



DISSERTATIONES CHIMICAE UNIVERSITATIS TARTUENSIS

43

**INVESTIGATIONS  
OF THE ELECTROCHEMICAL PROPERTIES  
OF POLYPYRROLE  
MODIFIED ELECTRODES**

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Dissertation is accepted for the commencement of the degree of Doctor of Philosophy in Chemistry on June 4, 2004, by the Doctoral Committee of the Department of Chemistry, University of Tartu.

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Commencement:     August 27, 2004 at 2 Jakobi St. Room 430

Publication of this dissertation is granted by University of Tartu

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Tartu Ülikooli Kirjastus  
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Tellimus nr. 323

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## LIST OF ORIGINAL PUBLICATIONS

The present thesis consists of four original publications and a review. Roman numbers I–IV are used in text for referencing the articles. In publication I, II and III the part of work related to quantum chemical calculations and also in publication I part of the experimental electrochemical work was carried out by the other authors.

- I. J. Tamm, A. Alumaa, A. Hallik, U. Johanson, L. Tamm, T. Tamm; Influence of Anions on Electrochemical Properties of Polypyrrole-modified Electrodes, *Russian J. Electrochem.*, 38 (2002) 182–187.
- II. J. Tamm, U. Johanson, M. Marandi, T. Tamm, L. Tamm; Study of the Properties of Electrodeposited Polypyrrole films, *Russian J. Electrochem.*, 40 (2004) 344–348.
- III. U. Johanson, M. Marandi, T. Tamm, J. Tamm; Comparative Study of the Behavior of Anions in Polypyrrole Films, *Electrochim. Acta.*, *accepted*.
- IV. U. Johanson, M. Marandi, V. Sammelselg, J. Tamm; Electrochemical Properties of Porphyrine-doped Polypyrrole Films, *J. Electroanal. Chem.*, *submitted*.

## LIST OF ABBREVIATIONS

AFM	Atom Force Microscopy
CV	Cyclic Voltammetry
EDS	Energy Dispersive Spectrometry
EPR	Electron Paramagnetic Resonance
NMR	Nuclear Magnetic Resonance
PAn	Polyaniline
PPy	Polypyrrole
PTh	Polythiophene
SEM	Scanning Electron Microscopy
SPM	Scanning Probe Microscopy
TPPS <sub>4</sub>	5,10,15,20-tetrakis-(4-sulfonatophenyl)-porphine
XPS	X-ray Photoelectron Spectroscopy

## INTRODUCTION

For more than 25 years electrically conducting polymers have been studied intensively for practical purposes. Such polymers can be divided into inorganic and organic depending on the nature of the monomer. The field of electrically conducting organic polymers has achieved an especially big interest. For the very first works in this area, which has been revolutionary for all polymer chemistry, the founders of conducting polymers — Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa — were awarded the Nobel Prize of chemistry in the year 2000. Since the beginning in the late seventies this area of scientific study has been growing very fast. Due to the quite good electrical conductivity, ranging from poor semi-conductors to metallic level, such polymers are also called “synthetic metals”. What is even better, the conductivity of the polymers can be easily varied during their formation process and even in already formed structures. Such properties open nearly unlimited possibilities for the practical application of the polymers. Batteries, capacitors, anti-static materials, anti-corrosion coatings, sensors, electrochromic devices are only some examples.

While the first organic conducting polymer — polyacetylene doped with iodide-ions was not stable in air, the majority of later-developed conducting polymers are essentially more stable. Good examples of such type of polymers are polyaniline (PAn), polythiophene (PTh), polypyrrole (PPy), and their derivatives — the polymers formed from aromatic carbo- and heterocycles. Electrochemical studies of conducting polymers have not only a practical value, but are also important for chemistry in general, giving better understanding of processes of the synthesis and modification of the material.

Polymers, formed from heterocyclic aromatic compounds are produced either by chemical or electrochemical oxidation. They are long-chain polycations by nature, where the chains consist of conjugated double bonds. These polycharged chains are mainly responsible for the conductivity of the polymers. According to the principle of electroneutrality, these polymers must contain negatively charged anions to neutralize the positive charge of the chains. In terms of the semiconductor industry, such polymers can be called p-doped semiconductors. After synthesis, the conductive polymers can be reduced. During the reduction the chains of the polymers will lose their positive charge, and again, according to the principle of electroneutrality, the dopant-ions should leave the polymer. What and how exactly happens in this case is depending on the polymer structure, dopant-ion properties, solvent used, and many other things related to the formation process and the following treatment of the films.

This work is focused on the polypyrrole films formed in aqueous solutions by electrochemical polymerization. During the electrochemical synthesis different polymerization regimes and various supporting electrolytes are used. The electrochemical properties of the formed polypyrrole films are investigated.

Traditionally, in experimental electrochemical studies of conductive polymers the macroscopic methods like cyclic voltammetry, potentiometry, impedance measurements, EQCM, etc. are used — but doing so there is a possibility, that many different effects are summarized.

Typical other measurement methods, like X-ray spectroscopy, EPR, NMR, etc., which can be successfully used for the determination of the structural properties of a variety of polymer materials, give only limited information about the polymer studied in this work, because of the highly amorphous structure of PPy. Surface morphology, giving some information about the structure of bulk as well, can be studied by SEM, STM, and AFM methods. From these investigations very interesting and useful information has been extracted, but for collecting more informative data the investigations should be done with both STM and AFM measurements, with higher resolutions up to molecular level, and in *in situ* conditions as a must.

Another promising method for getting atomic level information is to perform quantum chemical calculations for the polymer structures. In this case it is necessary to do many simplifications due to the technical limitations. But nevertheless, already the very first results in this field gave good opportunity for the better understanding of atomic interactions inside the polymer.

According to the limitations of each method it can be concluded, that not one of the above methods can give a good enough description for all of the processes that take place in conducting polymers during their formation and the following reduction and re-oxidation. Therefore, it is necessary to combine the results from different methods — only this way gives reasonable explanations for the changes occurring.

In this work, in addition to cyclic voltammetry measurements the AFM, SEM and X-ray microanalysis methods are used for a more complete characterization of the electrochemical properties of polypyrrole films.



# 1. LITERATURE OVERVIEW

## 1.1. Short history and representatives of conducting polymers

Polymers are a type of materials (mainly organic, but not only), which are produced from a large number of identical parts — the monomers. According to older concepts, all polymers were well known as good insulators. A clear identification, that it is possible to produce polymers that can conduct electrical current was something really new.

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. This material was probably polyaniline [1]. But this work did not lead to a breakthrough in this field.

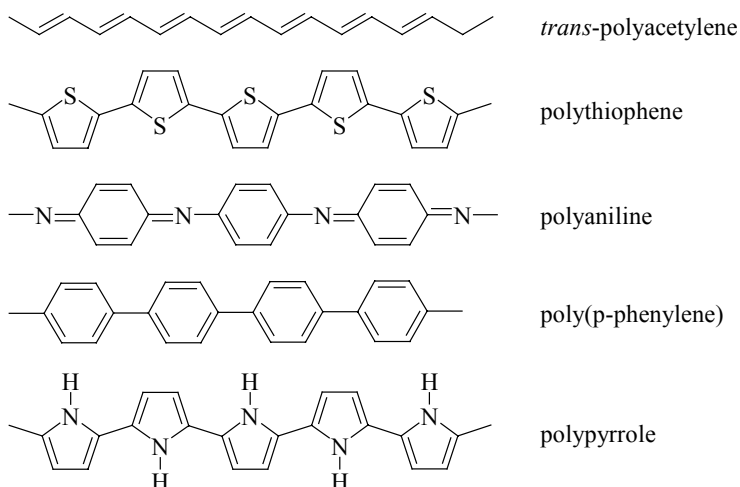
The next important work in the field of conducting polymers was probably related to melanine [2]. In this work it was clearly described that this well-known polymeric compound from biological systems is partly conductive.

