



Overpotential controls the morphology of electrolytically produced copper dendritic forms

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Abstract: The morphologies of copper dendritic forms obtained in both potentiostatic and galvanostatic regimes of electrolysis with various amounts of the electricity were analyzed by the scanning electron microscopy (SEM) technique. Irrespective of amount of passed electricity, 3D (three dimensional) pine-like dendrites with sharp tips were formed in the potentiostatic regime of electrolysis. On the other hand, the amount of passed electricity had a strong effect on the shape of the 3D pine-like dendrites formed in the galvanostatic regime of electrolysis. Dendrites with sharp tips were formed with smaller amount of passed electricity, while dendrites with globular tips were formed with larger amounts. The change in the shape of the galvanostatically synthesized 3D pine-like dendrites was explained by comparison with copper deposits obtained potentiostatically at overpotentials that corresponded to the final overpotentials during galvanostatic regime of electrolysis for the analyzed amounts of electricity. Based on the similarity of the obtained morphologies at the macro level, it was concluded that the overpotential plays a crucial role in the formation of the electrolytically synthesized dendrites and that the controlled conditions of electrolysis could represent a suitable way for a synthesis of spherical Cu particles by electrolysis.

Keywords: electrolysis; copper; powder; dendrite; scanning electron microscope (SEM).

INTRODUCTION

Due to its excellent electrical and thermal conductivities, copper in the form of powder has found wide application in oil lubrication, electric conductive pastes, medicine, biologic filters, and for other purposes.^{1,2} Although Cu powder

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can be obtained by different methods of synthesis, such as evaporation deposition, plasma approach, mechano-chemical approach, electrical explosion, micro-emulsion, mechanical commuting, chemical reduction and liquid metal atomization, the processes of electrolysis are widely used for the production of Cu powders. The advantages of electrolysis processes relative to the other synthesis processes are the low equipment and product costs, one-step, environmentally friendly, formation of the high purity products, low energy consumption, *etc.*²⁻⁴

Copper in the form of powders can be obtained by the both constant and periodically changing regimes of electrolysis. The potentiostatic⁵ and galvanostatic^{4,6-8} regimes of electrolysis are widely used for the production of Cu in powder form. From periodically changing regimes of electrolysis, the following regimes are used for Cu powder production: pulsating overpotential,^{9,10} pulsating and reversing current regimes.^{11,12} Although sulfate electrolytes are the most often used type of electrolytes,^{1,5,10,12} some other types of electrolytes, such as nitrate,¹³ are also used. Significant effects on the morphology of Cu powder particles can be achieved by the addition of specific substances, known as additives, to the electrolytes for Cu electrolysis.^{11,14,15} The design of the experiments also plays an important role in the production of Cu powder by electrolysis.^{1,16} From the other relevant parameters and factors of electrolysis affecting morphology of the particles, it is necessary to indicate temperature, circulation rate, type of working electrode, *etc.*^{10,17,18}

A decisive effect on the morphology of Cu powder particles has the quantity of generated hydrogen as a parallel reaction to Cu electrolysis in the powder production region.^{5,9,10} Depending on a quantity of evolved hydrogen, two types of particles can be produced: a) dendrites, this particle type is formed when the quantity of evolved hydrogen is insufficient to achieve any effect on the hydrodynamic conditions in the near-electrode layer, and b) cauliflower-like particles, these particles are produced under conditions of vigorous hydrogen evolution sufficient to achieve a strong effect on the hydrodynamic conditions in the near-electrode layer.

Comparison of Cu powder production in the potentiostatic and galvanostatic conditions onto different electrodes was presented by Popov *et al.*¹⁹ The critical conditions for the initiation of dendritic growth and powder formation in these two constant regimes of electrolysis have also been compared.²⁰ However, in spite of numerous investigations concerning the morphology of Cu dendritic particles, there is no clear evidence related to comparison of their morphology obtained in the potentiostatic and galvanostatic conditions of electrolysis. Simultaneously, a novel type of Cu dendrite obtained by a galvanostatic regime of electrolysis was recently presented.⁸ Having these facts in mind, with this investigation, comparative experiments were performed with the formation of Cu den-

drites in potentiostatic and galvanostatic regimes of electrolysis, with the aim of determining the similarity and difference in their morphology.

