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Electrochemical Study of Electroconducting Composite Material – Polypyrrole / Activated Carbon

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Electrochemical synthesis of PPy, and PPy / AC – composite films were carried out in the three electrode cell containing 0.1 M Py and 0.5 M $NaClO_4$ (used as doping agent) dissolved in ACN, and dispersed AC particles (10; 20; 30; 40 and 50 gL^{-1}). Polymerization was performed with constant current of 1.5 - 2.5 $mAcm^{-2}$ and the electrode potential varied with time between 0.95 and 1.05 V/SHE. The experimental data obtained by cyclic voltammetry and electrochemical impedance spectroscopy (EIS) show a significant increase of the redox capacitances (q_c), from ~200 Fg^{-1} for PPy to ~530 Fg^{-1} for the composite film, obtained in the presence of AC (50 gL^{-1} in the solution or 55 w% AC in the composite film). The corresponding increase of the limiting capacitance (C_L) from ~167 Fg^{-1} for a PPy films to ~358 Fg^{-1} for the composite PPy/AC, and enhanced electroconductivity of composites was observed as well. These findings can be mainly ascribed to the redox properties of the AC – particles and their impact to the polymer surface roughness. The decreased values of charge transfer resistance (R_{ct}) and limiting resistance (R_L) and increased of double layer capacitance (C_{dl}) and limiting capacitance (C_L), in both conducting and insulating state, at the same time, indicate the possibility for application of this material (PPy/AC) in supercapacitors and / or batteries.

Keywords: conducting polymers, composites, cyclic voltammetry, electrochemical impedance spectroscopy (EIS), electrical equivalent circuits (EECs)

1. INTRODUCTION

Electroconducting polymers are an attractive class of materials with outstanding environmental and thermal stability, biocompatibility, unique electronic, optical and electrochemical properties [1-3], and therefore they offer a wide range of application, starting from drug delivery [4] and encapsulation systems [5], to their application as electrodes in rechargeable batteries [6], sensors [7], actuators [8], electrochemical capacitors (supercapacitors) [9, 10], solar cells, magnet discs, displays, selective gas membranes [11], and for corrosion protection [12, 13].

Introduction of electroacive conducting polymers such as polypyrrole (PPy) as electrochemical pseudo(capacitor) material, was firstly suggested by Gottesfeld and Conway [14], taking into consideration its characteristic electrochemical behavior. Further investigations were concentrated to a possibility for PPy deposition on different substrates, using metals such as iron [15], steel [15, 16], copper, brass [16], noble metals (Pt, Au, Ti) [17] or inert materials like glassy carbon [18].

Conducting polymers offer possibilities for energy storage through their fast reversible redox reactions similar to those in transition metal oxides: RuO_2, Fe_3O_4, MnO_2 [10], that correspond to a "battery-type" behavior, but exhibiting electrical characteristics close to those of a capacitor. Such polymer materials have been much cheaper than RuO_2 or IrO_4, being not as stable over very long-term cycling ($10^5 \div 10^6$ cycle life), with a very loose mechanical properties [14].

One of the techniques implemented in improving the mechanical characteristics of electroconducting polymer materials are based on synthesis of block or graft copolymers [19], polymer blends, alloys and composites [20, 21] where a good electronic conductivity of a polymer is combined with a much better mechanical properties of some inert polymers (polyvinylchloride, polyvinylalcohol, polyester, etc.) [22]. However, this method does not provide the improvement of an electrochemical activity and stability of the composite. Achievement of satisfactory electrochemical features in electroconductive polymer materials has been accomplished combining two components, an electrochemically active material in a form of fibers or particles, usually based on carbon origin, distributed in an electrochemically active matrix [23].

Activated carbon is technically important material used in the industry for more than one century, but in the last years, the application as electrode in electrical double layer capacitors (EDLCs) (or supercapacitors), stimulates the interest for the characterization of their porous structure and electrochemical behavior [24-26]. Conducting capability of polymer system, among other factors, will depend on a type and capacity of charge storage of particular components in the system. For example, it is expected larger capacity values for systems including activated carbon particles having double layer capacitance (C_{dl}) around 10 to 15 μFcm^{-2} regarding those incorporating carbon black, with $C_{\mathrm{dl}} \sim$ 4.5 to 10 μFcm^{-2}, which is related to a higher porosity and oxygen containing groups at the surface of a material [10, 14].

So, the aim of our research was to synthesize a composite material comprising two electrochemically active components: activated carbon and PPy, from non-aqueous, acetonitrile (ACN) solution containing 0.1M Py and dispersed particles of activated carbon (AC). The obtained composites were investigated by cyclic voltammetry and electrochemical impedance spectroscopy (EIS).

The increased conductivity of PPy/AC films over that of the "pure" PPy film, has been discussed in relation with the developed microporosity of composite films enhancing the diffusion of doping anions in the films bulk.

2. EXPERIMENTAL

High grade chemicals: pyrrole (Py) (Merck), acetonitrile (ACN) (Merck), sodium perchlorate ($NaClO_4$) (Aldrich), and activated carbon (AC) (Merck, p.a., art. 2186) were used as received.

Specific area of activated carbon of ~ 540 m^2g^{-1} was determined using spectrophotometric method (λ ~ 570 nm) and methylene blue as an absorbent.

Electrochemical synthesis of PPy, and PPy / AC – composite films were carried out in the three electrode cell containing 0.1 M Py and 0.5 M $NaClO_4$ (used as doping agent) dissolved in ACN, and dispersed AC particles (10; 20; 30; 40 and 50 gL^{-1}).

