

Response to reviewer A:

Dear reviewer,

Thank you very much for reviewing our manuscript.

We fixed the grammatical-typical mistakes in the manuscript and correct the references. All the corrections have been made. Changes to the manuscript are shown in red.

We would be glad to respond to any further questions and comments that you may have.

Best Regards, Fatemeh Karimi

Response to reviewer B:

Dear reviewer,

Thank you very much for reviewing our manuscript.

We have answered each of points below:

1. Affiliation:

Fatemeh K. T. Shafiei is corresponding author.

2. Technical accuracy in writing:

- ✓ Refs. 8, 14, 26 and 27 added in appropriate place. (Are shown in green).
- ✓ In the line 243 we correct the overpotential amplitudes (2000 mV). (Are shown in green).

3. Figure 5b should be replaced by a microphotograph of the same magnification as Fig. 5a and Fig. 5c.

We repeat the experiment, obtain the copper deposits by pulsating overpotential regime from 0.30 M CuSO₄ + 0.50 M H₂SO₄ (solution (III)) at overpotential amplitudes of 1250 mV and prepare the microphotograph of the same magnification (×5000).

4. I suggest that the trace of oxides should be corrected.

The sample surface were slightly oxidized due to ambient air exposure. (Are shown in green).

5. References

Some irregularities in the list of references are corrected.

6. I strongly recommend a proofreading of complete paper by an expert for English language....

We fixed the grammatical-typical mistakes in the manuscript (Are shown in Red).

We would be glad to respond to any further questions and comments that you may have.

We also greatly appreciate the reviewers for their complimentary comments and suggestions.

Best regards, Fatemeh karimi

Copper deposits obtained by pulsating overpotential regime with a long pause and pulse duration from sulfated solutions

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Abstract: The morphologies of the copper deposits obtained by pulsating overpotential regime with prolonged pulse and pause durations from the solution of 0.15 M CuSO₄ in 0.50 M H₂SO₄ at overpotentials lower, higher and belonging to the plateau of limiting diffusion current density were compared with those obtained by the same electrodeposition regime from solutions of (0.075 and 0.30 M CuSO₄ in 0.50 M H₂SO₄) and (0.15 M CuSO₄ in 0.25 and 1.00 M H₂SO₄) at overpotentials outside the plateau of limiting diffusion current density. These samples characterized by scanning electron microscopic (SEM) analysis. The cathodic polarization characteristics from solutions compared. Increasing the Cu(II) concentration led to an increase in the limiting diffusion current density. Decreasing the H₂SO₄ concentration shifts both of the beginning and the end of the plateau of the limiting diffusion current density towards higher electrodeposition overpotentials. Also, electrodeposition in solutions (0.15 M CuSO₄ in 0.25 and 1.00 M H₂SO₄) led to the formation of morphological forms of copper deposits characteristic for electrodeposition of copper from higher CuSO₄ or lower H₂SO₄ in solution at some higher overpotentials.

Keywords: Electrodeposition; Pulsating overpotential; Morphology; Copper.

RUNNING TITLE: PULSATING OVERPOTENTIAL COPPER ELECTRODEPOSITION

INTRODUCTION

The open porous structures with the extremely high surface area are ideally suited for many electrochemical devices, such as batteries, fuel cells, sensors, capacitors, electrocatalysis and

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superhydrophobicity can be formed by a very suitable way named electrodeposition.⁰⁷ Morphology probably is the most important property of the electrodeposited metal. It depends mainly on the kinetic parameters of the deposition process, current density, overpotential which affect the grain size, nucleation and growth rate of the deposit.⁸ In the real condition, the size and shape of powder particles depend on electrolysis regime, solution composition, deposition time, temperature, hydrodynamic regime, cathodic material and etc.⁹

During the electrodeposition, the hydrogen gas evolution is a troublesome process and can adversely affect the metal coating quality.¹⁰ These H₂ bubbles used as a dynamic template to create a wide range of porous metal films.⁵ Templating mechanism and hydrogen bubble behavior on the morphology of porous copper foams have been reported.^{11,12} Open and porous copper deposits formation by the regimes of the pulsating current,¹³⁻¹⁵ pulsating overpotential¹⁶ electrodeposition and galvanostatic,¹⁷ potentiostatic^{15,18} modes has been the subject of many investigations. In pulsating electrodeposition, the potential or current is alternated between two different values and cause the ions easier passage through negatively charged layer around the cathode.¹⁹

The most often employed electrolytes for the electrodeposition of copper are those based on aqueous solutions of sulfuric acid (H₂SO₄) and cupric sulfate (CuSO₄).²⁰ Ionic equilibrium calculation of copper electrodeposition electrolytes species over a wide range of concentrations and temperatures was shown by Pinter's model. Increasing the copper concentration produces a sharp decrease in the hydrogen ion concentration while increasing the concentration of sulfuric acid produces an increase in the hydrogen ion concentration.²¹ Among the deposition parameters, the concentration of the metal ions greatly influences the morphology of the foam deposits, whereas the acidity and the applied current density had little effect on the foam structure.¹ The effect of different concentrations of copper (II) ions and overpotentials on the critical conditions for the formation of the honey-comb structure were determined on the processes of copper electrodeposition.²² Copper deposits obtained by different square-waves pulsating overpotential from 0.15 M CuSO₄ in 0.50 M H₂SO₄ were compared with those obtained by potentiostatic electrodepositions (1000 mV) from both 0.075 and 0.30 M CuSO₄ in 0.50 M H₂SO₄. It was shown that the effect of decreasing deposition pulse was equivalent to the increasing CuSO₄ concentration while the effect of the decreasing pause duration was equivalent to increase the H₂SO₄ concentration in the constant regime.¹⁶ Morphology of deposits obtained by constant overpotential electrodepositions in the hydrogen co-deposition range from six solutions with different concentration of CuSO₄ and H₂SO₄ were compared with those formed by the square-waves pulsating current with different pause to pulse ratio.¹⁴ Darko

