

Growth and dissolution of anodic antimony oxide in oxalic acid electrolytes

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The kinetics of anodic oxide growth on antimony in oxalic acid electrolytes was studied. The shapes of the voltage/time curves proved strongly to depend on the concentration of the electrolyte. Based on the different shapes, three electrolytes were chosen for investigations of the oxide film dissolution by means of impedance and open-circuit potential measurements. The rate of dissolution increases with increasing oxalic acid concentration. A relation is found between the shapes of the voltage/time curves and the proposed competitive process of film growth and dissolution, which includes the formation of an outer adherent layer of dissolution products. The proposed mechanism agrees well with some characteristics of the induction periods and explains adequately their appearance. The impedance studies indicate that the final thickness of the anodic oxide decreases with increasing concentration of the oxalic acid electrolyte. It is concluded that concentrations equal to or lower than 0.01 M (COOH)₂ have to be used in order to produce thick barrier-type anodic films.

Key words: anodic antimony oxide, oxide growth, oxalic acid anodizing, chemical dissolution, impedance measurements

INTRODUCTION

The anodic passivation of antimony in acid and alkaline electrolytes has been described by El Wakkad and Hickling [1] in the early fifties of the last century. Since then, the anodic behavior of antimony has been extensively investigated in view of its use as constituent of alloys for lead-acid batteries [2, 3] or of materials for lithium-ion batteries [4]. Anodizing has been carried out in sulfuric acid electrolytes [2, 3, 5–8] or sulphuric acid with additives [9, 10], in phosphoric acid [11, 12], buffered phosphate solutions [13, 14] or phosphate esters [15], in a boric acid electrolyte [16], as well as in different neutral and alkaline media [17,18].

During constant current anodization, broad or restricted regions of linear potential rise with time are reported, depending on the nature of the electrolyte [16, 17], the current density [12], and the potential attained [5, 13]. Deviations from the linearity are ascribed to a duplex anodic film structure, composed of antimony oxides at different oxidation stages [1], the formation of an outer porous layer [12, 19], the structural or mechanical defects [7], the crystallization [5], the formation of outer layers of hydroxo sulfates [20] or phosphates.

Retarded potential rise with time has been observed in a number of cases [15, 21, 22]. The related induction periods have been ascribed [12] to the initial formation of a semi conducting layer with its consequent conversion into a barrier sub layer. The main disadvantage of anodic antimony oxides is their instability in most of the forming electrolytes. The oxide films are easily dissolved in acid, neutral and alkaline media, as ascertained by open-circuit potential and impedance measurements [1, 5, 7, 17, 19], and by ellipsometric studies [14].

Preliminary data on the oxidation of antimony in oxalic acid pointed at the possible occurrence of relatively thick oxide films with bright interference colors after anodization up to high voltages. This work reports on the growth and dissolution kinetics of anodic antimony oxide in oxalic acid solutions.

EXPERIMENTAL

The specimens were cut from an antimony rod of 99.9995 % purity by means of a diamond disc. The cylindrical bodies were 1 cm thick; the working area of the antimony electrode was limited to one of the bases of the cylinder, having a surface of ca. 2.5 cm². A silver lead-out was welded to the opposite base of each cylinder and the non-working area was isolated by thermoplastic epoxy resin. The electrodes were polished with fine-grained emery papers and electro polished for 60 s in 1:9 volume parts of 70 % HClO₄ to (CH₃CO)₂O at 20 °C and

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0.3 A cm^{-2} . After rinsing with methanol and water, the electrodes were brightened at $20 \text{ }^\circ\text{C}$ for 10 min in 1: 1 volume parts of concentrated hydrochloric acid to water and thoroughly washed in deionized water.

Anodic growth and dissolution were studied in oxalic acid solutions with concentrations varying from 0.001 M to 0.1 M. In order to avoid some slowing down of the dissolution rate, due to saturation with ionic antimony species, large volumes of the most used solutions were prepared.

An especially designed galvanostat (0.5 A, 600 V) was used for the anodization at the constant current density of 2 mA cm^{-2} under controlled temperature conditions. In order to improve reproducibility of results, anodizing was carried out in unstirred electrolytes. The variation of the open-circuit potential with time was measured against a saturated calomel electrode (SCE); measurements started immediately after switching off the polarization.

