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## FORMATION OF ANODIC OXIDE FILMS ON ANTIMONY IN OXALIC ACID SOLUTIONS

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### Introduction

Anodic oxide films on antimony can be formed in different aqueous or non-aqueous electrolytes. Some aqueous oxalic acid solutions proved to allow the formation of relatively thick oxide films. The galvanostatic anodization in the concentration interval from 0.001 to 0.02 M  $(\text{COOH})_2$  was found to proceed in two stages [1]. During the first one, a linear increase of the formation voltage ( $U_f$ ) with time ( $t$ ) was observed, as typical for the anodization of valve metals. During the second stage, the voltage increase gradually slowed down, ending in electrical breaking down. In this work, studies on the formation of antimony oxide films and on their dissolution during anodic oxidation are presented in dependence of some parameters like electrolyte concentration, current density and process duration.

### Experimental

Specimens of high purity (99.999 % Sb) polycrystalline antimony were prepared and pre-treated as stated before [1]. Anodizing was carried out at 20 °C and a constant current density in the range from 0.8 to 20 mA cm<sup>-2</sup>. Aqueous  $(\text{COOH})_2$  solutions with different concentrations were used as forming electrolytes. The formation voltage vs. time curves were registered using a PC-based data acquisition system. The quantity of dissolved antimony during anodizing was determined by the ICP-OES method. An interferometric method was used to determine thicknesses of the oxides formed.

### Results and Discussion

#### Quantity of dissolved antimony

Anodic films can be formed on antimony using different in nature aqueous (solutions of acids, bases and salts) and non-aqueous electrolytes. Aqueous  $(\text{COOH})_2$  solutions allow the formation of oxide films at relatively high voltages, respectively with greater thickness. During anodization in the interval of concentrations 0.001 - 0.02 M  $(\text{COOH})_2$  two stages can be observed [1]: in the first one there is a linear increase in the applied voltage ( $U_f$ ) with time ( $t$ ), which results in a curve, typical for the anodization of valve metals. During the second stage the formation voltage increases at a delayed speed and the overall process ends with electrical breakdowns. In order to estimate the formation efficiency of the anodic antimony oxide, it is of interest to assess the quantity dissolved Sb depending on concentration ( $C$ ) of the oxalic acid, current density ( $J$ ) and the anodizing time ( $t$ ). Therefore, the dissolution of antimony was studied, varying the basic anodizing parameters. All experiments were carried out only in the first anodizing stage (the linear part of  $U_f(t)$ -dependencies), which corresponds to the flow of electric charge under than 0.6 C cm<sup>-2</sup>, and a forming voltage in the range of 100-180 V, respectively.

#### Influence of oxalic acid concentration

The influence of the oxalic acid concentration was followed by ascertaining the amount of dissolved antimony (ICP-OES method) during anodization at different current densities. Experiments were conducted galvanostatically until an electric charge of 0.4 C cm<sup>-2</sup> (first stage) was passed. An example of this effect is illustrated in Figure 1.