EXPERIMENTAL

Electrolysis of copper was performed from 0.10 M CuSO₄ in 0.50 M H₂SO₄ at room temperature using both potentiostatic and galvanostatic regimes of electrolysis. In the potentiostatic regime, the electrolysis was performed at overpotentials of 400 mV with an amount of the electricity (Q) of 9.6 mA h cm⁻², of 625 mV with a Q of 2.4, 4.8 and 9.6 mA h cm⁻², and of 700 mV with a Q of 2.4 mA h cm⁻². In the galvanostatic regime of electrolysis, a current density of 14.4 mA cm⁻² was used for the production of Cu powder particles. The times of electrolysis of 10.3, 20.6 and 41.2 min corresponded to the amounts of passed electricity of 2.4, 4.8 and 9.6 mA h cm⁻², respectively.

In the both regimes of electrolysis, the working, reference and counter electrodes were of pure copper. The working electrode was cylindrical in shape with an overall surface area of 0.50 cm². The counter electrode was Cu foil with a surface area of 144 cm². The counter electrode was situated close to the wall of the cell, while the working electrode was in the middle of the cell. The tip of reference Cu electrode was situated at 2 mm from the surface area of the working electrode. Analytical grade chemicals and doubly distilled water were used for the preparation of the electrolyte for Cu electrolysis.

The morphologies of Cu deposits were characterized by scanning electron microscopy (SEM) using a Tescan digital microscope, model VEGA3.

RESULTS AND DISCUSSION

In the potentiostatic regime of electrolysis, the overpotentials responsible for formation and growth of Cu dendrites were in the plateau of the limiting diffusion current density. For Cu solution containing 0.10 M CuSO₄ in 0.50 M H₂SO₄, the plateau of the limiting diffusion current density corresponded to a range of overpotentials between 300 and 750 mV.^{10,21} For synthesis of Cu dendrites in the galvanostatic regime of electrolysis, the current densities should be larger than the limiting diffusion current density, but not too large owing to the hydrogen evolution reaction as parallel reaction to Cu electrolysis that could have a strong effect on the hydrodynamic conditions in the near-electrode layer, and consequently, inhibit dendritic growth. The hydrogen evolution reaction, as a parallel reaction to Cu electrolysis, commences at some overpotential inside the plateau of the limiting diffusion current density, and intensification of this reaction occurs with increasing overpotential.¹⁰ For this system, an overpotential of 590 mV corresponds to the beginning of hydrogen evolution as a parallel reaction.²¹

The dependence of the current density on the time of Cu electrolysis at an overpotential of 625 mV is shown in Fig. 1a. The increase in the current density after an electrolysis time of 15 min indicates to the formation and growth of dendrites.²² The real current density remains constant, while the electrode surface area increases with time and as a result, the current density increases with time in the potentiostatic regime of electrolysis.^{19,23} The attained amounts of electricity of 2.4 and 4.8 mA h cm⁻² are denoted by vertical lines in Fig 1a. The chrono-

potentiometric dependence obtained at a current density of 14.4 mA cm^{-2} is shown in Fig. 1b. After the initial increase, the overpotential decreases with electrolysis time reaching a value of about 400 mV after a passed amount of electricity of 9.6 mA h cm^{-2} . This decrease in overpotential could be ascribed to an increase in the surface area of the electrode, and hence, to a decrease in the real current density with electrolysis time.¹⁹ The vertical lines in Fig. 1b denote attained amounts of electricity of 2.4 and 4.8 mA h cm^{-2} .

