

## Efficiency of formation of nanoporous alumina films in fluoride ion-containing electrolyte

Chr. A. Girginov\*, M. S. Bojinov

Department of Physical Chemistry, University of Chemical Technology and Metallurgy,  
8 Kliment Ohridski Blvd., 1756 Sofia, Bulgaria

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The formation of porous anodic films on Al was carried out in electrolytes based on 0.5 M  $(\text{NH}_4)_2\text{SO}_4$  with the addition of  $\text{NH}_4\text{F}$ . The anodization was performed in two stages. In the first stage the formation voltage is reached at a scan rate of  $50 \text{ mV s}^{-1}$ . In the second stage, the anodization was continued tensiostatically for up to 1 hour. Current density / formation voltage (first stage) and current density / time curves (second stage) were found to be in agreement with previous results of other authors. The current efficiency of film formation has been estimated by determining the concentration of Al, dissolved in electrolyte during anodization by inductively coupled plasma optical emission spectrometry (ICP-OES). Assuming that all the Al ions that migrate through the film are ejected in the solution, the transference number for  $\text{Al}^{3+}$  is also estimated. The obtained estimates allowed the determination of the total porosity of the alumina templates by re-anodization in 1 M AS/DMF (ammonium salycilate in dimethyl formamide) electrolyte. The obtained porosity values decreased with the increased voltage in the tensiodynamic stage and slightly increased with the time during the tensiostatic stage, in general agreement with the results, reported during porous anodization of Al in acidic electrolytes.

**Key words:** alumina films, sulphate-fluoride electrolyte, anodic films, oxides, nanoporous templates

### INTRODUCTION

Nanoporous oxide templates are formed during the anodic polarization of aluminum in suitable electrolytes. These self-organised structures grow as comparatively thick layers with very large surface area. The structures are well reproducible and their properties (pore diameter, distribution and length) are easily controlled by the parameters of the anodization process. Subsequent incorporation of a range of substances in the form of nanorods, nanodots, and nanotubes, results in the formation of a wide series of functional nanomaterials, characterized by unique magnetic, photocatalytic, semiconducting, and electrical properties [1]. Such materials find increasing application as high density storage media, functional nanomaterials exhibiting quantum size effect, highly selective chemical sensors [2], nano electronic devices [3], and functional bio-chemical membranes [4]. Active centres can be created in the porous templates via incorporation of suitable compounds, resulting in

effective catalyst materials [5]. Besides classical electrolytes for porous anodization of Al (sulphuric, oxalic, phosphoric and chromic acids) [6], a range of organic acids have been also successfully employed (sulfamic acid [7], malonic acid [8, 9], tartaric acid [9], etc.).

It has been reported recently that acidic and neutral electrolytes, containing fluoride ions are also suitable for the formation of self-organized alumina templates on Al [10, 11]. Such electrolytes are widely used for porous anodization of several valve metals such as Ti [12], Nb [13] and W [14]. It has been proposed that during anodic oxidation in the presence of fluoride, nucleation of ordered pores takes place with subsequent formation of self-organized nanotube arrays. In order to be able to propose a mechanism for such pore nucleation and growth processes, data on the relative importance of the processes of film growth and metal dissolution through the film are needed. In that respect, the present paper aims at estimating the charge density efficiency for porous alumina formation on Al in a neutral fluoride-containing electrolyte by electrochemical methods.

\*To whom all correspondence should be sent:  
E-mail: christian.girginov@gmail.com.

Sheets of high purity (99.999%) and technical purity (99.5%) aluminum were electropolished in a phosphoric acid-chromic acid electrolyte at 343 K. The electropolished samples were then anodized in an electrolyte based on 0.5 M  $(\text{NH}_4)_2\text{SO}_4$  with the addition of 0.075 M  $\text{NH}_4\text{F}$  at 293 K. A two-electrode cell with a platinum mesh counter electrode, situated symmetrically around the working electrode, was used. The anodization was performed in two stages. In the first stage, a range of voltages were reached at a scan rate of  $50 \text{ mV s}^{-1}$ . In the second stage, the anodization was continued tensiostatically ( $U = \text{const}$ ) for up to 1 h. The anodization was carried out using a high voltage potentiostat/galvanostat (600 V, 0.5 A), precision multimeters (Mastech MS 8050), and a PC-based data acquisition system were employed. The amount of dissolved Al in the forming electrolytes has been estimated by ICP-OES (Prodigy, Teledyne Leeman Labs). Pore-filling of the alumina templates, formed under different conditions, was achieved via re-anodization in 1 M AS/DMF (ammonium salicylate in dimethyl formamide), current density being of  $1 \text{ mA cm}^{-2}$  at 293 K.

