

Practical Considerations Regarding the Electrodeposition of Ni-Cu Layers as Potential Supercapacitors Plates

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In this paper the properties of some Ni-Cu layers deposited onto a steel substrate were discussed. One has investigated the influence of the electrodeposition process on the final properties of the Ni-Cu layers, in order to see if these electrodeposited layers could be used as supercapacitor plates. The structural characterization was investigated by scanning electron microscopy and their composition by dispersive energy spectrometry. One has built a number of functional supercapacitors using Ni-Cu layer plates inserting in between them a separation membrane and their capacitance values were determined.

Keywords: electrodeposited Ni-Cu layers, SEM, EDS, supercapacitor plates, capacitance

The rapid development of the global economy, the associated problems of fossil fuels, the increase in environmental pollution and the high energy consumption in the industrial and public sector lead to a continuous race for the development of clean, sustainable energy sources, as well as new technologies associated with conversion and storage of produced energy [1]. Some of the most practical and efficient technologies for converting and storing the energy is directly related to the electrochemical devices such as batteries, fuel cells and electrochemical supercapacitors [2-3].

Supercapacitors are energy storage devices with improved features over conventional capacitors: the ability to act as a secondary battery and to store a high amount of energy and have attracted great attention as energy storage devices as they can replace batteries due to a high power density, a fast loading electrical charge and a high lifespan [4-8].

Copper alloys are more resistant to corrosion than copper itself due to the incorporation of corrosion resistant metals such as nickel [9].

Electrodeposition is the most common method of forming Ni-Cu thin films. This method allows the control of the properties of this type of alloy, the phase composition and its morphology by adjusting the electrochemical deposition conditions such as: current density, deposition time, deposition temperature, electrolyte concentration and pH [2, 10-11].

Nanoporous metal structures obtain in the form of foam are 3D structures with interconnected walls, showing porosities greater than 50% [10]. These structures allow rapid diffusion of active species through the material and provide a greater surface area for electrochemical reactions [12-15].

The aim of this paper is to characterize some Ni-Cu deposits obtained on steel substrates that may be employed as supercapacitor plates. The morphological and chemical properties of the Ni-Cu depositions was performed by scanning electron microscopy, dispersive energy spectrometry and the properties of the obtained supercapacitors were determined by measuring their capacitance.

Experimental part

The metallic substrate

A steel plate with a deposition area of 1.6 cm² was used as metallic substrate. The plates were mechanically polished with different emery paper grains: coarse 800µm and fine 2000µm, rinsed with distilled water and ethanol, and dried at room temperature. After drying, the plates were electrically isolated on one side with Lackstift isolating paint, so that the Ni-Cu deposition takes place only on one side of the plate.

The deposition solution

The deposition solution was prepared at room temperature and it consists of a mixture of 0.5M CuSO₄·5H₂O (Sigma-Aldrich), 0.01M NiSO₄·7H₂O (Sigma-Aldrich), 1.5M H₂SO₄ (Chim Reactiv), 1M HCl (Chim Reactiv). The deposition was performed in a 120 mL electrolyte solution galvanic cell [15].

The electrochemical deposition cell had a steel plate that worked as a cathode, a platinum mesh with a surface area of approximately 5cm² as anode and the above said electrolyte solution (fig. 1). The Ni-Cu depositions were performed at room temperature. Once the current is set, the experiments started with the experimental parameters requiring the longest time and the highest current density, changing the electrolyte solution after every 9 depositions. Each plate was rinsed with distilled water and dried in the

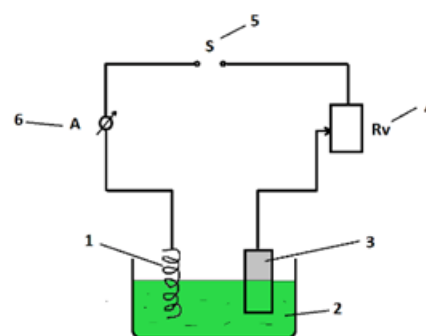


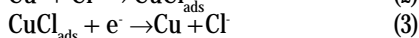
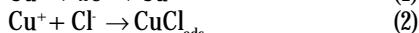
Fig. 1. Schematic representation of the deposition cell of the Ni-Cu layers. 1. Platinum mesh, 2. Electrolyte solution, 3. Steel plate, 4. Variable resistance, 5. Power source, 6. Ammeter

