The limited oil resources and hydro-electric projects and the portability issues have catalyzed the scientific community to develop efficient and cost effective alternative energy conversion technologies and storage devices. A great deal of attention has been given to supercapacitors due to their high specific capacitance (ability to store an electrical charge), long-term cycleability and high power density [1,2]. Due to their many advantageous properties, such as large capacitance, high power density, and long cycle life, the electrochemical capacitors (ECs) or supercapacitors (ES) play an increasingly important role in modern power source application [3,4]. Electrochemical capacitors have many potential applications in the power sources field [5,6]. They can be divided into electric double layer capacitors (EDLCs) and pseudo capacitors according to their mechanism of charging the double-layer on the electrode surface (non-faradaic process). The capacitance of an EDLC is determined by the interfacial area between the electrolyte and electrode. Carbon materials are the most widely used electrode materials in EDLCs, owing to their high surface area, accessibility, chemical stability, and relatively low cost [6,7]. A pseudo capacitor is based on the redox reaction at the interface of the electroactive species. A metal oxide or conducting polymer is commonly used as the electrode material for pseudo capacitors [6–13].

In the past few decades, both carbon nanotubes (CNTs) and electrically conducting polymers (ECPs) have attracted great attention in many fields, especially in the applications of energy storage [14,15]. Recent studies have found that the combination of CNTs and ECPs demonstrated significant advantages, such as low electrode impedance, high capacitance and fast charge transfer rate, as well as good mechanical stability [16]. The carbon nanotubes have excellent electrical and mechanical properties and promising applications, including conductive and high-strength composites, energy storage and energy conversion devices [17]. Because of the high electrochemically accessible surface area of porous nanotube arrays, combined with their high electronic conductivity and useful mechanical properties, CNTs are attractive as electrodes for supercapacitors [18]. However, the specific electrical capacitance of a CNTs layer is slightly low (generally <100 F g\(^{-1}\)) [19].

The growing interest in application of polymeric (PPy) for electrodes of electrochemical supercapacitors is attributed to high specific capacitance, relatively large voltage window, high electrical conductivity, low cost, and advanced chemical and mechanical properties of this material [20]. The high specific capacitance of PPy results from redox reactions, which allow charge storage in the bulk of the electrode material. Many fundamental investigations have been conducted with the objective to investigate the charging mechanism of PPy in different electrolytes and to utilize high theoretical specific capacitance of PPy (620 F g\(^{-1}\)) [20-23] in electrodes of ES [24]. The electrolysis of PPy can be controlled by adjusting electrolyte ionic strength and \(\phi H\); in this case, a high electrolyte concentration and a neutral or slightly acid \(\phi H\) value increase the quality of the polypyrrole film [25,26]. Also, the electrochemical method employed in the electropolymerization process strongly affects the properties of the obtained film.

In this paper, cyclic voltammetry was chosen as the electrochemical synthesis method for PPy-CNTs composite films instead of galvanostatic or potentiostatic methods. There are two reasons: cyclic voltammetry allows to yield smoother coatings [27] and it is possible to monitor the redox properties of the deposits during the experiment, while galvanostatic and potentiostatic polymerizations allow the evaluation of the electrochemical properties only in the end of the experiment. PPy coatings show weak mechanical properties that can be improved by the addition of carbon nanotubes, as has been observed previously for several polymeric matrices [28–30], thus obtaining a more resistant and durable support. Nanotubes also improve the electrical conductivity of polymer films, lowering the impedance modulus of these materials [31]. The electrochemical stability of polypyrrole is also increased by the addition of carbon nanotubes [32,33]. On the other hand, the electrochemical activity of PPy in dedoped state (which is the discharge state in supercapacitor) could be
a serious problem because of the typical volumetric shrinkage during ejection of counterions (doped ions). Furthermore, the conductance of ECPs is very low at dedoped state, which would result in high ohmic polarization of supercapacitor and low reversibility and stability of supercapacitor, as well. The problem has to be solved before the application. It has been already confirmed that composite materials based on Ppy-CNTs coatings are very interesting electrode materials for supercapacitor application [6,19]. The mesoporous structure of CNTs can adapt to the volume change of PPy, and the high electric conductance of CNTs could make up the low conductance of polymer on dedoped state.

The aim of this study is to investigate electrochemical behaviour as supercapacitor electrodes of Ppy-CNTs composite layers in sulfuric acid and oxalic acid solutions. We expect that the large surface area and high conductivity of the CNTs enhance the energy storage capacity. PPy provides not only additional capacitance as an active material, but also improves the adhesion between the CNTs and substrate. Furthermore, PPy acts as a conductive binder for connecting every individual CNT leading to an increase of the electrochemical capacitance.

