Chemistry Proceedings

MDPI

Proceedings

Electrocatalytic properties of Co nanoconical structured electrode produced by one-step and two-step method†

Katarzyna Skibinska[1,*], K. Kolczyk-Siedlecka[1], D. Kutyla[1], A. Jedraczka[1] and P. Zabinski[1]

[1] AGH University of Science and Technology, Faculty of Non-Ferrous Metals, al. Mickiewicza 30, 30-059 Krakow, Poland; kkolczyk@agh.edu.pl (K.K.-S.); kutyla@agh.edu.pl (D.K.); kwiec@agh.edu.pl (A.J.); zabinski@agh.edu.pl (P.Z.)

* Correspondence: kskib@agh.edu.pl (K.S.)

† Presented at the 1st International Electronic Conference on Catalysis Sciences, 10–30 November 2020; Available online: https://sciforum.net/conference/ECCS2020

Published: 10 November 2020

Abstract: One-dimensional (1D) nanostructures, such as nanotubes, nanopores, nanodots and nanocones, are characterized by better catalytic properties than bulk material due to their large active surface area and small geometrical size [1]. There are several methods of synthesis these structures, including the one- and two-step methods. In the one-step method, a crystal modifier are added to the solution in order to limit horizontal direction of structures growing during electrodeposition. In this work, cobalt nanoconical structures were obtained from an electrolyte containing $CoCl_2$, H_3BO_3 and NH_4Cl as the crystal modifier. Another way of production of 1D nanocones is electrodeposition of metal into porous anodic alumina oxide (AAO) templates. This method is called the two-step method. In this case, AAO template was obtained using two-step anodization. Then, electrodeposition of cobalt was performed from an electrolyte containing $CoSO_4$ and H_3BO_3. Nanocones obtained by two-step method shows smaller geometrical size. The bulk sample was electrodeposited from the same electrolyte. The electrocatalytic properties of materials fabricated in one-step and two-step method were measured in 1M NaOH and compared with bulk materials. Co cones obtained by one-step method shows the worst electrocatalytic properties. The hydrogen evolution reaction started the earliest for Co nanocones electrodepsited in the templates.

Keywords: 1D nanocones; anodization; crystal modifier; cobalt; electrodeposition; hydrogen evolution reaction;

1. Introduction

One-dimensional (1D) nanostructures are characterized by two nanometric dimention in three perpendicular directions. They can be synthesized using several methods such as electrodeposition with crystal modifier, two-step anodization, chemical vapor deposition (CVD) and etc.

In case of one-step method, the addition of crystal modifier causes promoting of a parallel direction of structures growth and blocking a horizontal one. This effect is connected with the screw dislocation driven crystal growth [2]. There are several examples of used crystal modifier such as EDA·2HCl [3], $CaCl_2{\cdot}2H_2O$ [2] or NH_4Cl [4]. This method allows to cover large-area fastly. Fabricated structures are ended with sharp tip. Another advantage of this method is no use of chromic acid, which is dangerous for environment. In case of cobalt, shell-like materials were obtained instead of conical ones [5].

Two-step method uses pre-produced templates. They are obtained by two-step anodization, which is the simply and low-cost process. Two-step method allows to obtain the round-ended nanocones. The advantage of this method is a possibility of controlling the geometrical features of synthesized structures. Produced structures show better electrocatalytic properties than bulk materials due to their small geometrical size [6].

Cobalt is an element from Fe-group. It shows ferromagnetic properties. Obtaining conical structures allow to apply them as magnetic devices and memory sensors. In this case they are also characterized by superhydrophobic properties.

In this work cones obtained by two methods from the same, base electrolyte. They were compared in terms of morphology, real active surface area and electrocatalytic properties.

2. Materials and Methods

One-step method of synthesis the conical Co structures consisted of the electrodeposition process. Used electrolyte included an addition of NH_4Cl as a crystal modifier. Copper foil was an substrate. The electrodeposition process was carried out galvanostatically with a Pt sheet as a counter electrode. The electrodeposition conditions are shown in Table 1.

