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Polypyrrole: a conducting polymer; its synthesis, properties and applications

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Abstract. The synthesis, properties and applications of polypyrrole (PPy), a representative of conducting polymers, are reviewed. Chemical and electrochemical methods for the preparation of PPy and PPy films and the effect of the reaction conditions on the properties of the polymer produced are discussed. The mechanisms of electrochemical polymerisation of pyrrole are compared. The physicomechanical properties of the polymer, its morphology and structure are discussed. The mechanism of charge transfer in PPy is considered within the framework of the model of quasi-equilibrium concentrations of polarons and bipolarons. The methods for modification of the electrochemical performance of PPy are reviewed, in particular, synthesis of PPy from pyrrole derivatives with the appropriate electroactive groups and introduction in the PPy of electroactive dopant anions and the effect of those on the electrochemical performance of PPy films are considered. Examples of the use of PPy are given and the prospects for its application in various areas are discussed. The bibliography includes 254 references.

I. Introduction

Not more than two decades ago, researchers considered exclusively polymeric dielectrics or semiconductors that could be made conductive only by means of dramatic changes in their chemical nature (*e.g.*, by heat causing pyrolysis and partial graphitisation of the polymer). The discovery in 1977 of the high conductivity of doped polyacetylene[1–4] stimulated studies on the synthesis and study of various conjugated polymers. As a result, an entire class of polymeric conductors was developed. Typical representatives of this class are poly(*p*-phenylene),[5] polypyrrole,[6] polythiophene[7] and its 3-methoxy- derivative,[8] polyaniline.[9] The common feature of the structure of conducting polymers is polyconjugation in the π-system of their backbone (for polyaniline, this holds only in the case of doped polymer).

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The conducting polymers (also called synthetic metals) are polyconjugated, which possess electronic (conductive, magnetic, optical) properties of metals, while retaining the mechanical properties and processibility of conventional polymers. They acquire high conductivity due to incorporation of a small concentration of dopants into the matrix of the initial polyconjugated polymers having conductivity ranging from 10^{-10} to 10^{-5} S cm^{-1}. The resulting materials have conductivities typical of metals or semiconductors, 1 to 10^5 S cm^{-1}.

The doping is performed by means of chemical or electrochemical oxidation (*p*-doping) or reduction (*n*-doping) of a polymer. As a result, the polymeric chains acquire positive or negative charges, respectively.[10] Electroneutrality of the material as a whole is preserved by incorporation of dopants (counterions) from electrolyte solution into the polymeric matrix. The doping is reversible; as a result of dedoping (removal of dopant), the initial polymer can be obtained with its polymeric structure intact. Regulation of the level of doping provides a possibility to prepare polymers with widely varied electric conductivity, from insulating or semiconducting forms of the polymer in the undoped state to highly conductive ones in the strongly doped state.

The conducting polymers attract attention of researchers and engineers from a variety of fields in science and technology as promising electrode materials for energy storage devices (electrochemical batteries and capacitors), electrocatalysts and biosensors based thereon, photoluminescent and electroluminescent materials, 'artificial muscles', gas separating membranes, anticorrosive coatings, electromagnetic shields, materials for microlithography, electrophotography, *etc.*[11] In addition, the possibilities to produce conducting polymers electrochemically and to control their properties by electrochemical means are of interest on their own. To date, a number of reviews and books on conducting polymers have been published. Unfortunately, the topic is not extensively reviewed in the Russian literature. In this paper, we review the properties of polypyrrole (PPy), which is a typical representative of conducting polymers and manifests characteristic features of this class of materials.

II. Methods of polypyrrole preparation

1. Chemical synthesis

Among other conducting polymers, PPy and its derivatives are of particular interest, owing to their high conductivity, stability in the oxidised state and interesting redox properties. The simplicity

of the synthetic procedures and availability of the initial monomers are also attractive features of PPy.

Chemical synthesis of PPy has a long history.[12] Polypyrrole prepared by oxidation of the monomer with chemical oxidants has a form of black powder. Aqueous or anhydrous $FeCl_3$,[12–15] other salts of iron(III) and copper(II) are widely used as chemical oxidants.[16–19] The use of halogens and organic electron acceptors as oxidants for PPy synthesis has also been reported.[20,21] The yield and conductivity of the PPy produced are affected by a variety of factors, among which are the choice of solvent and oxidant, initial pyrrole/oxidant ratio, duration and temperature of the reaction. At the optimal ratio[13] of Fe(III)/monomer which is 2.4, the yield of PPy approaches 100%. Shorter times of polymerisation and lower temperatures (0 to 5 °C) result in enhanced conductivity of PPy produced.[18] For PPy prepared by monomer oxidation with $FeCl_3$ in various solvents (water, alcohols, benzene, tetrahydrofuran, chloroform, acetone, acetonitrile (AN), dimethylformamide),[14] the highest conductivity was observed for PPy prepared in methanol solution (190 S cm^{-1}). Controlled variation of the oxidising potential of the reaction medium [it was changed through the ratio of $FeCl_3$ to $FeCl_2$ (Ref. 14) and also using a binary AN/methanol solvent[22]], provided a possibility to enhance conductivity of PPy to 220 S cm^{-1} in the former case and to 328 S cm^{-1} in the latter. When PPy is produced by oxidation in the presence of $FeCl_3$, the polymer is doped with Cl^- anions; the overall reaction can be represented by the following stoichiometric equation [12,14]

$$n\,C_4H_5N + (2+y)n\,FeCl_3 \rightarrow [(C_4H_3N)_n^{y+}\,ny\,Cl^-] + \\ + (2+y)n\,FeCl_2 + 2n\,HCl,$$

where y is the degree of PPy oxidation (doping level).

In earlier works, the degree of PPy oxidation was determined from the Cl/N ratio using the data from elemental analysis. The Cl/N ratio varied from 0.21 (see Ref. 12) to 0.34 (Refs 13, 14). In Ref. 19, the Cl/N ratio for PPy prepared from aqueous solution was 0.33 and substantially exceeded that for the polymer produced from methanol and AN. X-Ray photoelectron spectroscopy (XPS) revealed that chlorine atoms in the polymer are in three chemical states, namely, ionic, covalently bonded and an intermediate one; the latter is similar to the chloride anions in metal chlorides (including $FeCl_3$ and $FeCl_2$). It was noticed [12] that when PPy was treated with solution of $FeCl_3$ in nitromethane, the iron-containing $FeCl_4^-$ anions were incorporated in the polymer. Possibly, the intermediate species of chlorine is related to iron chlorides.[19] In spite of the high concentration of incorporated chlorine, only a Cl/N ratio equal to 0.25 corresponded to y (25% of oxidised monomer units). Thus, the elemental analysis is insufficient to determine the true degree of PPy oxidation.

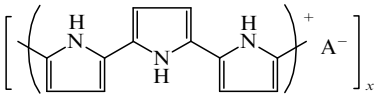
The conductivity and stability of PPy powder produced by means of chemical oxidation were substantially improved. However, formation of PPy films or coatings on another material remained problematic. This problem was partially solved by PPy deposition from gas with $FeCl_3$ used as an oxidant.[23–25] This method provided a possibility of producing free film or PPy coatings having high mechanical properties on substrates of any shape. The mechanical performance of PPy powder could also be improved by preparation of composites filled with it, composites with poly(ethylene oxide) in particular.[23,26,27]

The method of chemical oxidative polymerisation constituted a basis for the layer-by-layer deposition of PPy and polyaniline (PAni).[28] The authors of this work report that the polymers have more regular structure and higher crystallinity than those produced electrochemically.

2. Electrochemical synthesis

Electrochemical polymerisation provides a number of advantages over chemical methods. The first is that the reaction product is an electroactive film attached to the electrode surface and having high conductivity. Second is that the yield in charge terms is close to 100%; this provides a possibility of controlling the mass and thickness of the film. And finally, the properties of the film produced can be controlled directly in the course of preparation. In 1968, Dall'Olio *et al.*[29] obtained a PPy film with conductivity of 8 S cm^{-1} by electrolysis of pyrrole solution in the presence of sulfuric acid; the polymer was obtained in the form of powder deposited on the electrode surface. In 1979, Diaz *et al.*[6,30] prepared the polymer in the form of flexible films with conductivity of 100 S cm^{-1} by electrolysis of an aqueous solution of pyrrole. This work gave a start to the extensive use of electrochemical synthesis of PPy (and other conducting polymers). The PPy films are obtained in doped (conducting) form directly in the course of synthesis; they can be transferred to neutral (insulating) form by means of electrochemical reduction.

Electropolymerisation (EP) of pyrrole (and electrosynthesis of other conducting polymers) differs from other polymerisation reactions, including the radical ones, that are initiated electrochemically.[31] The anodic oxidation, which results in the formation of conducting polymer, has the stoichiometry of 2.07 to 2.6 F per mole of monomer.[32,33] Of those, only 2 F mol^{-1} are related to the polymerisation as such and extra charge, to the oxidation (doping) of the polymer film. Since the oxidation potential of the monomer is always markedly higher than that for the polymer, the two processes, the formation of polymer and its oxidation proceed in parallel and are accompanied by the incorporation of counterions into the polymer matrix. The structure of the PPy formed can be represented as [34]



where A^- is an anion.