Experimental part

3D CNTs network was achieved by chemical vapour deposition (CVD) growth on SiO2/n-type silicon (100) substrate covered with a catalyst layer based on nickel, obtained previously through electron beam evaporation method. Preceding the CNTs growth process, the Ni catalyst recrystallization was carried out at a temperature of 750°C for 15 min inside the quartz tube of CVD equipment. The general parameters for annealing process of nickel catalyst particles are presented in table 1. During the CNTs growth by CVD method in argon and hydrogen atmosphere, ethylene (C2H4) was used as gas source of carbon. General parameters of CVD process for nanotubes growth on the substrate (SiO2/n-type silicon (100)) covered with Ni catalyst, are shown in table 2.

Conductive polymeric coatings were achieved by using cyclic voltammetry in either 0.2M H2SO4 or 0.2M oxalic acid aqueous solutions. Pyrrol electropolymerization was carried out by potential cycling (50 successive cycles) between 0.2-0.85V/SCE, at a constant scan rate of 20 mVs-1. Chemical reagents of analytical grade used for electrochemical polymerization of pyrrole were pyrrol, 99% purity (purchased from Acros Organics), and sulfuric acid (98%) and oxalic acid dihydrate (both purchased from SC Chimreactiv). The solutions containing dissolved pyrrole were prepared using bidistilled water; to encourage pyrrol dissolution, 3-5 mL of ethanol were added. Before the beginning of each electrochemical polymerization the solutions were kept in darkness to avoid air oxidation and pre-polymerization. 0.2M H2SO4 and 0.2M oxalic acid solutions without pyrrole were the media for investigation of electrochemical behaviour of Ppy-CNTs composite films. A VoltaLab 40 potentiostat/galvanostat with dynamic impedance measurements was performed on the frequency range between 100kHz and 10mHz with an AC wave of 10 mV (peak-to-peak) overlaid on a DC bias potential; the impedance data were obtained at a rate of 10 points per decade change in frequency. AFM and SEM micrographs were obtained using a model Ntegra AFM/STM, NT-MDT microscope and a CARL ZEISS AURIGA scanning electron microscope with OXFORD INCA ENERGY EDX probe, respectively.

Results and discussions

Microscopy studies

Figure 1 shows the AFM images concerning the catalytic layer morphology before and after thermal treatment of nickel grains grown on SiO2/Si surface. SEM micrographs of the obtained CNTs layer on Ni/SiO2/Si surface, in the intermediate preparation step, are presented in figure 2.

In figures 3 and 4 are presented the SEM micrographs for electropolymerized polypyrrole film, grown from different aqueous electrolytes, 0.2M H2SO4 and 0.2M oxalic acid solutions before and after annealing. Table 1 presents the temperature, time and pressure parameters for Ni catalyst annealing.

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Table 2

A VoltaLab 40 potentiostat/galvanostat with dynamic EIS (Electrochemical Impedance Spectroscopy) connected to a computer through VoltaMaster 4 Software interface was used for the electrochemical measurements. The electrochemical polymerization and behaviour of the samples were studied in a classical electrochemical cell with three electrodes. The working electrode is a plate with surface area of 1 cm2 consisting in Ni/SiO2/Si support that will be covered with Ppy-CNTs composite coating. The cell contains, apart from the working electrode, a Pt counterelectrode and a saturated calomel reference electrode (SCE). The experiments were carried out in stationary conditions at room temperature. Impedance measurements were performed on the frequency range between 100kHz and 10mHz with an AC wave of 10 mV (peak-to-peak) overlaid on a DC bias potential; the impedance data were obtained at a rate of 10 points per decade change in frequency.
Electrochemical characterization

Figure 5 presents the variation with electrode potential (E) of electrical capacitance (C) for PPy-CNTs sample at constant frequencies, in aqueous solutions of 0.2M H₂SO₄ and 0.2M oxalic acid, without pyrrole monomer content. Measurements of capacitance in each solution were performed at frequency of 48Hz and at frequency of 100Hz, respectively. It can be observed from C=f(E) curves that the capacity values in oxalic acid solution are with around one order of magnitude lower than in the case of H₂SO₄ solution. The maximum capacity value is clearly registered at 550mV/SCE in the case of H₂SO₄ solution. In the case of oxalic acid solution, after a potential region of almost constant value the capacitance has a tendency to increase slowly up to 850mV/SCE electrode potential; we consider this last value to be favourable for pyrrol electropolymerization as successive cyclic voltammograms performed by us showed, too.

Electrochemical behaviour of PPy-CNTs samples was characterized in 0.2M H₂SO₄ and 0.2M oxalic acid aqueous solutions, without pyrrole monomer content, by the electrochemical impedance spectroscopy (EIS). Figures 6 and 7 show comparatively the Nyquist plots at open-circuit potential (OCP, which is a stationary potential) of composite electrode (281mV/SCE in H₂SO₄ and 401mV/SCE in oxalic acid, respectively) and at more positive potentials corresponding to the maximum electrical capacitance (550mV/SCE and 850mV/SCE, respectively), according to C = f(E) plots. In all cases it can be observed the appearance of a well evidenced capacitive semicircle (Debye semicircle) at high frequency, followed by a linear straightline. These correspond to the existence of two distinct processes: the first is the charging of double layer, and the second is the formation of some reaction products deposited as an adjacent diffusion layer near electrode. The electrical parameters corresponding to each Debye semicircle were determined by circular regression and