Table 1. Conditions of the electrodeposition process in one-step method.

Conditions of the electrodeposition process	
Electrolyte composition	200 g/l $CoCl_2$, 100 g/l H_3BO_3, 100 g/l NH_4Cl
Current density i [mA/cm^2]	20
Temperature [^{o}C]	60
Time [min]	20

In case of two-step method, the electrodeposition process was conducted into an AAO template. The template was obtained using two-step anodization. This method cosists of a long-period anodization of an aluminium AA1050 sample in 0.3 M oxalic acid at 2 ^{o}C for 1 h at 45 V. Then, obtained Al_2O_3 layer was removed for 1 h at 60 ^{o}Cusing a mixture of 1.6 wt% chromic acid and 6 wt% phosphoric acid. Alternating short-anodization and pore widening processes are called second-step of anodization. Time of short-anodization was 25 sec and 20 sec for the frist-step and next ones respectively. It was conducted in 0.3 M $H_2C_2O_4$ at 45 V as well. The temperature of solution was 9 ^{o}C. Pores were winded in 5 wt.% phosphoric acid solution for 12 min at 30 ^{o}C. The template with conical pores was obtained after 4 cycles.

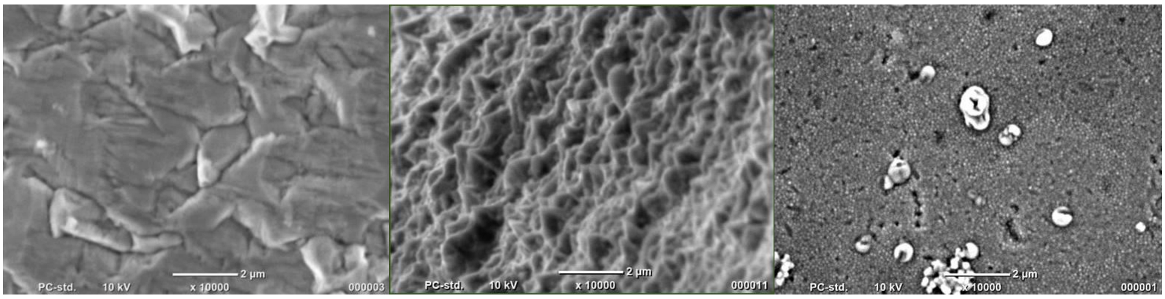
The electrodeposition process was conducted using the same condition as in one-step method for two-step method and synthesis of the bulk sample. There was no presence of the crystal modifier in the electrolyte. To obtain the free-standing Co nanocones, the template was removed in a dilute NaOH solution. In case of bulk material, the copper sample was also the substrate. Surface area for all materials was 2.8 cm^2.

Obtained structures were observed using scanning electron microscope JEOL - 6000 Plus. SEM photos were also used for determination of real active surface area.

Electrocatalytic properties of synthesized materials were investigated in the process of hydrogen evolution in a three-electrode cell. Cobalt layer was the working electrode, a platinum sheet was the counter electrode and a saturated calomel electrode SCE was the reference one. Process was carried out at room temperature in 1 M NaOH. The values of E_{ONSET} were determined from the figures. It is connected with starting of hydrogen reaction.

3. Results and discussion

In order to confirm obtaining desired structures samples were observed using SEM JEOL - 6000 Plus. Photos are shown in the Figure 1.

