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## The ionic equilibrium in the $\text{CuSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ system and the formation of the honeycomb-like structure during copper electrodeposition

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**Abstract:** The ionic equilibrium of the species in the  $\text{CuSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$  system was employed to systematize the conditions of copper electrodeposition leading to the formation of the honeycomb-like structure. The reason why  $\text{CuSO}_4$  concentrations higher than 0.15 M are unsuitable for the formation of honeycomb-like structures is shown. The range of  $\text{H}_2\text{SO}_4$  concentrations enabling the formation of this type of structure was also determined. The conditions leading to the formation of the honeycomb-like structures are: electrodeposition from solutions with lower concentrations of Cu(II) ions (0.15 M  $\text{CuSO}_4$  and less) in a concentration range from 0.25 to 1.0 M  $\text{H}_2\text{SO}_4$ , at a temperature of  $18.0 \pm 1.0$  °C and at overpotentials outside the plateau of the limiting diffusion current density at which hydrogen evolution is vigorous enough to change the hydrodynamic conditions in the near-electrode layer.

**Keywords:** electrolysis; hydrodynamics; morphology; hydrogen; copper.

### INTRODUCTION

Aqueous solutions of sulfuric acid and cupric sulfate are frequently found in copper hydrometallurgical processes, such as leaching, solvent extraction, electrowinning and electrorefining.<sup>1</sup> Irregular deposits, such as powder deposits<sup>2–5</sup> and open and porous structures with an extremely high surface area,<sup>6</sup> denoted as honeycomb-like ones,<sup>7–9</sup> are most often formed by electrodeposition from these solutions. The main species present in aqueous sulfuric acid solutions containing Cu(II) are: bisulfate ions ( $\text{HSO}_4^-$ ), cupric ions ( $\text{Cu}^{2+}$ ), aqueous cupric sulfate ( $\text{CuSO}_4(\text{aq})$ ), hydrogen ions ( $\text{H}^+$ ) and sulfate ions ( $\text{SO}_4^{2-}$ ).<sup>1</sup> In an aqueous so-

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lution of sulfuric acid and cupric sulfate, two weak electrolytes,  $\text{HSO}_4^-$  and  $\text{CuSO}_{4(\text{aq})}$  are formed and the equilibriums between  $\text{HSO}_4^-$ ,  $\text{H}^+$  and  $\text{SO}_4^{2-}$  ions, as well as between  $\text{CuSO}_{4(\text{aq})}$ ,  $\text{Cu}^{2+}$  and  $\text{SO}_4^{2-}$  species are constituted.<sup>1</sup>

Electrochemical processes dealing with the formation of irregular deposits are very suitable for the analysis of the ionic equilibrium in the  $\text{CuSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$  system, due to the hydrogen evolution reaction which occurs parallel to copper electrodeposition. The first report which investigated the effect of this ionic equilibrium on the formation of these deposits was reported recently.<sup>10</sup> Considering the high technological significance of honeycomb-like structures as possible electrodes in many electrochemical devices, such as fuel cells, batteries and sensors,<sup>6</sup> a detailed analysis of the ionic equilibrium in the  $\text{CuSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$  system on the formation of this type of deposit was until this study necessary.

#### EXPERIMENTAL

Copper was potentiostatically deposited from the following solutions: 0.075 M  $\text{CuSO}_4$  + 0.50 M  $\text{H}_2\text{SO}_4$ , 0.30 M  $\text{CuSO}_4$  + 0.50 M  $\text{H}_2\text{SO}_4$ , 0.60 M  $\text{CuSO}_4$  + 0.50 M  $\text{H}_2\text{SO}_4$  and 0.15 M  $\text{CuSO}_4$  + 0.125 M  $\text{H}_2\text{SO}_4$ .

The electrodepositions were performed in an open cell at a temperature of  $18.0 \pm 1.0$  °C using a Wenking 7103 Girh potentiostat. Doubly distilled water and analytical grade chemicals were used for the preparation of the solutions for the electrodeposition of copper.

The electrodepositions of copper were performed at an overpotential of 1000 mV onto cylindrical copper cathodes previously covered by a thin copper film.

