

Electrodeposition of Cu 3D structures suitable for CO₂ reduction

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Porous Cu foam electrodes, suitable for cathodic CO₂ reduction, were deposited in an acidic sulphate solution with different additives to obtain structures with a high real surface area and an adequate mechanical stability. The influence of the electrodeposition time and solution composition on the porosity parameters, microstructure and stiffness of Cu 3D structures was evaluated. Neither ammonium acetate nor polyethylene glycol were found to be effective additives to the Cu sulphate electrolyte to achieve the main objectives. Only the presence of Cl⁻ ions in the deposition solution resulted in a threefold increase in the real surface area and the achievement of a sufficient mechanical stability of the Cu 3D structure. The latter effect is related to the specific influence of Cl⁻ ions during the electrodeposition process on the microstructural characteristics, such as the size of micropores in the walls of holes and crystallite aggregates that form dendritic branches. These structural changes, in contrast to the Cu samples deposited in a solution without additives, resulted in larger real surface areas, while the denser structures deposited in the presence of Cl⁻ ions ensured the mechanical stability of the 3D structure.

Keywords: copper, CO₂ reduction, real surface area

INTRODUCTION

A unique feature of the Cu surface is the ability to convert CO₂ into hydrocarbons with a significant faradaic efficiency [1]. The catalytic activity of the metal is highly sensitive to electrolysis conditions, including surface structure, morphology and real surface area (S_r) [2, 3]. Simple polycrystalline Cu electrodes have a rather small S_r and therefore their efficiency is low. Meanwhile, nanostructured Cu electrodes exhibit a high electrochemical activity for CO₂ reduction. Cu foam, which can be successfully prepared by the electrodeposition process, possesses a highly open porous dendritic nanostructure, which is suitable for electrocatalytic applications. The pore sizes and wall structures of foams are tunable by adjusting

the deposition conditions, such as current density, deposition temperature, pH and electrolyte composition [4].

Usually, an acidic Cu sulphate bath is used for Cu foam electrodeposition [5, 6]. The morphology of the porous structure is mainly caused by the competing reaction of hydrogen evolution. Increasing the overpotential increases the evolution of H₂ bubbles during electrodeposition and is therefore beneficial for the porosity of the Cu foam and consequently for large values of S_r . However, these structures have two major problems that arise due to the rapid Cu deposition at an extremely high cathodic overpotential. The first is the low mechanical strength due to fragile Cu dendrites in the foam walls, while the second is the poor surface coverage of electrode materials due to the current concentration on Cu dendritic deposits during the electrodeposition process [7].

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For the practical use of Cu 3D foam samples in CO₂ reduction, additional studies should be carried out to increase the effective surface area while maintaining a sufficient mechanical stability of the structure. In addition, dendritic structures can be easily overgrown into a thick film with a very low porosity, hindering gas-liquid transport which is important in electrochemical applications [8]. Therefore, optimisation of the Cu 3D formation process is a challenge.

The problem of determining the S_r of porous Cu nanostructured materials was solved in our previous work [9], where it was shown that double layer capacitance measurements using voltammetry give the most reliable results.

It is necessary to reduce the size of the pores in the foam and the branches in the foam wall in order to increase the specific surface area and hence the effectiveness/activity of the porous electrodes [3]. These microstructural characteristics can be improved by adding specific substances, called additives, to the plating solution [10–12].

Attempts to reduce the pore size have focused on bubble stabilizers, such as acetic acid [10]. This compound was found to be effective in preventing bubble coalescence and thus reducing the pore size. The addition of chloride ions to the electrolyte affects the wall structure of the foam, dramatically reducing the size of Cu branches [11]. This phenomenon was related to the accelerating effect of Cl⁻ on the Cu reduction mechanism. Meanwhile, polyethylene glycol (PEG) has been widely used as a levelling agent and suppressant for sulphuric acid Cu plating, and has been found to improve the morphology of the foam deposit even at an extremely high cathodic polarization [12].

As far as systems using copper 3D structures as catalysts are concerned, the literature reveals a lack of data on the influence of the Cu deposition parameters on both the S_r and the mechanical stability of the deposit. The aim of this study was to determine the optimal conditions for producing Cu 3D structures with maximum S_r and good mechanical properties. This involved optimising the plating process and using additives in the plating electrolyte.

EXPERIMENTAL

Sample preparation

The substrate used for sample preparation was a polycrystalline copper foil with a geometric area

of 1 cm². Firstly, to prepare a 'plain' electrode with a known surface roughness ($f_R \sim 2$), a Cu layer of 8 μm thickness was deposited from the acidic sulphate solution [9]. Secondly, Cu 3D structures were electrodeposited on the plain electrode in an electrolyte containing 0.2 M Cu₂SO₄ and 1.5 M H₂SO₄. The following substances were used as additives to the plating solution: 0.5 M CH₃COONH₄, 0.0001 M PEG (2000) and HCl in the concentration range 0.001 M to 0.2 M. All samples were deposited at a cathodic current density of 3 A cm⁻² for 5, 10, 15, 20 or 25 s.

Analytical grade chemicals and deionised water were used in the preparation of all of the electrolytes.

