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Electroconducting materials based on polypyrrole

ABSTRACT

Polypyrrole, along with polyacetylene, polyparaphenylene polyaniline, polythiophene and other polymers structured by conjugated double bonds, is considered as one of the most attractive conducting materials for various applications, such rechargeable batteries, supercapacitors, sensors, gas membranes, magnetic shields, etc. Regarding their biocompatibility and biodegradability in addition to the possibility of controlling their porosity, as well as incorporation of different biological species, and latter by stimulation (e.g. applying electrical field) to control the release of these moieties from polymer matrix, make these polymers suitable for preparation of drug delivery systems, as well as tissue engineering applications. On the other hand, problems concerning poor mechanical properties and environmental instability could be compensated by preparation of blends, copolymers or composite materials. Systems including two components, e.g. conjugated polymers and carbons, supplement the two diverse electrochemical behaviors of both. Lately, composites of polypyrrole, with pseudocapacitance properties and/or carbons (activated carbon, carbon nanotubes) showing double layer capacitance, have been reported in the literature. So, we have made an effort to outline some of most significant results published.

Keyword: *electroconductive polymers, polypyrrole, activated carbon, carbon nanotubes, composite materials.*

1. INTRODUCTION

Development of new materials recognizable by excellent electronic conductivity comparable to that of conductivity of metals is in the focus of the scientific interest. One of the most interesting materials of this kind are electroconducting polymer materials (ECP) regarding the possibility of reversible change of their reduced (insulating) and oxidized (conducting) state by the means of the processes of reduction (undoping) and oxidation (doping). This feature, offers very broad application areas of electroconducting polymer materials, as electrodes in rechargeable batteries [1], electrochemical capacitors (supercapacitors) [2,3], sensors [4], actuators [5], solar cells [6], selective gas membranes [7], in the corrosion protection [8, 9], and even in the field of drug delivery [10] and tissue engineering systems [11].

The interest for electroconducting materials (ECM) in general started back in the '70s of the last century by the discovery of changes in the electroconducting properties of polyacetylene, firstly synthesized in 1958, by its treatment with oxidizing agent, e.g. iodine [12]. The ECM became more attractive after the Nobel Prize in chemistry was awarded to Heeger, MacDiarmid and Shirakawa for their revolutionary results in developing high conductive polyaniline [13].

Regarding the charge carriers, ECM could be classified as ionic and electronically conducting materials.

Solid polyelectrolytes based on poly(ethylene oxide) [14], poly(acrylic acid), poly(acryl amide) [15] are typical ECM characterized by ionic conductivity. It is considered that the ionic conductivity occurs as a result of detachment of differently charged ions followed by replacement of ions between coordination spots produced by slow segmental movement of polymer chains. Conductivity of polyelectrolytes is sensitive to moisture, the higher humidity results in increased conductivity [14,15].

On the other hand, polymer materials with electronically conductivity might be categorized into two groups, intrinsically and extrinsically conducting polymers [16]:

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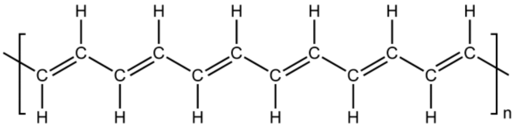
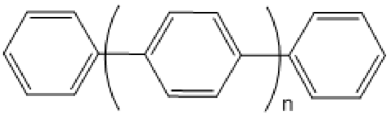
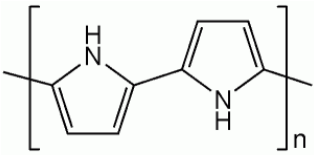
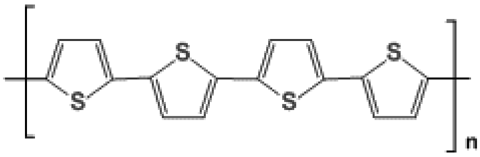
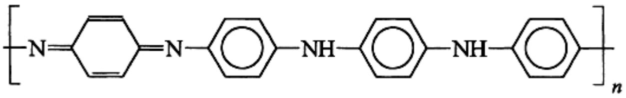
- Intrinsically conducting polymers contains conjugated π -electrons in the backbone which is responsible for the conductivity. Due to the overlapping of these electrons through the polymer chain both, the valence as well as conduction band are formed, but being separated by a considerable band gap. In this class of polymers electronic conduction could occur only after thermal or photolytic activation of electrons, so that they achieve needed energy to jump the gap and reach the conduction band. But, on the other hand only existence of the conjugated electrons is not satisfactory condition, a doping of positive or negative polymer backbone. The conductivity can be increased by creating positive or negative charge on polymer backbone by oxidation or reduction. These polymers have doping of positive or negative charge on polymer backbone. Conductivities of previous type can be increased by creating positive or negative charge on polymer backbone by oxidation or reduction. Examples are: polyacetylene, polyaniline, polythiophene, polypyrrole, etc.
- The conductivity of extrinsically conducting polymers is the result of the inserted conducting fillers in them. In this case a naturally insulating polymers act as matrix which holds the conducting species, such as carbon black, metallic fibers, metal oxides, etc. In order to gain the conductivity, a minimum concentration (called a percolation threshold) of an additive is required. Properties of such fillers, for example, a high surface area, bigger porosity and filamentous nature, assist the development of systems of higher conductivity.

