CONSIDERATIONS REGARDING THE OPTIMIZATION PROCEDURE OF THE ELECTRODEPOSITION OF NICKEL-COPPER FILMS USED FOR SUPERCAPACITORS AND/OR RECHARGEABLE BATTERIES PLATES

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Abstract.

The search for new ways of storing electrical energy, particularly produced from non-constant supplying sources, such as photovoltaic panels and wind generators is continuously expanding. One possible solution would be to employ supercapacitors, which may level the peak output as well as short term increased demands. One of the requirements for producing such supercapacitors is the possibility for a better structural deposition control of the supercapacitor plates, depending on the intended use. This paper presents the results of an optimization procedure applied to the electrodeposition parameters during the manufacture of some nickel-copper alloys intended for the supercapacitor plates use.

Key words: optimization procedure, Ni-Cu electrodeposited films, supercapacitors

1. Introduction

In the recent years, the development of alternative, efficient and sustainable energy sources has been of key importance and efforts have been made to ensure the energy requirements in a fast developing global economy. In the context of decreasing of available fossil fuels and the environmental problems caused by their intense use, the use of alternative energy sources is a prerequisite for sustainable development. However, one of the main issues that need to be addressed as regards energy production is the development of efficient conversion and storage devices. In this purpose, a practical and suitable technology is represented by electrochemical devices, i.e. batteries, fuel cells and electrochemical supercapacitors (SC) [1-4]. The later have been intensively studied over the last 50 years and may represent a viable alternative to

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conventional energy storage by means of batteries as their particular structure and surface area may provide the storage of a higher amount of energy and ensure a higher lifespan or as an additional top-up back-up system for overloaded rechargeable batteries [5-9].

Our previous research proved that SC based on Ni-Cu foams [10-13] have high equivalent/specific capacitance. Depending on their application, specific procedures are required for the optimization of the working parameters for the electrodeposition process so that the desired performances of the Ni-Cu coatings are achieved.

In this context, this paper presents a method to identify the optimum values of the parameters for the electrodeposition of nickel-copper layers in order to achieve better equivalent capacitance, pore diameter/bridge thickness ratio and Ni/Cu concentration ratio for different applications.

The actual values of the electrodeposition parameters, namely five current densities, five values for the deposition time and three temperatures of the electrolyte solution, as well as the primary data, were previously published in [10-13], this paper dealing only with the optimization procedure.

2. Experimental

Procedure

The identification of the optimum domains of nickel-copper films electrodeposition so that they exactly correspond to the operating requirements is a step that quantifies the parameters of the obtaining process, in an easily interpretable form. For an easy identification of the optimum fields of the electrodeposition process in order to obtain alloys for different applications types, one may use the contour charts, which allow the delimitation of some well-defined intervals of the parameters that can be used during the electrodeposition process.

In order to obtain the contour charts, one has used the OriginPro 8 software. The data used to draw the contour chart were processed so that the variables are dimensionless, more precisely the values of the considered parameters were normalized by referring to the maximum values of the respective parameters.

The variables used to construct an optimization procedure are:

- Deposition temperature (T) - the value of the temperature used is expressed in K;
- Current density (i), $A\cdot cm^{-2}$;
- Normalized temperature - the ratio between the working temperature value and the maximum temperature value used in the deposition process;

$$\overline{T} = \frac{T}{T\,max} \quad (1)$$

- Current flow (Ø)- the ratio of the value of current density to that of the deposition time, $A\cdot cm^{-2}\cdot s^{-1}$;
- Normalized current flow - the ratio between the average value of the current density and that of the deposition time on its highest value:

$$\overline{\emptyset} = \frac{\frac{i}{t}}{\left(\frac{i}{t}\right)max} \quad (2)$$

- Capacitance (C) - average capacitance values, µF;
- Pore diameter (D_{pore}), µm;
- Bridge thickness (G_{bridge}), µm;
- Nickel content, %;
- Copper content, %;
- Electrical charge (Q), A·s.
- Normalized electrical charge - normalized values of the electric charge obtained from the ratio of the product to the current density value, deposition time and surface reported to its highest value:

$$\overline{Q} = \frac{itS}{(itS)max} \quad (3)$$

The parameters considered relevant for the use of these nickel-copper deposits in the construction of supercapacitors are the deposits composition, namely the nickel and copper content, the capacitance values, the active surface of the deposits expressed by the pore diameter and the thickness of the bridges. Therefore, three representative groups have been built to identify the optimum domains:

