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# Review
# Anodic oxidation of titanium and its alloys

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This review deals with the procedures used in the anodic oxidation of titanium and its alloys, the nature and properties of the oxide films, their uses, and the trends in research and development.

## 1. Introduction and historical notes

Titanium was discovered in 1791 by W. Gregor, identified and named in 1794 by H. Klaproth, and isolated in an impure form by Berzelius in 1825. The metal was purified in 1910 by Hunter (reduction of the chloride by sodium) but substantial quantities of metallic titanium became available only after the industrial adoption of the Kroll process (reduction of $TiCl_2$ by magnesium), in 1949. High-purity titanium has been prepared in small amounts since 1925 by the so-called "iodide process" (thermal dissociation of titanium iodides) [1].

Early research on the electrochemistry of titanium showed that it cannot be electrodeposited (except as an alloy) from aqueous electrolytes; however, many authors have prepared massive titanium by electrodeposition from molten salts [2].

In view of its position in the periodic table and its electrochemical behaviour, titanium was classified as a "film-former", i.e., a metal whose surface is always covered with a "natural" oxide film, when exposed to air, water or other oxygen-containing media. Titanium shares that classification with many other metals, notably Ta, Nb, W, Al, etc. The "natural" oxide film on titanium ranges in thickness from 5 to 70 Å, depending on the composition of the metal and the surrounding medium, the maximum temperature reached during the working of the metal, etc. [3, 4]. The nature of that oxide film is controversial; it has been reported to consist of $TiO_2$ rutile [1], anatase [5], or lower amorphous oxides [1]. Different oxides are probably formed under different conditions, and the oxide composition may also depend on the purity of the metal.

Titanium is a very reactive metal; nevertheless, it exhibits a high resistance to corrosion, which should be attributed to the protective effect of the surface oxide films. Such films, and in particular $TiO_2$, are inert with respect to most natural environments and many chemicals. Corrosion is believed to occur through "weak spots" in the oxide; a forced increase in film thickness (e.g., by electrolytic or thermal oxidation) would eliminate such weak spots and could increase the corrosion resistance. The electrochemical behaviour of titanium attracted attention as early as 1927 [6] and research in that field advanced with the rapid expansion of the uses of titanium in particular after the development of its alloys, combining a low density with a high strength.

In this review, an attempt has been made to collect and present all available (to the middle of 1972) data on the anodic oxidation of titanium and its alloys; the subject has been discussed in a number of general reviews on the oxidation of metals or on the chemistry of titanium [7-13] but the coverage of the literature on the anodic oxidation of titanium in those reviews was only partial. The oxidation of titanium alloys has received much less attention than the oxidation of titanium; the available data are included in the review, together with the data for the pure metal. Qualitatively, the anodic behaviour of the alloys and the properties of the anodic films are similar to those for the pure metal [14]. It should be noted that certain titanium compounds (e.g., titanium nitride) may also be anodized in aqueous acid solutions, yielding oxide films which are essentially the same as those formed on metallic titanium [15].

## 2. Anodic oxidation procedures

Many electrolytes, under different conditions, have been used for the anodic oxidation of titanium and its alloys; data on the electrolyte compositions and the process conditions are listed in Table I (see the Appendix). In addition to the electrolytes listed below, special electrolytes have been developed to solve certain specific problems, e.g., localized anodic oxidation of titanium has been carried out through the use of viscous electrolytes and apertured templates [16]. In certain cases, mainly in patent information on devices based on anodized titanium, little detail has been reported on the bath composition and process conditions; in other cases, titanium is mentioned as one in a group of metals, without specific details. In those cases, as well as in a few cases in which the original article could not be obtained and had to be cited on the basis of some other reference or abstract, the relevant listing is only partial. Except when noted otherwise, the solutions listed in Table I are aqueous.

We should mention here a number of electrolytes in which anodic oxidation of titanium is not possible; those include $AlCl_3$ solutions in ether [17], 0.5 N HF [18], acid sulphate solutions containing fluoride [19], the Jacquet electropolishing baths (acetate-perchlorate solutions) [20]. In 5 to 10 N KOH at 25° C [21] a passivating oxide film may be formed on titanium, but active anodic dissolution begins after a certain time. Anodic polarization in a solution containing 16 to 132 g $l^{-1}$ ammonium sulphate, 15 to 98 g $l^{-1}$ alkali dichromate and 10 to 17 g $l^{-1}$ HF (at 0 to 100° C, 0.0015 to 0.7 A $cm^{-2}$) caused descaling, rather than oxidation of titanium and its alloys [259]. The addition of chlorides to non-oxidizing aqueous electrolytes hinders the anodic oxidation of titanium and shifts the critical potential for passivation to more positive values [22], while the addition of certain organic inhibitors (e.g., $[p\text{-}(HOCH_2CH_2)_2NC_6H_2O]P(S)(OEt)_2$) favours passivation [23].

In most cases, conventional d.c. sources with a continuously variable output range from 0 to 150 V or higher, are used for the anodic oxidation of titanium; usually, the equipment allows automatic transition from constant current to constant voltage, when a preset maximum voltage has been reached. For a description of such equipment adapted to the anodic oxidation of titanium, see [24]. In certain cases the use of a.c. (e.g., in trisodium phosphate solutions [25]) produces thicker oxide films, as compared with the use of d.c. anodic oxidation with pulsed (20 Hz) current in 20% HCl at 3 to 10 mA $cm^{-2}$ [26] produces a passivating oxide at potentials more negative than in the case of uninterrupted d.c.

## 3. Formation mechanism, thickness, growth rate and breakdown of the anodic films

### 3.1. Formation mechanism

The formation mechanism of anodic oxide films, and in particular those on aluminium and tantalum, has been the subject of extensive research [11]. Although the general rules governing the anodic oxidation of titanium are roughly the same as for other "valve" metals (i.e., the ionic current during anodic polarization leads to film formation, and the relatively great contribution of ionic current is probably associated with the high heats of formation of the respective oxides [27, 28]), the controversial data on the composition and structure of the anodic films on titanium (see Section 4) lead to certain controversies in published discussions on the nucleation and growth of such films.