In order to prevent sedimentation of AC particles during the process of electrochemical synthesis, the solutions were efficiently agitated with purified nitrogen (~120 bubbles min^{-1}). Polymerization was performed with constant current of 1.5 - 2.5 $mAcm^{-2}$ and the electrode potential varied with time between 0.95 and 1.05 V/SHE. The thicknesses of the films were regulated by anodic (polymerization) charge of 0.36 $Ccm^{-2}\mu m^{-1}$, while the content of AC in the composites was determined by elemental analysis (EA).

A thermostated glass cell (25 °C) with three electrode system, consisting of working, auxiliary and referent electrode was used during the synthesis and characterization of the polymer and composite films. A platinum electrode with surface area, A = 1.7 cm^2, was used as working electrode; platinum foil (~ 20 cm^2) as an auxiliary electrode and saturated calomel electrode as referent electrode. All potentials were measured versus saturated calomel electrode (SCE) and are referred to the standard hydrogen electrode (SHE).

PPy and composite PPy / AC films were investigated using cyclic voltammetry and electrochemical impedance spectroscopy (EIS) at constant potentials in acetonitrile (ACN) solution containing 0.5 M $NaClO_4$.

The cyclic voltammetry measurements were performed in the potential window from 0.95 to -0.6 V/SHE, and sweep rates ranging from 2 to 30 mVs^{-1}.

EIS measurements were carried out in the frequency range from 100 kHz to 10 mHz at constant potential of 0.2 V/SHE, for the characterization of doped, and -0.6 V/SHE, for the undoped state of PPy and / or PPy / AC composite films; with a.c. signal of 5 mV. Electrical equivalent circuits (EEC) for the best fit of the experimentally obtained data were obtained using software developed by B. A. Boukamp [27].

3. RESULTS AND DISSCUSION

3.1. Cyclic Voltammetry Study

Synthesis of electroconducting polymer films and a polymer / activated carbon composites were performed by constant current from a solution containing 0.1M pyrrole in 0.5M $NaClO_4$/ACN and dispersed particles of activated carbon.

The quantity of activated carbon incorporated in the composite films determined by elemental analysis is given in Fig. 1. The ratio of carbon versus nitrogen atoms (C/N) in pure PPy film is 4, which is in accordance with its chemical composition (C_4H_5N).

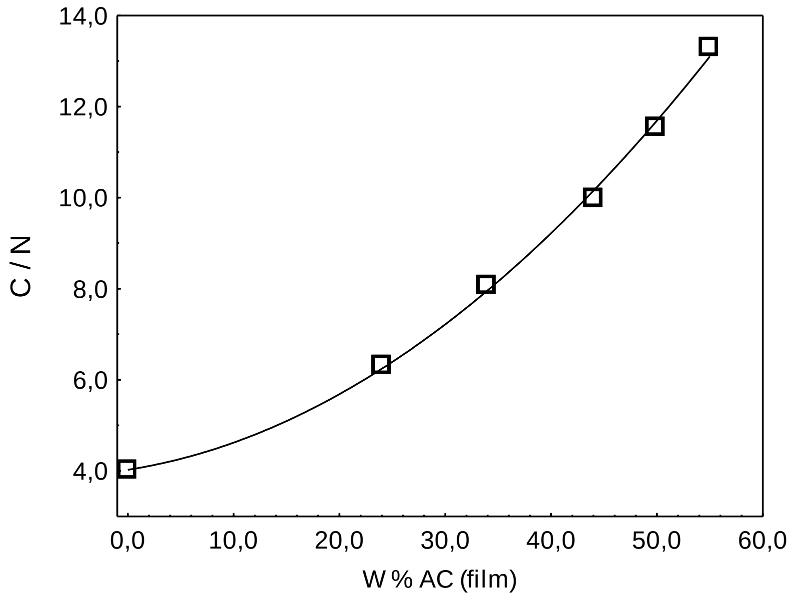

Figure 1. C/N dependence on weight percentage of AC in the PPy/AC - composite.

Table I Electrochemical features of PPy/AC – films synthesized with anodic charge of 1.8 Ccm^{-2} (PPy – film thickness: 5 μm)

C (AC) (gL^{-1})	**AC in films (w %)**	**m$^{f}_{PPy/AC}$**	**m$^{f}_{AC}$**	**L$_f$ (μm)**	**q$_C$ (mFcm^{-2})**	**q$_{red}$ (mCcm^{-2})**
		(mgcm^{-2})				
0	0	0.750	0	5	150	190
10	24	0.987	0.237	~ 6.5*	170	215
20	34	1.154	0.404	~ 7.6*	185	230
30	44	1.339	0.589	~ 9.0*	216	270
40	50	1.500	0.750	~ 10.0*	340	372
50	55	1.667	0.917	~ 11.0*	410	425

*assuming $\rho_{PPy} \approx \rho_{PPy/AC}$; 1.51 gcm^{-3}
$m^{f}_{PPy/AC}$ – mass of the composite film
m^{f}_{AC} – mass of activated carbon in the composite film
L_f – thickness of the composite film

q_C – capacitance calculated from the voltammograms, by the relation: $C = j_C \Big/ \left(\frac{dE}{dt}\right)$

q_{red} – redox capacitance, obtained by the graphical integration of the area under anodic and cathodic processes on the volatammograms

The weight percentages of AC inserted in composite films, based on elemental analysis and theoretical dependence curve are given in the Table I. As it was expected a higher concentration of AC in the solution leads to their increased incorporation in the films.

