly adsorbed, and so replacement of phosphate ions by hydroxyl ions may be the most difficult.<sup>299, 300</sup> The importance of the anions present upon the oxide surface prior to hydration has been shown<sup>281, 282</sup> to be reflected in an initiation time—a short time interval immediately following immersion in hot water when no appreciable changes (no detectable changes in barrier layer thickness) were observed. During this initiation period the replacement by hydroxyl ions of the electrolyte anions, adsorbed upon the oxide surface, is then seen as the first stage in the hydration process whether the film is porous or nonporous. This anion adsorption may result in compound formation with the alumina, as has been suggested by Hunter, Towner, and Robinson.<sup>281</sup> Strong electrolyte anion adsorption is then sufficient to retard sealing; *i.e.*, immersion of a porous film, formed in sulfuric acid, in a 2% solution of sodium phosphate considerably retards the subsequent hydration processes involved in sealing.<sup>281, 297</sup> Silicates have been reported to be similar to phosphates in this respect.<sup>301</sup>

The present authors consider that the two models proposed for sealing—the plugged pore and the model of Murphy<sup>288</sup>—can be regarded as complementary to each other; the Murphy model is applicable during the initiation period and the plugged-pore model is applicable for sealing times longer than the initiation time. The sealing mechanism in water is then seen as the following.

(1) During the initiation time hydroxyl ions replace those electrolyte anions adsorbed to the pore walls and other internal surfaces. The result of this is the formation of a skin of inert hydrated oxide upon the pore walls; this will effectively initiate the pore diameter decrease.

(2) Also during the initiation time, water diffuses down the pore length to the barrier layer where hydration occurs, producing the less dense monohydrate of alumina. This process effectively reduces the pore length by filling in the pore from its base.

(3) At sealing times in excess of the initiation period, the decrease in pore diameter away from the pore mouth and the decrease in pore height are very much reduced. Eventually these processes cease owing to the formation of a plug of hydrated alumina in the pore mouth due to easy access of pure sealant at this point.

(4) As sealing proceeds, this plug becomes longer as more and more of the pore is completely blocked. Since this mechanism requires the migration of  $H_2O$  or  $OH^-$  through the initial plug of crystalline boehmite, an ion-transport mechanism similar to the "advance proton" mechanism proposed by Hoar and Wood<sup>167, 289</sup> is suggested. Since ionic transport, involving either applied or locally induced electric fields, is

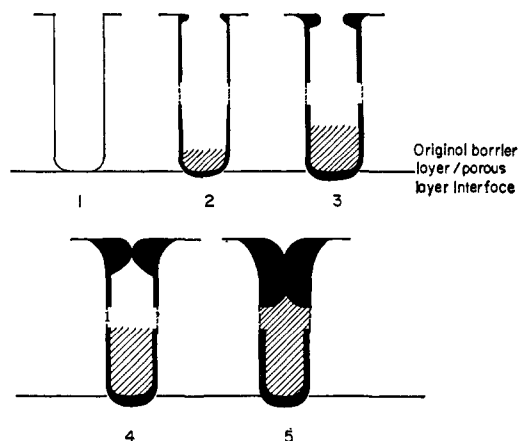


Figure 15. Successive stages 1–5 in the sealing of a porous anodic oxide film, illustrating the decrease in the barrier layer thickness, decrease in the pore radius, and the closure of the pore mouth. Diagonal shading represents a voluminous gel-like material which is transformed into solid, compacted boehmite as sealing proceeds (dark shading).

necessarily a function of the distance over which the field is applied, then as this plug of alumina lengthens the field will decrease. Therefore complete sealing throughout the pore length may never be attained.

Figure 15 illustrates these four stages in hot-water sealing. This model is similar to that proposed by Hoar and Wood,<sup>167, 289</sup> with the exception that complete blockage is envisaged by the present authors together with the possible formation of a surface recess which could be identified as something similar to a pore opening.

Sealing procedures in nickel and/or cobalt acetates and potassium dichromate and chromate in aqueous solutions are seen to be similar to that for sealing in hot water except that ions from these sealants are trapped, either adsorbed or chemically combined, within the pores. The sealing mechanism, involving pore blockage by boehmite, appears equally valid for these sealants as it does for water.<sup>284, 286, 287, 302, 303</sup>

As sealing appears to involve an initiation period during which ion exchange between the film and the sealant occurs, it can be said that the ions present in the sealant and their adsorbability upon alumina will decide (a) whether or not sealing will be effective, and (b) the time required to attain satisfactory sealing. Evidence for this has been obtained by Richaud<sup>301</sup> in his work with various added ions, and by Spooner,<sup>304</sup> who has reported that sealing in deionized water, pH 6.1, at 100° for 30 min produces a coating which was at least equal to that produced by all other sealing conditions. Further evidence is provided by the inability of tap water, particularly hard water, to produce sealing of the same effectiveness as deionized water.<sup>293</sup>

Attempts made to compare the effectiveness of sealing by different sealants are often confused by the contradictions that exist between work by different authors, this being due to the unsatisfactory nature of many accelerated corrosion tests as qualitative measurements of sealing efficiency. However, the following trends do appear. Whitby<sup>305</sup> and Spooner

(298) H. B. Weiser, "Colloid Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, Chapter 16, p 251.

