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# Aluminium anodizing in selenic acid: electrochemical behaviour, porous structure, and ordering regimes



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## ABSTRACT

Porous anodic alumina films are of great practical importance in membrane science and nanotechnology due to their unique structure possessing the arrays of aligned cylindrical channels. The most promising functional properties are observed for anodic alumina with an ordered porous structure. However, the pore ordering occurs only in a narrow range of anodizing conditions, which are commonly chosen by the empirical search. Here, recently proposed kinetic approach is applied to a directed search of self-ordering anodizing conditions in selenic acid electrolyte. We have developed a new self-ordering regime at the anodizing voltage from 60 to 100 V, which covers a novel interpore distance interval from 120 to 160 nm. Anodic alumina films obtained in this voltage range are free of cracks and possess a highly ordered porous structure, where more than 75% of pores have hexagonal coordination. Current efficiency of aluminium anodizing, anodic alumina formation efficiency, mass fraction of selenate impurities, interpore distance, thickness-to-charge density ratio, and volume expansion factor are determined as a function of anodizing voltage.

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# 1. Introduction

Anodizing of valve metals in acidic electrolytes is an efficient technique for the fabrication of porous oxide films. Anodic oxide coatings are industrially used for surface finishing and are promising for a variety of high-tech applications in nanotechnology, energetics, membrane science, optoelectronics, and sensorics. Nowadays, porous anodic oxides, possessing arrays of vertically aligned cylindrical channels, are routinely prepared on aluminium [1], titanium [2], zirconium [3], and hafnium [4]. The unique property of anodic aluminium oxide (AAO) among anodic oxides of valve metals is the possibility to obtain two-dimensional highly ordered hexagonal arrangement of pores resulting in narrow pore size distribution and extremely high density of pores (up to  $10^{11} \text{ cm}^{-2}$ ). The structural parameters of AAO can be precisely tuned by the variation of concentration [5,6] and temperature of electrolyte [7,8], applied voltage [9], anodizing duration [10], and crystallographic orientation of aluminium substrate [11–13].

Common electrolytes for the preparation of AAO with hexagonal

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acids [14–16]. Selenic acid is a new inorganic electrolyte, which has great potential for practical applications owing to low porosity and high transparency of the resulting anodic oxide films [17,18]. The first results on the aluminium anodizing in the selenic acid electrolyte was reported in 2013. The authors have shown the rapid formation of the self-ordered porous structure with a 10-nm-scale pore diameter at the bottom part of oxide film within 1 h [17]. Later, it has been shown that the formation of oxide films with regular porous structure with interpore distance from 95 to 110 nm occurs in the range of anodizing voltages from 42 to 48 V, respectively, regardless of the concentration of H<sub>2</sub>SeO<sub>4</sub> in electrolyte in the range from 0.1 to 3.0 M [18]. The "burning" of oxide layer has been observed for the higher voltages. In 2015, the improvement of AAO regularity was achieved during anodizing in 3 M selenic acid by optimization of Al surface roughness, electrolyte stirring rate, and process duration [19], however the degree of pore ordering was estimated only qualitatively.

arrangement of the pores include sulfuric, oxalic, and phosphoric

In galvanostatic mode, the shift of the current density, at which the regular porous structure forms, from 2 to 20 mA cm<sup>-2</sup> with the increase in electrolyte concentration from 0.04 to 2 M H<sub>2</sub>SeO<sub>4</sub> has been reported [20,21]. These self-ordering regimes lie between the growth of AAO with disordered structure at low current densities and abnormal growth in "burning mode", which occurs when the





applied potential difference reaches the value of about 50 V.

According to empirically performed experiments in galvanostatic and potentiostatic regimes the following advantages of aluminium anodic oxidation in selenic acid solutions have been observed: (i) high growth and self-ordering rates; (ii) very small pore diameters; (iii) colorlessness and transparency. Contrary to the porous alumina films obtained in organic acids electrolytes (e.g. oxalic acid), AAO formed in selenic acid does not exhibit photoluminescence [22,23].