The voltammometric characteristics of the synthesized PPy and PPy/AC composite films (Figs. 2 and 3), clearly indicate the following:

- Reversible redox behavior in the given potential range (0.9 ÷ -0.6 V/SHE);
- Dominant participation of the capacitance component of the current ($\boldsymbol{j}_C$) (especially at slow polarization rates) which have been confirmed by the linear plots of $\boldsymbol{j}_C$ vs. $\mathbf{d}\boldsymbol{E}/\mathbf{d}\boldsymbol{t}$ in a relatively wide potential range of sweep rates.
- Very fast anodic / cathodic current switching at 0.9 V (confirming the existence of relatively large capacitance).
- The presence of dispersed AC particles (0 – 50 gL^{-1}) in the solution for electrochemical synthesis, Fig. 3, indicates a significant increase of the redox capacitance, q_{red}, and the capacitance (q_C) as well, Table I. In this case, q_{red} was obtained by integration of the area under the anodic and cathodic processes, and the values of the capacitance (q_C) were calculated according the equation: $C = j_c \Big/ \left(\frac{dE}{dt}\right)$, (as a slope of the linear j_C / (dE/dt) plots) [28, 29].

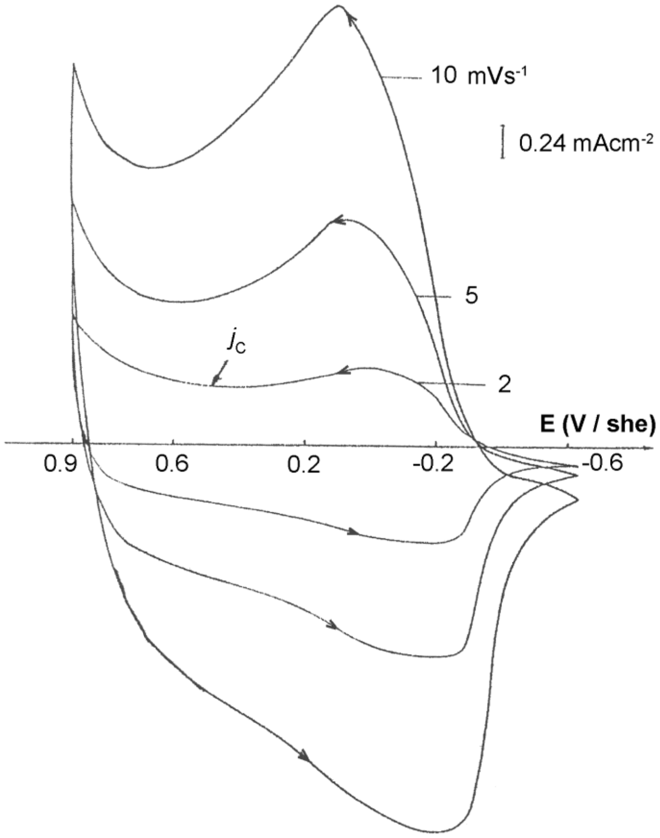

Figure 2. Voltammograms for PPy/AC composite film synthesized from 0.1 M Py in 0.5 M $NaClO_4$ / ACN with C_{AC} = 30 gL^{-1}; j = 1.5 $mAcm^{-2}$; $Q_{pol.}$ = 1,8 Ccm^{-2}.

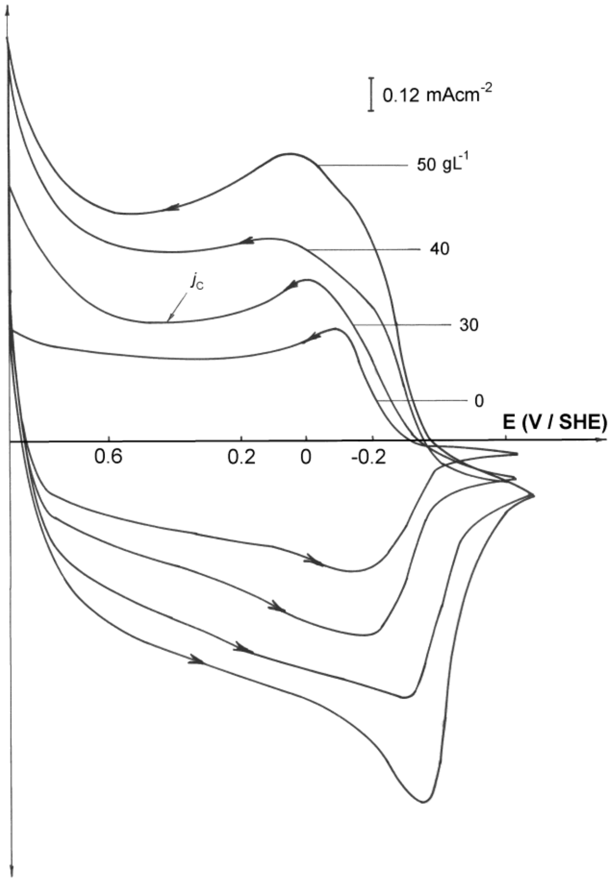

Figure 3. Voltammograms for PPy/AC composite film synthesized from 0.1 M Py in 0.5 M $NaClO_4$ / ACN with C_{AC} = 0, 30, 40, 50 gL^{-1}; sweep rate = 2 mVs^{-1}.

The considerable increase of q_{red} and q_C values of composites, in respect to those of the "pure" PPy evidently results from the incorporated AC particles, which significantly increase the area of the solution / composite film interface, and / or its capacitance, which per se, show reversible behavior, similar to that shown for glassy carbon, pyrographite and carbon fibers [30-32]. Thus, the values of q_C ranges from 150 mFcm^{-2} (~ 200 Fg^{-1}) for PPy to 410 mFcm^{-2} (~ 530 Fg^{-1}) for the composite film obtained in the presence of 50 gL^{-1} AC in the solution or 55 w% AC in the composite film. In the case of the composite film, mainly two processes take place: charging / discharging of the AC – particles / solution double layer and the redox processes of the PPy - film component. This statement has been confirmed by polymerization of PPy film using previously activated carbon fibers [30-32]; as it was shown the redox capacity (q_{red}) of an unactivated carbon fiber surface ranges between 0.2 and 0.5 mCcm^{-2}, while after the optimal electrochemical oxidation, q_{red} drastically increases up to 35 mCcm^{-2}.