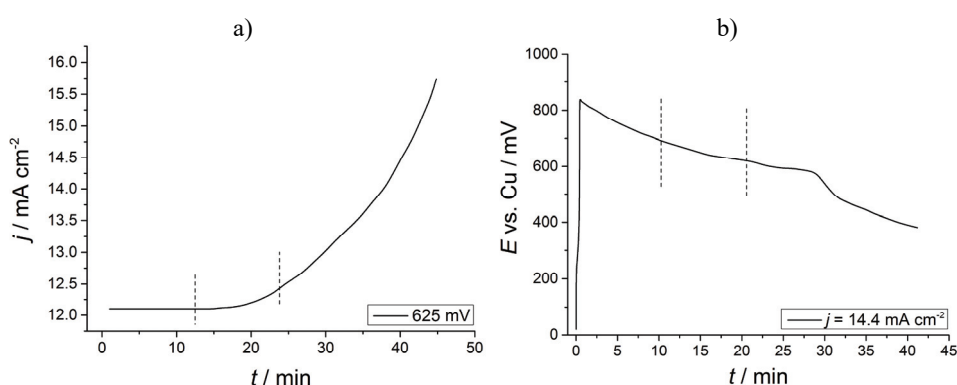


Fig. 1. a) The chronoamperometric curve obtained at an overpotential of 625 mV, and b) the chronopotentiometric curve obtained at a current density of 14.4 mA cm^{-2} . In the both cases, the amount of passed electricity was 9.6 mA h cm^{-2} .

A Cu deposit potentiostatically electrodeposited at an overpotential of 625 mV with an amount of the electricity of 2.4 mA h cm^{-2} is shown in Fig. 2, from which it could be seen that cauliflower-like agglomerates of Cu grains were formed with this amount of electricity. An increase in the amount of passed elec-

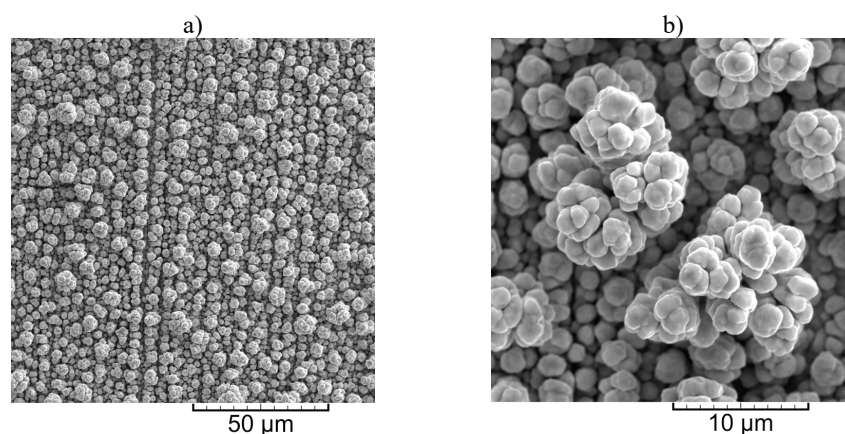


Fig. 2. The cauliflower-like Cu particles obtained by potentiostatic electrolysis at an overpotential of 625 mV, with an amount of electricity (Q) of 2.4 mA h cm^{-2} .

tricity led to formation of dendrites, as shown in Fig. 3. The very branchy three dimensional (3D) pine-like dendrites (Fig. 3a and b) constructed from corn-cob-like forms (Fig. 3c) with relatively sharp tips (Fig. 3d) were formed with an amount of the electricity of 4.8 mA h cm^{-2} . Aside from the 3D pine-like dendrites, individual holes formed from detached hydrogen bubbles and small cauliflower-like agglomerates of Cu grains were also formed (Fig. 3e). The amount of generated hydrogen at 625 mV corresponded to an average current efficiency of hydrogen evolution ($\eta_{\text{I,av}}(\text{H}_2)$) of 2.0 %.²⁴ No further difference in the surface morphology of Cu was obtained with a further increase of passed amount of the electricity (Fig. 4). Growth of the 3D pine-like dendrites, cauliflower-like forms and hole size were observed on increasing the amount of passed electricity from 4.8 to 9.6 mA h cm^{-2} .