Conducting polymers can be divided into organic and inorganic depending on the nature of the corresponding monomer. The next conducting polymer to be discovered was inorganic by nature and had the formula  $(\text{SN})_x$  [3].

In 1977 the articles by Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa [4, 5] about an organic conducting polymer — iodine doped polyacetylene — were finally published which did bring along the breakthrough. Starting with these revolutionary works a new era of a very fast growing field in chemistry was opened. It is necessary to add that some of the first evidences of possible conductance of polyacetylene were published more than 15 years earlier by M. Hatano et al. [6] but at that time this compound remained a scientific curiosity.

In terms of semiconductor industry, all semiconductors can be divided into p-doped and n-doped types. Similar types of conducting polymers also exist — for example iodine doped polyacetylene is p-doped. In such polymers the conjugated carbon chain is positively charged and negative iodide-ions are compensating this charge. The opposite situation occurs with polyacetylene containing sodium-atoms — in this case the carbon-chain with conjugated double bonds has a negative charge and the positive sodium-ions are compensating this charge.

While the conductivity of doped polyacetylene was not very stable in air, numerous other organic conducting polymers discovered later were already more stable. Organic conducting polymers that are formed from carbocyclic or heterocyclic aromatic compounds (e.g. tiophene, aniline, benzene, pyrrole, and their derivates) are of greatest interest and also probably better studied [7,8]. Some structures of the most popular conducting polymers are shown in Figure 1.



**Figure 1.** The structures of conducting polymers.

## 1.2. Formation and properties of polypyrrole

The first published work about one of the most studied organic conducting polymers — polypyrrole — is from 1979 [9]. An intensive study of this polymer started after the discovery.

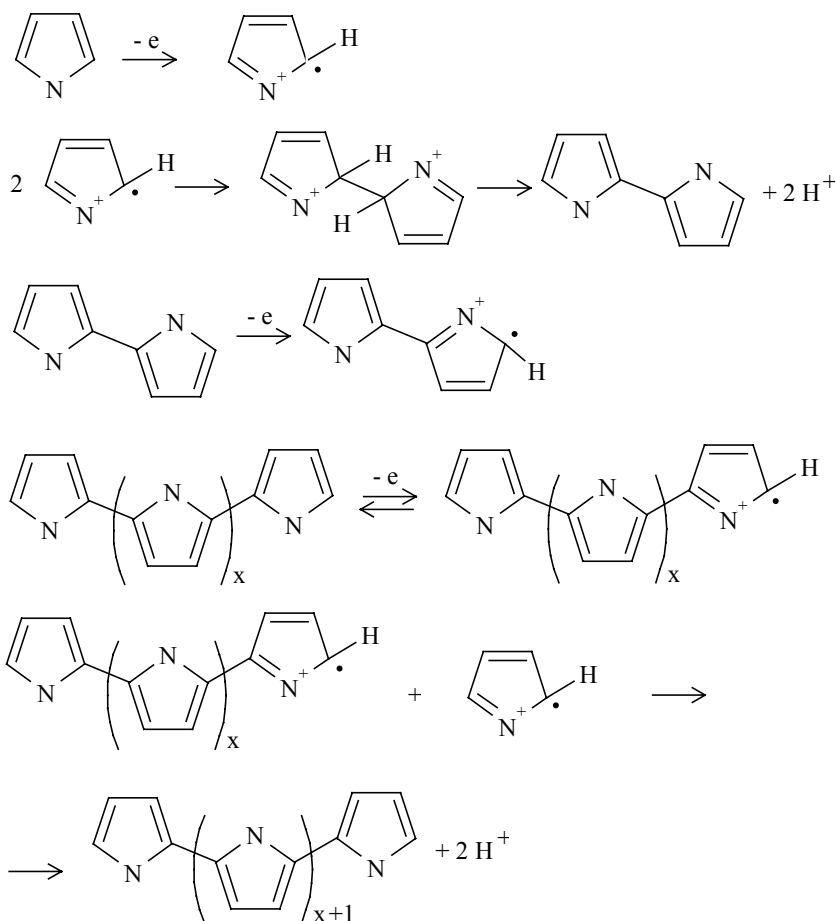
The formation of polypyrrole can be carried out by the chemical [7,10] or electrochemical [8] oxidation of pyrrole. In case of chemical oxidation, it is possible to use a wide range of oxidants like  $\text{FeCl}_3$ ,  $\text{Br}_2$ ,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and many others. In case of chemical oxidation, it is usually possible to produce highly porous polymer powder (called also pyrrole black) because the polymerization starts already in solution and after the formation of colloidal particles those aggregate and precipitate. Such oxidative polymerization is not very well controllable and the properties of such highly amorphous polymeric material are less predictable. But such method has also some advantages for example the possibility to cover insulators with conducting polymers.

A more commonly used method of preparing polypyrrole is the electrochemical oxidation of pyrrole. In this case, the polymer formation process is well controllable by the applied potential/current. Good electrical contact with the base electrode surface is another advantage of electrochemically produced polypyrrole films. The polymerization process can be described by the following summarized equation:



This equation shows that a large amount of hydrogen ions is produced in the process of the polymer formation. In the as-prepared state some part of the hydrogen ions stay in the film and make such polymers acidic [11].

The following scheme for the description of polypyrrole formation has been proposed in the literature [12, 13]:



**Figure 2.** Polypyrrole formation during oxidation.

According to the scheme in Figure 2. radical-cations are initially produced from monomers. The following stages consist of the formation of oligomers and finally the formation of polymer.

Such as-prepared polypyrrole films contain quite a large amount of anions. From the results of chemical analysis it follows that such polypyrrole films have one positive charge for every 3 until 4 monomer units and an equivalent

quantity of anions are also incorporated into the film. From Raman spectroscopy and XPS data it is found that the amount of incorporated anions depends on the polypyrrole film thickness and is lower in case of very thin polymer films and in the surface of thicker films [14]. During polymer formation an essential amount of solvent molecules is also incorporated into the polymer film.

Polypyrrole is one of the most popular in the group of organic conducting polymers because of its good mechanical durability and chemical stability. From X-ray diffraction spectra it is established that electrochemically formed polypyrrole is a typical amorphous polymer [15]. SEM measurements performed on PPy films did show that such polymers contain a large amount of pores [16].

Polypyrrole has different color in different redox states. Changes in color are depending on charge transfer in the films. Oxidized polypyrrole is usually black and reduced polymer is yellowish-green. Very thin PPy films are usually blue or brown in oxidized state and nearly colorless when reduced. In case of thick films ( $> 4 \mu\text{m}$ ), the color remains black also in the reduced state. It is possible to explain this phenomenon with oxidized areas remaining in such reduced films. The same conclusion can be made also from the elemental analysis of this type of films, where some part of the elements corresponding to the anions can be found even in the reduced polymer.

### **1.3. Ion transport during redox cycling**

An essential part of the interesting and useful properties of electrochemically formed polypyrrole films is connected with ion transport during electrochemical reduction and re-oxidation. An as-prepared polypyrrole film is in the conductive oxidized state. What is happening during reduction is essentially depending on the mobility of the incorporated anions. In case of small mobile anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{Br}^-$ ), the transport of the same anions is predominantly responsible for maintaining electroneutrality during redox processes. Medium sized and also small double-charged anions are less mobile. Both anions from the film and cations from the electrolyte solutions take a part in redox processes of polypyrrole films with medium sized dopants. In case of polypyrrole films doped with big immobile anions, only the transport of cations from the electrolyte solution is possible. Such division to the three groups is very approximate because the processes proceeding during reduction and re-oxidation are also essentially depending on polymerization conditions, electrolyte used during the measurements etc.

