Influence of Annealing Time of Aluminum AA1050 on the Quality of Cu and Co Nanocones

Katarzyna Skibinska , Grzegorz Smola, Lukasz Bialo, Dawid Kutyla, Karolina Kolczyk-Siedlecka, Anna Kwiecinska, Marek Wojnicki, and Piotr Zabinski

Submitted: 13 April 2020 / Revised: 21 July 2020 / Accepted: 7 October 2020 / Published online: 16 November 2020

Anodization is a widespread surface treatment method for aluminum and its alloys; it also allows the formation of 1D nanostructures by a two-step process. Microstructure of the Al substrate and crystallographic texture after rolling and annealing have influence on the properties of AAO templates with conical nanopores. Synthesized free-standing 1D nanostructures ensure better electrocatalytic properties than bulk materials due to larger active surface area. In this work, the influence of annealing time at 500 °C on Vickers hardness and microstructure of aluminum AA1050 used in a two-step anodization process was investigated. The geometrical features of the templates such as interpore distance and number of pores per 1 μm^2 were determined and compared. There is dependence between the time of the annealing process and surface quality of synthesized 1D Cu nanocone layers. The template, after 1 h of annealing, due to the largest active area and satisfactory quality of the nanocone surface, was chosen for synthesis of Co nanocones. The electrocatalytic properties of samples were measured in 1 M NaOH solution and compared with bulk material electrodeposited in the same conditions. The open circuit potential, connected with starting of hydrogen evolution reaction, was determined from the LSV curves. Active surface areas were determined for all samples using SEM photographs and taken into consideration during electrocatalytic tests. Possible behavior of hydrogen bubbles for the formation of nanostructures was considered.

Keywords 1D nanocones, annealing, electrodeposition, hydrogen evolution reaction

1. Introduction

Anodization is one of the commonly used surface treatment methods for aluminum and its alloys. The simplest process is carried out galvanostatically or potentiostatically. Porous anodic alumina oxide (AAO) consists of a close-packed hexagonal array of parallel nanopores perpendicular to the surface of aluminum called honeycomb structure (Ref 1). Anodic oxidizing can be also applied for other metals like Ti (Ref 2, 3), Sn (Ref 4), Fe (Ref 5), W (Ref 6), etc.

Two-step anodization used for fabrication of high-quality and well-ordered 1D nanostructures is characterized by the simplicity and low cost of the process. In the case of nanocones, the first step usually consists long-period anodization in oxalic acid. Before the second step of anodization, an oxide layer has to be removed in a mixed solution of phosphoric and chromic acids. Repeated anodizing in oxalic acid and a pore-widening process in phosphoric acid are called usually the second step of anodization.

Geometrical features of AAO can be influenced by changing the electrolyte and its concentration (Ref 7-9), anodization's

time (Ref 10), applied voltage and temperature (Ref 11, 12). In the case of two-step anodization, the number of cycles and duration of anodization in second step can control these properties. The influence on effects of anodization has also microstructure of aluminum sheet like grain orientation, boundaries and texture after rolling and annealing.

The annealing temperature affects the optical and photoluminescent properties of AAO (Ref 13, 14).

Cold rolling of aluminum before two-step anodization in 0.3 M oxalic acid at 20 ÷ 60 V worsens the pore ordering and increases number of pores (Ref 15). The interpore distance decreased at 30 V and increased at 50-60 V. Rolling texture of aluminum correlates with irregularity of pores (Ref 16). Recrystallization process is a solution to this problem, but only for high-purity aluminum. There is no influence of density of dislocations, boundaries and shape of grains on regularity of AAO. The most regular pores could be obtained for grains with (100) orientation. Moreover, in the initial stage oxide starts growing at the grain boundaries (Ref 17).

Annealing temperature influences on microstructure of AAO. With the increasing of annealing temperature (from 250 to 650 °C), the refractive index increases and the optical losses decrease due to the decrease in the alumina porosity and structure modification (Ref 13). Increasing of temperature of annealing causes also more regular ordering of pores for AA1050 and pure aluminum samples annealed under the same conditions (200 °C and 1 h) (Ref 18). For the anodized materials, the sheets represent similar surface textures but more regular pores arrays are obtained for pure aluminum. Al 1050 sheets characterized by different textures were also annealed at the same conditions. There is no influence of texture on arrangements of AAO.