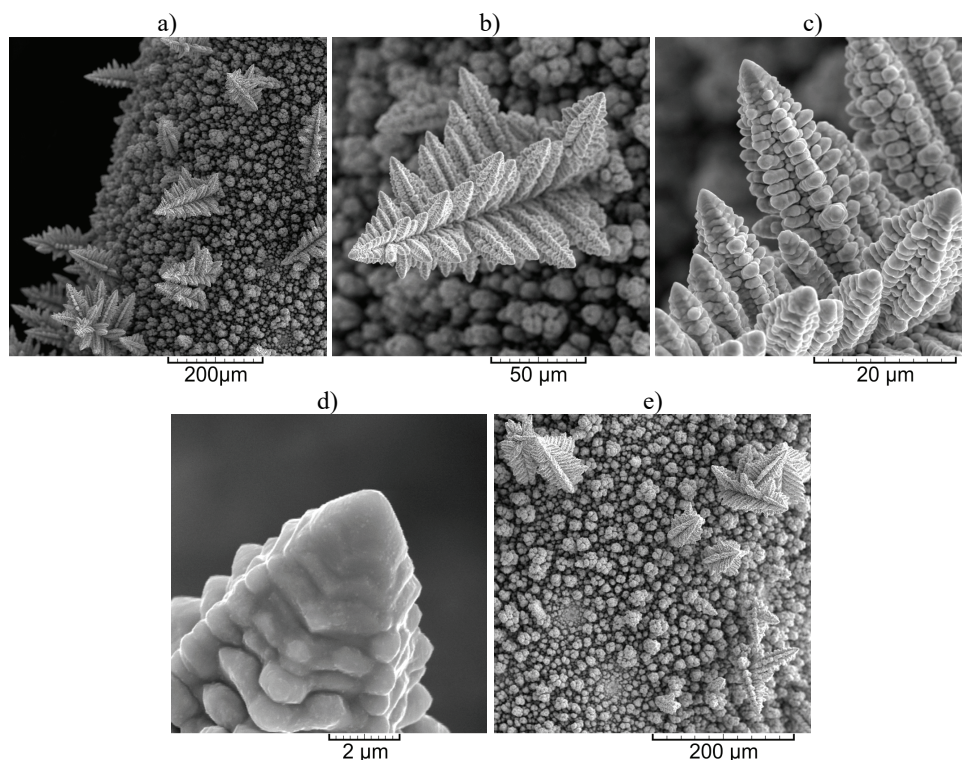


Fig. 3. Morphologies of Cu potentiostatically electrodeposited at an overpotential of 625 mV with a Q of 4.8 mA h cm^{-2} : a) the top view, b) dendrite, c) the corn-cob-like form as a constructive element of a dendrite, d) the tip of dendrite and e) top view with holes formed from detached hydrogen bubbles and cauliflower-like agglomerates of Cu grains.

A Cu deposit obtained in a galvanostatic regime of electrolysis using a current density of 14.4 mA cm^{-2} and an amount of passed electricity of 2.4 mA h

cm^{-2} is shown in Fig. 5. The rare holes formed from the detached hydrogen bubbles (Fig. 5a and b) and cauliflower-like agglomerates of Cu grains (Fig. 5a and c) were obtained with this amount of the electricity. The amount of evolved hydrogen at this current density corresponded to $\eta_{l,av}(\text{H}_2)$ of 6.6 %.⁸ The value of the overpotential at the end of the passed amount of the electricity was about 700 mV.

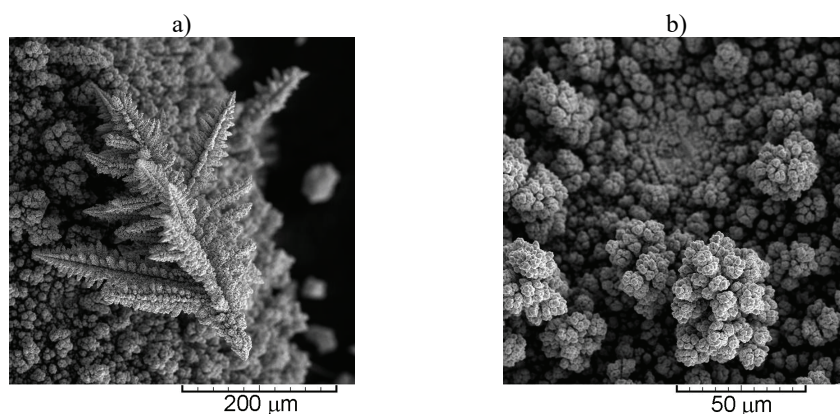


Fig. 4. Morphologies of Cu potentiostatically deposited at an overpotential of 625 mV with a Q of 9.6 mA h cm^{-2} : a) dendrite and b) hole formed by detached hydrogen bubble and cauliflower-like agglomerates of Cu grains.