Grujicic has studied the nucleation mechanisms of copper during the electrodeposition of thin films from sulfate solutions. It was found that with increasing the hydrogen ion and copper concentration, the nuclei size increased while the nuclei population density decreased. An increase in the deposition potential produced smaller nuclei size and higher nuclei population density.²³

However, in spite of investigation of copper deposits structures obtained at high overpotentials in the constant regime and pulsating overpotential regime with prolonged pause duration,¹⁸ the effect of prolonged pulse and pause durations in pulsating overpotential regime on copper electrodeposition from the solutions with different concentrations of sulfuric acid and cupric sulfate is not explored. For this reason, our investigation aimed to examine copper deposited morphologies by utilizing SEM to provide the correlation between the morphological information and H₂SO₄ and CuSO₄ concentrations on the prolonged both pulse and pause in pulsating electrodeposition of copper at cathodic overpotentials outside the plateau of the limiting diffusion current density.

EXPERIMENTAL

The cathodic polarization curves for electrodeposition of copper were recorded potentiostatically by changing the overpotential in 5 mV steps from the following solutions:

- (a) 0.15 M CuSO₄ + 0.50 M H₂SO₄; solution (I)
- (b) 0.075 M CuSO₄ + 0.50 M H₂SO₄; solution (II)
- (c) 0.30 M CuSO₄ + 0.50 M H₂SO₄; solution (III)
- (d) 0.15 M CuSO₄ + 0.25 M H₂SO₄; solution (IV) and
- (e) 0.15 M CuSO₄ + 1.00 M H₂SO₄; solution (V)

Square-wave pulsating overpotential technique was used for copper film electrodeposition from these solutions on the high purity copper (99.8% Cu) foil as the working electrode. Electrodepositions were performed in a three-electrode experimental open cell with Pt grid auxiliary electrode and Ag/AgCl (3 M KCl) as reference electrode at a temperature of 18.0 ± 1.0 °C. The geometric surface area of the working electrodes was 4.7 cm². The distance between the working and the counter electrode was 1 cm. In all experiments, constant pulse and pause durations were 30 and 100 ms, respectively. The deposition time was 480 s and the overpotential amplitudes at which copper was electrodeposited from all solutions were: 1100, 1250, 1400 and 2000 mV. The overpotential amplitude values for deposition from solution (I) was selected to be 200, 500, 800, 1600 and 1800 mV. After electrodeposition, copper deposits were immediately rinsed in distilled water and acetone and then dried by the warm air flow.

SEM microphotographs corresponding to morphologies of copper deposits obtained at desired overpotential amplitudes were characterized using a TESCAN Digital Microscopy. Energy dispersive microanalysis (EDS) of deposits at desired overpotential amplitudes were performed during SEM measurements. Doubly distilled water and analytical grade chemicals were used for the preparation of the solutions for polarization curve record and electrodeposition of copper. All experiments were performed by using Autolab (GTSTAT101).

RESULTS AND DISCUSSION

The polarization curves for the electrodeposition of copper from all solutions with well-defined plateaus of the limiting diffusion current density as the typical representatives of the group of intermediate metals are given in Fig. 1. Each curve was swept from the zero potential into more negative potentials with the scan rate of 5 mVs⁻¹.

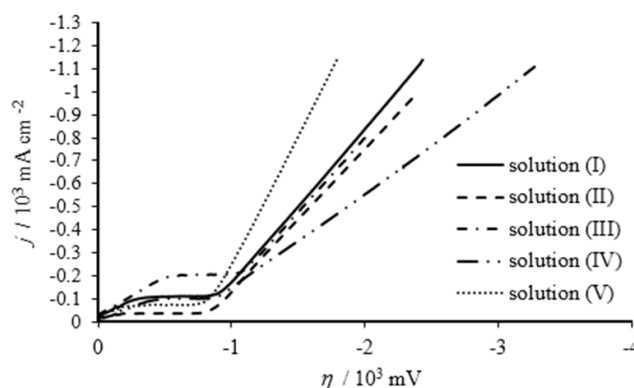


Fig. 1. Polarization curves for the cathodic process of copper deposition from the solutions.

The polarization curves consisted of three parts. The first linear part of the dependence of the current density on overpotential is the activation control. After the inflection point, the end of the plateau is determined as the overpotential at which current density started to grow with the increasing overpotential.²² This rapid grow is due to the hydrogen evolution as a parallel reaction.^{24,25} As can be seen from Fig. 1, decreasing the Cu(II) concentration leads to the decrease of the limiting diffusion current density, as well as shifting of both the beginning and the end of the plateau of the limiting diffusion current density towards lower deposition overpotentials. This can be explained by Nernst limiting current density equation. 1.

$$j_L = nFDc_0 / \delta \quad (1)$$

Where j_L is the limiting diffusion current density, D is the diffusion coefficient, nF is the number of Faradays per mole of consumed ions, c_0 is the concentration of Cu(II) ions and δ is the thickness of the diffusion layer. Therefore, a change of the Cu(II) concentration of the solution affects the limiting diffusion current density. Increasing the depositable Cu(II) ions in the cathode diffusion layer leads to decrease the concentration type of polarization.²² Also, an increase in the concentration of Cu(II) ions clearly leads to a corresponding decrease in the length of the plateau of the limiting diffusion current density.²² As can be seen from Fig. 1, with the decreasing concentration of H₂SO₄, the beginning of the plateau of the limiting diffusion current density was slightly shifted to higher electrodeposition overpotentials. The small shifting of the end of the plateau of the limiting diffusion current density to lower overpotentials can be neglected.²⁵ The decrease of the H₂SO₄ concentration leads to the decrease in the current grow at overpotentials outside the plateau of the limiting current density.