The dissolution rate was evaluated by means of ac impedance measurements at a frequency of 1000 Hz. An EG&G Instruments PAR model 273 potentiostat and 5208 two phase lock-in analyzer connected to an IBM personal computer via GPIB-II interface, and a M378 and M342 software were used to run the tests, to collect and evaluate the experimental data. The impedance measurements started about 30 s after switching off the polarization in order to avoid overloading of the potentiostat, due to non-dissipated space charge in anodic antimony oxide. The initial reciprocal specific capacitance, $1/c_{s,0}$, assumed to be proportional to the final thickness of the growing oxide film, was determined by extrapolation to zero time of the corresponding $1/c_s(t)$ -curves.

RESULTS AND DISCUSSION

Anodic oxide films on antimony were grown in a series of oxalic acid solutions with concentrations varying from 0.001 M to 0.1 M $(\text{COOH})_2$. The voltage/time dependence of the film growth under constant temperature (293 K) and current density (2 mA cm^{-2}) conditions without stirring is shown in Fig. 1 for six $(\text{COOH})_2$ concentrations. No induction periods are observed in most of the solutions used. In the solutions with concentrations from 0.01 M to 0.03 M, the initial linear potential rise is followed by slowing down, arrest or passage through maximum values of the forming voltage. Except for the 0.01 M solution, a second potential rise up to high voltages always takes place. This second potential rise is only partially shown in the

figure. It can be concluded that the shape of the voltage/time curves gradually changes with the

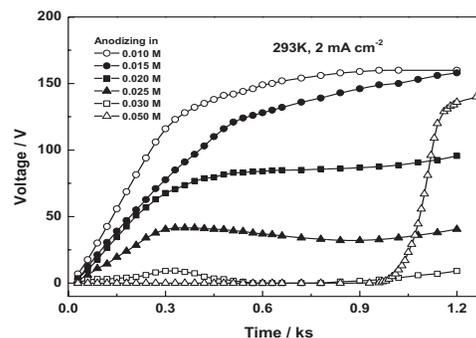


Fig. 1. Time variation of the forming voltage during anodization of antimony at 293 K and 2 mA/cm^2 in unstirred aqueous solutions of oxalic acid with different concentrations.

increasing concentration of oxalic acid. Moreover, the ‘induction period’, observed in 0.05 M solutions, appears to be a reasonable sequence of the changes in shape. In this case, the assumed initial formation of a semi conducting layer can hardly account for the retarded potential rise [12].

Previous investigations, mentioned in the Introduction, have furnished unambiguous evidence both for the formation of duplex films on antimony and for their dissolution in the forming electrolytes. These facts could be useful in the attempt to explain the anodic behavior of antimony. For the purpose, three oxalic acid solutions with concentrations of 0.01 M, 0.03 M and 0.05 M were chosen as representative of forming electrolytes with different shapes of the voltage/time curves. The dissolution rate of films, grown up to 5 V, 40 V and 140 V, was studied in the above solutions by means of ac impedance measurements at 1000 Hz. The results are shown in Fig. 2. It can be seen that the anodic oxide dissolves at a high rate.

Only about 7 minutes are needed for the film, formed up to 140 V in 0.01 M $(\text{COOH})_2$, to dissolve almost completely (Fig. 2a); the essential decay in film thickness takes less than 2 minutes in the other two solutions (Figs. 2b and 2c). The graphs in the latter figures are presented in a large scale; the thickness changes after the second minute of dissolution numerically correspond to the range of $1/c_s$ -values in Fig. 2a for the almost dissolved films.

After the initial decay in the film thickness during dissolution in 0.03 M and 0.05 M $(\text{COOH})_2$, the reciprocal specific capacitance consecutively passed through a minimum, gradually increased to a maximum, and afterwards, slowly decreased with

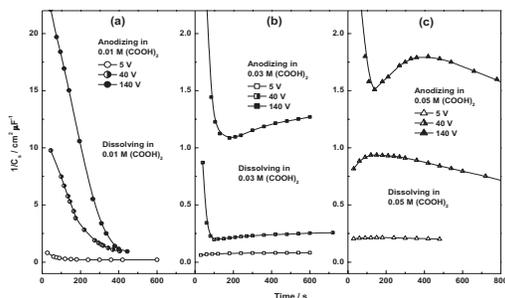


Fig. 2. Time variation of the reciprocal specific capacitance, $1/c_s$, of anodic antimony oxides grown without stirring in 0.01 M (a); 0.03 M (b) and 0.05 M (c) $(\text{COOH})_2$ at 293 K and 2 mA cm^{-2} up to 5 V, 40 V and 140 V.

