Electrodeposition of Polypyrrole on Carbon Nanotubes/Si in the Presence of Fe Catalyst for Application in Supercapacitors

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The electrochemical properties of composite films prepared from electrically conducting polypyrrole (PPy) and carbon nanotubes (CNTs) have been investigated for supercapacitor applications. The Ppy coatings for obtaining hybrid PPy-CNTs electrodes were achieved by cyclic voltammetry under the following conditions: 50 successive cycles in the potential domain of 0.2-0.85 V/SCE, at a scan rate of 20 mV/s, using aqueous solutions of either 0.1 M pyrrole in 0.2 M H2SO4 or 0.3 M pyrrole in 0.2 M oxalic acid as electrolytes. The CNTs were grown on the oxidized Si substrate by the chemical vapour deposition and PPy was subsequently coated on them by electrochemical polymerization. The large surface area and high conductivity of the CNTs on the Si/Fe catalyst substrate enhance the energy storage capacity. PPy provides additional capacitance as an active material. Furthermore, PPy acts as a conducting binder for connecting every individual CNT to increase the capacitance. The morphology of composite films was observed by scanning electron microscopy (SEM). The electrochemical capacitance properties of the composite films in 0.2 M H2SO4 or 0.2 M oxalic acid aqueous solutions were measured by electrochemical impedance spectroscopy technique.

Keywords: polypyrrole, carbon nanotubes, supercapacitors, Fe catalyst

Electrochemical supercapacitors (ES) have become an attractive alternative in electrical energy storage devices and found many applications in a number of industrial areas due to the advantages of both high power density and stable cycle life. The development of ES requires fabrication of advanced electrodes with novel materials and using new techniques. Conducting polymers such as polypyrrole (PPy) have been found to be promising electrode material for ES due to their high pseudo capacitance, good electrical conductivity, low cost and easy fabrication [3]. The carbon nanotubes (CNTs) have attracted much attention in recent years because of their excellent electric and mechanical properties and promising application including conductive and high-strength composites, energy storage and energy conversion devices [4]. 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 [5] and there is a considerable effort aimed at improving electrical conductivity using a variety of carbonaceous materials.

Recent studies have found that the combination of conducting polymers with carbon nanotubes demonstrated significant advantages, such as low electrode impedance, high capacitance and fast charge transfer rate as well as good mechanical stability [6]. It has been already confirmed that composites based on conducting polymers and CNTs are very interesting electrode materials for supercapacitor application [7].

For instance a polypyrrole based composite electrode with multi-walled carbon nanotube has been proved to enhance the electrochemical performance of ES [8]. The high specific capacitance of PPy results from redox reactions, which allow electric charge storage in the bulk of the electrode material. A number of investigations have been conducted in order to investigate the charging mechanism of PPy in different electrolytes and to utilize high theoretical stored charge of PPy (620 F/g) [9-12]. However, one of the major challenges for the electrochemical polymerization of pyrrole is to form adherent PPy coatings on reactive metal substrates, because the dissolution of the metal occurs prior to the coating formation [13,14]. The electrosynthesis of PPy can be favored by adjusting electrolyte ionic strength and pH. It was shown that both high electrolyte concentration and neutral or slightly acid pH increase the quality of the polypyrrole film [15]. The electrochemical stability of polypyrrole is also improved by the addition of carbon nanotubes [16-19] although the specific capacitance of raw CNTs was slightly low (generally <100 F/g) [20]. Nanotubes improve the electrical conductivity of polymer films and decrease impedance modulus of these materials [21].

The aim of this study is to investigate the properties of PPy/CNTs composite film on silicon substrate in the presence of iron catalyst films electropolymerized as supercapacitor electrodes.

Experimental part

The 3D CNTs network was achieved by the chemical vapour deposition (CVD) on n-type silicon (100) substrate using a catalyst layer based on iron obtained through e-beam method. Previous the CNTs growth process, a catalyst recrystallization was carried out at a temperature of 750°C for 15 min inside the quartz tube of CVD equipment. The operation parameters for recrystallization process of catalyst particles are presented in table 1. Within the CNT growth experiment by CVD method, ethylene (C2H4) was used as gas source of carbon. The operation parameters of CVD process to growth nanotubes on the substrate (type n silicon (100)) covered with Fe catalyst are shown in table 2.
The conductive polymeric coatings were achieved by electrochemical polymerization using a Voltalab 40 potentiostat/galvanostat with specific data acquisition and electrochemical processing software. The technique used was cyclic voltammetry. The potential was scanned for 50 successive cycles between 0.20 - 0.85 V/SCE, at a scan rate of 20 mV/s at room temperature. The experiments were carried out in stationary conditions. The electrochemical cell contained a CNTs covered oxidated Si wafer as working electrode (1 cm²), a Pt plate with large surface area as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode.