2. INTRINSICALLY CONDUCTING POLYMERS WITH CONJUGATED DOUBLE BONDS

Predecessor of electroconducting polymers systems with conjugated double bonds is considered to be polythiazyl (polymeric sulfur nitride), $(SN)_x$ which is of inorganic origin. The presence of one unpaired electron on each S-N unit leads to the existence of delocalized electrons and just half filled valence band, and by the application of an electric field enables easy movement of electrons to the conduction band.

Among the electroconducting polymer materials which electronic conductivity is a result of their structure, the highest scientific and practical significance belongs to the polymers with conjugated π electrons, as part of them are listed in the Table 1.

Table 1 - The effect of counter anion on the quality of polypyrrole (PPy) [17]

Polymer		Conductivity [$S\cdot cm^{-1}$]
	Polyacetylene	$10^3 – 1.7\cdot10^5$
	Polyparaphenylene	$10^2 – 10^3$
	Polypyrrole	$10^2 – 7.5\cdot10^3$
	Polythiophene	$10 – 10^3$
	Polyaniline	30 – 200

Before polyacethylene was synthesized in a form of film [12], it was considered that the sufficient prerequisite for a high electroconductivity in polymers is the presence of alternating double and single bonds in their structure. But, very low conductivity of these polymers, e.g., polyacethylene of 10^{-8} S cm^{-1}, indicated that a system of conjugated double bonds is not sufficient condition in acquiring a good electronic conductivity. In fact, two segments for achievement of good electronic conductivity in polymers is presence of charge carriers and appropriate orbital system. Conjugated double bonds provide continuous overlapping of p-orbitals along polymer chains, allowing increased electron movement and decrease of the energy gap between the valence and conduction bands, leading to a better conductivity. [17], but the conductivity can be improved by treatment (doping) with suitable species. When polymer is “doped”, a transfer of charges occurs, resulting in a partial oxidation or reduction of polymers, and thus changes of electronic properties. Doping process by oxidation designates removal of part of the delocalized electrons from p_z orbitals forming a p-type material. Namely, treatment of conjugated double bonds polymers, using Lewis acids, such $FeCl_3$ or I_2, promotes oxidation of macromolecule, generating a polycation formation. But, if conjugated polymers are treated with Lewis bases, e.g., sodium napthilide, as a result of reduction, a polyanion is created throughout backbone, ensuing n-type polymer [18].

For p-type of doping

$$\text{Polymer} + X \rightleftharpoons \text{Polymer}^{n+} + X^{n-}$$

where X: I_2, Br_2, AsF_5, etc.

For n-type of doping

$$\text{Polymer} + M \rightleftharpoons \text{Polymer}^{n-} + M^{n+}$$

where M: Na^+, Li^+, etc.

3. SYNTHESIS OF ELECTROCONDUCTING POLYMERS

Electroconducting polymers can be synthesized using chemical [19-21] or electrochemical polymerization [22-25]. Polymerization by ectropolymerization, metal-catalyzed coupling reactions, and chemical oxidative polymerization was successfully used for synthesis of polymers constructed of heterocyclic (pyrrole, thiophene, furan, etc) [26-30] and aromatic units (phenylene derivatives, aniline) [31-37], but also photochemical polymerization and polymerization cathalyzed by enzimes has been also applied [38, 39] Method of chemical polymerization can be applied for synthesis of all types of conducting polymers, including those which cannot be obtained electrochemically [40]. On the other hand, the electroconductivity of polymers obtained chemically is lower compared to the electrochemically synthesized equivalent [41]. Moreover, electrical properties of electroconducting polymers depend on their morphology, which is better controlled during electrochemical polymerization, which could be performed by three methods: galvanostatic, potentiostatic and potentiodynimic [42]. In all three cases the set up for electrochemical polymerization consists of electrode system immersed in the solution containing monomer and doping agent. Galvanostatically conditions offer the formation of the polymer film on the working electrode (anode) with a constant current, in the potentiostatic conditions the deposition of the polymer was controlled with the application of variable potential, while in potentiodynamically settings, the potential sweeps between minimal and maximal value of the potential in the cycle. Most common polymers synthesized electrochemically are polypyrrole, polythiophene, polyaniline and their derivatives, among which, polypyrrole (PPy) attracts bigger attention because of its good electrical properties, biocompatiblitiy, and suitable environmental stability [43].

3.1. Electrochemical synthesis of polypyrrole

The first electrochemically synthesized polypyrrole was crumbly and showed very low conductivity of around 8 S cm^{-1} [44,45]. Importance of electrochemically obtained polymer films was highlighted when continuous stable films, with a higher electronic conductivity (~100 Ω^{-1} cm^{-1}) were successfully synthesized [44-46].

