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Influence of dopant anions on
the electrochemical properties of
polypyrrole films



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LIST OF ORIGINAL PUBLICATIONS

The thesis is based on the following papers, which are referred to in the text by their Roman numerals I–IV.

- I. Tamm, J., Raudsepp, T., Marandi, M., Tamm, T.; Electrochemical Properties of the Polypyrrole Films Doped with Benzenesulfonate, *Synth. Met.* 157 (2007) 66–73.
- II. Raudsepp, T., Marandi, M., Tamm, T., Sammelselg, V., Tamm, J.; Study of the factors determining the mobility of ions in the polypyrrole films doped with aromatic sulfonate anions. *Electrochim. Acta.* 53 (2008) 3828–3835.
- III. Raudsepp, T., Marandi, M., Tamm, T., Sammelselg, V., Tamm, J.; Redoping – A simple way to enhance the redoxcapacity of polypyrrole films; *Electrochem. Commun.* 12 (2010) 1180–1183.
- IV. Raudsepp, T., Marandi, M., Tamm, T., Sammelselg, V., Tamm, J.; Influence of redoping on electrochemical properties of the polypyrrole films; submitted.

Author's contribution:

- I The author performed all the experimental work (including the synthesis of polypyrrole and the electrochemical measurements), the data analysis, and contributed to writing the text of the paper.
- II–IV The author performed all electrochemical measurements (including the synthesis of polypyrrole and the electrochemical measurements), and data analysis. Wrote the first draft of the manuscript and was involved in the final editing and submission of the manuscript in cooperation with the co-authors. The author is responsible for the interpretations of electrochemical results.

LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
CV	Cyclic Voltammetry
Py	pyrrole
PPy	polypyrrole
PTh	polythiophene
PAn	polyaniline
EQCM	electrochemical quartz crystal microbalance
BS	benzenesulfonate (anion)
<i>p</i> TS	p-toluenesulfonate, tosylate (anion)
NDS	naphthalene-1, 5-disulfonate (anion)
NS	naphthalene-2-sulfonate (anion)
DDS	dodecylsulfate
EDS	electronprobe X-ray microanalysis
STM	scanning tunneling microscopy
Q_d	deposition charge
Q_{red}	reduction charge
j_d	deposition current density
f_e	electrochemical doping level
f_a	analytical doping level

INTRODUCTION

Electronically conducting polymers are an interesting class of materials that gained popularity at the end of last century. For a long time it was believed that all polymers are dielectrics. The discovery that some polymers might be semi-conductors or even conductors was the inducement to a new branch of research – the study of conducting polymers. Conducting polymers have also been called “synthetic metals”.

The importance of this discovery was recognized in 2000 when the Nobel Prize for Chemistry was awarded to the scientists who discovered electrically conducting polyacetylene in 1977: Alan MacDiarmid; Alan Heeger and Hideki Shirakawa [1,2]. In fact, as early as in 1862 H. Letheby from the Collage of London Hospital obtained the first partly conductive material by using the anodic oxidation of aniline in sulfuric acid [3]. This material was probably polyaniline. But this work did not lead to a breakthrough in this field.

The high interest in conducting polymers is based on their high conductivity, good mechanical properties, structural flexibility, versatility of properties, lightness and already also on the long-term technological applications. In particular, polypyrrole is one of the most promising conducting polymer, because it has higher conductivity and environmental stability in the conductive (oxidative) state than most other conducting polymers. Furthermore, polypyrrole has been shown to be biocompatible when “doped” with particular counter anions [4–7].

Since the Nobel Prize awarded discovery that some polymers or “plastics” can be made electronically conducting, the scientific field of organic electronics has arisen. Many new conducting polymers have been synthesized such as polypyrrole (PPy), polythiophene (PTh), polyaniline (PAn), polyparaphenylene (PPP) etc., [1,8] and much attention has been paid to the application of these materials. Already at this moment, the potential applications of PPy, PAn, PTh, PPP are numerous and will grow as the improvement in the characteristics of these materials continues.

Conducting polymers have been used in many areas like medicine, the military, aeronautics, industry of semi-conductor device etc. There have been many potential applications suggested for these materials, including sensors [9–11], electrochromic devices [1,8,12–14], polymeric batteries [1,8,15], transistors [8,16], photodiodes [8,16], light emitting devices, electrochemical actuators (artificial muscles) [18–24], membrane separations and smart selective ion-exchange membranes [25–31], capacitors [32–34], antielectrostatic coatings[35], protective clothing for the military [36], implantates [4–7], as radar absorbing material [37] etc. In addition, there are a number of publications showing that conducting polymer coatings on metal electrodes have remarkably good corrosion protective effect [38–40].

This wide range of applications is possible in part due to the possibility to alter the electrochemical, optical, chemical, and mechanical properties of these polymers by changing synthesis conditions. In other words, the effect of the different adjustments can be used to the advantage to custom-tailor the

properties of the resulting materials. The second possibility to modify the properties of polypyrrole is mixing it with other compounds. For example, interesting and promising materials are also the conducting composites based on polypyrrole and other conducting polymers. Composites are prepared by adding carbon black, carbon fiber, nickel-coated graphite fiber, metal powders etc. to the conducting polymers [41–42]. The materials obtained in this way have distinctive features of both components. For instance, the composites of carbon nanotubes and conducting polymers are promising materials for supercapacitor devices due to their unique nanostructure that combines the redox charge storage mechanism of conducting polymers with the high surface area and nanoporosity of carbon nanotube films.

It is very well known that the synthesis conditions, as an example the pretreatment and material of electrode [1,43–45], polymerization method (potential regime, current density [46–48] or potential of polymerization [49]), the composition of synthesis solution (solvent [50–51] monomer[45], dopant [29,48,52–66], temperature [67–68], pH [69] and additives [56–57]) have great effect to the final properties of conducting polymers. From the aforementioned factors, the nature of the dopant has the most significant and dramatic effects on the properties (electrical, mechanical, physical and morphological) of the polymer, because this has remarkable influence on the structure of the polymer, especially in the case of aromatic sulfonates such as tosylate or polyanions like poly(styrenesulfonate) or poly(vinylsulfonate) [70–71].

After the synthesis, the polymer chains are positively charged and to neutralize this positive charge of the oxidized form of polymer, anions from the synthesis solution insert into the polymer. In addition to the electrostatic interactions between the anionic group and the positive charge on polymer chains in the case of conducting polymers based on aromatic or heterocyclic compounds (including pyrrole), the aromatic anions have π -interaction with the aromatic rings of polymer chains. Thus, it is reasonable to suppose that the structure of polymer films doped with aromatic anions has some specific features.

It is well known that polypyrrole (PPy) films electrodeposited in the presence of aromatic anions such as toluenesulfonate have a good electrical conductivity [28,53], mechanical properties and the best stability towards degradation compare with other PPy films[72], but not so good redoxactivity [55]. It is known that the electronic conductivity of a conducting polymer depends on the regularity of polymer chains (conjugation length) and inter-chain packing. As resistivity of the conducting polymers is mainly determined by inter-chain hopping of electrons it is evident that good conductivity is related to the ability of the aromatic anions to stimulate the formation of a more regular structure of the polymer. Therefore it is reasonable to believe that high conductivity indicates that the polymer has a well-packed structure. It is, however, not so simple to establish, how exactly the suitable structure is realized (e.g. by crystalline blocks, π -stacking, quasi-metallic states induced by desolvation of the polymer).

The main objectives of this study are to gain a better understanding of the behavior of electronically conducting polypyrrole films doped with aromatic anions. The present work is the first systematic study of the electrochemical properties of the PPy films doped with aromatic anions, such as BS, *p*TS, NDS by cyclic voltammetry, which is carried out under exactly the same preparation conditions and the experimental timescale. In this work, the electrochemical properties of the PPy films electrodeposited in the presence of middle sized organic anions: benzenesulfonate (BS), *p*-toluenesulfonate (*p*TS) and naphthalene-1,5-disulfonate (NDS) were investigated in two types of electrolytes: a) containing the same anion as used in the electrodeposition solution and, b) in solutions of small inorganic anions.

Direct comparison of the data registered in the literature is not so easy, because the conditions of electrodeposition and electrochemical measurements are very different, but certain conclusions can be drawn from those.

Our aim was to investigate if the polypyrrole films doped with these relatively similar aromatic sulfonate anions have any differences, whether the structure of the films is preserved upon redoping, and whether the anions themselves are mobile during redox cycling. Cyclic voltammetry (CV) is the main experimental method used. In addition to CV measurements, AFM, XDS and the quantum chemical methods are used for a more complete characterization of the properties of PPy films.

I. LITERATURE OVERVIEW

I.1. The synthesis of polypyrrole.

Polypyrrole was one of the first, and is still one of the very few electrochemically prepared conductive polymers, it has been extensively studied since 1968.

Polypyrrole, in general, is prepared by oxidation of the monomer (pyrrole) using electrochemical or chemical methods [74].

Typically, chemical polymerization uses a chemical oxidant such as FeCl [75–76] $(\text{NH}_4)_2\text{S}_2\text{O}_8$ [75,77], $\text{Fe}(\text{ClO}_4)_3$ [78] or $\text{Fe}_2(\text{SO}_4)_3$ [76] etc., which simultaneously oxidizes the monomer and provides the dopant anion. This approach to producing conducting polymers is extensively used in industry, but is limited to the small number of oxidants that can both oxidize the monomer and provide a suitable dopant.

The electrochemical method is more useful for small-scale and variable dopant applications, as it provides greater control over the rate of polymerization and results in a more reproducible product. In other words, in the case of electrochemical polymerization, properties of final material (polypyrrole) are much more controllable than by chemical polymerization. Furthermore, chemically polymerized PPy has lower conductivity and was found to be more active towards oxidative degradation [79].

The electrochemical synthesis of polypyrrole is based on the anodic oxidation of the pyrrole monomer on the working electrode. During the polymerization, the resulting polymeric film is simultaneously oxidized and in conductive state, and becomes doped with the anions present in the background electrolyte. The electropolymerization can take place in either aqueous or non-aqueous solutions. It should be noted, however, that even non-aqueous solutions must contain a little bit of water (generally 1 VOL %). This is necessary for the facilitation of the deprotonation process

Many mechanisms for the electropolymerization of pyrrole have been proposed [80], but the most widely referred one is that of Diaz et al [80] The polymerization of conducting polymers is classified as a free radical propagation reaction, and consists of a number of steps, which are clearly seen in Figure 1. The first step is the oxidation of the monomer, resulting in the formation of a radical cation which exists in three resonance forms. The most stable of these resonance forms couples with another α -radical producing a dicationic dimer. The dicationic dimer undergoes a (double) deprotonation reaction leaving a neutral dimer. The neutral dimer is oxidized to a new radical cation. This dimer couples with other radical cations leading to chain propagation.

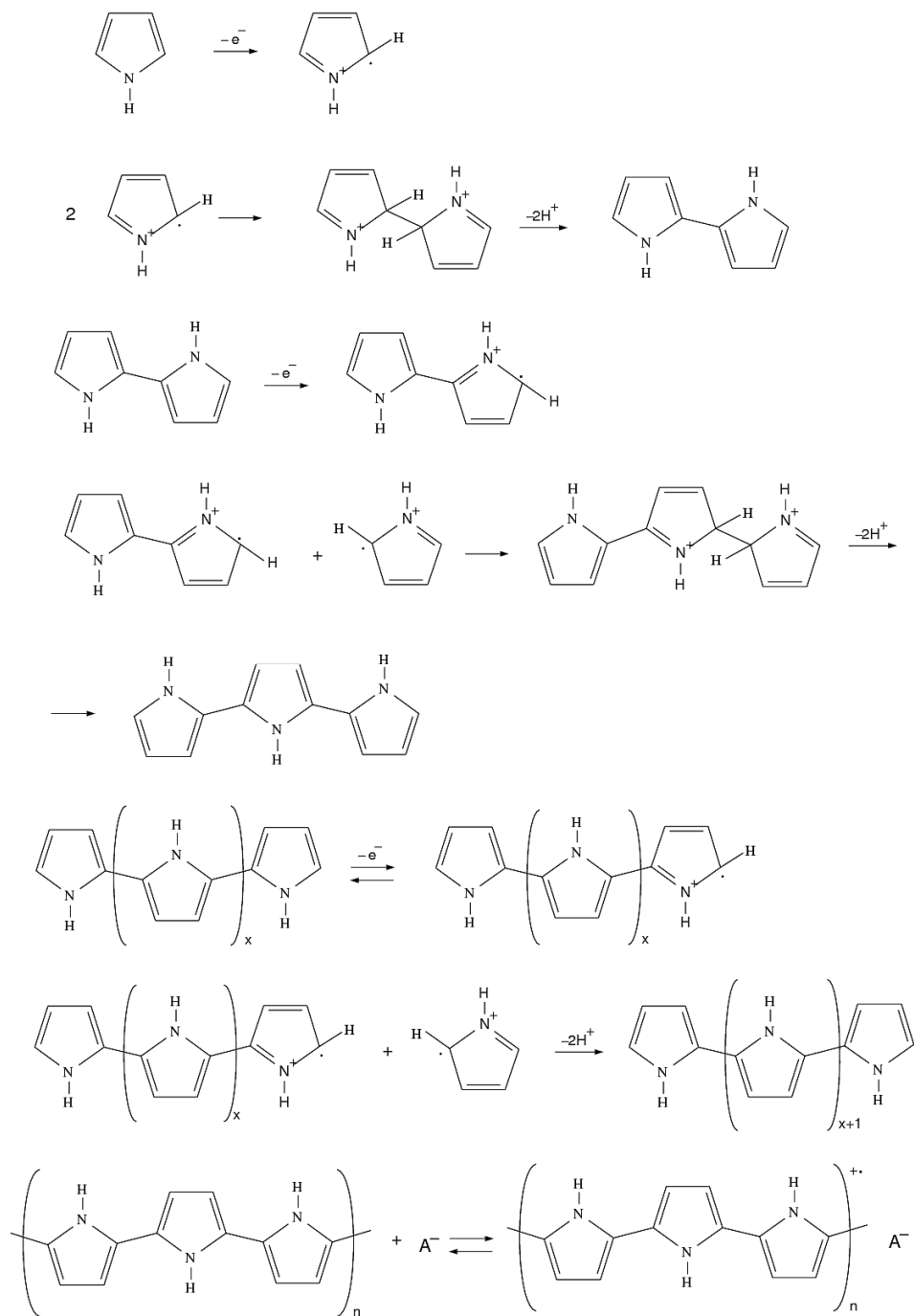


Figure 1. The electrochemical polymerization of pyrrole.