Chemical reagents used on electrochemical polymerization were: pyrrole (99%), purchased from Acros Organics, and sulfuric acid (98%), oxalic acid dihydrate (98%) and ethanol (p.a) all purchased from Chimreactiv, Bucharest.

The aqueous solutions containing either 0.1 M Py in 0.2 M sulfuric acid or 0.3 M Py in 0.2 M oxalic acid were prepared before the beginning of each electrochemical polymerization and these solutions were kept in darkness to avoid air oxidation and chemical polymerization. To improve pyrrol dissolution in water 3-5 mL/L of ethanol were added.

The electrochemical activity of hybrid polypyrrole-CNTs coating based electrodes in 0.2 M sulfuric acid or in 0.2 M oxalic acid aqueous solutions was studied by electrochemical impedance spectroscopy (EIS) using the same equipment, VoltaLab 40 equipment, connected to a computer through VoltaMaster 4 software interface. A platinum plate electrode and a saturated calomel electrode (SCE) were used as auxiliary and reference electrode, respectively. Impedance measurements were performed on the frequency range between 100 kHz and 10 mHz with an AC wave of 10 mV (peak-to-peak) overlapped on a DC bias potential; the impedance data were obtained at a rate of 10 points per decade change in frequency. Bode and Nyquist diagrams were recorded at stationary potential for each sample. The frequency corresponding to the maximum phase angle (θ) was selected from Bode diagrams; then, the capacity (C) vs. potential (E) curves were drawn at this frequency (fmax). The Nyquist and Bode diagrams were drawn again for the potential at which the capacity was maximum, determined from C = f(E) curves.

Micrographs of samples were obtained using FESEM/FIB/EDS Auriga equipment produced by Carl Zeiss, having minimal resolution of 1 nm at 15 kV and 1.9 nm at 1 kV acceleration voltage with SESI type (combined Secondary Electron Secondary Ion) detector.

AFM measurements were performed using an Integra AFM / STM, NT-MDT microscope.

Results and discussions

Microscopy studies

Figures 1 show the AFM images concerning the morphology of catalytic layer before and after the growth of Fe grains by thermal treatment of recrystallization. Figures 2 show FESEM micrographs of the deposited carbon nanotubes.

Table 1

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Time [min.]</th>
<th>Pressure [mm Hg]</th>
<th>H₂ flow rate [mL/min]</th>
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<tbody>
<tr>
<td>750</td>
<td>15</td>
<td>760</td>
<td>500</td>
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</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Time [min.]</th>
<th>Pressure [mm Hg]</th>
<th>Ar flow rate [mL/min]</th>
<th>H₂ flow rate [mL/min]</th>
<th>C₂H₄ flow rate [mL/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>750</td>
<td>300</td>
<td>760</td>
<td>1000</td>
<td>400</td>
<td>300</td>
</tr>
</tbody>
</table>

Figure 3 shows, as examples, some voltammograms registered for polypyrrole film growth (PPY/CNT sample) on oxidated Si substrate covered with Fe catalyst in 0.2 M oxalic acid supporting electrolyte with 0.3 M pyrrole concentration. One can observe that on anodic branche of voltammograms the current density increases with increasing the number of cycles, from 450 μA/cm² up in the first cycle up to 500 μA/cm² in the 25th cycle, at the same polarization potential (+0.85 V). This means an
increase in the electrical conductivity of the modified electrode as well as in the polymerization rate. By potential cycling at more than the 25th cycle, the current density decreases a little bit and reaches 480 μA/cm² at 50 th cycle; this proves a decrease of polymerization rate by deposit thickening.

As a further characterization of PPy/CNT samples, in Figure 4 are presented the SEM micrographs for electropolymerized polypyrrole film over 3D CNT network grown from 0.3 M pyrrole in 0.2 M oxalic acid electrolyte. It can be seen very clearly a similar vermicular morphology of polypyrrole film electrodeposited by cyclic voltammetry with CNT 3D network.

Characterization by impedance measurements

During EIS measurements we have noticed from preliminary recorded Bode diagrams a maximum of phase angle at 3.20 kHz frequency in the case of H₂SO₄ solution and at 31.64 kHz in the case of oxalic acid solution. Therefore, the capacity - potential diagrams (C = f(E)) were first drawn at these frequencies. These dependencies at an established frequency of AC current for PPy-CNT sample in 0.2 M H₂SO₄ solution (3.20 kHz constant frequency) and in 0.2 M oxalic acid solution (31.64 kHz constant frequency) are represented in Figure 5. As this figure shows, capacity values in oxalic acid solution are with two orders of magnitude lower than in H₂SO₄ solution; actually, values of less than 1 μF/cm² were recorded in this last electrolyte for entire electrode potential domain. The maximum capacity values were registered at +850 mV/SCE in H₂SO₄ solution and at 0 mV/SCE in oxalic acid solution.