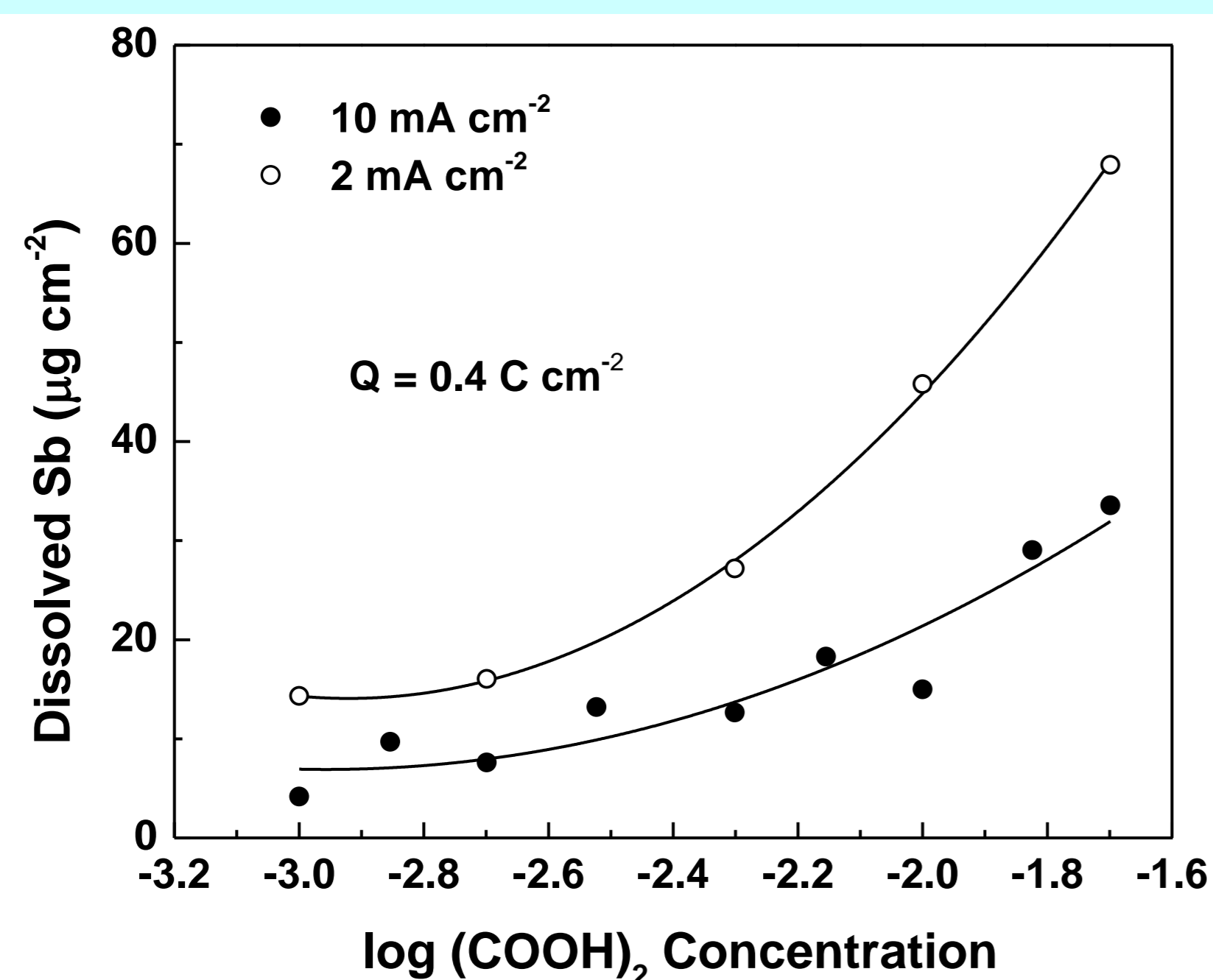


Fig. 1. Amount of dissolved antimony vs. oxalic acid concentration during anodization at two current densities

The results show that at all studied current densities, the amount of antimony increases with the concentration of the oxalic acid solution.

#### Influence of the applied current density

The influence of applied current density had been studied in more detail in two of the investigated electrolytes (0.001 and 0.01 M  $(\text{COOH})_2$ ). It was varied in the interval of (0.8 - 20 mA cm<sup>-2</sup>). The anodization duration has been chosen so that the charge density passed is (0.4 C cm<sup>-2</sup>). Again it should be noted, that the passing of this electric charge corresponds to the linear (stage 1) part of the kinetic  $U_f(t)$ -dependence. The results are presented in Figure 2.

The obtained results are logical – the decrease of current density and the increase of oxalic acid concentration lead to an increase of the dissolved antimony.

#### Influence of anodizing time

The influence of anodizing time ( $t$ ), respectively, the density charge density passed ( $Q$ ) on the amount of dissolved antimony was registered at various current densities. In all cases (in the first anodizing stage) this amount is proportional to anodization time.