3.2. Electrochemical Impedance Spectroscopy (EIS)Study

The observed electrochemical behavior of PPy and PPy/AC composite films was also confirmed by electrochemical impedance spectroscopy (EIS). Bode plots (log Z – log f and φ - log f)

for PPy and/or PPy/AC - composite films in their conducting state (at 0.2 V / SHE), presented in Figs. 4a and 4b, indicate the following:

○ In the frequency region (from 100 kHz to ~30 Hz), the impedance, *Z*, and the phase angle, φ, slightly depends on the frequency, *f*, indicating a pronounced ohmic behavior ($Z \approx R_{sol} = 10$ and 15 Ωcm^2).

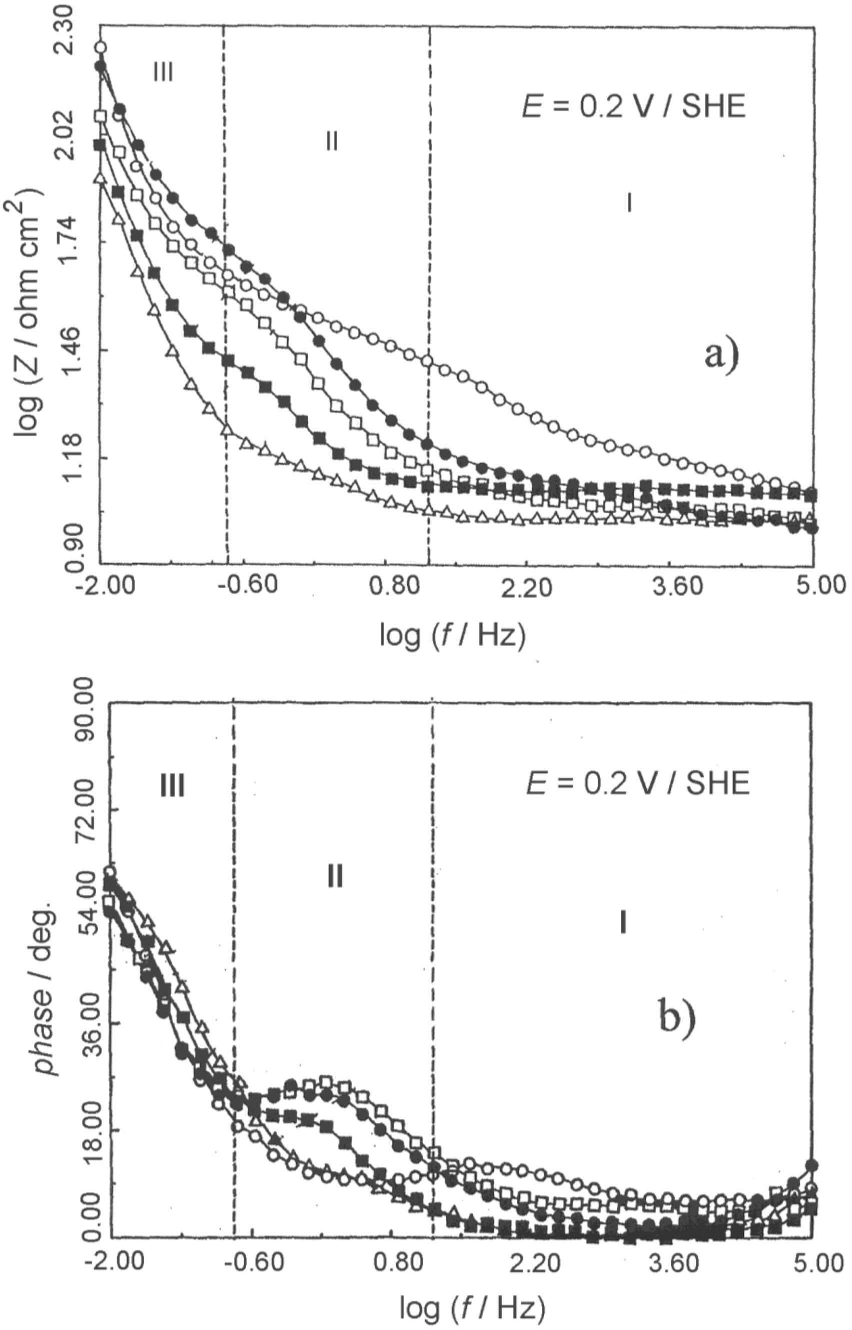

Figure 4. Bode plots of PPy – film (-○-) and PPy / AC composites (Table I): (-●-) 10, (-□-) 20, (-■-) 40, and (-Δ-) 50 gL^{-1} AC in the 0.5M $NaClO_4$ / ACN solution, for oxidized (doped) state (a) log *Z* – log *f*; and (b) Phase – log *f* dependences.

- The second region (from ~30 Hz to 0.5 Hz) with linear log Z / log f plots, and the value of the phase angle up to -25°, is characteristic for the processes taking place at the polymer and/ or composite film / solution interface. In this region the presence of the AC particles at the PPy / AC – composite film / solution interface is evident.
- At lower frequencies ($f < 0.25$ Hz) a nearly linear log Z – log f plots, and phase angles ranging between -54° and -63° has been obtained. Such an behavior is characteristic for very slow, doping / undoping controlled, processes in the bulk of the PPy and / or composite PPy / AC - films in accordance with the “finite diffusion model” of Ho et al [33, 34].