According to several authors [29, 30] the first step in the anodic oxidation of titanium involves the formation of an adsorbed layer of oxygen (or some oxygenated species) on the metal surface, or, more accurately, on the surface of the pre-existing "natural" oxide film. The nature of such adsorption has not been elucidated, and Hoar [31] believes that the problem of the existence or non-existence of such an adsorbed layer should be regarded merely as a semantic argument. In any case, the exact mechanism of primary passivation is difficult to establish, and requires further clarification [32]. Still, it seems certain that the formation of a separate-phase layer is preceded (or at least accompanied) by electric charging of the double layer at the metal electrolyte interface [33]; this is supported by data indicating that passivity may be repeatedly lost and acquired by switching off and on the polarizing current, even after the build-up of the anodic film [34]. The presence of oxidizing species is essential for oxidation [35]. At low anodic potentials, the relationship between the anodic current and the electric field across the oxide film is described by the following equation [36, 37]

$$i_+ = A \exp BE$$

where $i_+$ is the ionic current, $E$ is the field strength and A and B are constants. The halfwidth of the energy barrier for ion migration through the film on a Ti-Zr alloy (under the conditions for which the above equation is valid) increases with increasing zirconium concentration of the alloy [36].

Evidence exists that the anodic film on titanium grows as a result of the transfer of $Ti^{2+}$ cations through the film, i.e., that growth takes place at the oxide solution interface [38-40]; however, other authors have reported that the film grows by oxide ion transfer [41, 42]. Thus, it is most probable that both $Ti^{2+}$ and $O^{2-}$ transfer contribute simultaneously to the growth of anodic films on titanium [43] and it has been suggested that the growth mechanism is similar to that of oxidation in a gas [43]. When a titanium hydride film is present on the metal, titanium ions migrate through that film and the oxide is formed over the hydride [44, 45], but when a thermal oxide is present the anodic film is formed beneath the thermal [46].

The role of the electrolyte in the formation mechanism has not been studied in detail. Although in most cases there are no diffusion hindrances within the bulk of the electrolyte [47], the nature of the anions influences both the initial passivation and subsequent growth stages [24, 48-50]; it has been suggested [51] that an anodic oxide film is formed only if the conditions (including the nature of the electrolyte) favour the formation of $Ti^{4+}$ rather than $Ti^{3+}$ ions.

The steady decrease in current after the establishment of a constant voltage (in the final stages of oxidation) has been attributed to a gradual decrease in the concentration of $Ti^{3+}$ ions in the film [40] or to an increase in the degree of perfection of the film [52]; in both cases there would be an increase in the apparent resistivity of the film.

### 3.2. Thickness and growth rates

The thickness of anodic oxide films is often expressed in terms of the apparent growth rate, i.e., angstroms per volt of applied voltage. Most authors assume a linear relation between final voltage and thickness, independently of current density [53]. The methods used to determine the thickness include weighing [54-56], the Drude-Tronsted polarized light method (which has shown that thickness depends on substrate orientation) [57, 58], absorption of alpha-particles in films stripped by dissolution of the substrate in alcoholic halid solutions [59, 60], measurements of the oxygen content through nuclear reactions [61], interferometry [39, 62], ellipsometry [63] etc. For thickness measurements (or for other purposes, e.g., transmission electron microscopy) the film may be stripped by scratching the surface and immersing in 5% $Br_2$ in methanol [64] or by dissolving the substrate in a mixture of 350 ml concentrated HCl, 650 ml $H_2O$ and 10 g NaF [65].

The growth rate is of the order of 20 Å $V^{-1}$, the scatter in reported values is not too great, bearing in mind the great variety of measuring techniques. The reported values range from 18 [63] to 22 [66] and 23.8 Å $V^{-1}$ [39]. The thickness of the oxide film on alloys seems to be lower, e.g., on a 50% Ti-50% Nb alloy oxidized to 100 V in an aqueous tartrate solution, the thickness reached only 1700 Å [67].

According to Palkina [68] the thickness of the anodic film formed on titanium in 4 N sulphuric acid at 40° C may reach 0.2 to 0.3 μm, but the final thickness at any voltage depends on an equilibrium between competitive growth and dissolution processes [69]. The thickness increases with increasing temperature [55] and the value of about 20 Å $V^{-1}$ refers to room temperature.

The experimental growth rates are somewhat lower than the faradaic rates calculated by assuming that the film consists of $TiO_2$; the deviations from ideality have been attributed to oxygen evolution [70] or to partial dissolution of the oxide [68]. Thus, the current efficiency for film formation depends on temperature, the nature of the electrolyte, and other factors. For anodic oxidation in weakly-acid aqueous solutions the efficiency is near 70% [70, 71]; in aqueous hypochlorite solutions the efficiency depends on pH and has a maximum at pH 2 [72]. The assumption of a stoichiometric ($TiO_2$) composition is not strictly correct (see Section 4) and, in addition, the titanium may dissolve during the oxidation at a lower-than-accepted valency [73], so that the efficiency should be corrected for such deviations. The growth-dissolution equilibrium during anodic oxidation (and thus the efficiency) could be affected by catalytic phenomena at the oxide-electrolyte interface; it has been reported that the anodic dissolution of titanium in sulphuric acid solutions is catalysed by hydrogen [74].

### 3.3. Breakdown during oxidation

The exact nature of the breakdown of anodic oxide films, which occurs above certain critical potentials, is controversial, but in all cases it involves a loss of passivity and in certain cases it leads to pitting of the metal. In many cases, e.g., tantalum, the breakdown voltage under a certain set of conditions is well-defined and reproducible, and breakdown is often accompanied by sparking (the so-called "anode" effect). Titanium is different in this respect; breakdown voltages are spread over a wide range, reproducibility is poor even if great care is taken to ensure similarity of conditions, there is no sparking (except under exceptional conditions) and breakdown is generally manifested by a subtle change in the slope of the oxidation curve or in the rate of oxygen evolution rather than by an abrupt change in current or by thermal effects. Moreover, in the case of titanium the breakdown voltage is strongly affected by the nature of the electrolyte.