There are theoretical models for prediction of the conditions for self-ordering of porous anodic oxide films [24,25]. Although the satisfactory agreement between the theory and experimental data has been achieved for some experimental conditions in oxalic and sulfuric electrolytes, a universal theory is still absent. To simplify the calculations, a lot of assumptions have been made in the existing models. In particular, in Ref. [24] the effects of anodic oxide dissolution at the oxide/electrolyte interface as well as nonlinear metal- and oxygen-ion transport through the barrier layer are considered, whereas the mass transport in the pores is not taken into account. Contrary, the model suggested in Ref. [25] is based on the effect of electrolyte concentration changes along the pores length in terms of acids dissociation formalism. It is postulated that unchanged concentration of free hydrogen ions at the pore basis is a necessary condition for self-ordering of porous structure of anodic alumina films. The influence of the mass-transport in the pores on structure ordering is discussed, but only in the case of the quasi-steady-state anodizing. Thus both of the models could be applied just to the kinetic regime of anodizing (also known as mild anodizing), when current density at a given voltage does not change with thickness of porous oxide film. The conditions of selfordering in hard anodizing regime could not be predicted using these models. Moreover, the existing models have not been applied earlier for the prediction of self-ordering conditions in selenic acid electrolytes.

Here we apply our recently proposed kinetic model of selfordering of AAO structure [9] for the intentional choice of proper anodizing conditions in 0.3 M selenic acid. Our approach does not use any simplifying assumptions and is based exclusively on the experimental analysis of electrochemical responses recorded during aluminium anodizing. A new self-ordering window in the high voltage region of 60–100 V, which covers a novel interpore distance interval from 120 to 160 nm, is found. Oxide formation efficiency, volume expansion factors, AAO structural parameters, pore ordering degree, thickness-to-charge density ratio, and content of impurities are determined systematically as a function of anodizing voltage.

# 2. Experimental

# 2.1. Surface pre-treatment of aluminium foils

High-purity aluminium foils (99.999%, 0.5 mm thick) were utilized for the study of porous anodic alumina formation in selenic acid electrolyte. At the preliminary stage, aluminium was annealed in the air using the heating rate of  $5 \,^{\circ}$ C min<sup>-1</sup> and a two-step regime: at 150  $^{\circ}$ C for 12 h and then at 500  $^{\circ}$ C for 24 h. Prior to anodizing, the surface of Al foils was polished to a mirror finish as described elsewhere [26].

All solutions were prepared using deionized water (18.2 M $\Omega$  cm) obtained by water purification system MilliQ Integral 5 (Millipore).

#### 2.2. Anodizing setup

Samples were anodized in 0.3 M selenic acid electrolyte in a two-electrode electrochemical cell with the volume of ca. 1 L using

the DC power supply N8741A (Agilent Technologies). Aluminium foil was pressed to the bottom side of the cell with a Viton o-ring seal that guaranteed constant anodizing area of 1.13 cm<sup>2</sup>. The electrolyte was cooled down to 0 °C using Petite Fleur thermostat (Huber) and vigorously stirred during overall electrochemical experiments. Aluminium plate with the surface area of about 40 cm<sup>2</sup> served as a cathode. The distance between electrodes was 15 cm.

# 2.3. Linear staircase voltammetry

The linear staircase voltammetry (LSCV) with the voltage scan rate of 0.05 V s<sup>-1</sup> (step height of 0.025 V) was used for the characterization of the kinetics of anodizing process. In order to perform LSCV for the aluminium substrates covered with 20, 40, and 80  $\mu$ m thick porous layer, preliminary anodizing of aluminium at 45 V was carried out. After the formation of a porous oxide layer with a certain thickness at pre-anodizing step, the voltage was decreased to 10 V with the rate of 0.01 V s<sup>-1</sup>(step height of 0.005 V) before the recording of the linear voltammograms. This stage leads to thinning of the barrier layer at the pore basis and is essential for correct LSCV tests of pre-anodized aluminium foils in a low voltage range (see Fig. S1 in Supplementary Information).

# 2.4. Aluminium anodizing

Aluminium anodizing was carried out in the voltage range from 35 to 100 V. The applied voltage was increased to the target value with the rate of 0.05 V s<sup>-1</sup>(step high of 0.025 V) and then kept constant. Anodizing was stopped when the electrical charge density at the constant voltage stage reached 100 C cm<sup>-2</sup>. In the range from 35 to 45 V, this value corresponds to the thickness of the porous alumina film of about 50  $\mu$ m.

# 2.5. Scanning electron microscopy and energy dispersive X-ray analysis

The morphology of the bottom side of anodic alumina films were studied using field emission scanning electron microscope (SEM) Supra 50 VP (LEO). For this purpose, the aluminium substrates were selectively removed in a mixture of CH<sub>3</sub>OH and Br<sub>2</sub> with volume-to-volume ratio of 10 : 1 at room temperature. Barrier oxide layer was dissolved in 0.5 M H<sub>3</sub>PO<sub>4</sub> at 60 °C for 2–5 min. SEM images were processed with Voronoi algorithm using self-developed software [27]. A percentage of pores with a hexagonal coordination environment was chosen as a parameter of ordering degree of AAO porous structure. Thickness of AAO films was measured using cross-sectional SEM images.