The limiting capacitance, C_L, is calculated from the fairly good linear ($-Z''$ / ($1/\omega$)) plots, Figure 5, using the equation:

$$1/C_L = \mathrm{d}(-Z'')/\mathrm{d}(1/\omega),$$

where Z'' is the imaginary part of the impedance, $Z'' = 1/\mathrm{j}\omega C$, and ω is the angular frequency, $\omega = 2\pi f$.

According to the “finite diffusion model” [33]:

$$C_L = L^2/3DR_L$$

the value of C_L is closely related with the film thickness (L; given in Table I), diffusion coefficient (D) of the doping (ClO_4^-) anions of the polymer film, and the value of the limiting ohmic resistance (R_L) of the PPy and/or PPy/AC composite films, in this case.

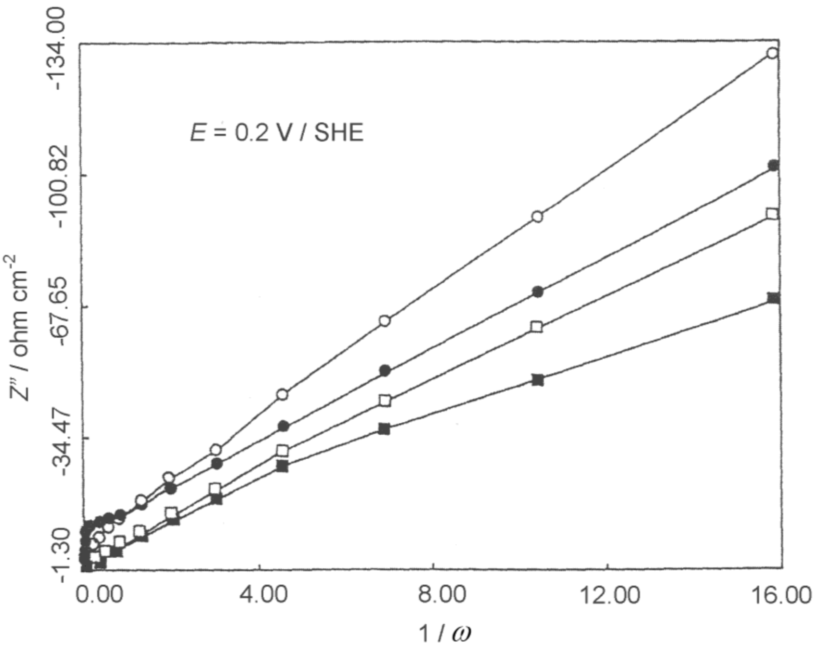

Figure 5. Z'' – $1/\omega$ plots for PPy (-○-) and PPy / AC composites (Table I): (-●-) 20, (-□-) 30, and (■-) 50 gL^{-1} AC in the 0.5M $NaClO_4$ / ACN solution; for oxidized (doped) state of PPy.

Taking into consideration the above mentioned results, the impedance behavior of PPy and / or PPy / AC – composite films, in the conducting state, E = 0.2 V/SHE, can be described with the equivalent electrical circuit (EEC) [27, 32, 35] presented in Fig. 6., where: R_{sol} is the ohmic resistance of the electrolyte; the element Q_1 (with its exponential coefficient n_1), is the so called constant phase element (CPE), and represents the double layer capacitance C_{dl} ($C_{dl} = Q^{1/n}$) at the polymer / solution interface; the element R_{ct} is the charge transfer resistance; the Warburg impedance (W); the element Q_2 (with exponent n_2), characterizing the bulk of the film, is proportional to the limiting capacitance C_L.

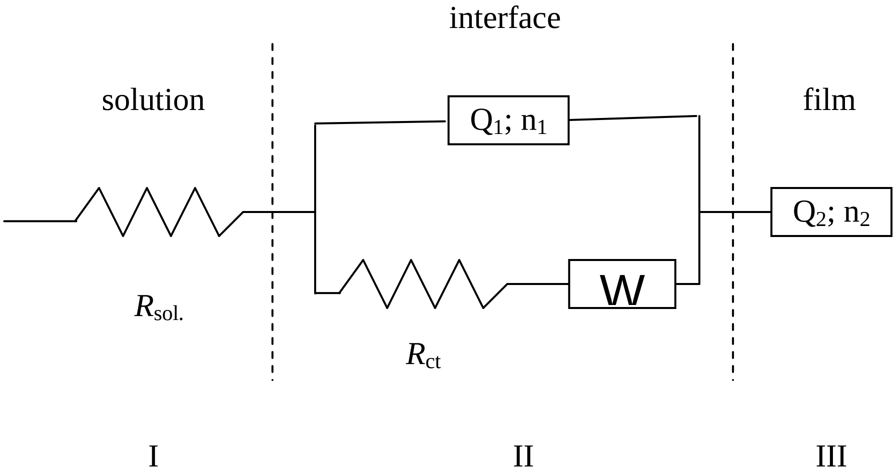

Figure 6. Equivalent electrical circuit (EEC), for doped state (0.2 V/SHE) of PPy and PPy / AC composite films.