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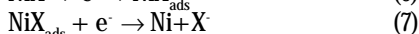
oven at 200°C for one hour [15]. In order to obtain deposits with different properties, the deposition of the Ni-Cu films was performed using various combinations of operating parameters as follows: the deposition time (50s, 100s, 150s) and the current density (0.7A/cm², 1.1A/cm², 1.5A/cm²). High current densities are considered effective for high concentration of copper deposits [16].

Reactions occurring in the electrochemical cell

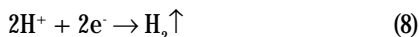
Generally, in an electrochemical cell, there are 2 types of characteristic reactions: an oxidation reaction, that occurs at the anode and a reduction one that takes place at the cathode. The mechanism of the Ni-Cu layer deposition is a complex one. At the cathode, the copper deposition reactions take place in two stages, the first stage is the reduction of the Cu²⁺ to Cu, which is the rate determining step, and the second one is the complexation of the Cu ions due to chlorine and CuCl adsorption on the Cu surface [15, 17].



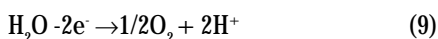
Also, at the cathode, nickel deposition reactions take place in two consecutive stages and form an intermediate complex of NiX_{ads} type where the anion X is chlorine [15].



A secondary reaction that takes place at the cathode, is the reduction of H⁺.



At the insoluble anode of the deposition cell, the reaction that takes place is the evolution of oxygen:



Methods of investigation

In order to determine the morphological and compositional properties of the Ni-Cu layers, one has employed some non-destructive methods, such as Scanning Electron Microscopy (SEM) for the determination of the morphology and structure of the crystals deposits and Dispersive Energy Spectrometry (EDS) for the determination of the composition of the layers.

The tests were performed on a ZEISS Merlin Gemini II scanning microscope with a resolution of 0.9 nm. The detector used to perform the qualitative and semi-quantitative analysis was an EDS OXFORD Instrument X-Max 50 detector. The working distance between the sample and the microscope column was 8.5 mm. An acceleration voltage of 15keV and an electron beam intensity of 2nA were used. Electronic images were made at different magnifications in order to observe the structure of deposits at different deposition current densities and times.

Supercapacitors and capacitance measuring

Capacitance measurement was performed on each built supercapacitor consisting of two steel plates having Ni-Cu alloy deposited at identical parameters and an activated Nafion 117® membrane hydrated with distilled water, which serves as a dielectric separator. Measurements have

been made with a dedicated professional LCR-Multimeter 4095, Germany, in order to determine the capacitance of the supercapacitor.

Unlike the methods reported in the literature, where the capacity assessment was done through electrochemical impedance spectroscopy (EIS), this method has the advantage of a direct measurement in a system whose configuration is similar to that reported in [18-20].

Results and discussions

Substrate composition

Prior to deposition, the steel substrate was analyzed in order to determine its characteristics. The composition of the metal substrate was determined using EDS. The substrate used is an alloy of 94.63% Fe with 4.44% Cu and 1,15% C. In figure 2 is shown the image of the steel substrate obtained with the electron microscope, where one may see the traces left behind by the mechanical preparation of the surface.