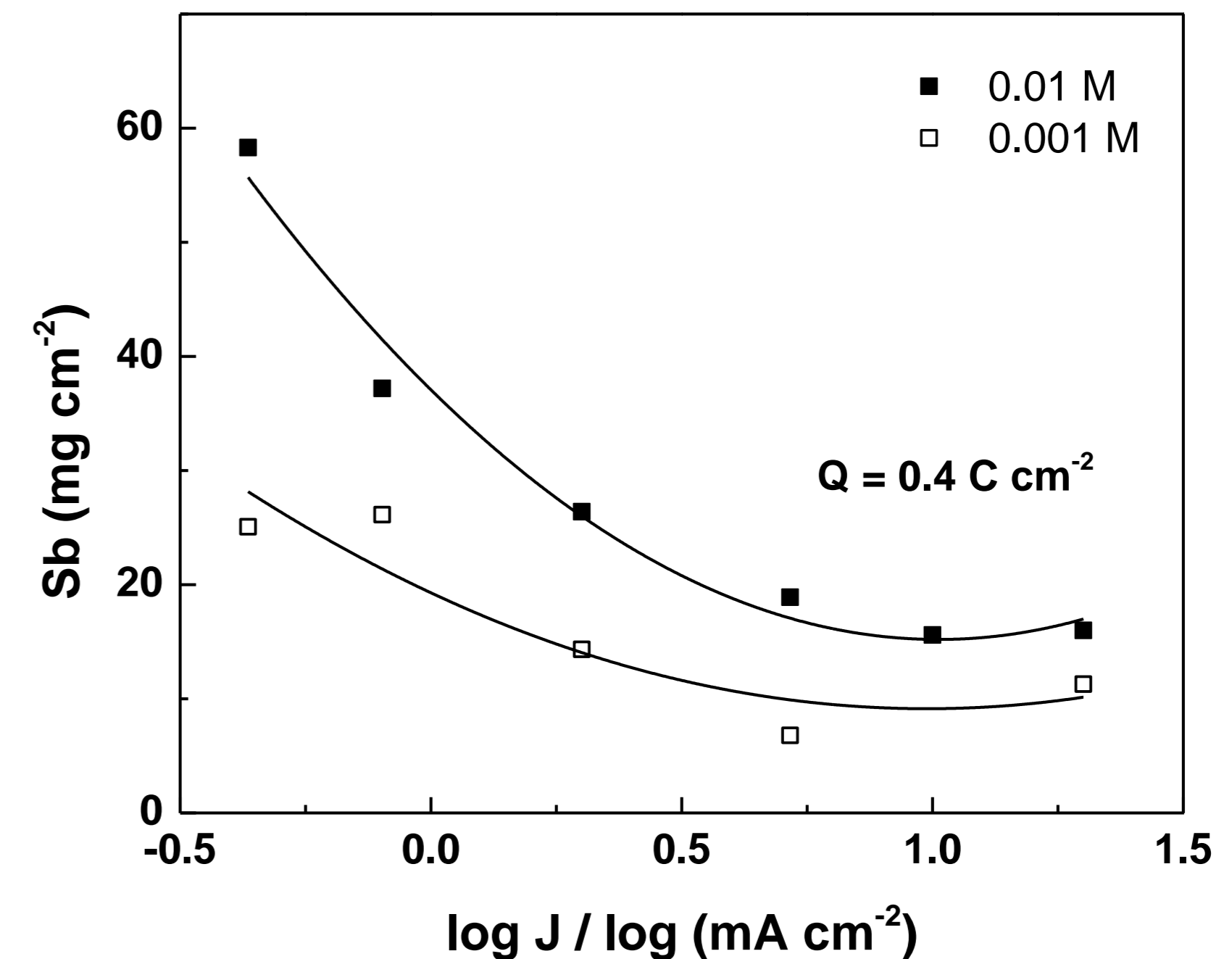


Fig. 2. Dissolved antimony vs. current density in oxalic acid solutions with two concentrations

#### Thickness of $\text{Sb}_2\text{O}_3$ -films

One problem which has long been discussed is related to the composition of the formed oxide films. Different opinions have been expressed that formed films can be  $\text{Sb}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_5$ ,  $\text{Sb}_2\text{O}_4$  or have a more complex composition. The thicknesses of the films formed in 0.01 M  $(\text{COOH})_2$  with different current densities are shown in Figure 3.

