

Membrane-assisted fabrication of copper nanostructures and their characterization

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Abstract

The aim of the present study is to prepare new copper nanostructured electrodes by copper electroplating in porous nonconductive membranes and to examine them by scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS).

Keywords: Nanomaterials, copper nanostructures, electron microscopy, electrochemical impedance spectroscopy

Introduction

Nanomaterials and nanotechnology have received considerable attention recently due to the potential applications and properties that differ from those of bulk materials. For example, biologically important species can be immobilized on the nanostructures and also the area of the nanostructured electrode is larger in comparison to the flat electrode. Nanostructured surfaces seem to be promising in the field of sensing and biosensing as well as fuel cells, electronic elements, magnetic storage media, microsensors, optical devices, etc. (Hubalek et al. 2007; Metzger et al. 2000; Ramanathan et al. 2006). One of the most effective ways to produce dense arrays of metal nanostructures is metal electrodeposition into nanoporous nonconductive membrane.

Materials and methods

The membranes were composed of Al_2O_3 and vapour deposited with copper on one side in order to provide an ohmic contact and to cover the nanopores. During copper electroplating (from 0.8M CuSO_4 and

0.4M H_2SO_4 with current density 60 mA/cm^2 , anode Cu wire, temperature 22°C), copper ions in a solution are attracted to the metal film at the bottom of the nanopores where they deposit in the form of solid metal. After filling the nanopores with copper, nanoporous membrane is dissolved in NaOH and the nanostructured surface is obtained (Fig 1).

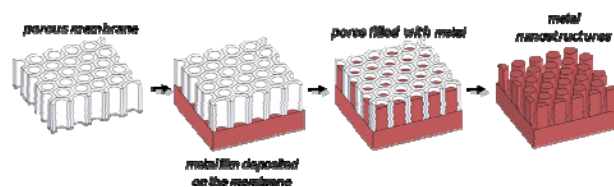


Figure 1: Illustration of copper nanostructure fabrication

The created copper nanostructures were examined using scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS). The conditions, under which majority of EIS experiments were performed, are summarized in Table 1.

Table 1: EIS experiment

electrolyte	1 mM KCl
frequency range	1MHz - 1kHz
potential	0 V
amplitude	0,01 V
number of frequencies	60
frequency step	logarithmic
wave type	single sine
auxiliary electrode	Cu
reference electrode	Ag/AgCl/3MKCl
temperature	22°C
device	Autolab 302N (EcoChemie)
software	Nova 1.5

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Results and Discussion

An example of real copper nanostructures, formed by electroplating into membrane, is in Fig 2. Apart from SEM, the copper

nanostuctures were also characterized by EIS (Barsoukov 2005). The impedance has been carried out before and after electrodeposition into membrane, as well as after dissolution of the membrane. The EIS exhibited two semicircles (one in the high frequency region and one in the low frequency region) if the nanoporous membrane was present. In the case of EIS measured after dissolution of the membrane, the semicircle in the low frequency region was usually replaced with a straight line. An example of Nyquist plot is in Fig 3. The two semicircles in the Nyquist plot, obtained from the measurements with porous membranes, have been simulated using software Nova 1.5. The proposed equivalent circuit consists of one RC element, in which the capacitance C is usually replaced with the constant phase element Q, and the second part of the circuit is composed of another Q in parallel with finite Warburg impedance O. After dissolution of the membrane, the electrode behaves as an imperfect electrode coating.

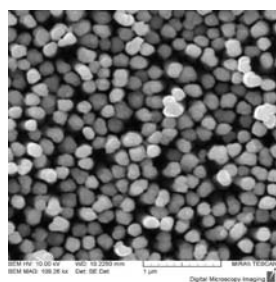


Figure 2: An example of copper

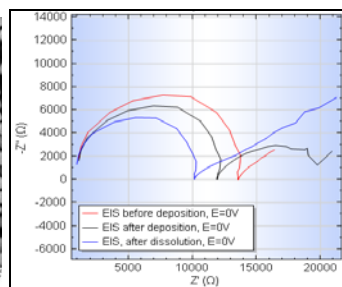


Figure 3: EIS measured with copper auxiliary electrode

Conclusion

Membrane-assisted fabrication of copper nanostructures was used for the preparation of an array of nanostructures on a vapour deposited film. These nanostructures were examined by SEM and EIS. An equivalent electrical circuit for measured impedance spectra has been proposed.

Acknowledgement

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