The quantity of impurities in the walls of anodic alumina films was recalculated from the Se/Al mass content ratio determined by the energy dispersive X-ray (EDX) analysis using the spectrometer X-Max 80 (Oxford Instruments) installed in the scanning electron microscope. The mass fraction of impurities in the AAO walls should be interpreted as an average over volume value because the locality of EDX analysis area is much larger than structural features of AAO (e.g. thickness of outer oxide layer containing electrolyte impurities).

#### 3. Results and discussion

Linear staircase voltammetry was applied to determine the range of anodizing voltage in which anodic alumina film forms uniformly in  $0.3 \text{ M} \text{ H}_2\text{SeO}_4$  electrolyte at the temperature of  $0 \,^{\circ}\text{C}$ . There are three characteristic regions on the current density (j) – voltage (U) plot (Fig. 1a). Up to ca. 50 V (*region I*) the growth of current density is observed in accordance with the high-field



**Fig. 1.** Linear staircase voltammetry data obtained in 0.3 M  $H_2$ SeO<sub>4</sub> electrolyte at a voltage sweep rate of 0.05 V s<sup>-1</sup>. (a) LSCV curve recorded on a bare Al foil. Three characteristic regions are shown. Inset represents photographs of AAO films formed during LSCV experiments stopped at 100 and 120 V. (b) LSCV curves recorded on a bare Al foil and on the Al substrates with different thickness of porous oxide layer, obtained by preliminary anodizing at 45 V.

conduction theory [28]. The maximum at 54 V is followed by a decrease in current density (*region II*). Above 110 V (*region III*) the non-uniform growth of the anodic alumina over film surface (see the inset in Fig. 1a) is accompanied by the stochastic oscillations on the *j*-U curve. Such behaviour is typical for the transition regime between the hard anodizing and the plasma electrolytic oxidation (PEO) process [29].

The nature of a rate-limiting stage in the wide voltage range in selenic acid electrolyte was proved based on the LSCV data using earlier reported protocol [9]. A set of LSCV measurements recorded on a bare Al foil and on the Al substrates covered with 20, 40, and 80  $\mu$ m thick porous alumina layers is shown in Fig. 1b. All *j*(*U*) curves coincide at least with an accuracy of 0.2 mA cm<sup>-2</sup> at low current densities (at voltage up to ca. 51 V), manifesting that the rate of anodizing is limited by the kinetics of a reaction occurred at the pore bases. Contrary, at higher voltages the current density decreases significantly with the thickness of a pre-oxidized porous layer because the anodizing rate is limited by the diffusion of ionic species in the pores of growing AAO film [9,30].

It is worth to note that significantly different behaviour is observed at voltages higher than 55 V for initially bare Al foil and pre-anodized substrates. When bare Al foil is used as a starting material, current densities are very high (ca.  $1 \text{ A cm}^{-2}$ ) resulting in fast increase in the diffusion path length and, as a consequence, causing a decrease in current density (black curve in Fig. 1b). Contrary, in the case of pre-anodized Al substrates, the growth rate of AAO has suppressed substantially. As a consequence, the thickness of the porous oxide film changes slightly during LSCV recording, and the increase in the strength of electric field in barrier layer with applied voltage becomes more important. Finally, it leads to the increase in current with voltage (see a green curve for the 80 µm thick porous layer in Fig. 1b).

According to coulometric analysis at the end of linear staircase voltammograms, all samples possess nearly the same thickness of porous oxide layer, and thus current densities at 100 V nearly coincide (see Fig. S2 in Supplementary Information).

Current efficiency ( $\eta$ ) of aluminium anodic oxidation (Al – 3e<sup>-</sup>  $\rightarrow$  Al<sup>3+</sup>) was calculated from gravimetric measurements:

$$\eta = \frac{(m_1 - m_2)nF}{QM_{Al}}.$$
 (1)

Here,  $m_1$  is the mass of the Al foil before anodizing,  $m_2$  is the mass of the Al foil after anodizing and selective dissolution of porous alumina film, Q is the total charge passed during anodizing process,  $M_{Al}$  is the molar mass of Al, n = 3 is the number of electrons involved in the electrochemical reaction, F is the Faraday constant.

The obtained values of  $\eta$  are close to 100% for all the samples within the accuracy of the measurements (see Table S3 in Supplementary Information).

