# METALLIC MICROELECTRODES OF DIFFERENT GEOMETRIES PREPARED BY 3D ELECTROCHEMICAL PRINTING TECHNIQUE

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Palavras Chave: 3D electrochemical printing, microelectrodes, electrode geometry

Abstract

Metallic microelectrodes with geometries such as positive and negative hemispherical and cylindrical were prepared using the recently developed 3D electrochemical printing technique.

#### Introdução

Three-dimensional (3D) electrodes have superior electrochemical performance than two-dimensional (2D) or even chemically modified electrodes (CME). For example, the electrochemical reaction of paminophenol at a 3D electrode was compared to that at a 2D electrode<sup>1</sup>. The anodic and cathodic currents were, respectively, around 10 and 8 times higher at the 3D electrode. Besides, a review showed the influence of electrode geometry on voltammetric sudies<sup>2</sup>. The 3D electrochemical printing technique developed in our laboratory allows obtaining metallic micro- and macro-structures from solutions containing the cation of the metal to be printed. The main goal of this study was evaluate the ability of the developed 3D electrochemical printing to build microelectrodes with different geometries, in view to use them in electrochemical applications. Microelectrodes of different metals and geometries were shaped. For copper microeletrodes, a solution of 0.20 mol  $L^{-1}$  KNaC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>.4H<sub>2</sub>O was used as supporting electrolyte. As source of Cu<sup>2+</sup>, a mixture of 0.30 mol  $L^1$  CuSO<sub>4</sub> and NH<sub>4</sub>OH was employed. The solution pH was adjusted to 6.4 with 0.50 mol L<sup>-</sup> <sup>1</sup> H<sub>2</sub>SO<sub>4</sub>. The hydrodynamic flux was 5.0 L min<sup>-1</sup>. A current of 75 mA was applied to the negatively charged printing table. The 3D electrochemically printed copper microelectrodes were obtained at ambient temperature.

### **Resultados e Discussão**

Figures bellow show copper microelectrodes with different geometries acquired by 3D electrochemical printing technique. As can be seen, well-defined high-resolution printed 3D microelectrodes were obtained. The ability to fabricate high-resolution 3D structures suggests substantial promise to build electrodes with different geometries and sizes as vertical, helical and zigzag-shaped pillars and others. In addition, the capability to print multiple functional metals directly with high resolutions structures is a key attribute of 3D electrochemical printing technology for extending its potential applications.



**Figure 1.** Optical microscopy of a positive hemispherical copper microelectrode ( $r = 50 \ \mu m$ )



Figure 2. Optical microscopy of a negative hemispherical copper microelectrode (r =  $50 \ \mu m$ )



Figure 3. Optical microscopy of a cylindrical copper microelectrode (r = h = 50  $\mu$ m)

#### Conclusões

This work demonstrates the capability of the developed 3D electrochemical printing technique to build high-resolution 3D microelectrodes using various functional metals and its potential application for the fabrication of 3D structures that are difficult to achieve by means of conventional methods.

## Agradecimentos

CAPES, CNPq, UFSC.

39ª Reunião Anual da Sociedade Brasileira de Química: Criar e Empreender

<sup>&</sup>lt;sup>1</sup> Honda, N. et al.; Bioesens. Bioelectron. 2005, 20, 2306.

<sup>&</sup>lt;sup>2</sup> Molina, A. et al.; J. Electroanal. Chem. 2015, 756, 1.