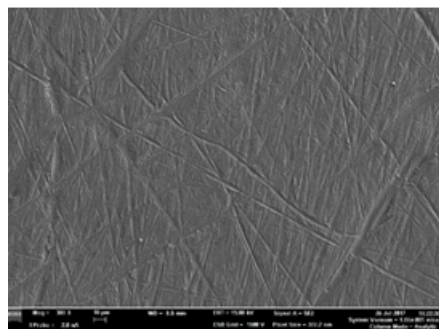


Fig. 2. SEM image of the steel substrate (300x magnification)

The structure of the Ni-Cu deposits

The structure of Ni-Cu electrochemical deposits was studied by SEM. The structure has been studied at elevations from 40x and over 14kx in order to identify the shape of the pores and their density. One may see from the images obtained that the morphology varies depending on the deposition parameters, that the upper surface of the film is matte, with cracks and that the formation of dendritic crystals on the first layer is perpendicular to the steel plate.

Figures 3A and 3B show the SEM images of the Ni-Cu layers, deposited at a current density of 1.5A/cm² for 150 s. One may see that the deposition is one with well defined pores and very thick connecting bridges with the dendritic

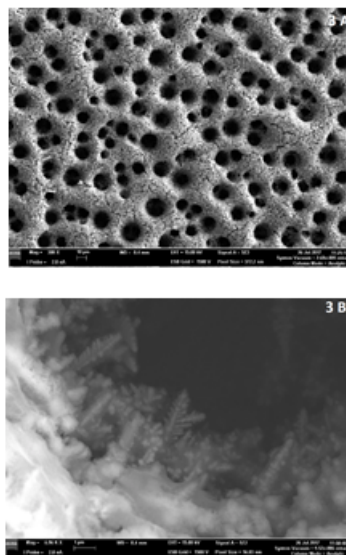


Fig. 3. SEM images of Ni-Cu deposition obtained at a current density of 1.5A/cm² for 150 s, 300x magnification (3A) and 7 000x (3B)

shape of the crystals. The pore diameter is approximately $13\mu\text{m}$ and the thickness of the connecting bridges is approximately $20\mu\text{m}$. Also, on the surface of the deposit is a film formed by the hydrogen bubble convection process.

Figures 4A and 4B show the electronic images of Ni-Cu deposits obtained at a current density of $1.5\text{A}/\text{cm}^2$ for 100 s. One may see that the deposition is one with well defined and very thick pores with the dendritic shape of the crystals. The pore diameter is approximately $8\mu\text{m}$ and the connecting bridges thickness is approximately $18\mu\text{m}$. As in the above case, there is a very thin film on the surface of the crystals.

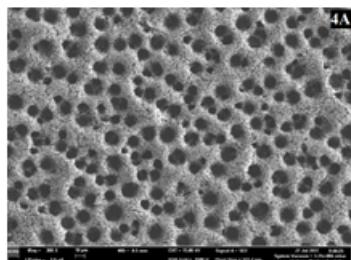
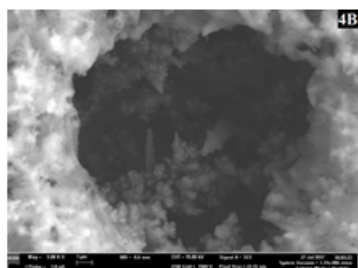


Fig. 4. SEM images of Ni-Cu deposition obtained at a current density of $1.5\text{A}/\text{cm}^2$ for 100 s, 300x magnification (4A) and 5 000x (4B).



Figures 5A and 5B show the electronic images of Ni-Cu deposits obtained at a current density of $1.5\text{A}/\text{cm}^2$ for 50 s. One may see that the deposition is one with defined and thick pores with the dendritic shape of the crystals. The pore diameter is approximately $10\mu\text{m}$ and the connecting bridges thickness is approximately $10\mu\text{m}$.

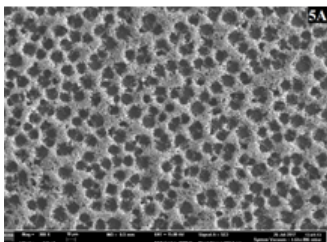
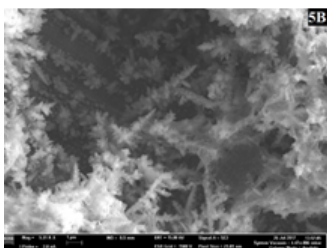


Fig. 5. SEM images of Ni-Cu deposition obtained at a current density of $1.5\text{A}/\text{cm}^2$ for 50 s, 300x magnification (5A) and 5 000x (5B).