(299) A. F. Bogoyavlenskii and V. T. Belov, *J. Appl. Chem. USSR*, **39**, 2540 (1966).

(300) A. F. Bogoyavlenskii and V. T. Belov, *ibid.*, **39**, 2221 (1966).

(301) H. Richaud, ref 1, p 181.

(302) R. C. Spooner and W. J. Forsyth, *Nature*, **200**, 1002 (1963).

(303) C. Th. Speiser, *Electroplating Metal Finishing*, **9**, 109 (1956).

(304) R. C. Spooner, *Tech. Proc. Amer. Electroplaters' Soc.*, **48**, 69 (1961).

(305) L. Whitby, *Metal Ind.* (London), **72**, 400 (1948).

and Forsyth<sup>302</sup> have reported that nickel acetate sealing is more effective than hot-water sealing, but less effective than dichromate sealing. Wood and Marron<sup>284</sup> have shown from impedance measurements that acid dichromate or alkaline chromate sealing is more effective than concentrated nickel acetate (60 g l.<sup>-1</sup>), but less effective than dilute nickel acetate solution (6 g l.<sup>-1</sup>). Nickel or cobalt acetate sealing is usually carried out at 100°, during which the acetates hydrolyze to produce hydroxides. Thus to prevent pH changes during these hydrolysis reactions, aqueous solutions of nickel or cobalt acetates are buffered, usually with boric acid, to pH 5–6.

The use of a particular sealant depends, to a great extent, upon the type of finish required on the final article, *i.e.*, whether for architectural or purely protective uses. Dichromate sealing, which usually imparts a slight color to the sealed film, could not be used for those purposes where color would be unsightly. Nickel acetate sealing is usually used for porous films produced in sulfuric acid, as it produces a more satisfactory finish. For details of the industrial and decorative uses of sealed anodic films, the work of Wernick and Pinner<sup>293</sup> should be consulted.

## 2. Dyeing

The most satisfactory films for decorative purposes are those films which are transparent and colorless after anodizing, adsorb colored substances readily, and possess good light fastness in both dry and wet environments when sealed.

Sulfuric acid films are transparent and colorless and, because of their high porosity, adsorb dyes readily. Oxalic acid films usually possess a slight yellow coloration after anodizing, and, since they are more expensive to prepare, are usually used only where very thick films are required (maximum porous film thickness is much greater for oxalic than for sulfuric acid, as mentioned earlier) or where pale yellow or gold decorative finishes are required. Some chromic acid films, *e.g.*, those films prepared by the now-obsolete Bengough-Stuart process, are considered unsatisfactory for decorative uses unless dark color tones are required, as the anodized film is usually gray and opaque, and also, as they are much less porous and thinner than sulfuric acid films, the dye adsorption characteristics are considered inferior. Satisfactorily dyed chromic acid films can, however, be obtained from the constant-voltage chromic acid process,<sup>306</sup> which has largely replaced the voltage cycle process originated by Bengough and Stuart.<sup>307</sup>

Several factors are important in the dyeing of a porous film. (a) The dye adsorption and the color tone increase as the film thickness increases. For films formed in a sulfuric acid dc process at 15 A ft<sup>-2</sup> and 25–28°, Schenk<sup>308</sup> has reported the anodizing times required for light, medium, dark, and very dark colors as 25, 30, 40, and 45 min, respectively. Dye bath concentration is also important in defining color tone.<sup>308</sup> As the porosity of a film increases, at constant film thickness, dye adsorption also increases, since the dye adsorption is a function of film surface area.

(b) A second factor is the color of the anodized film. As has been indicated previously, sulfuric acid films are the most satisfactory in this and other respects.

(c) The film should be free from any defects resulting either

from faulty anodizing or from metallurgical causes. The latter is usually avoided by using only pure metals or alloys, the so-called "anodizing grade" purity. The former is a question of adequate process control. Consequently, these factors are not as important as those in (a) or (b).

The degree of dye adsorption by those porous films which possess these three requirements is also dependent on time of dyeing, temperature of dyeing, and the volume of dye solution to oxide film weight ratio. These three latter factors will now be considered in detail.