Real surface area measurements

Cyclic voltammetry was used to evaluate the S_r of electrodeposited Cu 3D samples from the double layer capacitance measurements. All electrochemical measurements were performed using an AUTOLAB 302 potentiostat/galvanostat at ambient temperature in a 0.1 M NaOH solution in a three-electrode electrochemical cell. The cell was equipped with a Pt counter electrode, a Hg/Hg₂SO₄ (sat. K₂SO₄) reference electrode. Prior to the measurements, all electrolytes were purged with Ar gas for at least 20 min. All potentials in the text are reported versus a standard hydrogen electrode (SHE). Cyclic voltammograms were recorded in the non-Faradaic range (–0.57 V – –0.42 V SHE), at different scan rates. The capacitive currents at –0.5 V were then plotted against the scan rate. The slope of the resulting line gives the double layer capacitance value, C . At least three double layer capacitance measurements were performed.

The copper real surface area (S_r) and surface roughness factor (f_R) were calculated according to the following formulas,

$$S_r = \frac{C}{C_{sp}}, \quad (1)$$

$$f_R = \frac{S_r}{S_G}, \quad (2)$$

where C is the measured copper electrode double layer capacitance, mF, C_{sp} is the copper specific capacitance in an alkaline solution of 0.02 mF cm⁻² [13]), f_R is the surface roughness factor, and S_G is the geometrical surface area of an electrode in cm².

Structure and phase composition characterisation

A Helios Nanolab 650 dual beam system (FEI) was used in the secondary electron mode at an accelerating voltage of 3 kV to study the morphology of the coatings. The porosity of the Cu 3D coatings was assessed by the visual analysis of the SEM images.

The phase composition of the Cu electrode and the grain size were evaluated using an XRD SmartLab, Rigaku X-ray diffractometer (Rigaku, Japan, 2011). A grazing incidence method with the angle of incidence of $\omega = 0.5^\circ$ was applied.

Measurement of mechanical properties

Microhardness measurements were performed on a Hysitron Ti Premiere (Bruker) micro indentation device using an Omniprobe piezoelectric transducer. A Berkovich type diamond indenter was used as a probe. The displacement controlled trapezoid load function was used for indentation, and hardness (H) and reduced modulus (E_r) were measured at 1, 5 and 10 μm displacements. A 3×3 grid of indentations 200 μm apart were performed for every selected displacement. Measurement is performed by loading the surface and analysing the release curve. The stiffness (SF) of the object was fitted directly from the curve.

RESULTS AND DISCUSSION

Electrodeposition in an electrolyte without additives

Typically, Cu 3D crystalline structures (foams) are deposited from the acidic sulphate solution using high current densities. We started our studies

with samples deposited in an electrolyte without any additives. The process was carried out on Cu substrates using a method described in Refs. [5–7]. Typical SEM images of the surface morphology of Cu foams deposited at 3 A cm^{-2} are shown in Fig. 1. The evolution of hydrogen gas at an electrode surface is significant during Cu electrodeposition when current densities higher than $>0.5 \text{ A cm}^{-2}$ are maintained [14]. The evolution of hydrogen gas hinders the electrodeposition of Cu directly on the cathode by temporarily preventing a contact between the Cu cathode and the electrolyte containing Cu sulphate. Eventually, a thin film of electrolyte surrounding a bubble of H_2 comes into contact with the cathode, completing the electrochemical circuit and allowing Cu to be electrodeposited [4]. The resulting foam is an interconnected network of Cu pores patterned by H_2 bubbles (Fig. 1a). Meanwhile, the deposited structure was composed of ramified dendrites extending in all directions and cross-linked with each other, resulting in a loose structure with empty spaces (Fig. 1b). The number and size of the holes, as well as the wall width between them, depend on the conditions of electrodeposition and the electrolysis regime.

The hydrogen evolution reaction during the electroplating process creates two types of pores [14]. The first type are macropores (or holes) formed by detached hydrogen bubbles. The origin of the second type of pores are hydrogen bubbles generated at the tops of the agglomerates of Cu grains during the growth process (the current density distribution effect) [14]. Therefore, due to the intensive H_2 evolution resulting in a discontinuous pore size distribution, together with the formation of dendritic walls, the Cu 3D structure assumes a large surface

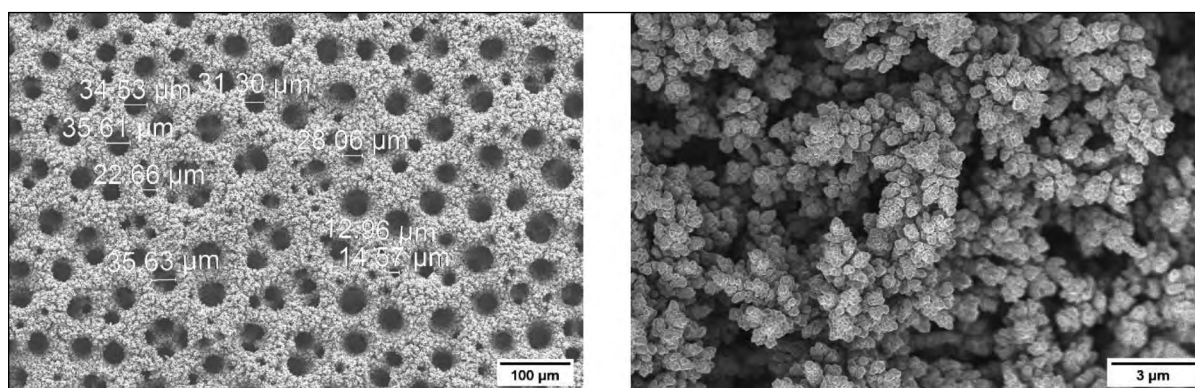


Fig. 1. SEM images at different magnifications of Cu 3D structures electrodeposited in a $0.2 \text{ M Cu}_2\text{SO}_4$ and $1.5 \text{ M H}_2\text{SO}_4$ solution at 3 A cm^{-2} current density