1.2. The effect of dopant

In order to obtain optimum conditions for the electrochemical synthesis of polypyrrole, the effect of various experimental parameters have been studied.

The most studied of all variables is the counterion. Numerous workers have shown that the counterion incorporated has a dramatic effect on the PPy mechanical properties (the tensile strength, Young's modulus, viscoelasticity etc.), electrical properties (conductivity), hydrophobicity/hydrophilicity and also on properties, more related to PPy film porosity as pore size, film density, the distance between PPy chains, degree of structure order, degree of electrostatic cross-linking, isotropy/anisotropy [1,8].

The spatial order in conducting polymers is determined by the order of the polymer backbone, dopant anion and their mutual interaction. The exact location of the counter anions with respect to the PPy chains is in most cases not known at present, but it is determined by their size and the conditions of the polymer preparation.

Polypyrrole can be doped by anions such as halogen, nitrate, perchlorate, tetrafluoroborate, hexafluorophosphate or sulfonate anions etc, and the doped PPy shows conductivity in the range 10^{-5} to 100 S/cm depending on the dopant structure and doping level. In situ conductivity measurements of relatively thick PPy films doped with p-toluenesulfonate *p*TS, benzenesulfonate (BS) and naphthalene-1,5-disulfonate (NDS) deposited at charge densities 1.2Ccm^{-2} [29] and 7.2Ccm^{-2} [43] have shown that specific conductivity decreases in the order *p*TS > NDS > BS and the highest conductivity were obtained in the case of tosylate anion synthesized in aqueous solution at roomtemperature. These results showed good agreement with the findings of Vork, who reported that the polypyrrole synthesized using organic anions such as benzenesulfonate, toluenesulfonate 1,3 benzenedisulfonate, 1,3,5 benzenetrisulfonate were more flexible and more highly conductive than that using Cl^- and ClO_4^- . However, diffusion coefficient values of $4.8 \times 10^{-11} \text{ cm}^2\text{s}^{-1}$ for benzene sulfonate and $4.3 \times 10^{-11} \text{ cm}^2\text{s}^{-1}$ for toluene sulfonate were smaller than the $3.1 (\pm 0.6) \times 10^{-9} \text{ cm}^2\text{s}^{-1}$ for Cl^- and $3.1 (\pm 1) \times 10^{-9} \text{ cm}^2\text{s}^{-1}$ for ClO_4^- [81].

In addition, it has been reported that PPy films doped with ClO_4^- , BF_4^- and PF_6^- were quite sparse, with more than 70% void volume. On the other hand PPy films doped with the counter anions such as *p*TS, SO_4^{2-} and NO_3^- showed compact structure (less than 20% void volume) with apparent densities close to their flotation densities [82].

It has been established that PPy layers doped with amphiphilic dopant anions like dodecylsulfate and dodecylbenzenesulfonate give layers with short range order, whereas small BF_4^- or ClO_4^- or (trifloro)methylsulfonate anions produced amorphous porous layers, with rough surface morphology [82].

Osaka compared the electrosynthesis of polypyrrole with different anions (PF_6^- , CF_3SO_3^- , ClO_4^- , PF_4^-) and found that the porosity of polypyrrole followed the order $\text{PF}_6^- > \text{CF}_3\text{SO}_3^- > \text{ClO}_4^- > \text{BF}_4^-$.

Other researches have shown that the void volume of PPy films doped with different anions increases in the order $\text{NS}^- < \text{DDS}^- < \text{NDS}^{2-} < p\text{TS}^- < \text{NO}_3^- < \text{Cl}^- < \text{SO}_4^{2-} < \text{ClO}_4^-$, and the most compact structure of the PPy films was obtained in the case of large oligomeric surfactants as dodecylsulfate and naphthalene(di)sulfonate anions [83].

Porosity and compactness of the PPy films depends also on film thickness. For example ellipsometric as well as SEM observation on electrodeposited films have also indicated that thin electrodeposited films (<150 nm) are rather more compact, having porosity <10%. On the other hand, thicker films are porous having porosity value in the range of 84–90% [84].

In general, most investigations have shown PPy films to have rather low crystallinity and anisotropy [1,8].

However, when the structures of PPy films formed in the presence of different dopant anions are compared, it can be concluded that PPy can form at least two major types of structures depending on the dopant anions. One of them is very disordered, porous and is formed with small anions (ClO_4^- ; Cl^-) or polyanions. The second of them is more ordered sandwich-like structure, where the planes of the PPy units and anions lie preferentially parallel to the electrode surface and is formed in the presence of aromatic anions [43,64–65].

This does not mean that some other dopants can not induce ordered structure. The experiments made at very low temperature give evidence that even in presence of small anions like PF_6^- in non-aqueous solution it is possible obtain PPy films with good crystallinity and order [85].

The above-presented data indicates clearly that the influence of dopant-anions on the properties of PPy films is not clear and needs further investigation.

1.3. Electrochemical properties of polypyrrole.

The study of the electrochemical properties of conducting polymers carries not just practical value, but it also helps to understand the mechanism of polymerization, the peculiarity of the structure of the polymer, and other properties of similar modified materials.

Polypyrrole has different redox-states. In general, it is possible to reversibly switch the polymer between these different oxidation states, resulting in significant change in the electrical, mechanical, physical, chemical, and morphological properties of the material.

The switching involves several subsequent or parallel processes, namely: charge transfer between the polymer and the conducting substrate, exchange of ions between the polymer film and the electrolyte solution, reconfiguration of the polymer chains, and swelling or shrinking of the polymer matrix (due to the motion of solvent). The rate of each of the stages depends on several factors that are difficult to define, like the morphology of the polymer film, the content of structural defects, the concentration and size of the counterion entering the film

to neutralize the positive polymer charge, the solvation properties of the ion and of the polymer itself, as well as the stacking mode of the polymer chains. Their influence on the electrochemical response upon polymer doping-undoping is a subject of continuous scientific discussion. Nevertheless, at that level, there are many open questions – most of which are in some form related to the structure of the polymer.

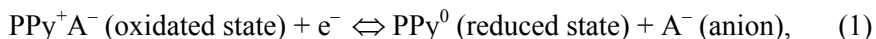
The redox process (oxidation and/or reduction) of PPy films in different electrolyte solutions has been studied by a number of research workers using a variety of techniques. The most common methods are cyclic voltammetry or cycling voltammetry coupled with electrochemical quartz crystal microbalance (EQCM).

1.3.1. Ion transport properties during cycling

What is happening during reduction and oxidation is essentially depending on the mobility of the incorporated anions (charge, charge density, size etc), but not only. The transport behavior of the anions may be controlled also by the film properties – by the film structure and morphology. It is very well known that the mobility of anions depends on both how densely the chains of the polymer film are packed, and how strong is the interaction between the conducting polymer chains and the anions.

Usually, the mobility of anions in PPy films depends on the size of the anions: small anions have good mobility, medium anions have average or bad mobility, and large polyanions are not able to leave the PPy film at all. This does not mean that some other factors as the nature of the solvent or the electro-deposition conditions of the polymer film do not influence the film properties. For instance the mobility of dodecylsulfate in PPy films in aqueous solutions is very low, but rather essential in methanolic or ethanolic solutions [86].

In general, in the case of small mobile anions, the transport of the same anions is predominantly responsible for maintaining electroneutrality during redox processes. This process is described by the following simplified equation:



where PPy^+ represents the doped (oxidized) state of the polymer, PPy^0 the undoped (reduced, neutral) state.

In the case of polypyrrole films doped with big immobile anions (polyanions), only the transport of cations from the electrolyte solution is possible. In a cation-transporting conjugated polymer, the electrochemical reaction can be described by



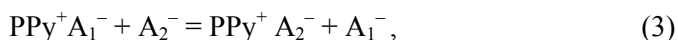
where PPy^+ represents the doped (oxidized) state of the polymer, PPy^0 the undoped (reduced, neutral) state, and C^+ , the compensating cation. PPy^+A^- indicates that the anion is incorporated in the polymer as a dopant and, $\text{PPy}^0\text{A}^- \text{C}^+$ indicates that cations inserted during reduction.

The real situation is actually even more complicated. In the case of medium sized and double-charged anions, both anions from the film and cations from the electrolyte solutions take part in redox processes of polypyrrole films.

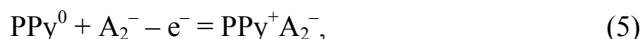
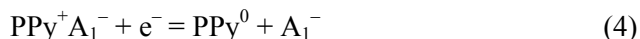
However, this situation may also occur in case of well-moving small ions, it all depends on synthesis conditions and cycling speeds. For example, by decreasing the rate of the electrodeposition it is possible to produce polypyrrole films in which the mobility of even small inorganic anions is not free any more but rather restricted [87]. Based on the data found in the literature it can be argued that the participation of cations in redox process increase by growing of film thickness [89].

1.3.2. Redoping

One very interesting way to get information about the ion-transport properties, and also about other properties of the polymer is redoping. Redoping is an ion-exchange process, where original dopant anions will be replaced by other anions. There are two general ways in which redoping can occur. The first option of redoping is self-exchange, which can be described by the following simplified equation:



where A_1^- are the initial anions (anion what will be exchanged); A_2^- the exchanging anions, PPy^+ represents the doped (oxidized) state of the polymer. A second way is to reduce an oxidized film under a constant cathodic potential in an aqueous or organic solvent electrolyte solution and then reoxidize electrochemically.



where PPy^0 is the undoped (reduced or neutral) polymer.

Anion exchange presents one method of replacing the dopant that has been applied by several authors [90–95], in order to understand the behavior of different PPy films.

The first time the replacement of the original dopant anions by other anions (ion-exchange) was mentioned in literature, was due to Münsterdt, who using X-ray spectroscopy attempted to determine the amount and composition of electrochemically synthesized relatively thick (20–30 μm) PPy films doped with

phenylsulphonate (bensenesulfonate) or perchlorate, which were soaked in NaOH or H₂SO₄ solution for 4 hours. Elemental analysis showed that the degree of replacement depends on film thickness, on the concentration of the electrolyte solution, and on the duration of treatment [90].

Pietro and his colleagues have studied self-exchange in 0.25 μm thick PPy films doped with perchlorate or tetrafluoroborate anions using Auger electron spectroscopy, keeping samples in acetonitrile or aqueous solution containing a variety of anions for one hour. Their data suggest that the replacement is anion-dependent. Redoping was complete when bathing medium contained BF₄⁻, I⁻, SO₄²⁻ or S₂O₈²⁻ anions. In the case of bigger and multi-valent anions such as [Fe(CN)₆]³⁻ the degree of replacement was partial. In some other cases (F⁻, PO₄³⁻) the ion-exchange does not occur [93].

Chien and co-workers have demonstrated that the exchange kinetics is very markedly depending on solvent, and they stress that solvent plays a major role in the transport of ions through bulk polymer. Diffusion coefficient obtained for the PPy/ClO₄ film was $D(\text{H}_2\text{O}) = 4.2 \cdot 10^{-8}$, $D(\text{ACN}) = 3.6 \cdot 10^{-10}$, $D(\text{PC}) = 3 \cdot 10^{-13}$ cm²s⁻¹ in water, acetonitrile and propylene carbonate, respectively [94].

Ionic transport properties and ion self-exchange has been studied spectrophotometrically in considerable extent by Reynolds and co-workers.

Their studies have been focusing on relatively thick (50–100 μm) PPy films doped with tosylate anions in acetonitrile (1 Vol% of water) solution at constant current density 1 mA·cm⁻². They have investigated the replacement of tosylate anions by OH⁻, F⁻, Cl⁻, SO₄²⁻ in aqueous solutions. The experimental work has shown that ion-exchange was the fastest in the case of OH⁻ ions, where diffusion coefficient reach to $1.9 \cdot 10^{-9}$ cm²s⁻¹. They also observed a change in the AC resistance, which slightly increased after the exchange of tosylate with another anion.[91]

Influence of replacing original dopant with other anions on the electrical conductivity of polypyrrole films has been studied by Hagiwara and co-workers, who found that redoped films preserve the conductivity of the parent films [95]. They concluded that the anions can be exchanged after growth with minimal effect on conductivity, suggesting that the polymer superstructure is determined during the synthesis, and the incorporation of other ions has minimal effect on this structure.

