Optimization of Ni nanofoams for assembling a Ni-Cap device

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ABSTRACT

The work in this thesis includes development and testing of novel electrodes based on nanostructured metallic foams of Ni and Ni hydroxide for application as electrode for hybrid supercapacitor. The first part of this thesis is dedicated to modification of morphology of the electrode current collector by Ni nano-foams using electrodeposition techniques. Next, the as prepared electrode supports were functionalized with active material Ni hydroxide.

The experimental results are presented to illustrate the influence of fabrication technique and electrode architecture on the overall electrode performance. Analysis of the produced composites was carried out using scanning electron microscopy and Raman spectroscopy. The electrochemical response was assessed by cyclic voltammetry and chronopotentiometry experiments. Obtained results showed that electrodes based on nickel hydroxide are very promising for hybrid supercapacitor applications. Introducing nanostructured composite as electrode support significantly improves overall performance of the electrode.

Keywords: Electrodeposition, supercapacitor, hybrid, energy storage.

1 INTRODUCTION

At the current energy consumption rate in order to meet future growing energy demands in a sustainable manner, it is critical to increase the share of energy generation that comes from renewable and clean energy sources. However, the intermittent nature of renewable sources (wind, solar) requires energy storage solutions for grid applications to ensure continuous and stable electricity supply [1], [2], [3]. Therefore, the development of advanced, environmentally friendly, efficient and low-cost energy storage solutions is of great importance.

The combination of supercapacitor and battery technologies can bring beneficial characteristics including relatively large storage capacity and very fast charge/discharge rates.

To achieve both characteristics in one device is a challenging task that can be potentially solved by integrating a battery-type electrode and capacitive electrode in a single electrochemical cell. An energy storage device with such kind of configuration is called hybrid supercapacitor and offers a promising way to achieve higher energy and power density [6]. For this purpose, it is critical to develop electrodes of a battery-type using inexpensive, environmentally friendly materials and techniques.

A superior performance can be achieved by designing an electrode with high surface area. In this regard, commercial nickel foam (CNF) has been widely explored as current collectors for different electrochemical energy storage devices, including supercapacitors and rechargeable batteries. CNFs have attracted great attention due to its excellent electric conductivity, low cost and high surface area [7]. Direct synthesis of nanostructured metallic foams onto current collector is expected to increase a number of electrochemical sites in the electrode [8].

The work in this thesis includes development and testing of novel electrodes based on nanostructured Ni foams and Ni hydroxide for application as electrode for hybrid supercapacitor.

The first part of this thesis is dedicated to electrodeposition of 3D porous nanostructured Ni foams (NF) over a commercial nickel foam (CNF) to prepare composite materials to be used as electrode supports.

Next, the as prepared electrode supports were functionalized with active material Ni hydroxide, using two techniques including electrochemical deposition in both galvanostatic and potentiostatic modes as well as chemical precipitation method.

2 METHODOLOGY

2.1 Electrodeposition of Ni foams

2.1.1 Materials and electrodeposition parameters

The first part of this work is dedicated to fabrication of a nickel composite, which would serve a double function for the novel electrode: current collector and active material support.

Here 3D-porous nanostructured nickel foams (NF) were electrodeposited on commercial nickel foam substrates (CNF) using the dynamic hydrogen bubble template [9] from an electrolyte solution containing 0.1 M $NiCl_2 \times 6H_2O$, 1M NH_4 and 1M NaCl. All chemicals were of analytical grade. Deionized water was used in the synthesis. The formation of nickel foam deposits on CNF was controlled by changing the values of applied current density (from -0.75 to -1.5 A cm^{-2}) and deposition time (from 300 to 1800 sec).

2.1.1 Thermal treatment

The effect of heat treatment on the electrochemical behavior of deposited materials was studied on the selected samples. The samples were subjected to heat treatment at temperatures of 350°C and 450°C.