The doping level for PPy (number of anions per monomer unit), depending on the nature of anions and conditions of synthesis, varies within 0.1 to 0.5. Switch-off of the current in the course of PPy electrosynthesis is immediately followed by the arrest of the chain growth; the mass of the polymer film is directly proportional to the charge passed.[35–37]

Electropolymerisation of pyrrole can be performed in both aqueous and non-aqueous media, such as AN, propylene carbonate (PC), dichloromethane.[32,38–41] However, with increasing nucleophilicity of solvent, the film growth is inhibited due to the interaction of solvent with the primary products of monomer oxidation. The film does not form in such nucleophilic aprotic solvents as dimethylformamide, dimethyl sulfoxide, hexamethylphosphoramide, unless the nucleophilicity of solvent is reduced by addition of a protic acid.[42] Apart from that, the side reactions occurring on the film surface can affect EP in these solvents. Thus, a thick PPy film was prepared from a $NaClO_4$ solution in dimethylformamide.[43] An increase in the rate of EP was observed when the temperature decreased. This increase was explained by the relative inhibition of the side reaction of film passivation, which resulted in lower conductivity. The rate of EP grew with increasing concentration of ClO_4^- anions that act as retardants for the passivating reactions in the electrolyte.

According to the extensively used procedure of Diaz,[30] 1% of water is added to AN solution; this results in improved properties of the film (adhesion to electrode, uniformity). The better PPy films were obtained with 2% of water in AN electrolyte.[44] However, a high content of water in the electrolyte (over 20%) results in deterioration of such film properties as tensile strength and electroconductivity.

The working electrode for electrosynthesis of conducting polymers is usually made of corrosion-resistant materials that are stable at high anodic potential, namely Pt, Au, Pd, Rh, Ir,[38,39,41] conducting $In_2O_3-SnO_2$ glasses,[45–47] carbonaceous materials (graphite, vitreous carbon).[39,40,48] Syntheses of conducting polymers on Al,[41,49,50] Ta,[41,51,52] Fe, Cu, Ti, Ni, Cr, Nb, stainless steel [41,53] were reported. It was found [41] that the nature of metal substrate virtually does not affect the kinetics of PPy

synthesis. Ta, Ti, Nb, and Al are exceptional; their behaviour is substantially affected by the oxide layer between a metal and PPy. The PPy film was reported to act as a protective coating on a Ta substrate.[54] Such semiconducting materials as Ge, GaAs,[55] CdS,[56,57] CdSe,[57] doped TiO_2 [58] were also used as electrodes; for these materials EP occurs under additional illumination.

In order to obtain reproducible results, one must carefully prepare the electrode surfaces before synthesis and also use high-purity chemicals.[39,55] High quality polymer films are usually produced in three-electrode cells with the regions of the working and the auxiliary electrodes separated with a diaphragm. Stirring of the electrolyte solution hinders polymer deposition on both pure and PPy-coated electrodes.[39,59] Prior to the experiment, the electrolyte solution should be purged with nitrogen or argon in order to remove oxygen, because films prepared in the presence of oxygen have inferior properties.[60]

In conventional EP of pyrrole, the polymer film grows as a coating on the anode immersed in electrolyte solution. When a platinum electrode floating on the surface of electrolyte was used,[61] a uniform thin film that grew along the gas–liquid interface from the electrode to the cell walls was formed. The structure and properties of this film differ from those of PPy films prepared using the conventional method. Supposedly, the polymer has a branched (possibly, three-dimensional network) structure.

Electropolymerisation of pyrrole can be performed in various regimes, in particular, potentiostatic,[32,62] galvanostatic,[35,40,63] potentiodynamic [36,64] and pulsed one.[65] The mechanical properties of the films, their morphology and electrochemical behaviour depend on the conditions of preparation, including the nature of solvent, pH of the electrolyte, the purity and concentration of the initial monomer, and the nature and concentration of electrolytic salt.[32,36,42,62,66–68]

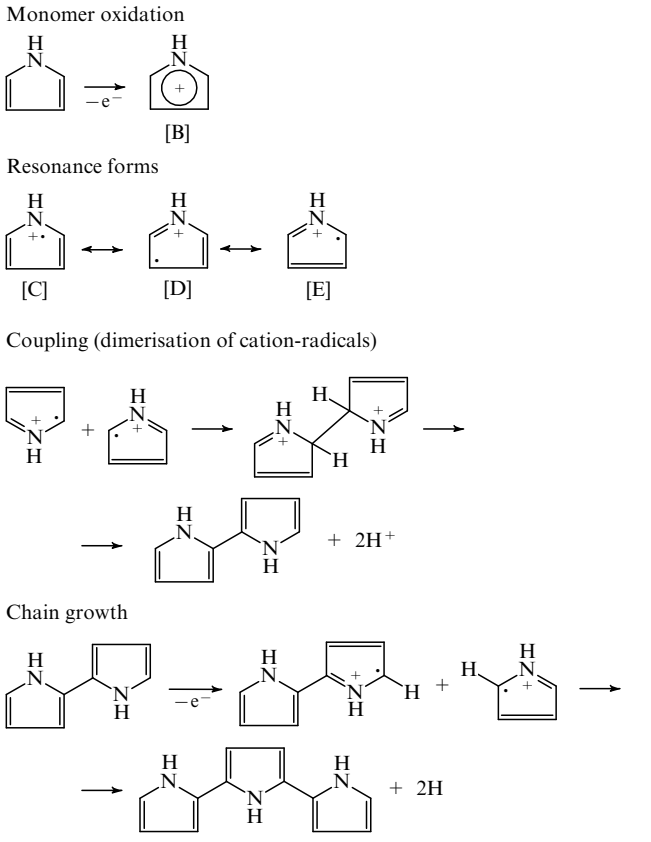
III. The mechanism of electrochemical synthesis of polypyrrole

The oxidation of pyrrole to PPy is irreversible. The mechanism of this reaction was extensively studied;[33,37–39,41,44,45,59,64,68–81] yet, the problem still remains not fully resolved. Among the mechanisms proposed, two have gained the greatest interest. One of those is the oxidative coupling of monomer molecules (Scheme 1).[37] The first stage of the reaction is the electrode oxidation of monomer molecules yielding radical cations with the radical state delocalised over the pyrrole ring (B). The maximum spin density is at the α-position;[69] hence, of the three possible resonance states, C, D and E, the latter is the most stable. The radical cations dimerise (this is the rate-controlling stage of the reaction[37,64,81]) and expel two protons. The dimers, owing to stronger conjugation, are more readily oxidised under the given reaction conditions than the monomer. The chain growth proceeds by addition of a newly formed radical cation to an oligomeric one. Some authors deny the possibility of dimerisation of radical cations because the latter experience strong Coulombic repulsion.[38,39,45]

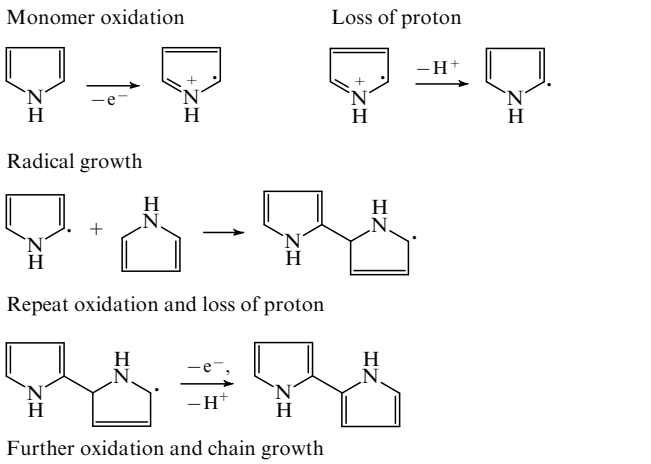
The alternative mechanism proposed for polymerisation of pyrrole is the free radical reaction (Scheme 2).[38,45] This scheme implies that formation of a radical cation on the anode is followed by the loss of a proton and attack of the radical on a neutral monomer. After reoxidation of the dimeric radical and proton loss, the dimeric molecule can experience subsequent oxidation, which results in chain growth. The release of protons in the course of oxidation of pyrrole was observed experimentally.[72]

Kinetic studies using isotopically labelled reactants and experiments with radical traps [70] showed that Scheme 1 is more probable. According to Scheme 2, any free-radical initiator would trigger the polymerisation of pyrrole, which is not the case. In addition to that, Scheme 2 cannot account for the experimentally observed fact that polymerisation proceeds only when monomer oxidation occurs in parallel with the oxidation of the polymer (the oxidation potentials for the dimer and oligomers of pyrrole are lower than that for the monomer).

Scheme 1



Scheme 2



The pyrrole dimers were detected in the electrolyte.[71,72] Spectroelectrochemical studies showed [64] that radical cations and dications of bipyrrole are the primary species observed at the early stages of electrolysis. Chronoamperometric methods with two-step variation of potential (using ultramicroelectrodes) showed [77] that EP of pyrrole proceeds according to the mechanism of oxidative coupling and that dimerisation of the radical cations is the rate-controlling stage. The lifetime of the radical cation was estimated [77] to be ~20 μs. The experiments using rotating ring-disc electrodes provided an estimate of the rate constant for the formation of the radical cations of pyrrole [82] within the range 10^7 to 10^8 litre mol^{-1} s^{-1}.

The stability of radical cations is an important factor in EP. The radical cations with moderate stability possess the chemical selectivity which favours radical coupling in the film formation. More stable radical cations diffuse away from the surface of the

electrode; this results in the formation of soluble oligomers. The radical cations with lower stability are more reactive and react with solvent or other nucleophiles close to the electrode surface. Therefore, EP of pyrrole in the presence of nucleophilic anions (halides, hydroxides, cyanides, acetates) results in lower yield and smaller molecular mass of the polymer and formation of soluble products.[83] The yield of polymer and its conductivity grow with the increasing donor number of the solvent (which reflects the strength of interaction between a solvent and radical cations) in the series nitromethane < nitrobenzene < benzonitrile < AN < PC.[84] In solvents with large donor numbers (AN, PC), the intermediate radical cations selectively react with the monomer in α-position; this results in formation of polymer with highly regular structure.