In sulphuric acid solutions the breakdown voltage does not exceed 60 to 70 V [56, 75-78] (however, a value of 150 V has also been reported [57]). It has been claimed that in such solutions, the introduction of chloride ions has little effect on the breakdown voltage [51]; however, the addition of sufficient $Cl^-$ to $H_2SO_4$ must decrease the breakdown potential [79]. Alloying of the titanium with palladium increases the upper limit of potentials at which the metal is still passive [80]. In chloride solutions breakdown occurs at 10 to 12 V [38, 51, 75, 81]; the range of passivity of titanium in such solutions may be widened by introducing into the solutions $Cu^{2+}$ or $Fe^{3+}$ ions [82, 83] or by preliminary cathodic treatment of the metal surface [84]. In contact with solid rutile at 1000°, breakdown during anodic oxidation occurred at current densities above 40 A $dm^{-2}$ [41]. According to Ammar [85] the breakdown voltage in aqueous acid solutions is about 100 V. In the anodic oxidation of titanium in ionized oxygen under 85 mTorr, breakdown is observed at 83 V [86]. In aqueous solutions of nitric acid the breakdown voltage is 10 V [87]; breakdown is accompanied by oxygen evolution, but there is no sparking. In buffered borate solutions the breakdown occurs above 100 V [88, 89] and may even occur above 120 V [34, 90] in the case of the pure metal, while the breakdown voltage of the Ti-6 Al-4 V alloy is somewhat lower and is further lowered if the alloy is heat-treated [34]. Burgers [91] has oxidized titanium in aqueous borate solutions up to 200 V. In non-aqueous formic acid solutions (containing $H_3PO_4$ and $Et_3N$) the breakdown voltage is 260 V, but drops to 60 to 70 V if water is added to the electrolyte [50]. The breakdown voltage is affected by agitation of the electrolyte, i.e., in ammonium tartrate solutions its values are 20 and 51 V without and with agitation respectively [92]; it is important to note that in such solutions breakdown starts at flat surfaces rather than on edges.

Yahalom and Zahavi [77] have shown that in sulphuric acid solutions partial breakdown occurs continuously during the anodic oxidation of titanium, but there is a noticeable change in mechanism above 65 V; the breakdown in such solutions leaves a crater-like structure. Breakdown may be associated with film cracking, caused by internal stresses in the oxide [52]. In his theory of dielectric breakdown of anodic films, Sato [93, 94] attributed a major role to the mechanical pressure $P$ exerted by the electric field $E$:

$$P = [(\epsilon(\epsilon - 1)\, E^2)/8\pi] - \gamma/L$$

where $\epsilon$ is the dielectric constant, $\gamma$ is the surface tension and $L$ is film thickness. Sato did not deal specifically with titanium but calculations show that for field strengths of the order of $10^6$ to $10^7$ V $cm^{-1}$ (i.e., similar to those existing during the oxidation of titanium) the pressure would exceed 1200 kg $cm^{-2}$; such pressures are above the compressive strength of the oxide and could cause cracking, with a loss of passivity.

The differences between the anodic behaviour of titanium and that of tantalum and other metals (and in particular the strong influence of the electrolyte in the case of Ti) indicate that the general theories on the breakdown of anodic films should probably be modified in order to apply to titanium. In that case, there may be more than a single breakdown voltage [77], and the breakdown is probably associated with a complicated relationship between partial anodic dissolution of the film, a passivity equilibrium at the oxide-solution interface, and phase changes or mechanical effects caused by the field and other factors.

## 4. Composition and structure of the anodic films

Metallic titanium exists in the close-packed hexagonal ("alpha-phase") or body-centred cubic ("beta-phase") forms. In alloys, aluminium and tin as well as oxygen and nitrogen stabilize the cph structure, while V, Cr, Mn, Fe, Mo, Si, Zr and Nb stabilize the bcc form. Titanium dioxide has three known modifications (rutile, anatase and brookite), and there are a number of lower oxides, notably TiO and $Ti_2O_3$.

Most investigators [27, 39, 72, 95-104, 181] agree that the anodic film on titanium consists of $TiO_2$; however, it has been reported that the anodic oxide is oxygen-deficient [40, 41, 51, 105], while some authors believe that oxygen is in excess [106-108]. In fact, a certain degree of non-stoichiometry in anodic films in general is regarded as inevitable [109]. This controversy is widened by reports according to which the anodic film is hydrated [110, 111], or consists of mixed oxides including TiO, $Ti_2O_3$ and $TiO_2$ (56, 78, 112]. According to Slomin [113] the film contains also $Ti_2O_5$, while Hall [38] reports that when titanium is oxidized at low potentials in neutral NaCl solutions, three oxygen atoms are deposited on the surface for each titanium atom. According to Isaacs and Leach [114] a fraction of the Ti in the oxide film may have a valence other than four.

The above controversy has its origins in the fact that only few of the authors (and in particular of the earlier ones) have made direct measurements of the Ti:O ratio in the anodic film; in fact, in most cases the conclusions concerning stoichiometry have been drawn on the basis of structural measurements (e.g., by electron diffraction), and such measurements are not very sensitive to slight deviations from stoichiometry. Moreover, it has been reported [39, 48, 115, 116] that both the composition and the structure of the anodic film depend on the composition, thermal history, etc., of the metallic substrate. Thus, it is most probable that the anodic film is not necessarily stoichiometric $TiO_2$, and that films studied by different authors had different compositions (because of differences in the materials used, in the conditions of oxidation, etc.). Indeed, one of the most adequate descriptions of the variation in composition has been provided by Huber [98]. According to Huber, the bulk of the film consists of $TiO_2$ (not necessarily stoichiometric) but the migration of Ti atoms across the metal-oxide interface produces an excess of titanium in the vicinity of that interface, while an excess of oxygen exists near the oxide-solution interface. Such an excess of oxygen near the electrolyte would be consistent with reports according to which oxygen is adsorbed or chemisorbed on the anodic film during its growth, and subsequently migrates into the bulk of the film [30, 41, 43, 106, 108, 117]. The formation of atomic oxygen is not essential and film growth may take place even below the oxygen evolution potential [118].

The valence changes of titanium in the oxide film are regarded as reversible [119]. The oxide composition may change with time (during the oxidation) even if conditions are kept constant. According to Krasil'shchikov [40] the film contains $Ti^{3+}$ ions which are responsible for its conductivity, but which migrate under the influence of the electric field and whose concentration thus decreases with time; a decrease in the concentration of excess $Ti^{3+}$ ions would be accompanied by a proportional decrease in the Ti:O ratio.

The differences in composition near the two interfaces of the film (film/metal and film/electrolyte) agree with the model of Van Rysselbergh and Johansen [118] for the potential drop across the anodic films formed on titanium in saturated ammonium borate solutions. According to that model, the potential drop occurs at the metal/oxide interface, across the bulk oxide, and at the oxide/solution interface. The above authors [118] reported also that the residual current (which is related to the degree of perfection of the film) at constant potential is not constant but varies by a factor of more than 2, as a function of more the purity of the titanium metal.

