SEM, EDS and Electrical Capacitance Study on Electrodeposited Ni-Cu Layers

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Nickel-Copper metallic layers were deposited onto a steel substrate by using the electrochemical method. The morphology and the chemical composition of the deposited layers were studied by scanning electron microscopy. The electrical capacitance was measured on a functional supercapacitor made of two Ni-Cu deposited layers and a Nafion 117® membrane hydrated with distilled water, which served as a dielectric separator.

Keywords: electrodeposited Ni-Cu; SEM; EDS; supercapacitor; capacitance; temperature

Supercapacitors are devices used for energy storage and release at demand intended to replace the conventional batteries [1-5]. The research in energy storage field is focused on improving the existing energy devices in terms of storage capacity, easy charging and extended lifetime [6].

Electrodeposition is a technique used to obtain materials with controlled structure and particular properties suitable to be used in the supercapacitors manufacture [7,8].

Several studies have been carried out to investigate the electrochemical behaviour of Ni-Cu alloys in acidic, neutral or slightly alkaline solutions, but few have been reported on this subject [9-11].

The high interest shown in the study of Ni-Cu alloys is related to their corrosion resistance, mechanical and magnetic properties, and optical properties. This type of alloy can be used to make optical mirrors due to its high reflection and gloss [12-14]. In addition to these properties, (such as: electrical and thermal conductivity, ductility and malleability are added [13-16].

The Ni-Cu electrochemical deposition process is carried out in two steps. In the first stage, a dendritic Ni-Cu deposition is formed by applying a controlled current density, and hydrogen bubbles are generated at the surface of the electrode. During Ni-Cu electrochemical deposition the hydrogen bubbles disrupt the continuous growth of metal layer generating dendritic morphologies. In the second stage, the production of the pores in the Ni-Cu layer occurs due to the selective Cu dealloying from the Ni-Cu dendritic structure. The convection created by detachment of hydrogen bubbles leads to the reduction of the diffusion layer from the surface of the electrode [4, 17].

The aim of this paper is to characterize some Ni-Cu deposits on steel substrates obtained at different deposition parameters that may be used as supercapacitor components.

Experimental part
Materials and methods

A steel plate of 1.6 cm² was used as metallic substrate for the deposition. The plates were mechanically polished with emery paper, rinsed with water and ethanol. They are electrically isolated on one side, so that the layer deposition takes place only on one side of the steel plate.

The electrochemical deposition cell contained a platinum mesh as anode (active surface area 5 cm²), the steel plate as a cathode, the electrolyte solution containing $NiSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$, H_2SO_4, HCl (Sigma-Aldrich, ChimReactiv) similar to that reported in [11]. The electrochemical installation is made of the cell, a variable resistance, a power source, an ammeter and a thermostatic water bath to maintain the temperature at constant values.

The Ni-Cu depositions working parameters: a). temperatures namely 30°C and 40°C, b). current densities namely 0.7A/cm², 1.1A/cm², 1.5A/cm², c). deposition times of 50s, 100s, 150s.

Methods of investigation

The morphological and compositional properties of the Ni-Cu deposited layers were studied by Scanning Electron Microscopy (SEM, Zeiss Merlin Gemini II) and Dispersive Energy Spectrometry (using SEM, OXFORD Instrument with X-Max 50 detector).

The electrical capacity performance was assessed by constructing a symmetrical capacitor supercapacitor made of two steel plates covered at identical parameters, with Ni-Cu layers containing an activated Nafion 117® membrane as a dielectric separator. The membrane was used in hydrated state in distilled water. The measurements were made with a dedicated professional LCR-Multimeter 4095 (Germany), the system configuration is similar as in [18].

Results and discussions
Morphology

An alloy of Fe, C and O having a dendritic structure of Ni-Cu deposits was used as the substrate.

Figure 1 A show the SEM images of Ni-Cu layers, deposited at a current density of 1.5A/cm² for 150 s, at a temperature of 30°C. One may see that the deposit is porous, cracked and very thick with the dendritic shape of the crystals same as the deposition obtain at 100s (B). As seen at the samples deposited at a high current and high density, the layer deposited is a thin film on the surface of the crystals formed by the hydrogen bubble convection process. The pore diameters are approximately 10μm and the connecting bridges thickness is approximately 18μm for the deposition at 150 s and for 100 s pore diameter is