Conditions of the preheating recrystallization such as holding time, heating and cooling rates affect the grain growth

Katarzyna Skibinska, Grzegorz Smola, Lukasz Bialo, Dawid Kutyla, Karolina Kolczyk-Siedlecka, Anna Kwiecinska, Marek Wojnicki, and Piotr Zabinski, Faculty of Non-Ferrous Metals, AGH University of Science and Technology, Kraków, Poland. Contact e-mail: kskib@agh.edu.pl.

and preferential crystal orientation of aluminum substrates (Ref 19). The grain size increases with increasing overall heating time. Smaller grains in the aluminum samples are obtained through quenching at a high heating and cooling rate. There are the preferential orientations (200) and (311) at all heating rate. For example, annealing preferential orientations were (311) and/or (422). To improve the pore regularity and thermal stability of AAO, slow heating and cooling rate are used during the recrystallization process.

Quality of AAO depends on purity of the aluminum sheets used. Using 99.999% pure aluminum during anodization leads to better ordered AAO compared to aluminum of lower purity (Ref 20). However, there is no difference between AAO using high- and low-purity aluminum during anodization in a mixture of 0.3 M sulfuric acid solution, water and glycol (3:2, v/v) at different voltages (Ref 21).

To obtain free-standing metal nanocones, the metal has to be electrodeposited using AAO. To produce Cu nanocones, DC electrodeposition in a three-electrode cell at room temperature in a 5 mA cm^{-2} for 60 min in aqueous solution containing 0.5 M CuSO_4 and 0.5 M H_2SO_4 can be performed (Ref 22). The AAO template is removed in a dilute phosphoric acid solution. The resultant nanostructures show better electrocatalytic activity compared with Cu bulk in reduction of H_2O_2 and they could be used as a non-enzymatic sensors.

Nanocones can be also synthesized by electroless deposition onto AAO (Ref 23). In this way, nickel can be deposited in a Watts bath in a three-electrode cell with Pt sheet as a working electrode and an Ag/AgCl electrode as reference electrode. To obtain free-standing nanocones, the sample is immersed into 30 wt.% NaOH.

Nickel, iron and cobalt hollow-nanocones are produced by electrodeposition after sputtering a thin, conductive Au layer (Ref 24). The bottom part of nanopores is not covered with sputtered metal. The electrodeposition is produced in a three-electrode electrochemical cell under the voltage of -1 V for 3 h at 30°C . There is no influence of applied current density on synthesis of these nanostructures.

The literature review shows that cold rolling, annealing and recrystallization processes effect on the regularity of AAO and then on the quality of obtained 1D nanocones. Therefore, the influence of time of annealing of aluminum AA1050 on AAO templates quality for Cu and Co nanocone synthesis was investigated in the work reported in this paper. The microstructures and hardness of aluminum sheets annealed for different times were investigated and compared. Copper and cobalt were electrodeposited using synthesized templates. Cobalt nanocones were successfully obtained. The electrocatalytic properties of Cu and Co 1D nanoconical layers were measured in 1 M NaOH and compared with electrodeposited bulk materials. The scale of increase in sample's active area was checked. Obtained results show the connection between annealing time and electrocatalytic properties of produced nanostructures.

2. Materials and Methods

Firstly, the chemical composition of aluminum AA1050 used was investigated using WD XRF method (Rigaku Primini) with palladium source of radiation. Table 1 presents the comparison of the chemical composition of AA1050 according to PN-EN 573-3:2014-02 norm.

The composition of aluminum used was in accordance with the standards and characterized by aluminum content 99.7% by weight.

The AA1050 rectangular samples ($50 \times 30 \text{ mm}$) were degreased using an ultrasonic cleaner by immersion into acetone. The thickness of aluminum sheet was 0.1 mm. The samples were annealed in a resistance furnace at 500°C in hydrogen atmosphere (5% hydrogen mixture with argon) for 20, 40, 60, 120, 180 and 240 min. Before carrying out the anodizing process, the samples were electrochemically polished using Struers LectroPol-5.