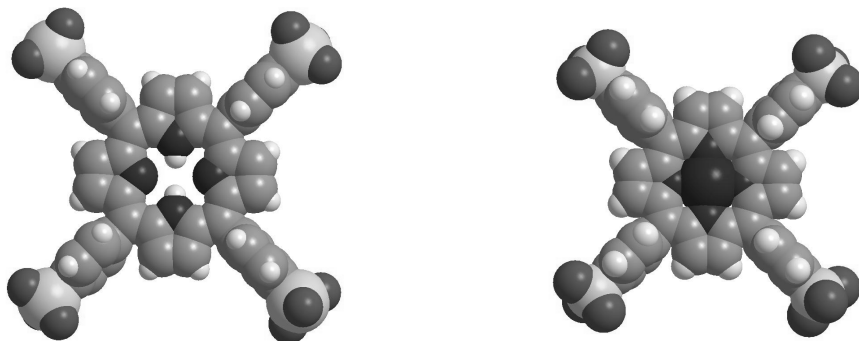
Very interesting information about the mass changes corresponding to anions, cations and solvent movement, can be obtained from EQCM measurements [17–23].

From the chemical analysis data it is possible to calculate real doping levels (charge per monomer unit) for the polymer in both reduced and oxidized states. The difference of these two doping levels is the effective doping level, corresponding to the doping level change during the electrochemical reduction of a PPy film [24]. The same effective doping level can be calculated also from the charges consumed during polymer formation and during reduction of the same polymer.

Bigger anions and anionic complexes can be also used as dopant ions. Such compounds are very well fixed into the polymer film so that during reduction the electroneutrality of films containing this type of anions can be achieved only by cation transfer into the film. Good examples for such systems are polymers containing immobile polyanions, for example poly(4-styrenesulphonat)-anion and poly(vinylsulphonate)-anion, but in aqueous solutions the anions of sulphonic acids with long alcylic chain, as for example dodecylsulphate and 4-dodecylbenzenesulphate [25–27], are also immobile.

Anions can be classified also into groups of electrochemically inactive and active dopants. Inactive anions do not give any additional redox-processes in the potential range where polypyrrole is stable [28]. Electrochemically active anions are such types of anions where redox processes also take place during the polymer reduction and re-oxidation. Anionic cyano-complexes of redox-active metal ions are probably most common representatives of such type of anions [29–32].

Tetra-sulphonated and tetra-carboxylated metalloporphyrines and metallo-phtalocyanines are both big and immobile, but if the metal ion in the porphine center is redox-active then also redox-active [33–43]. Such anions are very interesting for the possible use in the electrocatalytic reduction of different compounds. In Fig. 3 are presented anionic forms of porphyrines studied in this work.



**Figure 3.** Space-filling models of the structure of four-charged anions formed from 5,10,15,20-tetrakis-(4-sulfonatophenyl)-porphine (TPPS<sub>4</sub>) and 5,10,15,20-tetrakis-(4-sulfonatophenyl)-porphyrinato cobalt (II) (CoTPPS<sub>4</sub>).

## 2. EXPERIMENTAL

Pyrrole (Fluka) used for synthesis of PPy films was purified by distillation over calcium hydride under vacuum and stored in the dark under argon atmosphere at low temperature. *Meso*-tetra-(4-sulfonatophenyl)-porphine dihydrochloride purchased from Porphyrine Products, Inc. was neutralized with 0.05 M NaOH before use. All the salts used were of analytical reagent grade (mostly products from Fluka).

PPy films for electron probe microanalysis were prepared by potentiostatic or galvanostatic electropolymerization at various potentials/current densities in aqueous solutions, in case of electrochemical measurements the potentiodynamic regime was also used in addition to the two above mentioned polymerization methods.

Gold and platinum wire electrodes (products of Goodfellow) as working electrodes, graphite or platinum wire counter electrodes and saturated Ag/AgCl reference electrodes were used in conventional three compartment electrochemical cells. Two different cells were used — one for PPy film synthesis and the other for the electrochemical measurements. The film thickness was varied depending on the goal of the study.

Electrochemical measurements were performed mainly in 0.1 M solutions saturated with argon. The initial potential for CV measurements was 0.4 V, at which potential the films are in the oxidized and conductive state but where they are not yet undergoing any overoxidation.

Voltammetric measurements were carried out by using computer driven digital potentiostat/galvanostat equipment (in-house and PAR EG&G 263A).

The composition of the PPy films was determined by X-ray microanalysis using JXA-840 (JEOL, Japan) equipment supplied with an energy dispersive spectrometer (Voyager, Noran, USA). The analysis was performed with primary electron energies of either  $E_0=10, 15$  or  $20$  keV, depending on the film thickness, which varied from  $2$  to  $5$   $\mu\text{m}$ . The value of  $E_0$  was chosen such to guarantee adequate information collection from the entire film thickness. During the analysis the electron probe was defocused ( $\varnothing\sim 10$   $\mu\text{m}$ ) and the specimen was linearly scanned relative to the fixed probe. Thus, a lower dose density of primary electron irradiation and a wider area of the analysis were achieved. The  $K_\alpha$  lines were used as analytical X-ray lines for the determination of the content of S, Cl, Na and Co. Freshly-cleaved single-crystal pieces of NaCl for the analysis of Cl and Na, a conductive single crystal of ZnS for the analysis of S, and a high purity metal sample of Co were used as standards. The scanning electron micrographs were obtained using a JXA-840 scanning electron microscope (SEM) in secondary electron image mode with  $15$  keV primary electron energy. The investigated films were lightly rinsed in double-distilled water in order to remove excess electrolyte from the PPy film surface before the X-ray microanalysis and the SEM analysis and dried in argon flow.

The AFM experiments were performed using an multimode SPM AutoProbe CP (Park Scientific Instruments/Veeco) working in intermittent-contact mode.

## 3. RESULTS AND DISCUSSION

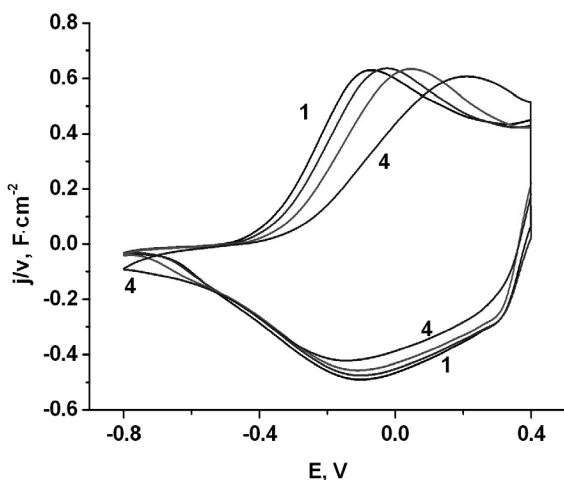
### 3.1. Transport of small ions in polypyrrole films

It is already well known that in case of polypyrrole films doped with small ions such as  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{Br}^-$  etc., the transport of the same anions is usually responsible for maintaining the electroneutrality during electrochemical reduction and re-oxidation. Two points have to be emphasized. Firstly, there is a good proportionality between the peak current  $i_{p,c}$  and the potential sweep rate  $v$ . Such behavior of a conducting polymer film can be described by the model of “free” ions inside the polymer film [44–46]. Secondly, if the mobility of anions is good there is no essential difference between the first, the second, and the following voltammograms. In this case the reduction charge determined from the voltammograms of the first scan  $Q_{1,r}$ , the second scan  $Q_{2,z}$  and for the continuous scanning  $Q_c$  are quite close and decrease only a little in the sequence  $Q_{1,r} \geq Q_{2,z} \geq Q_c$ .