Morphologies of copper deposited by pulsating overpotential regime from solution (I) and solution (II) at overpotential amplitudes of 1100, 1250, 1400 and 2000 mV are presented in Figs. 2 and 3, respectively. Copper dendrites obtained at the overpotential amplitude of 1400 mV (Figs. 2d and 3d) were more highly branched structures than the ones obtained at the overpotential amplitudes of 1100 and 1250 mV (Figs. 2a-b and 3a-b). As can be observed, the shape of copper deposits depends on the electrodeposition overpotential amplitude. It is well known that the increase in overpotential amplitude leads to the decrease in time needed for the initiation of dendritic growth.¹⁹ Then, further branched dendrites are formed.

Analysis of the copper deposits obtained at the overpotential amplitude of 2000 mV (Figs. 2d-e) shows two types of holes formed due to attachment hydrogen bubbles. One type of holes are very similar to those named honeycomb-like structure and the other with a larger diameter is dish-like holes.

This structure is very similar to that obtained from 0.30 M CuSO₄ in 0.50 M H₂SO₄ during potentiostatic deposition at the overpotential of 1000 mV.⁸ Increasing overpotential intensifies hydrogen evolution reaction and hydrogen evolution becomes vigorous at some overpotential outside the plateau of the limiting diffusion current density. Fig. 2f shows copper dendrite formed at the dish-like shoulders.

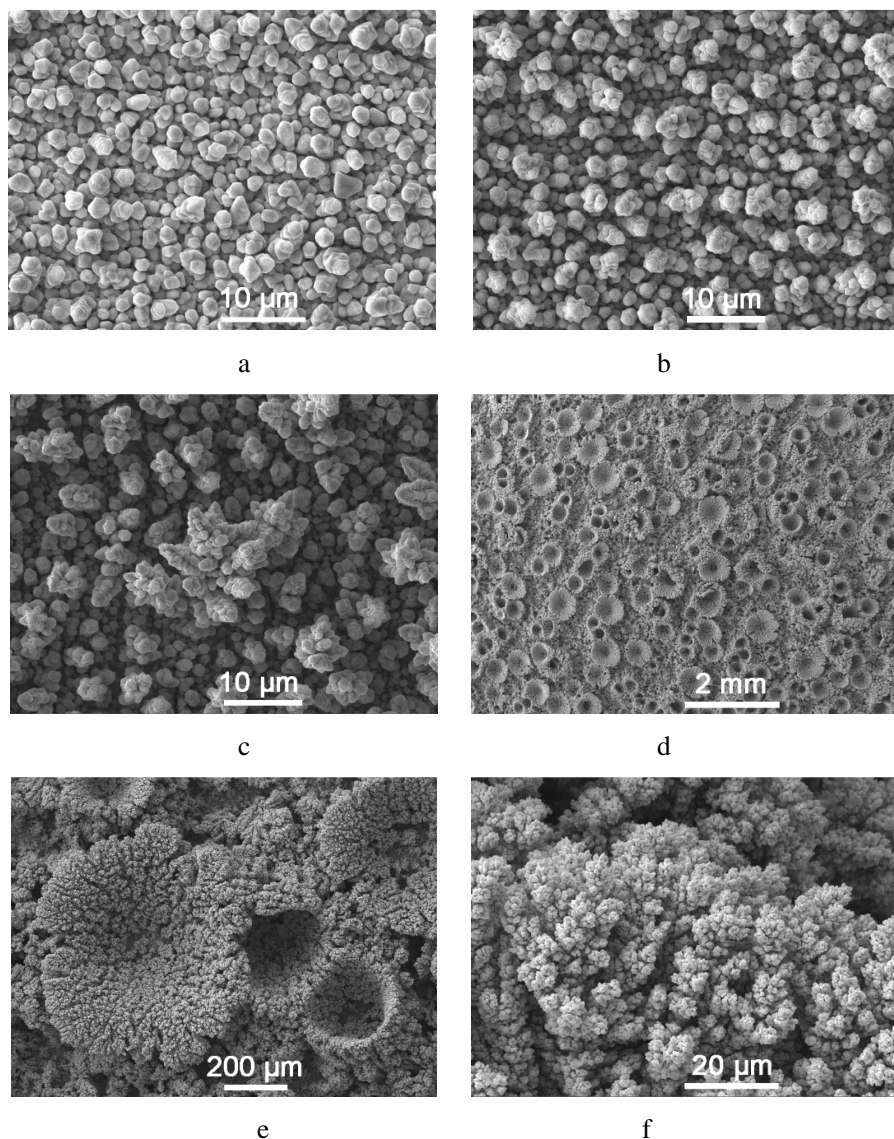


Fig. 2. Morphologies of copper deposits obtained by pulsating overpotential regime from 0.15 M CuSO₄ + 0.50 M H₂SO₄ (solution (I)) at overpotential amplitudes of: a) 1100, b) 1250, c) 1400 and d-f) 2000 mV. Pulse duration: 30 ms. Pause duration: 100 ms.