Figures 6A and 6B show the SEM images of the Ni-Cu layers deposited at a current density of $0.7\text{A}/\text{cm}^2$ for 150 s. The deposition is one with well defined and thick pores with the dendritic shape of the crystals. The pore diameter is approximately $12\mu\text{m}$ and the connecting bridges thickness is approximately $13\mu\text{m}$.

In figures 7A and 7B show the SEM images of Ni-Cu layers obtained at a current density of $0.7\text{A}/\text{cm}^2$ for 100 s. One may see that the deposit is porous with the dendritic form of the crystals. The pore diameter is approximately $12\mu\text{m}$ and the connecting bridges thickness is about $15\mu\text{m}$.

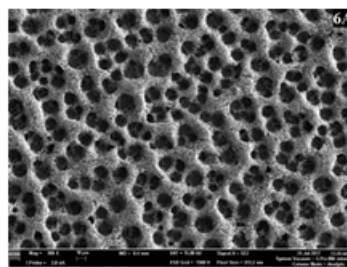


Fig. 6. SEM images of Ni-Cu deposition obtained at a current density of $0.7\text{A}/\text{cm}^2$ for 150 s, 300x magnification (fig. 6A) and 5 000 (fig. 6B)

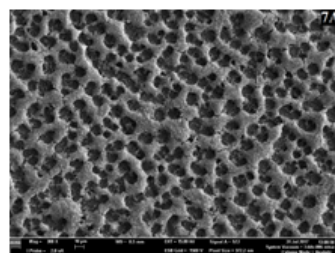
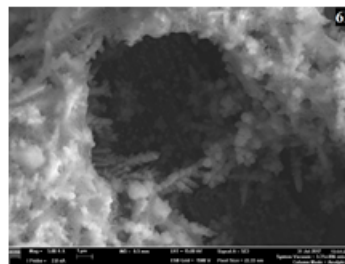


Fig. 7. SEM images of Ni-Cu deposition at a current density of $0.7\text{A}/\text{cm}^2$ for 100 s, 300x magnification (7A) and 5 000x (7B)

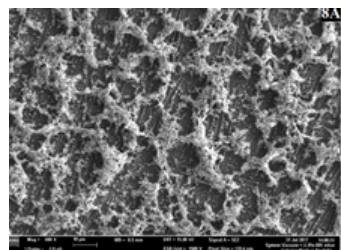
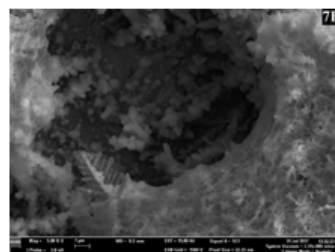
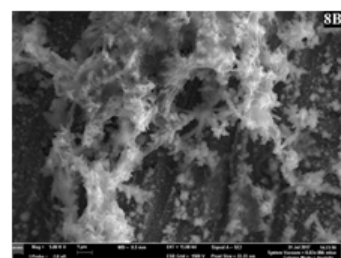


Fig. 8. SEM images of Ni-Cu deposition at a current density of $0.7\text{A}/\text{cm}^2$ for 50 s, 300x magnification (8A) and 5 000x (8B).



In figures 8A and 8B show the SEM images of Ni-Cu layers deposited at a current density of $0.7\text{A}/\text{cm}^2$ for 50 s. The deposit is one with undefined pores, with the dendritic shape of the crystals. In the middle of the pores one may notice the steel plate, thus leading to a thin deposition. The pore diameter is approximately $12\mu\text{m}$ and the connecting bridges thickness is about $15\mu\text{m}$.