If the mobility of anions in the polymer film is not high, the situation is much more complicated. The typical representative of such systems is polypyrrole film doped with sulfate anions. In this case the voltammograms are less reversible and, a very essential feature, the first and the following voltammograms are remarkably different. Such essential evolution of voltammograms during cycling is sometimes called “break in” phenomena [47]. In this case during the reduction of the PPy/SO<sub>4</sub> films, electroneutrality of the film is established not mainly by anions leaving the film but by the incorporation of cations from the solution into the film [24,48]. In this case the properties of the cations have essential influence on the electrochemical behavior of PPy films (publication I).

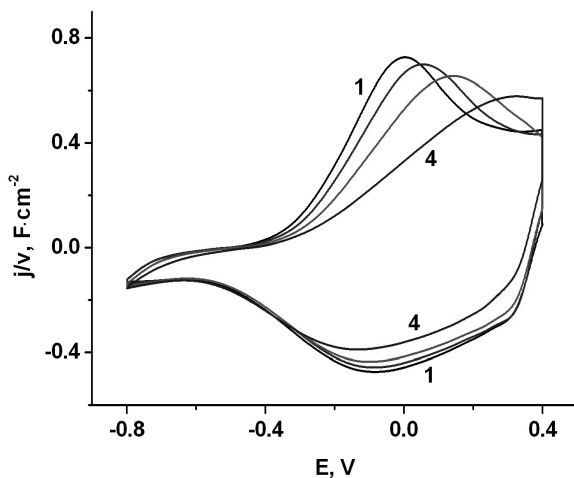
Nevertheless, the situation is more complicated even in case of small dopant ions. It is known that the properties of PPy films are dependent on the current density (potential) used during electrosynthesis [49]. In this part of work PPy films were deposited at low current density ( $0.4 \text{ mA}\cdot\text{cm}^{-2}$ ), and the total charge passed was  $Q_d = 0.8 \text{ C}\cdot\text{cm}^{-2}$ , which produces a film with  $2 \mu\text{m}$  thickness. Such relatively high thickness was used in order to increase the role of the diffusion process and to have a more uniform film as the morphology of the PPy films thinner than  $1 \mu\text{m}$  is very sensitive to the properties of the electrode used [50].

In Figs 4–6 the results of voltammetric measurements are presented in the form of current divided by the potential scan rate  $v$  (pseudo-capacitance curve) [45].



**Figure 4.** Dependence of the normalized current cyclic voltammograms on the scan rate 1:  $5 \text{ mV} \cdot \text{s}^{-1}$ ; 2:  $10 \text{ mV} \cdot \text{s}^{-1}$ ; 3:  $20 \text{ mV} \cdot \text{s}^{-1}$ ; 4:  $50 \text{ mV} \cdot \text{s}^{-1}$  of PPy film deposited at  $j_d = 2 \text{ mA} \cdot \text{cm}^{-2}$ ;  $Q_d = 0.8 \text{ C} \cdot \text{cm}^{-2}$  in  $0.1 \text{ M LiClO}_4 + 0.1 \text{ M pyrrole}$  and measured in  $0.1 \text{ M LiClO}_4$

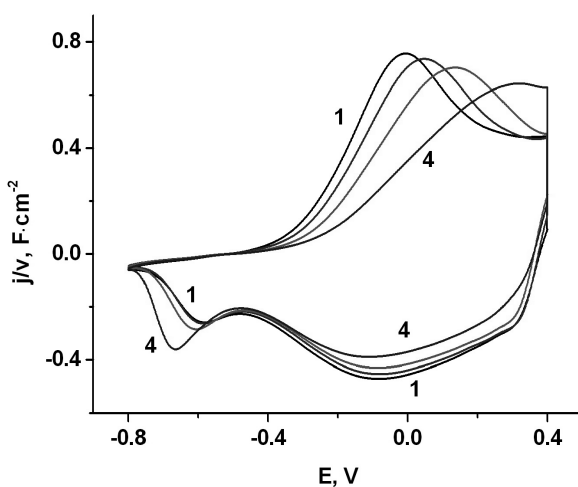
From the comparison of Fig. 4 and Fig 5, where only the polymerization rate is different, it follows that there are only some small differences especially in the area of higher negative potentials.



**Figure 5.** Dependence of the normalized current cyclic voltammograms on the scan rate 1:  $5 \text{ mV} \cdot \text{s}^{-1}$ ; 2:  $10 \text{ mV} \cdot \text{s}^{-1}$ ; 3:  $20 \text{ mV} \cdot \text{s}^{-1}$ ; 4:  $50 \text{ mV} \cdot \text{s}^{-1}$  of PPy film deposited at  $j_d = 0.4 \text{ mA} \cdot \text{cm}^{-2}$ ;  $Q_d = 0.8 \text{ C} \cdot \text{cm}^{-2}$  in  $0.1 \text{ M LiClO}_4 + 0.1 \text{ M pyrrole}$  and measured in  $0.1 \text{ M LiClO}_4$ .



The situation is remarkably different if the measurements are carried out in 0.1 M  $\text{KClO}_4$  (Fig. 6). One can see that the replacement of  $\text{Li}^+$  cations with  $\text{K}^+$  causes remarkable changes in the shape of the voltammograms. A new maximum has appeared at the high negative potential range and the size of this maximum depends on the scan rate. These phenomena can be easily explained if the mobility of cations is taken into account. The PPy film electrosynthesized at lower current density is more compact and the mobility of anions in this film is lower than in films synthesised at higher current densities. As the mobility of  $\text{K}^+$  ions in PPy films is higher than that of  $\text{Li}^+$  ions they take part in the realization of the electroneutrality of the polymer film in a much larger extent than the  $\text{Li}^+$  ions. During the reduction of the polymer (cathodic scan) especially at higher sweep rates some amount of  $\text{ClO}_4^-$  anions are not able to leave the film, and  $\text{K}^+$  ions are incorporated into the film to maintain the electroneutrality of the polymer (publication II).



**Figure 6.** Dependence of the normalized current cyclic voltammograms on the scan rate 1:  $5 \text{ mV} \cdot \text{s}^{-1}$ ; 2:  $10 \text{ mV} \cdot \text{s}^{-1}$ ; 3:  $20 \text{ mV} \cdot \text{s}^{-1}$ ; 4:  $50 \text{ mV} \cdot \text{s}^{-1}$  of PPy film deposited at  $j_d = 0.4 \text{ mA} \cdot \text{cm}^{-2}$ ;  $Q_d = 0.8 \text{ C} \cdot \text{cm}^{-2}$  in 0.1 M  $\text{LiClO}_4 + 0.1 \text{ M}$  pyrrole and measured in 0.1 M  $\text{KClO}_4$ .

In voltammograms of PPy films deposited and measured in the presence of the same anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ) the shape of the CV curves is apparently similar, but just apparently. The most essential differences appear in the case of  $\text{ClO}_4^-$  anions: the charge needed for the reduction or oxidization of the PPy/ $\text{ClO}_4$  film is remarkably larger (the deposition charge was the same 0.8 C). If to take the charge of PPy/ $\text{ClO}_4$  as one the charge of PPy/ $\text{NO}_3$  would be 0.80 and that of PPy/ $\text{Cl}$  0.75.

The reason for such phenomena may be differences in doping level or in the efficiency of the electrodeposition. It is essential to stress that the differences in redox activity are virtually independent of the nature of the anions used during the measurements. Therefore, the structure of the polymer (interaction sites — “places” for the anions) does not change essentially in case such relatively similar anions are used for the measurements.