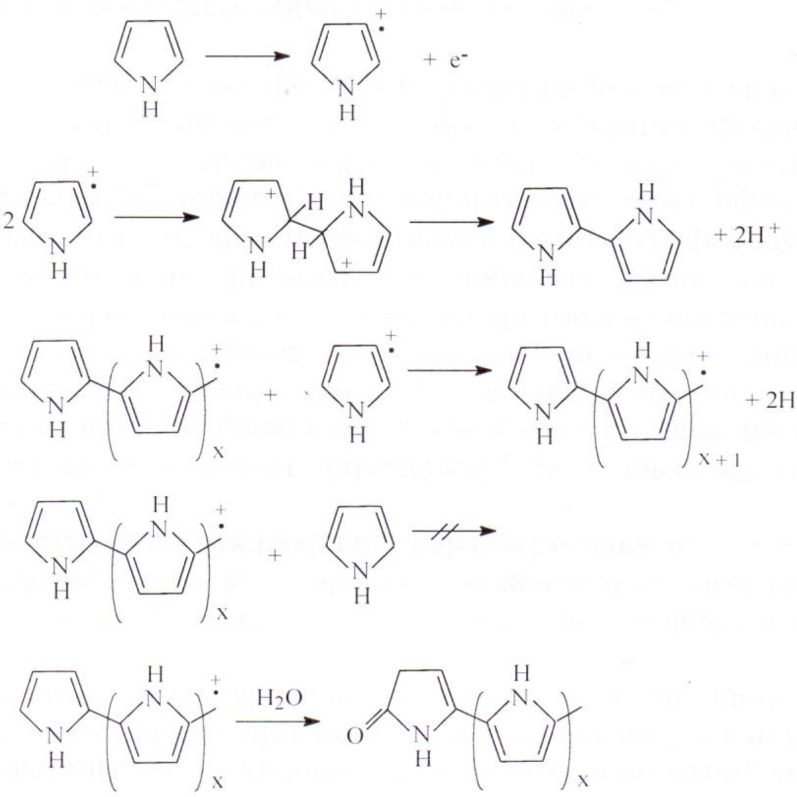
It is considered that the deposition on metal electrodes starts first with adsorption of monomer, than a generation of radical cations and their subsequent recombination. The rate of electrochemical polymerization is not directly dependent on the concentration of monomer in the solution, but it is influenced by its adsorption on the electrode surface, i.e. on the diffusion rate of the monomer molecules to the working electrode (anode).

Mechanism of electrochemical polymerization is very complex and it is not fully understand, but as accepted by Diaz et al., Scheme 1 [47], it is believed that the polymerization occurs by the formation of radical cation and further propagation reaction, accomplished by the coupling of existing radical cations in the system. [19,48].

In order to maintain the system in electroneutral condition, simultaneously to the polymerization process, an anionic doping of the polymer is performed according to the following equation:

$$\text{PPy} + yX^- \rightleftharpoons [(\text{PPy})^{y+}\, yX^-] + ye^-$$

where X: I^-, Br^-, ClO_4^-, etc.



Scheme 1 - *Electrochemical polymerization of pyrrole [48].*

Since the nature and the size of the anion influence the polymer properties, the doping anion should be selected very carefully [19, 48]. Classification of anions dopants according their size it is not done in accordance to the size of the solvated ions, but based on the similarity in in redox behavior of PPy films (shape of voltammograms, kinetics parameters, etc.). Thus, as small ions are considered: ClO_4^-, Cl^-, Br^-, NO3-, BF_4^-, PF_4^-, ions such as: tosylate (TsO^-), pentasulfonate (PS^-) benzenesulfonate (BS^-) are considered as medium sized, while into a group of big ions belong: dodecilsulfate (DDS), poly(styrene sulfonate) (PPS^-) poly(vinyl sulfate) (PVS^-). It was noticed that the best conductivity of PPy films of 60-200 Ω^{-1} cm^{-1} has been achieved when perchlorate (ClO_4^-) anions was used as a doping agent, and the smallest conductivity for the fluorosulfonate (FSO_2O^-) anions. It was also shown that the application of two-valent dopants (SO_4^{2-}, MoS_4^{2-}, HPO_4^{2-}, $C_2O_4^{2-}$, antrahinon anion, indigo disulfonate anion, etc.)-results in formation of a film with a lower conductivity [49, 50]. The nature of a dopant also impacts mechanical properties of polymer films, thus, PPy films containing toluenesulfonate, perchlorate, and fluoroborate anions showed significant mechanical strength, but low elasticity [19].

Except on the type of the anion incorporated into the polymer structure, the properties of electroconducting polymers depend on many factors among which: the nature of the solvent, pH of the polymerization solution, the water content, temperature of deposition, as well as the type of the working electrode [51,52].

For the electrochemical polymerization of pyrrole a wide spectra of aprotic solvents with low nucleophilic character, might be used, such as acetonitrile**,** methylene chloride, butanone, propylene carbonate, etc. The synthesis of polypyrrole in solvents with nucleophilic character leads to the irreversible oxidation of polypyrrole, resulting in disruption of its optical, electronic and electrochemical properties [53]. Polymerization in nonaqueous solutions, for example acetonitrile, produces films of better quality but poor adhesion to the metal electrode, compared to those grown in aqueous solutions.

Diverse conductivities observed in PPy films obtained by varying the current density, i.e. the polymerization charge of polymerization, is closely related to a degree of oxidation of PPy and chains growth [54].

Potentiostatic polymerization of PPy (0.95-1.25 V/SHE) indicated a strong influence of anodic potential on the rate of film growth which also affects the morphology of the deposited polymer [54]. Increased conductivity of a film, as the polymerization potential increases, indicates increased number of oxidized pyrrole units around deposition electrode. Contrary, it was also shown [52] that increasing the anodic potential, as a result of over-oxidized polymer film and inhibited redox processes, polymer conductivity decreases.

In potentiodynamic polymerization Zhou and Heinze [55] emphasized the occurrence that the other researchers tried to ignored, that is, the potential necessary to achieve the oxidation current decreases in each subsequent cycle, i.e., at constant potential, the current of oxidation decline in each following cycle. This phenomenon was explained such as the oxidation of monomer doesn't occur at the solution/electrode interface only, but in the polymer matrix as well.