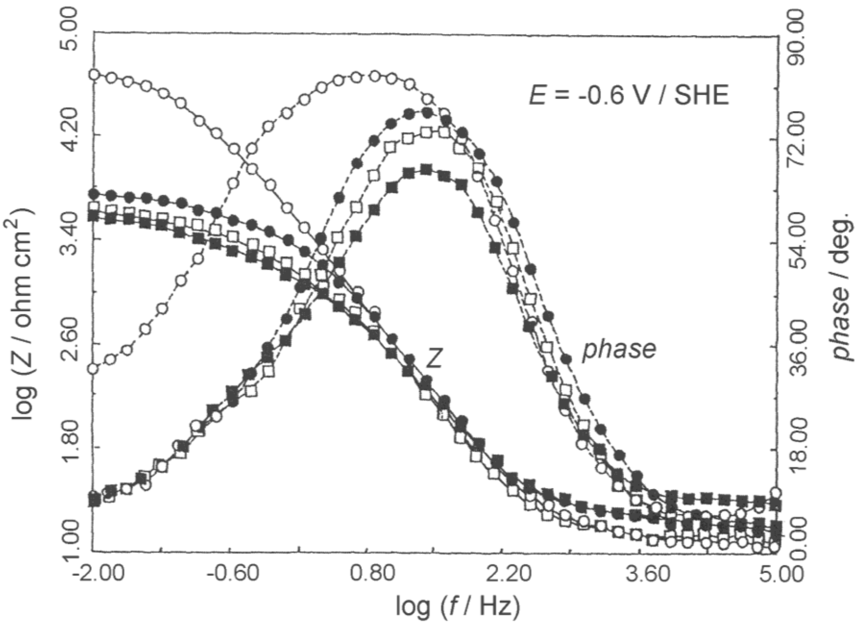

Figure 7. Bode plots for PPy – film (-○-) and PPy / AC composites (L_{PPy} = 5 μm): (-●-) 10, (-□-) 20, and (-■-) 50 gL^{-1} AC in the 0.5M $NaClO_4$ / ACN solution, for reduced (undoped) state.

The experimentally obtained impedance data for insulating state (-0.6 V/SHE) of PPy and / or composite films, Fig. 7, can be satisfactory explained by the simplified EEC presented in Fig. 8.

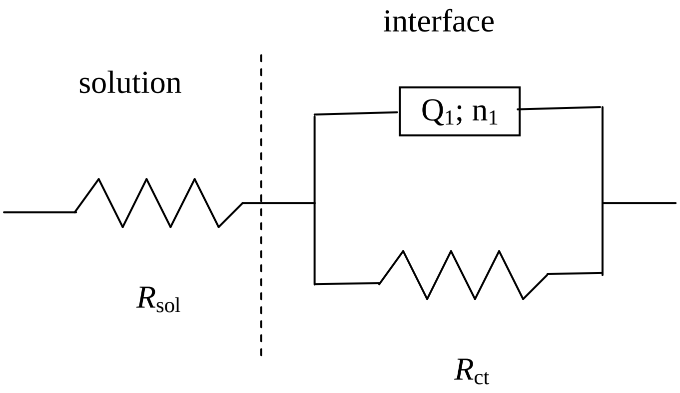

Figure 8. Equivalent electrical circuit (EEC), for undoped (-0.6 V/SHE) state of PPy and PPy / AC composite films.

The best fitting values of the EEC elements for PPy and PPy / AC-composite films in their doped (0.2 V/SHE), and undoped states (-0.6 V/SHE), Figs. 6 and 8, given in Table II, clearly indicate the following:

Table II The best fitting impedance parameters for oxidized (0.2 V/SHE) and reduced (-0.6 V/SHE) state of PPy and PPy / AC composites

C (AC) (gL^{-1})	**R_{ct} (Ω cm^2)**		**C_{dl} (mF cm^{-2})**		**R_L (Ωcm^2)**	**C_L ($mFcm^{-2}$)**
	0.2 V	-0.6 V	0.2 V	-0.6 V	0.2 V / SHE	
0	40	44.7 k	0.225	0.041 (0.93*)	40	125
10	36	5.6 k	4.7	0.054 (0.88*)	35	138
20	32	4.1 k	8.0	0.077 (0.86*)	23	171
30	24	3.4 k	10.0	0.128 (0.77*)	19	200
40	17	2.5 k	15.0	0.120 (0.73*)	15	220
50	5.5	2.3 k	17.2	0.136 (0.73*)	13	270

* Coefficient of homogeneity n; the electrolyte resistance (R_{sol}) was 12 ± 2 Ωcm^2

- Essential differences between conducting (doped) and insulating (undoped) state for both, PPy and PPy/AC - composite films:

The values of R_{ct} for polymer and / or composite films at 0.2 V/SHE (oxidized state) are much lower (about three orders of magnitude, $R_{ct}^{0.2V}/R_{ct}^{-0.6V}$ ~ 10^{-3}, Table II). The similar behavior has been observed for the limiting, and double layer capacitances; $C_{L}^{0.2V}/C_{dl}^{-0.6V}$ = (2 ÷ 3) · 10^{3}.

■ Increasing the concentration of AC particles in the solution for electrochemical synthesis of PPy films leads to the decreasing of both, the charge transfer resistance (R_{ct}) and the limiting resistance (R_L) of the obtained PPy/AC - composite films, Fig. 9.