- I: the ratio between the average values of the capacitance and the surface:

$$\left(\frac{\overline{C}}{S}\right) = \frac{\frac{C}{S}}{\left(\frac{C}{S}\right)max} \quad (4)$$

- II: the ratio between the pore diameter and the bridges thickness of the deposited alloy:

$$\left(\frac{\overline{D\,pore}}{G\,bridge}\right) = \frac{\frac{D\,pore}{G\,bridge}}{\left(\frac{D\,pore}{G\,bridge}\right)max} \quad (5)$$

- III: the ratio between the concentrations values of nickel and copper in the analyzed samples:

$$\left(\frac{\overline{Ni}}{Cu}\right) = \frac{\frac{Ni}{Cu}}{\left(\frac{Ni}{Cu}\right)max} \quad (6)$$

3. Results and discussions

The dependence of the normalized ratio of capacity on surface according to the normalized temperature and normalized current flow

Data previously published in [10-13] were transformed in normalized or dimensionless groups using equations (1-6). For the representation of the contour chart of the normalized ratio of capacitance and surface as a function of normalized temperature and normalized current flow (Fig.1.), the normalized values of current flow and temperature and those of capacitance reported at surface were used.

From fig.1, one may see that two domains of maximum values have been obtained for the normalized ratio of capacitance and surface. The first domain is recorded for values of the normalized current flow between 0.34 and 0.35 and for a normalized temperature within the range of 0.96 – 1. The second domain is recorded for values of the normalized current flow between 0.71 and 0.79 and at a normalized temperature range between 0.959 – 0.979.

Therefore, it can be concluded that in order to obtain a capacitor with high values of the capacitance reported to the surface, one may consider as optimal working range, the second domain identified above, due to the wider range of values of the respective normalized current flow, of the normalized temperature.

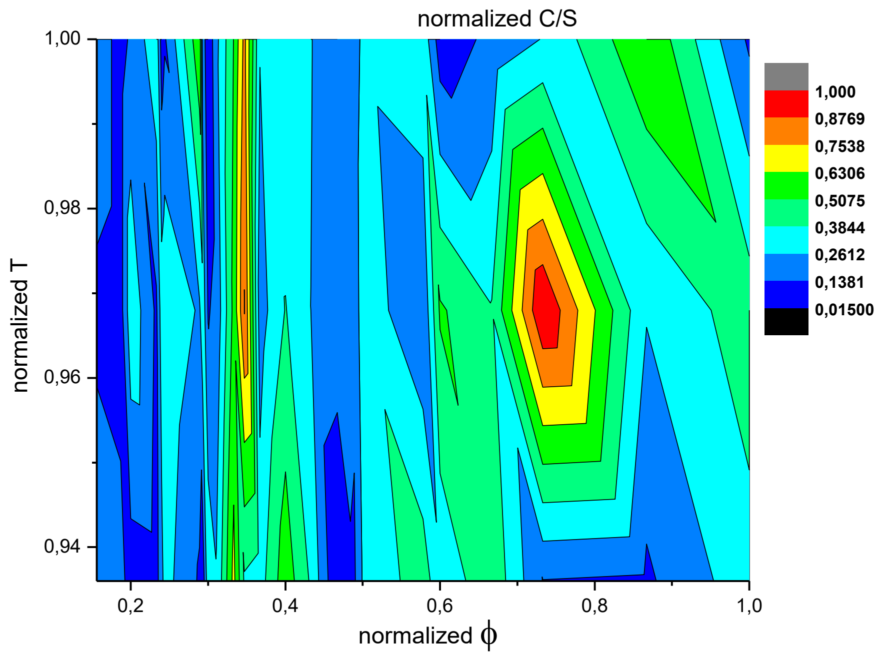

Fig.1. The contour chart of the normalized ratio of capacitance and surface according to normalized temperature and normalized current flow

The dependence of the normalized ratio between the diameter of the pores and the thickness of bridges by normalized temperature and normalized current flow

In order to represent the contour chart of the normalized ratio between the pore diameter and the bridge thickness depending on the normalized temperature and the normalized current flow (Fig.2.), one used the normalized values of the current flow obtained from the ratio of current density value to that of the deposition time on its highest value, the normalized values of the temperature obtained from the ratio of the average temperature to the highest temperature value.

In Fig.2. the optimum conditions may be observed in domain with the minimum ratio between the pore diameter on the bridge thickness. The optimum range of values for the normalized current flow is between 0.59 and 0.63, at a normalized temperature range between 0.97 and 1.

It can be concluded that the ratio between the pore diameter and the bridge thickness must be minimal, because if the alloy is used as catalyst, a material with potential catalytic properties and a maximum specific surface area is obtained.