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. From the comparison of the results follows that the PPy/ $\text{ClO}_4$  system is less reversible than the PPy/ $\text{NO}_3$  system: the shift of the peak on the oxidation curve in the case of PPy/ $\text{ClO}_4$  is more pronounced, especially at higher scan rates. Some amount of additional pseudocapacitance appears on the reduction curve in the negative potential area. This pseudocapacitance indicates that to some extent the cations also take part in the charge compensation process of the PPy/ $\text{ClO}_4$  film.

More information 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 structures of the PPy films are 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. Only at more negative potentials some differences in the shape of the CV curves become evident. Additional increase of the current at the end of the cathodic scan in the case of the  $\text{ClO}_4^-$  ions indicates that some amount of cations also take part in the processes of charge compensation during the cycling.

The mobility of anions studied does not differ too much, but increases in the sequence:  $\text{ClO}_4^- < \text{Br}^- < \text{Cl}^- < \text{NO}_3^-$ . Presumably, the mobility of the  $\text{ClO}_4^-$  anion is lower due to its larger crystallographic radius, and causes essential deviation of the points from the straight line at higher scan rates (publication III).

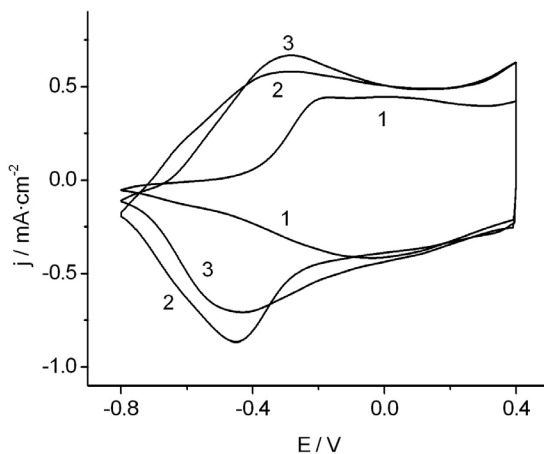
### 3.2. Porphyrine containing polypyrrole films

The electrodeposition of the *meso*-tetra-(4-sulfonatophenyl)-porphine (TPPS<sub>4</sub>) and  $\text{Cl}^-$  mixed-doped PPy- films was carried out from two TPPS<sub>4</sub> containing synthesis solutions with various concentration of NaCl: B — 2 mM TPPS<sub>4</sub> + 0.1 M NaCl + 0.1 M Py and C — 2 mM TPPS<sub>4</sub> + 4 mM NaCl + 0.1 M Py. Conventional 0.1 M NaCl + 0.1 M Py — synthesis solution A — was used for producing PPy/Cl — films. From the comparison of the polarisation measurements in synthesis solutions with and without TPPS<sub>4</sub> follows that the electrodeposition of PPy depends essentially on the presence of TPPS<sub>4</sub> in the solution. So, the electrosynthesis of PPy in the presence of TPPS<sub>4</sub> started at lower positive potentials and the rate of electrodeposition is remarkably higher at higher potentials. Such “catalytic” effect (TPPS<sub>4</sub> is not a real catalyst as it is incorporated into the PPy film, and thus, at least partly belongs to the products)

is almost the same for both porphyrine-containing solutions used. Such an influence of TPPS<sub>4</sub> on the rate of the electrodeposition may be caused by various reasons such as: the decrease of the energy of activation of the formation of the intermediates or/and the modification of the surface of the electrode due to adsorption or/and changes in the morphology of the surface.

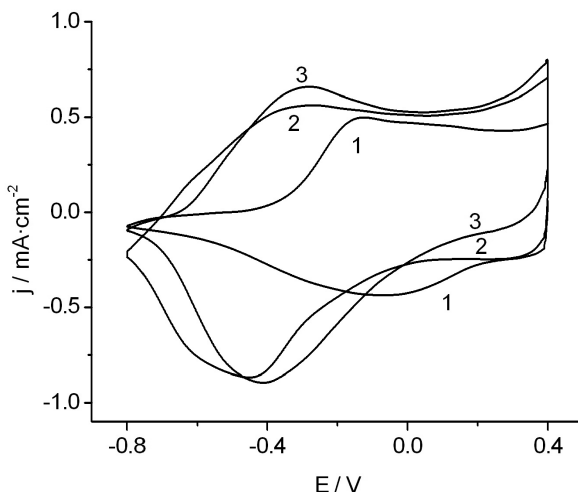
The influence of TPPS<sub>4</sub> on the morphology of the PPy surface was studied by SEM and AFM methods. These studies show that TPPS<sub>4</sub> essentially changes the morphology of the surface making it rougher, thus increasing the effective surface area of the polymer layer. Therefore, the presence of TPPS<sub>4</sub> decreases the effective current density per unit of film surface, and thus, decreases the potential of deposition.

For the cyclic voltammetry study, all the PPy films were electrodeposited at constant current density  $j_s = 235 \mu\text{A} \cdot \text{cm}^{-2}$  with total charge  $Q_s = 0.235 \text{ C} \cdot \text{cm}^{-2}$ . From the typical voltammograms (Figure 7.) it follows that TPPS<sub>4</sub> increases the redox activity of the PPy films at higher negative potentials. Such an increase in the redox activity is evidently connected with the behaviour of TPPS<sub>4</sub> as a big immobile dopant-anion. Some differences in the shape of the CV curves of the PPy films deposited from different solutions are obviously connected with the differences in the structure of PPy films. The most unexpected observation is that in the potential region between 0.4 and 0 V the CV curves for all three types of PPy films are very close. In this potential region the expulsion of anions has to be the dominating process during reduction and it is unreasonable that in these types of films the amount and mobility of Cl<sup>-</sup> ions is the same.



**Figure 7.** The voltammograms (second cycles) of the PPy films deposited from different solutions and measured in 0.1 M NaCl.  $v = 20 \text{ mV} \cdot \text{s}^{-1}$ . Total synthesis charge  $Q_s = 0.235 \text{ C} \cdot \text{cm}^{-2}$ . Compositions of synthesis solutions: 1) 0.1 M Py + 0.1 M NaCl; 2) 0.1 M Py + 0.1 M NaCl + 2 mM porphyrine; 3) 0.1 M Py + 4 mM NaCl + 2 mM porphyrine.

The situation becomes much clearer if to compare the results of the first voltammograms (Fig. 8). In this case the difference in the shape of the curves is essential. The current at the positive potentials increases with the increase of the role of  $\text{Cl}^-$  anions as dopants. The largest change takes place during the first cycle in the case of the PPy films deposited from the solution C, where the concentration of  $\text{Cl}^-$  anions is low.



**Figure 8.** The voltammograms (first cycles) of the Ppy films deposited in different solutions. The same scan rate and the compositions of solutions as in Fig. 7.

In order to have a more quantitative comparison, the changes of the CV curves (negative scan) were integrated from 0.4 V until 0.0 V (charge  $Q_1$ ) and from 0.0 V until  $-0.8$  V (charge  $Q_2$ ). From the EQCM measurements carried out in [51] it follows that in the case of PPy films doped with  $\text{CoTPPS}_4$  the essential increase of the mass of the film connected with the incorporation of sodium cations starts approximately at 0.0 V. So very roughly,  $Q_1$  can be connected with the expulsion of  $\text{Cl}^-$  anions and  $Q_2$  mainly with the incorporation of the cations and the total redox charge is  $Q_T = Q_1 + Q_2$ . In the case of the  $\text{Cl}^-$  doped PPy films total charge  $Q_T$  is divided also into two parts for comparison with porphyrine containing films, but it does not mean that in this case  $Q_2$  reflects the movement of cations.