Vickers hardness of the annealed samples was investigated using SHIMADZU HMV-G21 Series device with 100 g load for 10 s. For microstructure observation, samples were etched in Keller (mixing concentrated HNO_3 , HCl and HF acids in a volume ratio of 3:2:1) and Weck solutions from 10 to 120 s—depending on the annealing time.

Anodizing was carried out in a cell where the anode was an aluminum sample and the cathode was a platinum sheet. The process was carried out at 2°C in 0.3 M oxalic acid for 60 min. The obtained oxide layer was then removed by immersion into a 6 wt.% H_3PO_4 and 1.8 wt.% H_2CrO_4 (mixed in a 1:1 ratio) at 65°C for 60 min.

The process of nanopore growth and expansion consisted of 4 cycles of alternating short-anodizing of a pre-prepared aluminum sheet in 0.3 M oxalic acid at 9°C at 45 V and pore-widening process in 5 wt.% H_3PO_4 at 30°C for 12 min. The anodizing time in the first cycle was 25 s, for the next three cycles it was 20 s.

In order to ensure conductivity, a thin layer of Cu was sputtered on the prepared templates using EMITECH K575X. Then, the electrodeposition of Cu and Co was carried out at room temperature. In both cases, the sample was the cathode and Pt sheet was the anode. Copper was deposited from an electrolyte containing 0.5 M CuSO_4 , 0.5 M H_2SO_4 , and cobalt was deposited from an electrolyte containing 0.9 M $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, 0.4 M H_3BO_3 , 0.3 g L^{-1} SDS. A current density of 5 mA cm^{-2} and a time of 120 min were used.

After the electrodeposition process, the samples were immersed into a 5 wt.% H_3PO_4 solution (for Cu nanocones) and 5 wt.% NaOH (for Co nanostructures) to remove the AAO template. The SEM photographs of cross-sectional view of the $\text{Al}_2\text{O}_3/\text{Al}$ template with conical nanopores and free-standing copper nanocones were obtained using a Hitachi SU-70 scanning electron microscope. The nanocones obtained were observed using scanning electron microscope JEOL-6000 Plus. Mapping analysis was carried out using SEM-EDS, to confirm the synthesized metal nanocones.

The ANOVA test was applied, using OriginLab Software, to check the correlation between annealing time and features of AAO templates.

The synthesized layers of nanoconical structures were investigated for electrocatalytic activity in the process of hydrogen evolution. The measurement was taken in a three-electrode cell. The copper and cobalt layers obtained were the working electrode; a platinum sheet was the counter electrode. A saturated calomel electrode SCE was used as the reference electrode in the system. The measurement was taken in a 1 M NaOH solution at room temperature. The open circuit potential (OCP), connected with starting of hydrogen evolution reaction, was determined from the figures.

Figure 1 shows the scheme of conducted experiments.

Table 1 Chemical composition of the Al used

Element	Al	Si	Ti	Fe
wt.% according to PN-EN 573-3:2014-02 norm	Min 99.50	Max 0.25	Max 0.03	Max 0.40
wt.% XRF	99.70	0.13	0.01	0.16

Fig. 1 The scheme of performed experiments **Fig. 2** The comparison of samples (a) without annealing and (b) after 240 min of annealing

3. Results and Discussion

In order to find the optimal annealing time, the Vickers hardness of aluminum AA1050 was measured using the SHIMADZU HMV-G21 device with 100 g load. Additionally, a sample without annealing was tested as a reference. The hardness was measured 5 times for each sample. The example of indentations left in the samples without annealing and after 240 min of annealing is shown in Fig. 2.

It can be noticed that the indentations in the sample, which was annealed for 240 min at 500 °C, are two times larger than in the case of the non-treated sample. Microscopic observations were confirmed by the hardness measurement results given in Table 2.

The sample without annealing showed the highest hardness—the hardness of this sample on Vickers' scale was 41.86 HV. It was noticed that the other samples, annealed 20 min or more, have the same hardness (considering the measurement deviation) as the sample annealed at 500 °C for 240 min. Therefore, the hardness value for the annealed samples was averaged and amounted to 21.62 HV. It can be

concluded that the changes of hardness after 20 min or more of annealing are irrelevant. Hence, annealing time of 20 min is sufficient to prepare sample for next steps of template preparation.