Neither strong acid nor strong base solutions are required for synthesis of a quality, while lower temperature during polymerization leads to the formation of films with increased conductivity, compared to those gained at higher temperature.

The choice of the electrode material for electrochemical polymerization is restricted by the relatively high potential used for oxidation of monomer. Thus, at polymerization potentials some of the metals and their alloys, whether forms passive nonconductive layer (e.g., Zn) [56] or are dissolved in the solution used in the polymerization set up (iron, steel, etc.) [57-59]. Usually used substrates for polymer deposition are electrodes made of graphite, carbon fibers, glassy carbon, Indium-tin oxide (ITO), inert metals like Au and Pt [11, 43, 60-65].

4. ELECTROCHEMICAL PROPERTIES OF ELECTROCONDUCTIVE FILMS BASED ON POLYPYRROLE

Unlikely the redox systems in which only electrons transport is involved during oxidation and reduction processes, redox processes in PPy films includes both, ion and electron transfer through polymer chains which results in the change from insulating to a conducting state [66,67]. During doping processes, when a positive potential is applied to a neutral polymer, it is oxidized creating positive charges in the polymer chain which are balanced by incorporation of counter anions. Processes of reduction, undoping, realized at adequate negative potential translate the polymer into its neutral state, which is accompanied by the anion diffusion from polymer matrix into solution.

Redox characteristics of PPy films, actually its capacitance and kinetics of redox processes are very important features for their practical application, e.g. sensors, batteries, electrochemical capacitors, with controlled release of the anions out of polymer film being of particular significance during medical applications [10, 28, 68-74].

One of the most exploited techniques for determination of mechanisms and kinetics of redox changes is cyclic voltammetry.

The electrochemical synthesis technique showed very big impact on the electrochemical reaction activity of PPy. Voltamograms of PPy synthesized on glassy carbon using three different methods: galvanostatically, potentiostatically and sequential electrodeposition method, scanned in the potential range from -0.2 to 1.02 V/(Ag/AgCl) in 0.1 M phosphate buffer saline (PBS) indicated the biggest redox capacity for polymer deposited at constant current, while the worst electrochemical activity have shown film gained by sequential deposition method [60].

As far as the doping level concerns, it was reported that for PPy it ranges between 0.2 and 0.33 charge per monomer unit, and it is dependent on the polymerization potential and the nature of the solvent / doping media. So, when PPy is brought into contact with some media which act as electron acceptors, such as gasses I_2 or NO_2, electrons are removed from aromatic rings, leading to the formation of oxidized state of PPy, and thus an increased doping level and electronic conductivity of the film. In the contact to the electron donating gas, such as ammonia, it would be observed decrease of the conductivity of PPy as a result of the reduction reaction occurred. Contrary, for some polymers, e.g. polycarbazole films, it was noticed an increased conductivity in the presence of the electron donating gas [75]. Such a behavior of electroconducting polymers is very useful in their application as sensors for detection of gasses and volatile organic compounds [68, 75-78]. In addition to this, it was found that the potential at which the polymerization process is performed could also influence the doping level of a polymer. Raising the polymerization potential to a threshold point gives polymers with a higher doping level, but at potentials beyond the threshold results in a decreased doping level of the film. As reported by Grchev et al. [79], for the systems studied (PPy films (0.95-1.25 V/SHE) from acetonitrile (ACN) / 1M $LiClO_4$ / pyrrole solutions), at polymerization potentials higher than 1.15 V/SHE, over oxidation of PPy film takes place, thus processes of oxidation and reduction have been retarded and an unconducting (undoped) polymer is acquired.

Typical voltammograms of potentiostatically synthesized PPy films (0.95-1.25 V/SHE) from acetonitrile (ACN) / 1M $LiClO_4$ / pyrrole solutions are presented on Fig.1 [79]. Electrochemical activity has been monitored potentiodynamically in ACN / 1M $LiClO_4$ and H_2O / 0.2 M KCl, pyrrole free solutions. Current / potential (j vs. E) curves have indicated a typical reversible redox behavior, as well as a dominant participation of the capacitance in a given potential range, from 0.9 to -0.2 V/SHE for the electrolyte system ACN / 1M $LiClO_4$ and from 0.5 to -0.5 V/SHE for H_2O / 0.2 M KCl. The capacitance, q_C, read from the plateaus in the anodic and cathode regions, could be calculated from the linear relations of capacitance current, j_C and potential sweep rates, dE/dt, while the redox capacitance, q_{red}, by the graphical integration of the area under anodic and cathodic processes on the volatammograms. At constant sweep rates, a linear dependence for, both, q_C and q_{red}, on the thickness, L, of PPy films has been observed, too. The anodic currents, considering both, pick and capacitive currents are bigger, suggesting a pronounced Faradaic contribution in the electrochemical activity of polymer film. Polymer characterized in a water solution as a result of nucleophilic character of medium, have shown a decreased capacitances compared to that recorded in aprotic solution.