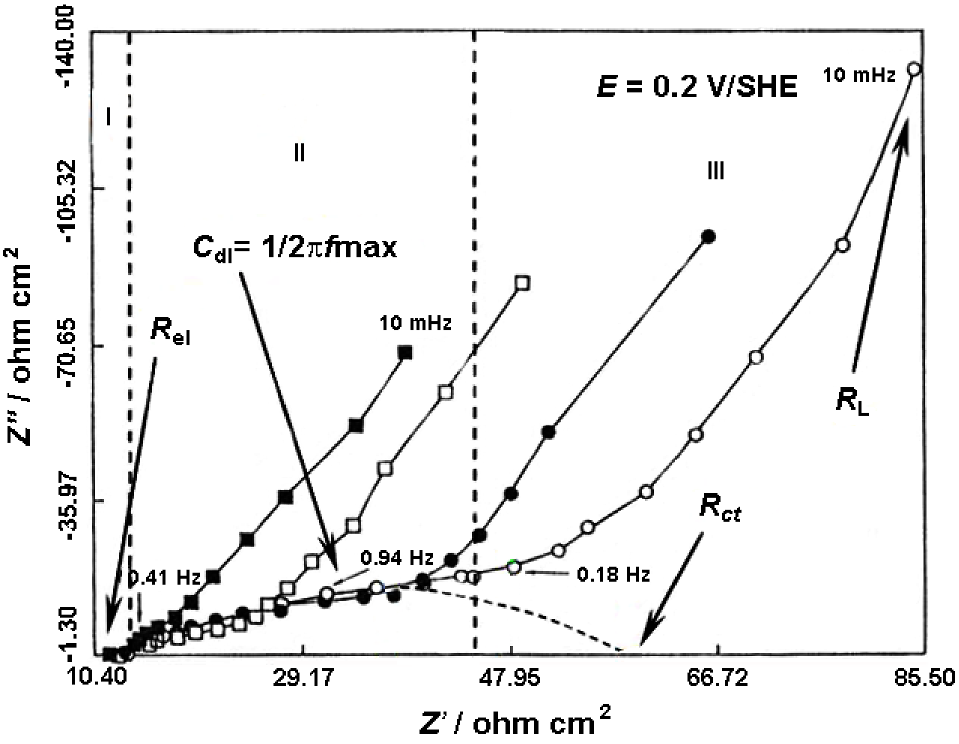

Figure 9. Nyquist plot for PPy / AC composites (L_{PPy} = 5 μm): (-○-)10, (-●-) 20, (-□-) 30, (-■-) 40 gL^{-1} AC in 0.5M NaClO$_4$ / ACN solution, in oxidized (doped) state.

■ The decreased values for R_{ct} with the increased participation of AC in the reduced state of the composite film (-0.6 V/SHE) could be also noticed, Fig. 10. Namely, for the "pure" PPy film (thick 5 μm) at -0.6 V/SHE, Table II, R_{ct} ~ 45 kΩcm^2, and the value of the volume resistivity, $\rho = \frac{45 \cdot 10^3}{5 \cdot 10^{-4}} \approx 10^8\,\Omega\text{cm}$, has been calculated. On the other hand, the PPy/AC - composite, with 55 w% AC (50 gL^{-1} AC), shows a value of volume resistivity, $\rho = \frac{2.3 \cdot 10^3}{11 \cdot 10^{-4}} \approx 2 \cdot 10^6\,\Omega\text{cm}$, (The thickness of the composite in this case (11 μm) is given in Table I).

These features of the composite films can be closely related with the significant increase of the electronic and / or ionic conductivity, surface roughness of these films, and probably with the significant changes in the film morphology, as well.

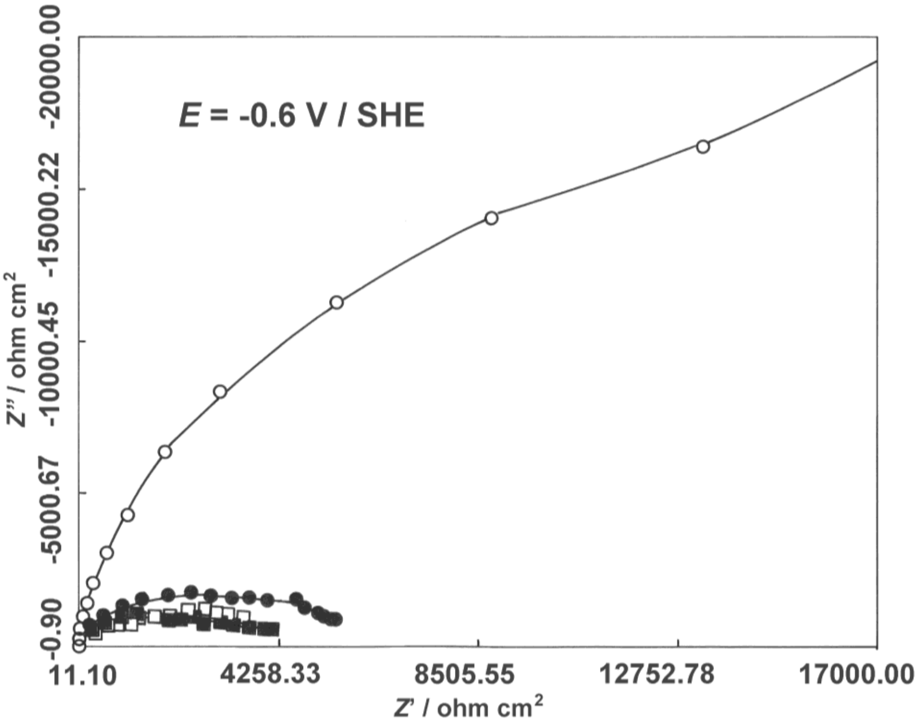

Figure 10. Nyquist plot for PPy – film (-○-) and PPy / AC composites (L_{PPy} = 5 μm): (-●-) 10, (-□-) 20, and (-■-) 50 gL^{-1} AC in the 0.5M $NaClO_4$ / ACN solution, in reduced (undoped) state.

In the reduced state, (-0.6 V/SHE, Table II) the double layer capacitance (C_{dl}) of the PPy/AC composites ranges from 40 to 136 μFcm^{-2} (depending on the concentration of AC in the composite), usual for the polymer / solution interface. Thus, increasing the concentration of AC particles in the solution and consequently in the polymer film, the value of the homogeneity coefficient, $0 < n \leq 1$, ($C_{dl} = Z^{-1}_{CPE} (j\omega)^{-n}$), significantly decreases (from 0.93 for the "pure" PPy to 0.73 for a composite film containing 55 w% AC). At the same time, the presence of AC particles in the composite films facilitates the transport of the doping (ClO_4^-) anions in the bulk of the film, expressed by the increased values of the diffusion coefficient (ranged between $1.7 \cdot 10^{-8}$ and $11.5 \cdot 10^{-8}$ cm^{2}s^{-1}) in the PPy and / or PPy / AC composite films, respectively.