There are three possible routes for the transport of  $Al^{3+}$  ions formed at the metal/oxide interface: (i) the incorporation into the barrier layer and further formation of AAO pore walls; (ii) transition into electrolyte due to the field-assisted dissolution of anodic alumina at the pore bases [31]; (iii) the direct ejection of  $Al^{3+}$  ions from the metal/oxide interface through the barrier oxide layer into the solution [32,33]. The fraction of  $Al^{3+}$  ions retained in the AAO film from the total amount of aluminium ions formed during aluminium anodizing – oxide formation efficiency ( $\varepsilon$ ) [24] – was evaluated gravimetrically as follows:

$$\varepsilon = \frac{2 \cdot (1 - \omega)(m_3 - m_2)}{m_1 - m_2} \cdot \frac{M_{Al}}{M_{Al_2O_3}}.$$
 (2)

Here,  $m_3$  is the mass of the Al foil with a porous alumina layer,  $\omega$  is the mass fraction of electrolyte impurities in AAO film,  $M_{Al_2O_3}$  is the molar mass of aluminium oxide.

The value of  $\omega$  was found by recalculation of the Se/Al ratio (determined by EDX analysis) to the mass fraction of selenate anions in the alumina matrix. Mass fraction of selenate impurities increases from 9 to 25% in the voltage range from 35 to 52 V and stabilizes at the level of about 24% for higher anodizing voltages (Fig. 2a and Table S3).

The dependence of AAO formation efficiency on the anodizing voltage is shown in Fig. 2b (numerical values of  $\varepsilon$  are given in Table S3). The formation efficiency grows from 60 to 90% when anodizing voltage increases from 35 to 60 V; it remains nearly constant at higher voltages in diffusion regime of anodizing. It is worth noting, that the oxide formation efficiency correlates with porosity – an increase in  $\varepsilon$  evidently leads to the decrease in the porosity. Thus, the porosity of AAO films obtained in selenic acid electrolyte in a diffusion regime (hard anodizing conditions,  $U \ge 60$  V) is expected to be lower than the corresponding value for the oxide films prepared under kinetic control (mild anodizing conditions,  $U \le 48$  V). The same tendency (the decrease in porosity with current density) was experimentally observed earlier for aluminium anodizing in oxalic, sulfuric, and phosphoric acid electrolytes [34–36].

Thickness-to-charge density ratio (*x*) correlates with the oxide formation efficiency. It grows up almost twice from 0.45 to 0.83  $\mu$ m cm<sup>2</sup>C<sup>-1</sup> when anodizing voltage increases from 35 to 100 V (see Table S3 and Fig. 2d). The values of *x* observed for *U* ranging from 35 to 48 V are close to the reported earlier thickness-to-charge density ratios for the kinetic anodizing regime in sulfuric,



**Fig. 2.** Influence of voltage on parameters of alumina porous films in the case of aluminium anodizing in 0.3 M selenic acid at 0 °C: (a) mass fraction of selenate impurities, incorporated into the pore walls from the electrolyte; (b) oxide formation efficiency (fraction of  $AI^{3+}$  ions retained in the oxide film); (c) interpore distance on the bottom side of porous alumina films; (d) thickness-to-charge density ratio. Dashed lines are given just for eye guide. For all the samples anodizing was stopped when the electrical charge density at the constant voltage stage reached 100 C cm<sup>-2</sup>.

oxalic and phosphoric acids [13,37]. Experimental values of x may be useful in the preparation of the AAO films with a desired thickness in the charge-controlled mode, in particular, for the fabrication of one-dimensional photonic crystals based on porous anodic alumina [38].

To calculate interpore distance (D<sub>int</sub>) distribution, SEM images of the bottom side of the prepared porous films after chemical etching of the barrier layer were statistically analysed. At least five SEM images each containing of about 10<sup>4</sup> pores were processed for each sample. Up to 48 V the  $D_{int}(U)$  dependence is linear with a proportionality constant ( $\xi$ ) of about 2.5 nm V<sup>-1</sup>, which is close to the corresponding value for the mild anodizing conditions in other electrolytes [39,40]. At anodizing voltage higher than 55 V the interpore distance-to-voltage ratio decreases to ca. 2 nm V<sup>-1</sup>. This behaviour is in good agreement with  $D_{int}(U)$  dependence observed earlier for hard anodizing conditions in oxalic and sulfuric electrolytes [34,41]. Sudden decrease in D<sub>int</sub> in the region of mixed kinetics (from 48 to 52 V) is caused by the temperature increase near the metal/oxide interface at high current densities (Fig. 1a). Impossibility to maintain the electrolyte temperature constant (in the used experimental setup) results in thinning of the barrier layer and, as a consequence, leads to the decrease in  $D_{int}$  (Fig. 2c).