In addition to the variations in oxygen stoichiometry, the anodic oxide films may contain various amounts of elements other than titanium and oxygen, depending on the composition of the metal and the electrolyte. Thus, $MnO_2$ is deposited at "weak spots" in anodic titanium oxide films when the anodic oxidation is carried out in acid electrolytes containing manganese sulphate [78, 274]. Anodic films consisting of $TiO_2$ with variable amounts of Ba, Ca, Mg, Sr, Li, and other oxides (i.e., films containing alkali or alkaline-earth titanates) are produced by anodic oxidation in electrolytes containing the respective alkali-metal or alkali-earth cations [120] or in molten alkali carbonates [121]. The amount of incorporated foreign ions depends on the conditions of electrolysis, e.g., when titanium is anodically oxidized in saturated $Ba(OH)_2$ solutions at 24° C a film containing barium (probably as the titanate) is formed at a c.d. of 70 mA $cm^{-2}$, but a barium-free film is formed at 5 mA $cm^{-2}$ [122]; the film containing

Ba has a rutile structure, while the Ba-free film is anatase. Anionic species may also be incorporated during anodic oxidation, e.g., phosphorus-containing films are produced in an aqueous solution of ethyl hydrogen phosphate [123]; it is assumed that the P is not taken-up in the dioxide lattice but forms part of an amorphous phase [123]. The semiconducting film formed on Ti in sulphamate solutions contains both metal-oxygen and metal-sulphur bonds [117]. Measurable quantities of radioactive sulphur-35 are incorporated in the anodic film (probably as sulphate ions) during anodic oxidation of Ti in 20% $H_2SO_4$ at 20° C, at 0.6 A $dm^{-2}$ [56].

The anodic oxidation of titanium alloys yields mixed oxide films. The oxidation of Ti-10% Al and Ti-9% Cr alloys produces films consisting of $TiO_2$-$Al_2O_3$ or $TiO_2$-$Cr_2O_3$ [3]. In such alloys, the presence of Al or Cr causes an increase in the corrosion current through the oxide film, in sulphuric acid solutions, while molybdenum reduces the current, i.e., Al and Cr tend to produce less perfect films. The favourable effect of molybdenum is attributed to a decrease in the number of oxygen ($O^-$) vacancies in the oxide film. When Ti-Nb or Ti-Ni alloys are oxidized in 0.1 N KOH, the Nb or Ni are incorporated in the $TiO_2$ lattice as $Nb^{5+}$ or $Ni^{2+}$ ions [124]. The cation ratio in the anodic oxide on alloys is not necessarily the same as in the metal; for example, anodic oxidation of a 50 at. % Ti-50 at. % Nb alloy in 3% ammonium tartrate at pH 2, to 100 V, yielded a 1700 Å film in which the Nb:Ti ratio was 6:1 [67].

The three crystalline forms of $TiO_2$ – rutile, anatase, and brookite – as well as amorphous constituents, have been found in the anodic oxide, mainly by electron diffraction. An amorphous (or partially amorphous) structure has been reported by several authors [39, 77, 99, 123, 125]; upon heating, the amorphous film is transformed first into anatase (at 150° C), then into rutile (above 700° C) [39]. However, most investigators claim that the oxide films on titanium are predominantly crystalline. A rutile structure has been found either by diffraction [5, 123, 126] or by optical or electrical measurements [109, 127-129], e.g., the widths of the forbidden band of the anodic film formed on Ti in 0.1 N NaOH is the same as that of rutile 3.65 eV [128]. On the other hand, Sibert [116] stated after a detailed study that the anodic films formed in aqueous solutions do not consist of rutile; many other authors report an anatase structure [76, 91, 130-134]. Brookite was found by Koyama [135] in anodic films formed in non-aqueous electrolytes, and by Yamaguchi [136] in films formed in sulphuric acid. Yamaguchi noted that reflection techniques had a poor sensitivity since the resulting electron diffraction pattern indicated an amorphous structure, while diffraction by transmission of "hard" (with a wavelength of 0.0272 Å) electrons showed a brookite structure, with a grain size of 50 Å.

The different conclusions of various authors on the structure of the anodic films are most probably based on genuine differences in structure, i.e., there probably is no experimental error, but different structures are formed under different conditions. Moreover, in a given experiment the structures may change when one parameter is changed; for instance, a gradual increase in current density causes a change from amorphous to anatase film, and a sponge-like substance is formed at high densities [123]. Yahalom [77] has shown that amorphous films are formed in 0.1 M $H_2SO_4$ below 5 V, but crystalline films are formed at higher potentials. The differences between the conclusions of various authors could also be explained by assuming that the films are composed of two or more phases; in that case, different measuring techniques would show different structures (e.g., the result would depend on the depth of penetration of electrons, the degree of sophistication of the optical method, etc.). Indeed, the presence of both rutile and anatase has been reported [137] for films formed in 2% $H_2SO_4$. A stratified structure has been observed by Fox *et al* [138] in films formed in molten carbonates at 300° C and up to 49 V; the layer near the electrolyte had a constant thickness (200 to 300 Å) and consisted of anatase, while the layer near the metal consisted of rutile and it alone grew when the potential was increased. The main component of a film grown to 8 V in 40% $H_2SO_4$ was anatase, but there were small amounts of rutile [139].

In addition to the differences in composition and crystalline structure, there may be differences in surface microstructure, porosity, etc. Micro-pitted films have been obtained after anodic polarization of Ti in chloride [38], formic acid [140, 141] and other electrolytes [142]. Porous films are formed in sulphuric acid [143, 144], in phosphate or borate solutions at high pH [145], or in electrolytes containing $Cl^-$ ions [146, 147].

The porosity increases with increasing temperature of oxidation [148]. According to Boddy [109], anodic $TiO_2$ films must be porous or cracked, since the anodic leakage currents depend on the nature of the electrolyte. The oxide films formed in acid chloride solutions containing $Cr^{2+}$ or $Cr^{3+}$ ions at 85° C are cracked, because of internal stresses [52], but the degree of perfection of such films increases with time. Anodic polarization curves show that even films formed under relatively mild conditions (in borate-phosphate solutions) are not completely impervious [34]. Vermilyea [149] also reports that such films are not rigid and uniform.

