QUANTITATIVE STUDIES OF ANODIC ANTIMONY OXIDE FORMATION AND DISSOLUTION IN OXALIC ACID ELECTROLYTES

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Introduction

The voltage-time curves obtained during galvanostatic anodization of antimony in oxalic acid solutions exhibited different shapes in dependence of the current density and/or the electrolyte concentration used. Variously long induction periods appear at current densities equal to or lower than 1.10^{-3} A.cm^{-2} and at electrolyte concentrations equal to or higher than 0.01 M. The shapes of the voltage-time curves and the lengths of the induction periods show a poor reproducibility. Data for the charge passed during the induction periods, as well as for the breakdown voltage and the frequency and amplitude of the voltage oscillations is obtained.

Experimental

Anodic oxide films on antimony were formed in dilute $(COOH)_2$ solutions at different current densities, thus obtaining kinetic curves. The working electrodes were mechanically polished antimony rods with high purity (99.999%). A two-electrode cell with platinum mesh as cathode was used. The formation voltage was measured by a precision multimeter. All experiments were carried out at 20°C.

Results and Discussion

Kinetic curves of galvanostatically anodized antimony with current density 2 mA cm^{-2} in aqueous solution of oxalic acid with three different concentrations are presented in Fig.1.

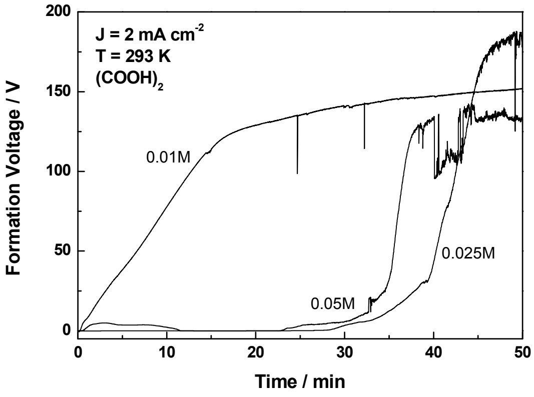

Fig. 1 Kinetic curves of galvanostatically anodized antimony in three electrolytes with different concentrations of $(COOH)_2$

The experiments show that depending on the concentration of oxalic acid the kinetic curves have different shapes. Only at the lowest concentration (0.01 M) a linear relation between the formation voltage (U_F) and time (t) is observed, which is characteristic for the galvanostatic anodizing of valve metals. This was the reason for choosing this electrolyte for subsequent experiments. It was of interest to trace the influence of current density (J) on the anodization kinetics. Figure 2 presents kinetic curves obtained at different current densities. The slopes $\left(dU_f/dQ\right)$ of these curves are also calculated.

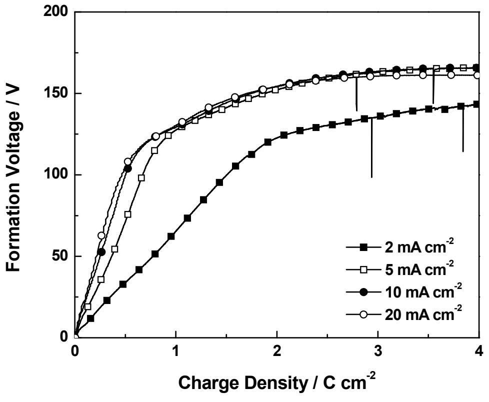

Fig. 2 $U_F(Q)$-dependencies obtained at different current densities

It is well known that the dependence $J_i(E)_T$ in the first approximation can be described by the equation of *Gunterschulze* and *Betz* [1]:

$$J_i = A_G \exp\,(B_G E)_T, \qquad (1)$$

where A_G and B_G are independent from the field intensity (E) constants. Interestingly, this equation describes well the kinetics of anodization of antimony in oxalic acid. Unfortunately, in the literature there are no reliable methods for determining the thickness of Sb_2O_3-anodic oxide films, which would allow calculating the intensity (E) of the electric field in the film. However, to make an assessment of the validity of equation (*1*), the intensity was calculated by *Faraday*'s law. Thus, from the experimental curves the intensity of the electric field (E) in the oxide film during anodizing can be determined:

$$E = \frac{6F\sigma\rho}{\lambda M}\left(\frac{\Delta U_{\mathrm{f}}}{\Delta Q}\right)_{J,T} \quad . \qquad (2)$$

Here F is the number of *Faraday*, M and σ are the molecular weight and density of the anode film respectively and $(\partial U_F/\partial Q)$ is the slope of the kinetic $U_F(Q)$-curve. The current effectiveness is indicated with λ, which depends on the total current density (J) and temperature (T). Assessment of the validity of the equation (*1*) was carried out by replacing the field in it with its proportional value $(\partial U_F/\partial Q)_T$ of equation (2):

$$J_i = A_G^* \exp\left[B_G^*\left(\partial U_f \big/ \partial Q\right)_T\right], \qquad (3)$$

where $B_G^* = \dfrac{6F\rho\sigma}{M\lambda}$

From data presented on Fig. 2 for the dependence of the slopes of kinetic curves on current density the averages of constants A_G^* and B_G^* were determined.

It was of interest to analyze the amplitude and frequency of the formation voltage during breakdowns. Fragments of these oscillations are presented in Fig. 3.

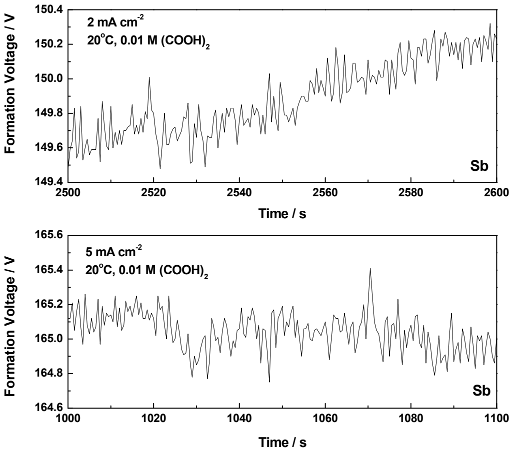

Fig. 3 Fragments of the kinetic curves during breakdowns at anodization with two current densities.

The results show that both frequency and amplitude of the formation voltage during breakdowns are insensitive to the applied current density. This result is in agreement with those obtained in the formation of oxide films on other typical valve metals.

Conclusions

Oxalic acid solutions are suitable for the formation of anodic oxide films on antimony. The common kinetics of linear increase of the formation voltage with time in galvanostatic conditions were observed only at current densities greater than 2 mA cm^{-2}. The kinetics of formation is subject to known relationships between current density and intensity of the field (*Gunterschulze* and *Betz*). The amplitude and frequency of oscillations of the formation voltage during electric breakdowns practically do not depend on current density.

References

1. A. Gunterschulze, H. Betz, *Z. Electrochem.*, **37** (1931) 730.