Figures 6 and 7 present the Nyquist diagrams for PPy/CNT sample in 0.2 M sulfuric acid and in 0.2 M oxalic acid aqueous solutions at its stationary potentials (+302 mV/ SCE and 301 mV/SCE, respectively). These spectra were recorded by polarization at potentials corresponding to the maximum capacity values which were selected from C = f(E) diagrams (+850 mV/SCE and 0 mV/SCE for sulfuric acid and for oxalic acid, respectively). In all cases it can be observed the occurrence of two well pronounced semicircles, corresponding to the impedance answer given by the existence of two distinct interfaces. Both capacitive loops continue with a linear portion, corresponding to the growth of polymer film.

Figures 8 and 9 present the Bode diagrams for PPy-CNT sample in 0.2 M H₂SO₄ solution and in 0.2 M oxalic acid solution at stationary potential and at potentials corresponding to maximum value of capacity chosen from C - E diagrams. The electrochemical parameters from both Nyquist and Bode diagrams were determined by circular regression and listed in table 3. Values of capacity calculated using the soft of equipment are higher in the case of 0.2 M oxalic acid solution and are in good agreement with its C = f(E) diagram.

In figures 10 and 11 are shown the capacity-frequency curves determined for PPy-CT electrode in 0.2 M oxalic acid solution and in 0.2 M H₂SO₄ solution respectively. It can be noticed that in both electrolyte solutions the capacity decreases monotonous with frequency.

Figures 12 and 13 show the variations with frequency of the angle for dielectric losses for PPy-CNT sample, in the frequency range of 100 kHz – 10 mHz. In both electrolytes, at stationary potentials and at polarization potentials corresponding to maximum capacity determined from C - E diagrams, the angle for dielectric losses has a minimum.
Fig. 8. Bode diagrams drawn at stationary potential (+302 mV/SCE) and at +850 mV/SCE potential in 0.2 M H2SO4 solution for PPy-CNT sample (the angle tangent has a maximum) in the middle of frequency region, while at high and low frequencies, the value of loss angle tangent increases significantly.

Conclusions

An experimental procedure for obtaining PPy-CNT hybrid electrodes was initiated. Firstly, CNT layer was obtained by CVD on Fe catalyst deposited on oxidized Si substrate. Over this CNT layer a polypyrrole film was deposited by electrochemical polymerization from a pyrrole monomer containing acid aqueous electrolyte; this may be either 0.2 M sulfuric acid or 0.2 M oxalic acid.

The electropolymerization process was indicated by stable multicyclic voltammograms (more than 25 cycles) at low scan rate (20 mV/s) in 0.2-0.85 V potential domain. Typical vermicular morphology of the investigated polymer films was similar with that of CNT deposit.

The PPy-CNT hybrid electrodes are suitable for supercapacitors due to their high capacity in acid aqueous electrolyte and low values of the angle of dielectric losses in the middle of frequency region, according to electrochemical impedance measurements.

Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solution</th>
<th>Potential, mV/SCE</th>
<th>Rs, Ω·cm²</th>
<th>Rp, Ω·cm²</th>
<th>C, µF/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPY/CNTs</td>
<td>0.2M H2SO₄</td>
<td>302</td>
<td>306.4</td>
<td>209.4</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td></td>
<td>560.3</td>
<td>20760</td>
<td>766.4</td>
</tr>
<tr>
<td>PPY/CNTs</td>
<td>0.2M oxalic</td>
<td>301</td>
<td>319.5</td>
<td>236.2</td>
<td>0.03</td>
</tr>
<tr>
<td>acid</td>
<td>0</td>
<td></td>
<td>576.5</td>
<td>248.7</td>
<td>2021</td>
</tr>
</tbody>
</table>

Fig. 10. The variation of capacity with frequency in 0.2 M oxalic acid solution at +302 mV/SCE (OCP) and +850 mV/SCE potentials for PPY-CNT sample

Fig. 11. The variation of capacity with frequency in 0.2 M H2SO4 solution at +301 mV/SCE (OCP) and 0 mV/SCE potentials for PPY-CNT sample

Fig. 12. The tangent of the angle of losses (β) vs. frequency in 0.2 M oxalic acid solution at +302 mV/SCE (OCP) and +850 mV/SCE potentials for PPY-CNT sample

Fig. 13. The tangent of the angle of losses (β) vs. frequency in 0.2 M H2SO4 solution at +301 mV/SCE (OCP) and 0 mV/SCE potentials for PPY-CNT sample

Fig. 9. Bode diagrams drawn at stationary potential (+301 mV/SCE) and at 0 mV/SCE potential in 0.2 M oxalic acid solution for PPY-CNT sample

Fig. 12. The tangent of the angle of losses (β) vs. frequency in 0.2 M oxalic acid solution at +301 mV/SCE (OCP) and +850 mV/SCE potentials for PPY-CNT sample
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References

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