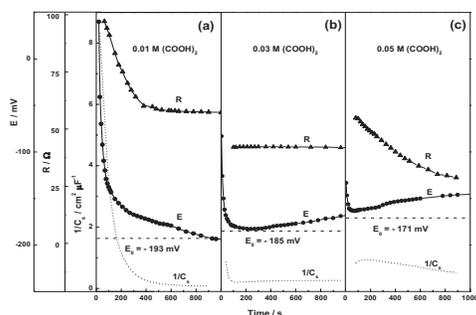


Fig. 3. Time variation of the resistance R and the open-circuit potential E of antimony oxide electrodes during dissolution in 0.01 M (a), 0.03 M (b) and 0.05 M (c) oxalic acid solutions after anodization up to 40 V at 293 K and 2 mA cm^{-2} . The dashed lines show the variation of the reciprocal specific capacitance, $1/c_s$, from Fig. 2. The dash-dotted lines mark the steady-state potential of non-anodized antimony in the electrolytes used. All potentials are measured versus saturated calomel electrode.

time, as illustrated in Fig. 2c, and partially in Fig. 2b. Such course of the curves could be attributed to the formation of an outer layer of dissolution products. The rapid dissolution of the oxide film in the oxalic acid electrolytes suggests the appearance of the outer layer since the very beginning of anodization as a result of the concurrence between film growth and dissolution. The layer grows further, parallel to the oxide film dissolution, and also dissolves in the electrolyte. Without deliberating about the nature of the dissolution products, a few suggestions can be made for the layer properties. First, a good adhesion to the oxide film is expected; second, the layer should dissolve in the contact electrolyte at a lower rate than that of the oxide, and finally, the layer should have a

porous structure which entangles but does not eliminate the migration of the electrolyte ions.

The above assumptions are in conformity with the experimental results. In addition, the time variation of the resistance and of the open-circuit potential was studied in order to gather more information about the dissolution process. The results in the three oxalic acid electrolytes are shown in Fig. 3.

The time variations of the open-circuit potential, the resistance and the reciprocal specific capacitance of the antimony oxide electrode in 0.01 M $(\text{COOH})_2$ correlate well, as seen in Fig. 3a. After the abrupt initial decay, all three quantities slow down; the potential reaches its steady-state value in the electrolyte.

In 0.03 M $(\text{COOH})_2$, the potential passes through a flat minimum near to the steady-state value, and shifts to less negative values in apparent correlation with the variation of $1/c_s$ (Fig. 3b). The reciprocal capacitance passes through a flat maximum after ca. 2.0 ks (not shown in the figure). This behavior was attributed to the final dissolution of the oxide film, the residual thickening of the layer formed from dissolution products and the on-going dissolution of the outer layer. The resistance passes through a flat maximum and decreases slowly with time, most probably due to the concurrence between the growth and the dissolution of the outer layer.

In 0.05 M $(\text{COOH})_2$, both, the resistance and the reciprocal specific resistance, pass through a maximum and decrease afterwards, as illustrated in Fig. 3c. Here, again, final dissolution of the oxide film, residual thickening of the outer layer and its dissolution in the electrolyte can account for the observed behavior. The relatively fast resistance drop appears to be connected to a stronger dissolving action towards the outer layer of the 0.05 M solution compared with the other two electrolytes.

The open-circuit potentials in 0.03 M and 0.05 M solutions vary in time in a quite similar way. The potential shift in 0.05 M $(\text{COOH})_2$ to less negative values, however, continues even after the decays in resistance and reciprocal capacitance have begun. Due to the various dissolution processes and the impeded diffusion in the unstirred electrolyte, its composition in the pores of the outer layer will be different from that in the bulk of the solution. Hence, the observed potential shift could be attributed to the electrolyte changes in the vicinity of the electrode rather than to the thickening of the outer layer.