It was supposed in the earlier studies[37,38] that, prior to oxidation, the neutral monomer molecule is adsorbed on the electrode surface. However, further studies using a rotating ring-disc electrode and differential ellipsometry showed that the first stage in polymer deposition is polymerisation in solution and that nucleation of PPy on the electrode surface occurs only after the oligomer chain acquires a certain length at which it becomes insoluble.[39,74]

The growth mechanism of nuclei of conducting polymers is debated in the literature. In a number of studies,[38,75,82] the EP is considered as nucleation and growth of the polymer coating analogous to the electrochemical deposition of metals. This analogy is supported by the nucleation loop present in the cyclic voltammograms[38,74,75] and by the increase in the current on the $I-t$ curve during potentiostatic EP.[27,38,44,75] The mechanism of these electrochemical phenomena (especially the rising $I-t$ transients) implies an increase in the electroactive surface of the electrode in the course of the process. It was reported[27,38,76] that addition of a pyrrole monomer to the end of a polymer chain does not bring about an increase in the electroactive polymer surface and implies unidimensional growth of the polymer; under such conditions, dendrites grow in the direction of the electric field on the electrode surface. The experiments on 10-μm-diameter electrodes[59] showed that the polymer growth resulting in the nuclei expansion occurs primarily due to deposition of oligomeric species on top of the existing nuclei rather than due to monomer addition to a polymer chain. Here, similar to electrochemical deposition of metals, the pyrrole and its oligomers from solution are preferentially oxidised on the polymer surface rather than on the electrode.

There are two regions in the Tafel plot of the synthesis current versus potential.[45,78] The inflection in the $\lg I-E$ curve indicates that the reaction mechanism gradually changes with the changing nature of the electrode surface. In the first region, the oxidation of pyrrole results in the polymer nucleation on platinum (the reaction order with respect to pyrrole is unity). When the electrode is covered with a polymer film, both the slope of the curve and reaction order with respect to pyrrole (equal to 0.5) change; the film growth is controlled by the electrochemical reaction on the polymer. The reaction order in the second region coincides with that measured using coulometry and microgravimetry *ex situ*.[64,79] The earlier electrochemical studies that considered the initial stages of electrochemical synthesis reported the pyrrole oxidation to be first order on a platinum electrode.[39,41,80] The reaction order of 0.5 with respect to pyrrole (at greater conversions) may indicate that the growth of polymer is fractal in its geometry.[85]

The rate of EP and yield of the polymer are substantially enhanced by addition of 2,2′-bipyrrole in the electrolyte in the course of the PPy synthesis.[86] The addition of 2,2′-bipyrrole also shortens the delay time associated with the stage of dimerisation of radical cations.

An increase in the rate of pyrrole EP is also observed with a trace of water in AN electrolyte;[68,81] this is related to reduced Coulombic repulsion of two hydrated radical cations of pyrrole. Addition of bromide anions to the electrolyte causes electrocatalytic promotion of pyrrole EP.[68] The electropolymerisation is also markedly accelerated in the presence of small amounts of iron(III) and copper(II) chlorides.[87]

In potentiodynamic regime, EP from aqueous solutions starts at lower potentials than in AN (0.35 V compared with 0.65 V *vs.* Ag/AgCl).[36,88] In aqueous solutions, the film grows faster than in AN (the increment of the mass in each cycle is higher). The measurements of anodic charge related to EP suggested that the film grew proportionally to the number of cycles. Use of electrochemical quartz microbalance showed that in both electrolytes the PPy films grow nonlinearly at the initial stage of EP and constant-rate growth is attained further.[88]

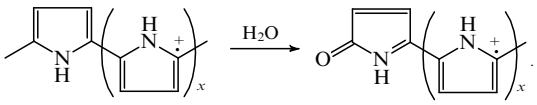
The rate of EP depends on the nature of the anions in electrolyte.[41,62,88] For example, the PP/poly(styrenesulfonate) film grows much faster than the PPy/Cl^- film. It is supposed[62] that larger anions are more strongly adsorbed on the electrode surface and this promotes the first stage of EP. Table 1 summarises the parameters of EP of pyrrole in the presence of various electrolytes.[62]

Table 1. Effect of the nature of organic anion on the rate of pyrrole EP and the properties of the film.[62]

Electrolyte anion	Conductivity /S cm^{-1}	Growth rate /nm s^{-1}	Yield of PPy /cm^3 mQ^{-1}
Dodecyl sulfate	15.3	25.6	1.3
Toluene sulfonate	9.8	20.1	1.0
Dodecylbenzene sulfonate	4.7	23.8	1.2
Poly(*p*-styrene-sulfonate)	7.3	7.9	0.4

A mechanism of electrochemical synthesis of PPy from aqueous solutions is proposed;[41] according to this mechanism, the EP involves a complex of pyrrole with anion and proton. The existence of such a complex was confirmed by means of IR spectroscopy. It was supposed[89] that protonated pyrrole is the active species.

EP of pyrrole, in the presence of water, in addition to the above-described dimerisation of the pyrrole cation radicals (see Scheme 1), can involve the side reaction of the cation radicals with water yielding undesirable electrochemically inert products.[90,91]



This polymer formed thus has shorter chains and, hence, poorer mechanical and electronic properties compared with PPy prepared from AN solution.

IV. Physical and mechanical properties of polypyrrole

PPy films thinner that 1 μm have different spectral properties depending on the conditions of synthesis and degree of PPy oxidation; with the increasing degree, the colour of the films changes from yellow to the blue and, ultimately, black.[32,92] The films have good adhesion to the substrate but at a thickness of over 10 μm are relatively easily peeled off the electrode.[34,93] The adhesion depends on a number of factors including the nature, coarseness, hydrophobicity of the electrode surface and the solvent used.[39,53,94]

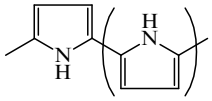
The stability in air of the doped PPy films is relatively high; their degradation occurs only above 150–300 °C (depending on the dopant anion).[6,34,93,95,96] Thermal degradation of PPy starts with the loss or decomposition of dopant.[97] Further deprotonation (or further dopant loss) at higher temperatures is always

accompanied by formation of imine-like structures in the polymer. The thermal stability of the films obtained by means of EP improves after their treatment with H_2SO_4, Na_2SO_4 or $NaHSO_4$; upon such treatment, no morphological changes are observed in the polymer.[98] The films of reduced (insulating) PPy are relatively stable when stored under an inert atmosphere and unstable in air; initially transparent and yellow, they rapidly turn dark, their conductivity increases to 0.01 S cm^{-1} and the films irreversibly lose their ability to undergo redox transition.[32, 94, 99]

The films prepared by electrodeposition in the presence of inorganic anions are relatively brittle; their mechanical properties are usually higher than those of the films doped with bulky organic anions.[42, 66, 100] The tensile strength for PPy films with different dopant anions varies from 8 to 100 MPa; the elongation at break, is within 2%–8%; the Young's modulus, 0.4–4 GPa.[42, 100, 101] The elongation at break can be substantially enhanced (to 70%), when PPy is synthesised at low temperatures.[101] According to Ref. 102, the elasticity of the freshly prepared films, which contain solvent, is higher, their elongation at break reaches 60%. The films reversibly absorb solvent (water, AN); they also absorb water vapour from air.[35, 103]

Studies by means of scanning and transparency electron microscopy showed that PPy films are compact and have no voids.[6, 32, 67] The apparent surface of the PPy-coated electrode measured using impedance spectroscopy and small-angle neutron scattering is 40–50 times higher than the area of underlying platinum electrode, according to scanning electron microscopy it is 2.2 times higher.[104] The latter method does not provide a possibility to assess microporosity of the polymer. The microstructure and porosity of the polymer depend on the dimensions of the dopant anion.[105] Thus,[106] the density of PPy/ClO_4^- films is 1.52 and that of PPy/toluenesulfonate, 1.37 g cm^{-3}. The films prepared from aqueous solutions are more porous and have lower density than those synthesised in AN.[36, 107] In microphotographs, the surface of PPy films prepared in aqueous solutions looks like a cauliflower.[32, 35] The films synthesised in non-aqueous media and those with large organic anions have a smoother-looking surface.[36, 62, 107, 108]

Polypyrrole is amorphous and usually gives only a diffuse halo in X-ray diffraction patterns.[6, 101] The electron diffraction showed that there are up 15% (of total volume) of crystalline domains in the bulk of amorphous PPy.[66] The experimental data indicate that the crystalline regions have a monoclinic lattice; the pyrrole rings are oriented so that nitrogens of neighbouring rings are oriented in opposite directions.



The data from IR spectroscopy,[109] NMR,[109, 110] analysis of the products of oxidative decomposition of PPy[111] indicate that pyrrole rings couple at $\alpha-\alpha'$-positions. This inference is confirmed by the fact that α-substituted pyrrole derivatives do not polymerise upon oxidation.[42] The calculations show that a certain number of bonds are formed at the β-position.[95] Electropolymerisation of 3-methyl- and 3,4-dimethyl-substituted monomer yields a polymer with a more regular structure and higher conductivity because for these monomers coupling at the β-position is blocked.[112]

The PPy chains are planar and are arranged in layers parallel with respect to the film surface; the interplane distance is 0.341 nm.[113] Alkyl substituents in PPy do not affect the planar arrangement of the chains.[114] The PPy chains within the planes are not oriented. The dopant anions intercalate the interplane spaces between the PPy chains.[115] X-Ray photoelectron spectroscopy showed that[116] electrostatic interactions between the oxidised PPy chains and dopant anions (ClO_4^-, polyvinylsulfonate) occur *via* the π-system of the rings rather than *via* heteroatoms of the rings. The sandwich structure is also formed in the case of PPy doped with alkylsulfate and arenesulfonate anions.[117] PF_6^- anions preserve their structure in the polymer matrix of PPy,[118] whereas $FeCl_4^-$ anions experience strong distortion of their tetrahedral structure due to the formation of hydrogen bonds.[119, 120] There are also indications that there is a strong interaction between charged PPy chains and dodecylsulfate anions.[121]

The data of electron diffraction indicate that polymer chains are ordered.[122] Studies of conductivity, which is related to both fast charge transfer along the polymer chains and rapid exchange between the macromolecules, also indicate that polymer chains are to some extent ordered.[109] The degree of polymer ordering strongly affects its conductivity.[123] X-Ray diffraction showed that PPy films prepared in the presence of multicharged anions are more regular than those with single-charged anions.[119]

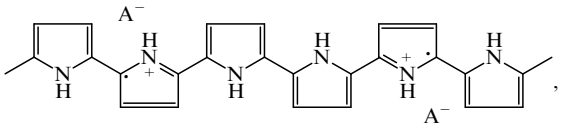
Numerous studies of the chemical structure of PPy indicate that its elemental composition fits the formula $C_4H_3NA_{0.3}$, where A is the anion in the presence of which electrosynthesis was performed.[6, 32, 34, 93] The percentage of carbon and hydrogen in the polymer often exceeds the theoretical values, sometimes oxygen is also present. The actual cause of these deviations is not unambiguously understood; it was however found that the polymer contains water or another solvent,[35, 103] and that PPy chemically reacts with the atmospheric oxygen.[6, 32, 40, 94] Polypyrrole is insoluble in organic solvents and this makes measurements of its molecular mass a difficult problem.