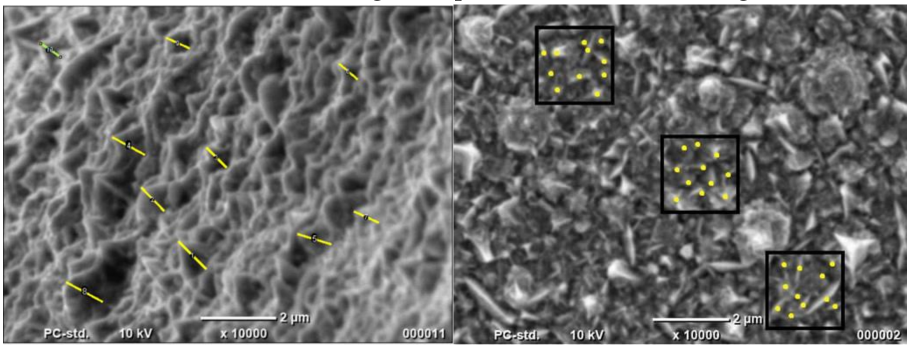


(a) **(b)** **(c)**

Figure 1. SEM photos of a) bulk material and Co nanocones synthesized using b) one-step method and c) two-step method.

Observations confirmed obtaining all expected types of materials. It can be noticed that the surface of fabricated bulk material is not a flat one. Synthesized by one-step method Co structures are not homogeneous. Single cones connected what means that NH_4Cl could not block the horizontal direction growth in an appropriate degree. The surface of Co nanocones obtained by two-step method shows numerous holes and precipitations on the surface. However, their geometrical size is several times smaller.

Knowledge about real surface area is necessary for an appropriate assessment of the electrocatalytic properties of materials. In case of structures synthesized using one-step method the geometrical features were determined using SEM photos. It is shown in Figure 2.



(a) **(b)**

Figure 2. Determination of a) nanocones height and b) number of nanocones using SEM photos.

Based on obtained results, the real surface areas were determined for all materials. Results are shown in Table 2.

Table 2. Determinated values of real active surface area for all samples.

Material	Height [nm]	Number of nanocones per 1 μm^2	Real active surface area [cm^2]
Co nanocones obtained in one-step method	866	2.75	8.05
Co nanocones obtained in two-step method	74	68	3.57

Co bulk	-	-	2.80

The results show that Co nanocones obtained in one-step method show the greater value of real active surface area. However, the determination was approximately in all cases. Firstly, the cones are heterogeneous. Their base is also not a round one. Nevertheless, this calculation confirmed that the height of Co nanocones obtained using one-step method is almost tenfold greater than for structures synthesized by two-step method. The height and the number of conical nanostructures for two-step method were determinated earlier using TEM photos .

The electrocatalytic properties of samples were measured in 1 M NaOH. The results are shown in Figure 3.

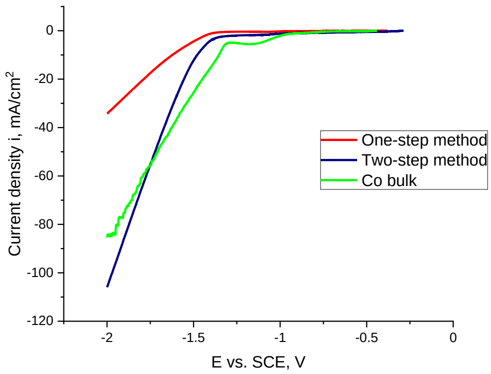


Figure 3. LSV curves of Co bulk and Co nanocones obtained using one-step and two-step method in 1 M NaOH solution.

Obtained results show that the Co structures fabricated by one-step methods show the worst electrocatalytic properties. Sharp character of curve for nanoconical Co structures is connected with blocked any areas on the sample surface by hydrogen bubbles. The values of determined E_{ONSET} are shown in Table 3.

Table 3. Values of E_{ONSET} for all samples.

Material	**E_{ONET} [V]**
Co nanocones obtained in one-step method	−1.47
Co nanocones obtained in two-step method	−1.29
Co bulk	−1.50

It can be notices that for the Co nanocones obtained in two-step method the process begun the earliest.

The surface of Co sample obtained by one-step method was observed using SEM. It is shown in Figure 4.