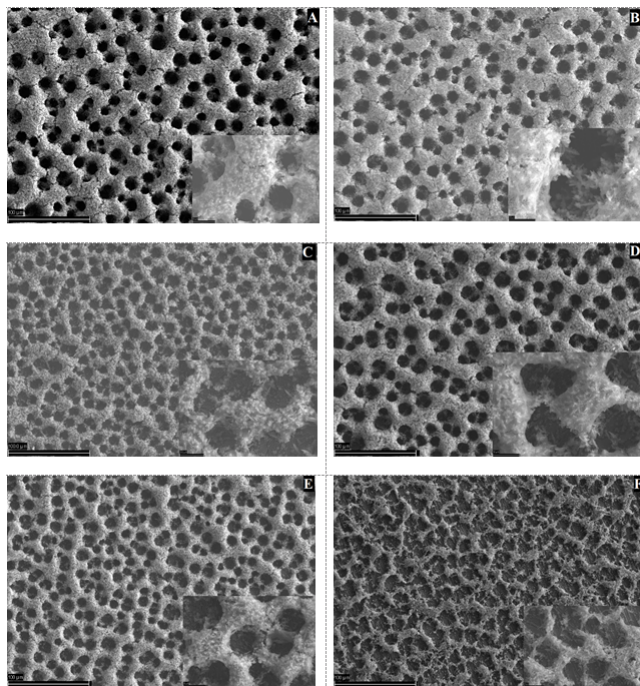Fig. 1. SEM images of Ni-Cu deposition obtained at a current density of 1.5A/cm², for 150s (A), 100s (B) and 50s (C), and a current density of 0.7A/cm² for 150s (D), 100s (E) and 50s (F) at a temperature of 30°C.
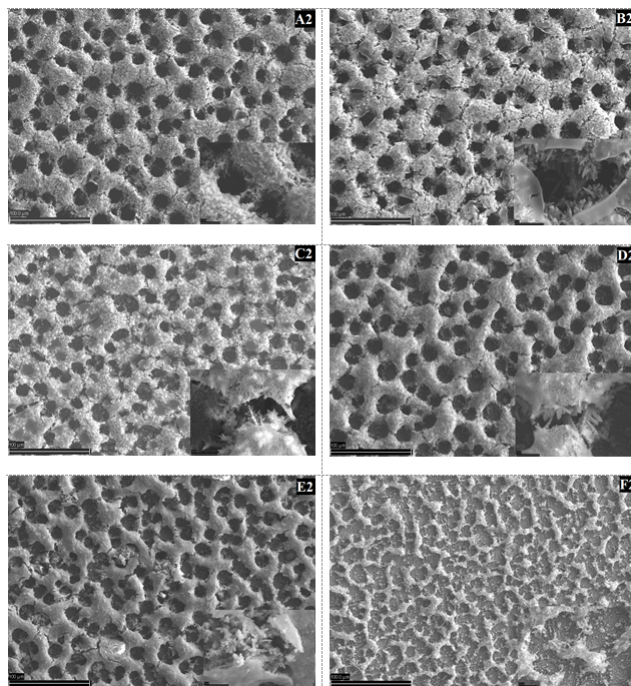

Fig. 2. SEM images of Ni-Cu deposition obtained at a current density of 1.5A/cm², for 150s (A2), 100s (B2) and 50s (C2), and a current density of 0.7A/cm² for 150s (D2), 100s (E2) and 50s (F2) at a temperature of 40°C

about 11μm and the connecting bridges thickness is about 14μm. For the same current density but a deposition time of 50 s (C), the deposition is one with defined but thin pores, that the steel substrate is visible between the bonding bridges. The pore diameter is about 10μm and the connecting bridges thickness is about 9μm.

At a deposition current density of 0.7A/cm² for 150 s (D) the Ni-Cu layer is very thick and porous. The pore diameter is approximately 14μm, while the bond bridge thickness is about 14μm. If the deposition time decreases at 100 s (E) the pore diameter drops down to approximately 9μm and the thickness of the connecting bridges is to 7μm. The deposition performed at 50 s (F) and at current density of 0.7A/cm² is very thin, the steel substrate can be easily seen, but still have a dendritic shape of crystals. The pore diameter is about 14μm and the connecting bridges thickness is about 7μm.

Figure 2 A2 shows the SEM images of Ni-Cu layers, deposited at a current density of 1.5A/cm² for 150 s, at a temperature of 40°C. One may see that the deposit is porous, cracked and very thick with the dendritic shape of the crystals same as the deposition obtain at 100s (B2). The pore diameter is approximately 15μm and the connecting bridges thickness is approximately 16ìm for the deposition at 150 s and for 100 s, the pore diameter is about 13ìm and the connecting bridges thickness is about 21μm.

For the same current density but a deposition time of 50 s (C2), the deposition is one with defined but thin pores, that the steel substrate is visible between the bonding bridges. The pore diameter is about 13μm and the connecting bridges thickness is about 18μm. At a deposition current density of 0.7A/cm² for 150 s (D2) the Ni-Cu layer is thick and porous. The pore diameter is approximately 19μm, while the bond bridge thickness is about 15μm.

If the deposition time decreases at 100 s(E2) the pore diameter drops down to approximately 17μm and the thickness of the connecting bridges is to 13μm. The deposition performed at 50 s (F2) and a current density of 0.7A/cm² is very thin, the steel substrate can be easily seen,

but still have a dendritic shape of crystals. The pore diameter is about 13 μm and the connecting bridges thickness is about 8μm.

Composition

The nickel concentration increases as the deposition time and current density decreases. At a deposition time of 50 s , a current density of 0.7A/cm² and a deposition temperature of 30°C, the Ni concentration is 16.13% and that of Cu is 57.7% while at a deposition time of 150 s and a current density of 1.5/cm², Ni concentration is 8.35% and Cu is 42.72%.