V. The nature of electronic conduction of polypyrrole

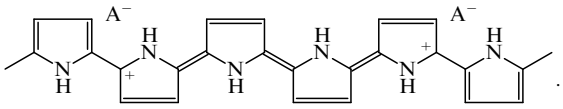
The interest in the electronic properties of polyconjugated polymers was boosted by the 1964 paper by Little,[124] where the possibility of superconductivity in unidimensional structures was predicted.

The neutral (undoped) PPy is a dielectric with the gap of 4 eV.[125] Upon oxidation (doping), the π-electrons are removed from the upper level of the valence zone with a simultaneous shift of the boundary π-levels (the highest occupied and the lowest vacant) to lower energies. The gap reduces to $\leqslant 2.5$ eV and the polymer becomes a semiconductor.

Of special interest in PPy conduction is the mechanism of charge transfer. The charge carriers are the polarons and bipolarons formed upon doping.[126, 127] In chemical terms, the formation of a polaron is equivalent to formation of a radical cation



and of a bipolaron, to dication



The polaron and bipolaron in PPy are extended structures spread over three to four monomeric units of the chain.[128]

The separation of the positive charge on the chain in the bipolaron structure predetermines the energy of the system. The further the positive charges are apart the lower the stability of the system, since it contains more rather unstable quinoid rings. The calculations of the energetics showed that formation of a bipolaron requires 0.45 eV less than formation of two polarons.[126, 127] This result led to a suggestion that bipolaron is the major charge carrier in PPy.[129, 130] This suggestion was to a certain extent confirmed experimentally by the studies of optical absorption spectra[131, 132] and ESR.[133, 134] The ESR spectroscopy is extensively used for studies of doping in PPy, because it provides a possibility to measure the concentration of spins associated with polarons ($S = \pm 1/2$). Bipolarons that are spinless ($S = 0$) are not detectable by means of ESR. The authors of Ref. 134 claim that

only spinless charge carriers are present in the polymer because there is no correlation between the conductivity and concentration of spins in the polymer. The experimental data of Refs 135 and 136 were interpreted in terms of quasi-equilibrium concentrations of polarons and bipolarons formed in the two-step redox process:

$$PPy^0 \xrightarrow{E_1} PPy^{\bullet+} + e^-,$$

$$PPy^{\bullet+} \xrightarrow{E_2} PPy^{2+} + e^-,$$

where E_1 and E_2 are the quasi-standard potentials of formation for polarons ($PPy^{\bullet+}$) and bipolarons (PPy^{2+}).

The data of Refs 135 and 136 agree well with the measurements of PPy conductivity as dependent on the partial charge per monomer unit.[137] The strong correlation between the enhanced PPy conductivity and concentration of polarons is illustrated by Fig. 1. When the conductivity reaches the plateau, the concentration of polarons decreases; this decrease can be attributed to the formation of bipolarons. The obvious relation of the conductivity to concentration of polarons at low doping levels disproved the previous hypothesis [133, 134] that conduction in PPy is solely spinless. The spectoelectrochemical measurements showed [138] that polarons in PPy and PAni are stable species and their maximum concentrations in respective polymer are 80% and 90% at 50% of the reversible charge. Further investigation of PPy by means of *in situ* impedometry[139] showed that polarons and bipolarons equally contribute to conductivity, being charge carriers with the same mobility. Further,[140] it was inferred that in PPy the polaron and bipolaron are partners and electron hopping is easier between a polaron and bipolaron than it is between a neutral chain fragment and polaron; this is due to the fact that in the former case planarity of the states is similar and this reduces the conformational activation energy. Similar results were obtained for PAni.[141]

The concentrations of polarons and bipolarons in PPy in the course of oxidation and reduction were studied using ESR spectroscopy and laser electroreflectance.[142] The equilibrium concentration of polarons in PPy increases with potential growing from 0 to 200 mV and reduces for $E > 200$ mV, owing to the formation of bipolarons.

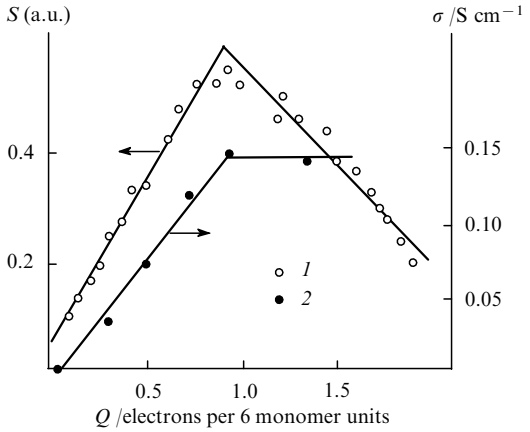


Figure 1. The dependences of (*1*) spin concentration[135] and (*2*) conductivity[137] on the oxidation charge (Q).

The conducting polymers are quasi-unidimensional conductors rather than unidimensional. Of particular interest are interchain interactions and charge transfer. It was noted [143] that dopant not only compensates the charge of the free charge carriers but also enhances the probability of interchain charge transfer due to a strong overlap of the atomic orbitals of the dopant with the π-orbitals of the carbon atoms. Since the polymer chains are oriented mainly parallel to the film surface, the conductivity along the surface ($s_\parallel$) is usually higher than that perpendicular ($s_\perp$). In the former case, conductivity involves less interchain charge hops. The anisotropy of conductivity ($s_\parallel/s_\perp$) amounts to 360.[144]

The most regular alignment of the macromolecules (more ordered structure) and, therefore, higher conductivity of the films is achieved when the synthesis is performed at low temperatures.[100, 101, 112] The conductivity of PPy films prepared in PC solution at -20 °C is 300 S cm^{-1} and for $+20$ °C it is 97 S cm^{-1}.[101] Due to the alignment of the polymer chains the highest conductivity achieved for PPy, 3000 S cm^{-1}, was attained under conditions of low-temperature electrosynthesis.[145]

The temperature dependence of the conductivity fits the equation

$$\lg \sigma = A + BT^{-1/(n+1)},$$

where $n = 1, 2, 3$.

Such a dependence is typical of the hopping mechanism of conduction with a variable hop length.[146] With decreasing temperature, the conductivity drops (which is characteristic of semiconductors). However, there are also reports (cf.[147]) that the conductivity increases with decreasing temperature (such behaviour is inherent in metals).

The conductivity of the polymers strongly varies depending on the conditions of their synthesis. Major changes in the conductivity usually occur at the earlier stages of doping, its further increase is insignificant.[100, 148]

The conductivity of PPy films varies by several decimal orders depending on the nature of an anion introduced into it during synthesis (Table 2). A change in the nature of solvent changes the order of anions in the series of conductivities. Usually, the PPy films prepared in AN electrolytes are more conductive than those synthesised in aqueous solutions. This is due to a larger conjugation length of the polymer and better contact with the metal electrode in the former case.[36] The electrical conductivity is, in the majority of cases, higher for anions with lower nucleophilicity.[149] Electrosynthesis of PPy in aqueous solutions in the presence of bulky organic anions (toluenesulfonate, dodecylbenzenesulfonate, dodecylsulfate) results in enhanced quality and conductivity of the films produced, compared with those of the PPy/Cl^- and PPy/ClO_4^- films (see Refs 62, 108, 149).

At the same time, the exchange of a counterion in as-grown PPy for other anions from electrolyte but slightly affects the conductivity of PPy; the replacement of an anion changes the structure of the polymer matrix, yet not to the extent that it will change the barrier height and hopping frequency.[40, 150] On the other hand, for the films being prepared with a particular anion, the structure of the forming polymer matrix substantially depends on the nature of dopant and, therefore, the conductivity is strongly affected by the nature of an anion.