![Fig. 5. Capacity variation with electrode potential in 0.2M H₂SO₄ solution at 48Hz frequency (curve 1) and in 0.2M oxalic acid solution at 100Hz frequency (curve 2) for PPy-CNTs sample](http://www.revistadechimie.ro)

![Fig. 6. Nyquist diagram plotted at stationary potential (OCP = 281mV/SCE) and by polarizing at 550mV/SCE for PPy-CNTs sample in 0.2M H₂SO₄ solution](http://www.revistadechimie.ro)

![Fig. 7. Nyquist diagram plotted at stationary potential (401mV/SCE) and by polarizing at 850mV/SCE for PPy-CNT sample in 0.2M oxalic acid solution](http://www.revistadechimie.ro)
listed in table 3. It is seen that the double layer capacity ($C_{dl}$) values calculated by circular regression are lower in the case of oxalic acid solution than in sulfuric acid solution, similarly to $C = f(E)$ diagrams.

In table 3 are also listed values of the solution resistance (ohmic resistance, $R_s$) between working and reference electrodes, as well as the polarization resistance ($R_p$) which is a measure of electron transfer rate in the electrochemical process. Values of the order 50-200 $\Omega$cm$^2$ for $R_s$ and values of 0.5-4.8 $k\Omega$cm$^2$ for $R_p$ are of usual order of magnitude.

Figures 8 and 9 present the Bode diagrams for PPy-CNTs sample in 0.2M H$_2$SO$_4$ and 0.2M oxalic acid solutions, at stationary potentials (281mV/SCE and 401mV/SCE, respectively) and at electrode potentials corresponding to maximum capacitance (550mV/SCE and 850mV/SCE, respectively). It can be noticed that the maxima of phase angle are recorded at 48Hz frequency in the case of H$_2$SO$_4$ solution and 100Hz in the case of oxalic acid solution. This was the reason for which the C=f(E) diagrams were drawn at these frequencies (fig.5).

Supplementary information of electrochemical capacitance behaviour can be obtained from semilogarithmic dependences of capacity vs. frequency in sulfuric acid or oxalic acid (figs.10 and 11). The C-log f curves presented in figures 10 and 11 show that no significant difference in the curve shape is recorded for capacity of PPy-CNTs sample in investigated acid solutions either at stationary potential (for non-polarized electrode, at OCP) or at more positive potentials (300-450mV overpotentials). It can be noticed that in both electrolyte solutions the capacity of electrode has a monotonically increase from high frequencies to low frequencies, but within the domain of average frequencies the increase of capacity is more pronounced and an intersection of curves occurs. For electrode at stationary potentials, the capacity has values between 1 $\mu$Fcm$^{-2}$ (at approx. $10^5$ Hz) and 10$^4$ $\mu$Fcm$^{-2}$ (at approx. $10^{-2}$ Hz) in both electrolyte solutions. However, different behaviour is recorded for capacity values of polarized electrode comparative with non-polarized electrode in high- and low frequency regions. While in H$_2$SO$_4$ electrolyte, the capacity values at the extreme frequencies remain approximately equal with those of non-polarized electrode, in oxalic acid electrolyte the polarized electrode (+850mV/SCE) has an increase in capacity by an order of magnitude at lowest frequencies (10$^{-2}$Hz) and also a decrease in capacity by an order of magnitude at highest frequencies (10$^{10}$Hz).

Figures 12 and 13 show the variations of loss angle tangent with logarithm of frequency in the 100kHz – 10mHz frequency range for PPy-CNTs sample in H$_2$SO$_4$ or oxalic acid electrolyte. It may be observed in both electrolytes that at...
stationary potential (OCP) the loss angle tangent has a minimum within the average frequency region, while at high and low frequencies, the value of loss angle tangent increases significantly. A similar behaviour is recorded by polarizing the electrode at potentials which correspond to maximum capacity, determined from C-f(E) diagrams, but with very higher loss angle tangent, especially at low frequencies. Values below 2-3 of loss angle tangent exhibited in these diagrams recommend PPy-CNTs electrode to be used in supercapacitors in the 10-10³ frequency range.

Conclusions

The PPy-CNTs composite electrodes were successfully obtained by CVD of carbon nanotubes on a Ni catalyst layer deposited on Si/SiO₂ substrate and afterwards by polymerization of pyrrole. The polypyrrole layer was electrodeposited from pyrrole monomer solution in acid polymerization of pyrrole. The polypyrrole layer was electrodeposited from pyrrole monomer solution in acid media (sulfuric acid or oxalic acid, 0.2M, aqueous solutions) by cyclic voltammetry at low scan rate (20mVs⁻¹). Morphology of the investigated films shows an uniform cover; in the case of oxalic acid electrolyte, the morphology is of spherulitic type.

The PPy-CNTs composite electrodes are suitable for supercapacitors due to their high capacitance in acid electrolyte and low values of loss angle tangent at medium frequencies, according to electrochemical measurements presented in this paper.

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References