Nikolic *et al.* explained the dish-like hole structures formation. The initial stage of the formation of dish-like holes and the honeycomb-like structure is the same. The number of the formed “nuclei” of hydrogen bubbles at active sites on the electrode surface was smaller than the number which led to the formation of the honeycomb-like structure.⁸ In the growth process, they have enough space to develop into large bubbles, making holes with a dish-like shape at the surface of the electrode.

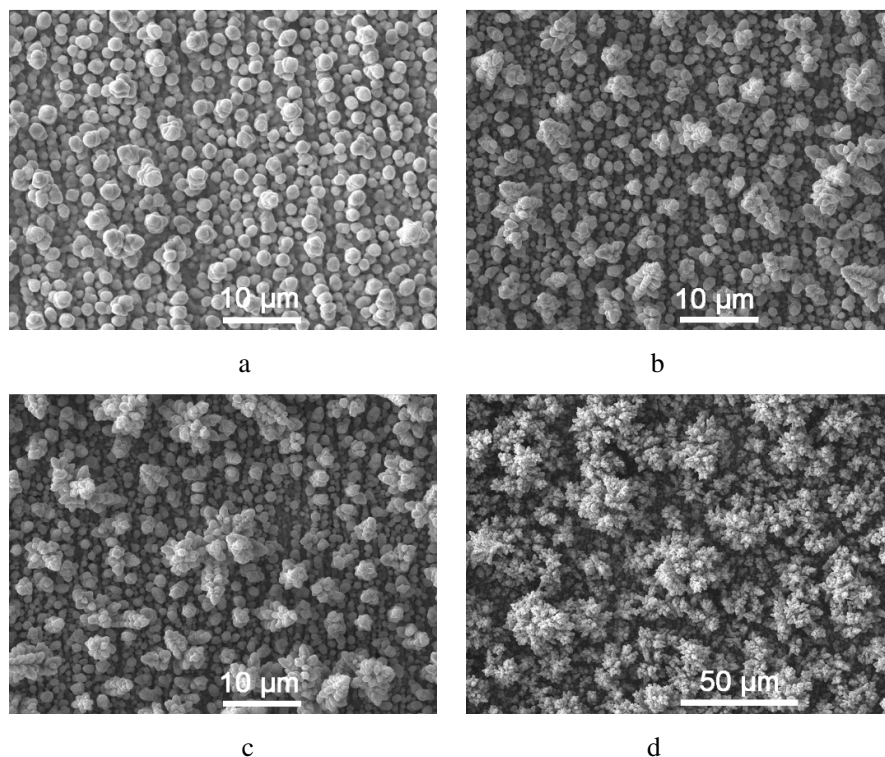


Fig. 3. Morphologies of copper deposits obtained by pulsating overpotential regime from 0.075 M CuSO_4 + 0.50 M H_2SO_4 (solution (II)) at overpotential amplitudes of: a) 1100, b) 1250, c) 1400 and d) 2000 mV. Pulse duration: 30 ms. Pause duration: 100 ms.

The copper morphologies consisted of dendrites, degenerate dendrites and channels (Fig. 3d) obtained by pulsating overpotential at overpotential amplitude of 2000 mV from solution (II), proves that there is no hydrogen evolution or evolved hydrogen is not sufficient to form holes. The change of copper deposit structures during the electrodeposition from solutions (I) and (II) with the increase of electrodeposition overpotential amplitude from 1100 to 2000 mV can be observed by Fig. 4 with further magnification. SEM images show that some grains grow from pyramid-like precursors of dendrites (Fig. 4a) to dendrites (Fig. 4b) and very branchy dendrites (Fig. 4c) or degenerate dendrites (Fig. 4d) by electrodeposition at overpotential amplitudes of 1100, 1250 and 1400 and 2000 mV, respectively.

One difference in morphology among copper deposits obtained at different overpotential amplitudes is the size and number of the branches. It can be explained by the fact that increasing the overpotential amplitude leads to the decrease of the height of protrusion at which dendrites start to grow instantaneously. Hence, increasing the overpotential amplitude means a large number of growth sites suitable for the growing of dendrites.

