

## COMPOSITION OF ANODIC FILMS ON ANTIMONY, OBTAINED IN WATER SOLUTIONS OF OXALIC ACID

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**Abstract:** ATR FTIR technique was used to study the composition of anodic films on antimony obtained in water solutions of oxalic acid with different concentrations. The results show, that the layer consists of antimony oxide and antimony oxalate. Increasing the concentration of the forming electrolyte increases the amount of antimony oxalate in the layer. That's probable reason for reduction of the width of the band gap of the resulting film with increasing of the concentration of the electrolyte.

**Key Words:** anodic film, anodic film composition, band gap, ATR FTIR technique, antimony oxide, antimony oxalate

### 1. Introduction

The problem about the composition of anodic films on antimony was discussed by a lot of authors. In the first systematic study on the anodic behavior of antimony [1] it was pointed, that this behavior can be explained by the initial formation of  $\text{Sb}_2\text{O}_5$  and gradually increase the amount of higher antimony oxide on the surface of the electrode. This amount depends on the access of oxygen to the surface. In another study [2] it is supposed that the possibility for the formation of oxides on the electrode depends on the characteristics of the electrolyte. In weak acid and alkali solutions antimony passivates at moderate current densities. During this process it forms relatively thick layer  $\text{Sb}_2\text{O}_3$  in the beginning, under which later it forms thick layer of  $\text{Sb}_2\text{O}_5$ . In case of very small current densities it could be formed intermediate layer of  $\text{Sb}_2\text{O}_4$ . In solutions of strong acids and bases in which antimony trioxide is soluble a film is not formed. Faizulin and Mironow [3] supposed that anodic layer obtained in alkali solutions consists of  $\text{Sb}_2\text{O}_4$ .

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Anodic films on antimony are obtained in phosphoric acid [4]. It is supposed that they are formed by partially hydrated  $\text{Sb}_2\text{O}_3$ , with big amount of defects, more than in the films, obtained in weak solutions of  $\text{H}_2\text{SO}_4$  [5, 6]. It was found that when the potential increases, the thin film composition changes from  $\text{Sb}_2\text{O}_3$  to  $\text{Sb}_2\text{O}_5$ . Formation of anodic layers in 0.1N  $\text{H}_3\text{PO}_4$  was studied [7]. Kinetic curves for the dissolution of the oxide film in most media show a two stage process that seems to be related to the dual nature of the oxide film. The film consists mainly of  $\text{Sb}_2\text{O}_3$ . The processes occurring consecutively during anodic oxidation of antimony in buffered phosphate solutions with pH varying from 2 to 10 are followed by *in situ* ellipsometry [8, 9]. In the first stages of anodization, it takes place formation of soluble species, followed by formation of a highly hydrated film. At higher voltages the film was composed by  $\text{Sb}_2\text{O}_3$ . Recently it was suggested that the layer consists of  $\text{Sb}_2\text{O}_3$ . However the controversial opinions given in the literature show that the problem with the composition of anodic films on antimony is not completely solved.

## 2. Experimental

To investigate the composition of the layers obtained during anodization of antimony in oxalic acid, cylindrical electrodes, made out of highly pure (99.999%) Sb, were used. A thick copper wire was soldered to one of the bases of the cylinder. This base and the surrounding surface were protected with epoxy resin. The working surface area of  $0.8 \text{ cm}^2$  was polished mechanically by polishing paste with decreasing size down to  $0.5 \mu\text{m}$ , washed with neutral detergent, rinsed with double distilled water and dried before anodizing. The forming electrolytes were prepared by solving of chemically pure  $\text{C}_2\text{H}_2\text{O}_4$  in double distilled water. A standard two electrode cell with a golden cathode was used. The anodizing was carried out in a galvanostatic mode with a current density  $5 \text{ mA cm}^{-2}$  at temperature  $20^\circ \text{C}$ . All samples were prepared aiming to obtain layers as thick as possible but with no breakdown. In case of anodizing of no induction period (at concentrations of the forming electrolyte lower than  $0.4 \text{ mol dm}^{-3}$ ) the process was carried out for 80 s (0.4 C), while in those of an induction period the anodization was stopped at about 70 V.

The Fourier transform infrared (FTIR) spectra of the samples were recorded on Bruker Tensor 27 spectrometer, equipped with a detector of deuterated triglycine sulphate (DTGS). The FTIR spectrum was collected by direct deposition of the sample on attenuated total reflectance (ATR) element (diamond crystal) in frequency region  $4000 \text{ cm}^{-1}$ – $600 \text{ cm}^{-1}$  (ATR) with 64 scanning and at resolution of  $2 \text{ cm}^{-1}$ . The spectrum of the sample was rationed against the background air spectrum.

## 3. Results and discussion

The oxalates have two strong peaks in the IR range [10, 11]. We used the band at  $1610 \text{ cm}^{-1}$  (Fig. 1) in order to establish the calibration curve and analyze the oxalate content.