1.4. Stability of Polypyrrole.

The large variety of ways to synthesize and modify the characteristics of PPy makes this material attractive for a wide range of applications, but a major obstacle to their commercialization is the relatively poor stability of conducting polymers, which can undergo several degradation mechanisms.

In its oxidized form, polypyrrole is quite stable in air, compared to most other conducting polymers, but the neutral insulating form of the polymer is rather unstable.

Over-oxidation was discovered in 1982 by Bard,[96] and is a widely discussed topic in several works, because the stability of conducting polymers is apparently one of the main limiting factors in their practical applications, especially the electrochemical stability of conducting polymers will be a key factor in their practical applications, because many potential applications of conducting polymers are based on their electrochemical activity such as in capacitors or artificial muscles.

There are many aspects of PPy stability: including thermal [97–103], environmental [104–106,111], and electrochemical stability [107–110].

Environmental stability is related to the reactivity of the charged polymer backbone towards oxygen, water or nucleophilic species.

A proposed mechanism for anodic over-oxidation of polypyrrole is shown in Figure and is described as an irreversible intrinsic redox reaction [96,106].

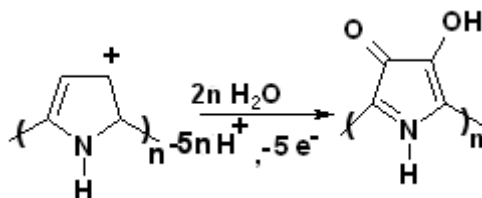


Figure 2. Over-oxidation of PPy.

The precise mechanism of overoxidation still remains unclear, but the formation of hydroxyl and then the carbonyl groups in the polymer chains, which make the properties of polypyrrole worse, has been demonstrated by X-ray photoelectron spectroscopy (XPS) [110], Raman spectroscopy [111] and IR-spectroscopy [111].

During overoxidation, the conjugation is interrupted and conductivity breaks down [97], hence the re-chargeability of the polymer is lost, and in the process, the mass of the polymer [107] also decreases, together with the irreversible loss of the electrochemical activity.

The extent and mechanism of degradation of conducting polymers depends on various factors. Therefore, their degradation properties under different conditions have been studied extensively. The main interest is usually in the effect of aging on the conductivity of PPy films [97–99,111,103–104]. Previous studies have shown that the dominating factor, which affects the overoxidation process, is the solution composition. The stability of conducting polymers is dependent on the solvent, on the dopant anion [99,102], on the type of electrolyte [106] and its concentration [106] and especially on the pH of the solution [97,99,101]. The presence of water and particularly, the presence of OH⁻ ions in the electrolyte solution have been implicated as the main cause of overoxidation of PPy. In addition, in electrochemical processes, the stability of PPy films depends on the electrode potential. The rate of overoxidation of PPy is higher at

higher electrode potentials and at higher pH of the solution. PPy degrades remarkably already during short-term ageing at potentials as low as + 0.5 V versus SCE. An improvement of PPy stability could be achieved by adding some amount of specific additives [106,109] or by doping of PPy with specific anions like aromatic sulfonates [105,112–113] or dodecyl sulfate [114]. PPy films doped with the tosylate anions have shown a higher degree of degradation. The corrosion of PPy can be inhibited also by using higher electrolyte concentrations.

The overoxidation processes have also one bright side namely, the over-oxidation process is used to generate overoxidized PPy, which has applications in the fabrication of sensor electrodes [115]. To avoid over-oxidation of PPy films, the above-mentioned factors were taken into account and 0.4 V was the maximum anodic potential used.

2. EXPERIMENTAL

Pyrrole (Fluka), used for the synthesis of PPy films, was purified by distillation over calcium hydride under vacuum and stored in the dark under Ar atmosphere at low temperature. The salts used were of analytical reagent grade. High purity water (MilliQ+) was used. Gold wire electrode (Goodfellow) as working electrode, graphite or nickel counter electrodes, and Ag/AgCl reference electrodes were used. Two different cells were used – one for PPy film synthesis, the other for the electrochemical measurements. Electrodepositing of the PPy films was carried out in a one-compartment cell with a large cylindrical nickel counter electrode, and the voltammetric (CV) measurements in conventional three compartment electrochemical cells. Electrochemical measurements were carried out using computer driven digital potentiostat/galvanostats (in-house and PAR EG&G 263A). Before the electrodepositing and voltammetric measurements the solutions were deoxygenated with Ar. All measurements were performed in 0.1 M electrolyte solutions saturated with argon.

Prior to each experiment, the gold wire electrode was electrochemically purified in 0.1 M H₂SO₄ solutions and annealed in flame. After electrochemical synthesis, the films were rinsed thoroughly with high purity water to remove excess monomers, oligomers, and electrolyte ions.

All PPy films for the electrochemical, AFM measurements and elemental analysis were prepared in the same conditions: by galvanostatic electropolymerization in aqueous solutions containing 0.1 M of pyrrole and 0.1 M of supporting electrolyte: sodium benzene sulfonate (Fluka), sodium tosylate (Aldrich) or sodium naphthalene -1, 5-disulfonate, NaNO₃, LiClO₄, NaCl, Na₂SO₄ in a one-compartment cell with a large cylindrical counter electrode at two current densities 0.4 mA·cm⁻² and 4.0 mA·cm⁻² with total charge passed $Q_d = 80 \text{ mC}\cdot\text{cm}^{-2}$ and $Q_d = 400 \text{ mC}\cdot\text{cm}^{-2}$. Considering that about 0.4 C·cm⁻² is consumed for the deposition of 1 μm thick films [116–117], the estimated thickness of the PPy films used in this work is approximately 1.0 μm and 0.2 μm. The solutions of 1,5 – naphthalenedisulfonic acid (Aldrich) disodium or calcium salt were prepared by adding a fixed amount of sodium hydroxide or calcium oxide to the appropriate concentration of acid solution up to pH ≈ 7.0. The pH of the solutions was determined using an Evikon pH meter E6121.

The PPy-electrodes were immersed in the investigated solutions saturated with Ar under the anodic potential $E = 0.4 \text{ V}$, at which the films are in the oxidized and conductive state, and polarized at this potential for 10 min before every scan. Potential scan rates were in the range of 5 to 50 mV·s⁻¹. All electrochemical measurements were performed in 0.1 M (or 0.05 M) electrolyte solutions (all PPy films doped with aromatic anions were measured in NaBS, NapTS, NaNDS, NaCl, Ca(Cl)₂, NaNO₃, Ca(NO₃)₂, NaClO₄, LiClO₄, Na₂SO₄, La₂(SO₄)₃ saturated with argon in conventional three-compartment cell.

Redoping of PPy films was carried out by two methods of self-exchange: a) as-prepared PPy electrodes were immersed in 0.1 M NaCl solution saturated with Ar under the anodic potential $E = 0.4 \text{ V}$, at which the films are in the

oxidized and conductive state, and polarized at this potential for 10 min before every scan (this time and anodic potential is adequate for almost complete self-exchange); b) self-exchange was carried out at open circuit potential (0.150... 0.170 V), and the first scan was started from this potential towards negative potentials.

The surface morphology of working electrodes was studied by an AFM/STM measurement system 5500 (Agilent Technologies) in non-contact mode. All AFM images were recorded in ambient conditions. The GwyddionTM ver. 2.19 free software was employed for image processing.

The composition of PPy films was determined by electron-probe X-ray microanalysis. The JSM-840 (JEOL Ltd., Japan) equipment with EDS System Voyager (Noran, USA) was used.

3. RESULTS AND DISCUSSION

3.1. The electrochemical properties of the PPy films in solution containing the same aromatic anion as used in the electrodeposition solution

Three aromatic sulfonate anions: benzenesulfonate (BS); tosylate (*p*TS) and naphthalene-1,5-disulfonate (NDS) were used as dopants in this work. *p*TS is a most studied single charged aromatic anion. BS seems to be with similar properties as *p*TS but as we established in this work, some differences are essential and the behavior of BS as dopant was studied in more detail in this work. NDS anion is large and double charged, so it is reasonable to suppose that the PPy films deposited from the electrolyte containing NDS anions have remarkably different structure and electrochemical properties.

3.1.1. Redoxactivity of PPy films

Electrochemical properties of the PPy films doped with different aromatic anions, as shown in figure 3: benzenesulfonate (BS); tosylate (*p*TS) and naphthalene-1,5-disulfonate (NDS), were studied by cyclic voltammetry. Cyclic voltammetry is a useful method for the determination of ion mobility and redoxactivity of the PPy films. However, it should be noted that without additional methods, it is very difficult to analyze the shape of voltammograms obtained during the cyclic voltammetry measurements (especially in the case of thin films), it is also difficult to assess the extent of the film that is electrochemically active, because response is obtained from only the part of the film, which takes part in the redox process. Therefore, elemental analysis was used in order to determine the amount of ions inside of PPy films.

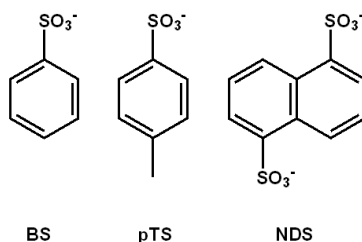


Figure 3. Schematic chemical structure of the aromatic anions used.

A good possibility to compare the mobilities of the anions in the polymer film is to study the influence of the sweep rate v on the shape of the CV curves. Cyclic voltammetric (CV) response of polypyrrole film doped with benzenesulfonate in contact with NaBS in aqueous solution is demonstrated in figure 4.

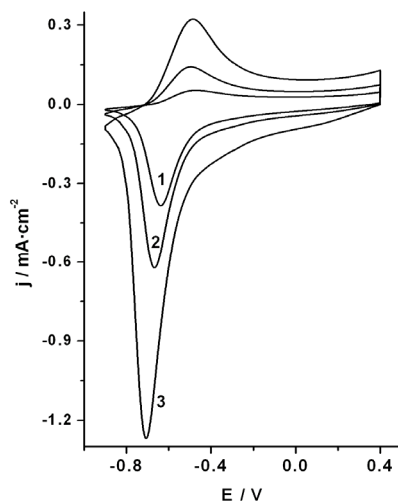


Figure 4. Voltammograms of PPy/BS film deposited at current density $j_d = 0.4 \text{ mA} \cdot \text{cm}^{-2}$ electrodeposition charge $Q_d = 400 \text{ mC} \cdot \text{cm}^{-2}$; and measured in 0.1 M NaBS solution at different scan rates v : (1) $5 \text{ mV} \cdot \text{s}^{-1}$; (2) $10 \text{ mV} \cdot \text{s}^{-1}$; (3) $20 \text{ mV} \cdot \text{s}^{-1}$.

However, such presentation of CV curves (frequently used in literature) does not make sense, because influence of the sweep rate v on the redoxactivity and the shape of the CV curves are not clearly expressed. Therefore, cyclic voltammograms measured at different scan rates should be presented in the form of pseudocapacitance (current density divided by scan rate) [118]. Typical results are presented in Figure 5.

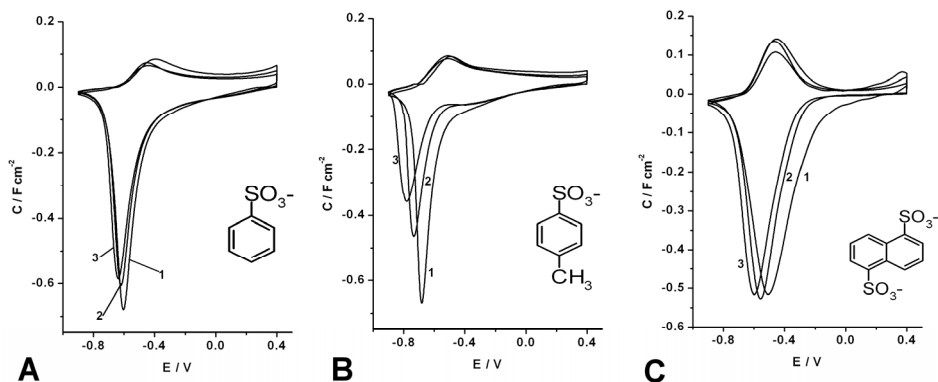


Figure 5. Pseudocapacitance curves of different PPy films: A) PPy/BS; B) PPy/*p*TS; C) PPy/NDS in solution containing the same anion as used in the electrodeposition solution. PPy films deposited at current density $j_d = 4.0 \text{ mA} \cdot \text{cm}^{-2}$; electrodeposition charge $Q_d = 400 \text{ mC} \cdot \text{cm}^{-2}$.

Generally, such shape of the cyclic voltammograms indicates that the mobility of anions in the polymer film is suppressed, and cations from the solution play a dominant role in maintaining the electroneutrality during the redox cycling.