According to the earlier reported protocol for the directed search of self-ordering conditions [9], self-ordering of AAO structure should occur on the upper limit of the kinetic control region and in the diffusion control regime. These regions on the voltage scale for 0.3 M selenic acidelectrolyte can be easily found out using LSCV data (Fig. 1b). Additional proving comes from the analysis of

the current-time transients, recorded under steady-state anodizing conditions in the voltage range from 35 to 100 V (Fig. S4 in Supplementary Information). One can see that at high voltages (60–100 V) the inverse of current density linearly increases with AAO thickness. This behaviour is a key feature of the diffusion limited regime. Contrary, at low voltages (below 50 V), the current density is almost independent of the porous film thickness, manifesting the kinetic regime of anodizing.

SEM images of the bottom side of porous AAO films after etching of barrier layer are shown in Fig. 3. Double-layer nature of the pore walls can be clearly seen at least for the samples obtained at high voltages (Fig. 3c and d). The degree of pore ordering on the bottom side of AAO films (Fig. 3a-d) correlates well with the nature of a rate-limiting step (Fig. 3e). The pores are self-organized in hexagonal arrays under kinetic control of anodizing process (mild anodizing) with a maximal ordering rate just below 50 V. This voltage range is in good agreement with anodizing conditions that has been found earlier by an empirical search [17,18]. The second self-ordering window is observed under diffusion control of anodizing process (hard anodizing) from 60V to the "burning" voltage. The upper limit of this voltage region depends on the efficiency of a cooling setup. In our case, the uniform AAO films were obtained at 100 V, whereas at 110 V inhomogeneous growth of oxide was observed. According to the model [9], under kinetic and diffusion control of anodizing the growth rates of all channels are close to each other.

On the voltage scale, two self-ordering windows are separated by the region of mixed kinetics, where porous films with



Fig. 3. SEM images of the AAO bottom side after etching of barrier layer. Porous films were prepared in 0.3 M selenic acid at the temperature of 0°C and different anodizing voltages: 40 V (a), 48 V (b), 60 V (c), and 100 V (d). Dependence of pore ordering degree in alumina films (e) and volume expansion factor (f) on anodizing voltage.

disordered structures are formed. The main reason for the porous structure disordering is morphological instability of growth front in mixed anodizing regime as was determined earlier for other electrolytes using SEM study of aluminium surface after selective dissolution of AAO film [9]. High dispersion of the average number of neighbouring pores is observed in the voltage range from 50 to 55 V (Fig. 3e). It is caused by a significant variance in the degree of pore ordering at the adjacent sample areas in this voltage range (Fig. S5 in Supplementary Information). Such behaviour cannot be explained solely by morphological instability and, most probably, is induced by the anisotropy of aluminium oxidation rates in various crystallographic directions at relatively high current densities [28]. The anisotropy of growth rate of anodic alumina has a strong influence on the long-range pore ordering, as was demonstrated for oxide films formed on single crystal [13] and polycrystalline substrates [11].

From theoretical point of view, the development of the ordered porous structure is predicted at the oxide formation efficiency from 65 to 70% [24]. As can be clearly seen from the comparison of the data presented in Figs. 2b and 3e, only one of the experimentally observed self-ordering windows is close to this  $\varepsilon$  range. Diffusion regime of anodizing cannot be described in the frames of the model [24], because only the interfacial kinetics (the alumina dissolution at pore bases and ionic transport through barrier layer) is considered.

A special attention should be paid to the AAO growth at the voltages below 48 V under the used anodizing conditions. Earlier, the slow self-ordering rate was experimentally observed for aluminium anodizing under kinetic control at low voltages [9]. To explain this tendency, a value of compressive stress, which is commonly accepted as a prerequisite for regular porous structure formation [42–44], was measured. For this purpose, a volume expansion factor ( $k_v$ ) was calculated as a ratio of the volume of a porous AAO film ( $V_{AAO}$ ) to the volume of consumed aluminium

 $(V_{Al})$ :

$$k_{\nu} = \frac{V_{AAO}}{V_{Al}} = \frac{S \cdot H \cdot \rho_{Al}}{m_1 - m_2}.$$
(3)

Here,  $\rho_{Al}$  is the density of aluminium (2.7 g cm<sup>-3</sup>), *S* and *H* are the visible area (1.13 cm<sup>2</sup>) and the thickness of AAO porous film, respectively. Obviously, that higher  $k_v$  values correspond to higher mechanical stress in the AAO film.