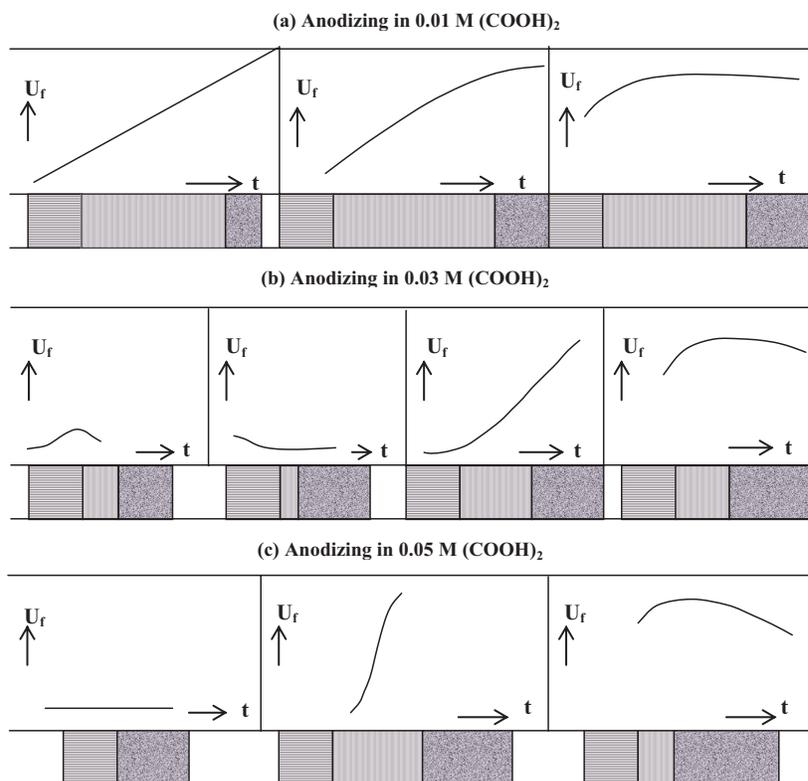


Fig. 4. Schematic presentation of the anodic behavior of antimony (■) in 0.01 M, 0.03 M and 0.05 M (COOH)₂. The stages in growth and dissolution of the oxide film (▨) and of the layer formed from dissolution products (□) are matched to the corresponding parts of the voltage/time curves. The width of the sectors is purely speculative and does not correspond to the real film or layer thicknesses.

Summarizing, the processes of film growth and dissolution of anodic antimony oxide in oxalic acid electrolytes are schematically depicted in Fig. 4. The relatively low dissolving effect of the 0.01 M solution permits the formation of a thick barrier-type anodic film up to voltages as high as 100 V. The continuous thinning of the oxide film and/or a field-assisted dissolution causes the consequent slowing down and the arrest of the voltage rise; the dissolution products adhere to the film surface, forming a porous outer layer which permits the migration of ions.

The stronger dissolving action of the 0.03 M electrolyte leads to the formation of a thin oxide film which gradually dissolves. For a given period of time, the rate of film growth equals to the dissolution rate, resulting in the thickening of the outer layer only. A larger coverage of the surface with dissolution products and/or an increased density of the outer layer provoke the increase of the real current density. The film growth starts then to prevail again over the dissolution. An almost linear voltage rise up to ca. 100 volts is observed, followed by a slowing down, and eventually by a

decrease, resulting in the reduction of the oxide thickness.

During almost 1 ks, no film growth is observed in the 0.05 M oxalic acid. This is the period of time, for which balancing of film growth and dissolution is assumed. Like in the 0.03 M solution, the accumulation of dissolution products in the outer layer leads to higher values of the real current density and an abrupt voltage rise is observed. The slow down and voltage decrease, as mentioned, resulted in lowering of the anodic film thickness.

Studies of the current density dependence of the induction periods of antimony in concentrated phosphoric acid [11] or in 0.05 M oxalic acid [22] showed a decrease of the induction period with increasing current density. The induction period appearance explanation, proposed in this work, agrees well with the above finding. A simple calculation indicates that the induction period disappears at a current density of ca. 5 mA cm⁻², so this value is expected to correspond to the real current density, needed to overcome the dissolution and to restart anodizing of the electrode, covered with dissolution products. Furthermore, the

reported poor reproducibility of induction periods in stirred media [15, 21, 22] is now better understood in view of the complex influence of the hydrodynamics on the oxide film dissolution and the formation and dissolution of the porous outer layer.