This method may represent an alternative with better pore size control over the method of obtaining Raney-nickel skeletal catalysts.

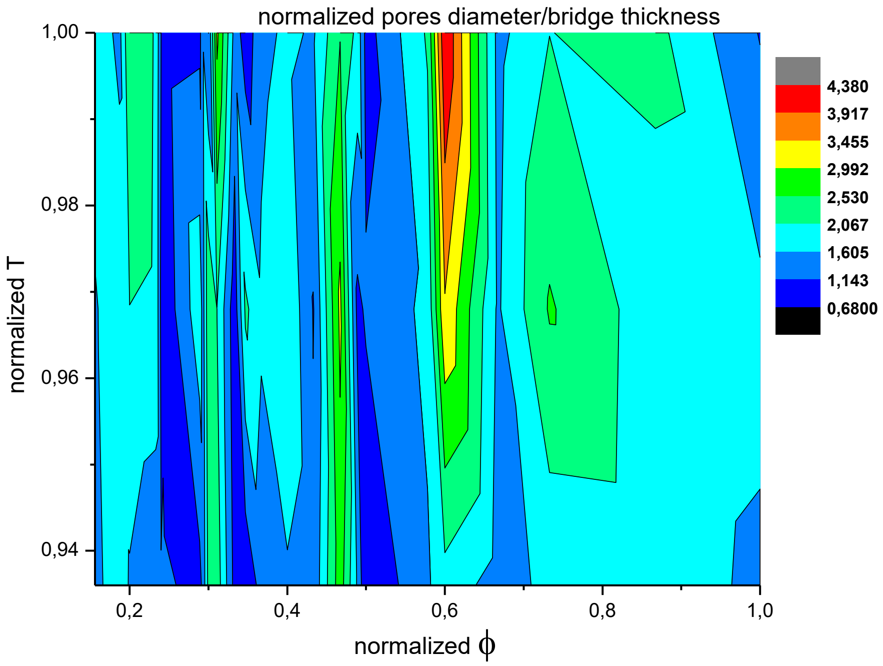

Fig.2. The contour chart of the normalized ratio between the pore diameter on bridge thickness according to normalized temperature and normalized current flow

The dependence of the normalized ratio between nickel and copper concentration according to normalized temperature and normalized current flow

In order to represent the contour chart of the normalized ratio between the nickel concentration on copper concentration according to normalized temperature and normalized current flow (Fig.3.), one has used the normalized values of current flow, obtained from the ratio between the average current density and the deposition time on its highest value, the normalized values of the temperature obtained from the ratio of average value of temperature to highest temperature value.

From Fig.3, one may observe two optimum intervals for the normalized ratio of the nickel on copper concentration depending on the normalized temperature and current flow. The first domain is recorded for values of the normalized current flow between values 0.71 and 0.8 and at normalized temperature within the range of values 0.952 – 0.979. The second domain is recorded for values of the normalized current flow between 0.42 and 0.43 and in a temperature range between 0.963 – 0.972.

It can be concluded that in order to obtain a capacitor with high values of the concentration of nickel relative to copper, it can be considered as the optimum working domain, the first domain due to the wider range of values of the current flow and the temperature.