As it was shown the double layer capacitance (C_{dl}) and the limiting capacitance (C_L) of polypyrrole (PPy) and (PPy/AC) composite films, significantly increase at higher concentrations of AC particles in the solution. The enhancement of C_L from 125 mFcm^{-2} (~ 167 Fg^{-1}) for a PPy film to 270 mFcm^{-2} (~ 360 Fg^{-1}) for the composite (PPy / AC), with 55 w% AC in the film was also observed. Such a behavior is mainly due to the increased quantity of AC particles in the composite films, and at the composite / solution interface, as well. The participation of the double layer capacitance in the overall capacitance of the conducting polymer films is negligible, Table II: $C_{dl} / C_L = 0.225 / 125 = 1.8 \cdot 10^{-3}$ (for PPy at 0.2 V/SHE) and $C_{dl} / C_L = 17.2 / 270 \sim 0.064$ (for PPy/AC composite at 0.2 V/SHE; containing 55 w% AC in the film).

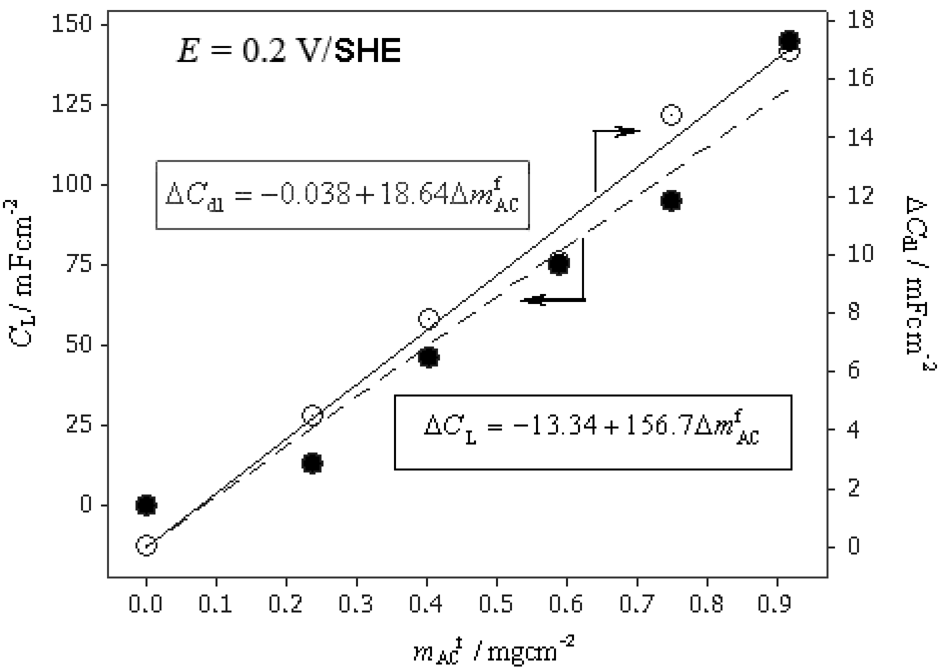

Figure 11. Impact of AC particles in the PPy – composite film (mgcm^{-2}) on the limiting capacitance (C_L) (-●-) and double layer capacitance (C_{dl}) (-○-) – obtained by EIS (Table II).

As can be seen from Fig. 11 the above mentioned findings were confirmed by EIS. The presence of AC particles in the composite films affected, both, the values of C_L and C_{dl}: $\partial(\Delta C_L)/\partial m^{f}_{AC}$ ~ 150 Fg^{-1} and $\partial(\Delta C_{dl})/\partial m^{f}_{AC}$ ~ 18 Fg^{-1}. These values are in a good agreement with the literature data [10, 25] for double layer capacitance of activated carbon in organic electrolytes.

4. CONCLUSIONS

On the basis of the obtained experimental results and discussion it can be concluded as follows:

- Electrochemically synthesized PPy and / or composite PPy / AC – films show a typical reversible redox behavior with the dominant participation of capacitance current component.
- The incorporation of the AC particles in the PPy – matrix sharply increases the electronic conductivity of the obtained PPy / AC – composite films, as well as, their limiting capacitance.

Thus, the electrochemical redox capacitance, q_C, ranges from ~ 200 Fg^{-1} (~56 Ahkg^{-1}) for a “pure” PPy films to ~530 Fg^{-1} (~148 Ahkg^{-1}) for the PPy / AC- composites synthesized in the presence of 50 gL^{-1} AC in the solution (~55 w% in the composite film).

The corresponding significant increase of the limiting capacitance (C_L) was also observed (from ~167 Fg^{-1} or ~47 Ahkg^{-1} for “pure” PPy films to ~358 Fg^{-1} or ~100 Ahkg^{-1} for the composite film).

- AC particles incorporated in the composite films have an appreciable impact on both, double layer capacitance, C_{dl}, and electronic conductivity, of these films. Thus, the double layer capacitance (C_{dl}) ranging from 4.7 to 17.2 mFcm^{-2}, almost linearly increases by increasing the concentration of AC particles in the solution or in the films.

On the other hand, the charge transfer resistance (R_{ct}) and the limiting resistance (R_{L}) significantly decrease; which is of a special interest as far as the application of this material (PPy / AC – composite) in batteries and / or supercapacitors is concerned.

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