2.2 Electrochemical synthesis of $Ni(OH)_2$/NF/CNF and $Ni(OH)_2$/CNF composites

2.2.1 Electrochemical synthesis of $Ni(OH)_2$/NF/CNF and $Ni(OH)_2$/CNF composites in galvanostatic mode

Electrodeposition of $Ni(OH)_2$ films was carried out in galvanostatic mode from 0.1 M $Ni(NO_3)_2 \cdot 6H_2O$ aqueous solution. Here, as a working electrode were used CNF substrate or the as-prepared NF/CNF composite. In order to study the effect of electrodeposition parameters on the mass load and structure of the deposits, experiments were performed varying both applied current density (from -0.05 to -1 A cm^{-2}) and deposition time (from 180 to 900 s).

2.2.2 Electrochemical synthesis of $Ni(OH)_2$/NF/CNF and $Ni(OH)_2$/CNF composites in potentiostatic mode

The nickel hydroxide films were obtained by potentiostatic electrodeposition from 0.1 M $Ni(NO_3)_2 \cdot 6H_2O$ aqueous solution. Depending on the experiment, working electrode was CNF or the as-prepared NF/CNF supports. All the active surface films were obtained at a potential of -1.1 V vs. saturated calomel electrode (SCE) during 1200 and 1800 s.

2.3 Synthesis of the electrode in C2C-NewCap laboratory

Synthesis of the Ni active electrode material on the as-prepared NF/CNF support was conducted in the laboratory of C2C-NewCap company. This is a multiple-step method, carried out under the company procedures (not disclosed). This procedure results in chemical precipitation of an active Ni compound onto the porous surface of the NF/CNF. All the details regarding used methodology remained confidential. The selected electrode samples were calendared.

2.4 Scanning electron microscopy

Scanning electron micrographs of selected samples with magnifications of 50X and 5kX were acquired with analytical microscope JEOL 7001-F operated at 15 kV.

2.5 Raman spectroscopy

Raman measurements were performed at room temperature (22°C) employing diode laser light at 532 nm from a LabRAM HR Evolution Raman spectrometer (HORIBA, Jobin Yvon, Edison, NJ) with integrated BX41 confocal microscope (Olympus) focused with a 50x objective lens. The Raman spectra of each sample were truncated in the range between 100 and 4000 cm^{-1}.

2.6 Electrochemical techniques

In the present work all electrochemical measurements were carried out in glass cell (100 mL) using 1 M KOH aqueous solution as the electrolyte at room temperature (25°C). Electroanalytical tests for single electrodes were conducted in a three-electrode cell connected to Gamry reference 600 potentiostat. Different samples to be studied were used as the working electrode, a platinum wire as the counter electrode, saturated calomel electrode (SCE) as the reference electrode.

2.6.1 Cyclic voltammetry

The cyclic voltammetry was conducted in a potential range between -0.2 and 0.8 V vs. SCE at various scan rates of 2; 5; 10; 20 mV s^{-1}. The potentiostat applied and maintained potential between the working and reference electrode while at the same time measured the current at the working electrode. The recorded values were used to plot the graph of current versus the applied potential.

2.6.2 Chronopotentiometry

Depending on the system under investigation, the constant current charge–discharge tests were carried out at various current densities from 7.5 to 25 mA cm^{-2} within a potential range of 0 to 0.42 V for testing single electrode, and of 0 to 2 V for the 2-electrode cell. The electrochemical stability windows of each electrode and of the full cells were evaluated by cyclic voltammetry.

The specific capacity C of the active material was estimated from discharge curves of single electrodes, using the following equation:

$$\mathrm{C} = \mathrm{I} \times \frac{\mathrm{t_{discharge}}}{3600 \times \mathrm{m}}\ [\mathrm{mAh\ g^{-1}}] \tag{1}$$

where I is the applied current [mA], $t_{discharge}$ is the discharge time [sec], and m is the mass of an active material [g].

To evaluate the rate capability of a single electrode, the specific capacity was measured at different discharge currents. The cycling stability test of selected electrodes was conducted by applying current density of 25 mA cm^{-2} for 1000 cycles.

3 RESULTS

3.1 NF/CNF composites for electrode supports.

3.1.1 Selection of samples

Optimization of the electrodeposition parameters (time and current density) resulted in a set of two optimized composites with a mass of nickel deposit of 60 mg cm^{-2} (NF_60/CNF) and 80 mg cm^{-2} (NF_80/CNF), which displayed the intended morphology.