Composition of the Ni-Cu layers

The properties of the Ni-Cu deposits are influenced by the working parameters employed in the deposition process. One may see that in figure 9, the time remains constant (150 s) and the current density varies, the Ni

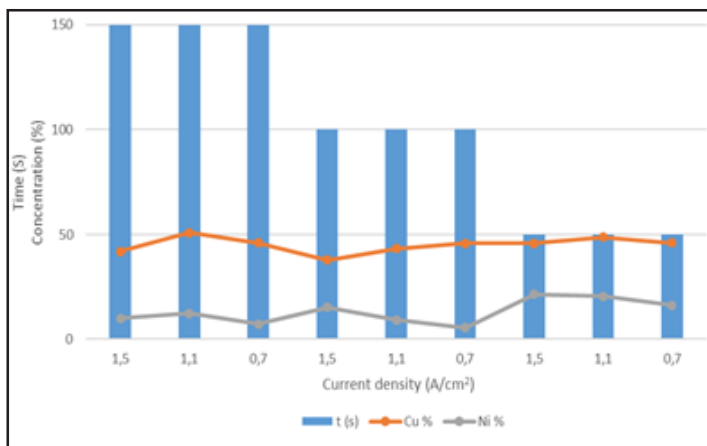


Fig. 9. The Ni-Cu composition in the tested layers

concentration drops from 10.02% at a current density of 1.5 A/cm^2 to 7.24% at a current density of 0.7 A/cm^2 . The Cu concentration also varies according to the current density applied during deposition, from 41.86% at a current density of 1.5 A/cm^2 to 50.92% at a current density of 1.1 A/cm^2 and then decreases to 45.9% at a current density of 0.7 A/cm^2 .

At a deposition time of 100 s and a variable current density, the Ni concentration also decreases from 15.36% at a current density of 1.5 A/cm^2 to a concentration of 9.22% at a current density of 1.1 A/cm^2 to 5.6% at a current density of 0.7 A/cm^2 . The concentration of Cu also in this case increases with decreasing the current density from 37.86% at a current density of 1.5 A/cm^2 to 43.36% at a current density of 1.1 A/cm^2 at 45.87% at a current density of 0.7 A/cm^2 .

If the deposition time is 50 s and the current density varies, the Ni concentration drops from 21.4% at a current density of 1.5 A/cm^2 to 20.56% at a current density of 1.1 A/cm^2 at a concentration of 16.29% at a current density of 0.7 A/cm^2 . Concentration of Cu increases from 45.83% at a current density of 1.5 A/cm^2 to 48.66% at a current density of 1.1 A/cm^2 and decreases to 45.92% at a current density of 0.7 A/cm^2 .

Element distribution in the electrochemically deposited Ni-Cu layers

The EDS results show that the Ni and Cu deposition is performed selectively. The Ni is more present close to the steel substrate than the concentration at the deposition surface where the Cu concentration is higher. This distribution is influenced by the deposition time and the current density at which the deposition was accomplished. The higher these parameters are, the lower the Ni concentration is over the deposition rate on the surface. This may be seen in the profile analysis and element distributions maps.

In figure 10 is shown the linear distribution profile of Ni and Cu deposition. One may see that in pores, the concentration of Ni is more pronounced than that at the surface of deposition. This is also confirmed by the element distribution maps shown in figure 11.

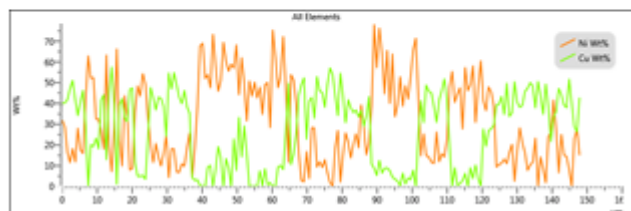
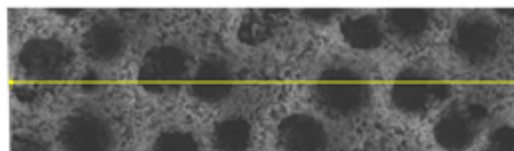


Fig. 10. Linear Ni-Cu deposition profile at a current density of 1.1 A/cm^2 , for 100s.