With a rise in anodizing voltage,  $k_v$  values grow nearly twice from 1.3 in mild anodizing regime to 2.4 in hard anodizing regime (Fig. 3f). The evidence of high mechanical stress generated at high applied voltages is the formation of cracks in porous oxide film, which are visible by naked eye in the case of some anodizing conditions [41,45]. Obtained  $k_v$  values are in good agreement with the earlier reported data on the low current density anodizing in the oxalic and sulfuric acids electrolytes [43,46]. Comparison of the dependencies of volume expansion factor and pore ordering degree on anodizing voltage allows one to conclude that highly ordered porous structures are formed at  $k_v$  higher than 1.7. Lower values of volume expansion factor are not sufficient for stress driven pore ordering into hexagonal pattern. It should be noted, that high value of  $k_v$  is prerequisite but not sufficient for self-ordered growth of anodic alumina. Under mixed anodizing regime, which is characterized by morphological instability of a growth front [9], porous AAO structure is disordered despite high compressive stress.

# 4. Conclusions

The formation of porous anodic alumina in 0.3 M selenic acid electrolyte at 0 °C in the range of anodizing voltages from 35 to 100 V was studied. Up to 50 V the anodizing occurs in the kinetic regime, at which the current density does not change with the thickness of a porous oxide layer. At higher voltages, the mixed

kinetics (from 50 to 60 V) and then diffusion control regime (above 60 V) are observed. Current efficiency of aluminium anodizing is close to 100% in the whole voltage range from 35 to 100 V. Oxide formation efficiency, volume expansion factor, thickness-to-charge density ratio, and the content of electrolyte impurities in AAO increase significantly with anodizing voltage in the range from 35 to 60 V and remain almost constant at higher voltages in diffusion-limited regime. Experimental values of the above mentioned parameters are useful for further refinement of existing theoretical models of self-organized growth of porous anodic alumina films.

The kinetic model of the self-ordering of anodic alumina porous structure was successfully applied for the targeted search of proper anodizing conditions for fabrication of alumina films with highly ordered structure. A new self-ordering regime for anodic oxidation in 0.3 M selenic acid electrolyte at the anodizing voltage from 60 to 100 V was developed. Anodizing in this voltage range occurs in diffusion-limited regime and can be classified as hard anodizing, which results in high volume expansion factor of  $2.30 \pm 0.18$  and high thickness-to-charge density ratio of  $0.80 \pm 0.08 \,\mu\text{m cm}^2 \,\text{C}^{-1}$ . Anodic alumina films obtained in 0.3 M selenic acid in the voltage range from 60 to 100 V are free of cracks and possess a highly ordered porous structure, where more than 75% of pores have hexagonal coordination. These anodizing conditions cover a novel interpore distance interval from 120 to 160 nm, which was not available before for ordered AAO structures.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.electacta.2019.03.098.

# References

- W. Lee, S.J. Park, Porous anodic aluminum oxide: anodization and templated synthesis of functional nanostructures, Chem. Rev. 114 (2014) 7487.
- [2] P. Roy, S. Berger, P. Schmuki, TiO<sub>2</sub> nanotubes: synthesis and applications, Angew. Chem. Int. Ed. 50 (2011) 2904.
- [3] S. Berger, F. Jakubka, P. Schmuki, Formation of hexagonally ordered nanoporous anodic zirconia, Electrochem. Commun. 10 (2008) 1916.
- [4] S. Berger, F. Jakubka, P. Schmuki, Self-ordered hexagonal nanoporous hafnium oxide and transition to aligned HfO<sub>2</sub> nanotube layers, Electrochem. Solid State Lett. 12 (2009) K45.
- [5] S. Ono, M. Saito, H. Asoh, Self-ordering of anodic porous alumina formed in organic acid electrolytes, Electrochim. Acta 51 (2005) 827.
- [6] C. Sun, J. Luo, L. Wu, J. Zhang, Self-ordered anodic alumina with continuously tunable pore intervals from 410 to 530 nm, ACS Appl. Mater. Interfaces 2 (2010) 1299.
- [7] L. Zaraska, W.J. Stepniowski, E. Ciepiela, G.D. Sulka, The effect of anodizing temperature on structural features and hexagonal arrangement of nanopores in alumina synthesized by two-step anodizing in oxalic acid, Thin Solid Films 534 (2013) 155.
- [8] W.J. Stepniowski, A. Nowak-Stepniowska, A. Presz, T. Czujko, R.A. Varin, The effects of time and temperature on the arrangement of anodic aluminum oxide nanopores, Mater. Char. 91 (2014) 1.
- [9] I.V. Roslyakov, E.O. Gordeeva, K.S. Napolskii, Role of electrode reaction kinetics in self-ordering of porous anodic alumina, Electrochim. Acta 241 (2017) 362.
- [10] K.S. Napolskii, I.V. Roslyakov, A.A. Eliseev, D.V. Byelov, A.V. Petukhov, N.A. Grigoryeva, W.G. Bouwman, A.V. Lukashin, A.P. Chumakov, S.V. Grigoriev, The kinetics and mechanism of long-range pore ordering in anodic films on aluminum, J. Phys. Chem. C 115 (2011) 23726.
- [11] K.S. Napolskii, I.V. Roslyakov, A.Y. Romanchuk, O.O. Kapitanova, A.S. Mankevich, V.A. Lebedev, A.A. Eliseev, Origin of long-range orientational pore ordering in anodic films on aluminium, J. Mater. Chem. 22 (2012) 11922.
- [12] I.V. Roslyakov, A.A. Eliseev, E.V. Yakovenko, A.V. Zabelin, K.S. Napolskii, Longitudinal pore alignment in anodic alumina films grown on polycrystalline metal substrates, J. Appl. Crystallogr. 46 (2013) 1705.
- [13] I.V. Roslyakov, D.S. Koshkodaev, A.A. Eliseev, D. Hermida-Merino, V.K. Ivanov, A.V. Petukhov, K.S. Napolskii, Growth of porous anodic alumina on low-index