The different features are clearly visible when the voltammograms of PPy films doped with aromatic dopants are compared to those of an inorganic anion, such as perchlorate (Fig.6). In the case of small anions, the reduction of the polymer starts immediately after applying the cathodic scan due to the good mobility of anions (Fig.4, curve 4), but in the case of aromatic dopants, the current (reduction rate) at these potentials is very low and reaches maximum value only at more negative potentials where the ingress of cations takes place. We do not analyze the anodic scans for the comparison of the properties of the PPy films as they are not as characteristic probably due to some relaxation phenomena taking place at the cathodic potentials [119–120]. The small maxima on the CV curves are probably connected with the expulsion of cations as they disappear if sodium is replaced by calcium ions. Very useful information could, in principle, be obtained from electrochemical quartz crystal microbalance (EQCM) experiments, however, this method cannot be utilized properly for films of this kind of thickness ($Q_d > 80 \text{ mC cm}^{-2}$), due to the visco-elastic effects [121]. On the bases of the results of the EQCM measurements carried out on thin PPy films [122], it is possible to suppose that the role of cations increases with the increased thickness of PPy film doped with aromatic sulfonates.

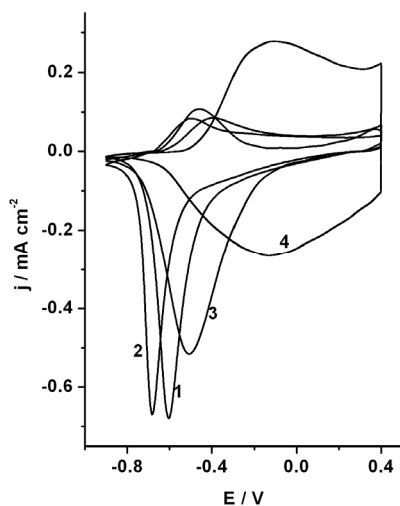


Figure 6. Voltammograms of different PPy films at scan rate 5 mV s^{-1} : 1 – PPy/BS film in 0.1 M NaBS ; 2 – PPy/pTS film in 0.1 M NapTS ; 3 – PPy/NDS film in 0.1 M NaNDS ; 4 – PPy/ ClO_4 in 0.1 M LiClO_4 . PPy films deposited at current density $j_d = 4.0 \text{ mA cm}^{-2}$; electrodeposition charge $Q_d = 400 \text{ mC cm}^{-2}$.

The importance of the nature of the cations was demonstrated by replacing sodium cations with calcium cations. We have carried out special experiments where sodium benzenesulfonate is replaced by calcium benzenesulfonate in the test solution.

As the double charged calcium ion is much more strongly solvated, the mobility of this cation is lower, and the maxima on the CV curves at $-0.5 \dots -0.7$ V disappeared, while the reduction charge Q_{red} decreased from 29.0 to 19.0 $\text{mC}\cdot\text{cm}^{-2}$ (Fig.7). From this follows that this maximum is connected with the penetration of cations into the PPy film. Also, similar behavior happens in the case of PPy/*p*TS films, where Ca^{2+} ions were too large for entering the polymer in order to stabilize the charge and take part in the redox process. A different situation is observed in the case of PPy/NDS films, where calcium ions were mobile. Redox cycling of PPy films doped with NDS in the solution containing calcium ions carried out in this work shows only a small increase of the insertion resistance. This also indicates that PPy films deposited in the presence of NDS anions have a less densely packed structure and the larger (more hydrated) calcium cations are indeed able to ingress into the polymer film.

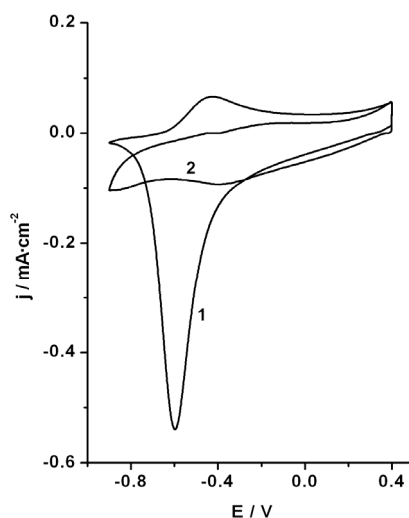


Figure 7. Voltammograms of PPy/BS film deposited at current density $j_d = 4.0 \text{ mA} \cdot \text{cm}^{-2}$ electrodeposition charge $Q_d = 400 \text{ mC}\cdot\text{cm}^{-2}$; and measured in (1) 0.1 M NaBS (2) 0.05 M $\text{Ca}(\text{BS})_2$ solution at scan rate $v: 5 \text{ mV} \cdot \text{s}^{-1}$.

The shape of the voltammograms (Figure. 5) of the PPy films doped with BS, *p*TS and NDS anions is similar only at the first approximation. From figure 6, where the voltammograms measured at the scan rate $5 \text{ mV}\cdot\text{s}^{-1}$ are presented, it is clearly seen that the cathodic peak potential (E_{cat}) depends markedly on the nature of the dopant anion. It is important to stress that, as in all these cases, the

moving ions which are responsible for the formation of maxima on CV curves are not the aromatic dopant-anions but the sodium cations, therefore, these differences characterize variations in some structural properties of the polymer films. The dependence of the values E_{cat} from scan rate is presented in Fig. 8. For comparison, the data for a perchlorate-doped PPy film is also presented in this figure. All these results show that the resistance to the insertion of sodium cations into PPy films depends on the nature of the aromatic dopant-anions increasing in the sequence $\text{NDS} < \text{BS} < p\text{TS}$.

The most densely packed structure of the PPy films synthesized in the presence of $p\text{TS}$ also causes remarkable decrease of the redox-capacitance with the increase of the scan rate (Fig. 5 B) – cations are not able to ingress into PPy film in this timescale. On the other hand, the cathodic peaks for the NDS-doped PPy films are broader which indicates that the structure of these films is less homogeneous.

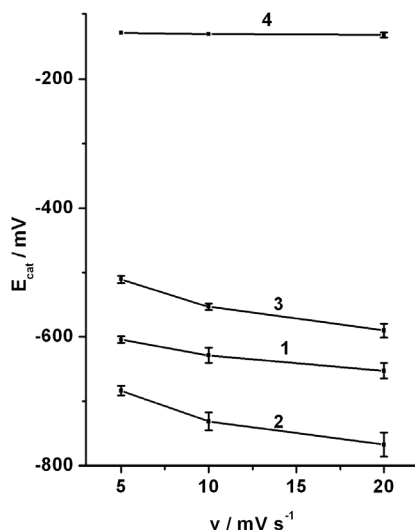


Figure 8. Dependence of the peak potential E_{cat} on scan rate: 1 – PPy/BS film in 0.1 M NaBS; 2 – PPy/ $p\text{TS}$ film in 0.1 M NapTS; 3 – PPy/NDS film in 0.1 M NaNDS; 4 – PPy/ ClO_4 film in 0.1 M NaClO_4 .

For a more quantitative comparison of the electrochemical properties of different PPy films, it is possible to use the term “redox activity”. In the present work we define the term as the charge released during the reduction phase (Q_{red}), previously stored in the polymer during the anodic sweep and the following polarization at 0.4V for 10 min. We also use a dimensionless value – the electrochemical doping level (f_e) calculated as $f_e = 2 Q_{\text{red}} / (Q_d - Q_{\text{red}})$. From the results obtained (Table 1) it is possible to state that the redox activity and f_e

of PPy films decreases in the sequences NDS>BS>*p*TS. It does not mean that the initial real value of the doping level is so low. The results of the electron-probe X-ray microanalysis show that as- prepared PPy films doped with aromatic dopants contain 9.5–10.5 mass % of sulfur, and the resulting analytical doping level f_a of PPy films calculated as in [123] is relatively high (0.40–0.43), decreasing during the first cycle. The exact determination of the values of f_a after cycling is very complicated as some part of the anions and cations (probably in the form of ion pairs) leave the polymer film during the washing of the electrode and, if the washing is insufficient, crystals of salt appear on the surface of the electrode during the drying process. Nevertheless, it is possible to say that in all cases $f_a > f_e$.

Table 1. Results of redox cycling at scan rate $5 \text{ mV}\cdot\text{s}^{-1}$. Q_{red} – charge of reduction ($\text{mC}\cdot\text{cm}^{-2}$) f_e -formal effective doping level calculated from the results of CV measurements. PPy films deposited at current density $j_d = 4.0 \text{ mA}\cdot\text{cm}^{-2}$ electrodeposition charge $Q_d = 400 \text{ mC}\cdot\text{cm}^{-2}$.

Electrodeposition	Measurement		
Solution	Solution	Q_{red}	f_e
NaBS	NaBS	29.59	0.15
NapTS	NapTS	25.74	0.14
NaNDS	NaNDS	36.15	0.2
NaNDS	NaBz	46.26	0.26
NaNDS	NapTS	41.28	0.23
LiClO ₄	LiClO ₄	40.82	0.23

Low ion mobility and dense packing of the PPy films electrodeposited in the presence of BS, *p*TS and NDS ions complicates the comparison of the mobility of the aromatic anions. As the PPy films prepared in the presence of NDS anions seem to be less densely packed, it is possible to compare the mobility of other anions in this polymer using redoping. A similar approach has been used earlier for the comparison of the mobilities of inorganic anions [87].

Voltammetric measurements showed that the redoping process of the aromatic sulfonates is quite fast, as during the first cycle and the following polarization at 0.4V, most of the NDS anions from the redox-active sites were replaced by the new anions. During the following cycling, the shape of the voltammograms remains almost the same, indicating the completeness of redoping. In this work, we have avoided long-time reduction of the polymer as it may cause deep conformation changes in the structure [119,120]. In Fig. 9 the voltammograms for PPy films synthesized with NDS anions and measured in the solutions of different aromatic anions are presented. These results are very interesting. In principle, there are two extreme possibilities: if the structure of the polymer film is rigid, redoping does not change the structure of the polymer and the voltammograms reflect the mobility of host ions in the parent matrix. In

contrast, if the polymer is more flexible, some changes in the structure take place and the shape of the voltammograms are closer to that for the polymer synthesized with the host anions. At first glance, the comparison of the voltammograms (Figs. 5 and 6) shows that the structure of the PPy films deposited in the presence of NDS ions is not too rigid and that considerable restructuration takes place, as the shape of reduction peaks are close to those for PPy films synthesized in the presence of BS and *p*TS ions. A more detailed comparison of the voltammograms shows that this is not the case. The peak potential E_{cat} is shifted in the less negative direction – $\Delta E_{\text{cat}} = 15 \text{ mV}$ for BS ions and 140 mV for *p*TS ions. It means that the mobility of cations is not as much restricted as in PPy films deposited in the presence of BS and especially for *p*TS. There is another more interesting phenomenon: the relative position of E_{cat} is drastically changed.

If for usual films the difference of peak potentials:

$$\Delta E_{\text{cat}} = E_{\text{cat}}(\text{BS}) - E_{\text{cat}}(p\text{TS}) \quad (6)$$

is -80 mV then for redoped films it is $+50 \text{ mV}$. It seems unbelievable – the mobility of sodium cations in PPy film redoped with *p*TS is better than that in films redoped with BS. The reason of such major changes is related to the essentially increased mobility of not only the cations but also the anions in the NDS films. The voltammograms presented in Fig. 7 clearly show that here, in the region of positive and small negative potentials, already some process is taking place, especially in the case of the BS anions. Most probably it is connected with the mobility of anions. The electrochemical doping level f_e in redoped PPy films is higher than that in PPy deposited in the presence of TS and especially BS, indicating that a part of more available sites of PPy chains is doped with BS or *p*TS anions which are able to leave the polymer film during the reduction and enter again during the oxidation of the polymer. From this follows that the mobility of BS anions in PPy film deposited in the presence of NDS anions is considerably higher than that of *p*TS anions and it is probably connected with the weaker interaction between BS anions and PPy chains. At the same time, these more active centers (pores) are not involved in cation exchange, which causes the shift of the cation peaks in the direction of more negative potentials.

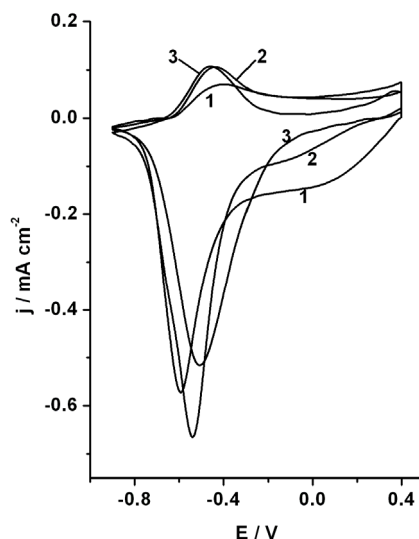


Figure 9. Voltammograms of different PPy films at scan rate 5 mV s^{-1} : 1 – PPy/NDS film in 0.1 M NaBS; 2 – PPy/NDS film in 0.1 M NapTS; 3 – PPy/NDS film in 0.1 M NaNDS. PPy films deposited at current density $j_d = 4.0 \text{ mA cm}^{-2}$; electrodeposition charge $Q_d = 400 \text{ mC cm}^{-2}$

3.1.2. Influence of deposition current density

The differences between the electrochemical behaviour of the polypyrrole films doped with aromatic anions are not significantly dependent on the current density used for the electrodeposition of the PPy films. All voltammograms of the PPy films doped with different aromatic anions deposited at current densities from 0.4 to 4.0 mA cm^{-2} show the same characteristics.