The electrical capacitance vary depending on the deposition time and the applied current density (table 1).

The higher the deposition time, the higher the value of electrical capacitance, at a deposition time of 150 s and 1.5 A/cm^2 current density, the value of electric capacitance is $52.9 \mu\text{F/cm}^2$; the electrical capacitance measured in a supercapacitor with plates deposited for 50 s and a current density of 0.7 A/cm^2 the value is $1.2 \mu\text{F/cm}^2$.

At a time of deposition of 100 s and a current density of 1.5 A/cm^2 , the value of electrical capacitance is $21.5 \mu\text{F/cm}^2$, it increases slightly if the deposition is made at a current density of 1.1 A/cm^2 at $26 \mu\text{F/cm}^2$, then decreases to $7.2 \mu\text{F/cm}^2$ at a deposition at a current density of 0.7 A/cm^2 .

In the case of a deposition made for 150 s at a current density of 1.5 A/cm^2 , the value of electrical capacitance is $52.9 \mu\text{F/cm}^2$, it decreases to $24.5 \mu\text{F/cm}^2$ at a deposition density currents of 1.1 A/cm^2 and up to $7.2 \mu\text{F/cm}^2$ at a deposition current density of 0.7 A/cm^2 .

The current density is an important parameter because at a deposition time of 50 s and a current density of 1.5 A/cm^2 the value of electrical capacitance is $26.8 \mu\text{F/cm}^2$ and at a deposition current density of 0.7 A/cm^2 the value of electric capacitance is $1.2 \mu\text{F/cm}^2$.

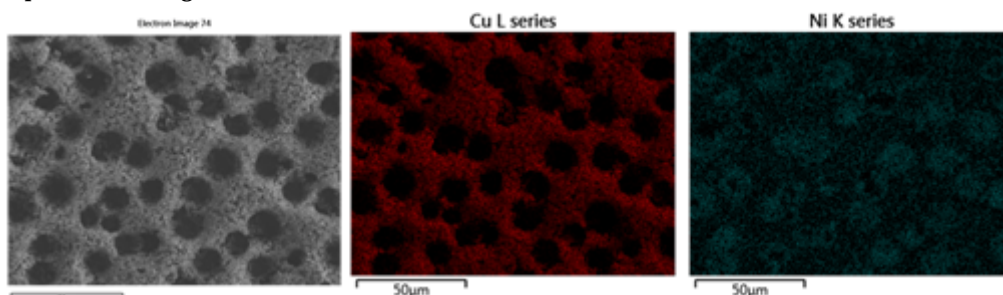


Fig. 11. Distribution map of Ni-Cu elements at a current density of 1.1 A/cm^2 , for 100s

Deposition parameters		Capacitance, $\mu\text{F}/\text{cm}^2$
Current density, A/cm^2	Time, s	
1.5	150	52.9
1.5	100	21.5
1.5	50	26.8
1.1	150	24.5
1.1	100	26
1.1	50	10.6
0.7	150	16.4
0.7	100	7.2
0.7	50	1.2

Table 1
VALUES OF THE CAPACITANCE FOR BUILT
SUPERCAPACITORS

Conclusions

This paper presents the effect of changing the deposition parameters in obtaining Ni-Cu deposits intended as charge plates for supercapacitors.

Depending on the parameters varied (current density and time), the deposition structure changes, as does the pore size. The higher the deposition current density and time, the more consistent the electrodeposits are.

The current density has a strong influence, as expected, on the thickness of the deposits, affecting also the pore diameters and the connecting bridges.

The values of the electrical capacitance varies between a few $\mu\text{F}/\text{cm}^2$ and tens of $\mu\text{F}/\text{cm}^2$, being strongly affected by the deposition time and current density.

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