**Table 1.** Charge (mC) consumed during anodic scans.

	PPy A			PPy B			PPy C		
	Q <sub>1</sub>	Q <sub>2</sub>	Q <sub>T</sub>	Q <sub>1</sub>	Q <sub>2</sub>	Q <sub>T</sub>	Q <sub>1</sub>	Q <sub>2</sub>	Q <sub>T</sub>
1 <sup>st</sup> cycle	7.5	9.6	17.1	4.7	23.5	28.2	2.1	22.4	24.5
2 <sup>nd</sup> cycle	6.6	9.9	16.5	6.6	22.3	28.9	6.8	20.6	27.4

From Table 1 it follows that in the case of as-prepared PPy C films the redox activity connected with the transport of chloride anions is essentially lower than that for PPy B but after one cycle the difference has almost disappeared. In the same time the values of  $Q_2$  for both types of porphyrine-containing PPy films decrease. As the increase of  $Q_1$  is more essential than the decrease of  $Q_2$  the total redox charge  $Q_T$  increases for both types of porphyrine containing PPy films but more remarkably in the case of the PPy C film. Some accumulation of the sodium salt into the TPPS<sub>4</sub> doped PPy films during the cycling was also established with EQCM measurements by Paik *et. al.* [51]. It seems that the mobility of chloride anions in the TPPS<sub>4</sub> doped PPy films is slightly higher than that of sodium cations, and therefore more salt will be accumulated into the film, and the role of the Cl<sup>-</sup> anions in guaranteeing the electroneutrality of the polymer increases.

In addition to this very simple mechanism of the accumulation of Cl<sup>-</sup> anions some re-doping process may take place. As TPPS<sub>4</sub> is able to act as a many-charged dopant-anion it is possible that during reduction configurational changes of the system of polypyrrole chains and TPPS<sub>4</sub> are quite essential. During the following oxidation of the PPy film the incorporation of the additional amount of Cl<sup>-</sup> ions may be more preferable and TPPS<sub>4</sub> ions in the PPy film remain partly in non-dopant salt form. A possible role of the reconfiguration of the polymer in determining the electrochemical properties of conducting polymers is discussed by Hillman and Bruckenstein [52–54].

From the values of the total redox charge  $Q_T$  and the charge consumed during the electropolymerisation of polypyrrole  $Q_s$  it is possible to calculate the effective doping level of the PPy films. The values of the doping level are 0.16 for PPy A, 0.27 for PPy B, and 0.23 for PPy C.

In this work X-ray microanalysis of the PPy films was carried out for quantitative determination of the concentration of dopant ions in the polymer films. As the method requires thicker films (a 15 kV electron beam was used) the deposition charge  $Q_s$  was  $1.2 \text{ C} \cdot \text{cm}^{-2}$ , which is approximately 5 times higher than for the CV measurements. From the X-ray microanalysis measurements it is possible to determine the amount of sulphur, chlorine and sodium but not oxygen (water) and protons (possible additional charge compensation of the TPPS<sub>4</sub> in polymer). The analyses were carried out on as-prepared films (without cycling) and also after the first reduction scan. From these measurements it is

possible to calculate the mole ratio of the ions to the pyrrole unit  $f_{m(\text{TPPS}_4)}$  and  $f_{m(\text{Cl})}$  in PPy films.

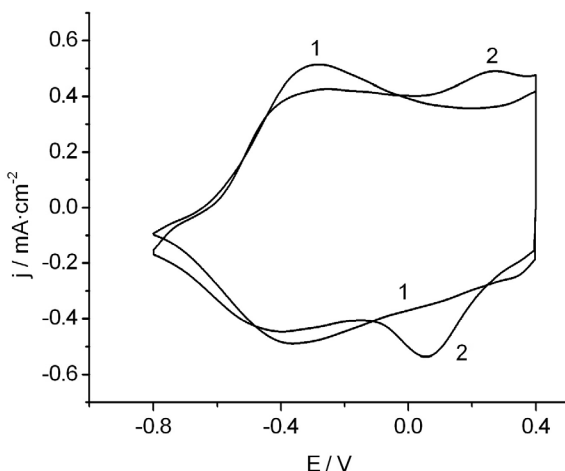
**Table 2.** The mole ratio of the ions  $f_m$  and the effective doping level  $f_c$  calculated from the results of CV measurements.

	$f_{m(\text{TPPS}_4)}$		$f_{m(\text{Cl})}$		$f_{m(\text{Na})}$		$f_c$
	ox.	red.	ox.	red.	ox.	red.	
PPy A	–	–	0.23	0.05	0.02	0.02	0.19
PPy B	0.02	0.02	0.20	0.04	0.01	0.09	0.24
PPy C	0.17	0.09	0.04	0.03	0.41	0.31	0.22

The results of the X-ray microanalysis are very interesting. The behaviour of the Cl<sup>-</sup> doped PPy film is quite simple — only the transport of Cl<sup>-</sup> anions is responsible for the redox-capacity of this PPy film. Redox-properties of the mixed-doped PPy films are more complicated. In the case of the PPy B, the quantity of TPPS<sub>4</sub> in the film is constant and Cl<sup>-</sup> and Na<sup>+</sup> are mobile ions. The most complicated is the behaviour of the PPy C film. The reduction of this film causes a decrease of the amount of both TPPS<sub>4</sub> and Na<sup>+</sup> ions. It means that a quite remarkable part of the TPPS<sub>4</sub> is on the surface of the PPy film and the charge of these TPPS<sub>4</sub> anions is at least partly compensated by Na<sup>+</sup> cations. During reduction these ions diffuse into the solution. From the values of the  $f_m$  and effective doping level  $f_c$  it is possible to calculate how TPPS<sub>4</sub> anions behave as dopant anions. These calculations show that in as-prepared PPy films TPPS<sub>4</sub> acts as double charged dopant-anion.

One problem related with porphyrine doped polypyrrole films not correctly solved until this time is: whether it is this possible to use an electrochemical method (voltammetry) for the registration of the redox process of the redox active metal ion introduced into the porphine centre. It is not a very simple question, because the determination of the waves of the redox couples of the metalloporphyrine immobilised into PPy film is very complicated as PPy itself has high redox-activity at the same potentials.

One possibility to show this phenomenon is to decrease the redox-activity of the PPy film through the depression of the mobility of the anions in this film. This can be achieved by increasing the compactness of the PPy film by decreasing the rate of the electrodeposition of the polymer [49,55–57].



**Fig. 9.** Voltammograms of the PPy films formed in aqueous solution of 0.1 M Py + 4 mM NaCl + 2 mM porphyrine in potentiostatic condition at +0.5 V with  $Q_s = 0.08 \text{ C} \cdot \text{cm}^{-2}$  and measured in 0.1 M NaCl solution: 1) before treatment in 0.1 M  $\text{Co}(\text{CH}_3\text{COO})_2$  solution, 2) after treatment. Scan rate  $50 \text{ mV} \cdot \text{s}^{-1}$ .

In this part of the work PPy films were electrodeposited at  $E = +0.5 \text{ V}$  with the total charge  $Q_s = 0.08 \text{ C} \cdot \text{cm}^{-2}$ . The  $\text{Co}^{2+}$  ions were introduced into the porphine centre by the immersion of TPPS<sub>4</sub> doped PPy film in aqueous 0.1 M cobalt acetate solution heated to  $90^\circ\text{C}$ . The incorporation of cobalt was determined by X-ray microanalysis. It was found that approximately 70% of the porphine centres contain a Co ion, which is a very good yield, considering the relatively high thickness of the film (5–15  $\mu\text{m}$ ). CV curves measured before and after the insertion of Co ions show a clear maximum appearing at 0.05 V on the cathodic scan and at 0.27 V on the anodic scan of the voltammograms recorded with the scan rate of  $50 \text{ mV} \cdot \text{s}^{-1}$  (Fig. 9). Treatment of the TPPS<sub>4</sub> doped PPy film at  $90^\circ\text{C}$  in a solution not containing  $\text{Co}^{2+}$  ions causes no additional maxima on the CV curves.