The counter electrode was a copper foil placed close to the walls of the cell; the working electrode was placed in the middle of the cell, while the overpotential was adjusted vs. a copper electrode which was positioned at a distance of 0.2 cm from the surface of the working electrode.

For the determination of the average current efficiency of hydrogen evolution, an electrochemical cell with the same arrangement of copper electrodes as that used for the preparation of the copper deposits for SEM analysis was employed. The electrodes were situated under a burette with the surface facing up so that the total amount of hydrogen evolved during the electrodeposition processes went into the burette. During the electrodeposition process, the volume of evolved hydrogen,  $V(\text{H}_2)$ , and the current of the electrodeposition,  $I$ , after a time,  $t$ , were recorded. Then, after graphical integration  $I\text{--}t$ , the average current efficiency for hydrogen evolution in a time  $t$ ,  $\eta_{I,\text{av}}(\text{H}_2)$ , was determined according to Eq. (1):

$$\eta_{I,\text{av}}(\text{H}_2) = \frac{nFV(\text{H}_2)}{V \int_0^t I dt} \quad (1)$$

where  $nF$  is the number of Faradays per mole of consumed ions and  $V$  is the molar volume of a gas under normal conditions (*i.e.*, 22.400 dm<sup>3</sup>).

The average current efficiency for hydrogen evolution,  $\eta_{\text{av}}(\text{H}_2)$ , is defined as the average value of the  $\eta_{I,\text{av}}(\text{H}_2)$  values over the total electrolysis time.

A detailed procedure for the determination of the average current efficiency of hydrogen evolution has already been given.<sup>7</sup>

SEM Microphotographs corresponding to morphologies of copper deposits, obtained with a quantity of electricity of  $10.0 \text{ mA h cm}^{-2}$ , were recorded on scanning electron microscope (SEM) JOEL, model T20, and a Tescan Digital Microscope.

#### RESULTS AND DISCUSSION

The copper deposits obtained at an overpotential of 1000 mV from 0.075, 0.30 and 0.60 M  $\text{CuSO}_4$  in 0.50 M  $\text{H}_2\text{SO}_4$  are shown in Fig. 1. For all these solutions, an overpotential of 1000 mV is for 250 mV higher than the plateaus of the limiting diffusion current density.<sup>11</sup> As can be seen from Fig. 1, holes formed due to attached hydrogen bubbles were the main morphological form obtained under these electrodeposition conditions. The shape of the obtained holes changed with increasing  $\text{CuSO}_4$  concentration, from those forming a honeycomb-like structure to dish-like ones and the mechanism of their formation has been widely studied.<sup>7,8,11</sup>