To check the surface quality of the samples, surface before and after electrochemical polishing (without etching) was observed and compared. The results are shown in Fig. 3.

It can be noticed that electrochemical polishing significantly improves the sample surface. The rolling scratches on the surface resulting from the rolling and transport process are less visible and the surface becomes uniform. Unfortunately, irregularity after electropolishing is still present, connected with insufficient leveling of the surface. It could be caused by heating of the electrolyte during polishing of aluminum. This may influence the quality of aluminum oxide templates obtained in the anodizing process. Therefore, the additional step, annealing process at 500 °C for different times, was added before the polishing step.

The samples of AA1050 aluminum were chemically etched in Keller and Weck solutions in order to reveal their microstructure. The microstructure changes occurring during

Table 2 Hardness measurement results after different times of annealing

Number of indentation	Sample without annealing, HV	Sample after 20 min of annealing, HV	Sample after 40 min of annealing, HV	Sample after 60 min of annealing, HV	Sample after 240 min of annealing, HV
Average value	41.86 ± 2.23	21.74 ± 0.87	20.90 ± 1.42	22.73 ± 1.89	21.14 ± 0.86

Fig. 3 Comparison of surface (a) before and (b) after polishing

the annealing process at different times were analyzed using Nikon ECLIPSE LV150 optical microscope. The microstructures of annealed samples were observed and compared. The results are shown in Fig. 4.

The non-annealed sample is characterized by long stretched grains. As the annealing time increased, changes in grain size were observed. The size of a single grain was measured using Jeffries method. The grain shape changed after 20 min of annealing—from long stretched grains to a more round one. There is no clear influence of annealing time on grain size of AA1050. Grain size increased from 20 to 120 min of annealing process time, then a decrease in this value is observed. In this case, we did not observe the process of grains growing: the motivation to be further explored. The resolution of photographs is $100\times$.

Samples prepared in such way were two-step anodized and then observed using JEOL 6000 Plus SEM. Observation consists of the porous anodic alumina oxide templates and obtained free-standing Cu and Co nanocones.

Observation of the AAO was carried out to check the surface quality after anodizing process, measure the distance between pores and calculate the density of pores per μm^2 . The distance between the two pores was measured using SEM—Jeol JCM-6000 Plus. The example of the image is shown in Fig. 5. Six measurements were taken for each sample. The results for all samples are shown in Fig. 6.

It has been observed that as the annealing time increases, the distance between two alumina pores decreases. This means that there are more pores on the surface of the template, which could be correlated with increasing of the active surface area. It was noticed that for an annealing time of 120 min the interpore distance slightly increased, this may be caused by a measurement deviation—there is possibility of choosing inappropriate point for measuring due to the size of pores. In addition, it was observed that the annealed samples after 180 and 240 min have similar distance values. It is possible that for this value of annealing time the average distance between pores does not vary. The template shows also the hexagonally ordered pores.

To confirm that there is the influence of annealing time on this distance, an ANOVA test was carried out—at the 0.05 level, the slope is significantly different from zero.

In order to calculate the number of pores per μm^2 using SEM photographs, a square of $1\mu\text{m} \times 1\mu\text{m}$ was drawn and all the pores within this square were calculated as it is shown in Fig. 7.

The results of all calculations are presented in Fig. 8; no influence of annealing time on the number of pores per μm^2 was observed. The average number of pores is about 67 per $1\mu\text{m}^2$.

An ANOVA test was carried out to confirm that there is no influence. In this case at the 0.05 level, the slope is not significantly different from zero.

To provide the conductivity for synthesis of free-standing nanocones, copper was sputtered on the obtained templates. Then, Cu was electrodeposited on the template in a solution of 0.5 M $\text{H}_2\text{SO}_4 + 0.5\text{ M CuSO}_4$ at room temperature for 120 min at 5 mA cm^{-2} . The obtained layers were immersed into a 5 wt.% H_3PO_4 solution to remove the AAO. The SEM photographs of the template before electrodeposition of copper and obtained free-standing Cu nanocones are shown in Fig. 9.