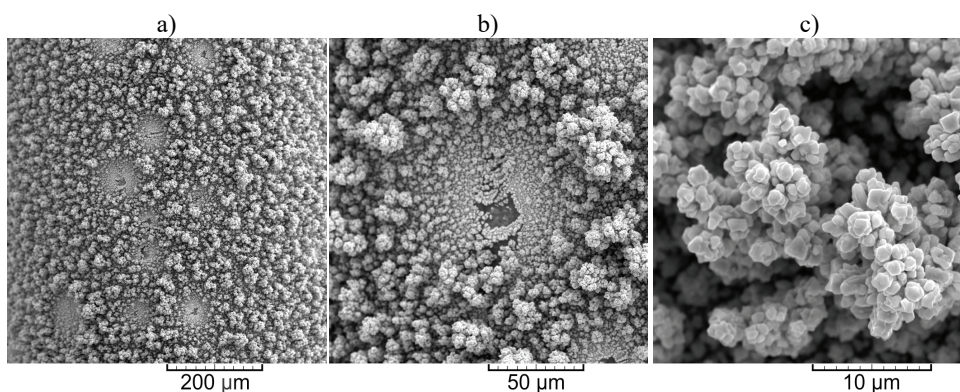


Fig. 5. Morphologies of Cu galvanostatically deposited at a current density of 14.4 mA cm^{-2} with a Q of 2.4 mA h cm^{-2} : a) top view, b) hole formed by a detached hydrogen bubble and c) cauliflower-like agglomerates of Cu grains.

Double the amount of passed electricity (4.8 mA h cm^{-2}) at this current density led to the formation of 3D pine-like dendrites (Fig. 6a and b). At first sight, the 3D pine-like dendrites were very similar to those obtained at an overpotential of 625 mV (Fig. 3b). This is understandable because the overpotential at

the end of passed amount of the electricity of 4.8 mA h cm^{-2} was about 620 mV. Both the stalk and the corncob-like forms as the basic element constructing this dendrite type had relatively sharp tips (Fig. 6c). The increase in the amount of passed electricity did not affect the hole size (Fig. 5b and 6d), which could be ascribed to suppression of the hydrogen evolution reaction with a decrease of overpotential in the galvanostatic regime of electrolysis.