The crystalline structure and surface microstructure of anodic $TiO_2$ films are not changed by irradiation for up to 60 days with gamma rays from a Co-60 source, at dose rates of $10^{18}$ eV $cm^{-3}$ $min^{-1}$ [161].

Thus, the anodic oxide films on titanium are rarely, if ever, stoichiometric $TiO_2$; in many cases the films contain also elements other than titanium and oxygen. The experimental data indicate that the films may be amorphous, or they may consist of any of the known modifications of $TiO_2$ or mixtures thereof.

## 5. Electrical and optical properties

The electrical and optical properties of the films are closely related, and are discussed in the same section.

The resistivity of anodic films on titanium is either similar to [150] or lower than [151] the resistivity of anodic films on tantalum; the resistivity of the film formed by anodic oxidation in an oxygen plasma is $6 \times 10^{17}$ Ω cm [86]. The dielectric constant of films formed in molten nitrates is 107 [152], but values for films formed at lower temperatures range from 21 to 47 [39, 135]. The dissipation factor is 0.01 [86, 102]. Reported values of the capacitance range from 0.1 μF $cm^{-2}$ or less [86, 102, 143] through 1 to 10 mF $cm^{-2}$ [87, 152, 153] to more than 10 μF $cm^{-2}$ [114]; according to Tajima [154] at 400 V the capacitance is 40 times that of anodic films on aluminium. The mean specific capacitance at 1 kHz is 7.6 to 7.9 μF V $cm^{-2}$ [39]; it decreases with increasing temperature of oxidation. It should be noted that the values reported by Isaacs *et al* [114] refer to extremely thin films; other values in excess of 1 μF $cm^{-2}$ correspond to films formed under rather unusual conditions (molten salts [152], oxidation to very high voltages [154]), and are not characteristic of films used in capacitors. The leakage current in the case of films formed in molten nitrates is 0.2 μA $(\mu F\ V)^{-1}$ [152]; for films tested at 80% the formation voltage, that current is only 1 μA $cm^{-2}$, as compared with up to 5 mA $cm^{-2}$ for films tested at the formation voltage [155]. The band gap is 3.0 eV [156]. The electrical properties of the oxide-electrolyte interface depend on the nature of the electrolyte, e.g., the capacitance of the double layer increases when fluoride ions are present in the solution [157]. The anodic film is semiconducting in contact with an electrolyte (no current passes upon anodic polarization) [34, 104, 138, 158-161]; for films oxidized to 1000 Å in an ethylene-glycol–oxalic acid mixture the rectification factor is $10^6$ [162]. Rectification occurs at the film–electrolyte interface; the activation energy for cathodic current flow through the film in contact with liquid $SO_2$ containing 0.01 N NaI is 6 to 16 kcal $mol^{-1}$ [163]. The carrier concentration in the film during its growth is $10^{20}$ to $10^{21}$ $cm^{-3}$ [164]; the electric field across the film at zero current and at 100 μA $cm^{-2}$ is $\sim 2.5 \times 10^6$ and $3.2 \times 10^6$ V $cm^{-1}$ respectively [165]. The activation barrier for anodic oxidation of titanium is $A^+ = 48.5$ mA $cm^{-2}$, $B_+ = -1.33 \times 10^7$ cm $mV^{-1}$ [105]. The energy of activation for the dissolution of the film (in 10 N HCl at 25 to 70° C) is 18.6 to 22.4 kcal $mol^{-1}$ (it decreases at lower temperatures) [273].

The refractive index of the film depends on its structure, and generally corresponds to that of the observed crystalline modification of $TiO_2$. Koyama [135] reports a value of 2.2 to 2.5. The film exhibits intense interference colours, which depend on the formation voltage, the composition of the metal, the formation temperature, etc. [34]. The film formed at 25 V in 10% ammonium sulphate is blue-purple [146]. Kendall [166] gives the following colour chart for films formed in $HBF_4$ solutions in dimethyl formamide (the formation voltages are in parentheses): indigo (20), dark blue (30), light blue (40), green (50), yellow (60), salmon (70 V). There is an optical absorbance peak at 3.65 eV and a minimum at 3.8 eV [128]. Phillippi and Lyon [167] report an asymmetric absorption band at 828 $cm^{-1}$, composed of superimposed modes at 828 and 809 $cm^{-1}$, for thermal oxide films on titanium; no such band exists in single-crystal $TiO_2$, and data for anodic films are not available. The threshold wavelength for photo-conductivity is 290 nm [53]; the maximum photo emf for 300 Å films (formed in ethylene-glycol–oxalic acid solutions) is 0.53 V (with ultra-violet or green light) [98]. Illumination of the Ti-$TiO_2$-electrolyte system with ultra-violet light reduces the anodic potential [90].

## 6. Applications of the anodic films

Most actual or proposed uses of anodic films on titanium are in the fields of electrical or electronic components (capacitors, resistors, diodes, photo-electric devices) and corrosion protection. Other uses include wear- and friction-resistance, reflective surfaces, preparation for electroplating, decorative coatings, accelerator targets and electrophotographic plates.

Although the volume of titanium used in the manufacture of electrolytic capacitors is small in comparison with aluminium or tantalum, titanium compares favourably with those metals from the standpoint of capacitor properties, and has important weight and price advantages [168, 169]; when the oxidation is carried out in oxalic acid–propanediol solutions the resulting capacitors are superior to those based on Ta-$Ta_2O_5$ [170], and the capacitance of films formed in borate solutions may be up to 40 times that of anodic $Al_2O_3$ films [154]. The use of anodic oxidation of titanium for the manufacture of capacitors has been studied by many authors [102, 171-176]; the electrolytes used in such studies include phosphate [177], borate [103, 154], nitrate [178], carbonate [179], formic acid [50] and glycolonitrile [180] solutions. Several authors have compared the relative merits of different electrolytes from the standpoint of capacitor manufacturing [143, 153, 182-184]; the recommendations differ, but there are indications that the use of organic electrolytes (e.g., ethylene-glycol adipate [184]) yields capacitors of improved properties.

Other methods for improving anodized titanium capacitors include the growth of mixed oxides such as Ba or Ca titanates [120], deposition of $MnO_2$ on weak spots of the anodic oxide [119], nitriding of the metal before anodizing [103], pretreatment in nitric acid [152], superposition of a.c. on the d.c. during the oxidation [143], the use of alloys (e.g., Ti-13% V-11% Cr-3% Al, anodized at 20 to 50 V in mixed $H_3PO_4$-$H_2O$-$C_2H_4(OH)_2$ electrolytes [169]) instead of unalloyed titanium, and the use of two-stage oxidation, in which the titanium was first anodized in 3% ammonium borate, a layer of titanium was deposited by vacuum plating on the anodic film, and the metal was again anodized [185]. Heating to 700 to 800° C converts the anodic film from anatase to rutile and also improves capacitor properties [132].