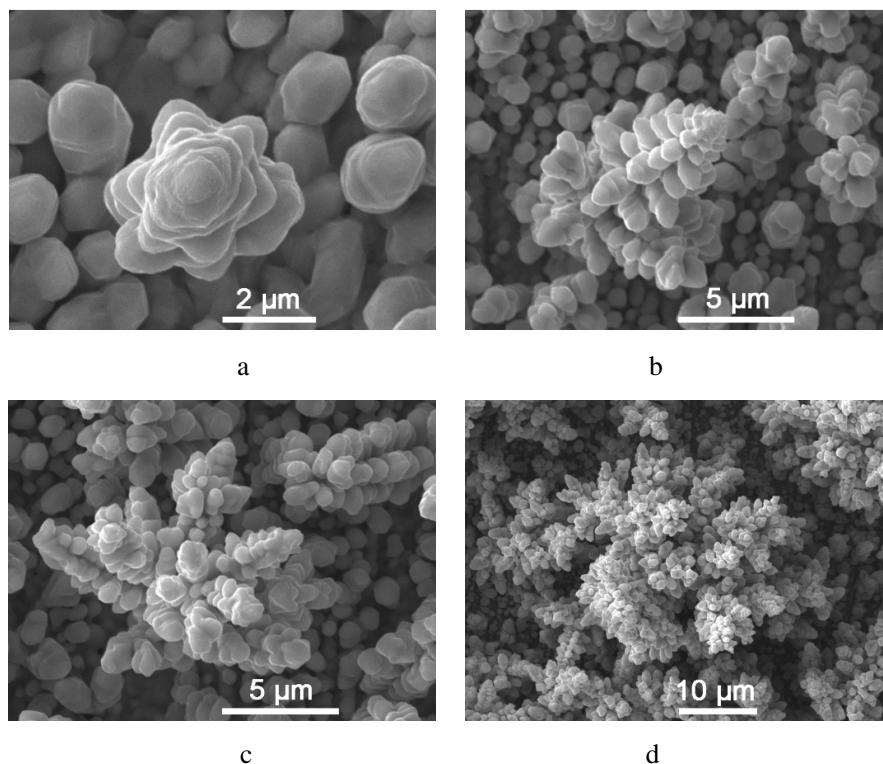


Fig. 4. Deposit structures obtained by pulsating overpotential regime from solutions (*I-II*): a) top wive of the pyramid-like precursors of dendrites at 1100 mV, b) dendrites at 1250 mV, c) branchy dendrites at 1400 mV and d) degenerate dendrites at 2000 mV. Pulse duration: 30 ms. Pause duration: 100 ms.

The deposits size and the optimal value of the dendrite tip decrease with increasing the applied overpotential amplitude.⁹ The uniform distribution of morphological forms of copper grains obtained at the overpotential amplitudes of 1100, 1250 and 1400 mV from solutions (*III*) and (*IV*) are shown in Figs. 5a-c and 6a-c. The type of electrolyte has a strong effect on the surface morphology. It can be noticed that a big increase in the copper concentration (solution (*III*)) or decrease of the sulfuric acid concentration (solution (*IV*)) lead to a big change in copper deposit morphologies. There is hardly hydrogen evolution as evident from the morphologies of Figs. 5 and 6a-c. The activity and available sites of hydrogen ions significantly decreased²⁷ and the obtained copper structures consisted of copper grains. The grains grown by electrodeposition on the initially formed nuclei practically touch each other and there is no new nucleation on already existing grains.²⁰ The difference in size between grains can also be observed. This is due to the fact that the nucleation does not occur simultaneously over the whole cathode surface. It is a process extended in time, therefore that crystals generated earlier may be considerably larger in the size than ones generated later (Figs. 5a and 5c).^{18,25}