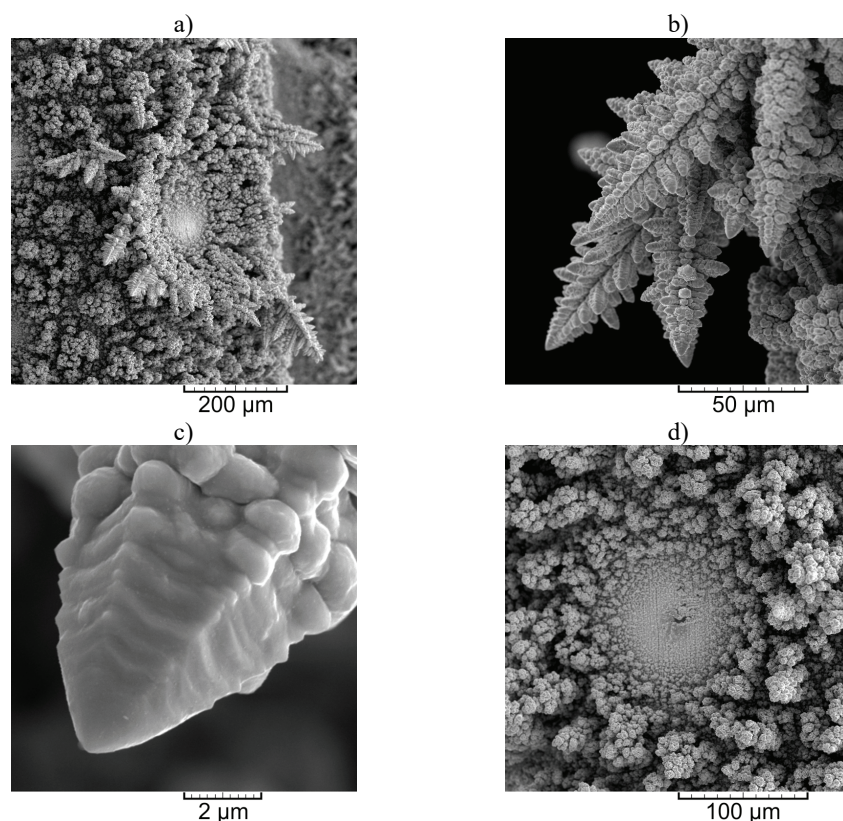


Fig. 6. Morphologies of Cu galvanostatically deposited at a current density of 14.4 mA cm^{-2} with a Q of 4.8 mA h cm^{-2} : a) top view, b) dendrite, c) tip of dendrite and d) hole formed by a detached hydrogen bubble.

The non-uniformity of the electrode surface produced at a current density of 14.4 mA cm^{-2} increased with a further increase in the passed amount of electricity (Fig. 7a). A mixture of 3D dendrites (Fig. 7a and b), cauliflower-like agglomerates of Cu grains (Fig. 7a and c) and holes formed by detached hydrogen bubbles (Fig. 7a and d) was formed at this current density. At first sight, it is necessary to note that the shape of dendrites differed from those obtained with an amount of passed electricity of 4.8 mA h cm^{-2} (Fig. 6), and of those synthesized

in the potentiostatic regime of electrolysis (Figs. 3 and 4a). Instead of relatively sharp tips (Figs. 3d and 6c), the tips of this dendrite type were globular (Fig. 7e). The globules were also the main constructive element of the corn-cob-like forms (Fig. 7f). The overpotential at end of the passed amount of electricity of 9.6 mA h cm^{-2} was about 400 mV.

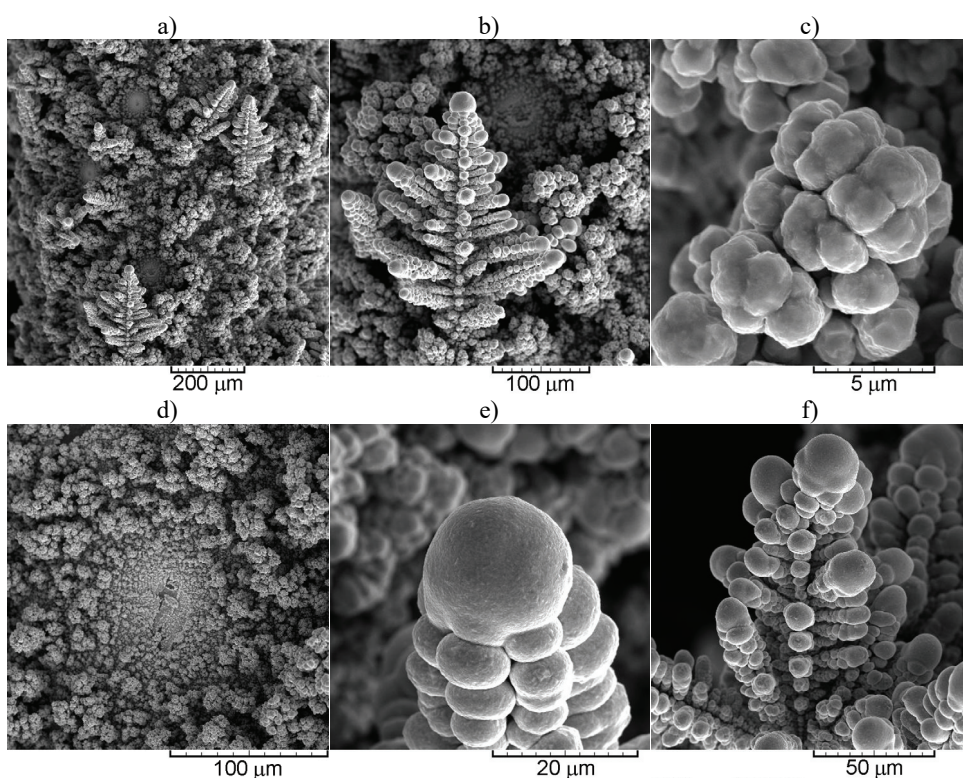


Fig. 7. Morphologies of Cu galvanostatically deposited at a current density of 14.4 mA cm^{-2} with a Q of 9.6 mA h cm^{-2} : a) top view, b) dendrite, c) cauliflower-like agglomerates of Cu grains, d) hole formed by detached hydrogen bubble, e) tip of dendrite and f) branches of dendrites.