3.1.2 Morphological characterization of electrodeposited Ni nanofoam

Morphological analysis demonstrated that Ni nanofoam, in agreement with literature [10], has a uniform sponge-like morphology where the pores result from hydrogen bubble evolution during the electrodeposition process. The deposit of the Ni nanofoam leads to reduction of the pore size compared to the CNF surface (Fig.1).

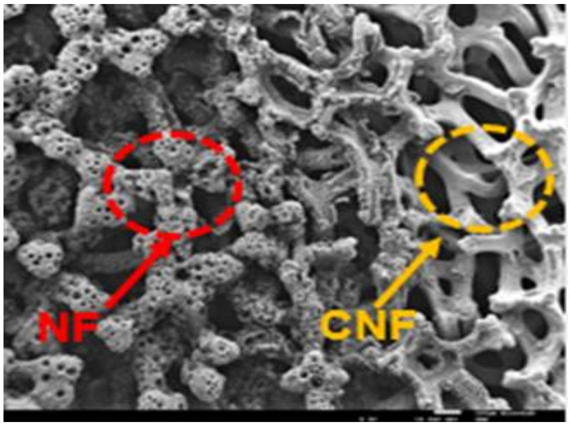

Figure 1 - NF_80/CNF on the edge with clean CNF at magnification 50X

3.1.3 Electrochemical characterization

Cyclic voltammetry of NF_60/CNF and NF_80/CNF measured in the potential window from 0 V to 0.55 V in 1M KOH revealed one pair of redox peaks for both composites (Fig. 2a). The CV curves of clean commercial foam CNF obtained in the same conditions are also depicted for comparative reasons. The phenomena are related to the faradaic reactions of nickel species that occurred in alkaline electrolyte.

Chronopotentiometry test carried out at current density of -7.5 mA cm^{-2} (Fig. 2b) are consistent with CVs. The specific capacity calculated from the GCD curves for NF_80/CNF composite is 8 mAh g^{-1} which is twice higher than that of 4 mAh g^{-1} for NF_60/CNF.

The electrochemical tests of heat treated samples showed that with increase of the heat treatment temperature, from 350ºC to 450ºC, the electrochemical response is poorer, meaning that there are more semiconducting nickel oxides being formed on the surface of the foam [11]. For this reason in the present work heat treatment was not considered for further experiments.

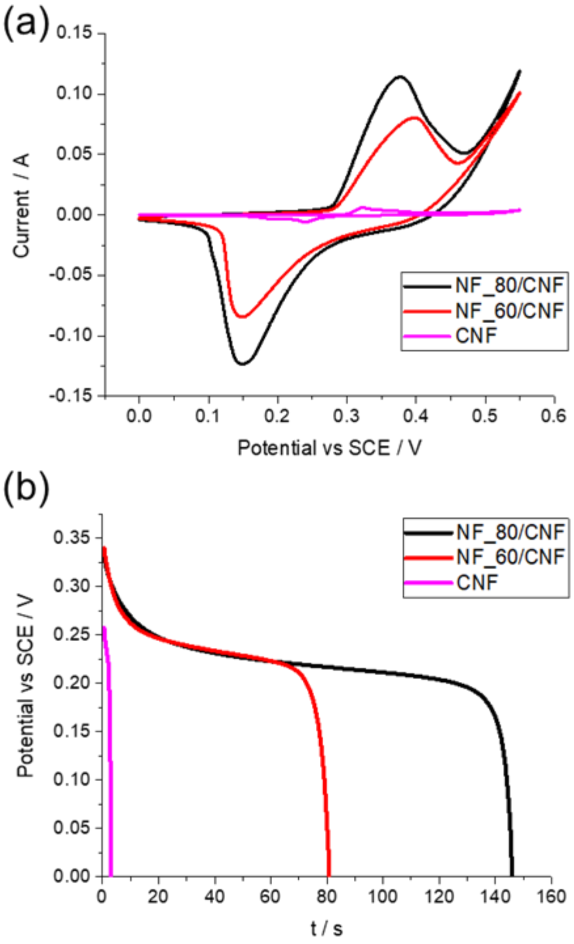

Figure 2 - Electrochemical response of the different materials (a) at scan rate of 5 mV s^{-1}, (b) at -7.5 mA cm^{-2}