It is well known that  $\text{CoTPPS}_4$  has high catalytic activity for  $\text{O}_2$  reduction. From the CV curves measured on  $\text{CoTPPS}_4$  doped PPy films in the 0.1 M NaCl solution under argon and air atmosphere it is clearly seen that an essential increase of the current connected with the ionisation of  $\text{O}_2$  starts at the same potentials where the reduction of  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$  started. These results additionally confirm that the maxima on CV curves are connected with the reduction of  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$  and not with the properties of the PPy film (publication IV).

## 4. CONCLUSIONS

The essential results of the present electrochemical study of polypyrrole films containing various types of anions can be listed as follows:

- The mobility of small mono-charged dopant-anions is high and the model of “free” ions inside of polymer film can describe it. In case of conventional quite porous PPy films doped with easily moveable anions such as  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{ClO}_4^-$ , or  $\text{NO}_3^-$ , the reduction charge determined from voltammograms of the first, the second and following scans are quite close and decreases only a little showing good electrochemical stability of the polymer.
- For the more compact polypyrrole films, the mobility of small, normally easily moveable anions is not high enough for achieving electroneutrality and cations will take part in the processes. In this case the results are depending on the cation mobility. From the results of the study of compact PPy films it can be concluded that the mobility of anions is essentially depending on the size of the anions used by electrochemical PPy film formation. From the results of exact experiments follows that the mobility of anions does not differ too much, but rises in the sequence:  $\text{ClO}_4^- < \text{Br}^- < \text{Cl}^- < \text{NO}_3^-$ .
- The presence of *meso*-tetra-(4-sulfonatophenyl)-porphine in the solution of the monomer during the electrosynthesis of PPy film essentially promotes polymer formation. The AFM and SEM studies showed that the surface of the PPy films containing porphyrine PPy film roughened.
- The cyclic voltammetry studies showed that in case of mainly porphyrine doped PPy films some re-doping processes with small anions will also happen. It can also be concluded from the same results that the effective doping level of the porphyrine containing PPy films is higher than of that without porphyrine.
- It also followed from the analysis, that in as-prepared PPy films doped mainly with porphyrine a quite remarkable part of the  $\text{TPPS}_4$  is on the surface of the PPy film and the charge of these  $\text{TPPS}_4$  anions is at least partly compensated by  $\text{Na}^+$  cations. The calculations based on the X-ray microanalysis and cyclic voltammetry measurements showed that in as-prepared PPy films  $\text{TPPS}_4$  acts as a double charged dopant-anion.
- The results of the X-ray microanalysis show that it is possible to carry out the insertion of  $\text{Co}^{2+}$  ions into the porphine centres in already formed porphyrine containing film with high efficiency — approximately 70% of the porphyrine centres were occupied even in the case of the relatively thick (5–15  $\mu\text{m}$ ) PPy films.
- For the first time, well-defined waves corresponding to the  $\text{Co}^{3+/2+}$  redox-transition in cobalt-porphyrine containing PPy films were established from the cyclic voltammetry study. It was established that the electroreduction of molecular oxygen starts just at the same potential as the wave on the voltammogram connected with the reduction of the  $\text{Co}^{3+}$  ions to  $\text{Co}^{2+}$ .



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## SUMMARY IN ESTONIAN

### Polüpürrooliga modifitseeritud elektroodide elektrokeemiliste omaduste uurimine

Käesoleva töö eesmärgiks oli uurida ühe enimtuntud orgaanilise elektrit juhtiva polümeeri — polüpürrooli — elektrokeemilisi omadusi. Tunnustatud arusaamade kohaselt mõjutavad polüpürrooli omadusi mitte ainult monomeeri omadused, vaid ka konkreetseid sünteesitingimused, nagu näiteks: sünteesimeetod (keemiline või elektrokeemiline), kasutatavate lahuste kontsentratsioonid, kasutatav solvent, sünteesi kiirus, temperatuur jne. Käesolevas töös kasutati elektrokeemilist sünteesimeetodit ja kõik katsed viidi läbi vesilahustes. Katsetati erinevate foonelektrolüütidega ja varieeriti sünteesikiirust. Lisaks viidi läbi ka aatom-jõu mikroskoopia ja skaneeriva elektronmikroskoopia mõõtmised kile pinnatopograafia iseloomustamiseks. Valmistatud kilede koostis määrati röntgen-mikroanalüüsi abil.

Olulisemad tulemused:

- Väikeste ühelaenguliste anioonide liikuvus tavalistes, suhteliselt poorsetes polümeerkiles on väga hea ja seda kirjeldab hästi “vabade” ionide liikumise mudel. Väikeste anioonide ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{ClO}_4^-$  ja  $\text{NO}_3^-$ ) korral on esimese, teise ja järgnevate tsüklite korral redutseerimiseks kuluv laenguhulk üsna sarnane ja see kahaneb vaid veidi tsükleerimise käigus.
- Tihedate kilede korral on ka väikeste, tavalistes tingimustes hästiliikuvate, anioonide liikumine pärsitud ja sellisel juhul osalevad redoksprotsessides ka katioonid. Kui suur on aga sellel juhul katioonide roll, see sõltub juba omakorda katioonide liikuvusest. Selliste tihedate polümeerkilede elektrokeemilistese omaduste uurimisest ilmnas, et anioonide liikuvus polüpürroolkiles on olulisel määral sõltuv sünteesis kasutatud dopantaniooni mõõtmest. Väga täpselt samades tingimustes tihedatel kiledel teostatud eksperimentidega tehti kindlaks, et väikeste anioonide liikuvus on üsna sarnane, kuid kasvab siiski reas:  $\text{ClO}_4^- < \text{Br}^- < \text{Cl}^- < \text{NO}_3^-$ .
- Polüpürrooli valmistamisel kasutatavasse sünteesilahusesse *meso*-tetra-(4-sulfonatofenüül)-porfiini lisamine soodustab oluliselt polüpürroolkile moodustumist. Aatom-jõu mikroskoopia ja skaneeriva elektronmikroskoopia mõõtmised näitasid, et porfüriini sisaldava kile pind on oluliselt ebatasasem, kui sarnastes sünteesitingimustes valmistatud ilma porfüriiniga polüpürroolkilede pinnad.
- Segadopeeriinguga, põhiliselt porfüriiniga dopeeritud polüpürroolkilel tehtud tsüklilise voltamperomeeria mõõtmised näitasid, et tsükleerimise käigus toimub polüpürrooli osaline ümberdopeerimine väikeste anioonidega (antud töös kloriidiga). Samadest andmetest järeldub, et porfüriini dopandina sisaldava polüpürroolkile efektiivne dopatsiooniaste on oluliselt kõrgem, kui porfüriiniga kilede korral.