Our data shows (see Figure 10) that overall the voltammograms of these films are similar with one remarkable difference: the peaks on the reduction curves of the PPy films deposited at lower current density are shifted towards more negative potentials, and at the same time, the charge consumed during the reduction is smaller (see table 2) compared to the films deposited at higher current densities. This indicates that PPy films deposited at lower current densities are more densely packed, offering more resistance to the ingress of cations.

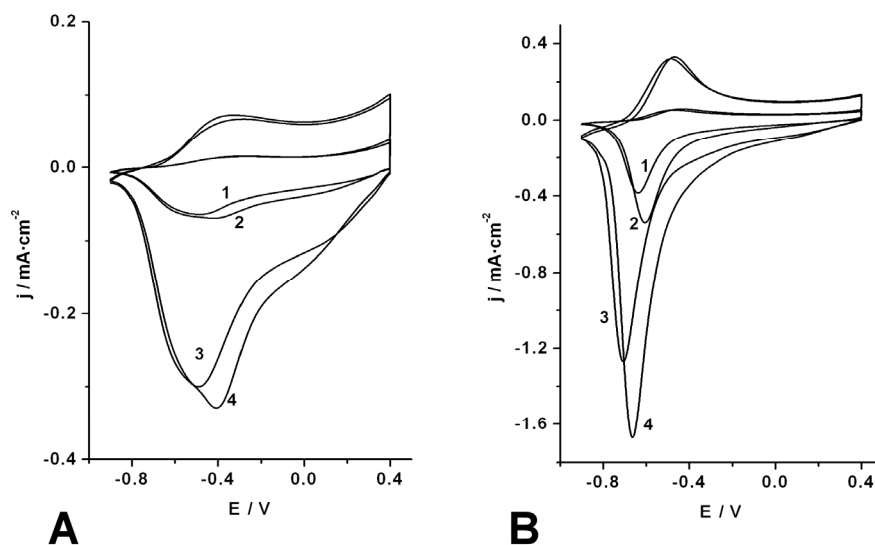


Figure 10 : Voltammograms of PPy/BS films deposited at current density (1 and 3) $j_d = 0.4 \text{ mA} \cdot \text{cm}^{-2}$; (2 and 4) $j_d = 4.0 \text{ mA} \cdot \text{cm}^{-2}$ and charge $Q_d = 80 \text{ mC} \cdot \text{cm}^{-2}$ (A); $Q_d = 400 \text{ mC} \cdot \text{cm}^{-2}$ (B) and measured in 0.1 M NaBS solution at scan rates v : (1 and 2) $5 \text{ mV} \cdot \text{s}^{-1}$; (3 and 4) $20 \text{ mV} \cdot \text{s}^{-1}$.

3.1.3. Influence of film thickness on the redoxactivity

The shape of the voltammograms of the thinner PPy films is remarkably different (see Fig. 10A). The much broader reduction wave indicates that in these films both anions and cations are moving in order to satisfy electroneutrality. The PPy films deposited at higher current density j_d are a little more active, in the same manner as in the case of the thicker films. However, the influence of the thickness of the films on redoxactivity is much more pronounced than variations in current density.

Results of voltammetric measurements are presented in Table 1. For comparison, also the data for PPy films deposited and measured in sodium nitrate solution is presented. The conditions of electrosynthesis and voltammetric measurements were the same as in the case of BS doped films.

Table 2. Results of redoxcycling at scan rate 5 mVs⁻¹. Q_d - electrodeposition charge (mC·cm⁻²); j_d – current density of electrodeposition (mA·cm⁻²); Q_{red} – charge of reduction (mC·cm⁻²); Q_{ox} – charge of oxidation(mC·cm⁻²); f_e -formal effective doping level calculated from the results of CV measurements.

Electrodeposition			Measurements			
Solutions	Q_d	j_d	Q_{red}	Q_{ox}	Q_{ox}/Q_{red}	f_e
NaBzSO ₃	80	0.4	10.78	3.13	0.29	0.31
NaBzSO ₃	80	4	11.75	2.98	0.25	0.34
NaBzSO ₃	400	0.4	20.75	7.25	0.34	0.1
NaBzSO ₃	400	4	29.1	8.57	0.29	0.15
NaNO ₃	80	0.4	10.57	7.19	0.68	0.3
NaNO ₃	80	4	10.59	7.48	0.7	0.31
NaNO ₃	400	0.4	33.3	30.76	0.9	0.18
NaNO ₃	400	4	35.38	31.28	0.88	0.19

It is clearly seen that the charge consumed during the reduction of the films, Q_{red} , is larger for films deposited at higher j_d . From the data presented follows that the reduction charge Q_{red} for the PPy films doped with benzenesulfonate and nitrate anions (as well as formal doping level f_e) is not very different if the deposition charge Q_d (and film thickness) is low. This difference increases with the increase of the value of Q_d .

The dependence of the redox activity on the thickness (deposition charge) of the PPy films is more essential. The formal doping level decreases more than twice with the fivefold increase of the Q_d in the case of BS doped PPy films and a little less than two times for nitrate doped films. Similar remarkable dependences of the redox properties of the polymer films on the thickness were observed in the case of titanocene derivatized polypyrrole films [124]. An additional possibility for the comparison of the redox activity of different PPy film is to compare the values of Q_{ox}/Q_{red} (see Table 2). This value is a measure of the reversibility of the redox behavior of the polymer films in the timescale used. It shows the extent of the PPy film reduced during the cathodic scan that can be reoxidized during the following anodic scan. From the data presented in Tab. 2 follows that redox-processes in the PPy/BS films are markedly more irreversible than in the case of the nitrate-doped films.

Influence of the deposition charge on the redoxactivity is illustrated in Fig. 11. In this figure the CV curves corresponding to the $Q_d = 400$ mC·cm⁻² (curves 1 and 2) are experimental and the rest (CV curves 3 and 4) are hypothetical, being recalculated from those for $Q_d = 80$ mC·cm⁻² as they would be if the redox activity would not depend on the thickness of the film.

The principal differences in the influence of the PPy film thickness on its redox properties are clearly seen. While in the case of the nitrate doped PPy films, redox activity of the films also decreases with the increase of the thickness but the shape of the CV curves remains generally the same, for BS doped films changes are more pronounced. However, there is no evidence that the real

doping level of the electrodeposited PPy films decreases so strongly with the increase of the thickness of the polymer film. Raman spectroscopic analysis of PPy films carried out in [125] have shown that the doping level with BF_4^- ions increases during the film growth process, and in the case of β -naphthalene-sulfonate anions does not depend markedly on the film thickness. From all these results follows that some part of the thicker PPy films does not participate in the redox processes in the timescale used in this work (scan rate 5 mVs^{-1} or higher) which indicates that the mobility of BS anions in thicker PPy films is much more depressed than that of nitrate anions.

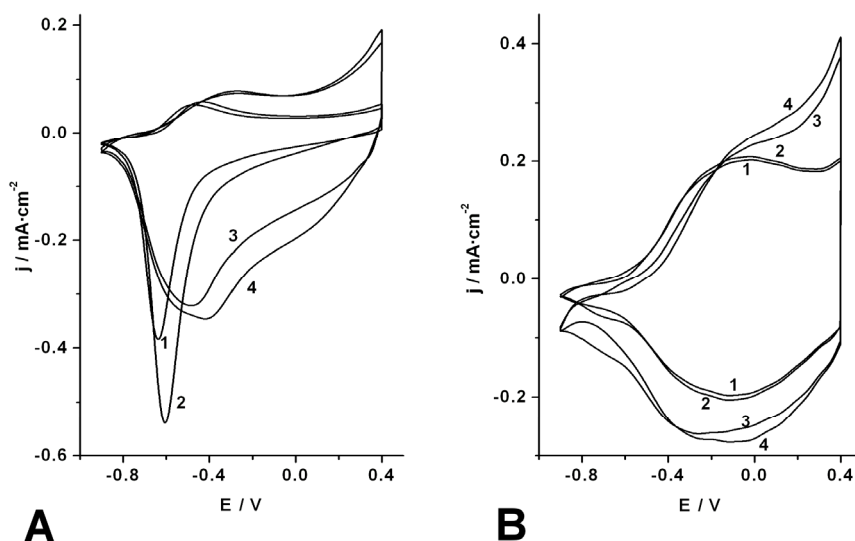


Figure 11. Voltammograms of PPy/BS (A) films measured in NaBS and PPy/ NO_3 (B) films measured in 0.1 M NaNO_3 deposited at current density: (1 and 3) $j_d = 0.4 \text{ mA}\cdot\text{cm}^{-2}$; (2 and 4) $j_d = 4.0 \text{ mA}\cdot\text{cm}^{-2}$; (1 and 2) deposited at charge $Q_d = 400 \text{ mC}\cdot\text{cm}^{-2}$; (3 and 4) deposited at charge $Q_d = 80 \text{ mC}\cdot\text{cm}^{-2}$ and recalculated to electrodeposition charge $400 \text{ mC}\cdot\text{cm}^{-2}$.

3.2. The electrochemical and ionic transport properties of the PPy films after redoping in solutions of small inorganic anions

In this chapter will be discuss electrochemical properties (redoxactivity, the mobility of anions) of PPy films originally doped with aromatic anions after redoping. Redoxcapacity (redoxactivity) depends on different parameters: the mobility of anions, doping level and reversibility of the processes during redoxcycling.

The aim of redoping experiments was to combine the beneficial properties of PPy films formed in the presence of benzenesulfonate (BS) or *p*TS with the higher mobility of small inorganic anions, like chloride, by redoping (ion-exchange).

3.2.1. Redoxactivity of PPy films after redoping

Upon immersing PPy films doped originally with aromatic anions in solutions of small inorganic anions, the redoping take place. Fig. 12 shows how the self-exchange of BS, *p*TS and NDS (Fig. 12. curve 2) to nitrate anions at potential of 0.4 V changes the voltammograms of the PPy film and how during this the redoxactivity changes (the second scan). CV curve of PPy film synthesized from solution containing 0.1 M NaNO₃ (Fig. 12. curve 3) is presented for comparison. The different features are clearly visible when the voltammograms of PPy films doped with aromatic dopants are compared to those of an inorganic anion, such as as nitrate (Fig. 10. curve 3). In the case of small anions, the reduction of the polymer starts immediately after applying the cathodic scan due to the good mobility of anions, but in the case of aromatic dopants, the current (reduction rate) at these potentials is very low and reaches maximum value only at more negative potentials where the ingress of cations take place[126]. After redoping, the situation is quite different. The evaluation of the shape of the CV curves indicates both common parts and remarkable differences. In general, for all PPy films after redoping, a broad maximum appears on the reduction curve similar to that on curve (Figure 12. curve 3) which is connected to the expulsion of nitrate anions [127]. The charge consumed during the reduction of the redoped PPy film is remarkably larger than that for the original PPy film in the same potential interval and even greater than that for the PPy films doped with nitrate anions and measured in 0.1 M NaNO₃ aqueous solution. The reduction charge increased in 0.1 M NaNO₃ approximately 76 %, in the case of PPy/BS film. For the PPy/*p*TS films, the increase of reduction charge was larger by approximately 110 % and for PP/NDS films by approximately 37 %.

It is important to emphasize that the same phenomenon (increase in the electrochemical doping level and reduction charge) was recognized in all cases of measuring PPy film doped with aromatic anions in the solution containing small inorganic anions. Summary of these results are presented in table 3.

Table 3. Increase in redoxactivity of different PPy films in the percentage in various solutions. PPy films deposited at current density $j_d = 4.0 \text{ mA}\cdot\text{cm}^{-2}$; electrodeposition charge $Q_d = 400 \text{ mC}\cdot\text{cm}^{-2}$.

	PPy/BS	PPy/ <i>p</i> TS	PPy/NDS
NaNO ₃	76 %	110 %	37 %
NaCl	78 %	124 %	36 %
NaClO ₄	67 %	75 %	42 %
Na ₂ SO ₄	89 %	124 %	46 %

The increase of the effective redoxactivity in the case of 5 times thinner films was not very significant compared to the thicker films. The redoxactivity of thin films (deposition charge $80 \text{ mC}\cdot\text{cm}^{-2}$) will be discussed later.