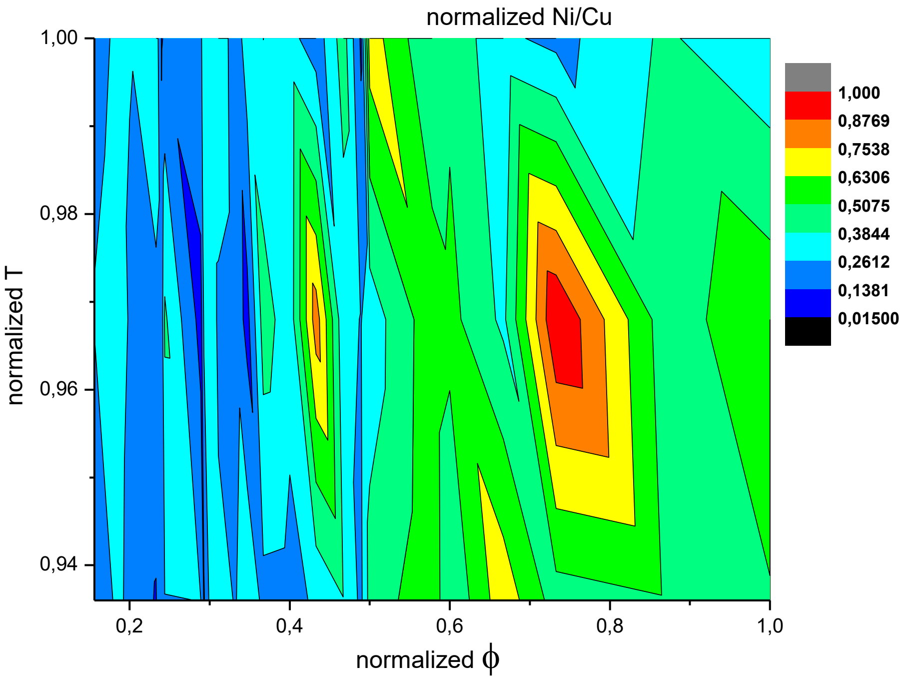

Fig.3. The contour chart of the normalized ratio of nickel on copper concentration according to normalized temperature and normalized current flow

The dependence of the normalized ratio between nickel and copper concentration according to normalized temperature and normalized electrical charge

In order to represent the contour chart of the normalized ratio between the concentration of nickel on copper depending on the normalized temperature and the normalized electrical charge (Fig.4.), one has used the normalized values of the electric charge obtained from the ratio of the product to the current density value, deposition time and surface reported to its highest value, the normalized values of the temperature obtained from the ratio of the average temperature value to highest temperature value.

From Fig.4. it can be observed that two optimum intervals are obtained for the normalized ratio of nickel on copper concentration depending on the normalized temperature and electric charge. The first domain is registered for normalized electric charge values in the range 0.24 – 0.27 and at a normalized temperature in the range of 0.952 – 0.98, while the second domain is recorded for normalized electric charge values in the range 0.57 – 0.59 and at a temperature range between 0.964 – 0.972.

It can be concluded that in order to obtain a capacitor with high values of the concentration of nickel reported to copper, it can be considered as the optimum working range, the second domain due to the wider range of values of the electric charge and the temperature.

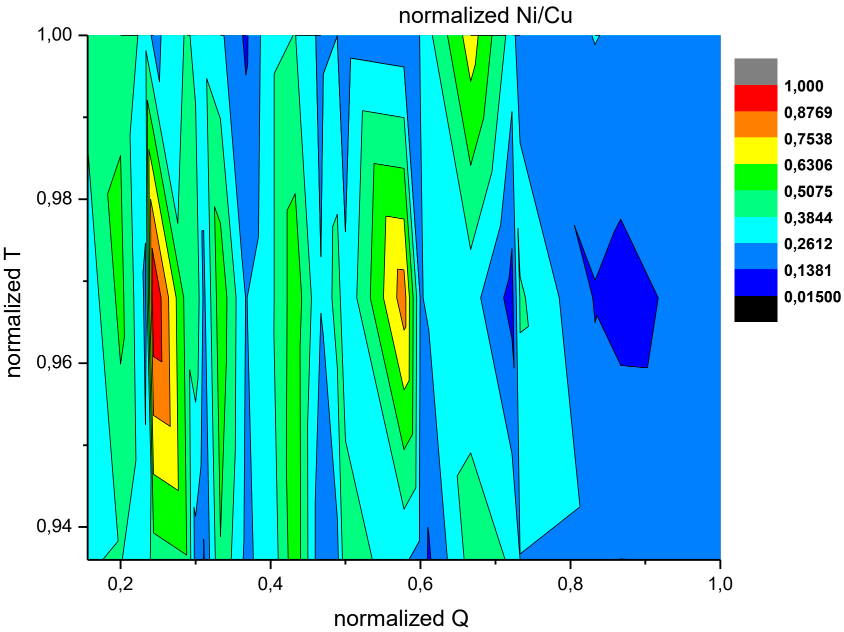

Fig.4. The contour chart of the normalized ratio of nickel to copper concentration according to normalized temperature and normalized electrical charge

4. Conclusions

Optimum domains for the electrodeposition of nickel-copper alloys have been established so that they correspond to the specific requirements of use. The processing of the experimental data obtained was done in an easily interpretable form that correlated the parameters of the obtaining process with the final characteristics of the nickel-copper deposits, using the contour-type charts from which the optimum domains for each interest parameter were extracted. Thus, the interest parameters for the performance of supercapacitors were identified, namely: the ratio between the average values of the capacitance and surface, the ratio between the pore diameter and the bridges thickness of the deposited alloy, the ratio between the values of the concentrations of nickel and copper in the analyzed samples.

Acknowledgement: Miss Ioana-Alina Ciobotaru has been funded by the Operational Programme Human Capital of the Ministry of European Funds through the Financial Agreement 51668/09.07.2019, SMIS code 124705.

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