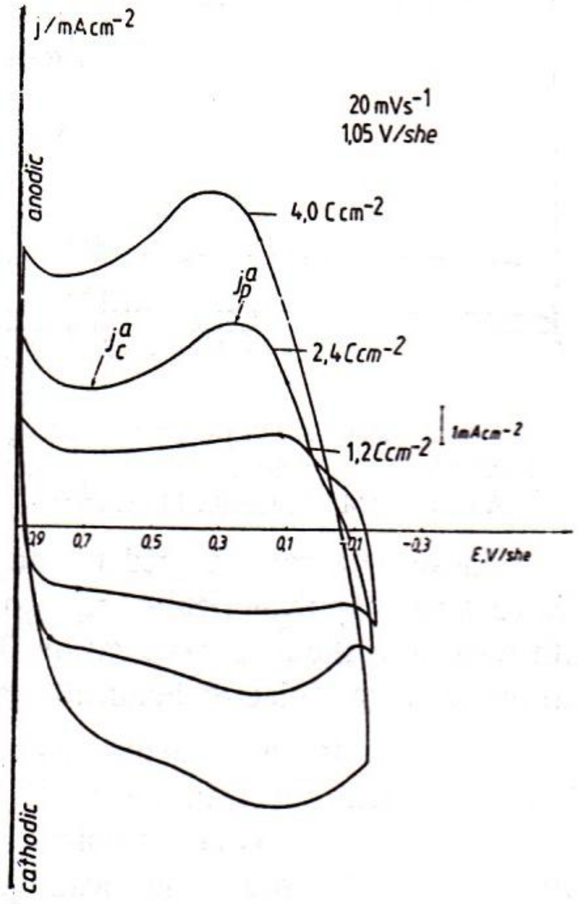


Figure 1 - Voltammograms of PPy films with several thicknesses (3.35, 6.7 and 11.2 µm) [79]

As far as the battery application is concerned, it is known that conducting polymers that can be doped just by p-type of doping, can be used as cathodes, hence in this case it is accepted that the capacitance in the cathodic area is more relevant parameter. [33, 69, 80]. Still, n-doped polymers could be synthesized by incorporation of large polymeric anions in polymer films during their polymerization. Thus, PPy doped with two different dopants, e.g., para (toluene sulfonic acid) (pTS) and indigo carmine (IC), can act as cathode (system PPy/*p*TS) or anode (system PPy / IC) in the combination with polymer-based electrolyte or commercial organic electrolyte. [69]. As far as the stability of these systems concerns, it was observed retention of 76 and 90% of the initial reversible discharge capacity after 50 cycles in the system PPy–pTS / PPy–IC (electrolyte) for polymer-based and commercial based-electrolytes, respectfully.

Development of systems with high specific capacities [81,82] as well as introduction of new techniques for electrode fracture prevention, occurred as a result of volume expansion during cyclic processes [83,84], or inhibition active material dissolution, resulted in application of conducting polymers as coatings in rechargeable lithium-ion batteries [85,86]. Conductive PPy has been also verified as appropriate material in improving electrical properties of lithium-ion batteries, by the preparation of anode materials as: C / PPy [61], and TiO_2 / PPy [87] , SnO_2 / PPy [88], and Si / PPy [89], Ge / PPy [90]. Polypyrrole coatings on α-MoO_3 and also those on composites based on V_2O_5 prevent the dissolution of molybdenum and vanadium ions and improve the cyclic stability of the material. Even it was expected that PPy at the redox potentials of α-MoO_3 would be in its unconducting, neutral state, increase of the electronic conductivity was observed, without suggesting the mechanism for such a behavior. On the other hand, sufficiently thin PPy coatings on $NaTi_2(PO_4)_3$, allows transport of electrons through polymer film, such that, an increased electronic conductivity of the system was observed [91].

Composite materials based on polypyrrole and nano-particles of germanium (Ge) [90] or tin (Sn) [92] indicated superior electrochemical behavior capacity compared to the virgin germanium. Better electrochemical properties of nanocomposites could be attributed to the PPy matrix, which affords an efficient electrons transportation route, but also prevent and/or reduce the agglomeration of nanoparticles. Thus, the system consisting on Ge nanoparticles coated on the surface of PPy indicated approximately 2.5 times higher discharge capacity after 50 cycles of charging-discharging processes of composite (1014 mAh g^{-1}) compared to that of pure Ge (439 mAh g^{-1}), which makes this system as a suitable anode material in the lithium-ion batteries [90].

Composite films with a developed porous structure, based on polypyrrole and reduced graphene oxide acting as dopant (PPy/r-GO) was successfully prepared. When used as a cathode material this film showed an outstanding cycling stability, but also conveyed a large discharge capacity when used as an anode material, that is mostly ascribed to the reduced graphene oxide (r-GO) component. [93].

Very fast processes of charging / discharging, which in the power devises such as electrochemical capacitors (ECs) occur within seconds, give a crucial role of these energy storage systems making them very popular with the intention of complementing or substituting conventional batteries [94]. Based on the active material used and the mechanisms of charge storage, ECs can be categorized as:

1. Double layer capacitance ECs involving carbon-based active materials which energy-storage characteristics depends on physical and chemical characteristics of carbon electrodes. In order to acquire material with a high activity and reproducible behavior, chemical or electrochemical activation of carbon electrode is required [95]. Electrochemical stimulation - oxidation, could be performed potentiodynamically, by cycling in a given potential range, galvanostatically (constant current) or potentiostatically (constant potential). An extent of power and energy-storage capabilities is closely related to the physical and chemical characteristics of carbon electrodes. Thus, some of the investigations [96] of electrochemically oxidized carbon fiber (CF) electrode at constant current, indicated charge densities of oxide layer (which is pseudo capacitance in origin) itself of 290-300 Ah kg^{-1}, and for untreated CF electrode it was shown only 5 Ah kg^{-1}. The values of capacitances and / or charge densities of treated CF is proportional to the quantity, i.e., thickness of oxide layer [96]. Thus, decreasing the size of carbon material, and thus increasing its surface area, e.g. carbon black (CB) with surface area bigger than 1000 m^2 g^{-1}, increases the capacitance of the material [97].
2. Pseudocapacitors or redox supercapacitors belong to a second group of ECs, featured by fast and reversible reactions, Faradaic chemical processes occurring at the surface or near-surface of the electrode. Supercapacitors as energy storage devices act a role of a bridge between high power capacitors and high energy batteries [98]. Transition metal oxides and electrically conducting polymers (polyaniline, polypyrrole, polythiophene and their derivatives) have been observed as pseudocapacitance materials in EC applications [2], which capacitance was suggested to embrace Faradaic processes of chemical / electronic changes. [2, 59, 99].

Very small charge capacity is a major weakness of conducting polymers, and it can be improved by combination with a high-charge capacity redox molecule, such as 1,4-benzoquinone. System comprising polypyrrole electrodes doped with 1,4-benzoquinone displayed increased charge capacities of 104 mA h g^{-1} in comparison to 50 mA h g^{-1} of a neat PPy electrode. [98]. Similarly, arrangement consisting of two diverse electrochemically active components [97-99]: double layer capacitance (CF or CB) and a component with Faradaic character, i.e., pseudo-capacitance behavior such electroconducting polymers [61,100,101].

4.1. Electrochemical properties of PPy based composites

Recently [100,101], two types of PPy / activated carbon (AC) composites have been synthesized from non-aqueous acetonitrile (ACN) solution containing 0.1M Py, 0.5 M sodium perchlorate ($NaClO_4$) used as a doping agent, and dispersed AC particles with variable concentrations, between 10 and 50 gL^{-1}, but fixed PPy thickness of 5 µm, or fixed concentration of AC in the solution for electrochemical synthesis of 30 gL^{-1}, and different thicknesses of PPy from 1.5 to 15 µm. and/or composite films, using constant current (2.0 mA cm^{-2}) and polymerization potential varied between 0.95 and 1.05 V/SHE. Control of the thicknesses of polymer and composite films, in both cases, has been accomplished by the application of polymerization charge of 0.36 C cm^{-2} μm^{-1} [79]. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy analysis were performed in acetonitrile solutions containing 0.5 M $NaClO_4$, and free of pyrrole and activated carbon particles. As this system is made of two components, polymer matrix which is liable for ionic conductivity and activated carbon particles responsible for electronic conductivity, it covers both types of conductivity.

The voltammometrics curves of these composite materials, resembled those voltammograms presented on Fig.1 for “pure” PPy, specifying existence of reversible redox behavior, as well as prevailing contribution of capacitive component of a current in total current. PPy / AC composite films with bigger thicknesses, in addition to the increase of the concentration of AC particles in the polymerization solution and films as well, showed significant increase of both, redox capacitance, q_{red}, and the capacitance, q_C. [100].

Electrochemical characteristics of polymer and composite films of varying thicknesses as well as different concentration of AC particles in the polymerization solution and/or obtained composite film, monitored by electrochemical impedance spectroscopy (EIS), supplemented the findings gained by cyclic voltammetry.

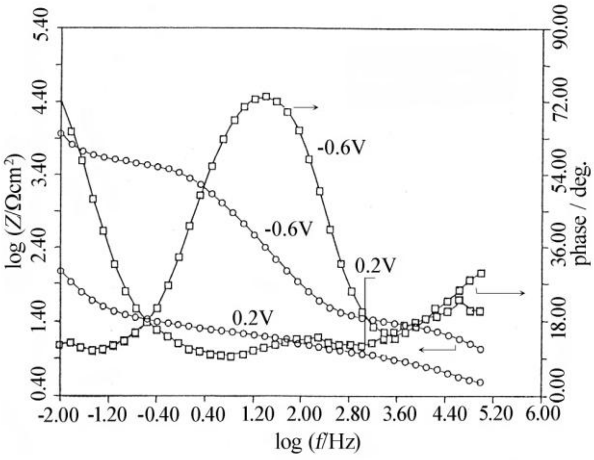


Figure 2 - Bode – plots (log Z – log f, and φ - log f) for PPy film (5 μm) in doped (E = 0.2 V/SHE) and undoped (E = -0.6 V/SHE) states, in 0.5 mol dm^{-3} NaClO$_4$ / ACN solution [101].

The typical log Z – log f, and φ - log f plots of polymer and composite films for the doped (E = + 0.2 V/SHE) and undoped states are shown in the Fig. 2.

Regarding conducting state of polymer / composite films the following frequency regions could be identified.