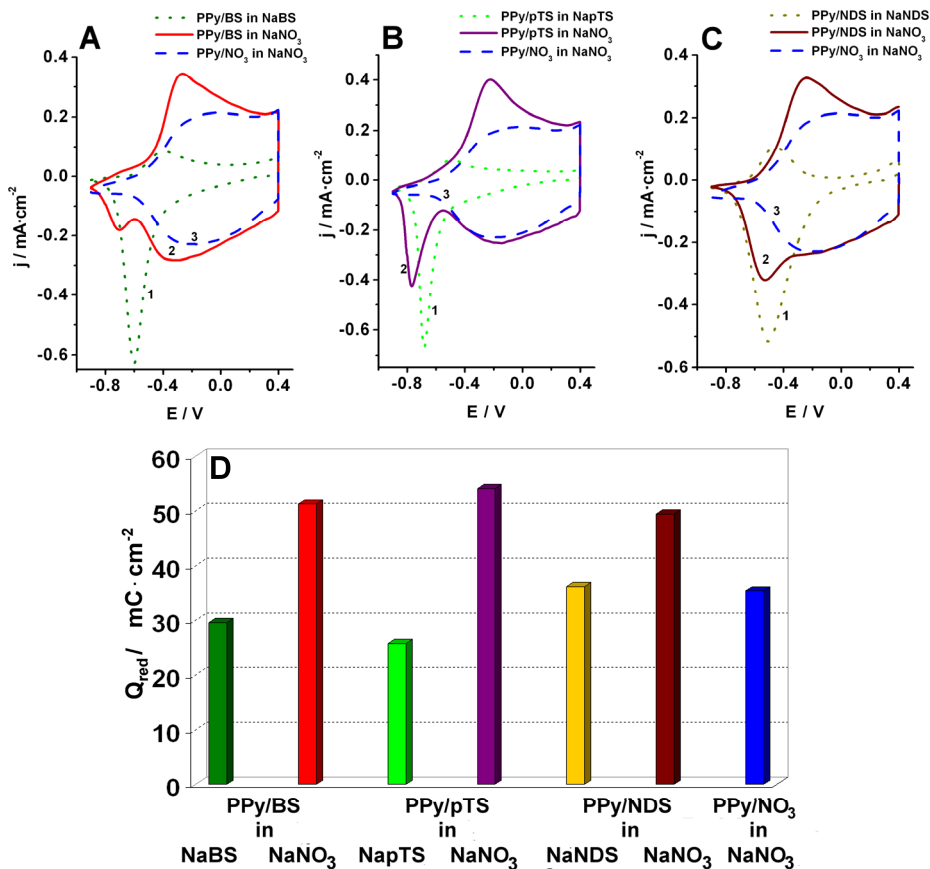


Figure 12. Cyclic voltammograms and the corresponding reduction charge (Q_{red}) of the PPy films measured in various electrolyte solutions at scan rate 5 mV s^{-1} . $Q_d = 400 \text{ mC}\cdot\text{cm}^{-2}$, $j_d = 4.0 \text{ mA}\cdot\text{cm}^{-2}$.

As in the case of PPy films redoped with nitrate anions, it is difficult to distinguish dopant from polymer using the EDS method because both contain nitrogen atoms, the elemental analysis was carried out and the extent of redoping was verified in the case of samples redoped with chloride anions. The chloride ions, in terms of their characteristics, have a similar behavior to the nitrate ions at same scan rates, with only some small differences in PPy films doped originally with aromatic anions, these results are presented in the figure 13.

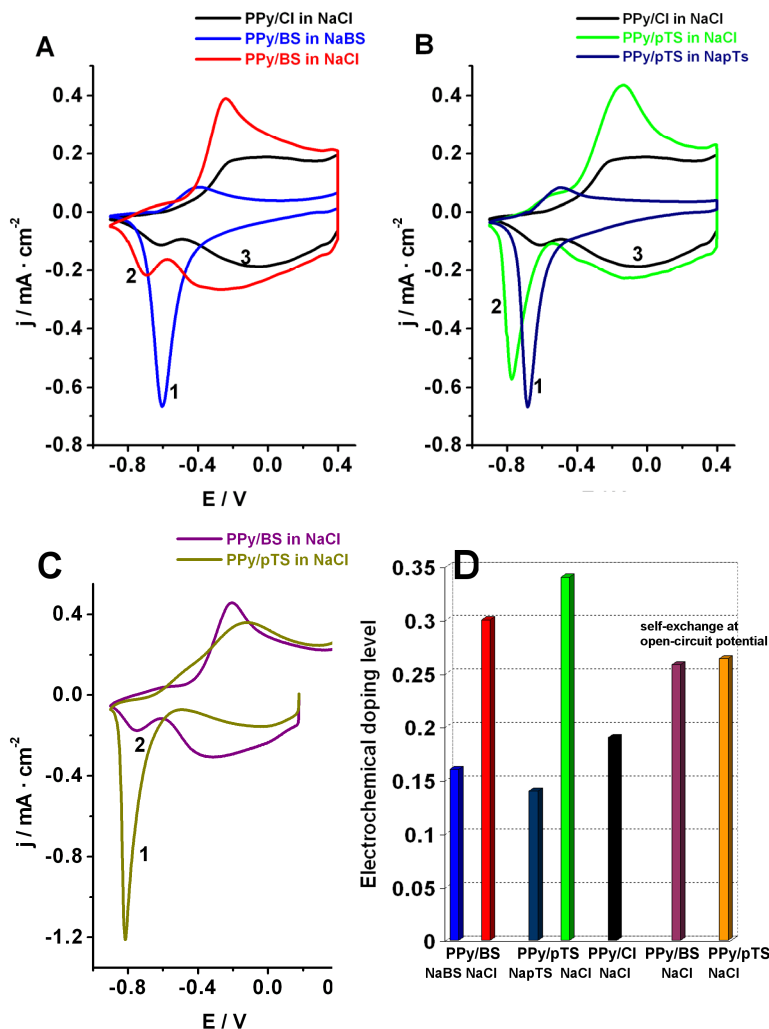


Figure 13. Cyclic voltammograms of the PPy films deposited and measured in different solutions. Scan rate 5 mV s^{-1} . The CV curves measured after 10 min self-exchange of PPy/pTS (curve C1) and PPy/BS (curve C2) films in NaCl solution. Electrochemical doping level of different PPy films before and after redoping (D).

Most significant differences in the electrochemical behaviour of the redoped PPy/BS; PPy/pTS and PPy/NDS films are observed at more negative potentials ($-0.4 > E > -0.9 \text{ V}$): while for PPy/BS films, the current maximum on the reduction curve connected with the insertion of cations [123] is drastically decreased, for PPy/pTS films, redoping only shifts this maximum towards more negative potentials.

In order to confirm and demonstrate that after redoping the maximum at negative potential ($-0.4 > E > -0.9$ V) is still related to the mobility of cations, a special test was carried out, where the cationic composition of the solution was exchanged. All films were studied in 0.05 M CaCl_2 solution. The disappearance of this maximum is clearly seen in Fig. 14 curve 2, as Ca^{2+} ions are not able to enter the PPy/BS or PPy/*p*TS film. Also, the oxidation of PPy films in this case starts at more positive potentials, as the more negative area of the maximum of the oxidation curve is connected to the expulsion of cations.

In the case of the PPy/NDS films, the maximum on the CV curve undergoes a more complicated redistribution between anionic and cationic parts. In the case of PPy/NDS film, there is only a small resistance to the mobility of calcium ions. It seems that Ca^{2+} ions do not block all possible cation exchange positions in this film. Influence of cations on the redoxactivity will be also discussed later.

The EDS analysis of the redoped PPy/*p*TS films showed that most *p*TS anions are replaced by chloride anions. Further cycling of PP/*p*TS films in NaCl solution increases the amount of Cl^- anions in the film but approximately 10 % of *p*TS anions remain unexchanged. Apparently, the cationic maximum on these reduction curves is due to the compensation of the charge of two types of anions: the unexchanged *p*TS anions, but also some part of the Cl^- anions, which having replaced *p*TS anions in the areas of the film with low anionic mobility became immobile themselves. The comparison of the results of EDS analysis and CV indicates that in the timescale used (5 mV s^{-1}) approximately 65 % of the charge of the peak of the insertion of Na^+ cations is due to the compensation of Cl^- anions and 35% of *p*TS anions. The EDS analysis for PPy/BS films showed that less than 5% of BS anions are non-exchangeable.

The self-exchange of ions was also carried out at open circuit potentials. The CV curves measured after 10 min self-exchange of the PPy films doped with BS and *p*TS anions in 0.1 M NaCl solution are presented in Fig. 13C. As can be seen from the figure, the self-exchange of ions at open circuit potentials take place to a somewhat lesser extent than at the potential of 0.4 V.

The shift of the maximum related to the incorporation of Na^+ cations into PPy film towards more positive potentials can be explained in framework of the electrochemically stimulated conformational relaxation model developed by Otero [128–129]. From the comparison of the voltammograms (Fig. 12B curves 1 and 2), it is clearly seen that up to potential -0.5 V only a small part of the total reduction charge is consumed in case of the original film, meaning that it remains in the oxidised (and swelled) form – the polymer matrix is not closed or just slightly closed. In the case of redoped film, however, an essential part of the film is reduced, the matrix is much more closed, and the incorporation of cations into this film requires higher negative potentials.

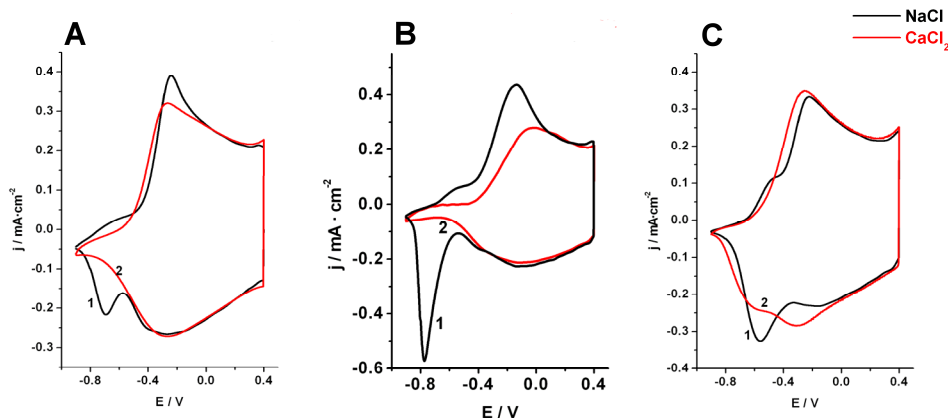


Figure 14. Cyclic voltammograms of the PPy films: A – PPy/BS; B-PPy/*p*TS; C-PPy/NDS measured in 1) 0.1 M NaCl and 2) 0.05 M CaCl₂ solution, scan rate 5 mV·s⁻¹. PPy films deposited at current density $j_d = 4.0 \text{ mA} \cdot \text{cm}^{-2}$; electrodeposition charge $Q_d = 400 \text{ mC} \cdot \text{cm}^{-2}$.

The difference between the mobility of the BS and *p*TS anions can in principle be explained by either steric or interaction factors. However, the more dense packing and higher conductivity of *p*TS doped PPy compared to (the somewhat smaller) BS doped PPy indicates that these chemically rather similar anions differ in their interactions with the PPy chains. As discussed previously, the differences in the interaction with the PPy chains for these anions are most probably due to the different partial charge distribution (II). While both sulfonate groups interact similarly, the less uniform partial charges of *p*TS induce stronger interaction between the benzene ring and the (charged) pyrrole rings.

For a quantitative comparison of the electrochemical behaviour of the various PPy films during cycling, the formal electrochemical doping level f_e was calculated from the CV curves. Figure 13D summarizes the results for different PPy films. Apparently, the largest increase in effective doping level is achieved in the case of PPy films originally doped with *p*TS ions. It is interesting to note that while the initial doping level (redoxcapacity) of the PPy films originally doped with Cl⁻ is remarkably higher than of those doped with BS or *p*TS, the situation is totally reversed after redoping – the electrochemical doping level of the PPy/*p*TS film is increased more than two times. This indicates that the mobility of chloride anions in the PPy matrix originally formed by BS and especially by *p*TS is much less restricted than in the PPy films formed by Cl⁻ anions. There are two main reasons – the aromatic sulfonates are larger and the inner structure of the PPy films is more regular.

3.2.2. The mobility of small inorganic anions (NO_3^- , Cl^- , ClO_4^-) in PPy films doped originally with aromatic anions

More information about structural specificity and others properties of the PPy films can be obtained from the comparison of the voltammograms measured in the presence of different anions with PPy films synthesized in the same solution. In these cases, the structure of the PPy films is identical or at least very similar and the changes in the shape of the CV curves are more directly linked to the mobility of anions. Results of this kind of measurements are presented in figure 15. From this figure is clearly see differences in ion mobility. The voltammograms show that in all cases the increase of the redox charge is generally similar. A more detailed comparison of reduction curves allows identifying some small but typical differences: the PPy films redoped with nitrate ions (Fig. 15 curves 1) show higher values of charge connected with the mobility of anions and smaller charge connected with ingress of cations. The reduction charge of the PPy films connected with mobility of ClO_4^- anions is the smallest. Another possibility to compare the mobilities of the anions in the polymer films is to study the influence of the scan rate on the shape of the CV and on the charge of reduction and on the oxidation. Influence of scan rate is also see in figure 15. Increase the scan rate from 5 to 50 mV s^{-1} amplifies these differences (Fig.15 A2, B2 and C2). From these follow that mobility of anions studied in these polymer films changes in sequences $\text{NO}_3^- \geq \text{Cl}^- > \text{ClO}_4^-$.