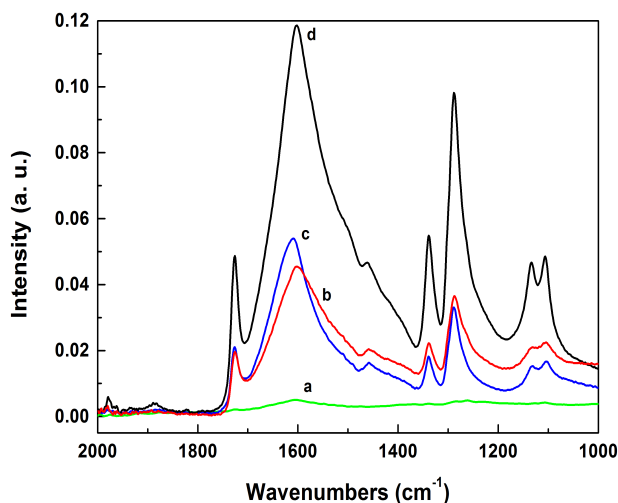


Fig. 1 Variation of the peak at  $1610\text{ cm}^{-1}$  with the change of the concentration of the electrolyte: (a)  $0.025\text{ mol dm}^{-3}$  (in green); (b)  $0.03\text{ mol dm}^{-3}$  (in red); (c)  $0.045\text{ mol dm}^{-3}$  (in blue); (d)  $0.06\text{ mol dm}^{-3}$  (in black).

It becomes noticeable at a concentration of the forming electrolyte  $0.02\text{ mol dm}^{-3}$ . It is obvious that increasing the concentration of the forming electrolyte increases the area of the peak. On Fig. 2 it is shown the dependence of the area under the peak on the concentration of the solution. The point (0, 0) is added to the experimental data and the curve is fitted to pass thru it.

Mixtures of pure antimony oxalate and antimony oxide in the following weight ratios were prepared: 0% (pure  $\text{Sb}_2\text{O}_3$ ); 10%; 20%; 30%; 40%; 50%; 60% and 100% (pure  $\text{Sb}_2(\text{C}_2\text{O}_4)_3$ ). The ingredients were mixed thoroughly and well powdered. The area under the corresponding peak was measured. The weight ratios were recalculated in mol %, and the dependence of the peak area on the composition of the mixture was build. In this way was obtained calibration curve.

Fig. 3 is the calibration curve for the dependence of the area of the peak at  $1610\text{ cm}^{-1}$  on the composition of the sample.

Using Figs. 2 and 3 it can be determined the dependence of the composition of the formed anodic film on the concentration of the electrolyte (Fig. 4). It is obvious that increasing the concentration of the forming electrolyte increases the amount of oxalate in the anodic layer.

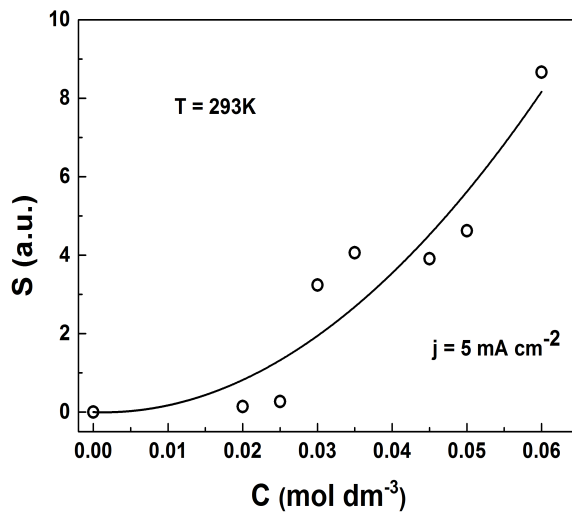


Fig. 2 Dependence of the peak area ( $S$ ) on the concentration of the forming ( $C_2H_2O_4$ )-electrolytes ( $C$ ).

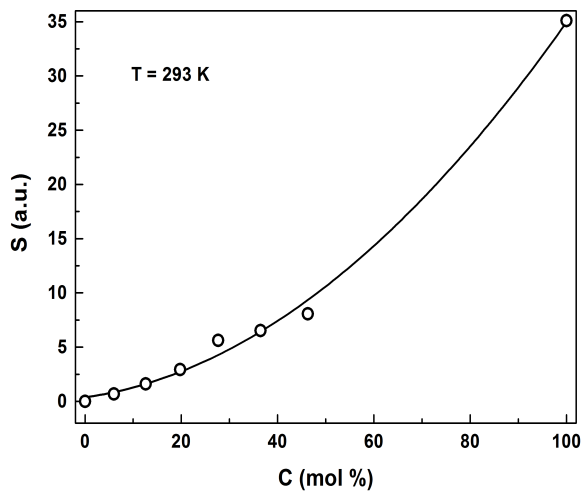


Fig. 3 Calibration curve – dependence of the peak area ( $S$ ) on the concentration of the antimony oxalate ( $C$ ).

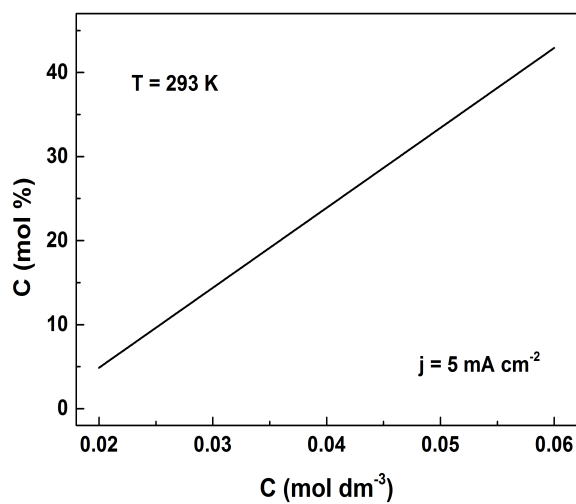


Fig. 4 Dependence of the amount of oxalate contained in the films on the concentration of the forming ( $C_2H_2O_4$ )-electrolytes ( $C$ ).

#### 4. Conclusion

The anode films on antimony formed in aqueous solutions of oxalic acid consists of antimony trioxide and antimony oxalate. Increasing concentration of the electrolyte increases oxalate content in the layer. This in turn should affect the physical properties of anodic film (width of the band gap, refractive index, etc.).

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