3.2 Ni(OH)$_2$/NF/CNF and Ni(OH)$_2$/CNF composites from electrodeposition experiments

3.2.1 Optimized composites obtained from galvanostatic and potentiostatic electrodeposition experiments

The optimization of the electrodeposition parameters (time and current density) resulted in a set of 4 optimized composites summarized in the Tab.1. In galvanostatic electrodeposition mode (Galv.) all the samples were obtained at the current density of -0.05 A cm^{-2}, while in potentiostatic mode (Pot.) at potential of -1.1 V.

Table 1 - Description of the composites prepared by electrodeposition

No.	Mode	Initial material	Index	Mass [mg cm^{-2}]
1	Galv.	CNF	g18	18
2	Galv.	NF_80/CNF	g16	16
3	Galv.	NF_60/CNF	g18	18
4	Pot.	NF_80/CNF	pot16	16

3.2.2 Morphological characterization of electrodeposited composites

Surface analysis shows that both electrodeposition conditions produce similar smooth films of Ni hydroxide with surface morphologies analogous to the morphology of the substrate. For both deposition techniques Ni hydroxide shows surface cracks, that may be caused by drying process. Though, a higher cracking tendency is observed in the galvanostatically obtained sample. This differences may be associated with different potential and current response during electrodeposition process.

3.2.3 Raman spectroscopy analysis

The Raman spectra of the films obtained in galvanostatic and potentiostatic electrodeposition modes showed very similar profiles. The peak positions, intensities and peak width, in both samples, correspond well to the spectra of α-$Ni(OH)_2$ prepared from $Ni(NO_3)_2$ as described in a literature [12].

3.2.4 Electrochemical characterization

The cyclic voltammograms of different samples of electrodeposited $Ni(OH)_2$ were measured at rate of 2 mV s^{-1} within a potential window from 0 V to 0.55 V. The CV curves evidence the presence of a pair of broad peaks with correspond to Faradic processes for charge storage in the hydroxide film. The current response of the active material deposited over NF_80/CNF composites is stronger than over the blank commercial foams.

The highest specific capacity of 192 mAh g^{-1} and 177 mAh g^{-1} correspond respectively to the active material electrodeposited galvanostatically and potentiostatically on the NF_80/CNF substrate.

However, further observations demonstrate significant capacity decrease for both samples associated with detachment of the active material from the surface of the electrode support, an effect that was experimentally observed during the GCD measurements. The electrode produced galvanostatically demonstrated higher capacity fade compared to galvanostaically deposited electrodes, probably due to morphological differences associated with the electrodeposition route.

3.3 Electrodes with active material $Ni(OH)_2$ fabricated in C2C-NewCap laboratory.

3.3.1 Optimized $Ni(OH)_2$/NF/CNF and $Ni(OH)_2$/CNF

The fabrication of the electrodes by C2C-NewCap method resulted in the set of 3 electrodes depending on the number of fabrication cycles (L1 and L2) and whether the electrodes were calendared or not. The calendared electrodes were marked with an additional index “cal” (Tab.3).

Table 2 - Composites prepared at C2C-NewCap laboratory

Index	Initial material	$Ni(OH)_2$ [mg cm^{-2}]
L1 _cal	NF_80/CNF	15
L2	NF_80/CNF	20
L2 _cal	NF_80/CNF	15

3.3.2 Morphological characterization of the electrodes with active material $Ni(OH)_2$ fabricated with C2C-NewCap method

The micrograph of as-prepared L2 electrode (Fig.3a) demonstrates that precipitated Ni compounds does not hinder the porous morphology of the NF_80/CNF substrate, however the distribution of the active material is not fully homogeneous. Fig.3b (L2_cal) shows that after roll pressing the porosity of the electrode is significantly reduced compared to its as-prepared equivalent. The electrode demonstrates well-compacted surface.