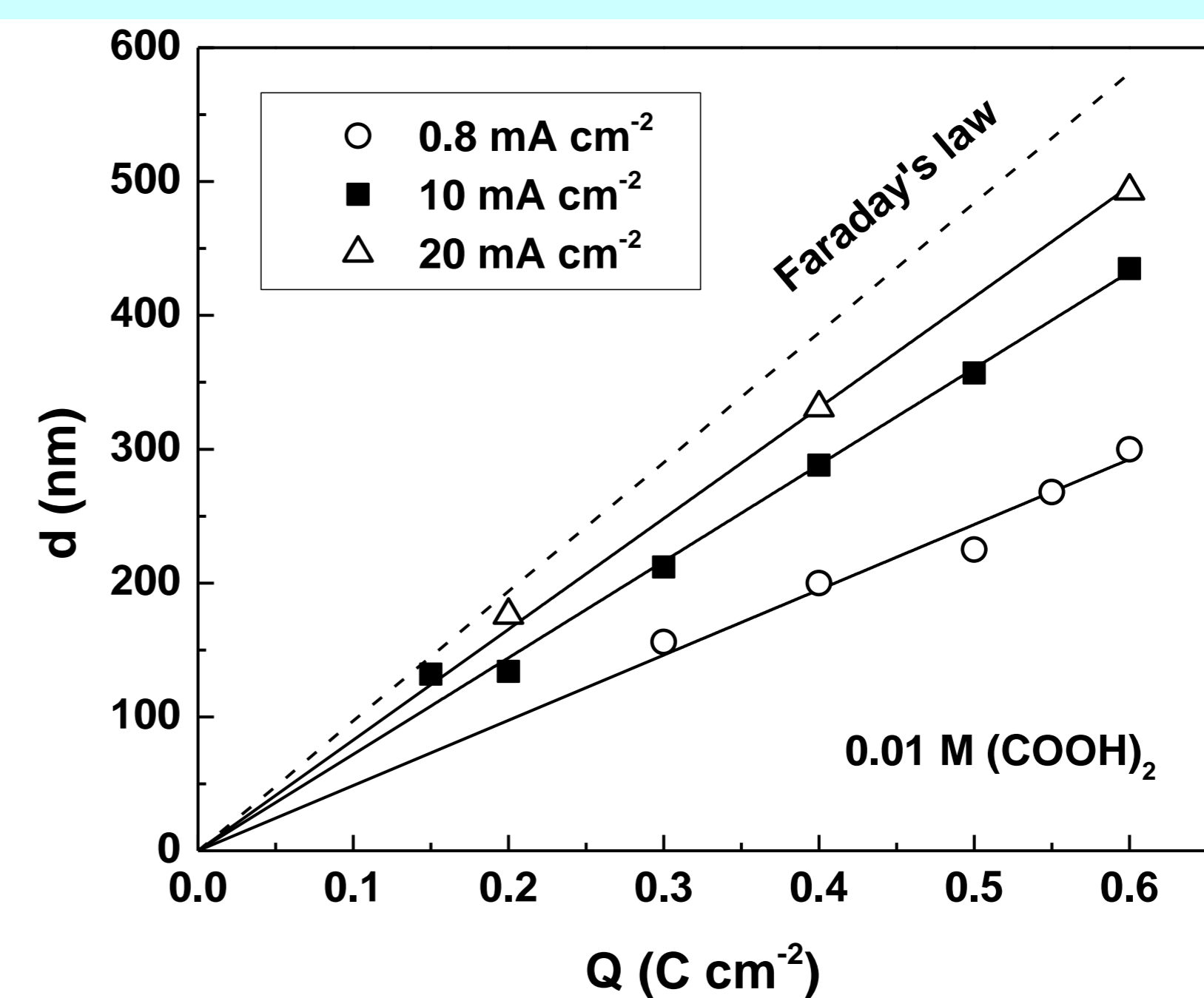


Fig. 3. Thickness of anodic oxide films, anodized in 0.01 M  $(\text{COOH})_2$  at three current densities (20 °C). The theoretical thickness, calculated using Faraday's law, has been shown for comparison.

The calculations indicate that under these conditions anodic  $\text{Sb}_2\text{O}_3$ -films are being formed. Assuming that the anodic polarization current is only ionic, the theoretical thickness can be calculated using Faraday's law. The presented in Figure 3 results show that the experimentally determined thicknesses are smaller than the theoretical ones. Obviously, during the anodic polarization, part of the passed electricity is consumed for the electrochemical dissolution of antimony.

#### Electric charge for the electrochemical dissolution of antimony

The part of the electrical charge consumed for the dissolution of antimony can be determined from the mass of dissolved antimony ( $m_{\text{Sb}}$ ) in the electrolyte. At lower current densities the ascertained thicknesses are smaller than those expected after considering the electrochemical dissolution.

This could be due to the presence of an electronic component ( $J_{\text{el}}$ ) in the total current ( $J_{\text{total}}$ ). Moreover, the value of ( $J_{\text{el}}$ ) is greater, as the current density gets smaller ( $J_{\text{el}}$ ), which is in agreement with similar results for anodic films, formed on other valve metals.

#### Field intensity

In galvanostatic-isothermal regime, the intensity of the electric field is constant and can easily be calculated using the formation voltage and the thickness of the anodic film. The resulting value of the field ( $2.37 \times 10^6$  V cm<sup>-1</sup>) in the investigated interval ( $J = 0.8 - 20$  mA cm<sup>-2</sup>) is relatively high.

### Conclusions

The diluted  $(\text{COOH})_2$  solutions provide the formation of sufficiently thick barrier oxide films on antimony. This, however, is always accompanied by a certain antimony dissolution, which strongly depends on the current density. Analysis of the process parameters suggests a possible existence of an electronic current component.

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### References

[1] E. Lilov, Ch. Girginov, E. Klein, *Advances in Natural Science: Theory & Applications*, 1 (2012) 115-120