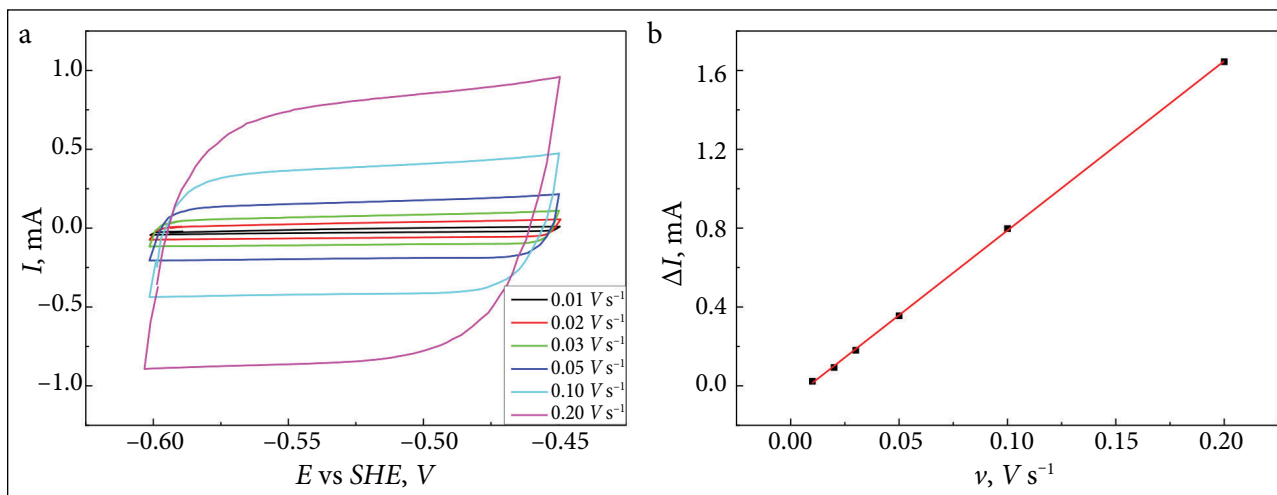


Fig. 2. (a) Voltammograms of Cu foam recorded in the non-Faradaic region at different scan rates; (b) the linear dependence of capacitive currents at -0.5 V on the scan rate

area.

The numerical values of S_r were determined from the voltametric double layer capacitance measurements using cyclic voltammetry [15]. Typically, CV curves are recorded in the double layer charging region at different scan rates.

Figure 2a shows the CV curves recorded in a 0.1 M NaOH solution in the non-faradaic region (-0.57 V – -0.42 V for the Cu 3D electrode deposited in the acidic sulphate solution without additives). The obtained capacitive current values were plotted against the scan rate (Fig. 2b), and the slope of the obtained linear dependence gave the double layer capacitance values. The S_r and f_R values were calculated using Eqs. (1) and (2).

The first step was to study the influence of the electrodeposition time on the porosity characteristics and the values of S_r of the Cu 3D structure. In general, the topography of all deposited samples was very similar to that shown in Fig. 1. Meanwhile, the obtained values of f_R parameters are listed in Table 1. It is evident that the average

pore density decreases while the average pore size and the real surface area increase with the increase of the deposition time. It can be stated that the optimal deposition time, which results in the highest values of S_r and the high quality of deposited Cu samples, is 20 s, as the longer deposition process causes the appearance of numerous structural defects, like crevices, in the Cu 3D structure.

The influence of additives on Cu 3D layer formation

The additives used to improve the micro- and nanostructural properties of Cu 3D electrodes are usually the same as those used in bright copper electroplating [11, 14]. As the morphology of the porous structure is mainly caused by the competitive reaction between hydrogen evolution and Cu deposition, it has been shown that additives such as acetic acid, NH_4^+ , Cl^- ions or PEG have a good effect in preventing bubble coalescence and hence pore size reduction [7, 12, 16]. It is also known that the addition of chloride ions to the deposition solution dramatically reduces the size of the dendritic copper branches. However, despite numerous investigations on the effect of additives on the deposition process of Cu 3D structures [7, 11–14, 16], there are no reliable data on their influence on the deposit morphology, S_r values and mechanical stability.