- Röntngen-mikroanalüüsi ja tsüklilise voltamperomeetria andmete alusel tehtud arvutustest ilmnes, et värskeltvalmistatud kiledes käitub porfüriin kahelaengulise dopandina. Samadest andmetest järeldub ka see, et värskeltvalmistatud, põhiliselt porfüriiniga dopeeritud kilede korral on üsnagi märgatav osa porfüriini seotud kile pinnaga ja et porfüriin on vaid osaliselt dopandi rollis — märgatav osa anioonse porfüriini laengutest on kompenseeritud naatriumioonidega.
- Röntngen-mikroanalüüsi andmetest tehti arvutuste teel kindlaks, et ka suhteliselt paksude (5–15  $\mu\text{m}$ ) porfüriini sisaldavate polüpürroolkilede korral on võimalik viia koobalt(II)ioone porfiini tsentritesse küllalt suure saagisega (70%).
- Kasutades koobaltioone sisaldava porfüriiniga dopeeritud polüpürroolkilede tsüklilist voltamperomeetriat jälgiti esmakordselt elektrokeemilise uurimismeetodi abil selgelt väljendunud  $\text{Co}^{3+/2+}$  redoksüleminekule vastavaid redoksmaksimume. Samuti leiti elektrokeemilistest mõõtmistest abil, et molekulaarse hapniku redutseerumine algab täpselt samal potentsiaalil, kui koobalt(III)ioonide üleminek koobalt(II)ioonideks.

## **ACKNOWLEDGEMENTS**

I wish to express my gratitude to my doctoral advisors Prof. Jüri Tamm and Prof. Väino Sammelselg for the professional guidance and advice they provided through the years of collaboration.

I am very thankful to my colleagues, the inorganic chemistry group, and especially Mr. Margus Marandi and Dr. Tarmo Tamm for very useful and successful teamwork.

Last but not least, I would like to thank my parents for continuous support during the long years of my studies.

## **PUBLICATIONS**

# CURRICULUM VITAE

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### Education

1995–2000 University of Tartu, Ph.D. student  
1992–1995 University of Tartu, graduate student, M.Sc.  
(chemistry) 1995  
1988–1992 University of Tartu, student, B. Sc. (chemistry)  
1977–1988 Viljandi 5<sup>th</sup> Secondary School

### Work experience

2004– University of Tartu, Institute of Physical, 0,5 chemist  
2002–2003 University of Tartu, Institute of Physical, chemist  
1999–2001 University of Tartu, Institute of Physical, 0,5 chemist

### Professional self-improvement

1994 University of Barcelona, 5 months in the group of Prof.  
Dr. Josep M. Ribó

## Publications

### Scientific publications in major international journals:

1. Tamm, J.; Alumaa, A.; Hallik, A.; **Johanson, U.**; Tamm, L.; Tamm, T.; Influence of Anions on Electrochemical Properties of Polypyrrole-modified Electrodes, *Russian J. Electrochem.*, 2002, 38, 182–187.
2. Tamm, J.; **Johanson, U.**; Marandi, M.; Tamm, T.; Tamm, L.; Study of the Properties of Electrodeposited Polypyrrole films, *Russian J. Electrochem.*, 2004, 40, 344–348.
3. **Johanson, U.**; Marandi, M.; Tamm, T.; Tamm, J.; Comparative Study of the Behavior of Anions in Polypyrrole Films, *Electrochim. Acta.*, *accepted*.
4. **Johanson, U.**; Marandi, M.; Sammelselg, V.; Tamm, J.; Electrochemical Properties of Porphyrine-doped Polypyrrole Films, *J. Electroanal. Chem.*, *submitted*.

### Abstracts of meetings and conferences:

1. Johanson, U.; Tamm, J.; Electrochemical Properties of Porphyrin Doped Polypyrrole Films “Baltic Conference on Interfacial Electrochemistry, Extended abstracts”; Tartu, 1996, 103–105
2. Tamm, J.; Johanson, U.; Some Electrochemical Properties of the Polypyrrole Films, “XXII Eesti Keemiapäevad. Teaduskonverentsi teesid”; Tartu, 1996, 196
3. Tamm, J.; Alumaa, A.; Hallik, A.; Johanson, U.; Silk, T.; Tamm, L.; Tamm, T.; Sammelselg, V.; Ion Sensitive Properties of Conducting Polymers, “2<sup>nd</sup> Baltic Conference on Electrochemistry, Extended Abstracts”; Palanga, 1999, 160
4. Tamm, J.; Alumaa, A.; Hallik, A.; Johanson, U.; Tamm, L.; Sammelselg, V.; Influence of Ion Mobility on Redox Behaviour of Polypyrrole; ”50th ISE Meeting, Abstracts”; Pavia, 1999
5. Tamm, J.; Tamm, T.; Johanson, U.; The Theoretical and Experimental Study of Pyrrole Oligomers and Polypyrrole, “51<sup>st</sup> Annual ISE Meeting, Extended abstracts”, Warsaw, 2000, s-5 639.
6. Tamm, J.; Johanson, U.; Alumaa, A.; Hallik, A.; Tamm, T.; Sammelselg, V.; Ion Mobility and Electrochemical Properties of Polypyrrole, “NATO Advanced Research Workshop on Electrochemistry of Electroactive Polymer Films, Extended abstracts, Oral Presentation”, Poraj, 2000, 40.
7. Tamm, J.; Tamm, T.; Johanson, U.; Tamm, L.; Alumaa, A.; Hallik, A.; Role of Ions in Polypyrrole Films, ES and ISE joint meeting, San Francisco, 2001.
8. Tamm, J.; Johanson, U.; Tamm, T.; Alumaa, A.; Hallik, A.; Tamm, L.; Sammelselg, V.; Ions in Polypyrrole Films, “53<sup>rd</sup> Annual ISE Meeting, Book of Abstracts”, Düsseldorf, 2002, 362.



# ELULOOKIRJELDUS

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### Üldandmed

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### Haridus

1995–2001 TÜ doktorant  
1992–1995 TÜ magistrant, keemiamagister, M.Sc. 1995  
1988–1992 TÜ üliõpilane, keemiabakalaureus, B. Sc. 1992  
1977–1988 Viljandi 5. Keskkool

### Teenistuskäik

2004– füüsikalise keemia instituudi (keemik 0,5 kohaga)  
2002–2003 füüsikalise keemia instituudi keemik  
1999–2001 füüsikalise keemia instituudi (keemik 0,5 kohaga)

### Enesetäiendus

1994 Barcelona Ülikool, 5 kuud prof. Dr. Josep M. Ribó grupis

## Teadustööde loetelu

### Teaduslikud artiklid rahvusvahelise levikuga väljaannetes:

1. Tamm, J.; Alumaa, A.; Hallik, A.; **Johanson, U.**; Tamm, L.; Tamm, T.; Influence of Anions on Electrochemical Properties of Polypyrrole-modified Electrodes, *Russian J. Electrochem.*, 2002, 38, 182–187.
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4. **Johanson, U.**; Marandi, M.; Sammelselg, V.; Tamm, J.; Electrochemical Properties of Porphyrine-doped Polypyrrole Films, *J. Electroanal. Chem.*, submitted.

### Konverentside teesid:

1. Johanson, U.; Tamm, J.; Electrochemical Properties of Porphyrin Doped Polypyrrole Films “Baltic Conference on Interfacial Electrochemistry, Extended abstracts”; Tartu, 1996, 103–105
2. Tamm, J.; Johanson, U.; Some Electrochemical Properties of the Polypyrrole Films, “XXII Eesti Keemiapäevad. Teaduskonverentsi teesid”; Tartu, 1996, 196
3. Tamm, J.; Alumaa, A.; Hallik, A.; Johanson, U.; Silk, T.; Tamm, L.; Tamm, T.; Sammelselg, V.; Ion Sensitive Properties of Conducting Polymers, “2<sup>nd</sup> Baltic Conference on Electrochemistry, Extended Abstracts”; Palanga, 1999, 160
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8. Tamm, J.; Johanson, U.; Tamm, T.; Alumaa, A.; Hallik, A.; Tamm, L.; Sammelselg, V.; Ions in Polypyrrole Films, “53<sup>rd</sup> Annual ISE Meeting, Book of Abstracts”, Düsseldorf, 2002, 362.