A few authors have reported that titanium is an unsatisfactory material for electrolytic capacitors since the oxide film is non-insulating [71, 182]. However, it seems that the relation between capacitance and film properties is complex, and the exact nature of the layer responsible for capacitance is not well understood; at least in the case of films formed in borate solutions [114] the layer responsible for capacitance is extremely thin (about 1 Å) and the capacity increases with increasing thickness and is associated with changes in the valence of titanium in the oxide. Equations for the dielectric properties of the films used in titanium capacitors have been presented by Miyata *et al* [186], and equations for the shape dependence of the electrical properties of such capacitors have been proposed by Nakata and Minami [187].

Other uses of anodically oxidized titanium in electric components include diodes and rectifiers [97, 104, 117, 138, 162, 163, 188] and film resistors [189]; the observed photoelectric [121, 162] and piezoelectric [98] effects could also be put to use.

The corrosion resistance of titanium and its alloys in many media, e.g., ammonium sulphate liquors, sulphuric acid, NaCl solutions, inhibited HCl solutions, chlorinated organic solvents, bromine, etc., is improved by anodic oxidation [56, 146, 190-201, 275]. Sealing of the anodic films with palmitic, stearic and other organic acids further improves the corrosion resistance [144].

The effect of anodic oxide films on the stress corrosion cracking of titanium alloys is difficult to measure by direct tests, since such tests usually require the use of fatigue-cracked samples and anodic oxidation inside the hairline crack is ineffective [34]; direct comparative tests with notched (but not precracked) anodized and non-anodized samples are not very sensitive [196], but indicate that the anodic oxidation may have a favourable influence on the resistance to stress-corrosion cracking. This is confirmed by indirect studies of environmental and metallurgical factors [34, 63] which show that those factors which suppress the anodic activity of titanium alloys (i.e., reduce the residual current at a given voltage, increase the breakdown voltage of the anodic film, etc.) have at the same time, an inhibiting effect on stress corrosion cracking. This favourable effect of anodic films is probably associated with the fact that the films reduce the rate of penetration of hydrogen into the metal (it is considered that hydrogen plays an important role in the stress corrosion cracking of titanium alloys in certain environments [202, 203]. For example, after 7 h of exposure to 40% sulphuric acid at 60° C the hydrogen concentration in anodized titanium remained the same as before the immersion (11 ppm) while that in non-oxidized samples increased to 145 ppm [204]. The anodic oxide film slows-down the penetration of hydrogen at 500 to 700° C [205], and improves the fatigue resistance of titanium alloys [144, 206]. However, in general the film on titanium alloys is less protective than the film on non-alloyed titanium [207]; it should also be noted that partially crystalline films (such as the anodic films on titanium and its alloys) are less protective than fully amorphous films (such as those on tantalum) [208].

Anodic oxidation of titanium and its alloys reduces friction, abrasion and wear [148, 201, 209] and prevents seizing and galling, e.g., in cold forming [140, 210-213]; this is attributed to a micropitted state of the oxidized surface, which is thus able to hold lubricants.

As a result of their strong interference colours, anodic films on titanium find use as "coloured" coatings [166, 214, 215]. Anodic coatings have also been used as intermediate layers in electroplating on titanium [216, 217] or as a base for selective electroplating [215]. Anodizing of vacuum deposited titanium is a step in the manufacture of reflecting surfaces [218]. Electrophotographic plates have been made by anodic oxidation of titanium in a borate solution [219]. Finally, anodic oxidation is a convenient method for binding oxygen in the form of $TiO_2$, which has a high radiation stability and may be used as an accelerator target or in other devices that have to accommodate high radiation fluxes [60].

## 7. Trends in present research and conclusions

The advances in modern science and technology have been reflected in the development of research techniques for the study of anodic films on titanium, and the early electrochemical, capacitance, corrosion, and other measurements are today supplemented by a wide use of electron microscopy and diffraction, ellipsometry, the use of particle accelerators, etc. The next few years would probably witness the application to the anodic oxidation of titanium of even more advanced techniques (some of which have already been applied to the oxidation of other metals) such as acoustic measurements [220], ion microprobe mass spectrometry [221], shifts in X-ray fluorescence lines [222], radioisotopic tracing [223], automated ellipsometry [224], Auger electron spectrometry [225], reflection [167] and infra-red [226] spectroscopy, optical studies in electric fields [227], optical absorbance to infra-red emittance ratios [262] and computerized anodization control [228]. The major remaining problems in the anodic oxidation of titanium, and in the first place the question of the exact relation between oxidation conditions and the composition, structure and properties of the resulting film, would probably be the subject of more detailed studies. There is still controversy concerning the nature of breakdown, the mechanism of ionic transfer through the growing film, the growth rate in different electrolytes, and the distribution of the electric field across the oxide [34, 229, 230, 270]. New oxidizing techniques, including plasma anodizing [231, 232] and the use of non-aqueous electrolytes [233–235] could be used on a wider scale, and the range of practical applications could be extended to optical measuring instruments, medical engineering, nuclear instrumentation, etc.

In conclusion, it could be said that the anodic oxidation of metals is a true interdisciplinary field which employs steadily increasing numbers of physicists, electrochemists and metallurgists in a search for better understanding of its basic phenomena and for improving and extending the uses of the resulting films.