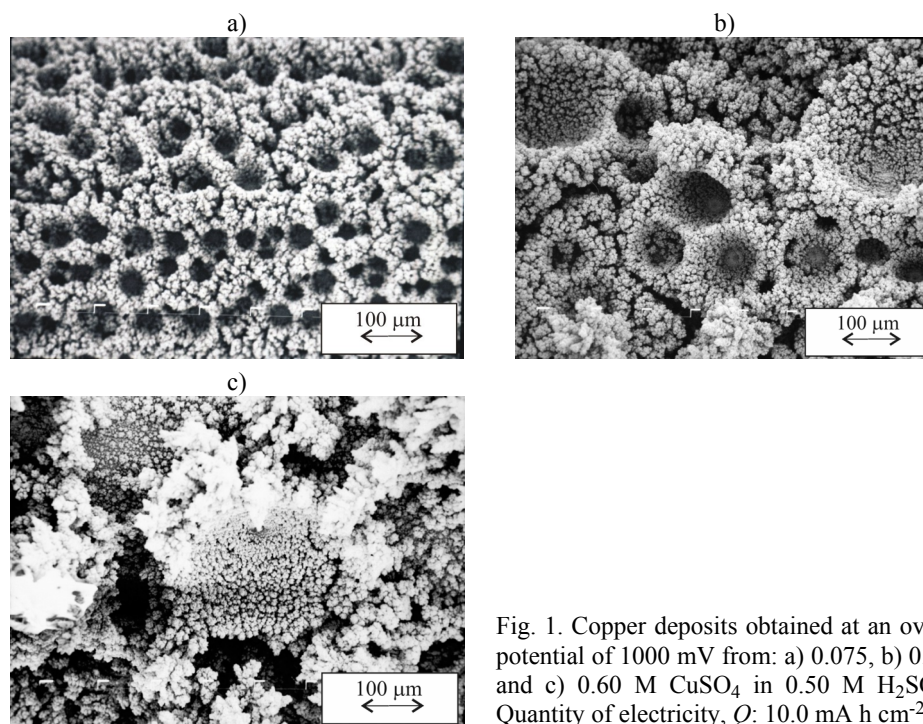


Fig. 1. Copper deposits obtained at an overpotential of 1000 mV from: a) 0.075, b) 0.30 and c) 0.60 M  $\text{CuSO}_4$  in 0.50 M  $\text{H}_2\text{SO}_4$ . Quantity of electricity,  $Q$ :  $10.0 \text{ mA h cm}^{-2}$ .

The average current efficiencies of hydrogen evolution,  $\eta_{\text{av}}(\text{H}_2)$ , obtained under these electrodeposition conditions were 68.7, 16.0 and 4.6 % from 0.075, 0.30 and 0.60 M  $\text{CuSO}_4$  in 0.50 M  $\text{H}_2\text{SO}_4$ , respectively.<sup>11</sup> These values were derived from the dependences of the current of electrodeposition and the volume of evolved hydrogen on the electrodeposition time, as shown in Fig. 2. It can be seen from Fig. 2 that increasing the concentration of  $\text{CuSO}_4$  led to a decrease of

the quantity of evolved hydrogen and, hence, the average current efficiencies of hydrogen evolution. At the first sight, this was unexpected because the concentration of  $\text{H}_2\text{SO}_4$  was the same in all the solutions. The explanation for it can be obtained by analysis of the ionic equilibrium of the species in the  $\text{CuSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$  system. The dependence of the relative concentration of hydrogen ions ( $\text{H}^+$ ) on the  $\text{H}_2\text{SO}_4$  concentration for different concentrations of copper ions is shown in Fig. 3. According to this equilibrium, increasing the copper ion 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.<sup>1</sup> The reason for this is that the addition of sulfuric acid to the solution decreases the concentration of free sulfate ions due to the formation of bisulfate ions, while the addition of cupric sulfate to the solution increases the concentration of bisulfate ions and decreases the concentration of hydrogen ions.

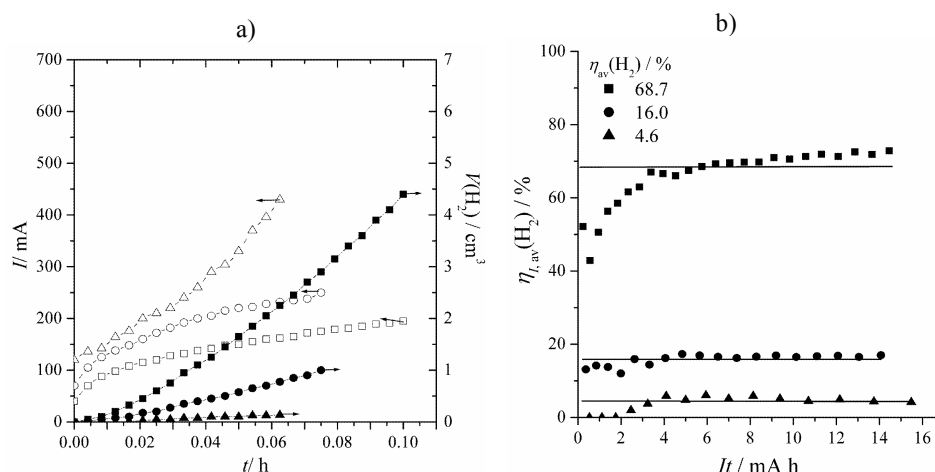


Fig. 2. The dependences of the current of copper electrodeposition and the volume of evolved hydrogen on the electrodeposition time (a) and the average current efficiencies for hydrogen evolution reaction on the quantity of used electricity (b) for copper electrodeposition at 1000 mV from 0.075 ( $\square$ ,  $\blacksquare$ ), 0.30 ( $\circ$ ,  $\bullet$ ) and 0.60 M ( $\triangle$ ,  $\blacktriangle$ )  $\text{CuSO}_4$  in 0.50 M  $\text{H}_2\text{SO}_4$ .