The photographs show the template and 1D nanocones obtained using the sample annealed for 180 min. They confirmed synthesis of 1D nanostructures by electrodeposition onto AAO template. It can be noticed that fabricated nanostructures are homogeneous in shape and size. They do not form the clusters. Obtained nanocones show the cone tops, which are not sharp but rounded. It is the characterizing phenomenon for 1D metal nanocones produced using AAO (Ref 22, 23).

The copper nanocones were analyzed using SEM, and the compositions of the samples were examined using mapping analysis mode of EDS.

It was noticed that for the nanocones obtained after 240 min of annealing, the surface with the best quality was achieved (Fig. 10). The other samples are characterized by a large number of defects (e.g., 20 min of annealing) and surface

Fig. 4 Comparison of optical microscopy images ($\times 100$) of microstructures and the average grain size after different times of annealing

unevenness (e.g., sample annealed for 120 min). However, samples after 40 and 60 min show sufficient quality.

Analysis of the surface composition for layers of copper nanocones, obtained under different conditions of annealing, showed that the distribution of Cu on the surface is homogenous.

For the calculation of the active surface area of the copper nanocones, the diameter of the nanostructures was measured (Fig. 11a) and the number of nanocones per $1 \mu\text{m}^2$ was calculated (Fig. 11b). The area between nanocones was also included in calculations. Then, using equations: $P_b = \pi \cdot r \cdot l$,

$l = \sqrt{h^2 + r^2}$ [where P_b is the lateral surface area of the cone (nm^2), r —cone base radius (nm), l —length of the cones forming line (nm), h —cone height (nm)], the lateral surface of the cone was calculated. The results are shown in Table 3. Figure 12 shows the geometrical features for nanocones.

The highest increase in active surface area compared with reference layer (1.2 cm^2) was observed for sample after 60 min of annealing (1.5 cm^2). It suggests that 60 min is an optimal time to obtain a sample with the highest active surface area. All measurement results are shown in Table 3.

Fig. 5 Measuring the distance between the two Al_2O_3 pores for a sample annealed for 40 min

Fig. 6 Influence of annealing time on average distance between pores

Fig. 7 Calculation of the number of pores for the sample annealed for 40 min

Fig. 8 Number of pores per μm^2 depending on annealing time

Fig. 9 SEM photographs of (a) cross-sectional view of the $\text{Al}_2\text{O}_3/\text{Al}$ template with conical nanopores and (b) Cu nanocones after removing the AAO template

Used in calculations height of nanocones was investigated using the TEM photograph. We assumed that this value is constant for all templates. The amount of nanocones should be higher for the smaller diameter; however, due to not perfect

Fig. 10 SEM photographs and mapping analysis of Cu nanocones with annealing time of Al

ordering and quality of nanocones, it is difficult to determine it. The potential differences should not strongly influence on the results of electrocatalytic properties.

The electrocatalytic properties of the obtained nanocones were measured in non-stirred 1 M NaOH in a three-electrode

Fig. 11 Calculation of (a) cone diameters on the Cu layer and (b) number of Cu nanocones per μm^2 for sample annealed for 60 min

cell with the analyzed sample as working electrode, platinum foil as an anode and saturated calomel electrode (SCE) as a reference electrode. The LSV measurements were taken in a range from the open circuit potential (OCP) value to -2 V versus SCE with a scan speed of 5 mV s^{-1} . Additionally, for comparison, the copper electrode without nanocones (bulk material) was used.

To determine the potential E_{ONSET} , at which the hydrogen evolution reaction (HER) begins, two tangents were plotted on the curve of the potential dependence on the current density. It marked the point of intersection of the potential at which the process began. This determining is shown in Fig. 13.

The LSV curves of copper nanostructures and Cu bulk as a reference are shown in Fig. 14.

Sample obtained using aluminum annealed for 60 min shows the best electrocatalytic properties. It can be connected with the larger active surface area of this sample. Samples obtained after 180 and 240 min of annealing give the worst electrocatalytic properties. These samples show lower slope of LSV curve.

E_{ONSET} measured for copper bulk was about -1.72 V . It was noticed that there is no dependence of annealing time on value of this potential. The best results were obtained for the nanocones obtained using aluminum sample annealed for 60 min (-1.69 V). The results are shown in Table 4.