Table 2. Conductivity of PPy films synthesised from aqueous electrolytes and from AN.[42, 93, 149]

Dopant anion	Conductivity (S cm^{-1})	
	aqueous solution	AN
BF_4^- (fluoroborate)	2–2.5	30–100
ClO_4^- (perchlorate)	5–6.5	60–200
AsF_6^- (hexafluoroarsenate)	2.4–2.8	30–100
HSO_4^- (hydrosulfate)	3.5	0.3
$CF_3SO_3^-$ (triflate)	3.4	0.3–1.0
CF_3COO^- (trifluoracetate)	1.0–1.3	12
p-$CH_3C_6H_4SO_3^-$ (tosylate)	89–121	20–105

The effect of pH of electrolyte on conductivity of PPy films synthesised therein was extensively studied [38, 62, 117, 149] (Fig. 2). In alkaline media, thin insulating films are formed.[38] The conductivity goes through a maximum at the synthesis potential of 0.6 V (*vs.* saturated calomel electrode) in aqueous solution[100] (Fig. 3), the

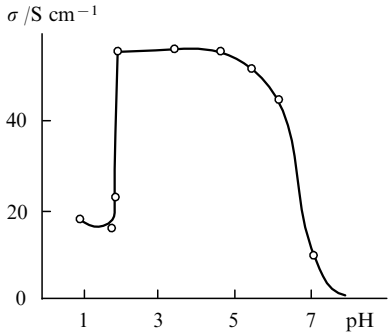


Figure 2. The dependence of PPy conductivity on pH of the electrolyte.[117]

corresponding maximum is observed in the dependence of conductivity on the current density.[117, 151] Electrosynthesis of PPy films at current densities over 5 mA cm^{-2} results in reduced conductivity of the films with both organic and inorganic dopant anions.[108]

The structure of PPy films doped with ClO_4^-, BF_4^- and,

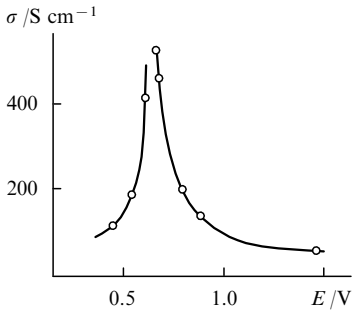


Figure 3. The dependence of conductivity of PPy films on oxidation potential (*vs.* saturated calomel electrode); synthesis from aqueous solution of 0.25 M pyrrole + 0.8 M sodium tosylate.[100]

correspondingly, their conductivity depend on the nature of solvent (due to above-described causes). The films doped with strongly basic anions (high pKa)[84] do not show such a dependence (Fig. 4).

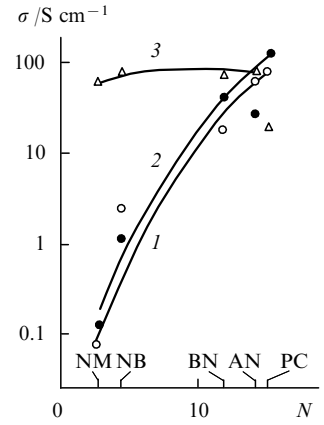
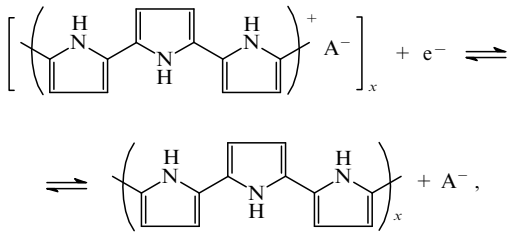


Figure 4. The dependence of conductivity (σ) of PPy films prepared in the presence of ClO_4^- (*1*), BF_4^- (*2*), tosylate anion (*3*) on the donor number of solvents (*N*):[84] nitromethane (NM), nitrobenzene (NB), benzonitrile (BN), acetonitrile (AN), propylene carbonate (PC).

When conducting PPy films are stored in air, their conductivity decreases.[151] The conductivity of the films with bulky organic anions reduces much more slowly. Thus, the electrical properties of PPy/dodecylbenzenesulfonate do not change after a 6-month storage in air.[149]

VI. Electrochemical properties of polypyrrole

The very first electrochemical studies showed that PPy is sufficiently stable and can be used as a non-metallic electrode material.[30, 93, 152] Its intrinsic redox reaction associated with doping and dedoping must be taken into account as was first shown by Diaz *et al.*[32, 93, 153] in 1980. The following equation for this reaction was proposed on the basis of electron balance and elemental composition.



where A^- is the anion.

The positive charge of oxidised segments in PPy chains is counterbalanced by the anions of electrolyte that are incorporated in the polymer; the anions leave the polymer matrix and return to the solution when PPy is reduced. The method of cyclic voltammetry (CVA) is extensively used in studies of redox processes in conducting polymers. In this method, the potential is linearly scanned up to a certain preset limit and then is reversed to the initial value.[32, 38, 88, 91, 107, 154–158] Figure 5 shows a typical voltammogram (VA) of a PPy film. The anodic peak in VA is related to the oxidation of PPy, the cathodic one, to its reduction to the neutral form according to the above equation. The maxima of the peaks in VA correspond to the maximum polaron concentration in PPy.[159] In the cycling of PPy films to potentials lower than −0.8 V, the currents are close to zero and down to −2.3 V (in AN solution) no peaks are observed because at these potentials the neutral film has low conductivity. At anodic potentials over 0.8–1.0 V, irreversible oxidation of PPy starts; it results in the loss of electrochemical activity and a drop in the conductivity of

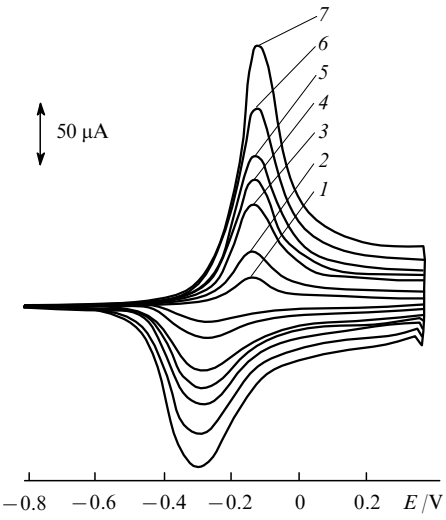


Figure 5. The cyclic voltammograms of 20-nm PPy/BF_4 film in Et_4NBF_4/AN solution [32] at varied scan rate 10 (*1*), 20 (*2*), 40 (*3*), 50 (*4*), 60 (*5*), 80 (*6*), 100 mV s^{-1} (*7*) (*E vs.* saturated calomel electrode).

the films.[32, 35, 91, 160] The films can be repeatedly cycled without any sign of polymer degradation within a certain potential range where no side reactions occur (the so-called stability window); here the redox reaction of PPy is reversible.[32, 35, 54, 107, 161]

A distinctive feature of VA of PPy films is, in the case of anodic oxidation, the steep anodic wave at the start of doping followed by a flat plateau. In the reverse scan of the potential, a cathodic wave appears at the end of the capacitive-type plateau; this wave is shifted in potential with respect to the anodic one. The current of the cathodic peak is usually lower than that of the anodic (whereas the surface areas of the anodic and cathodic parts of VA are the same). Such a behaviour is not typical of redox-active films. The theory predicts that thin redox-active films must show mirror-symmetric anodic and cathodic waves with identical peak potentials and currents.[162] However, even the high quality films of conducting polymers manifest this potential shift between the anodic and cathodic peaks in their VA. The theory of redox-active polymers interprets such a behaviour as a kinetic effect of slow heterogeneous charge transfer.[32]

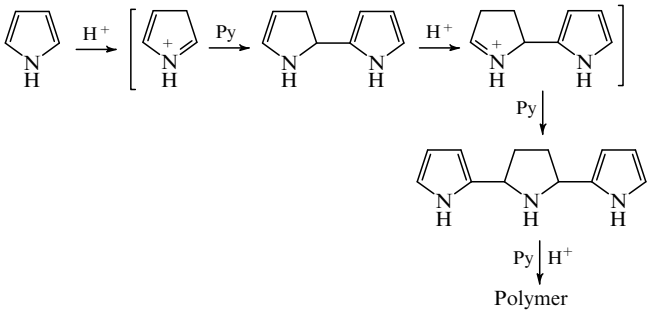
The thermodynamic redox potential of the system is defined as the mean of the anodic and cathodic maxima ΔE_p (for the PPy film in Fig. 5 it is -0.2 V). As a first approximation, one can assume that the interaction between the charged segments of the polymer chains can be neglected and that there is only one redox state with a characteristic redox potential depending on the nature of the monomer unit. However, one must keep in mind that the redox potential of nominally the same system depends on the conditions of measurements and the regime of PPy synthesis (chemical nature and composition of the solvent and electrolyte, scan rate, thickness of the PPy film).[32, 154, 163, 164] The redox potential of a polymer also depends on the time during which it was stored in a dielectric state.[165]

The interrelation between the Faradaic and capacitive processes in the course of reduction and oxidation is closely related to the redox mechanism. It was reported[166] that in CVA, the Faradaic oxidation associated with the charge transfer *via* interphase boundary is limited to the region of peaks, whereas the broad anodic plateau corresponds to the large capacity of the double layer at the surface (charge accumulation at the interphase boundary); the interphase surface is largely due to the porosity of the film. This problem remains debatable.[167] On the basis of the studies using impedance spectrometry and CVA, the following model for redistribution of charges in polymer was proposed.[168] In the electrochemical redox cycling of a polymer film, which is associated with penetration and removal of the anions, the polymer becomes subdivided in aggregates with the diameter about 6 nm. The capacity of the double layer formed reaches 200 F cm^{-2}. The capacitive behaviour of the conducting polymers is due the fact that they are porous and conductive and also due to the number of electroactive sites in the polymer not being fixed but dependent on the potential. The Faradaic charge results from the penetration of dopant anions into the aggregates, which is diffusion-controlled. The rate of the Faradaic process is lower than that of the capacitive.