## RESULTS AND DISCUSSION

### Influence of the Al purity on porous anodization

Preliminary investigations have shown that the current densities during porous anodization are influenced to a certain extent by the purity of the metal substrate. It turned out that the current density of tensiodynamic anodization of pure (99.999%) Al in all cases is larger compared to that of the technically pure (99.5%) Al. This trend is illustrated on Fig. 1, where the current vs. voltage curves during the first stage of anodization of the two types of Al substrates are superimposed. A tentative explanation of that phenomenon is the slower rate of oxidation of secondary phases, most probably present at the surface of the electropolished technically pure Al, although further investigations are planned to get a deeper insight into that experimental fact.

### Kinetics of porous film formation

The formation of porous anodic films was carried out in an electrolyte (0.5 M  $(\text{NH}_4)_2\text{SO}_4$ ) with added  $\text{NH}_4\text{F}$  (0.075 M). A formation voltage  $U = 20 \text{ V}$  is reached at a scan rate of  $50 \text{ mV s}^{-1}$  in the first stage. The respective current density vs. voltage curves were recorded. Subsequently, the anodization was continued tensiostatically ( $U = 20 \text{ V}$ ) with different durations (up to 1 h). The current density vs. time

dependences obtained in stage 1 and 2 are shown on Fig. 2.

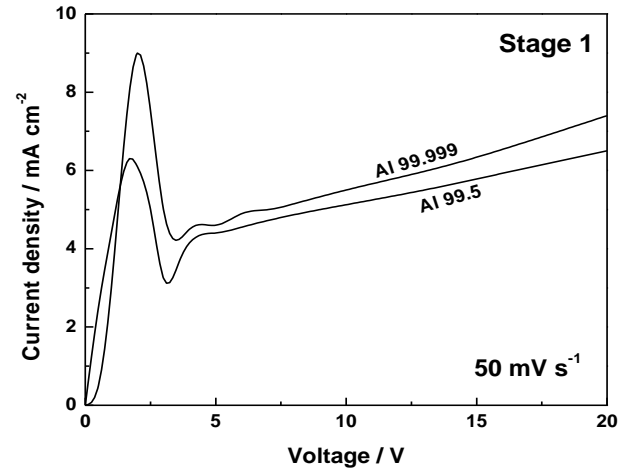


Fig. 1. Current density vs. voltage during tensiodynamic anodization of Al with different purity in (0.5 M  $(\text{NH}_4)_2\text{SO}_4$  + 0.075 M  $\text{NH}_4\text{F}$ ) at 293 K.

### Charge density efficiency

Numerical integration of  $J(t)$ -curves, resulted in estimates of the total charge density ( $Q_{\text{total}}$ ), passed during the two stages of anodization:

$$Q_{\text{total}} = \int_0^t (Jt) dt \quad (\text{C cm}^{-2}). \quad (1)$$

The amount of dissolved aluminum ( $m_{\text{Al}}$ ) was estimated by determining the concentration of Al, dissolved in the electrolyte during anodization by ICP-OES. The dependence of  $m_{\text{Al}}$  on total charge density ( $Q_{\text{total}}$ ) during anodization in 0.5 M  $(\text{NH}_4)_2\text{SO}_4$  + 0.075 M  $\text{NH}_4\text{F}$  is presented on Fig.3.

Starting from the estimated amount of dissolved Al, the quantity of charge for dissolution of Al ( $Q_{\text{dissolving}}$ ) was easily calculated using Faraday's law

$$Q_{\text{dissolving}} = \frac{m_{\text{Al}}}{A_{\text{Al}}} zF \quad (\text{C cm}^{-2}), \quad (2)$$

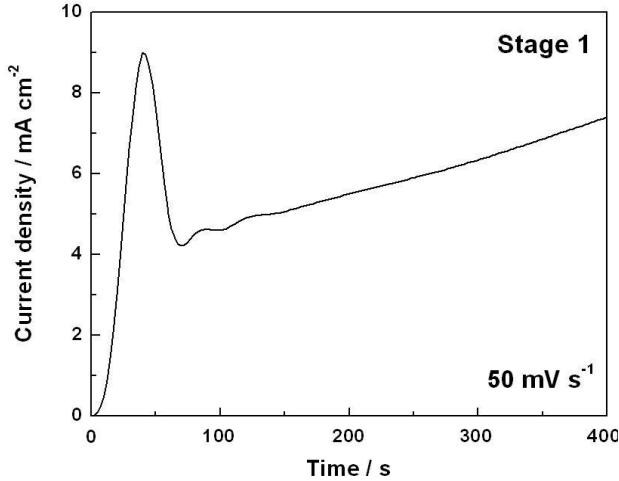
where  $A_{\text{Al}}$  is the atomic weight of Al,  $F$  is the Faraday constant, and  $z = 3$ .