Table 3 The results of the calculation of the surface of the active of layer with Cu nanocones

Annealing time, min	Nanocone diameter d , nm	Nanocone height h , nm	Lateral surface area of the cone, μm^2	Amount of nanocones per, μm^2	Active surface area, cm^2
0	115	73.5	0.015	66	1.29
20	97		0.013	64	1.35
40	96		0.013	67	1.40
60	87		0.012	72	1.50
120	84		0.011	69	1.46
180	75		0.010	68	1.46
240	82		0.011	63	1.39

Fig. 12 Geometrical features of nanocones: h height, d diameter, D_{int} distance between the nanocones **Fig. 13** Determining the potential E_{ONSET} for starting the hydrogen evolution process

For synthesis of Co nanocone, sample template produced using AA1050 material after 60 min of annealing was chosen. This time ensures obtaining the template characterized by the best quality and allows to synthesis nanocones with the highest active surface area. The electrodeposition of cobalt was performed in cell with a template as a cathode and a platinum foil as an anode for 120 min. To remove the template, the sample was immersed into dilute NaOH solution. The SEM image and mapping analysis of obtained Co nanocones are shown in Fig. 15.

Mapping analysis of nanomaterial confirmed that it is possible to produce free-standing Co nanocones with uniform

Fig. 14 LSV curves of Cu bulk and Cu nanocone materials in 1 M NaOH solution

distribution of this metal on the surface of the sample. The electrocatalytic properties of obtained Co nanocones were compared with Co, Cu bulk and Cu nanocones. The results are shown in Fig. 16.

In case of synthesized Co nanocones, the material is characterized by worse electrocatalytic properties in comparison to bulk material. It could be caused by the destruction of the thin nanocones layer during intensive hydrogen evolution reaction. Cobalt materials show worse properties also compared with Cu. This might be related to different activities of materials made of different metals. Values of E_{ONSET} of used materials are shown in Table 5.

Determination of this potential shows that, for Co bulk and Co nanocones, HER started earlier compared with copper. This result also confirmed that Co bulk is characterized by better electrocatalytic properties because the value of E_{ONSET} is less negative.

Electrocatalytic properties of material can be increased by changing the composition of material (alloying) or by increase in active surface area or by change surface properties. In case of Cu or Co nanostructures, the increase in these properties cannot be assumed with change of composition of material—nanocones are synthesized using only one element: Cu or Co.

It was shown that electrocatalytic properties of nanocones increase in comparison with bulk material, due to higher degree of surface development. It is connected with an enlargement of active surface area by about 16%. Synthesis of nanocones had

Table 4 Sample and its E_{ONSET} potential

Sample	E_{ONSET} , V
Cu bulk	− 1.72
Annealing time, min	E_{ONSET} , V
<i>Cu nanocones</i>	
0	− 1.72
20	− 1.74
40	− 1.70
60	− 1.69
120	− 1.73
180	− 1.67
240	− 1.66

Fig. 15 (a) SEM image and (b) mapping analysis of cobalt nanocones **Fig. 16** LSV curves of Cu and Co bulks and Cu, Co nanocone materials in 1 M NaOH solution**Table 5** Sample and its E_{ONSET} potential

Material	E_{ONSET} , V	Calculated active area, cm ²
Cu bulk	− 1.72	1.20
Cu nanocones (60 min)	− 1.69	1.64
Co bulk	− 1.40	1.20
Co nanocones (60 min)	− 1.42	1.64

Fig. 17 A scheme of hydrogen bubbles behavior on (a) the bulk material surface and (b) nanocone surface

also an effect on physicochemical properties of materials such as, for example, wettability.

As it is shown in Fig. 17, surface made from nanocones should characterize by smaller contact surface with hydrogen bubbles. Additionally, it should be expected that small hydrogen bubbles will assemble into bigger ones more easily in case of nanoconical surface, due to occurrence of verticals components, that enhance coalescence of hydrogen. However, these postulates require further confirmation in experimental way.