The concentration of anions was found to play an important role in the film growth. Thus, the antimony oxide dissolution has proven to be promoted by phosphate ions [13]. A voltage/time dependence, similar to that of the antimony in 0.03 M (COOH)₂, has been obtained for the same metal in KOH and Na₂CO₃ solutions [23]. The shape of the curves was attributed to the presence of carbonate ions. Our studies showed an increasing dissolution rate with increasing concentration of the oxalic acid. As discussed before (Fig. 2), dissolution in 0.03 M and 0.05 M (COOH)₂ started at lower initial film thicknesses compared to the 0.01 M solution. This observation was considered when composing Fig. 4. Moreover, an additional check was undertaken. For the purpose, the initial parts of the capacitance/time or reciprocal capacitance/time curves for films, formed up to different voltages in the three studied electrolytes, were extrapolated to zero time, and the calculated values for the initial reciprocal specific capacitance $1/c_{s,0}$ were plotted against the forming voltage. The curves for the films, formed in the 0.01 M and 0.05 M solutions, are shown in Fig. 5.

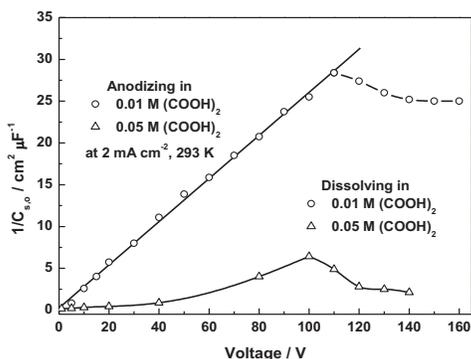


Fig. 5. Dependence of the initial reciprocal specific capacitance $1/c_{s,0}$ of anodic antimony oxide on the final voltage attained during anodization in 0.01 M and 0.05 M (COOH)₂ at 293 K and 2 mA cm⁻².

A linear increase of $1/c_{s,0}$ with increasing voltage of up to about 100 V is observed for the films, grown in 0.01 M oxalic acid. Quite surprisingly, the attendant chemical film dissolution proved not to affect linearity, and relatively high film thicknesses were attained. Above 100 V, the

lowering of the film thickness is possibly related to additional field-assisted dissolution. The anodization in both 0.03 M (not shown) and 0.05 M solutions proved to be severely affected by chemical dissolution of the oxide films. The restricted non-linear increase of $1/c_{s,0}$ with increasing voltage to up to 100 V would mean that the main contribution to the overall thickness is due to the outer porous layer. Above 100 V, the final film thickness decreased like that in the 0.01 M solution but films formed up to 120 V had almost the same residual thickness as those formed in 0.01 M solutions up to 10 V. The above results indicate that relatively thick barrier-type films on antimony can be obtained only in diluted oxalic acid solutions with concentrations equal to or lower than 0.01 M.

CONCLUDING REMARKS

The studies of the growth and dissolution of anodic antimony oxide in oxalic acid electrolytes permitted to limit the concentration range for effective barrier anodizing of the antimony. A scheme of film dissolution was proposed, relating adequately the shapes of the voltage/time curves to the thickness changes, ascertained by impedance measurements. Additional analytical methods have to be used, however, to confirm the assumptions made.

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ОБРАЗУВАНЕ И РАЗТВАРЯНЕ НА АНОДЕН АНТИМОНОВ ОКСИД В РАЗТВОРИ НА ОКСАЛОВА КИСЕЛИНА

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(Резюме)

Изследвана е кинетиката на образуване на анодни оксидни филми върху антимон в разтвори на оксалова киселина. Установено е, че формата на кривите напрежение-време силно зависи от концентрацията на оксаловите електролити. Три електролита, в които се получават кинетични криви с различна форма, са избрани за изследвания на химичното разтваряне на филмите с помощта на импедансни измервания. Предложен е механизъм на основата на конкурентно нарастване и разтваряне на анодния филм, предполагащ образуването на външен порест слой от продуктите на разтварянето. Намерено е добро съответствие между експерименталните резултати и предложената схема за образуване и разтваряне на филмите. Установено е, че сравнително дебели анодни филми от бариерен тип се получават само в 0.01 моларна оксалова киселина.