surfaces of Al single crystals, J. Phys. Chem. C 121 (2017) 27511.

- [14] H. Masuda, F. Hasegwa, S. Ono, Self-ordering of cell arrangement of anodic porous alumina formed in sulfuric acid solution, J. Electrochem. Soc. 144 (1997) L127.
- [15] H. Masuda, M. Satoh, Fabrication of gold nanodot array using anodic porous alumina as an evaporation mask, Jpn. J. Appl. Phys. 35 (1996) L126.
- [16] H. Masuda, K. Yada, A. Osaka, Self-ordering of cell configuration of anodic porous alumina with large-size pores in phosphoric acid solution, Jpn. J. Appl. Phys. 37 (1998) L1340.
- [17] O. Nishinaga, T. Kikuchi, S. Natsui, R.O. Suzuki, Rapid fabrication of selfordered porous alumina with 10-/sub-10-nm-scale nanostructures by selenic acid anodizing, Sci. Rep. 3 (2013) 2748.
- [18] T. Kikuchi, O. Nishinaga, S. Natsui, R.O. Suzuki, Self-ordering behavior of anodic porous alumina via selenic acid anodizing, Electrochim. Acta 137 (2014) 728.
- [19] S. Akiya, T. Kikuchi, S. Natsui, R.O. Suzuki, Optimum exploration for the selfordering of anodic porous alumina formed via selenic acid anodizing, J. Electrochem. Soc. 162 (2015) E244.
- [20] Y. Nazarkina, S. Gavrilov, H. Terryn, M. Petrova, J. Ustarroz, Investigation of the ordering of porous anodic alumina formed by anodization of aluminum in selenic acid, J. Electrochem. Soc. 162 (2015) E166.
- [21] Y. Nazarkina, K. Kamnev, A. Dronov, A. Dudin, A. Pavlov, S. Gavrilov, Features of porous anodic alumina growth in galvanostatic regime in selenic acid based electrolyte, Electrochim. Acta 231 (2017) 327.
- [22] Y. Nazarkina, S. Gavrilov, A. Polohin, D. Gromov, P. Shaman, Application of porous alumina formed in selenic acid solution for nanostructures investigation via Raman spectroscopy, in: The International Conference on Microand Nano-Electronics, Zvenigorod, Russia, 3-7 October 2016, vol. 102240, SPIE, 2016, p. 102240].
- [23] Y. Nazarkina, K. Kamnev, A. Polokhin, Y. Shaman, The effect of annealing on the Raman spectra of porous anodic alumina films formed in different electrolytes, in: IEEE Conference of Russian Young Researchers in Electrical and Electronic Engineering (ElConRus), St. Petersburg, Russia, 1-3 February 2017, IEEE, 2017, p. 1409.
- [24] K.R. Hebert, S.P. Albu, I. Paramasivam, P. Schmuki, Morphological instability leading to formation of porous anodic oxide films, Nat. Mater. 11 (2012) 162.
- [25] R.A. Mirzoev, A.D. Davydov, S.I. Vystupov, T.B. Kabanova, Conditions for selfordering of porous structure of anodic aluminum oxide in weak and strong acids, Electrochim. Acta 294 (2019) 276.
- [26] A. Mozalev, S. Magaino, H. Imai, The formation of nanoporous membranes from anodically oxidized aluminium and their application to Li rechargeable batteries, Electrochim. Acta 46 (2001) 2825.
- [27] Software for Analysis of Pore Ordering in Anodic Alumina. http:// www.eng.fnm.msu.ru/en/software/.
- [28] L. Young, Anodic Oxide Films, Academic Press, New York (N.Y.), 1961.
- [29] A.L. Yerokhin, X. Nie, A. Leyland, A. Matthews, S.J. Dowey, Plasma electrolysis for surface engineering, Surf. Coating. Technol. 122 (1999) 73.