This change in the shape of the tip of a dendrite could be explained from electrochemical point of view as follows: it is known that the velocity of dendrite growth is maximal for some optimal tip radius.^{19,25} The optimal tip radius increases with decreasing overpotential. The difference between the maximal velocity and the actual velocities for dendritic growth with tip radius different from the optimal one becomes smaller with decreasing overpotential. In this way, because of the decrease in overpotential during galvanostatic electrolysis, a change in the morphological characteristics of the dendritic particles was expected.

The similar shape of Cu dendrites obtained in the potentiostatic regime of electrolysis at an overpotential of 625 mV (Figs. 3 and 4) and in the galvanostatic regime of electrolysis at a current density of 14.4 mA cm^{-2} with an amount of electricity of 4.8 mA h cm^{-2} (Fig. 6), when the overpotential at the end of electrolysis was about 620 mV, clearly indicates that the overpotential plays a crucial role in the final morphology of Cu dendrites. To prove this, experiments from the same electrolyte in the potentiostatic regime of electrolysis at an overpotential of 400 mV with an amount of the electricity of 9.6 mA h cm^{-2} , and at an overpotential of 700 mV with an amount of the electricity of 2.4 mA h cm^{-2} were performed. These overpotentials corresponded approximately to the final values of overpotentials attained in the galvanostatic regimes of electrolysis with the stated amounts of passed electricity. According to expectation, Cu globules were formed at an overpotential of 400 mV with an amount of the electricity of 9.6 mA h cm^{-2} (Fig. 8a and b).

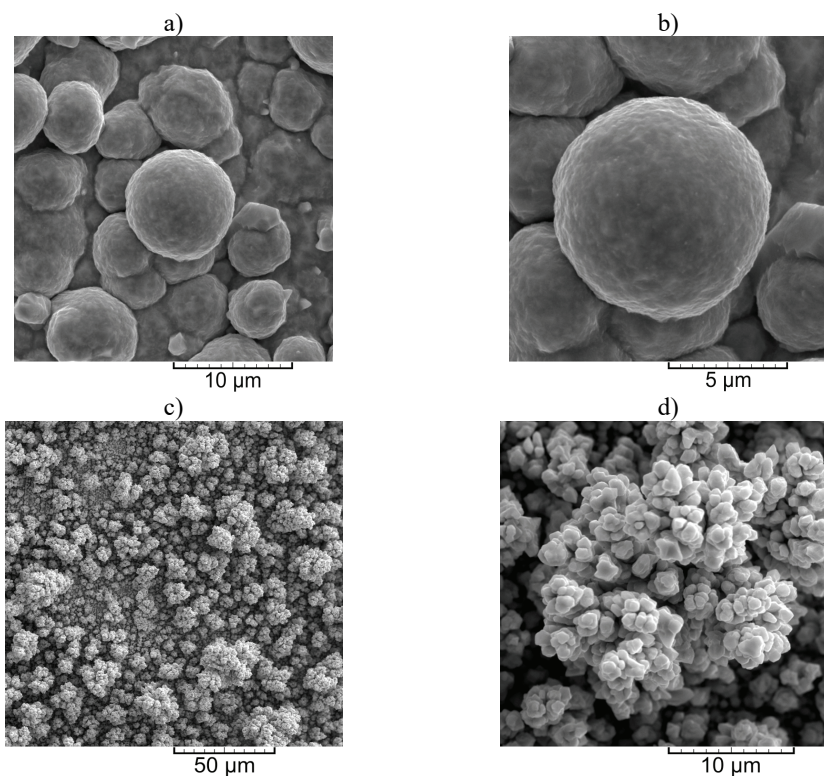


Fig. 8. Morphologies of Cu potentiostatically deposited at overpotentials of: a) and b) 400 mV, $Q = 9.6 \text{ mA h cm}^{-2}$ (globules), and c) and d) 700 mV, $Q = 2.4 \text{ mA h cm}^{-2}$ (cauliflower-like agglomerates of Cu grains).