At a current density of 1.1A/cm² regardless of the time of deposition, the Ni concentration is the highest. At a deposition time of 150 s , the Ni concentration is 15.94%, at 100 s, is 17.39% and at 50 s, is 30%.

At a deposition temperature of 40°C, the Ni concentration has the highest values at a deposition of 100 s and a current density of 1.5 A/cm², it does not exceed 22.69% and the Cu concentration is 34.71%.

The lowest Ni concentration, 6.9%, is recorded for a deposition at a current density of 1.1 A/cm² for 150 s and the equivalent Cu concentration is 45.4%.

Electrical capacitance measurements

In figure 3 is shown that the values of the electrical capacitance varies between 16.9μF/cm² at a deposition temperature of 30°C and 16.4μF/cm² at a deposition temperature of 40°C for a current density of 0.7A/cm² and 50 s deposition time. If the time deposition increases up to 150 s, the electrical capacitance varies between 8.8μF/cm² at a deposition temperature of 30°C and 17.9μF/cm² at a deposition temperature of 40°C.

If the deposition current density increases at 1.5 A/cm², the electrical capacitance at a deposition time of 50 s increases up to 35.8μF/cm² at a deposition temperature of 30°C and decreases to 9.3μF/cm² when the deposition temperature is 40°C. If the time deposition increases up to 150 s, the electrical capacitance varies between 42.9μF/
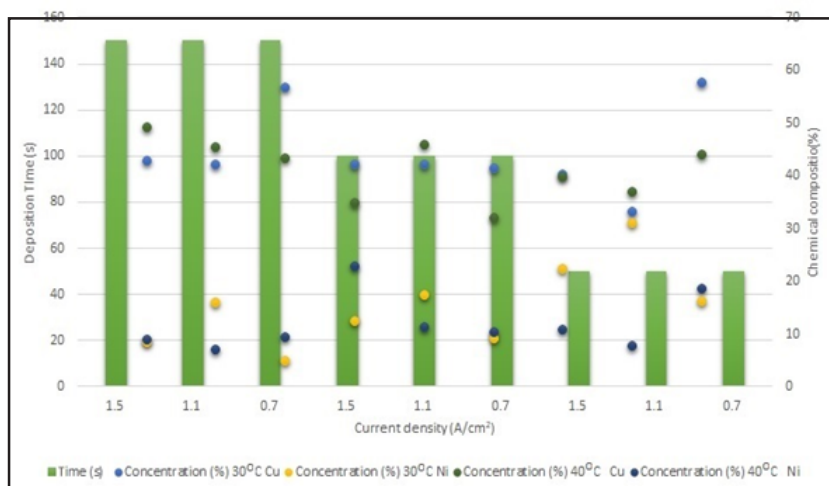
Fig. 3. The Ni-Cu composition in the deposited layers

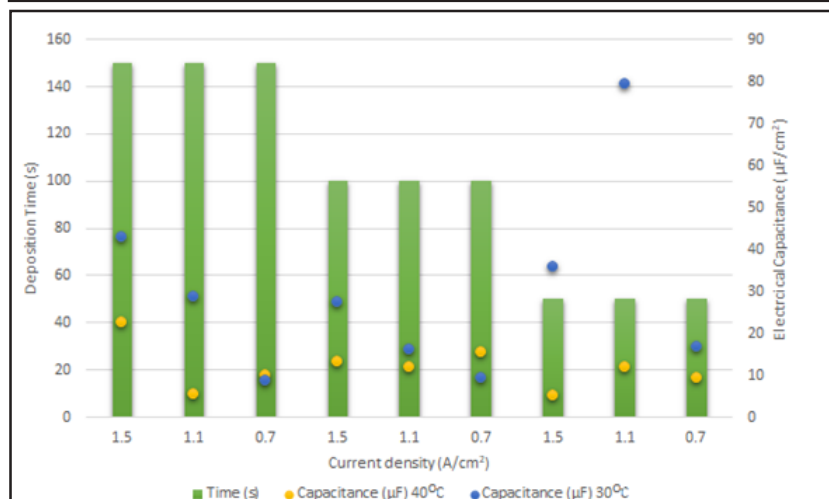Fig. 4. The variation of the capacitance depending on temperature, time and current density

cm^2 at a deposition temperature of 30°C and 40.4μF/cm^2 at a deposition temperature of 40°C.

The highest value of electrical capacitance, 79.4μF/cm^2, is measured at a deposition performed at a current density of 1.1A/cm^2 at 50 s deposition time and 30°C deposition temperature.

Conclusions

Electrodeposition of Ni-Cu alloys carried out in acidic electrolyte solutions was used to obtain a nanostructured metallic foam in order to be used as electrode plates for supercapacitors. The Ni-Cu deposits on steel plates have randomly distributed circular pores with dendritic crystal structure. The parameters applied to the deposition stage, have a strong influence on the thickness, morphology of the final deposits, affecting also the pore diameters and the connecting bridges and the Ni-Cu ratio.

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