First region (from 100 kHz to ~30 Hz) characterized with a pronounced ohmic behavior of the electrolyte between the working and the reference electrode. [100, 101]. The second region, appearing usually in the frequency region with moderate frequencies, e.g., between 30 and 0.5 Hz, is characteristic for the processes at the interface solution / polymer and/or composite film, while the third region attributed to the lower frequencies, represents very slow, diffusion controlled processes of doping / undoping, inside films, represented by the “finite diffusion model” of Ho et al [79, 100-102]:

$$w \ll 2D / L^2 \tag{1}$$

$$R_L = \frac{V_{m.} \cdot L}{z \cdot F \cdot A \cdot 3 \cdot D}(dE / dy) \tag{2}$$

$$C_L = \frac{z \cdot F \cdot L \cdot A}{V_m}(dy / dE) \tag{3}$$

$$R_L \cdot C_L = L^2 / 3 \cdot D \tag{4}$$

$$C_L = (k / 3 \cdot D) \cdot L \tag{5}$$

where D is the diffusion constant of doping ions with charge z; L is the thickness of polymer; V_m is the molar volume of the polymer film; dE/dy is the variation of the potential with doping level; F – Faraday constant; R_L is a limiting resistivity of polymer film in the total resistance ($R_{total} = R_{el.}+R_L$) computed for low frequencies ($f \rightarrow 0$); C_L is the limiting capacitance of the film, calculated from the linear plots: – Z'' / ($1/\omega$) where ω is an angular frequency ($\omega = 2\pi f$); k is the ionic conductivity (L/R_L), and A is the electrode surface area [79].

Electronic conductivity of the obtained pPy / AC – composite films, as well as, their limiting capacitance is significantly enhanced by the synthesis of polymer and composite PPy/AC films with higher thicknesses, but also increasing the percentage of AC particles in the polymerization solution and / or pPy – matrix. Thus, the noteworthy increased values of the limiting capacitance from ~180 Fg^{-1} (~50 Ahkg^{-1}) for “pure” pPy films to ~358 Fg^{-1} (~100 Ahkg^{-1}) for the PPy/AC composite film of the same thickness and ~55 w% presence of AC particles [100].

As the result of higher thicknesses of polymer and composite films and / or increased amount of AC particles incorporated in the composite films leads to the differences in the morphology of the film, which will increase the values of diffusion coefficient of doping ions. The nature of the doping ions influences the value of diffusion coefficient [103, 104], so for perchlorate ions, the observed values were in the order of magnitude from 10^{-7} to 10^{-9} cm^2 s^{-1} [79, 100, 101].

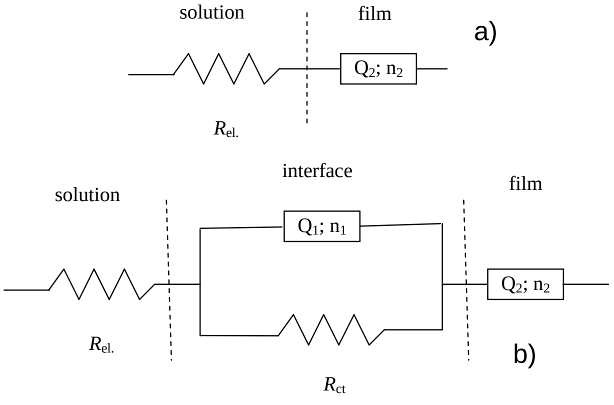


Figure 3 - Electrical equivalent circuits for doped (E = 0.2 V/SHE) state of PPy in the PPy / AC – composite film with 30 wt% of AC in the polymerization solution; (a) L_{PPy} < 2.5 µm, (b) L_{PPy} ≥ 2.5 µm [100].

In terms of the explanation of impedance behavior of polymer and composite films in the conducting state of PPy film (E = +0.2 V/SHE), according the simulation software developed by Boukamp [105], RQ - equivalent electrical circuit

(EEC), Fig. 3a, as well as R(RQ)Q EEC, Fig. 3b for the best fit to the experimentally obtained data has been suggested [100, 101].

The charge transfer resistance, R_{ct}, of the doping ions from solution to the polymer and or composite surface determines the value of electrolyte ohmic resistance, R_{el}. Double layer capacitance, C_{dl}, ($C_{dl} = Q^{1/n}$) explaining the diffusion or mixed (ohmic-diffusion) processes at the solution / polymer interface is represented by constant phase element (CPE) - the element Q_1 (with the exponential coefficient n_1) [106, 107]. The element Q_2 shows the processes inside polymer and/or composite films, approaching the behavior of an ideal capacitor with the exponent n_2 takin value very close to 1 [107].

The electrochemical behavior of polymer and/or PPy / AC composite films in their conducting - doped and insulating - undoped state, (-0.6 V/SHE) shows some essential differences, Fig. 3. When system is in its insulating state, the charge transfer resistance, R_{ct}, shows higher, while double layer capacitance, C_{dl}, smaller values of about three orders of magnitude in respect of same parameters of PPy and or PPy / AC composite film in insulating state [100]. As a result of increased microprosity and at the same time conductivity of thicker polymer and composite films (particularly for those having bigger amount of AC particles), lower volume resistivity was observed in contrast to a pure PPy [101]. Similarly like in the conducting state, electrochemical features of PPy and PPy / AC composites in their insulating state could be explained by simple EEC, Fig. 4a, for thinner films, and more complex EEC, Fig. 4b, for thicker ones, where diffusion controlled processes, (Warburg impedance) [100, 101, 107], at the solution / film interface are pronounced.

Comparable behavior was also observed for systems, such as graphene / polypyrrole composites, obtained by chemical oxidative polymerization of PPy onto graphene substrate [108].

Nanotechnology and synthesis of nano-sized materials are expanding part of science especially in the field of conducting materials, offering superior features compared to their larger scale counterparts.