The shape and parameters of VA are affected by a number of factors including the range of potential cycling, the scan rate, solvent used, composition of the electrolyte, film thickness, conditions under which it was prepared and its treatment and storage history. Synthesis under similar conditions does not always provide a possibility of obtaining similar VA of PPy films. Stirring of the solution of background electrolyte does not affect the shape of VA.[32]

The shape of VA is indicative of the quality of PPy films. The rate of the charge transfer in conducting polymer and, therefore, its conductivity correlate with sharp anodic and cathodic peaks and narrow ΔE_p.[103, 160, 169] The redox capacity of the film (the surface area under the anodic and cathodic branches of VA), in its turn, is related to the doping level of the polymer.[32, 38]

The EP of pyrrole in galvanostatic regimes in the $LiClO_4$/PC system at low current density ($i \leqslant 0.3$ mA cm^{-2}) yields PPy with a high degree of conjugation (the energy of $\pi-\pi^*$ transition is 2.83 eV) and high doping level ($y = 0.37$), which shows narrow peaks in VA.[63] At high density of polymerisation currents ($i \geqslant 0.5$ mA cm^{-2}), the VA of the polymer produced is distinguished by broad peaks, its doping level and degree of conjugation are low (the energy of $\pi-\pi^*$ transition is 3 eV). A similar effect of the EP current density on electrochemical properties of the polymer was reported in Ref. 81; overoxidation of the polymer at high anodic potentials of EP (0.8 – 1.2 V *vs.* saturated calomel electrode), results in reduced redox capacity of PPy films (Fig. 6). This effect is most pronounced in anhydrous electrolytes. It was supposed[170] that the decrease in conductivity is due to formation of saturated oligomers in the reaction initiated by the protons released in the oxidation of monomers near the electrode surface at high current density.



Addition of water to the electrolyte inhibits this reaction due to solvation of the protons.

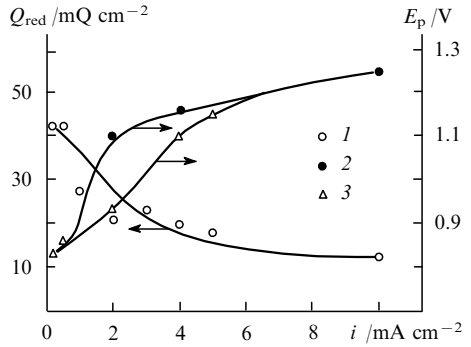


Figure 6. The dependence of anodic potential of polymerisation (E_p *vs.* saturated calomel electrode) and redox capacity (Q_{red}) of 1 μm PPy films on the current density (i) in galvanostatic electropolymerisation[81] from solution of 0.1 M pyrrole + 0.1 M Bu_4NBF_4 in AN (*1*) with addition of 10 (*2*) and 50 (*3*) mM H_2O.

The thickness of a PPy film (and, correspondingly, charge in EP) is one of the major controlling parameters for VA of the films. The charge of reduction and oxidation of PPy during cycling (redox capacity) is proportional to the charge in synthesis. The redox capacity of PPy during cycling in AN comprises 8% – 12% of the EP charge in the Diaz electrolyte (AN + 1% H_2O) and up to 19% for EP in aqueous solution; this corresponds to a doping level of 20% – 30% in the former case and 47% in the latter.[38]

An important electrochemical characteristic of the redox reaction on the electrode is the dependence of the anodic peak current i_{pa} on the scan rate v:

$$i_{pa} = Av^x,$$

where A is a constant and x is the exponent, which characterises the mobility of counterions in the PPy matrix. The redox reaction is controlled by the rate of electron transfer (adsorption, $x = 1$) for PPy films doped with small mobile anions (Cl^-, ClO_4^-) or in the opposite case of polymer doped with very bulky multicharged

anions (*e.g.*, benzenetrisulfonate anion). For PPy films with medium-size anions (benzenesulfonate, toluenesulfonate) the electrode reaction is diffusion-controlled ($x = 0.5-1$).[46, 108] When the film thickness increases (over 1 μm), the electron transfer is superimposed by the diffusional restrictions, which result in broadening of the peaks in VA and their wider separation.[32, 35, 46]

The VA of PPy films differ substantially when the latter are tested in aqueous media and aprotic solvents.[88, 103, 107] In the former case, the currents are higher, owing to higher mobility of anions in the porous film. At the same time, the films synthesised in AN have better electrochemical reversibility of redox transition than those synthesised in aqueous electrolytes.[36, 107] The former films are distinguished by a higher rate of electron transfer and narrower ΔE_p. The PPy films obtained in aqueous solutions are more porous and manifest higher capacitive currents in VA (their capacity is 460 F cm^{-3} compared with 390 F cm^{-3} for PPy synthesised in AN).[36]

In the course of cycling, the PPy can exchange its initial dopant anion for another anion of electrolyte.[88, 154, 155] The diffusion processes are controlled by the dimensions of the pores and the nature (dimensions, mobility) of the penetrating anion. The Cl^- anions in PPy/Cl^- upon cycling are replaced by the electrolyte anions F^-, ClO_4^- (Fig. 7).[164] In a solution of sodium poly(styrenesulfonate) (Na/PSS^-), PPy/Cl^- film loses its electroactivity as the anions of the polyelectrolyte are too large to penetrate into the film, while diffusion of Cl^- anions through the adsorbed layer of PSS^- anions is suppressed.

PPy synthesised in aqueous $NaNO_3$ solution, upon reoxidation, manifests selectivity with respect to anions in the solution decreasing in the following series[171] $NO_3^- > ClO_4^- > Br^- > Cl^- > F^-$.

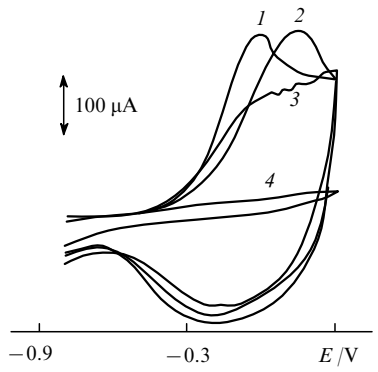


Figure 7. The voltammograms of PPy/Cl^- in 0.1 M aqueous solutions of:[164] NaCl (*1*), $NaClO_4$ (*2*), NaF (*3*), NaPSS (*4*) (*E vs.* Ag/AgCl).

Active control of the ion transport is possible when the mobile species can be identified. The problem is complicated by the fact that several ionic species are often present in the system. There are two pathways for the charge transfer in the oxidation–reduction of the polymer[46, 154, 155, 164, 172]

$$PPy^+/A^- \rightleftharpoons PPy^0 + A^-,$$

$$PPy^+/A^- \rightleftharpoons PPy^0/A^-/C^+.$$

The former process implies diffusion of A^- anions away from the film upon reduction of oxidised polymer, while the latter, penetration of C^+ cations, which compensate the negative charge of immobile anions that become redundant after reduction of the polymer. Use of an electrochemical quartz microbalance provided a possibility of following the changes in the mass of the film during cycling in solution and, thus, of elucidating the nature of the ions penetrating into the film.[88, 164, 173] The anionic transport predominates when small single-charged anions (Cl^-, ClO_4^-, $H_2PO_4^-$, NO_3^-) are used in electrochemical synthesis of PPy. In such a film,

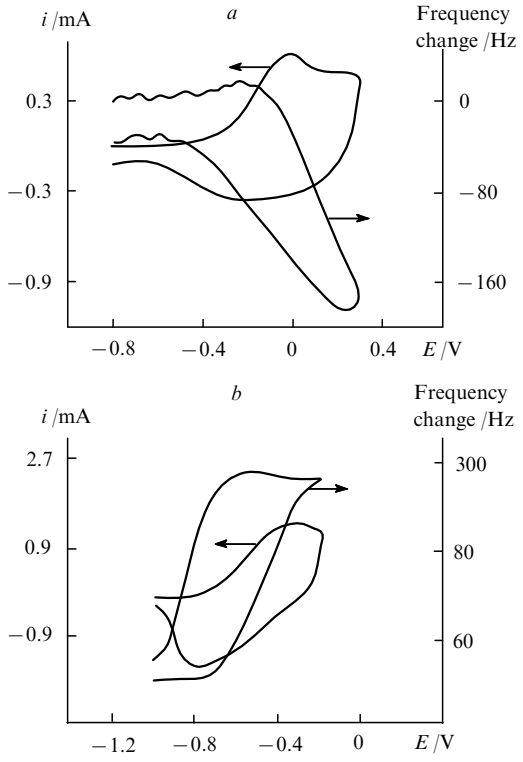


Figure 8. The changes in currents and frequency shifts of quartz resonators for the films:[164] PPy/Cl^- (*a*) and PPy/dodecyl sulfate (*b*) in aqueous solution of 0.1 M NaCl (*E vs.* Ag/AgCl).

anions rather than cations penetrate into the film and are removed in the course of cycling. When the polymer is synthesised with bulky immobile anions, multicharged anions or polyelectrolytes [dodecylsulfate, toluenesulfonate, phthalocyanine tetrasulfonate, SO_4^{2-}, HPO_4^{2-}, poly(styrenesulfonate)], which are firmly fixed in PPy, then the cationic transport through the polymer–electrolyte boundary predominates. Figure 8 shows the VA of PPy/Cl^- and PPy/dodecylsulfate films and also the change (decrease/increase) in the resonance frequency due to the changed (higher/lower) effective mass related to electrochemical processes.

The cationic transport also predominates in self-doped polymers where dopant anions are covalently bonded with the polymer matrix, *e.g.*, poly{pyrrole-*co*-[3-(pyrrol-1-yl)propanesulfonate]}, and for a molecular PPy/Nafion composite where the dopant anion is polymeric.[164] The frequency response of these films depends on the nature of the cation of the electrolyte in which the films are tested.