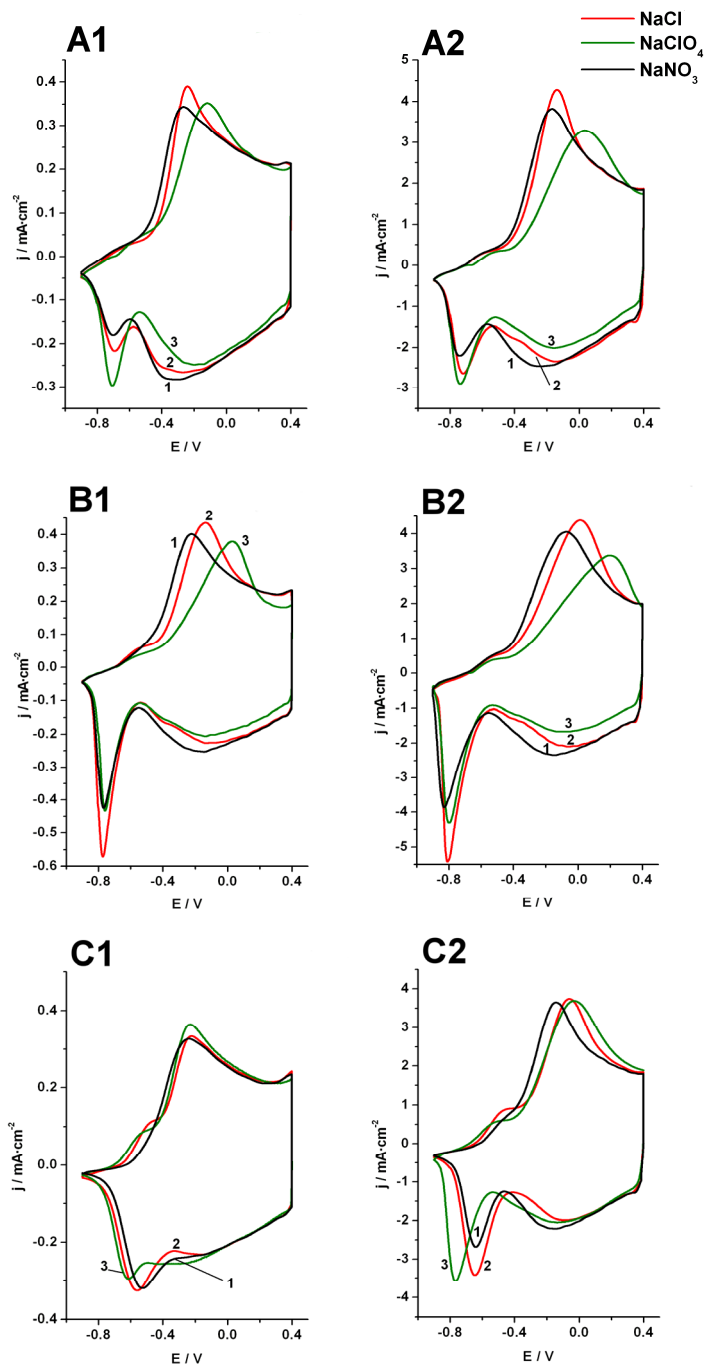


Figure 15. Influence of PPy matrix (A – PPy/BS; B-PPy/*p*TS; C-PPy/NDS) and scan rate (5 mV s^{-1} : A1; B1; C1 and 50 mV s^{-1} : A2; B2; C2) to the shape of CV curves. PPy films deposited at current density $j_d = 4.0 \text{ mA cm}^{-2}$; electrodeposition charge $Q_d = 400 \text{ mC cm}^{-2}$.

3.2.3. The features of PPy films doped originally with NDS anions

It is reasonable to suppose that PPy films synthesized in the presence of NDS anions must have some peculiarities as the NDS anion is double charged and remarkable larger than BS or *p*TS anions. The comparison of the shape of the first and second voltammograms presented in Fig. 16 show very important differences: if in the case of PPy/BS and PPy/*p*TS films the shape of the first and the second voltammogram is very close, it is not the case for the PPy/NDS films.

The shape of the first voltammogram is closer to that of PPy/NDS films in NaNDS solution (Fig. 5C) than to the redoped film. From the results presented in Fig. 16 follows that in the case of PPy/BS and PPy/*p*TS films, redoping is almost completed during 10 min polarisation in 0.1 M solution of NaNO₃, NaCl or NaClO₄ – the self-exchange is fast; in the case of PPy/NDS films, self exchange is restricted and the ingress of the cations into the film during the first cycle essentially increases the rate of the self-exchange of anions. The incorporation of cations during the first cycle drastically changes the electrochemical properties of the film. Such activation (break-in) of the polymer by the cycling is very common [130,131,132].

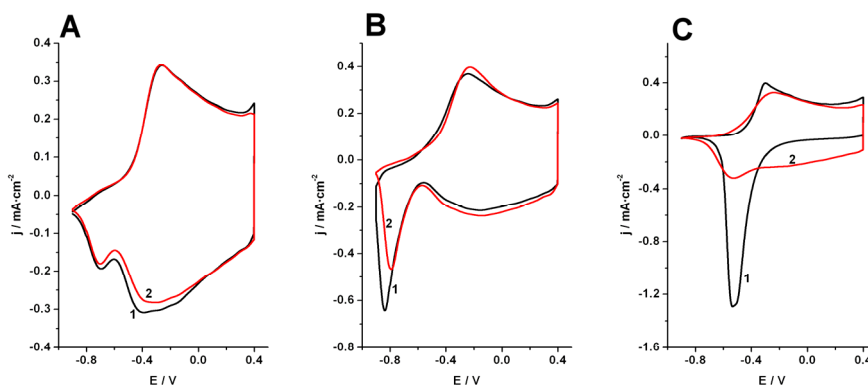


Figure 16. First (1) and second cycle (2) of the PPy films: A – PPy/BS; B-PPy/*p*TS; C-PPy/NDS obtained in 0.1 M NaNO₃ solution, scan rate 5 mV s⁻¹. PPy films deposited at current density $j_d = 4.0 \text{ mA cm}^{-2}$; electrodeposition charge $Q_d = 400 \text{ mC cm}^{-2}$.

3.2.4. Redoxactivity of PPy films doped with aromatic anions in Na₂SO₄

Radically different shapes of the CV curves (Fig 17.) were obtained by measuring PPy films doped with aromatic anions in 0.05 M Na₂SO₄. The voltammograms are presented in the figure 17 A. As sulfate anion carries a larger negative charge than the other inorganic anions used in this work and is more strongly hydrated, it is reasonable to suppose that in this case ion exchange is

much more restricted. The results were totally different: ion exchange was practically complete in 10 min. Unfortunately, we can operate only with the results of electrochemical measurements here, as it is not possible to separate the sulfur atoms belong to sulfate from those of the sulfonate anions by XDS.

The most striking result is that that the shape of the voltammograms measured after redoping are practically identical (Fig. 17A) while the PPy films redoped with other small inorganic anions show essential differences at high negative potentials (Fig. 17B). The very close shape of the parts of the voltammograms where the main process is the expulsion of the small inorganic anions indicates that the possible differences in the inner structure of the different PPy films do not cause remarkable variation in mobility of anions. But a hydrated sulfate anion is not so small and the shape of the CV is also remarkably different. One possible explanation is that cations do not take part in the maintenance of electroneutrality of the PPy films redoped with sulfate. Possibility of the occurrence of such mechanism is, however, low and an experiment with $\text{La}_2(\text{SO}_4)_3$ confirmed that. Large differences in the shape of the CV curves of redoped in sulfate PPy/*p*TS film measured in sodium and lanthanum sulfates (Fig. 17C) is evident. It is clear that cations do take part in the redox processes. Another possible explanation is that sulfate anions, due to the double charge, interact so strongly with polymer chains during redoping that they induce remarkable changes in the inner structure of the polymer, and as result, the mobility of sodium ions in the redoped PPy films becomes independent of the previous structural differences. The strong interactions of sulfate anions with the polymer matrix during redoping may also change the distribution of charge in the polymer and so stimulate quicker ion exchange. The model calculations of charged pyrrole oligomers and various anions using the PM6 semi-empirical method revealed this (IV).

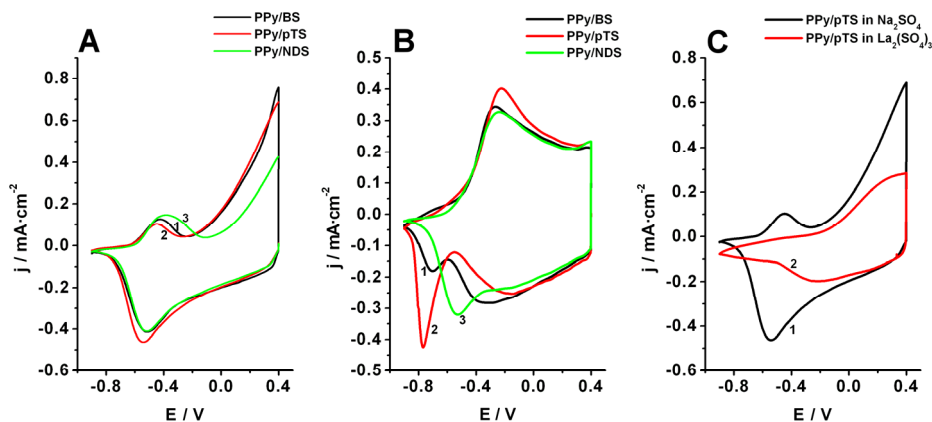


Figure 17. Cyclic voltammograms of different PPy films measured in: A) 0.05 M Na_2SO_4 and B) 0.1 M NaNO_3 solution at scan rate 5 mV s^{-1} . C – PPy/*p*TS film in 0.05 M $\text{La}_2(\text{SO}_4)_3$. PPy films deposited at current density $j_d = 4.0 \text{ mA cm}^{-2}$; electrodeposition charge $Q_d = 400 \text{ mC cm}^{-2}$

3.2.5. Stability of the redoped PPy films.

It has been suggested that redoped PPy films lose their high activity very quickly and the structure of PPy films collapse after ion-exchange [133]. The tests carried out in this work do not confirm this supposition. Long term cycling (300 cycles, 50 mV s^{-1}) showed that the reduction charge was decreased by just around 6 % during the experiment. The special reverse redoping experiments also demonstrate the good stability of the structure of the films under study. In these experiments, PPy films synthesized in the presence of *p*TS and redoped with Cl^- anions were redoped again with the native anions after the voltammetric measurements.

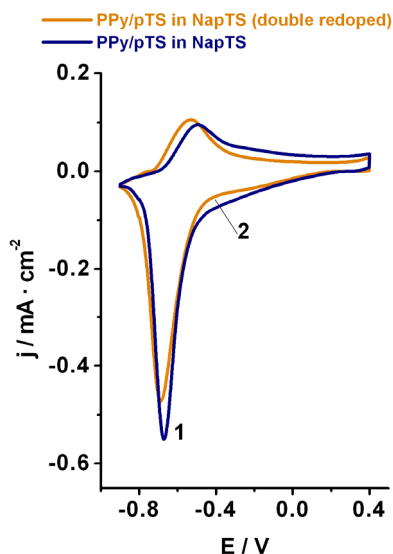


Figure 18. The CV curves of PPy/*p*TS films measured in NapTS solution. PPy synthesised in the presence of *p*TS, redoped with Cl^- anions, and again reverse redoped with *p*TS anion (curve 2). PPy films deposited at current density $j_d = 4.0 \text{ mA} \cdot \text{cm}^{-2}$; electro-deposition charge $Q_d = 400 \text{ mC} \cdot \text{cm}^{-2}$

The comparison of the CVs (Fig.18) shows that the decrease of redoxcapacity after reverse redoping is very low (approximately 7%).

The comparison of AFM images measured before and after redoping do not shows major changes in the morphology of the polymer films either (see publication III).

3.2.6. Redoxactivity of thinner films after redoping

It is well known that the diffusion coefficients of the ions in the PPy films are relatively low 10^{-8} – 10^{-10} [91,94]. One possibility to increase the effective redox-capacity of a PPy films is to decrease the thickness and so shorten the diffusion way. The ion exchange behavior of PPy films with deposition charge $80 \text{ mC}\cdot\text{cm}^{-2}$ (5 time difference between deposition charges) were examined. The volt-ammograms of redoped films are presented in Fig. 19. In order to simplify the comparison, the current density measured for the thinner films was multiplied by 5.

As one can see, the shape of the CV measured on thinner films is remarkably different: on the reduction curve there is one large maximum. Such large shift of the maximum (385 mV for PPy/pTS 380 mV for PPy/BS films) to the more positive potentials is probably not connected with the simple increase of the mobility of cations but with the essential facilitation of the mobility of anions. The tests with the electrolytes containing larger cations confirmed this supposition. The CV measurements in CaCl_2 and LaCl_3 solutions do not show remarkable changes in the shape of the CV curves. The special tests were carried out also by EDS method. The electrodes were taken out from the cell at potential of the maximum and after very short washing analyzed by EDS. No cations were found in the PPy films. From this follows that the maximum on the reduction part of the thin redoped films is mainly connected with the mobility of anions. It is in agreement with the results of EQCM measurements that are carried out, as rule, on thinner films. The effective redoxcapacity of the thinner films is larger than that of the more thick films. The electrochemical doping level f_c of the redoped thinner films is 0.36–0.41 and for thicker films 0.25–0.33 depending on type of the films and anions used for redoping. It is essential to stress that in contrast to the thicker PPy films, where analytical doping level in all cases is larger than the electrochemical doping level indicating that not all parts of the PPy films take part in redox cycling, in the case of the thinner films such difference practically disappears. This means that almost all of the film takes part in the redox processes. In the case of thin films, the increase of redoxcapacity after redoping was not large, only 5–10% in the case of PPy/BS films and 25–33% in the case of PPy/pTS depending on the composition of solution.