Many efforts were made in building systems with an extended life cycles of electrodes applied in supercapacitors and composite materials including carbon nanotubes (CNTs) are one of them. Great electronic conductivity, very high surface area, excellent chemical and mechanical stability make CNTs suitable in a compensation of disadvantages of conducting polymers synthesized for supercapacitor applications [109-113]. Very high specific capacitance and good high-rate capability of electrode material has been achieved by synthesis of PPy/CNT composite with controlled pore size in a three-dimensional entangled structure of a CNT film using an electrostatic spray deposition process [112].

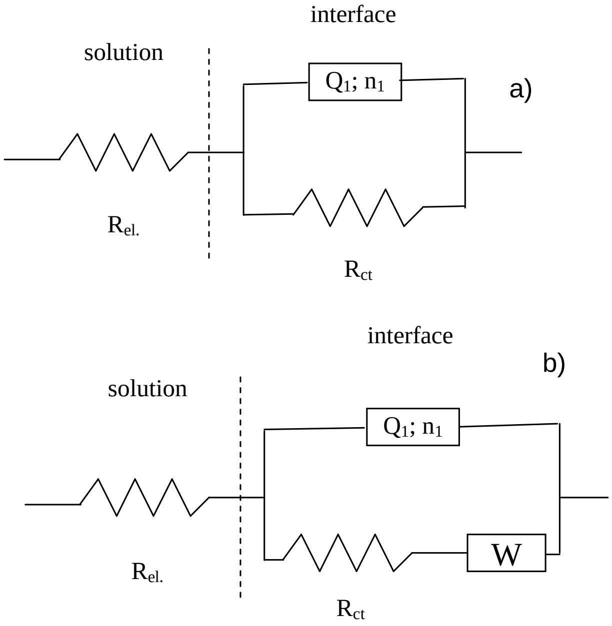


Figure 4 - Electrical equivalent circuits for undoped (E = -0.6 V/SHE) state of PPy in the PPy / AC – composite film with 30 wt% of AC in the polymerization solution; (a) $L_{PPy} < 2.5$ μm, (b) $L_{PPy} \geq 2.5$ μm [100].

Recently, Paul et al. synthesized polypyrrole (PPy) / multi-walled carbon nanotube (MWCNT) / conductive carbon (CC) composites by chemical oxidative polymerization method using anhydrous $FeCl_3$. The impedance behavior of PPy / MWCNT / CC electrodes in their insulating state, have been taken before and after performed charging-discharging 500 cycles in the potential range from 0 to 0.6 V. Charge transfer resistance, R_{ct}, of composites comprising 10, 15 and 20 wt% of MWCNT determined before cycling processes have shown values of 7.4, 2.1 and 4.3 respectively, which indicated that only optimal amount of MWCNT could facilitate the charge transfer throughout the system [113].

The areas of applications of CNT based composites are constantly increasing, so except electrodes in the supercapacitor cells, such and similar systems might be applied as sensors for heavy metals detection [114,115], but lately their application as microbial fuel cells where biomass, through the metabolic activity of microorganisms, successfully converted into electricity has been reported [116].

In spite of importance of carbon nanotubes as nanomaterials for many industrial application, and their production, their serious impact on human health is consider as their serious weakness [117, 118]. Thus, the further scientific intersect should be focused on special regulatory attention and special safety measures during manipulation with CNT which can reduce and/or eliminate their adverse effects.

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IZVOD

ELEKTROPROVODLJIVI MATERIJALI NA BAZI POLIPIROLA

Polipirol zajedno sa poliacetilenom, poliparafenilenom, polianilinom, politiofenom i drugim polimerima, koji u svojoj strukturi sadrže konjugovane dvojne veze, smatraju se jednim od najatraktivnijih provodnih materijala sa širokim spektrom primene, kao što su baterije sa višekratinim punenjem, superkondenzatori, senzori, gasne membrane, štitovi od magnetnih uticaja itd. Zahvaljujući njihovoj biokompatibilnosti i biorazgradljivosti, nadopunjavajući mogućnost za kontroliranje njihove poroznosti, kao i sposobnost za inkorporiranje biološko-aktivne komponente, koje se kasnije kao rezultat stimulacije (na pr. primena električnih polja) oslobađaju iz polimerne matrice, daju pogodnost provodljivim polimerima za izradu sistema za kontrolirano oslobođenje lekarstava, a isto tako su pogodne i kao matrice za inženjering tkiva. Sa druge strane, loša mehanička svojstva i nestabilnost ovih polimera se mogu poboljšati sa priprenom kompozitnih materijala, blendi, ili metodom kopolimerizacije. Kompozitni sistemi, koji se sastoje od polimera sa konjugiranim dvojnim vezama i aktivnog uglja, nadopunjavaju različite elektrohemijske karakteristike obe komponente. Kasnije se u naučnoj literaturi pojavljuju informacije o kompozitnim materijalima na bazi polipirola sa pseudokapacitivnim karakteristikama i/ili materijale na bazi uglja (aktivni ugalj, nanocevčice) koji se sa druge strane karakterišu kapacitetom dvojnog sloja. Dakle, u ovom radu potrudili smo se da izdvojimo neke od najznačajnijih objavljenih rezultata.

Ključne reči: *elektrosprovodljivi polimeri, polipirol, aktivni ugalj, nanocevi, kompozitni materijali.*

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