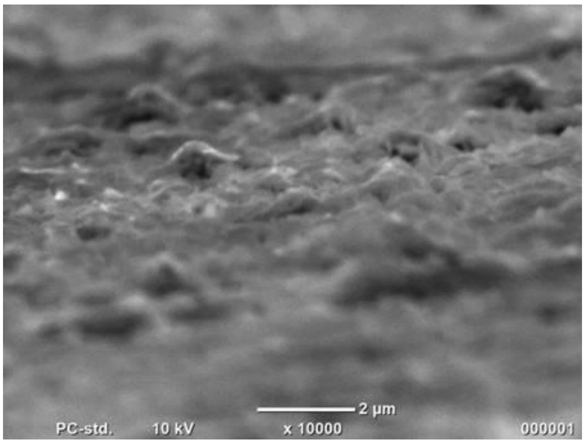


Figure 4. Co cones obtained using one-step method after hydrogen evolution reaction.

There is no noticeable changed on the sample surface after the evolution of hydrogen. Unfortunately, nanoconical Co structures obtained from template were destroyed during this process.

4. Conlusions

1. It is possible to obtain Co nanocones from the electrolytes with the same composition using one-step and two-step method.

2. Synthesized by one-step method Co structures are characterized by greater geometrical size. However, there are several microshells structures.

3. Value of real active surface area was determined approximately using SEM photos. It is connected with heterogeneous Co cones obtained by one-step method. There was also assumption that their base is round. Inexactness is connected also with quality of Co nanocones produced using two-step method. Their height and diameter were determined earlier using TEM photos.

4. The worst electrocatalytic properties are shown by Co cones obtained by one-step method. It can be connected with assumptions during determination of active surface area. However, in this case the hydrogen evolution reaction started earlier than for Co bulk.

5. The hydrogen evolution reaction started the earliest for Co nanocones fabricated by two-step method.

6. The SEM photo after hydrogen evolution reaction does not show any change on the sample surface. Taking photo of the Co nanocones after this reaction was impossible due to destruction of the layer by the hydrogen bubbles. It can be noticed in the sharp character of the curve.

Author Contributions:

K.S. preparation of the AAO templates, electrodeposition of Co by one-step method, writing—original draft preparation. K.K.-S. SEM analysis. D.K. measurement of electrocatalytic properties. A.J. electrodeposition of Co. P.Z. Supervision, writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Polish National Centre of Science, grant number UMO-2016/23/G/ST5/04058.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

[1] Kurowska E.; Brzozka A.; Jarosz M.; Sulka G.D.; Jaskula M. Silver nanowire array sensor for sensitive and rapid detection of H_2O_2. *Electrochimca Acta* **2013**, *104*, 439–447.

[2] Lee J. M.; Jung K. K.; Lee S. H.; Ko J. S. One-step fabrication of nickel nanocones by electrodeposition using $CaCl_2 \cdot 2H_2O$ as capping reagent. *Applied Surface Science* **2016**, *369*, 163–169.

[3] Hang T.; Li M.; Fei Q.; Mao D. Characterization of nickel nanocones routed by electrodeposition without any template. *Nanotechnology* **2008**, *19*.

[4] Darband G. B.; Aliofkhazraei M.; Dolati A.; Rouhaghdam A. S. Electrocrystallization of Ni nanocones from chloride-based bath using crystal modifier by electrochemical methods. *Journal of Alloys and Compounds* **2020**, *818*.

[5] Xiao H.; Hu A.; Hang T.; Li M. Electrodeposited nanostructured cobalt film and its dual modulation of both superhydrophobic property and adhesiveness. *Applied Surface Science* **2015**, *324*, 319–323.

[6] Brzozka A.; Szeliga D.; Kurowska-Tabor E.; Sulka G. D. Synthesis of copper nanocone array electrodes and its electrocatalytic properties toward hydrogen peroxide reduction. *Materials Letters* **2016**, *174*, 66–70.