Ammonium acetate, hydrochloric acid and PEG were used as additives to the acidic sulphate electrolyte to determine their influence on the S_r values of electrodeposited Cu 3D structures. SEM images

Table 1. Influence of deposition time on the Cu 3D layer porosity parameters and surface roughness factor values

Deposition duration, s	Average pore size, μm	Average pore density, cm^{-2}	Surface roughness factor, f_R
5	7.3	$3.2 \cdot 10^7$	90 ± 4
10	16.5	$1.2 \cdot 10^7$	290 ± 11
15	21.5	$8.0 \cdot 10^6$	600 ± 22
20	25.3	$4.0 \cdot 10^6$	814 ± 29
25	28.8	$3.0 \cdot 10^6$	900 ± 35

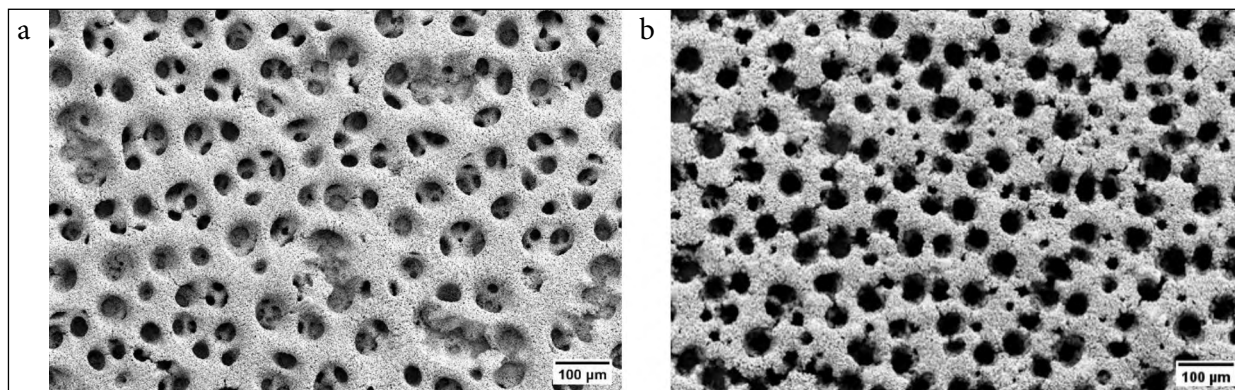


Fig. 3. SEM images of the Cu 3D structures electrodeposited from the acidic sulphate solution containing additives: (a) $\text{CH}_3\text{COONH}_4$, (b) PEG

of the surface morphology of Cu foam samples deposited in solutions with ammonium acetate and PEG additives are shown in Fig. 3, while those deposited with hydrochloric acid are shown in Fig. 4, respectively. Meanwhile, the values of the surface roughness factors of deposited samples are listed in Table 2. All the deposits showed the porous foam structure, however, the average pore size and density, as well as a degree of crystallite compactness in the foam walls looked different.

Despite the reports that NH_4^+ ions improve

Table 2. Effect of acidic sulphate electrolyte additives on the Cu 3D layer real surface area values (surface roughness, f_R)

Electrolyte additives	Surface roughness factor, f_R
–	814 ± 29
0.5 M $\text{CH}_3\text{COONH}_4$	576 ± 116
0.0001 M HCl	622 ± 119
0.001 M HCl + 0.0001 M PEG	567 ± 63
0.05 M HCl	2512 ± 247