It is very clear that the decrease of the quantity of evolved hydrogen, and consequently, the average current efficiencies of hydrogen evolution (Fig. 2) is the result of decreasing the hydrogen ion concentration with the increasing copper concentration. Moreover, the acceleration of the electrochemical processes with increasing  $\text{CuSO}_4$  concentration had an unfavorable effect on the formation of the honeycomb-like structures. It was found<sup>12</sup> that the maximum  $\text{CuSO}_4$  concentration (in 0.50 M  $\text{H}_2\text{SO}_4$ ) which allowed the formation of the honeycomb-like structure was 0.15 M. Hydrogen evolution, which leads to the formation of the honeycomb-like structures, was vigorous enough to change the hydrodynamic conditions in the near-electrode layer. For copper sulfate solutions containing 0.15 M

CuSO<sub>4</sub> and less, in 0.50 M H<sub>2</sub>SO<sub>4</sub>, the critical quantity of evolved hydrogen leading to a change in the hydrodynamic conditions was estimated to correspond to  $\eta_{av}(H_2)$  of 10.0 %.<sup>12</sup> This was attained by electrodeposition at an overpotential of 800 mV from 0.15 M CuSO<sub>4</sub> in 0.50 M H<sub>2</sub>SO<sub>4</sub>.<sup>7</sup>

Vigorous hydrogen evolution is only one of the possible ways of changing the hydrodynamic conditions in the near-electrode layer. For example, a change in the hydrodynamic conditions can also be realized under imposed magnetic field (magnetohydrodynamic effects),<sup>13–15</sup> in an ultrasonic field<sup>16</sup> or by rotating the electrode.<sup>17</sup>

The above analysis of the electrodeposition processes with the different CuSO<sub>4</sub> concentrations and the same H<sub>2</sub>SO<sub>4</sub> concentration corresponds to a vertical analysis of the ionic equilibrium of the species in the CuSO<sub>4</sub>–H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O system. Horizontal analysis of this ionic equilibrium can be performed by analysis of the electrodeposition processes with a constant CuSO<sub>4</sub> concentration and different H<sub>2</sub>SO<sub>4</sub> concentrations.

For the horizontal analysis, 0.15 M CuSO<sub>4</sub> was selected, while the selected H<sub>2</sub>SO<sub>4</sub> concentrations were higher (1.0 M) and lower (0.125 and 0.25 M) than 0.50 M. According to the ionic equilibrium shown in Fig. 3, the H<sup>+</sup> concentration is higher for these solutions (the position of the Cu<sup>2+</sup> concentration of 0.15 M can easily be calculated) than for copper solutions containing 0.30 and 0.60 M CuSO<sub>4</sub> in 0.50 M H<sub>2</sub>SO<sub>4</sub>. This was confirmed by the higher average current efficiencies of hydrogen evolution obtained at an overpotential of 1000 mV from these solutions than those obtained from 0.30 and 0.60 M CuSO<sub>4</sub> in 0.50 M H<sub>2</sub>SO<sub>4</sub>. The average current efficiencies of hydrogen evolution,  $\eta_{av}(H_2)$  were: 20.3 % from 0.15 M CuSO<sub>4</sub> in 0.125 M H<sub>2</sub>SO<sub>4</sub>, 26.4 % from 0.15 M CuSO<sub>4</sub> in 0.25 M H<sub>2</sub>SO<sub>4</sub> and 45.7 % from 0.15 M CuSO<sub>4</sub> in 1.0 M H<sub>2</sub>SO<sub>4</sub>.<sup>18</sup> Based on the obtained values, it was expected that honeycomb-like structures would be obtained by electrodeposition from these solutions. However, honeycomb-like structures were only formed from 0.15 M CuSO<sub>4</sub> in both 1.0 M and 0.25 M H<sub>2</sub>SO<sub>4</sub> but not from 0.15 M CuSO<sub>4</sub> in 0.125 M H<sub>2</sub>SO<sub>4</sub>.<sup>18</sup> The copper deposit obtained at an overpotential of 1000 mV from 0.15 M CuSO<sub>4</sub> in 0.125 M H<sub>2</sub>SO<sub>4</sub> is shown in Fig. 4. Analysis of this copper deposit identified the presence of holes with shoulders of degenerated dendrites, and irregular channels formed by evolved hydrogen around the dendritic and cauliflower-like particles. The appearing of these morphological forms clearly indicates that the hydrodynamic conditions in the near-electrode layer remained unchanged during electrodeposition from this solution. This was very surprising owing to the very high average current efficiency of hydrogen evolution under which this deposit was formed. This indicates that the quantity of evolved hydrogen is not the only parameter responsible for a change in the hydrodynamic conditions in the near-electrode layer. Therefore, the recognition of the properties of the electrodeposition solutions, such as density