In turn, the charge density efficiency for film formation was determined as follows:

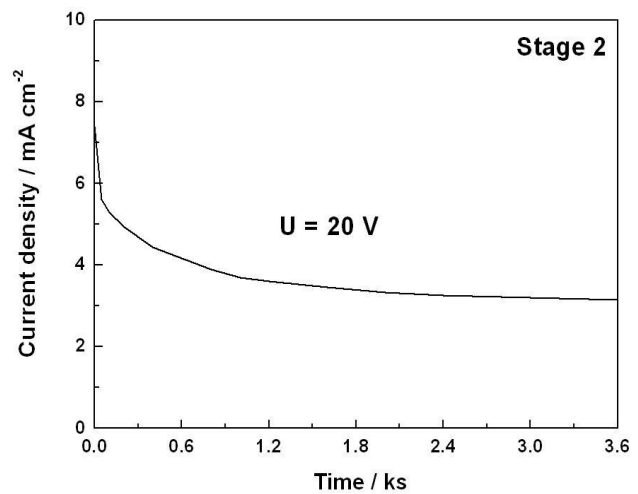
$$\Lambda = 100 \frac{Q_{\text{total}} - Q_{\text{dissolving}}}{Q_{\text{total}}} \quad (\%). \quad (3)$$

The  $\Lambda$ -( $Q_{\text{total}}$ ) -dependence is shown on Fig.4. During Stage 1, the anodization efficiency increases with applied voltage. In the second stage ( $U = \text{const}$ ), however, it was found that the efficiency slightly decreases with time (or

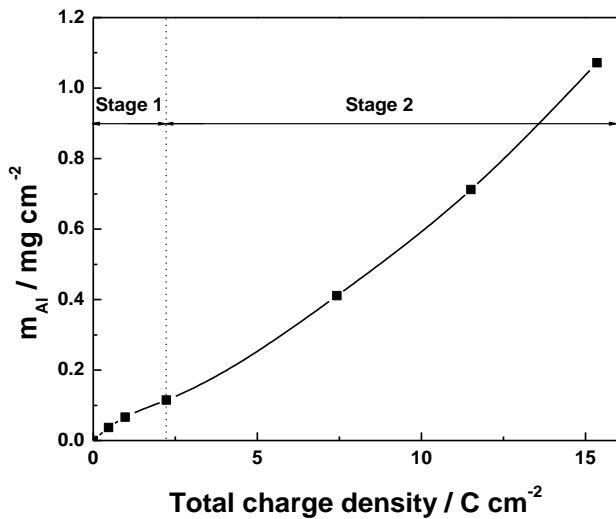
equivalently, with the thickness of the porous oxide



layer).



**Fig.2** Current density vs. time during the first and second stages of anodization of pure Al in (0.5 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> + 0.075 M NH<sub>4</sub>F) at 293 K.



**Fig. 3.** Amount of dissolved Al vs. total charge density during anodization

#### Porosity of alumina templates

The total porosity ( $\alpha$ ), i.e. the ratio of pore volume to the total oxide volume, is an important characteristic of the anodic alumina templates. As the mean pore radius does not change significantly in-depth, porosity can be also expressed as the ratio of the area of pores to the total sample area.

It is well known that porous anodic films on Al can be re-anodized in a non-dissolving electrolyte. The current during re-anodization is transferred through the barrier oxide via Al<sup>3+</sup> and O<sup>2-</sup> electromigration, as a result of which new oxide is formed both at the metal/film and the film/electrolyte interfaces [15, 16]. The pores are gradually filled and as a result of ionic migration, the thickness of the barrier oxide increases with re-anodization time. The increase of the formation voltage in galvanostatic conditions is a measure of barrier film growth, which gives a

possibility to estimate  $\alpha$  via analysis of kinetic  $U(t)$ -curves. Takahashi and Nagayama [16] have analyzed the kinetics of pore-filling during re-anodization. In galvanostatic conditions, the formation voltage ( $U$ ) increases linearly with time ( $t$ ), the slope of the straight line changing from

$m_I = \left(\frac{\partial U}{\partial t}\right)_I$ , when anodization takes place in the