### a. Time of Dyeing

The dyeing of a porous substance is a slow process, and, in the case of a porous anodic film, it has been reported<sup>309</sup> that equilibration may require more than 10 hr at 60°. It has also been shown<sup>309</sup> that the rate of dye adsorption is proportional to the square root of time, thus suggesting that slow diffusion is the rate-controlling process. This slow diffusion process was suggested by Giles<sup>309</sup> to be the slow inward diffusion of dye from a layer of dye rapidly adsorbed at the outer porous-layer surface.

Light fastness of the final film is dependent, to a large extent, on the dyeing time and on the dye bath concentration, better light fastness being obtained by dyeing in low concentration dye solutions for a few minutes rather than in concentrated dye solutions for a few seconds.<sup>310</sup> Light fastness is then clearly related to the depth to which the dye penetrates, as might be expected.

### b. Temperature of Dyeing

As expected for a diffusion-controlled process, increase in dyeing temperature increases the rate of dye adsorption. Since light fastness is related to the degree and the depth of dye adsorption and penetration, then light fastness should be a function of dye-bath temperature. This is found to be the case.<sup>310</sup> The light fastness increases with temperature until a temperature is reached (90°) where adequate dye adsorption is hindered by a competitive sealing process. The normal dye-bath temperature is usually between 65 and 70°, where the competition from sealing is low and where dye adsorption is at an optimum.

### c. Volume of Dye Solution to Oxide Film Weight Ratio

It has been reported<sup>311</sup> that, for anodic oxide films prepared in chromic acid, as the ratio of volume of dye solution to oxide film weight increases, the adsorption of dye increases. The proposed explanation of this unusual phenomenon was that the aqueous dye solution dissolves small quantities of alumina, thus producing an increase in the film real surface area. This dissolution, it was proposed, increases as the volume of a constant dye composition solution to oxide film weight ratio increases, and therefore the dye adsorption increases. The degree of dissolution of the alumina film was reported<sup>311</sup> to be increased from 0.5 to 2% while the concentration of dye within the film increased fourfold, both being observed for a tenfold increase in the ratio between the volume of dye solu-

(306) S. Wernick and R. Pinner, ref 59, p 298.

(307) G. D. Bengough and J. McA. Stuart, British Patents 223,994 and 223,995 (1925); *Chem. Abstr.*, 19, 1101 (1925).

(308) M. Schenk, "Werkstoff Aluminium und seine Anodische Oxidation," A. Francke, Berne, 1948.

(309) C. H. Giles, ref 1, p 174.

(310) S. Wernick and R. Pinner, ref 59, p 445.

(311) C. H. Giles, H. V. Mehta, S. M. K. Rahman, and C. E. Stewart, *J. Appl. Chem.*, 9, 457 (1959).



tion to the film weight. It is difficult to see how such a small change of 2% in the original film (judged by weight loss) could produce the large changes in the dye adsorption (assuming, as Giles does, that the extent of adsorption is dependent on the real surface area of the porous film), unless perhaps large changes in the original film weight are compensated by the formation of a second phase.<sup>281</sup>

Dye-bath pH is also of considerable importance in defining both the degree of adsorption of dye and the final light fastness of films. The general trend of light fastness and color tone, with respect to dye-bath pH, appears to show that a slight acidity (pH 3–5) is the most satisfactory.<sup>308, 310</sup>

The dyes which are used today can generally be divided into classes according to their chemical nature and to the nature of the dyeing process involved. Giles<sup>309, 311, 312</sup> has suggested that the following three dye types exist.

(a) Acid-wool-type dyes where there is covalent bonding between the sulfonate group of the colored anions and the aluminum atoms.<sup>309</sup> Speiser,<sup>308</sup> in contrast, has reported that these dyes do not react with the positively charged alumina surface,<sup>269, 270</sup> but are simply physically adsorbed. Examples of this type of dye are shown in Figure 16a.

(b) Mordant-type dyes. These dyes form chelate complexes with the anodic film.<sup>309</sup> These dyed films would therefore be expected to be stable and to lose dye only under chemical attack, *e.g.*, sulfuric acid. A typical example of this type of dye is shown in Figure 16b.

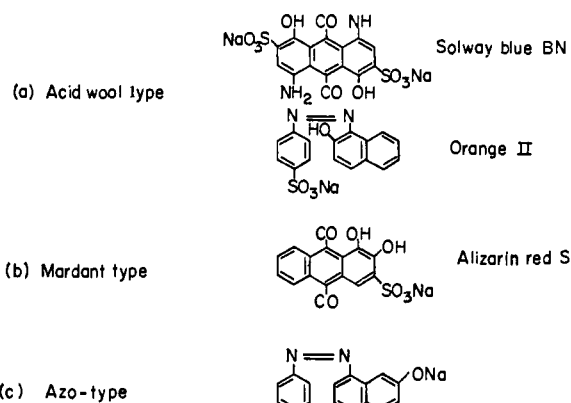


Figure 16. Organic structures of the three classes of dyes used to color porous alumina films.