For the PPy/SO_4^{2-} film in an aqueous solution of CsCl, a mixed anionic–cationic transport is observed depending on the cycling potential.[173] The migration of cations into electrolyte prevails at the initial stages of oxidation of PPy/poly(styrenesulfonate), but upon further growth of the potential this process is complicated by the anionic counterflow.[174] The mixed type of charge transfer often results in the appearance of several peaks in anodic or cathodic parts of VA.[107, 175]

The type of charge transfer is governed also by the choice of a solvent. The bulky dodecylsulfate anion is always firmly fixed in the PPy film synthesised in its presence, irrespective of the solvent used. However, the mobility of the ions in the bulk of the film during redox switching depends on the solvent. Upon reduction in AN, dodecylsulfate anions leave the film, whereas in aqueous solutions they remain trapped in the polymer matrix;[176, 177] upon reduction, Na^+ cations are inserted into the film. The stronger interaction between the charged polymer chains and dodecylsulfate anions in aqueous solutions is due to the hydrophobic nature of the aliphatic part of the anion. For the polymer doped with the

highly mobile ClO_4^- anion, prolonged cycling in aqueous solution results in the cationic transport substituting for anionic.[88] In AN, the anionic transport prevails in this film.

The exchange of the dopant anion in the polymer can result in a changed type of ionic transport.[156] The ionic charge transfer can be controlled by creating in the polymer an ion pair of immobilised anion and multicharged cation of electrolyte.[173]

The contribution of anionic and cationic charge transport strongly depends on the EP potential.[178, 179] The redox switching in PPy synthesised at 1.0 V (*vs*. Ag/AgCl) are accompanied by simultaneous mass transport of anions and cations, whereas in the films prepared at lower potentials of EP, the charge transport is separated into either anionic or cationic regions. The cathodic shift of the first cycle of reduction in VA is related to the phase transition in the polymer and indicates that cations are inserted into the film. This was confirmed using an electrochemical quartz microbalance and X-ray emission analysis.[103] The potential of the anomalous reduction peak in the first reduction cycle of PPy film depends on the size of electrolyte cation (in AN solution).[177] During the first reduction cycle, a large uptake of electrolyte by the film is observed (up to 3 M). The measurements using impedance spectroscopy[103] showed that over several initial cycles the resistance of the PPy film drops (ionic conductivity grows) and remains virtually unchanged in further cycling. In reoxidation of the polymer, the uptake of the anions by the film exceeds the release of cations (the anionic type of the charge transport predominates); this results in formation of a non-equilibrium state in the polymer containing excess of the electrolyte. The mobility of the anions in such a polymer is greatly enhanced; the redox transition in AN solution proceeds fast only for the non-equilibrium form of the polymer. The PPy films prepared from aqueous solution with Et_4NClO_4 originally possess a high ionic conductivity. The strong difference between the ionic conductivity of the PPy films prepared from aqueous and AN solutions can be related to lower mobility of anions due to the better solvation of the polymer in aqueous solution.

Possibly, it is the excess of electrolyte in the film that causes wide scatter of the data for the diffusion coefficient of anions measured using different methods, 10^{-11} to 10^{-9} $cm^2\ s^{-1}$ for ClO_4^-, BF_4^- in AN[32, 34, 35, 37, 47] and 10^{-10} to 10^{-8} for Cl^-, ClO_4^- in aqueous solutions.[108, 180, 181]

Since the properties of the polymer are to a large extent governed by the dopant anion, the choice of the latter depends on the properties to be imparted to the polymer. If hydrophilic anions such as ClO_4^- or BF_4^- are used in EP, the polymer produced also becomes hydrophilic, in contrast to PPy doped with hydrophobic polymeric counterions. In the latter case, sensitivity of PPy to humidity is greatly reduced. In the presence of optically active anions (*e.g*., camphorsulfonic acid), the polymer acquires optical activity, which can be used to separate chiral stereoisomers.[66] In order to prepare flexible and smooth films that easily detach from the electrode, organic dopant anions are used. Aromatic and bulky surfactant sulfonate anions provide better conductivity and stability of the polymers. Thin PPy films with small anions manifest the most pronounced electrochromic properties and the fastest response.[182, 183] In order to make PPy coating with strong adhesion to aluminium electrode, hydroxyanthraquinonesulfonic acid is recommended, because it forms a complex with aluminium.[66]

VII. Modification of the properties of polypyrrole films

Modification of the electrochemical properties of PPy is a promising and diverse field of research. This can be achieved using a variety of methods, *viz*. by the synthesis of polymer from pyrrole derivatives with corresponding electroactive substituents, by introduction of electroactive dopant anions, by modification of the film surface through immobilisation of certain reactants thereon. These methods are supplemented by copolymerisation and preparation of PPy-based composites.[184–186]

Numerous examples of preparation of PPy derivatives containing electro- and catalytically active groups are given in Ref. 187. The *N*-substituted PPy with grafted electroactive groups, derivatives of viologen,[188] anthraquinone,[189] and porphyrins of Co, Ni, Mn were studied.[190, 191] The PPy with a covalently bonded three-nuclear rhuthenium cluster showed high chemical and electrochemical stability, especially at positive potentials. This electrode was used for electrocatalytic oxidation of benzyl alcohol.[192] The cluster $[Fe_4S_4(SPh)_4]^{2-}$ was inserted in the electrode surface covered with the ion-exchange polymers based on *N*-substituted PPy.[193]

EP of pyrrole with bulky alkyl substituents provides a route to prepare a polymer soluble in organic solvents. This facilitates its further processing, including preparation of coatings of well defined structure and thickness using the Langmuir–Blodgett technique.[194]

Substitution in the monomer ring causes a decrease in the conductivity of PPy films.[32] However, in many cases, the conductivity does not change strongly when dopant anion is replaced with another one.[149] Various organic and inorganic electroactive anions were used as dopants for PPy matrix; these include tetrathiomolybdate,[195–197] tetrachloroferrate,[151, 198, 199] ferrocyanide,[61, 119, 155, 172, 200] metal phthalocyanines and porphyrins,[73, 201–205] ferrocenesulfonates,[206, 207] sulfonates of quinones,[208, 209] isopolyanions,[210] heteropolyanions.[211–216] A wide array of conducting polymers with various incorporated functional molecules is described in Ref. 217.

Studies on the growth of PPy in the presence of the above-mentioned anions and on the properties of the polymers obtained revealed a number of common features inherent in these polymers: (1) the rate of EP in the presence of multicharged anions is unusually fast; (2) it is difficult to replace electroactive anions in the polymer matrix with another anion; (3) ΔE_p shifts to the cathodic region; (4) the electroactivity of a polymer doped with electroactive dopant anions is substantially enhanced due to the inherent redox reaction of the anions incorporated in the polymer matrix. The enhanced electroactivity of the conducting polymers is a desirable feature for the ones to be used as electrode materials in rechargeable batteries.

The synthesis and electrochemical properties of PPy films doped with $FeCl_4^-$ anions were discussed in Refs 198, 199. The introduction of tetrachloroferrate anions to the electrolyte at the stage of EP results in acceleration of the process and brings about enhanced coarseness of the PPy films formed.[198] Supposedly, the large $FeCl_4^-$ anion, which is connected to the polymer matrix with hydrogen bonds,[120] decreases the Coulombic repulsion of two radical cations thus promoting the dimerisation. The incorporation of $FeCl_4^-$ into PPy improves the reversibility of the redox transition and permits the synthesis of conducting films in galvanostatic regime without degradation of the polymer material even at high current density (2 mA cm^{-2}, further studies showed that the current density up to 8 mA cm^{-2} can be used). It was assumed on the basis of CVA studies [199] that due to the cage effect $FeCl_4^-$ anions are reversibly reduced in the polymer matrix. This contributes to the redox capacity of the polymer. The VA of PPy/$FeCl_4^-$ films are stable in the course of cycling in acetonitrile solutions of Et_4NClO_4 and Et_4NFeCl_4, whereas in solution of $NaClO_4$ they are unstable. In AN/Et_4NFeCl_4 electrolyte, the PPy/$FeCl_4^-$ films do not experience degradation even when the cycling range is extended to +1.5 V, the redox capacity of the films increasing more than threefold. The surface of PPy/$FeCl_4^-$ films is covered with crater-like [199] or dendrite-like structures [151] depleted of $FeCl_4^-$ anions.

The VA of PPy film doped with $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ anions shows two pairs of redox peaks,[61] the additional pair near 0.1 V appears due to the reversible redox transition $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$. The PPy film doped with $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ is more electroactive than PPy/ClO_4^-, its redox capacity is higher, the current

peaks are sharper and are shifted to more negative potentials. Upon cycling of PPy/$Fe(CN)_6^{4-/3-}$ in a broad range of potentials including the region of redox reaction of the polymer, the NO_3^- anions of electrolyte substitute for $Fe(CN)_6^{4-/3-}$. When the cycling range is restricted to the oxidised state of the polymer, this system behaves as a conducting ion-exchange membrane. Oxidation (reduction) of $Fe(CN)_6^{4-/3-}$ immobilised in the polymer matrix is accompanied by migration of the cations of electrolyte from (into) the film.[155] The $Fe(CN)_6^{4-}$ anions leave the film at potentials more negative than -0.4 V for thick and -0.6 V for thin films.[172] Reduced PPy contains, in addition to ferrocyanide anions, cations that neutralise the anionic charge. At the same time, there are indications[200] that cations penetrate the film already at the stage of synthesis, because each positive charge of the polymer matrix is compensated with a multicharged ferricyanide anion. X-Ray diffraction revealed that PPy/$Fe(CN)_6^{4-}$ has a more regular structure than PPy doped with single-charged anions.[119] Mössbauer spectroscopy showed that PPy film prepared at anodic potential of 0.75 V (*vs.* saturated calomel electrode), when the ferrocyanide–ferricyanide transition must have occurred, contains only $Fe(CN)_6^{4-}$ anions.[119] In other words, the charge is redistributed between the anions and polymer matrix.