- [30] V. Vega, J. Garcia, J.M. Montero-Moreno, B. Hernando, J. Bachmann, V.M. Prida, K. Nielsch, Unveiling the hard anodization regime of aluminum: insight into nanopores self-organization and growth mechanism, ACS Appl. Mater. Interfaces 7 (2015) 28682.
- [31] J.P. O'Sullivan, G.C. Wood, The morphology and mechanism of formation of porous anodic films on aluminium, Proc. R. Soc. Lond. Ser. A 317 (1970) 511.
   [32] J. Siejka, C. Ortega, An O<sup>18</sup> study of field-assisted pore formation in compact
- [32] J. Siejka, C. Ortega, An O<sup>1o</sup> study of field-assisted pore formation in compact anodic oxide films on aluminum, J. Electrochem. Soc. 124 (1977) 883.
- [33] Z. Wu, C. Richter, L. Menon, A study of anodization process during pore formation in nanoporous alumina templates, J. Electrochem. Soc. 154 (2007) E8.
- W. Lee, R. Ji, U. Gosele, K. Nielsch, Fast fabrication of long-range ordered porous alumina membranes by hard anodization, Nat. Mater. 5 (2006) 741.
   S. Ono, M. Saito, M. Ishiguro, H. Asoh, Controlling factor of self-ordering of
- anodic porous alumina, J. Electrochem. Soc. 151 (2004) B473.
- [36] R.A. Mirzoev, A.D. Davydov, D.K. Kurmyalevskaya, A.N. Bazylyk, S.I. Vystupov, Conditions for transition from barrier to porous oxidation of aluminum in phosphoric acid solutions, Electrochim. Acta 184 (2015) 214.
- [37] A. Santos, P. Formentin, J. Pallares, J. Ferre-Borrull, L.F. Marsal, Structural engineering of nanoporous anodic alumina funnels with high aspect ratio, J. Electroanal. Chem. 655 (2011) 73.
- [38] S.E. Kushnir, K.S. Napolskii, Thickness-dependent iridescence of onedimensional photonic crystals based on anodic alumina, Mater. Des. 144 (2018) 140.
- [39] A.P. Li, F. Muller, A. Birner, K. Nielsch, U. Gosele, Hexagonal pore arrays with a 50-420 nm interpore distance formed by self-organization in anodic alumina, J. Appl. Phys. 84 (1998) 6023.
- [40] K. Nielsch, J. Choi, K. Schwirn, R.B. Wehrspohn, U. Gosele, Self-ordering regimes of porous alumina: the 10% porosity rule, Nano Lett. 2 (2002) 677.
- [41] K. Schwirn, W. Lee, R. Hillebrand, M. Steinhart, K. Nielsch, U. Gosele, Selfordered anodic aluminum oxide formed by H<sub>2</sub>SO<sub>4</sub> hard anodization, ACS Nano 2 (2008) 302.
- [42] O. Jessensky, F. Muller, U. Gosele, Self-organized formation of hexagonal pore arrays in anodic alumina, Appl. Phys. Lett. 72 (1998) 1173.
- [43] I. Vrublevsky, V. Parkoun, V. Sokol, J. Schreckenbach, G. Marx, The study of the volume expansion of aluminum during porous oxide formation at galvanostatic regime, Appl. Surf. Sci. 222 (2004) 215.
- [44] J. Liao, Z. Ling, Y. Li, X. Hu, The role of stress in the self-organized growth of porous anodic alumina, ACS Appl. Mater. Interfaces 8 (2016) 8017.

- [45] S.Z. Chu, K. Wada, S. Inoue, M. Isogai, A. Yasumori, Fabrication of ideally ordered nanoporous alumina films and integrated alumina nanotubule arrays by high-field anodization, Adv. Mater. 17 (2005) 2115.
- [46] I. Vrublevsky, V. Parkoun, J. Schreckenbach, G. Marx, Effect of the current density on the volume expansion of the deposited thin films of aluminum during porous oxide formation, Appl. Surf. Sci. 220 (2003) 51.