(c) Azo-type dyes. These dyes are considered to be bonded to the alumina surface in a manner similar to the acid-wool-type dyes,<sup>309, 311</sup> but are considered as a separate class due to their chemical nature. Bonding of azo dyes to the alumina surface has also been suggested by Speiser.<sup>308</sup> Examples of this type of dye are numerous. Figure 16c shows an example of the bright red dye resulting from the coupling of benzenediazonium chloride and  $\beta$ -naphthol.

The positive charge that this type of porous surface possesses has been attributed to a layer of acidic anions, held either covalently or present as hydrated ions, on the surface of the porous layer following formation.<sup>309, 311</sup> Cutroni<sup>313</sup> has pro-

posed that the complex ion  $\text{Al}(\text{H}_2\text{O})_4(\text{OH})_2^+$  is formed during anodizing, and it is this anion which complexes with the dye anion. The unhydrated form of this complex ion, *i.e.*,  $\text{Al}(\text{OH})_3^+$ , has also been suggested by Morfopoulos and Parreira<sup>269</sup> to account for the positive charge of alumina films in acidic solutions. The surface charge will change polarity when the pH of the medium, in which it is immersed, exceeds the isoelectric point, or when small concentrations of ions with high negative charge densities are added to the medium. For example, it has been reported<sup>312</sup> that the surface charge on chromic acid-porous alumina films changes sign when NaCl in excess of 0.09% is added to an aqueous suspension of the oxide.

Inorganic dyes as well as organic dyes can be used to color the anodic alumina film; *e.g.*, a yellow coloration is obtained from lead chromate, orange from antimony sulfide, green from copper arsenite, and blue from ferrocyanide complexes.<sup>310, 314</sup>

In conclusion, it is mentioned that the lack of adsorption of a dyestuff by a sealed film, in the absence of a better test, is unfortunately still being used as a standard test<sup>315, 316</sup> to determine sealing effectiveness. It has been realized,<sup>294</sup> however, that the lack of adsorption of a colored anion does not necessarily mean effective sealing, only that the pore mouth is smaller than the diameter of the dye molecule, *i.e.*, 12 Å or less.<sup>312</sup> Hence there is the necessity for a new test, preferably nondestructive, to determine sealing effectiveness, *e.g.*, impedance measurements. Many tests to determine effectiveness of sealing are largely unsatisfactory owing to irreproducibility, but one of the more satisfactory is the determination of the breakthrough time when a small cathodic current is applied to the sealed film in an aqueous solution of 2% nitric acid.<sup>294, 317</sup> This test has been shown to produce results which confirm trends obtained by other more tedious methods.

### 3. Electrical Characteristics

Since porous-type films and barrier-type films both possess a thin compact oxide layer lying adjacent to the aluminum substrate, it might be expected that, under certain conditions, their electrical characteristics are similar. Two aspects have been studied; these are (i) capacitance and (ii) ionic conduction, especially the validity of the high-field expression (eq 1). In order to relate these two properties of barrier-type films to porous-type films, conditions are required where the characteristics of the porous layer are negligible when compared to those of the underlying barrier layer. Such conditions are easily achieved.

#### a. Capacitance and Its Relationship to the Voltage of Formation

Figure 17 shows the electrical analog for one pore of a porous film as proposed by Jason and Wood;<sup>318</sup>  $R_p$  and  $C_p$  are the resistance and capacitance of the barrier layer,  $R_e$  is the resistance of the electrolyte occupying the pore ( $R_p$ ,  $C_p$ , and  $R_e$  here as essentially similar to that analog shown in Figure 6a), and  $R_o$  and  $C_o$  are the resistance and capacitance of the solid

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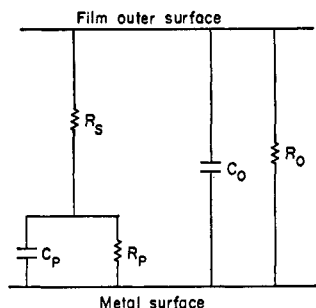


Figure 17. Electrical analog proposed by Jason and Wood to represent the electrical characteristics of an unsealed porous alumina film.

alumina which lies between the metal surface and the film outer surface.