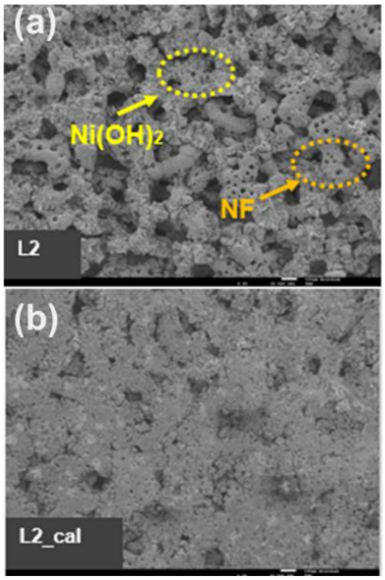

Figure 3 - SEM images at different magnifications of Ni hydroxide on the NF_80/CNF substrate before (a) and after (b) calendaring

3.3.3 Raman spectroscopy analysis

Raman experiments provided some chemical insights regarding the chemical composition of the Ni electrode synthesized by C2C-NewCap method.

3.3.4 Electrochemical characterization

The cyclic voltammograms measurements of the electrodes produced at C2C-NewCap laboratory were taken in KOH electrolytes with the sweep rate of 2 mV s^{-1} ranging the potential from -0.2 V to 0.8 V. The shape of the CV curves confirmed the typical redox reaction of Ni compounds in alkaline solution (Fig.4a). The chronopotentiometry test was carried out at current density of -7.5 mA cm^{-2}. The plateau-like profiles of the discharge curves depict the performing of a battery-type redox reaction (Fig. 4b). Here, the calendared electrodes possess the longer discharge time compared to the as-prepared equivalent. The results are consistent with the CV curves. The specific capacity of the synthesized L1_cal, L2, L2_cal electrodes calculated from the GCD curves at differen applied current densities is summarized in Tab.3.

Among the tested electrodes, L1_cal and L2_cal showed the best results, which lead to conclusion that calendering improved electrochemical performance of the electrodes. This is probably because after the roll pressing the uniformity of the active material in the electrode is increased, which may improve an electric contact between the active material Ni hydroxide and current collector Ni_80/CNF.

Next, the cyclic stability of nanostructured L2_cal electrode was carried out in charge-discharge test at constant current density of 25 mA cm^{-2} for 1000 cycles. The results indicate that after 1000 cycles L2_cal electrode demonstrate specific capacity drop by 75% of the initial value at the second discharge cycle. The specific capacity fade of L2_cal electrode is the consequence of degradation mechanism in which the active material detached from the current collector.

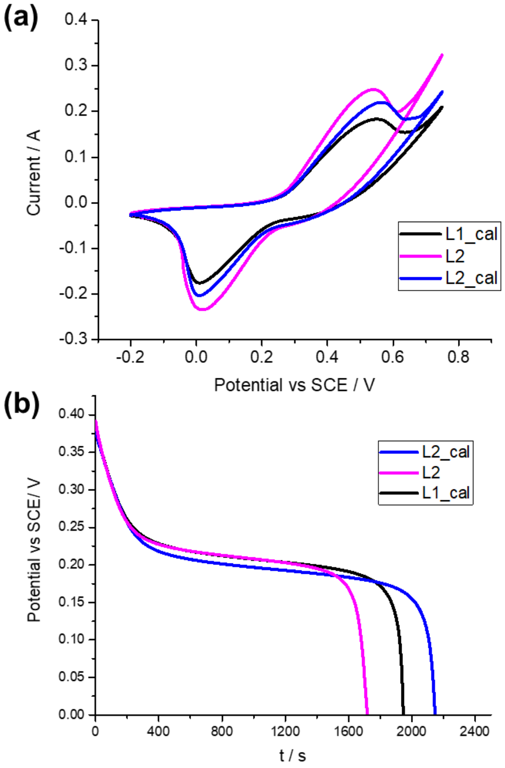

Figure 4 - Electrochemical response of the electrodes with an active material fabricated by C2C-NewCap method (a) at scan rate of 2 mV s^{-1}, (b) at -7.5 mA cm^{-2}

Table 3 - Calculated specific capacity of the electrodes in mAh g^{-1} at different currant densities

Index	-7.5 [mA cm^{-2}]	-15 [mA cm^{-2}]	-25 [mA cm^{-2}]
L1_cal	253	153	119
L2_cal	298	220	72
L2	179	127	43

4 CONCLUSIONS

The objective of the present thesis was to develop and to test a novel nanostructured electrode for the hybrid supercapacitor. The work included fabrication of the electrode supports and then filling the pores of the as-prepared electrode supports with an active material nickel hydroxide.