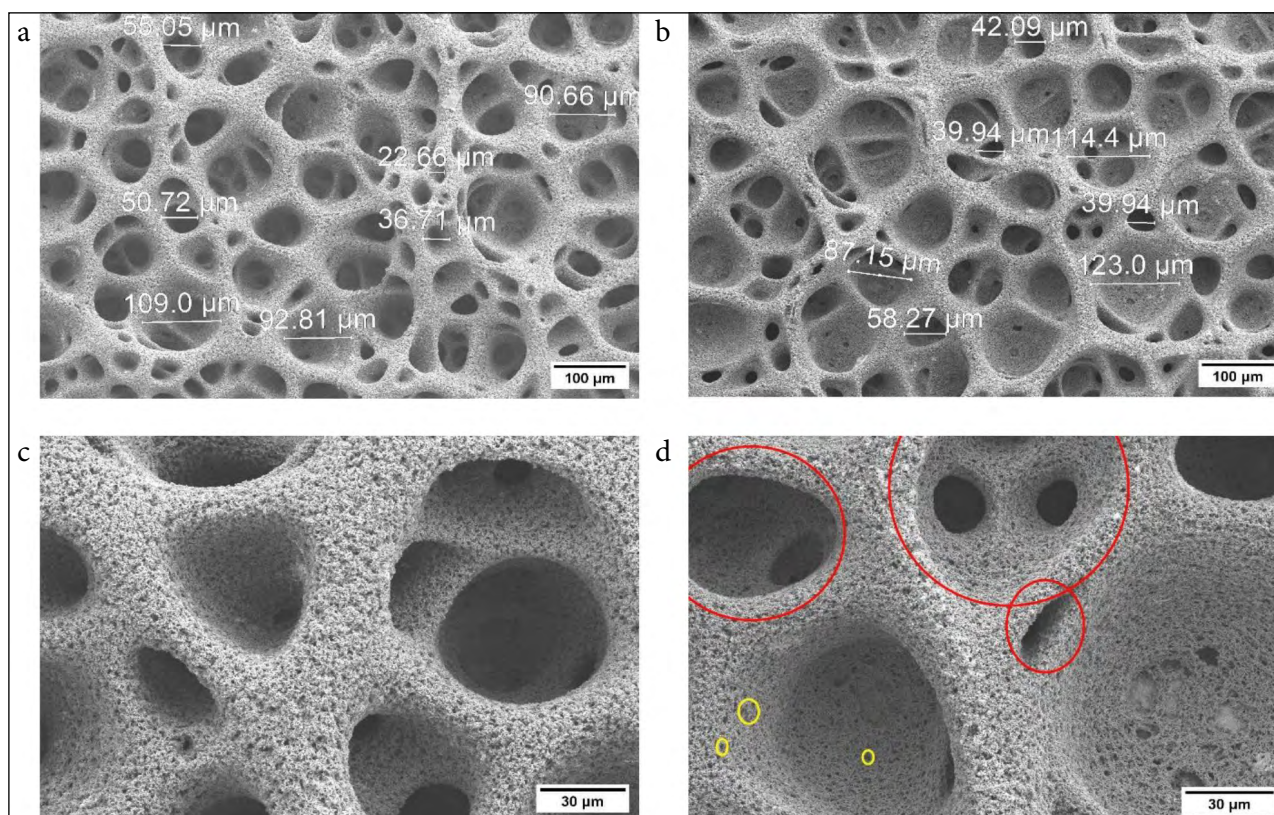


Fig. 4. SEM images of the Cu 3D structures, deposited in solutions containing an HCl additive: (a, c) 10 mM, (b, d) 50 mM. A red mark is the first type pores; a yellow mark shows the second type pores

the porosity of Cu foam, since they produce H_2 gas during the cathodic reaction and inhibit bubble coalescence in an aqueous solution [7], we have not observed any significant influence of ammonium acetate on the morphology of the deposited Cu foam (Fig. 3a). In addition, the values of S_r of those samples were even lower with respect to those deposited in the solution without additives. Similar conclusions can be drawn for the samples deposited in the solution containing PEG. Besides, some structural defects such as cracks in the walls of these samples can be observed (Fig. 3b). On the basis of the results obtained, further studies were carried out without the aforementioned additives.

The most obvious and effective influence on morphology and S_r values was observed when chloride ions were added to the deposition solution. If comparatively low concentrations of Cl^- (0.1 mM) do not significantly affect the S_r values of Cu 3D deposited samples, the addition of 50 mM increases this figure more than threefold (Table 2). Therefore, the detailed analysis of the influence of HCl on the morphology and properties of deposited Cu foam structures was investigated.

Effect of Cl^- ions on the Cu foam structure and properties

It is known that the trace amount of Cl^- could have an obvious catalytic effect on Cu deposition because these ions are able to modify the mechanism of electron transfer through a Cl^- bridge, greatly increasing the exchange current density and lowering the overpotential of the Cu^{2+}/Cu^+ reaction, which is the rate-controlling step of the Cu reduction reaction [18]. From the data presented in Table 2, it is clear that with the addition of 50 mM HCl in the acidic sulphate solution, it is possible to form a structure with significantly higher values of S_r compared to the sample deposited in the solution without Cl^- ions. The next step was to investigate how this increase relates to the structure of the deposited Cu 3D layers.

The macropores or holes (the first type pores) of the samples deposited in the solutions without HCl were smaller and more uniform in size (14–34 μm , average 25 μm , Fig. 1a), but with a high average pore density ($3.5 \cdot 10^5$). Meanwhile, the addition of HCl resulted in the formation of coalesced holes with a dispersed hole size (22–129 μm) and

a lower number of holes per mm^2 of the geometric surface area (Fig. 4a, b). The results on the effect of Cl^- concentration in the deposition solution on the porosity parameters and S_r values of deposited Cu 3D structures are summarised in Table 3. The increase in the Cl^- concentration resulted in an increase in the mean values of the first type pore size and a decrease in the mean values of pore density. At the same time, an increase in the S_r values, for the deposited samples was observed. The highest f_R values (2614 ± 294) were found for the Cu 3D structure deposited in the solution containing 100 mM HCl; however, the samples deposited in the presence of the high concentration of HCl (100 and 200 mM), showed the presence of additional powdered Cu aggregates on the top layer of the deposited samples and therefore, were not further investigated.

Table 3. The influence of Cl^- concentration in the deposition solution on the porosity and S_r of Cu 3D structures

HCl concentration in deposition solution, mM	Surface roughness factor, f_R	Average pore size, μm	Average pore density, cm^{-2}
0	814 ± 29	25.3	$3.5 \cdot 10^5$
0.1	622 ± 119	27.4	$8.4 \cdot 10^5$
10	1792 ± 503	33.8	$2.6 \cdot 10^4$
20	1979 ± 141	53.1	$2.2 \cdot 10^4$
50	2512 ± 247	65.4	$1.7 \cdot 10^4$
100	2614 ± 294	79.6	$1.1 \cdot 10^4$
200	2458 ± 403	61.4	$1.8 \cdot 10^4$