When  $R_o$  is very large and  $C_o$  is very small (as is the case), the impedance of the  $R_o C_o$  combination is very high compared to the impedance of the  $R_p C_p$  combination. Therefore the measured capacitance, which is  $(C_p + C_o)$ , can be placed equal to  $C_p$ , and the measured resistance placed equal to  $R_p$  (provided that  $R_s$  is small in comparison to  $R_p$ ). The impedance of a capacitance-resistance network is dependent on the ac frequency used, decreasing as the frequency increases. This frequency dependence is the property through which the capacitance characteristics of barrier films are related to those of porous films. Hoar and Wood,<sup>167, 289</sup> in an investigation of the frequency dependence of porous oxide films formed in 15% w/v sulfuric acid found, in agreement with Jason and Wood,<sup>318</sup> that for unsealed films the measured capacitance and resistance decreased as the ac frequency increased. Above  $10^3$  Hz the measured resistance remained approximately constant, at a value identifiable with  $R_s$ , owing to the low impedance of  $C_p$  completely bypassing  $R_p$ . Below  $10^3$  Hz the measured resistance increases as the impedance of  $C_p$  increases.

The measured capacitance below  $10^4$  Hz was identified with  $C_p$ , since at this frequency  $C_o$  is negligible compared to  $C_p$ . From the frequency dependence study, Hoar and Wood were able to place the following values on the analog circuit shown in Figure 17 for a 15- $\mu$  porous oxide film formed at 20 V and immersed in nickel acetate at 19°:  $C_p = 0.39 \mu\text{F cm}^{-2}$ ,  $R_p = 700 \text{ k}\Omega \text{ cm}^{-2}$ ,  $R_s = 25 \Omega \text{ cm}^{-2}$ ,  $C_o = 0.001 \mu\text{F cm}^{-2}$ , and  $R_o = 5 \text{ M}\Omega \text{ cm}^{-2}$ .

Hence, below  $10^4$  Hz measuring frequency (ac techniques) the capacitance of unsealed porous films is then seen as equivalent to a barrier film whose thickness is also obtained from  $C_p$ . This capacitance  $C_p$  can be written as  $\epsilon A/4\pi d$  if the parallel-plate equation applicable to condensers is assumed valid. Since  $d$ , the barrier layer thickness, is dependent upon the formation voltage used in the porous film preparation, the relationship

$$V = \left( \frac{\epsilon A}{4\pi} E \right) \frac{1}{C} \quad (26)$$

verified for barrier-type films can be tested.

A question arises here as to the identity of  $A$ , the dielectric surface area. Does the area correspond to the metal-oxide interface area, *i.e.*, the geometric area, or to the pore base area? Dekker and Urquhart<sup>319</sup> suggested the use of the former

area. Subsequent results by Hoar and Wood<sup>289</sup> confirm this suggestion: the area  $A$  is the metal-oxide interface area, as is the case for barrier-type films.

Equation 26, when applied to porous films, is subject to the same error concerning the validity of assuming that  $V$  in the above equation is the applied voltage, and hence it is more correctly written as

$$V_{\text{applied}} = \left( \frac{\epsilon A}{4\pi} E \right) \frac{1}{C} + \Sigma\phi \quad (29)$$

where

$$\Sigma\phi = (\eta_o + \sigma iR) - V_{\text{reaction}} \quad (30)$$

Equation 29 has been found to be valid for porous films in some work by Petrocelli<sup>320</sup> and also by the present authors.<sup>321</sup>  $\Sigma\phi$ , in agreement with the work of Vermilyea<sup>201</sup> and McMullen and Pryor<sup>197</sup> with barrier-type films, was found to be negative as required by eq 30, since  $V_{\text{reaction}}$  is positive and numerically greater than  $(\eta_o + \sigma iR)$ .

#### b. Current Density-Voltage Characteristics

In section IV.A, IV.C, and in Figure 14 it was shown that although barrier-type films and porous films possess similar characteristics, they differ in one important aspect, the relationship of the current density to the applied voltage. When the applied voltage is increased across a barrier-type film, the current density undergoes the transient shown in Figure 14. When new growth is complete, the current density drops to an electronic level; this electronic current is slightly dependent on the applied voltage. In the case of porous films, however, the current density increases, linearly at first, then exponentially with applied voltage;<sup>51</sup> this current density in the case of alumina films is almost completely ionic.