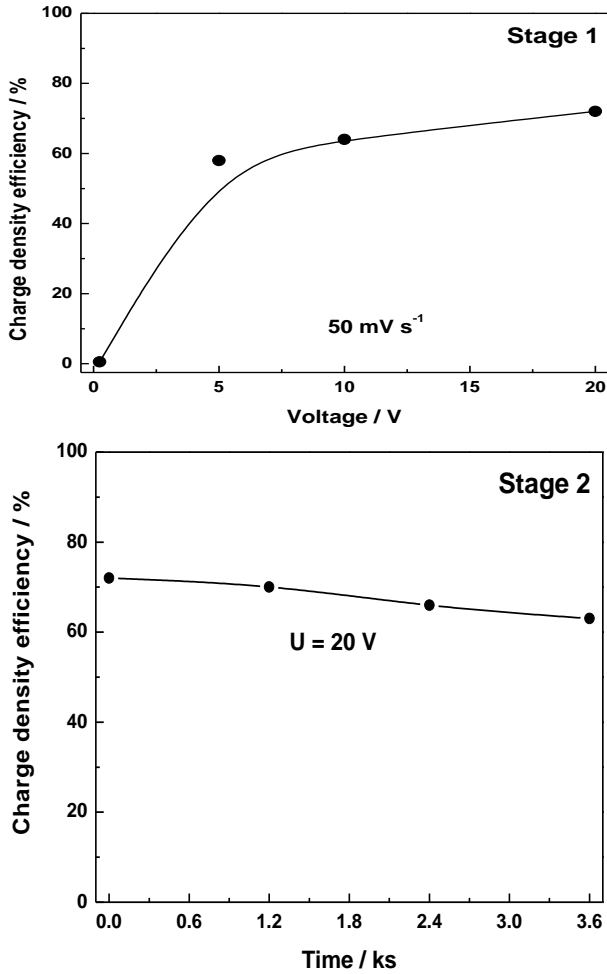
pores, to  $m_{II} = \left(\frac{\partial U}{\partial t}\right)_{II}$ , when the pores are totally filled. At the moment of total pore-filling, the area of the barrier sublayer/electrolyte interface increases sharply, i.e. the apparent “porosity” assumes a value of 1. This explains the smaller rate of increase of the barrier film thickness after pore-filling, which is expected to be equal to that during direct anodization in non-dissolving electrolytes. As a result of this analysis, the total porosity of the alumina template is expressed as [16]:

$$\alpha = \frac{t_{Al^{3+}} m_{II} / m_I}{1 - \left[ \left(1 - t_{Al^{3+}}\right) m_{II} / m_I \right]}, \quad (4)$$

where  $t_{Al^{3+}}$  is the transference number of Al<sup>3+</sup> in the barrier oxide.

Using this method,  $\alpha$  can be estimated from experimental kinetic data, received from the ratio of the two slopes ( $m_I$  and  $m_{II}$ ), if the transference number  $t_{Al^{3+}}$  is known.

Several authors [17, 18] have proposed that the growth of the oxide in porous anodization is due to the migration of oxygen ions alone, i.e. they grow at



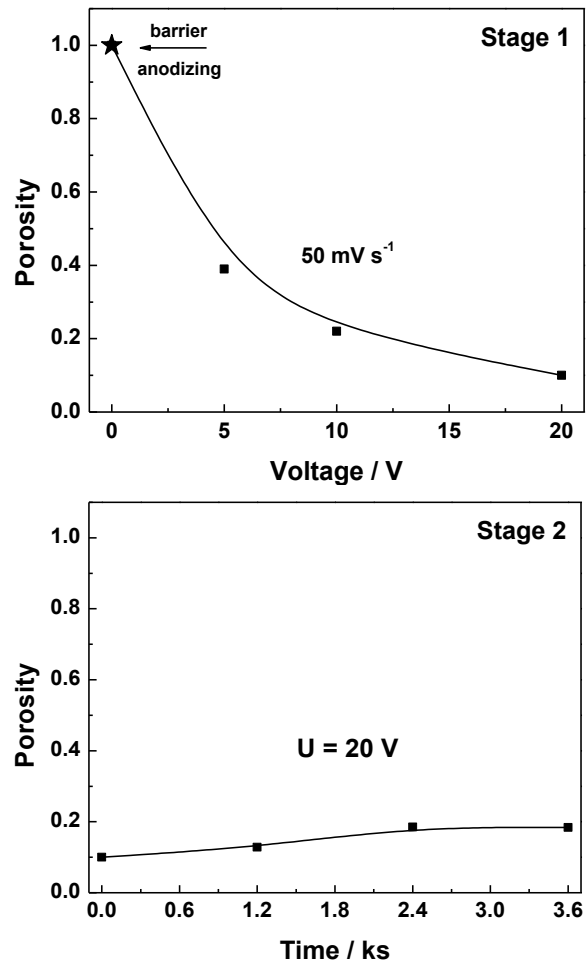
**Fig. 4.** Charge density efficiency vs. formation voltage (stage 1) and vs. time (stage 2) during anodization in 0.5 M  $(\text{NH}_4)_2\text{SO}_4 + 0.075 \text{ M NH}_4\text{F}$ .