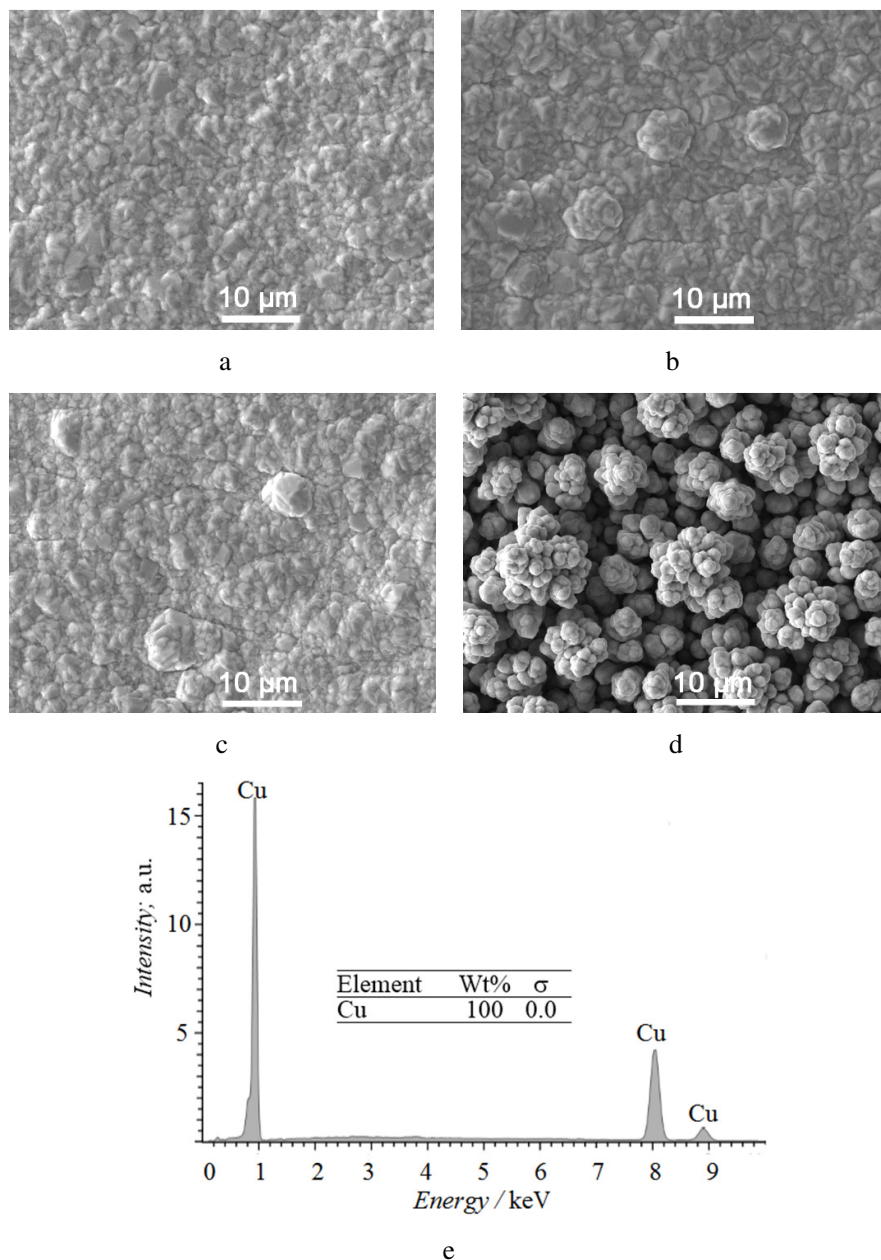


Fig. 5. Morphologies of copper deposits obtained by pulsating overpotential regime from 0.30 M CuSO_4 + 0.50 M H_2SO_4 (solution (III)) at overpotential amplitudes of: a) 1100, b) 1250, c) 1400 and d) 2000 mV., e) EDS analysis of the obtained typical copper grain microstructure. Pulse duration: 30 ms. Pause duration: 100 ms.

Fig. 5d shows the cauliflower-like agglomerates of grains were formed at the potential amplitude of 2000 mV. As shown in Fig. 5e, energy-dispersive spectroscopy (EDS) analysis demonstrated that the foil was successfully covered with pure copper electrodeposited from solution (III) at 1250 mV, (Fig. 5b).

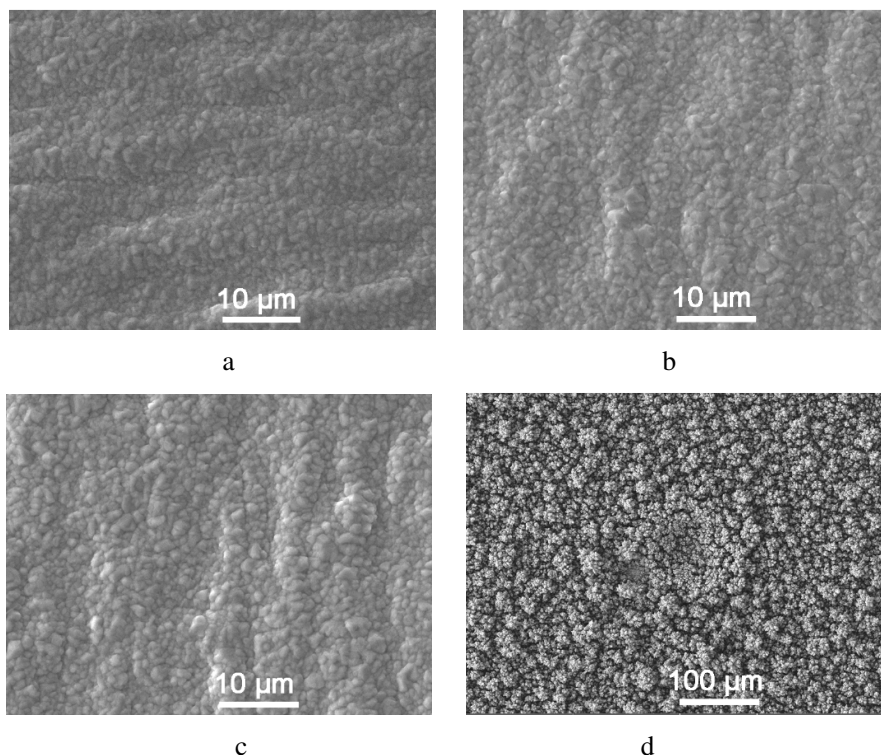


Fig. 6. Morphologies of copper deposits obtained by pulsating overpotential regime from solution 0.15 M CuSO_4 + 0.25 M H_2SO_4 (solution (IV)) at overpotential amplitudes of: a) 1100, b) 1250 c) 1400 and 2000 mV. Pulse duration: 30 ms. Pause duration: 100 ms.

Top view of the morphology of copper deposited at an overpotential amplitude of 2000 mV with lower magnification shows a semi dish-like hole, compacted dendritic agglomerates and small dendrites on them (degenerate dendrite) (Fig. 6d).

Morphologies of copper deposits obtained from solution (I) at lower overpotential amplitudes of (200 mV), inside (500 and 800 mV) and outside (1600 and 1800 mV) the plateau of the limiting diffusion current density is presented in Fig. 7a-e. The careful analysis of the morphologies of copper deposits shown in Figs. 5, 6 and 7 indicated the electrodeposition from solution (solution III) and solution (IV) at overpotential amplitudes outside the plateau of the limiting diffusion current density (1100, 1250 and 1400 mV) led to the formation of regular, compact and well-dispersed deposits with small grain size (Figs. 5a-c and 6a-c) are very similar to deposits formed at overpotential amplitudes at lower and inside the plateau of the limiting diffusion current density (200, 500 and 800 mV) from the solution (I), (Fig. 7a-c). Dendrites formation at these applied potentials illustrates that the hydrogen evolution is insufficient to change the hydrodynamic condition in the near-electrode layer.²⁴