If the high-field conduction expression is assumed, the exponential dependence of the current density on the voltage is then seen to be due to the nonequality of the linear dependences of the electric field strength on the potential drop across the barrier layer ( $V$ ) and on the barrier layer thickness ( $d$ ). The change in the electric field strength, as the applied voltage increases, will be dependent on the relative changes of the potential drop and the thickness of the barrier layer across which this potential drop occurs. If the changes produced in  $V$  and  $d$  are such as to produce an identical ratio at every applied voltage, *i.e.*, constant anodizing ratio, then the current density would be independent of the applied voltage. Since this is not the case, the anodizing ratio is not constant; non-equal changes in  $V$  and  $d$  will produce the exponential relationship between the applied voltage and the current density in those areas where eq 1 is valid. At low electric field strengths, where eq 1 is no longer valid, the general expression for the ionic current density  $i_+ = 2A_+ \sinh B_+ E$  reduces to  $i_+ = (\text{constant})E$ , *i.e.*, a linear relationship between ionic current density and the field;<sup>322</sup> the constant is representative of the oxide conductivity. In the low-field strength range, a linear relationship between the applied voltage and the current density may then be expected; this is found experimentally.<sup>321</sup>

Can this seemingly linear and then the exponential variation

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of current density, with applied voltage, be accounted for other than by changes in  $E$  caused possibly by changes in the anodizing ratio  $V/d$ ? Can errors arise due to the neglect of factors which vary with either current or voltage, *e.g.*, terms  $\eta_o$  and  $\sigma iR$  in eq 27? Since 15% sulfuric acid is used, the term  $\sigma iR$  can be shown to be negligible compared to  $V_{\text{applied}}$  at all current densities encountered.

The cathode overpotential  $\eta_o$  is related to the current density through the Butler-Volmer equation, and hence the current density can depend either linearly or exponentially on the applied voltage. This assumes, however, that  $\eta_o$  is comparable to the applied voltage and that the Butler-Volmer equation passes from the linear to the exponential law at the point where the applied voltage-current density tends from linear to exponential. It can be established that the Butler-Volmer equation passes from linear law to exponential law at a very low current density (microampere range), while the experimental applied voltage-current density relationship tends from linear to exponential in the milliampere range,<sup>321</sup> *e.g.*, at 30° linear up to 4 V and 3 mA cm<sup>-2</sup>.

Calculations show that  $\eta_o$  can be an appreciable quantity, and hence, although changes in  $\eta_o$  do not appear to account for the linear and exponential relationships between the applied voltage and the current density, corrections to  $V_{\text{applied}}$  should always be applied *via* eq 27 to obtain  $V_{\text{true}}$ . This procedure has been amply demonstrated by Hoar and Yahalom.<sup>199</sup>

It is therefore tentatively concluded that the relationships found between the current density and the applied voltage and between the current density and the anodizing temperature (as discussed earlier in section IV.A.1) are due to small changes in the anodizing ratio  $V/d$ , decreasing with increasing applied voltage and temperature.

### c. Applicability of the High-Field Ionic Conduction Expressions

Efforts to verify the high-field ionic conduction expression (eq 1) have, up to the present time, been largely fruitless and have been subject to considerable experimental scatter from an assumed theoretical  $\log i_+ \text{ vs. } E$  plot.<sup>199</sup> This has doubtlessly been due to a lack of experimental accuracy in the barrier layer thickness determination ( $\pm 1\%$  would be required). The present authors consider that such accuracy could be obtained by ellipsometry and the application of a technique such as that reported by Barrett.<sup>2</sup>

It might be expected that the high-field conduction expression will be found to be valid for barrier layers underlying porous films, although definite proof of this may be experimentally difficult.

### 4. The Phenomenon of "Open Circuit" Dissolution

In the study of porous alumina films formed by anodic oxidation, the lack of information concerning the dissolution of such films when immersed in solutions, and the important parameters in such dissolution, is noticeable. Often in the literature<sup>228</sup> the statement is made, "... the film was left in the sulfuric acid electrolyte upon open circuit to enlarge the pores," or other similar statements, and yet, until recently,<sup>218</sup> no theory existed as to the mechanism of such pore widening and its relation to the porous film thickness.

In a study of the dissolution of unsealed porous alumina films in stirred aqueous solutions of 10% sulfuric acid at 27°

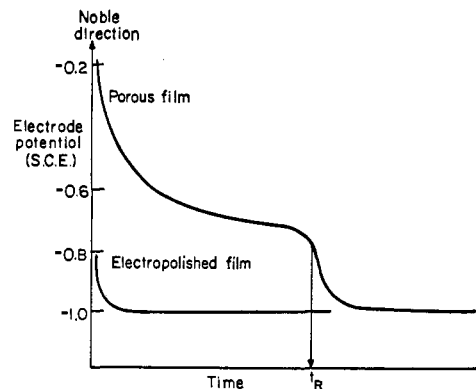


Figure 18. Electrode potential-time behavior for a porous alumina film and an electropolished aluminum surface when immersed in sulfuric acid. The time  $t_R$  is typically 120 min, when the dissolution medium is 10% sulfuric acid, for a porous film prepared in 10% sulfuric acid with a formation voltage of 11.9 V<sup>218</sup>.