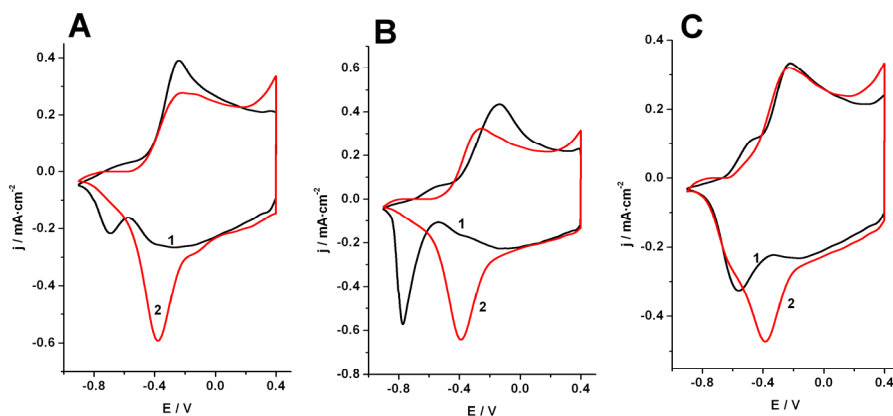


Figure 19. Influence of deposition charge on the shape of the PPy films: A – PPy/BS; B – PPy/pTS; C – PPy/NDS measured in 0.1 M NaNO₃ solution. Deposition charge $Q_d = 400 \text{ mC cm}^{-2}$ (curves 1) and $Q_d = 80 \text{ mC cm}^{-2}$ (curves 2) and recalculated to $Q_d = 400 \text{ mC cm}^{-2}$.

3.2.7. Doping level of the PPy films

An important characteristic for charge storage and other electrochemical properties of polypyrrole is the extent of doping. It is concluded that a high degree of doping may be necessary for optimum electrical and environmental performance of polypyrrole. Charge–discharge capacities of conducting polymer films are limited by the maximum amount of electrolyte anions. In the literature, the proposed doping level of polypyrrole have remained in ranges between about 0.15–0.33 moles per mole polypyrrole, depending mainly on the type and the charge of incorporated anion and its concentration in electropolymerization solution as well as the solvent used for electropolymerization. Based on the data collected from the literature, it can be concluded that the level of doping can be increased by using higher concentrations of doping anions [134–135] or by using aromatic dopant ions for the electrochemical polymerization. In many cases the same researchers who to have achieved higher doping levels, have also applied higher electrode potentials, this, however, normally results in the overoxidation or degradation effects.

In this work, two different methods were used to calculate the doping level of the PPy films before and after redoping. We refer to them as follows: electrochemical f_e and analytical doping level f_a . Electrochemical doping level (f_e) was calculated from the results of CV measurements and the analytical doping level (f_a) was calculated from the elemental analysis as mentioned above. In all cases, the analytical doping level was somewhat higher than f_e in the case of thicker films. These results confirm the fact that some areas from polypyrrole films do not participate in redox processes in t time scale of the operation used in this work. The situation was radically different in the case of 5 times thinner films,

where f_e and f_a were numerically much closer. One possible explanation for this might be that the zones of different structures of polypyrrole films differ in swelling and ion-exchange properties. Wallace and co-workers proposed that polypyrrole consist of highly conducting islands and an amorphous “sea” of conducting polymer regions, which are less-conducting [1].

The results of the redoping measurements of the PPy films deposited with total charge 400 mC cm^{-2} are summarized in Fig.20 in the form of a bar graph. From this Fig. one can see that the highest doping levels are shown by PPy films redoped with the sulfate anions ($f_e=0.30\text{--}0.34$). On the second place are PPy films redoped with chloride anions ($f_e=0.29\text{--}0.33$). In all cases, the electrochemical doping level is essentially higher than that of the PPy films doped with aromatic sulfonates ($f_e=0.14\text{--}0.20$). Comparison of the electrochemical doping level f_e of the PPy films redoped with the same anions show that in all cases, excluding ClO_4^- , the doping level decreases in the the sequences $p\text{TS} > \text{BS} > \text{NDS}$. The ClO_4^- anion is relatively larger than other single charged anions used in this work and has good mobility only in the less compact PPy/NDS film and correspondingly the higher f_e value. If to compare the values of f_e of the PPy films doped with native anions with f_e values of redoped films it seems that there are some contradictions: the native PPy/ $p\text{TS}$ films have the lowest value of f_e but the highest after redoping. It is connected with two reasons: a) the PPy/ $p\text{TS}$ matrix is more organized and more compact which restrict mobility of $p\text{TS}$ anions but not small inorganic anions; b) the essential ingress of the cations during the thirst reduction cycle causes also the incorporation of solvent molecules and swelling of the polymer. As the result, the redoped PPy/ $p\text{TS}$ films are in swollen not only at positive potentials as typical anion exchangers but also at negative potentials which stimulates the mobility of the small ions in the film.

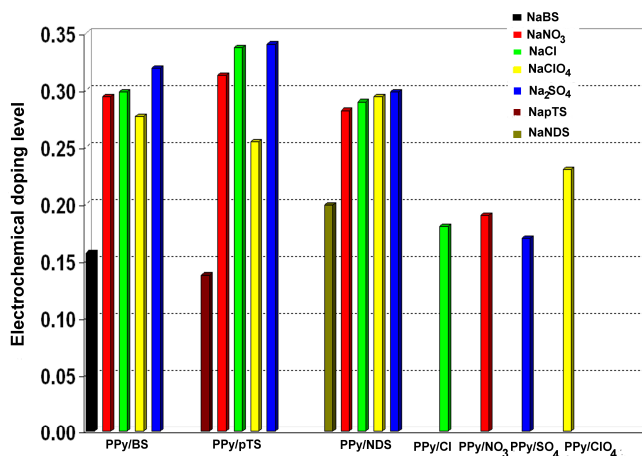


Figure 20. Electrochemical doping level of the PPy films at scan rate 5 mV s^{-1} . PPy films deposited at current density $j_d = 4.0 \text{ mA cm}^{-2}$; electrodeposition charge $Q_d = 400 \text{ mC cm}^{-2}$.

4. CONCLUSIONS

The essential results of the present electrochemical study of polypyrrole films doped originally with aromatic anions such as BS; *p*TS and NDS and measured in various types of electrolytes can be listed as follows:

- The comparative study of the properties of PPy films doped with three different aromatic sulfonate anions using four methods revealed that these similar-looking anions have quite different behavior as dopants.
- It was established, that the process of reoxidation of the PPy film after reduction in solution containing the same anion as used in the electrodeposition solution is slow and the restoration of the initial redox charge needs additional polarization for more than 10 min. Due to the compact structure of PPy films doped with aromatic anions the mobility of anions and cations is restricted which causes irreversibility of redox processes.
- The voltammetric measurements show that redox activity (in solution containing the same anion as used in the electrodeposition solution) of the polypyrrole films doped with these sulfonate ions increases in the sequence *p*TS < BS < NDS, mostly due to the different mobility of cations. The mobility of the ions in these films is mainly determined by how densely the films are packed, which in turn partly depends on the interactions between the dopant-anion and polymer chains.
- The results of voltammetric measurements and XDS analyses show that ion exchange between PPy films and solution is relatively quick. It was established that small inorganic anions as NO_3^- , Cl^- , ClO_4^- can relatively easily replace aromatic sulfonates in PPy/BS and PPy/*p*TS films simply during 10 min polarization at 0.4 V. Only one potentiodynamic cycle needed for essential increase of the rate and completeness of the self-exchange of the anions.
- The highest redox activity and doping levels in the case of all films originally doped with aromatic anions were obtained in the Na_2SO_4 solution. The self-exchange ability of the double charged SO_4^{2-} anion is more pronounced and the exchange process does not need electrochemical activation.
- The redox capacity and corresponding electrochemical doping level of the redoped PPy films are essentially higher than that before ion exchange, showing that the PPy matrix formed in the presence of sulfonate anions does not collapse after ion exchange, and it creates good conditions for the mobility of smaller inorganic anion.
- The results of the electrochemical measurements show clearly that the PPy films synthesized in the presence of BS, *p*TS and NDS and redoped by self-exchange with chloride, nitrate, perchlorate and sulfate anions have good redox capacity and stability.

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SYMMARY IN ESTONIAN

Dopant anioonide mõju polüpürrooli elektrokeemilistele omadustele

Käesolevas töös uuriti detailselt kolme aromaatsse-aniooni: benseensulfonaat-aniooniga (BS); para-tolueensulfonaat-aniooniga ja naftaleen-1,5-disulfonaat-aniooniga dopeeritud polüpürrooli (PPy) elektrokeemilisi omadusi vesilahustes. Erineva paksusega kilesid sünteesiti elektrokeemiliselt konstantsel voolutihe-
dusel. Põhiliseks kasutatavaks uurimismeetodiks oli tsükliline voltampero-
meetria. Täiendavat informatsiooni saadi mikroanalüüsist (EDS), kvantkeemi-
listest arvutustest ning pinnauuringutest aatomjõu mikroskoopia meetodiga
(AFM.).

Ekspimentaalsed uuringud näitasid, et need võrdlemisi sarnaste dopantiooni-
dega (benseensulfonaat vs *para*-tolueensulfonaat) sünteesitud kiled omavad üsna
erinevaid elektrokeemilisi omadusi sõltuvalt lahuse koostisest ning paksusest.

Olulisemad tulemused:

- Elektrokeemiliste mõõtmiste tulemused näitasid, et nende dopantidega (BS, *p*TS, NDS) dopeeritud kilede redoksprotsessi pöördumus on madal sama iooni sisaldavas lahuses (mida kasutati sünteesil), mistõttu täiendav polari-
seerimine positiivsel potentsiaalil on vajalik kile oksüdeerimiseks. Antud
süsteemide korral tagati neutraalsus põhiliselt katioonide liikuvusega.
- Väikeste ühelaenguliste anioonide liikuvus maatriksis, mis oli moodustunud
aromaatsete dopantidega juuresolekul, oli oluliselt parem kui kilede korral,
mis on sünteesitud väikest dopant-iooni sisaldavas lahuses. ning ionide
liikuvus antud maatriksites kahanes reas $\text{NO}_3^- \geq \text{Cl}^- > \text{ClO}_4^-$.
- Elektrokeemiliste mõõtmiste tulemused näitasid, et PPy/*p*TS kile on kom-
paktsem võrreldes teiste kiledel.
- Röntgen-mikroanalüüsi tulemused näitasid, et ümberdopeerimine PPy/BS
ja PPy/*p*TS korral on suhteliselt kiire ning ulatuslik polariseerimisel 10 min
0.4 V väikest aniooni sisaldavas lahuses. Samadest andmetest järeldub ka
see, et 5–10 % algsest dopandist ei ole väljavahetatav antud tingimustes.
- Paksemates ümberdopeeritud kiledes tagati elektroneutraalsus nii katioonide
kui anioonide liikuvusega kiles.
- Röntgen-mikroanalüüsi antmetest tehti arvutuse teel kindlaks, et paksude
kilede dopeerimisastmed olid suhteliselt kõrged, jäädes vahemikku 0.40–
0.43 võrreldes elektrokeemiliste dopeerimisastmetega (0.3–0.34). Antud
tulemused kinnitavad aga tõsiasja, et osa paksust kilest ei võta osa redoks-
protsessist. Täiesti erinev olukord oli õhemate kilede korral, mille efektiivne
redoksaktiivsus oli suurem võrreldes paksemate kiledel.
- Elektrokeemilised mõõtmised näitasid, et aromaatssete dopantidega dopee-
ritud kilede redoksaktiivsust on võimalik oluliselt tõsta ümberdopeerimisega
2 korda ning suurim redoksaktiivsus saavutati kõikide kilede korral
naatriumsulfaati sisaldavas lahuses.

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PUBLICATIONS

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List of publications

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2. **Raudsepp, T.**, Marandi, M., Tamm, T., Sammelselg, V., Tamm, J.; Study of the factors determining the mobility of ions in the polypyrrole films doped with aromatic sulfonate anions. *Electrochim. Acta.* 53 (2008) 3828–3835.
3. **Raudsepp, T.**, Marandi, M., Tamm, T., Sammelselg, V., Tamm, J.; Redoping – A simple way to enhance the redoxcapacity of polypyrrole films; *Electrochem. Commun.* 12 (2010) 1180–1183.
4. **Raudsepp, T.**, Marandi, M., Tamm, T., Sammelselg, V., Tamm, J.; Influence of redoping on electrochemical properties of the polypyrrole films; submitted.

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1. T. Tamm, **T. Raudsepp**, M. Marandi, J. Tamm, Some interesting aspects of aromatic dopant anions in polypyrrole, 57th ISE Annual Meeting, Edinburgh, UK, 27 aug – 1 sept 2006. Book of Abstract, S7, P-77
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Teaduslikud artiklid rahvusvahelise levikuga väljaannetes:

1. Tamm, J., **Raudsepp, T.**, Marandi, M., Tamm, T.; Electrochemical Properties of the Polypyrrole Films Doped with Benzenesulfonate, *Synth. Met* 157(2007) 66–73.
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Konverentside teesid

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