and surface tension, is very important.<sup>18</sup> The addition of H<sub>2</sub>SO<sub>4</sub> to an electroplating solution increases the density<sup>18,19</sup> and decreases the surface tension of an electroplating solution.<sup>18</sup> An increase of the density and a lowering of the surface tension of the solution decreases the break-off diameter of a hydrogen bubble<sup>18,20</sup> and, consequently, reduces the time required to achieve the critical size for its detachment from the electrode surface. Electrodeposition processes from such solutions will produce an sufficient amount of hydrogen bubbles which can cause an effective stirring of solution in the near-electrode layer and change the hydrodynamic conditions. This can be confirmed by the analysis of number of holes formed per mm<sup>2</sup> of surface area of the copper electrodes and the average diameter of holes obtained from 0.15 M CuSO<sub>4</sub> in 0.50 M H<sub>2</sub>SO<sub>4</sub> at 800 mV (the formed honeycomb-like structure with a  $\eta_{av}(H_2)$  of 10.8 %; changed hydrodynamic conditions in the near-electrode layer) and from 0.15 M CuSO<sub>4</sub> in 0.125 M H<sub>2</sub>SO<sub>4</sub> at 1000 mV (the honeycomb-like structure was not formed with a  $\eta_{av}(H_2)$  of 20.3 %; insufficient change of the hydrodynamic conditions in the near-electrode layer). The number of holes formed due to the attached hydrogen bubbles from 0.15 M CuSO<sub>4</sub> in 0.50 M H<sub>2</sub>SO<sub>4</sub> at 800 mV was 10 per mm<sup>2</sup> of surface area of the copper electrode,<sup>7</sup> while their average diameter was 98.7  $\mu$ m. This number was for about 40 % larger than the number of holes formed from 0.15 M CuSO<sub>4</sub> in 0.125 M H<sub>2</sub>SO<sub>4</sub> at 1000 mV. The average diameter of the holes formed from 0.15 M CuSO<sub>4</sub> in 0.125 M H<sub>2</sub>SO<sub>4</sub> at 1000 mV was about 20 % larger than the average diameter of those formed from 0.15 M CuSO<sub>4</sub> in 0.50 M H<sub>2</sub>SO<sub>4</sub> at 800 mV.

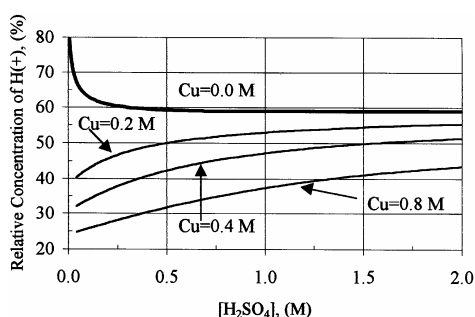


Fig. 3. Relative concentration of hydrogen ions as function of sulfuric acid and total copper concentrations, at 25 °C ( $c_{RH^+} = [H^+]/[HT]$ ) (Reprinted with permission of Elsevier).<sup>1</sup>