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## Appendix

TABLE I Anodic oxidation procedures

| Electrolyte composition | Operating condition and remarks | References |
|---|---|---|
| 1. 10 N sulphuric acid | Use of a.c., 10 to 10 000 $H_2$. Oxide film formed only at low frequencies | [29, 26] |
| 2. 22% $H_2SO_4$, with small amounts of Al, Cu and Zn salts | 0 to 60° C, 5 to 80 V, Al cathode | [214] |
| 3. Solutions of borate, phosphate, succinate, citrate or tartrate in organic acids, alcohols or esters | Various | [236] |
| 4. 54.6% methanol – 31.6% adipic acid – 9.7% sodium adipate, 5.1% water | 3.5 V, $3 \times 10^{-6}$ A $cm^{-2}$ | [237] |
| 5. 2% $HNO_3$ | 4 V, ambient temp. | [216] |
| 6. Buffered borate solutions | At pH 6.7 to 12.5 | [145] |
| 7. 8% $H_2C_2O_4$ | 0 to 60° C, 5 to 80 V | [214] |
| 8. 3% ammonium tartrate | pH 7, 10 mA $cm^{-2}$ | [92, 151] |
| 9. 1 to 5% NaOH | Ambient temp., 4 V | [212, 216] |
| 10. Mixed nitrates (sodium-calcium) | 348° C, up to 50 V | [152, 178] |
| 11. Sulphuric acid (various concentrations, from 0.2 N to concentrated) | 1 to 20 mA $cm^{-2}$, various temps. up to 100° C | [3, 43, 44, 55, 56, 68, 75, 77, 136, 137, 139, 142, 190, 193, 198, 201, 202, 213, 217, 238, 241, 255, 257, 260, 265, 267, 269, 276] |
| 12. 5% tartaric acid, or 20% $H_3PO_4$, or 5% oxalic acid | 1.5 to 7.5 mA $cm^{-2}$, up to 130 V | [142] |
| 13. Dilute HCl (2 g $l^{-1}$) containing $Cr^{3+}$ (175 g $l^{-1}$) and $Cr^{2+}$ (15 g $l^{-1}$) ions | pH 1.0, 85° C | [52] |
| 14. 2 N $Na_2SO_4$ + 0.1 N $H_2SO_4$ | | [164, 247] |
| 15. Dilute HCl, with organic inhibitors | 11 to 14 V, form unstable films | [81, 248, 249] |
| 16. 1% $CrO_3$ in dilute $H_2SO_4$ or $H_3PO_4$ | 20 min at 5 A $ft^{-2}$ | [250] |
| 17. 15% $H_2SO_4$ + 40% $H_3PO_4$ | 1 A $dm^{-2}$ | [251] |
| 18. $H_3PO_4$ (50 g $l^{-1}$) – NaF (930 g $l^{-1}$) | | [46] |
| 19. Concentrated (> 350 g $l^{-1}$) NaOH or KOH | 30 to 80° C, 25 to 80 V, 5 to 60 sec | [215, 252] |
| 20. Sulphamic acid in formamide | Room temperature | [234] |
| 21. 450 g $l^{-1}$ $CrO_3$, small amount of HF | 250 mA $cm^{-2}$, 3 min | [119] |
| 22. 8% $H_3PO_4$ in tetrahydrofurfuryl alcohol | 2 mA $cm^{-2}$, 50 to 150 V up to 100° C | [97] |
| 23. Various sulphuric-phosphoric acid mixts. | 40 to 50° C | [147] |
| 24. 5 to 20% ammonium sulphate | 108 A $m^{-2}$, 10 to 40 V | [204] |
| 25. 1 N sodium sulphate | | [129] |
| 26. 10% oxalic acid | 25 to 75° C | [207, 253] |
| 27. 0.1 to 11.0 M HCl | Solutions in methanol with 10% $H_2O$ | [115] |
| 28. Hot concentrated HCl | Up to 9 V | [258] |
| 29. Saturated oxalic acid | 25 to 60° C, 5 to 60 mA $cm^{-2}$ | [105] |

| Electrolyte composition | Operating condition and remarks | References |
|---|---|---|
| 30. 0.1 M $HClO_4$ | | [239] |
| 31. Molten 1:1 $NaNO_3$:$Ca(NO_3)_2$ mixture | 300° C, Al cathode | [138] |
| 32. 5 N $H_2SO_4$ with 1 mol $l^{-1}$ KI | Above 1 mA $cm^{-2}$ | [261] |
| 33. 1:1 mixture of ethylene-glycol and saturated oxalic acid | 12 V | [98, 162] |
| 34. Oxygen-free HCl containing >0.115 mol $l^{-1}$ trivalent Fe | 35° C; dissolution of Ti occurs if the Fe concentration is reduced | [83] |
| 35. 0.12 N NaF in 5% sulphuric acid | | [189] |
| 36. Borax in diethylene glycol | | [256] |
| 37. 18% HCl | Use of a.c., 50 Hz 5000 A $m^{-2}$ | [215] |
| 38. 2 to 8% NaOH or KOH, 1 to 3% EDTA or other complexants (gluconate, nitriloacetate) | 20 to 40 min, 10 to 12 A $ft^{-2}$ 150 to 212° F | [196] |
| 39. 5 N $H_2SO_4$ with inhibitors (e.g., *p*-nitroaniline) | | [254] |
| 40. 40% $H_2SO_4$, up to 0.186 g $l^{-1}$ titanyl ions | 0.4 mA $cm^{-2}$ | [49] |
| 41. 3.0 to 3.5% NaCl | | [63, 191] |
| 42. HF 11.5, $H_2O$ 6.2, tetrahydrofuran 15, ethylene glycol 67.3% | 30 to 55° C, interrupted current (500 Hz) | [263] |
| 43. 10% $NH_4$ borate in ethylene-glycol | 12 to 85° C, up to 200 mA $cm^{-2}$ | [264] |
| 44. 8 to 40 oz $gal^{-1}$ NaOH or KOH, 3 to 10 oz $gal^{-1}$ NAF | 35 to 40 V, 5 min | [113] |
| 45. Ethylene-glycol 100 ml, $H_2O$ 100 ml, $H_3PO_4$ 10 g | First at 200, then at 4 to 8 mA $in^{-2}$ | [132] |
| 46. Mixed (e.g., Na-ammonium) phosphates, 70 g $l^{-1}$ | pH 3 to 12 | [199] |
| 47. NaOH 214.5, $Na_2SiO_3$ 18.75, $TiO_2$ 15.0, activated carbon 3.75 g $l^{-1}$ | pH 13 to 14, 66 to 68° F, 10 A $ft^{-2}$ Pb cathode | [206] |
| 48. Various solutions (0.01 to 0.4% NaF, KF, $NH_4F$; 1 to 10% $NH_4HB_4O_7$, $KH_2PO_4$, $H_3PO_4$; or in 0.1 to 5.0% $NH_4BF_4$, $(NH_4)_2SiF_6$, $SnF_2$, $ZnF_2$, $CdF_2$ dissolved in water with glycerol, methanol, formamide, ethanolamine) | 50 to 80° C, 10 min, 80 to 200 V | [246] |
| 49. 0.1 N KCl | 12 V | [111] |
| 50. 0.5 N $Na_2S$ or $HClO_4$ | 25 to 65° C | [18, 269] |
| 51. 0.05 M $Na_3BO_4$ | 1 mA $cm^{-2}$, 30 min | [268] |
| 52. Ethyl hydrogen phosphate | In aqueous solutions | [123] |
| 53. 20% $NHO_3$ + 3% HF | | [266] |
| 54. 20% sulphuric acid saturated with $H_2$ | Room temp, above 140 mA $cm^{-2}$ | [101] |
| 55. 0.5% ammonium hydrogen phosphate | 85 V | [218] |
| 56. Dilute HCOOH solutions | 200 to 250 V, 5 to 20 A $ft^{-2}$, 0 to 40° C | [140, 141] |
| 57. 70% glycolonitrile | 90 min at 75 V | [180] |
| 58. Various electrolytes (comparative study): nitric, sulphuric, phosphoric, boric, oxalic, tartaric, citric acids, $K_2Cr_2O_7$, $Na_2MoO_4$, $(NH_4)_2S_2O_8$, $Na_2WO_4$, $NH_4HSO_4$ | 24 V, 18 to 20° C | [181] |
| 59. 10 parts ethyl hydrogen phosphate, 5 parts 85% $H_3PO_4$, 20 parts glycerol, 65 parts $H_2O$ | 250 V, 10 mA $cm^{-2}$, 30 min | [102] |
| 60. Two step anodizing: | | |
| I: 100 ml ethylene-glycol, 100 ml $H_2O$, 10 g phosphoric acid | 200 mA $in^{-2}$ | [272] |
| II: 10% $H_3BO_3$ | Constant voltage, to a residual current of 1 mA $in^{-2}$ | |
| 61. 7% ammonium carbonate | | [179] |