Analysis of the Cu 3D structures also showed a decrease in the portion of holes formed by coalesced H_2 bubbles with an increasing HCl concentration. Meanwhile, analysis of the interior of those holes showed that the dimensions of the second type pores in the walls were lower and their density was higher for the sample deposited in the solution containing a higher amount of HCl (Fig. 4c, d). The walls of pores and holes were also very porous, consisting of dispersed small aggregates of Cu crystallites, and their formation depended on the presence of Cl^- in the electrolyte. The addition of Cl^- ions dramatically reduced the size of the copper branches and the dimensions of the Cu crystallite aggregates in the branch, whose average size was 215 and 115 nm for the samples deposited in the solution without Cl^- (Fig. 5a) and with

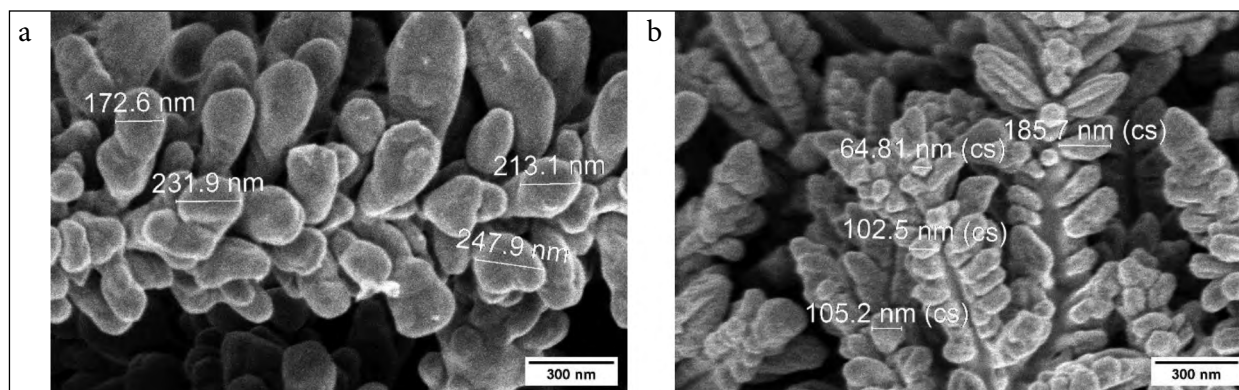


Fig. 5. SEM images of dendritic branches of Cu 3D layers deposited in the solutions without (a) and with addition of 50 mM Cl^- (b)

Cl^- (Fig. 5b), respectively. It can be observed that the compactness of the agglomerates of Cu crystallites formed along the holes was also increased, as the dendrites were reduced in size and closely stacked when the sample was deposited in the presence of Cl^- (Fig. 5b).

The presence of Cl^- ions in the deposition solution significantly affects not only the dimensions of the branches but also the thickness of the deposited Cu layer. The latter parameter was determined from the cross-section SEM images, which are presented in Fig. 6.

The average thickness of the Cu 3D layer deposited in the Cl^- free solution at 3 A cm^{-2} is close to $\sim 80 \mu\text{m}$ (Fig. 6a), while the thickness of the Cu sample deposited under the same condition in the presence of 50 mM Cl^- reaches $\sim 120 \mu\text{m}$ (Fig. 6b). The thickness of the Cu 3D layers can even reach $\sim 200 \mu\text{m}$ when higher HCl concentrations (100 or 200 mM) were applied, but such deposits showed a lot of structural defects. It is also evident from the presented cross-section images that the Cu 3D layer deposited in the solution containing Cl^- ions

exhibit a significantly denser structure. The pore size distribution and the compactness of the agglomerates of Cu crystallites formed between the holes determine the uniformity of such structures, which exhibited large S_r values with respect to the samples deposited in the solution without Cl^- additives.

It can be stated, therefore, that the specific surface area of Cu electrodes is determined by the size of the second type pores and agglomerates of Cu grains in the walls of the holes. The presence of Cl^- in the solution reduces the size of these pore and dendritic branches at the same time facilitating the transport of electroactive species through the interior of the structure and simultaneously increasing the value of S_r .

Phase composition and the grain size

The XRD patterns of the Cu samples deposited in the solutions without and with Cl^- ions do not differ from each other, nor does the Cl^- concentration show any influence on the phase composition and lattice parameters. Therefore, only one diffractogram, corresponding to the sample deposited in

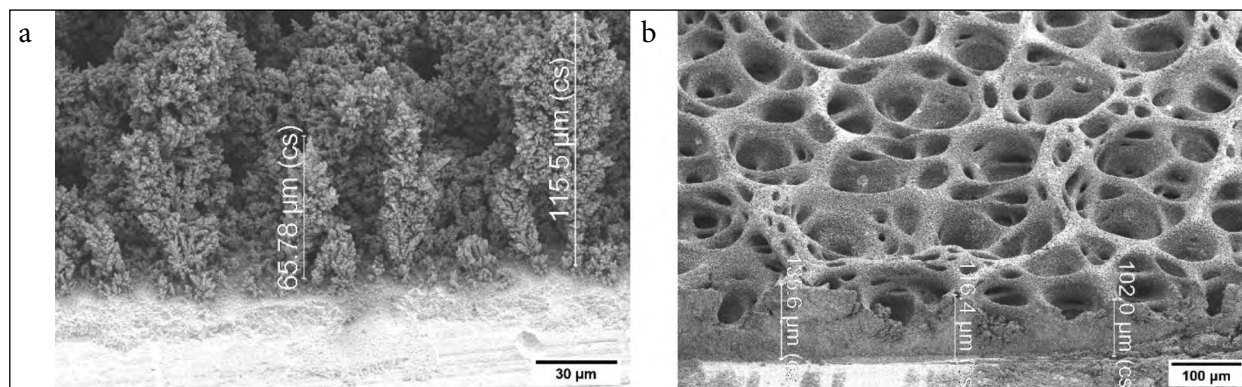


Fig. 6. Cross-sectional SEM images of the Cu 3D layers deposited in the solutions without (a) and with addition of 50 mM Cl^- (b)