4. Conclusions

These results could lead to the following conclusions:

1. Twenty minutes of annealing of AA1050 is sufficient time for obtaining constant value of Vickers hardness (21.62 HV).
2. After 20 min of annealing, the grain shape changed from long to round but there is no clear dependence of time of this process on grain size.
3. The distance between two pores decreases with the annealing time. The biggest difference in distance was noticed for annealing times under 60 min—then distance does not change.
4. There is no influence of annealing time on number of pores per $1\ \mu\text{m}^2$.
5. The sample annealed for 240 min is characterized by the best quality compared with others. All samples uniform distribution of copper on the surface.
6. Calculations show that the largest active surface area ($1.50\ \text{cm}^2$) was observed for sample after 60 min of annealing. This sample shows the best electrocatalytic properties in 1 M NaOH.
7. It has been proved that 60 min is the best annealing time that allows satisfactory results; therefore, Co nanocones were obtained using aluminum annealed for 60 min.
8. Obtained Co nanomaterial was characterized by homogeneous distribution of this metal on the surface but shows the worst electrocatalytic properties compared with bulk Co.
9. Co nanocones show worse electrocatalytic properties than bulk material; it is caused probably by the destruction of thin nanomaterial layer by intensive hydrogen evolution. However, the value of E_{ONSET} is less negative for Co bulk, which confirmed that this material shows better electrocatalytic properties in comparison with Cu.
10. It can be postulated that nanocone surface is characterized by smaller contact surface with small hydrogen bubbles. The presence of vertical components can cause easier coalescence of hydrogen bubbles into bigger ones, due to enhancing coalescence of hydrogen.

Acknowledgments

This work was financially supported by Polish National Science Center (NCN) under Grant UMO-2016/23/G/ST5/04058.

Open Access

This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence

and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

1. A.M.M. Jani, D. Losic, and N.H. Voelcker, Nanoporous anodic aluminium oxide: advances in surface engineering and emerging applications, *Prog. Mater. Sci.*, 2013, **58**(5), p 636–704 (in English)
2. H. Habazaki, M. Teraoka, Y. Aoki, P. Skeldon, and G.E. Thompson, Formation of porous anodic titanium oxide films in hot phosphate/glycerol electrolyte, *Electrochim. Acta*, 2010, **55**(12), p 3939–3943 (in English)
3. M. Liao, H. Ma, D. Yu, H. Han, X. Xu, and X. Zhu, Formation mechanism of anodic titanium oxide in mixed electrolytes, *Mater. Res. Bull.*, 2017, **95**, p 539–545 (in English)
4. L. Zaraska, K. Gawlak, D. Gilek, and G.D. Sulka, Electrochemical growth of multisegment nanoporous tin oxide layers by applying periodically changed anodizing potential, *Appl. Surf. Sci.*, 2018, **455**, p 1005–1009 (in English)
5. B. Lucas-Granados, R. Sánchez-Tovar, R.M. Fernández-Domene, and J. García-Antón, Iron oxide nanostructures for photoelectrochemical applications: effect of applied potential during Fe anodization, *J. Ind. Eng. Chem.*, 2019, **70**, p 234–242 (in English)
6. K. Syrek, L. Zaraska, M. Zych, and G.D. Sulka, The effect of anodization conditions on the morphology of porous tungsten oxide layers formed in aqueous solution, *J. Electroanal. Chem.*, 2018, **829**, p 106–115 (in English)
7. W.J. Stepniowski, M. Moneta, M. Norek, M. Michalska-Domanska, A. Scarpellini, and M. Salerno, The influence of electrolyte composition on the growth of nanoporous anodic alumina, *Electrochim. Acta*, 2016, **211**, p 453–460 (in English)
8. S. Ateş, E. Baran, and B. Yazıcı, The nanoporous anodic alumina oxide formed by two-step anodization, *Thin Solid Films*, 2018, **648**, p 94–102 (in English)
9. R. Syed, D. Sen, K.V. Mani Krishna, and S.K. Ghosh, Fabrication of highly ordered nanoporous alumina membranes: probing microstructures by SAXS, FESEM and AFM, *Microporous Mesoporous Mater.*, 2018, **264**, p 13–21 (in English)
10. S.H. Su, C.S. Li, F. Bin Zhang, and M. Yokoyama, Characterization of anodic aluminium oxide pores fabricated on aluminium templates, *Superlattices Microstruct.*, 2008, **44**(4–5), p 514–519 (in English)
11. W.J. Stepniowski, A. Nowak-Stepniowska, A. Presz, T. Czujko, and R.A. Varin, The effects of time and temperature on the arrangement of anodic aluminum oxide nanopores, *Mater. Charact.*, 2014, **91**, p 1–9 (in English)
12. W.J. Stepniowski, A. Nowak-Stepniowska, and Z. Bojar, Quantitative arrangement analysis of anodic alumina formed by short anodizations in oxalic acid, *Mater. Charact.*, 2013, **78**, p 79–86 (in English)
13. M. Ghrib, R. Ouertani, M. Gaidi, N. Khedher, M. Ben Salem, and H. Ezzaouia, Effect of annealing on photoluminescence and optical properties of porous anodic alumina films formed in sulfuric acid for solar energy applications, *Appl. Surf. Sci.*, 2012, **258**(12), p 4995–5000 (in English)
14. S. Stojadinovic, Z. Nedici, I. Belca, R. Vasilic, B. Kasalica, M. Petkovic, and L.J. Zekovic, The effect of annealing on the photoluminescent and optical properties of porous anodic alumina films formed in sulfamic acid, *Appl. Surf. Sci.*, 2009, **256**(3), p 763–767 (in English)
15. W.J. Stepniowski, M. Michalska-Domanska, M. Norek, E. Twardosz, W. Florkiewicz, W. Polkowski, D. Zasada, and Z. Bojar, Anodization of cold deformed technical purity aluminium (AA1050) in oxalic acid, *Surf. Coat. Technol.*, 2014, **258**, p 268–274 (in English)
16. G. Beck and K. Petrikowski, Influence of the microstructure of the aluminum substrate on the regularity of the nanopore arrangement in an alumina layer formed by anodic oxidation, *Surf. Coat. Technol.*, 2008, **202**(21), p 5084–5091 (in English)
17. T. Kikuchi, T. Yamamoto, and R.O. Suzuki, Growth behavior of anodic porous alumina formed in malic acid solution, *Appl. Surf. Sci.*, 2013, **284**, p 907–913 (in English)