| Electrolyte composition | Operating condition and remarks | References |
|---|---|---|
| 62. Various electrolytes ($NH_4HB_4O_7$, $NH_4$ molybdate, citrate, tartrate, succinate, or borax, $NH_4H_2PO_4$) in organic solvents (methanol, ethanol, propanol, glycol, glycerol, propionic acid, diethylamine, ethylene glycol, pyridine, $Ac_2O$) | | [183] |
| 63. 0.1 N $NaBO_2$ | 1.0 to 5.0 mA $in^{-2}$ | [134] |
| 64. HCOOH containing 2% phosphorous acid, 5 to 10% $H_2O$, 400 to 700 ppm HF | 60 to 70 V (or 260 V in absence of water) | [50] |
| 65. Ethylene-glycol adipate | | [184] |
| 66. 2.5% $H_3BO_3$ with 0.05% borax | 150 to 250 V | [219] |
| 67. Eutectic mixture of molten alkali carbonates | 600 to 800° C | [121] |
| 68. 3% ammonium borate | | [185] |
| 69. Mixed Li-Na-K carbonate | 600 to 700° C, above $10^{-3}$ A $cm^{-2}$ | [271] |
| 70. Saturated $Ba(OH)_2$ | 25° C, 5 to 70 mA $cm^{-2}$ | [122] |
| 71. 70% $HNO_3$ | 25° C, 10 V, 1 mA $cm^{-2}$ | [87] |
| 72. Solid rutile | 900 to 1000° C, up to 40 A $dm^{-2}$ | [41] |
| 73. Distilled $H_2O$ | Boiling | [240] |
| 74. Ammonium borate solution, containing starch–iodine | 4 to 5 V | [88] |
| 75. 1 to 43% $HBF_4$ in dimethyl formamide | 10 to 60 sec, 20 to 70 V | [166] |
| 76. Dilute cyanide solutions | | [244] |
| 77. 3% ammonium tartrate | pH 2, 100 V | [67] |
| 78. Saturated $H_3BO_3$ or dilute $CrO_3$, LiOH, KOH, citrate or tartrate | 50 to 2000 V, below 100° F | [201] |
| 79. Mixed $H_3PO_4$-$H_2O$-$C_2H_4(OH)_2$ solution | 20 to 50 V, suitable for alloys | [169] |
| 80. 50% $C_2H_5PO_2(OH)_2$ - 50% $H_2O$ | 300 to 400 mA $dm^{-2}$ to 150 to 400 V, then at constant voltage to below 10 mA $dm^{-2}$ (residual current) | [176] |
| 81. Saturated ammonium borate | 25° C, 100 mA $cm^{-2}$ | [154] |
| 82. 0.01 M $Na_2SO_4$ | 29° C, 12.5 mA $cm^{-2}$, to 70 V | [131] |
| 83. 0.1 N KOH | | [124] |
| 84. Oxygen plasma ionized at 800 V | 85 mTorr, 80 V | [86] |
| 85. 20 vol conc. $HNO_3$ + 80 vol conc. $H_2SO_4$ (electrolyte "SN") | | [39] |
| 86. Dilute solutions of organic acids | | [277] |
| 87. Mixed chlorate electrolytes | | [245] |
| 88. 2% $H_3BO_3$ + 0.5% $(NH_4)_2B_4O_7.4H_2O$ | | [149] |
| 89. Saturated oxalic acid, with 1-2-propanediol | | [170] |
| 90. 5 N $H_2SO_4$, >0.01 mol $l^{-1}$ $SbCl_3$ | 40° C | [242] |
| 91. NaCl, or K dichromate, or K phosphate solutions | 10 V | [243] |
| 92. Dilute $H_3BO_3$ | pH 9 to 10, 60 V | [114] |
| 93. Acid methyl-ethyl phosphate solutions (5 to 25%) | pH 0.4, 14 mA $cm^{-2}$, up to 400 V | [143] |
| 94. 10% NaCN, or alkaline K-Ti oxalate | 10 V (maximum voltage) | [143] |
| 95. 5% HF, or 70% $HNO_3$ | 20 V (maximum voltage) | [143] |
| 96. 5 to 10% oxalic-citric-lactic acid, or 5% $Na_2HPO_4$ | Up to 300 to 400 V | [143] |
| 97. Ammoniacal tartaric acid solutions | | [66] |
| 98. 3% $H_3PO_4$ + 1% $H_3BO_3$ | Room temp., up to 110 V | [34] |
| 99. Molten $HNO_2$ or $HNO_3$ | 315° C, constant current 4 mA $cm^{-2}$ | [278, 279] |

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