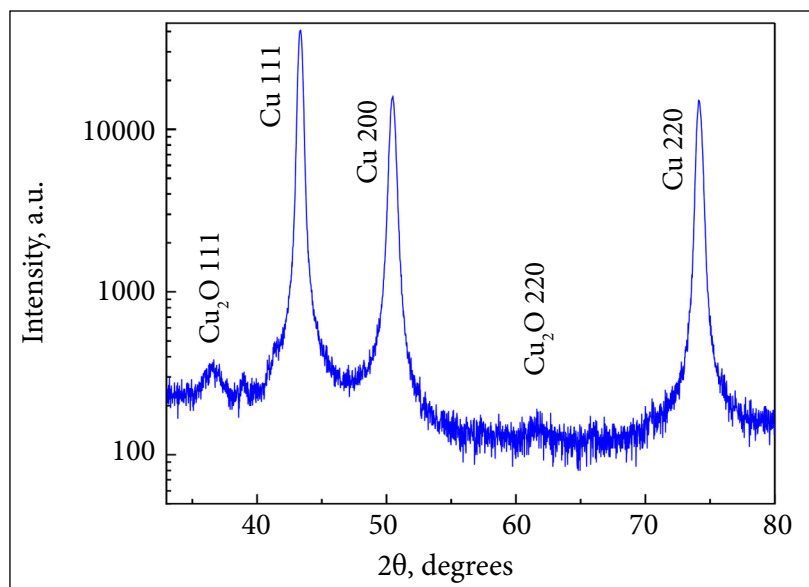


Fig. 7. XRD pattern of the Cu 3D structure deposited in the solution containing Cl^- ions

the solution with Cl^- ions, is presented in Fig. 7 and shows that Cu deposits have a face centred cubic (fcc) structure with a high crystallinity and peaks corresponding to the (111), (200) and (220) crystal facets. Besides, polycrystalline Cu deposits do not exhibit a dominant crystallographic orientation. Small peaks seen together with Cu peaks were attributed to the Cu_2O phase. It is important to note that the oxide appears on the Cu foam samples immediately after electrodeposition, indicating that this porous material is highly sensitive to surface oxidation.

A polycrystalline Cu 3D material is composed of crystallites that 'stick' together and can vary in size from a few nanometers to several millimeters, as it can be observed in Figs 1–5. While in the XRD field, the crystallite is considered to be the smallest single crystal or part of the grain that has no lattice defects and in which coherent scattering of X-rays takes place [19, 20]. In a certain case, the grain may coincide with the crystallite. The grain size values of the Cu 3D structures were determined on the basis of XRD measurements and it appeared that the grain size values of the samples deposited in the solutions without and with Cl^- ions are very close and vary within the range $16.8 - 17.3 \pm 5$ nm.

Mechanical properties

As the foam materials are composed of a solid, thin-walled matrix and hollow cells, the mechanical properties of such objects are related to the way

in which the constituent particles (crystallite aggregates) are arranged in the structure of the material [21, 22]. The stiffness (SF) is a parameter, which corresponds to the extent to which the material resists deformation in response to an applied force. SF values were determined from the microhardness measurements of the investigated samples, which were performed by loading the surface and analysing the release curves.

Two sets of experiments were carried out: the first one with the Cu 3D samples deposited in the solution without additives during 10 and 20 s, while the second one with the samples deposited in the solutions containing a different amount of HCl. The values of SF were fitted from the unloading curves and are summarised in Fig. 8. It can be seen that the samples deposited for 20 s are more resistant to deformation (Fig. 8a) compared to those deposited for 10 s. At all three loads applied SF values of the latter sample (pink points) are close to $5-7 \mu\text{N nm}^{-1}$, while those of the sample deposited for 20 s (black points in Fig. 8a) are close to $10-15 \mu\text{N nm}^{-1}$. The influence of the Cl^- ions concentration in the deposition solution on the mechanical properties of deposited Cu 3D structures is also apparent. The samples deposited in the presence of 10 mM of HCl exhibited the lowest SF values (blue points in Fig. 8b), which were close to the values of the samples deposited in the Cl^- -free solution. The addition of 50 or 100 mM of HCl resulted in the deposition of Cu 3D samples with