The experimental results proved that the mass of deposits increased with the increase of deposition time and the value of applied current density. The optimization of the electrodeposition parameters (time and current density) resulted in a set of two optimized composites with a mass of nickel deposit of 60 mg cm^{-2} (NF_60/CNF) and 80 mg cm^{-2} (NF_80/CNF), which displayed the intended morphology. Morphological characterization of the NF_80/CNF composite surface proved significant reduction of the pore size compared to the bare CNF. The nickel nanofoam deposit demonstrated a uniform sponge-like morphology where the pores were formed by hydrogen bubble evolution during the electrodeposition process. Higher magnification images revealed that the deposit is composed of small agglomerates of Ni grains.

The electrochemical tests showed superior performance of the composites with higher nickel deposit mass. NF_80/CNF composite demonstrated higher current response in cyclic voltammograms and longer discharge time during chronopotentiometry tests if compared to NF_60/CNF. The specific capacity calculated from the GCD curves at 7.5 mA cm^{-2} for NF_80/CNF composite is 8 mAh g^{-1} which is twice higher than that of 4 mAh g^{-1} for NF_60/CNF.

The electrochemical characterization of the heat-treated NF_80/CNF composites showed that with increase of the heat treatment temperature, from 350ºC to 450ºC, the electrochemical response is poorer in comparison with as-prepared composite, meaning that more semiconducting nickel oxides was formed on the surface of the nickel nanofoam deposit.

Raman spectroscopy analysis indicated that the structure of the synthesized active material $Ni(OH)_2$ prepared by electrodeposition in the present work corresponded to alpha phase. Therefore, the electrochemical characterization of the electrodes is demonstrating the crucial importance of the electrode architecture on the overall electrode performance.

The results obtained from electrochemical characterization revealed that specific capacity of the electrodes with the active material electrodeposited over nonporous nickel composites NF_80/CNF (up to 192 mAh g^{-1}) and NF_60/CNF (up to 116 mAh g^{-1}) is significantly higher than that of the electrodes with nickel hydroxide over the blank commercial foams CNF (up to 63 mAh g^{-1}). The superior performance may result from the enhanced ionic/electronic conductivity achieved by introducing nanostructured electrode supports.

All the electrodes with the active material obtained by electrodeposition showed high mechanical degradation during electrochemical tests. Electrodes with an active material electrodeposited galvanostatically demonstrated higher mechanical instability compared to the electrodes with potentiostatic electrodeposition. This is probably due to morphological differences associated with electrodeposition mode.

The fabrication of the electrodes by chemical precipitation method resulted in the set of 3 electrodes depending on the number of fabrication cycles (L1 and L2) and whether the electrodes were calendared or not.

The morphological characterization demonstrated that the surface of the calendared electrodes were well-compacted, and the porosity was significantly reduced compared to their as-prepared equivalents.

The electrochemical tests revealed that after calendaring the electrodes exhibited improved electrochemical performance. This is probably due to better electric contact between the precipitated nickel hydroxide particles and the electrode support after calendering.

The results of the cyclic stability test carried out at 25 mA cm^{-2} showed that after 1000 cycles specific capacity of the calendared electrode L2_cal decrease by 75% of the value at the second discharge cycle. This specific capacity fade is associated with the detachment of the active material from the current collector during the cycling experiments.

The experimental results demonstrate that the 3D nanostructured NF/CNF composites used as electrode supports can effectively promote the material utilization leading to improved electrochemical performance. It is possible to conclude, that electrodes based on nanostructured metallic foams of Ni and Ni hydroxide could be a promising candidate for electrochemical energy storage devices.

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