Nagayama and Tamura<sup>218</sup> have reported that the rate of dissolution increases slightly with dissolution time until a time  $t_R$  is reached. At this time  $t_R$ , the electrode potential, which was monitored *vs.* a reference electrode (sce), and which had been drifting in the base direction asymptotically to a plateau, underwent a rapid shift (200–300 mV) in the base direction in a short period (see Figure 18); the final electrode potential was reported as  $-1.0$  V (sce). The potential-time behavior of electropolished aluminum in the same solution is also shown in Figure 18; the potential-time behavior observed for porous films would thus appear to be related to the porous structure. Partially similar potential-time behavior has been observed for the potential decay curves of overcharged nickel oxide electrodes<sup>323, 324</sup> and for passivated iron in both aqueous<sup>325</sup> and nonaqueous media.<sup>326</sup>

Nagayama and Tamura have shown this time  $t_R$  to be independent of the porous layer thickness when the films are prepared at the same voltage, and independent of the presence of an imposed cathodic current density. This applied cathodic current density was sufficient to produce an electrode potential of approximately  $-1.0$  V (sce) throughout dissolution, and therefore the latter observation may indicate that the mechanism of oxide dissolution is chemical in nature.

The independence of the dissolution  $t_R$  on the porous film thickness would suggest, as Nagayama and Tamura<sup>218</sup> reported, that the dissolution proceeds *via* a pore-widening mechanism. The dissolution rate was reported as  $0.75 \text{ Å min}^{-1}$ , this representing the increase in the pore diameter and the decrease in the porous film thickness. As the pore diameter increased, the surface area increased to a maximum at  $t_R$ . Beyond  $t_R$  the pore diameter became equal to the oxide cell size, and at this point dissolution was complete; *i.e.*, the porous layer was absent. The rate of dissolution of the barrier layer, which in the Nagayama and Tamura<sup>217</sup> work would be approximately  $119 \text{ Å}$ , was also suggested to be  $0.75 \text{ Å min}^{-1}$ .

It would appear, therefore, that the important factor in porous film dissolution is not the depth of the film, but the

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pore wall thickness. Since the cylindrical pore model of the porous film proposes that the pore wall thickness is dependent on the applied voltage,<sup>52</sup> then the dissolution time  $t_R$  should also be dependent on the voltage. The higher the voltage, the greater the dissolution time. (A linear relationship between these two parameters should be found if both the above interpretation and the assumed Keller model for the porous film are correct.)

The final stage of the dissolution process reveals<sup>218</sup> an aluminum surface, which has undergone no self-dissolution during the oxide dissolution, covered with a thin highly protective layer of oxide, presumably the remainder of the eroded barrier layer, which, considering the dissolution media is sulfuric acid, will be quite stable. The potential of the aluminum at this point ( $-1.0$  V sce) clearly shows that the surface is still covered with an oxide, since the potential is at least  $0.9$  V anodic compared with the reversible potential. This final rest potential of  $-1.0$  V (sce) will therefore be a mixed potential, presumably due to hydrogen evolution and aluminum dissolution. The latter process requires the presence of an electric field, and hence the barrier layer is probably near to  $10$  Å in thickness at this potential. The anodic product resulting from aluminum dissolution has been reported<sup>278</sup> to be alumina, and therefore the rest potential will probably be defined by the potentials for the aluminum dissolution–alumina formation and the hydrogen evolution reaction (dissolution of the formed alumina film may also be expected to play a part in the definition of this rest potential).

The time  $t_R$ , from Figure 18, for an electropolished aluminum surface is much lower than that for the porous film. Assuming this pore widening mechanism as being correct, can the decrease in  $t_R$  be related to the much larger pore diameter in the case of an electropolished film (see Figure 12 and Table IX)?

The electropolishing agent used by Nagayama and Tamura<sup>217</sup> was a mixture of glacial acetic acid and 60% perchloric acid under conditions of  $120$  mA  $\text{cm}^{-2}$  for 8 min in 10-sec bursts, at a temperature of  $20$ – $30^\circ$  (10-sec bursts were used to overcome local heating problems due to high current flow). Since the structure of the electropolished film formed by this procedure is not known, it is uncertain whether the difference in  $t_R$  between a porous and an electropolished film can be accounted for in terms of differing pore diameters. It would appear that the difference between the values of  $t_R$  in Figure 18, if due to differing pore diameters, requires a greater difference than that shown in Table IX. Clearly then, a correlation between time  $t_R$  and the pore diameter at constant oxide cell size or between  $t_R$  and the oxide cell size at constant pore diameter would clarify this possibility; the latter conditions are probably more easily obtainable.