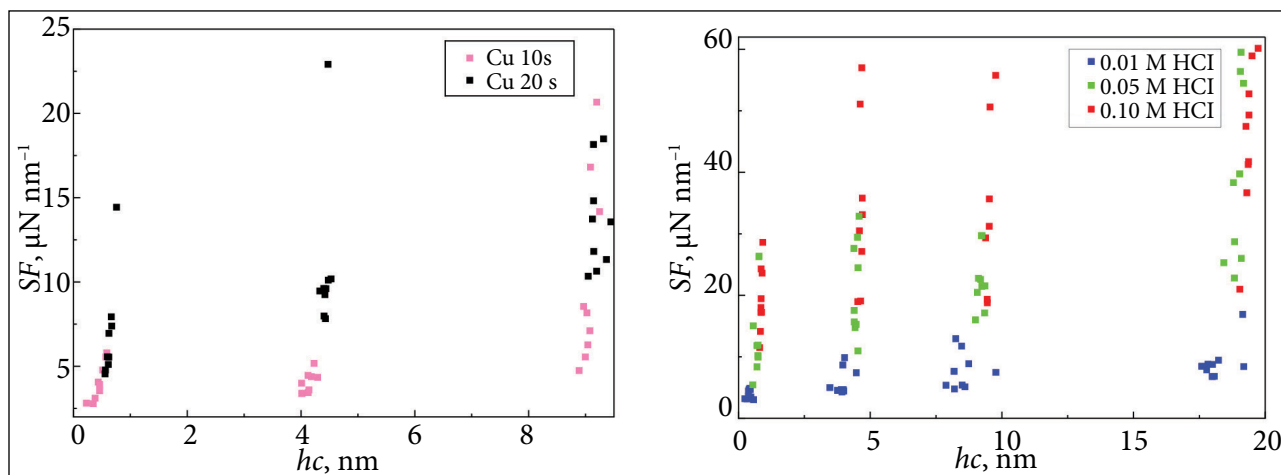


Fig. 8. The stiffness (S_f) values at various contact depth (h_c) of the Cu 3D electrodes deposited in different conditions: with 0.01 M HCl, 20 s deposition (blue); 0.05 M HCl, 20 s (green); 0.10 M HCl, 20 s (red); no additive, 10 s (pink); no additive, 20 s (black)

the 25–30 $\mu\text{N nm}^{-1}$ S_f values (green and red points in Fig. 8b). As it was already mentioned, the samples deposited in the solution with the Cl^- concentration exceeding 50 mM possess serious structural defects, which restrict further use of the mentioned Cu 3D foams. It is also evident that the properties of the sample change with a depth, which may be related to structural peculiarities of the porous structure.

The results of the mechanical properties of the deposited Cu foams are in agreement with the SEM analysis (Fig. 4), which indicates that the presence of a certain concentration of HCl in the deposition solution favours the formation of structures with a higher density, which are more resistant to deformation and have a significantly higher real surface area compared to the samples deposited in the solution without Cl^- ions.

CONCLUSIONS

Increasing the real surface area (S_r) and ensuring an adequate mechanical stability of the electrodeposited Cu foams were achieved by using Cl^- ions as additives to the acid sulphate electrolyte. Meanwhile, ammonium acetate and polyethylene glycol additives showed no positive effect on the properties of the electrodeposited Cu 3D structures. While relatively low concentrations of Cl^- (0.1 mM) do not significantly affect the values of S_r of Cu 3D deposited samples, the addition of 50 mM of Cl^- increases this value more than threefold. The increase of the Cl^- concentration in the deposition

solution resulted in an increase of the average pore size and a decrease of the average pore density. At the same time, the S_r values increased, except for the highest Cl^- concentrations (100 and 200 mM), when the formation of structural defects in the upper layer of the deposited samples was observed. The positive effect of Cl^- ions during electrodeposition is related to the specific influence on the microstructural characteristics, such as the size of micropores in the walls of the holes and crystallite aggregates, forming dendritic branches. These structural changes resulted in larger real surface areas, while the higher density obtained in the presence of Cl^- ions ensured the mechanical stability of the 3D structure.

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CO₂ REDUKCIJAI TINKAMŲ Cu 3D STRUKTŪRŲ ELEKTROCHEMINIS NUSODINIMAS

Santrauka

Porėti Cu elektrodai, skirti katodinei CO₂ redukcijai, buvo nusodinti iš rūgštaus vario sulfato tirpalo su skirtingais priedais, siekiant gauti struktūrą su dideliu tikroju paviršiaus plotu ir pakankamu mechaniniu stabilumu. Buvo įvertinta elektrodų nusodinimo laiko ir tirpalo sudėties įtaka Cu 3D struktūrų porėtumo parametrams, mikrostruktūrai ir standumui. Nustatyta, kad nei amonio acetatas, nei polietilenglikolis nėra veiksmingi Cu sulfato elektrolito priedai, leidžiantys pasiekti numatytus tikslus. Tik pridėjus Cl⁻ jonų pavyko tris kartus padidinti tikrąjį Cu 3D struktūrų paviršiaus plotą bei pasiekti pakankamą mechaninį stabilumą. Specifinis Cl⁻ jonų poveikis mikrostruktūros savybėms sietinas su mikroporų dydžiu skylių sienelėse bei kristalinių agregatais, sudarančiais dendritines atšakas. Šie struktūriniai pokyčiai, skirtingai nei Cu bandinių, nusodintų tirpale be priedų, lėmė didesnes tikrojo paviršiaus ploto vertes, o tankesnės struktūros, nusodintos esant Cl⁻ jonams, užtikrino 3D struktūros mechaninį stabilumą.