These globules had the appearance of almost ideal spheres and the similarity with those obtained in the dendrites produced in the galvanostatic regime with an amount of electricity of 9.6 mA h cm^{-2} is clear. Furthermore, the cauliflower-like particles obtained at an overpotential of 700 mV (Fig. 8c and d) were at the macro level very similar to those obtained in the galvanostatic regime with an amount of the electricity of 2.4 mA h cm^{-2} (Fig. 5c).

Cauliflower-like particles obtained under conditions of vigorous hydrogen evolution and dendrites are the most frequent shapes of electrolytically produced Cu particles.^{10,18} Particles of spherical shape, such as globules, are usually formed by non-electrolytic methods of synthesis, such as the gas-atomizing process,²⁶ the polyol process²⁷ and ultrasonic spray pyrolysis.²⁸ Copper particles of spherical shape have been obtained by electrolysis processes only in the presence of additives, such as a combination of potassium ferrocyanide and 2,2'-dipyridine.¹⁵ In this study, it was shown that it is possible to obtain spherical-shaped particles under controlled conditions of electrolysis from electrolytes without the addition of additives by regulation of the duration of the electrolysis time. Certainly, further investigations in this direction will be continued in the future.

CONCLUSIONS

Comparative analysis of the morphological characteristics of copper dendrites formed in potentiostatic and galvanostatic regimes of electrolysis was realized. 3D pine-like dendrites with sharp tips and corncob-like forms, as the basic element constructing them, were obtained in the potentiostatic regime of electrolysis at an overpotential of 625 mV. The corncob-like forms consisted of small agglomerates of Cu grains. The various amounts of passed electricity did not affect the shape of the formed dendrites. 3D pine-like dendrites, very similar to those obtained in the potentiostatic regime of electrolysis, were also obtained in the galvanostatic regime of electrolysis at a current density of 14.4 mA cm^{-2} with an amount of electricity of 4.8 mA h cm^{-2} . However, an increase in the amount of the electricity from 4.8 to 9.6 mA h cm^{-2} led to a change in the shape of the dendrites. Instead of sharp tips and small agglomerates of Cu grains, the ends and corncob-like forms in the 3D pine-like dendrites were constructed from globules.

The explanation for the change in the shape of dendrites is ascribed to control of the overpotential in the formation and growth of dendrites during the galvanostatic process of electrolysis. This was concluded by comparison with the copper deposits obtained in the potentiostatic regime of electrolysis at overpotentials of 400, 625 and 700 mV, which corresponded to the final overpotentials in the galvanostatic regimes of electrolysis with amounts of the electricity of 2.4, 4.8 and 9.6 mA h cm^{-2} . Furthermore, it follows that the controlled conditions of galvanostatic electrolysis represent a suitable way for obtaining spherical particles (globules) in electrolysis.

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ИЗВОД

ПРЕНАПЕТОСТ КОНТРОЛИШЕ МОРФОЛОГИЈУ ЕЛЕКТРОЛИТИЧКИ ПРОИЗВЕДЕНИХ ДЕНДРИТИЧНИХ ФОРМИ БАКРА

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Морфологије дендритичних форми бакра добијене потенциостатским и галваностатским режимима електролизе са различитим количинама наелектрисања су биле анализирани техником скенирајуће електронске микроскопије (СЕМ). Без обзира на количину пропуштеног наелектрисања, 3D (тродимензионални) дендрити налик стаблу бора са оштрим врховима су били формираны потенциостатским режимом електролизе. На другој страни, количина пропуштеног наелектрисања је имала строг утицај на облик 3D дендрита налик бору формираных галваностатским режимом електролизе. Дендрити са оштрим врховима су били формираны са мањом, док дендрити чији врхови су глобуле су били формираны са већом количином пропуштеног наелектрисања. Промена облика галваностатски синтетизованих 3D дендрита налик бору је била објашњена поређењем са потенциостатски добијеним талозима бакра на пренапетостима које су одговарале крајњим пренапетостима током галваностатског режима електролизе за анализирани количине наелектрисања. На основу сличности њихових морфологија на макро нивоу, закључено је да пренапетост игра пресудну улогу на облик електролитички синтетизованих дендрита, и да контролисани услови електролизе представљају погодан начин за синтезу сферичних честица бакра поступком електролизе.

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