In the absence of evidence concerning the structure of aluminum surfaces electropolished in an acetic–perchloric acid mixture, the possibility that  $t_R$  is not related to the structure, as seems the case for porous films, must be recognized. Perhaps some impurity from the electropolishing process is being desorbed, and the aluminum surface electrode potential moves cathodic in an attempt to reach the mixed potential of  $-1.0$  V (sce). Only further work will answer this question.

For alumina films to dissolve in any medium, the alumina must of course be soluble in that medium. It has been reported<sup>327</sup> that sealed porous alumina films are insoluble in citrate solutions of pH 3.5 and therefore undergo no dissolution. However, the addition of sodium fluoride to the citrate

solution promotes dissolution. This was considered to be due to the formation of readily formed AlF complexes which are soluble in citrate solutions. Evidence for the formation of fluoride complexes with aluminum includes the weight gains experienced when alumina films are immersed in fluoride solutions,<sup>327, 328</sup> i.e., 50% weight gain in 120 hr of  $0.1$  M NaF in the case of a sealed porous film, and the microscopic evidence for the existence of a second phase upon the surface of alumina films immersed in fluoride solutions.<sup>329</sup>

Dissolution of barrier-type films has also been reported<sup>118</sup> to occur in ethylene glycol–ammonium pentaborate electrolytes via the formation of a soluble aluminum–borate complex. This dissolution phenomenon has practical implications in that it is considered a mode of failure of aluminum electrolytic capacitors based upon the above electrolyte. Preferential dissolution was proposed<sup>118</sup> to occur at weak spots or flaws in the barrier layer, and the dissolution rate was found to be a function of the barrier-layer thickness. No explanation was given for the latter observation, apart from the fact that it is not due to variation in composition through the film nor to the defect concentration, i.e., the incorporation of electrolyte anions.

Alwitt and Hills<sup>118</sup> have also reported that the dissolution rate was dependent on the electrolyte and upon the presence or absence of water; the dissolution rate of an ethylene glycol–ammonium pentaborate electrolyte was increased by the addition of water. The rate of dissolution also increased from 7 to 9, but was independent of the pentaborate concentration. This all indicates the importance of the  $\text{OH}^-$  and/or the  $\text{H}^+$  ions, and the presence of water in nonaqueous environments (the water is probably involved in solvent equilibria reactions, possibly releasing  $\text{OH}^-$  ions), in the dissolution of alumina films; the importance of these entities in the formation was discussed earlier in section IV.C.

In conclusion, a great deal has yet to be elucidated concerning the dissolution of porous anodic oxide films. Such elucidation of this dissolution phenomenon may be advantageous in that it may indicate that some model of the porous film is more acceptable than another; e.g., the dissolution phenomenon reported by Nagayama and Tamura<sup>218</sup> can be most easily explained on the cylindrical or truncated pore model. Answers to the following questions would help in this elucidation.

- (i) Is the suggested pore widening mechanism correct?
- (ii) What is the behavior of the porous layer thickness during dissolution? Does it decrease in thickness at the same rate as the pore diameter increases?<sup>218</sup> The present authors consider this doubtful.
- (iii) What part does the barrier-layer thickness play in dissolution?
- (iv) How does dissolution rate depend on the film dimensions; i.e., which film dimension controls the dissolution rate?
- (v) How, and in what way, do the dissolution rates of sealed films differ from those of unsealed films?
- (vi) Is the dissolution rate chemical in nature as suggested in this review?
- (vii) If this is so, what type of kinetics does the dissolution rate follow?
- (viii) Since the dissolution proceeds through some soluble species, what is this species?

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(ix) Finally, what is the mechanism of dissolution in terms of dissolving alumina and putting  $\text{Al}^{3+}$  ions in solution?

## V. Summary

In this review the authors have attempted to show the present state of knowledge concerning anodic oxide films on aluminum, complete from formation to dissolution. It is clear that the formation, and the kinetics of formation of barrier-type films, involving high-field ionic conduction, is not yet clearly understood, although several promising theories are available.

The formation of a porous film from a preceding barrier-type film is not understood clearly, although the important characteristics of such a transformation are known. The importance of considering an external surface dissolution process during porous film formation has been explained and found to be consistent with several experimental observations. The structure of porous films has yet to be fully established, although a considerable weight of evidence supports the cylindrical or possibly the truncated cone pore model. Satisfactory correlation between this pore model and all experimental observations has yet to be achieved, although considerable progress in this direction has been made recently.

Finally, dissolution of porous oxide films was outlined. The importance of such a study to the elucidation of the porous structure was mentioned. Several basic questions concerning dissolution were posed, the answers to which would do much to forward our knowledge of the porous anodic oxide films on aluminum. For further reading and study note ref 300-335.

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