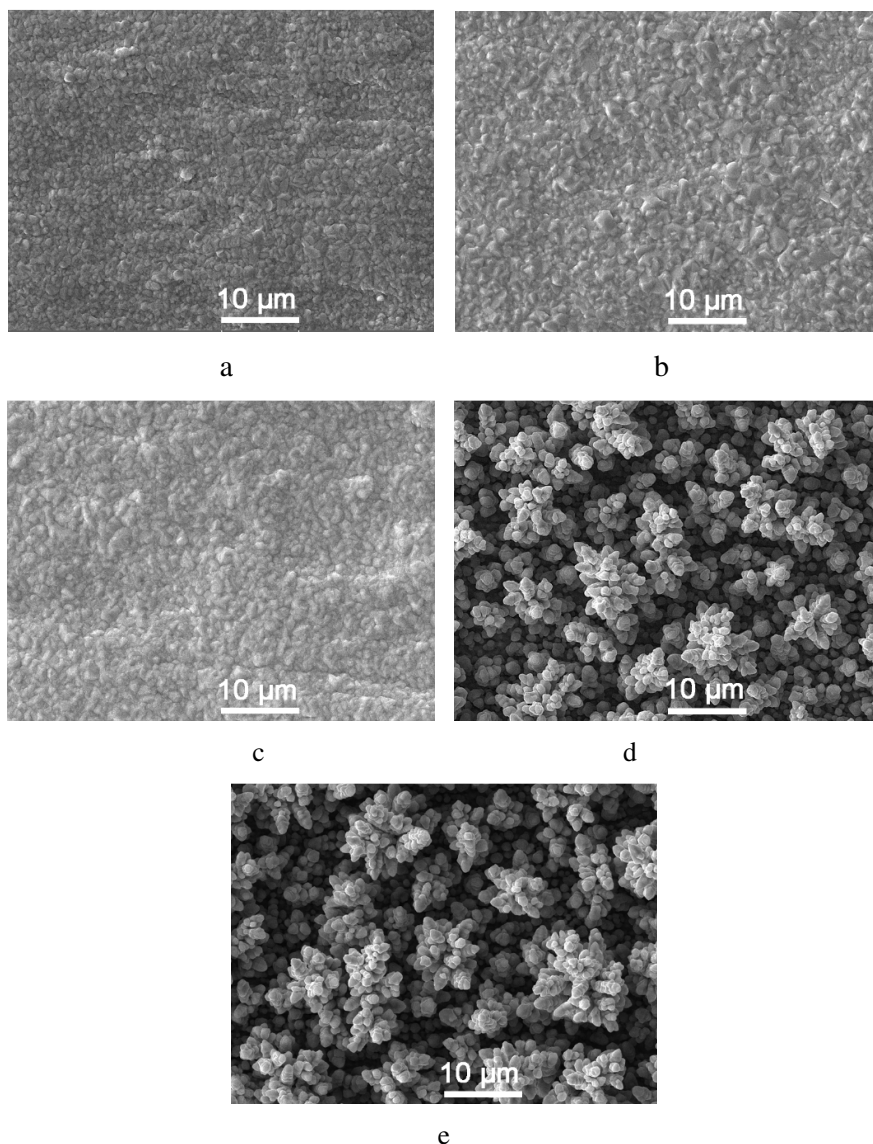


Fig. 7. Morphologies of copper deposits obtained by pulsating overpotential regime from 0.15 M $\text{CuSO}_4 + 0.50 \text{ M H}_2\text{SO}_4$ (solution (I)) at overpotential amplitudes of: a) 200, b) 500 and c) 800, d) 1600 and e) 1800 mV. Pulse duration: 30 ms. Pause duration: 100 ms.

Fig. 8 Shows the copper deposits obtained at overpotential amplitudes of 1100, 1250, 1400 and 2000 mV from solution (V). By electrodeposition at the potentials belonging outside the plateau of the limiting diffusion current density, dendrites or ramified dendrites are formed (Figs. 2, 3 and 7d-e). For the solutions with the concentration of 0.15 M CuSO_4 , by increasing the acid concentration from 0.25 (solution (IV)) to 0.50 (solution (I)) and 1.00 M (solution (V)), the morphology changes from compact grains (Fig. 6) and dendrite (Fig. 2) to dendrite and hole structure (Figs 8a-b and 8d). Increasing the acid concentration led to a higher rate of hydrogen

evolution and consequently producing of hydrogen bubbles. Adsorption of the hydrogen bubbles on the surface generates the holes.

