

# Microscopic analysis of electrodeposited copper in the hydrogen co-deposition range

Nebojša D. Nikolić<sup>1</sup>

1. ICTM – Institute of Electrochemistry, University of Belgrade, Njegoševa 12, Belgrade, Serbia

nnikolic@tmf.bg.ac.rs

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Electrodeposition is a very valuable way of obtaining open porous structures of copper with an extremely high surface area, because such structures are ideally suited for electrodes in many electrochemical devices, such as fuel cells, batteries and chemical sensors [1, 2]. Such copper structures, denoted as both 3-D foam [1, 2] and honeycomb-like ones [3, 4], are obtained at high current densities and overpotentials, where parallel to copper electrodeposition, the hydrogen evolution reaction occurs. The basic characteristics of these electrodes are: holes or pores formed due to attached hydrogen bubbles and agglomerates of copper grains or dendrites among them. The walls of the holes are very porous and they are also composed of disperse agglomerates of copper grains [4] or of dendritic particles [1].

SEM microphotograph of the typical honeycomb-like deposit obtained by electrodeposition from 0.15 M CuSO<sub>4</sub> in 0.50 M H<sub>2</sub>SO<sub>4</sub> at an overpotential of 1000 mV is shown in Fig. 1a. Formation of this copper electrode was accompanied by the quantity of evolved hydrogen which corresponded to an average current efficiency of hydrogen evolution of 30.0 % [3]. The number, distribution and pore size can be easily controlled by the choice of appropriate electrolysis parameters [5, 6]. Increasing overpotential, decreasing concentration of Cu(II) ions and increasing concentration of H<sub>2</sub>SO<sub>4</sub> as the supporting electrolyte intensifies the hydrogen evolution reaction and, consequently, the number of holes formed per mm<sup>2</sup> surface area of electrode is increased [5, 6].

The increase of the specific surface area of the porous electrodes manifested through the decrease of the size of the pores, as well as the branches in the foam or agglomerates of copper grains in the honeycomb-like structures can be achieved by the addition of specific substances, known as additives, to the plating solution [7-9], or by the application of pulsating overpotential (PO) regime with the constant deposition pulse and different pause durations [10].

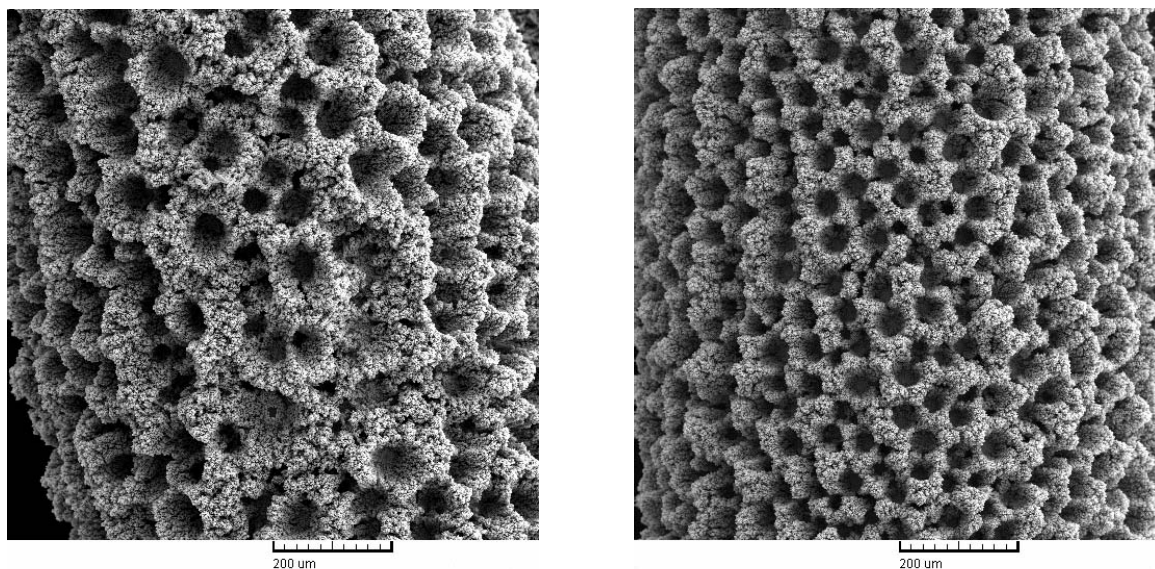
Figure 1b shows SEM microphotograph of the honeycomb-like structure electrodeposited from the same solution by square-wave PO with a deposition pulse of 10 ms and a pause of 10 ms. Amplitude overpotential applied for the production of this structure was 1000 mV. The average current efficiency of hydrogen evolution which corresponded to the formation of this structure was 27.2 %. The application of PO regime led to the decrease of the average diameter of holes for about 45 % [10]. On the other hand, the number of the holes formed by this square-wave PO was three times larger than the one obtained by electrodeposition in the constant potentiostatic regime. The increase of the number of the formed holes and the decrease of their number can be ascribed to suppressed coalescence of closely formed hydrogen bubbles.

The shortening of deposition pulse from 10 to 3 ms (keeping pause duration of 10 ms and amplitude overpotential of 1000 mV) led to change of copper morphology formed around holes from cauliflower-like agglomerates of grains to dendrites. The number, distribution and

hole size remained unchanged. This change of morphology of electrodeposited copper around holes can be ascribed to the change of effectiveness of stirring of solution by evolved hydrogen. Also, the shortening of deposition pulse duration from 10 to 3 ms led to energetic savings in production of honeycomb-like structures for about 15 %.

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**Figure 1.** Honeycomb-like deposits obtained by electrodeposition: a) at a constant overpotential of 1000 mV; b) by square-wave PO: amplitude overpotential of 1000 mV; deposition pulse of 10 ms and a pause of 10 ms. (Reprinted from Ref. [10] with permission from Elsevier.)