18. C.S. Chi, J.H. Lee, I. Kim, and H.J. Oh, Effects of microstructure of aluminum substrate on ordered nanopore arrays in anodic alumina, *J. Mater. Sci. Technol.*, 2015, **31**(7), p 751–758 (in English)
19. F. Rashidi, T. Masuda, H. Asoh, and S. Ono, Metallographic effects of pure aluminum on properties of nanoporous anodic alumina (NPAA), *Surf. Interface Anal.*, 2013, **45**(10), p 1490–1496 (in English)
20. W. Huang, M. Yu, S. Cao, L. Wu, X. Shen, and Y. Song, Fabrication of highly ordered porous anodic alumina films in 0.75 M oxalic acid solution without using nanoimprinting, *Mater. Res. Bull.*, 2019, **111**, p 24–33 (in English)
21. M. Michalska-Domanska, M. Norek, W.J. Stepniowski, and B. Budner, Fabrication of high quality anodic aluminum oxide (AAO) on low purity aluminum—a comparative study with the AAO produced on high purity aluminum, *Electrochim. Acta*, 2013, **105**, p 424–432 (in English)
22. A. Brzozka, D. Szeliga, E. Kurowska-Tabor, and G.D. Sulka, Synthesis of copper nanocone array electrodes and its electrocatalytic properties toward hydrogen peroxide reduction, *Mater. Lett.*, 2016, **174**, p 66–70 (in English)
23. T. Nagaura, F. Takeuchi, Y. Yamauchi, K. Wada, and S. Inoue, Fabrication of ordered Ni nanocones using a porous anodic alumina template, *Electrochem. Commun.*, 2008, **10**(5), p 681–685 (in English)
24. J. Li, L. Hu, C. Li, and X. Gao, Tailoring hexagonally packed metal hollow-nanocones and taper-nanotubes by template-induced preferential electrodeposition, *ACS Appl. Mater. Interfaces*, 2013, **5**(20), p 10376–10380 (in English)

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.