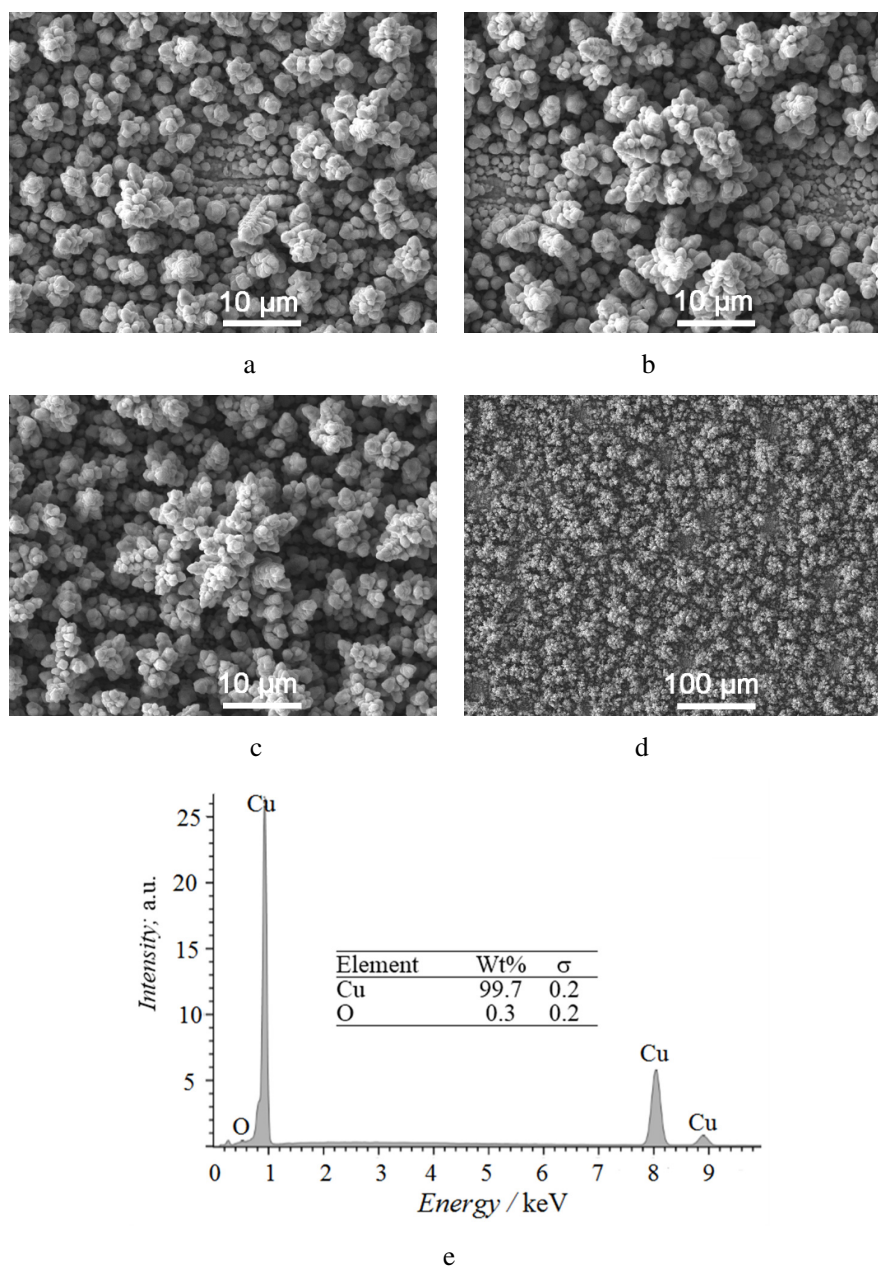


Fig. 8. Morphologies of copper deposits by pulsating overpotential regime from 0.15 M CuSO_4 + 1.00 M H_2SO_4 (solution (V)) at overpotential amplitudes of: a) 1100, b) 1250 and c) 1400 and 2000 mV., d) EDS analysis of the obtained typical copper dendrite. Pulse duration: 30 ms. Pause duration: 100 ms.

The appearance of dendritic forms indicates a decreased effectiveness of the stirring of the copper solution by the evolved hydrogen with prolonged pause duration.²⁸ The prolongation of deposition pulse duration led to the increase of both the rate of hydrogen evolution and copper

electrodeposition. The formed hydrogen bubbles number depends on the overpotential amplitude. Even though the overpotential amplitudes of 1100, 1250 and 1400 and 2000 mV corresponding to the outside the plateau of the limiting diffusion current density were used, holes which are the origin of the attached hydrogen bubbles were not formed.²⁹

The low number or absence of holes indicated that the deposition pause of 100 ms is too long to produce sufficient hydrogen to change the hydrodynamic conditions in the near-electrode layer which led to the formation of open and porous honeycomb-like structures. The proof for this is the branched dendrites (Fig. 8c) and rare holes (Figs. 8a-b and 8d) formed on the electrode surface.³⁰ Hydrogen bubbles detachment forms the individual holes.³⁰ From (EDS) analysis using, it is evident that foil was covered with copper deposits from solution (V) at 1250 mV (Fig. 8e). While the sample surface were slightly oxidized due to ambient air exposure. Analysis of Figs 3, 6 and 8 confirms that the solution stirring effectiveness does not increase with the increasing overpotential amplitude to form the honeycomb structure. Because of the lack of effective solution stirring by evolved hydrogen, the change in the morphology of electrodeposited copper from dendrite to degenerated dendrites and cauliflower-like agglomerates was observed.²⁷ These dendritic copper agglomerates are well-dispersed and surrounded by irregular channels as shown in Fig. 3d as well as Figs. 6d and 8d which show the typical cauliflower-like agglomerates of copper dendrites obtained by the square-wave pulsating overpotential at overpotential amplitude of 2000 mV with the prolonged deposition pulse and pause of 30 and 100 ms, respectively.

CONCLUSION

The effect of concentrations of copper sulfate and sulfuric acid on the copper electrodeposited by pulsating overpotential regime with a prolonged pulse and pause durations at overpotentials outside the plateau of the limiting diffusion current density was examined. By analyzing the morphological characteristics of copper deposits, the results obtained on the pulsating electrodeposition:

Copper grains obtained from a copper solutions containing 0.30 M CuSO₄ in 0.50 M H₂SO₄ (solution(III)) and 0.15 M CuSO₄ in 0.25 M H₂SO₄ (solution (IV)) at overpotentials amplitudes values outside the plateau of the limiting diffusion current density (1100, 1250 and 1400 mV) is very similar to deposits obtained from the solution containing 0.15 M CuSO₄ in 0.50 M H₂SO₄ (solution (I)) at overpotential amplitudes belonging to the plateau of the limiting diffusion current density and lower (200, 500 and 800 mV).

A very long pause duration suppresses the hydrogen evolution reaction. Only in two cases: dish-like holes obtained from 0.15 M CuSO₄ in 0.50 M H₂SO₄ (solution (I)) and 0.15 M CuSO₄ in 1.00 M H₂SO₄ (solution (III)) at high overpotential amplitude of 2000 mV.

Although the potentials outside the plateau of the limiting diffusion current density were used, no honeycomb structure was created in any of the solutions.

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