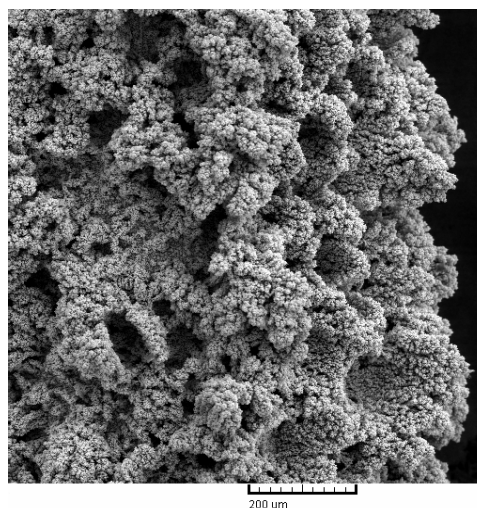


Fig. 4. The copper deposit obtained at an overpotential of 1000 mV from 0.15 M CuSO<sub>4</sub> in 0.125 M H<sub>2</sub>SO<sub>4</sub>. Quantity of electricity: 10.0 mA h cm<sup>-2</sup>.

The acceleration of electrochemical processes through increasing the temperature of electrolysis had an unfavorable effect on the formation of honeycomb-like structures.<sup>21</sup> Increasing the temperature led to a decrease in the number of holes because of the effect of temperature on some properties of the solutions, such as viscosity and surface tension.<sup>20–22</sup>

Horizontal and vertical analysis of the ionic equilibrium in the  $\text{CuSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$  system enabled the electrodeposition conditions leading to the formation of honeycomb-like structures to be systematized. It explained why  $\text{CuSO}_4$  concentrations higher than 0.15 M are unsuitable for the formation of this type of structures. The minimal  $\text{H}_2\text{SO}_4$  concentration of 0.25 M  $\text{H}_2\text{SO}_4$  (for 0.15 M  $\text{CuSO}_4$ ) allowing the formation of honeycomb-like structures was also determined.

#### CONCLUSIONS

Systematization of the electrodeposition conditions allowing the formation of honeycomb-like copper structures from acid sulfate solutions was made by analyzing the ionic equilibrium in the  $\text{CuSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$  system. The honeycomb-like structures can be formed by electrodeposition from solutions with low concentrations of Cu(II) ions (0.15 M  $\text{CuSO}_4$  and less) in an  $\text{H}_2\text{SO}_4$  concentration in the range from 0.25 to 1.0 M, at a temperature of  $18.0\pm 1.0$  °C, and at overpotentials positive with respect to the plateau of the limiting diffusion current density at which hydrogen evolution is vigorous enough to change the hydrodynamic conditions in the near-electrode layer.

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#### ИЗВОД

#### ЈОНСКА РАВНОТЕЖА У СИСТЕМУ $\text{CuSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ И ФОРМИРАЊЕ СТРУКТУРЕ ПЧЕЛИЊЕГ САЋА ЕЛЕКТРОХЕМИЈСКИМ ТАЛОЖЕЊЕМ БАКРА

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Анализирана је јонска равнотежа у систему  $\text{CuSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$  да би се систематизовали услови електрохемијског таложења бакра који доводе до формирања структуре пчелињег саћа. Показано је да су концентрације  $\text{CuSO}_4$  веће од 0,15 М непогодне за формирање структуре пчелињег саћа. Одређен је и опсег концентрација  $\text{H}_2\text{SO}_4$  у којем се формира оваква структура. Услови који доводе до формирања структуре пчелињег саћа су: електрохемијско таложење из раствора са концентрацијом Cu(II) од највише 0,15 М и опсегом концентрација  $\text{H}_2\text{SO}_4$  од 0,25 до 1,0 М, температуре од  $18,0\pm 1,0$  °C, и на пренапетостима позитивнијим од оних који одговарају платоу граничне дифузионе густине струје, на којима

је издвајање водоника довољно интензивно да промени хидродинамичке услове у прикатоном слоју.

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