the metal/film interface. This means that all the  $\text{Al}^{3+}$  that migrate through the oxide are ejected in the electrolyte. Following this assumption, the transference number  $t_{\text{Al}^{3+}}$  was estimated as:

$$t_{\text{Al}^{3+}} = \frac{100 - \Lambda}{100} \quad (5)$$

for templates in both stages of anodization. The oxide films, formed in different conditions, were re-anodized in 1 M AS/DMF (ammonium salicylate in dimethylformamide). The kinetic  $U(t)$ -curves were recorded and the porosity of the obtained templates was estimated from the  $m_I$  and  $m_{II}$  using the calculated values of  $t_{\text{Al}^{3+}}$ . The results are presented on Fig.5. During the first stage of anodization, porosity decreases with increasing voltage, reaching the value of ca. 0.1 at 20 V, and then slightly increases during the second stage of anodization. The obtained values and trends are in good agreement with the results of Ono et al.[19, 20], obtained by re-anodization of alumina templates, formed in sulphuric and oxalic acids at 293 K, as

well as those of Sulka and Parkola [21],



**Fig. 5.** Porosity vs. formation voltage (stage 1) and vs. time (stage 2) during anodization in 0.5 M  $(\text{NH}_4)_2\text{SO}_4 + 0.075 \text{ M NH}_4\text{F}$  at 293 K.

estimated from post-processing of scanning electron micrographs of nanoporous alumina, formed in sulphuric acid at 274 K.

## CONCLUSION

Well reproducible alumina templates are obtained during anodization of Al at room temperature in neutral sulphate electrolytes with the addition of fluoride. To assess the charge density efficiency during the two stages of film formation (tensiodynamic and tensiostatic), the amount of dissolved Al was quantified using ICP-OES. During Stage 1, the anodization efficiency increases with applied voltage. In the second stage ( $U = \text{const}$ ), however, it was found that the efficiency slightly decreases with time (or equivalently with the thickness of the porous oxide layer). Assuming that entire Al that migrates through the forming oxide is ejected into the solution, the transference number of  $\text{Al}^{3+}$  was estimated from the amount of dissolved Al and the charge density efficiency. Using pore-filling via re-anodization, the total porosity of the

templates, depending on the formation voltage (in tensiodynamic anodization) and anodization time (in tensiostatic anodization), is determined. The porosity decreases with increasing voltage in tensiodynamic anodization and slightly increases in the tensiostatic stage, in general agreement with the results from the porous anodization of Al in acidic electrolytes. Further investigations, aiming at elucidating the effect of fluoride concentration, formation voltage, and tensiostatic stage duration on the main characteristics of the alumina templates, are in progress and will be reported in the near future.

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## Ефективност на образуване на нано-порьозни филми от двуалуминиев триоксид в електролит, съдържащ флуоридни йони

Кр. А. Гиргинов\*, М. С. Божинов

Катедра „Физикохимия“, Химикотехнологичен и металургичен университет, бул. „Климент Охридски“ № 8, 1756 София

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(Резюме)

Формирани са порести анодни филми върху алуминий в електролит 0.5 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> с добавка на 0.075 M NH<sub>4</sub>F. Анодирането е проведено в два стадия. В първия стадий определено напрежение се достига с постоянна скорост (50 mV s<sup>-1</sup>) на нарастване на потенциала. Във втория стадий формирането продължава при постоянно напрежение (20 V) с различна продължителност (до 1 час). Определена е токовата ефективност на анодирането чрез аналитично определяне на количеството разтворен алуминий в електролита. Определени са стойностите на преносното число ( $t_{Al^{3+}}$ ) на алуминиевите йони. Формираните алуминиеви оксидни матрици са повторно анодирани (ре-анодирани) в неразтварящ филма електролит. Чрез анализ на кинетичните криви на ре-анодирание и получените стойности за  $t_{Al^{3+}}$  е изчислена пористостта на филмите в двата стадия на тяхното формиране. Пористостта намалява с повишаване на напрежението (в първия стадий) и слабо се променя с нарастване дебелината на филмите (във втория стадий) на анодирането.