The PPy/ferrocenemonosulfonate (PPy/FMS) and PPy/ferrocenedisulfonate (PPy/FDS) showed[206] a higher redox capacity and lower electrochemical stability than PPy/ClO_4^-. The PPy/poly(vinylferrocenesulfonate) films (PPy/PVFS) are smooth and uniform; the anion immobilised in the film is retained for hundreds of cycles. The maximum discharge capacity of a Li/PPy/PVFS battery was 120 A h kg^{-1}. The PPy/PVFS is a promising electrode material for rechargeable batteries. The instability of PPy/FMS and PPy/FDS is related to degradation of PPy, because in the region of redox transition of ferrocenesulfonates (0.7–1.2 V *vs.* Ag/AgCl) overoxidation of PPy can occur. In order to reduce the redox potential of ferrocenic (F) dopants, the polymeric dopant, poly(styrenesulfonate-*co*-vinylferrocene) (PVFSS) was synthesised.[207] In this polyanion, sulfogroup is not directly bonded with the ferrocene ring. PPy/PVFSS showed two pairs of redox peaks, at -0.1 V and $+0.35$ V (*vs.* Ag/AgCl), which correspond to PPy/PPy^+ and F/F^+ transitions. The latter transition is shifted by 0.4–0.5 V to cathodic region as compared with PVFS. The zinc battery with PPy/PVFSS showed a higher (1.5 times) discharge capacity and energy density and improved charging–discharging performance compared with a lithium cell. Its Coulombic efficiency remained unchanged during 500 cycles.

The preparation, composition and electrochemical properties of PPy films incorporating quinoid dopant anions was reported in Ref. 208. The redox transitions of the quinone/hydroquinone pair of tiron (T), naphthoquinone (NQ) and anthraquinone (AQ) are superimposed on the large background signal of PPy. The position of the redox pair of quinones on the potential axis depends on the dimensions of their conjugated π-systems; $\Delta E_T > \Delta E_{NQ} > \Delta E_{AQ}$. The electrochemical properties of their redox transition are similar to those for quinones adsorbed on the electrode. The redox capacity for AQ on the electrode reaches its limiting value, whereas for PPy/AQ it grows linearly with increasing charge in EP. The PPy/NQ film is highly stable, its VA did not change after a four-days' storage in electrolyte. The electrocatalytic oxidation of ascorbic acid was performed on a PPy/NQ electrode. Tiron plays the role of both a catalyst and dopant in EP of pyrrole ($\Delta E_T = 0.605$ V *vs.* saturated calomel electrode at pH = 1); initially it is oxidised to quinone and the latter oxidises pyrrole to a radical cation that initiates polymerisation. The charge–discharge properties of PPy/AQ, PPy/NQ and PPy/ClO_4^- films synthesised at the same charge of EP in the system of 0.1M Et_4NClO_4/AN at 0.02 mA cm^{-2} were investigated.[209] For PPy/AQ, the charge–discharge capacity (119 mQ cm^{-2}) and charge density (150 A h l^{-1}) more than twice exceed respective values for PPy/NQ and PPy/ClO_4^-. The choice of an electrolyte plays an important role; Li^+ cations in aprotic solvents form insoluble compounds with dianions of quinoid derivatives and this makes the redox transition irreversible.

The incorporation of metal porphyrins (MP) and phthalocyanines (MPhC), isopoly- and heteropolyacids (HPA) into the matrix of a conducting polymer can be useful for electrocatalysis. The immobilisation of catalysts in the films of conducting polymers provides a number of advantages over monolayers of catalysts grafted to or adsorbed on a support. First, the surface concentration of the catalyst can be electrochemically controlled due to the mechanism of polymerisation inherent in conducting polymers; the second is that the active form of the catalyst can be easily regenerated.

The effect of the nature of isopolymolybdate species on EP of pyrrole and aniline and the electrochemical behaviour of the polymer films doped with polymolybdate anions were investigated using CVA.[210] The number of molybdenum atoms in the polymolybdate anion that predominates in solution and is incorporated as a dopant in the growing polymer film was controlled through the ratio of acid and molybdenum in electrolyte. The polymolybdates promote the film growth and, owing to their intrinsic electrochemical activity, enhance its redox capacity. In the course of cycling polymer films, the polymolybdate anions are easily removed to the electrolyte from PPy, whereas they remain firmly immobilised in PAni due to formation of complex.

The electrochemical properties of Keggin-type tungstates and molybdates, the effect of pH on the properties of HPA and stability of HPA derivatives in strongly acidic aqueous solutions were studied in detail.[218] Pyrrole (and similarly, aniline) in aqueous and AN solutions forms soluble complexes with HPA, where it substitutes the co-ordinated water molecules

$$PW_{12}O_{40}(H_2O)_n^{3-} + m\,Py \rightleftharpoons \rightleftharpoons PW_{12}O_{40}(H_2O)_{n-m}(Py)_m^{3-} + n\,H_2O.$$

EP of these complexes results in formation of PPy films doped with anions of HPA.[211,212,214] The VA of these films are distinguished by the reversible peaks of the polymer itself and of multistep reversible redox transitions of HPA. The electrochemical behaviour of HPA immobilised in the polymer differs from the behaviour of the same HPA in solution due to low conductivity of PPy and poly(*N*-methylpyrrole) (PNMPy) in the potential range of HPA reduction.[211] The peaks of HPA are characterised by diffusion-controlled charge transport. Since HPA anions are firmly immobilised within the film, the charge transport involves the Li^+ cations. The maximum doping level for PPy is[214] 27% for $(PMo_{12}O_{40})^{3-}$, 26% for $(PW_{12}O_{40})^{3-}$, 23% for $(SiW_{12}O_{40})^{4-}$. The conductivity of the PPy/HPA films is 2.6 S cm^{-1}; PNMPy/HPA, 5×10^{-3} S cm^{-1}. The comparatively high conductivity (taking into account the very high molecular mass of HPA) can be explained by the contribution of a number of factors. First, the delocalisation of the negative charge in HPA anion facilitates the uniform charge distribution along the polymer chain. This factor also facilitates formation of the polymer with a more regular structure. And finally, the HPA anions can play the role of charge carriers between the polymer chains.

According to Ref. 212, PPy must be prepared from fresh aqueous solutions of HPA because fast trimerisation of pyrrole in solution results in formation of PPy films with poorly reproducible properties. Use of aqueous solutions with neutral salts of HPA allows one to prepare PPy with high conductivity and stable electrochemical properties. The PAni/HPA films are also stable in acidic solutions. The EP of pyrrole in aqueous solutions of Dawson-type HPA (which have the dimensions two times larger than the Keggin-type HPA)[215] and of aniline in AN solutions of these HPA[213] also yields electroactive and highly stable polymers. The redox capacity for PPy/$P_2W_{18}O_{62}^{6-}$ was[215] 50 mA h g^{-1} (or 190 mA h cm^{-3}, as the density of the film is very high, 3.9 g cm^{-3}). The incorporation of HPA anions in conducting polymers brings about substantial changes in their electrocatalytic and catalytic properties[219] due to interactions with the polymer matrix and molecular dispersion of the anions. In the case of PAni

doped with HPA ($PMo_{12}O_{40}^{3-}$, $PMo_{11}Fe^{2+}O_{39}^{4-}$, $PMo_{11}Mn^{2+}O_{39}^{4-}$), an enhanced selectivity in formation of acetone in catalytic decomposition of propan-2-ol was observed.[216] In catalytic conversion of ethanol on PAni/$PMo_{12}O_{40}^{3-}$, mainly acetaldehyde is formed (redox activity), whereas on PAni/$PW_{12}O_{40}^{3-}$ and PAni/$SiW_{12}O_{40}^{3-}$, ethene is the main product (acid–base properties).[220] The activity of the catalysts depends on the preparatory procedure for PAni/HPA.

The PPy films modified with MPhC (M = Fe, Co) showed high electrocatalytic activity in electroreduction of oxygen[201,203,204] and those modified with MP, in the oxidation of phenol derivatives.[205] Reduction of thionyl chloride was performed on PPy electrode modified with iron tetrasulfophthalocyanine.[221] The introduction of MPhC in the PPy matrix brought about enhanced currents of thionyl chloride reduction, compared with a PPy/ClO_4^- electrode and even with a platinum one. The reaction mechanism was not changed. Apparently, the enhancement of currents is due to elevated concentration of adsorbed $SOCl_2$ on the electrode surface, owing to formation of complexes with MPhC.

PPy was also modified by non-ionic species, in particular metals,[222] metal oxides,[223–225] and enzymes.[226,227] On a PPy film with peroxidase, direct bioelectrocatalysis of cathodic reduction of hydrogen peroxide was observed.[227]

VIII. The potential for polypyrrole applications

The PPy is a promising material for rechargeable lithium batteries.[228–230] The advantages of the polymeric electrodes include light weight combined with high energy storage capacity and a possibility to manufacture and use them in the form of thin films. Table 3 summarises some parameters of the polymer-based lithium batteries and, as a reference, also the properties of lead and nickel–cadmium batteries.[231]

Table 3. Comparison of characteristics of some electrochemical batteries.[231]

Battery	U /V	W /W kg^{-1}	Q /A h kg^{-1}	E /W h kg^{-1}
PAc/PC, $LiClO_4$/Li	3.7	3.5	105	80
PAc/PC, $LiClO_4$/PAc	3.0	1.1	85	50
PPh/PC, $LiClO_4$/Li	4.4	7.0	–	80
PPy/PC, $LiClO_4$/Li	3.2	2.8	85	55
PTh/PC, $LiClO_4$/Li	3.4	2.5	75	50
PAni/PC, $LiClO_4$/Li	3.3	0.4	–	60
Lead	2.1	1.2	–	40
Nickel–cadmium	1.35	–	–	35

Note. PAc is polyacetylene, PPh is polyphenylene, PPy is polypyrrole, PTh is polythiophene, PAni is polyaniline, PC is propylene carbonate.

A comparison of energy storage capacity shows that polymer-based batteries are superior. Note also that Li/PPy batteries have a high Coulombic efficiency. In addition to the energy storage advantages, the conducting polymers provide also operational ones. During discharge of the battery, the polymers do not dissolve and this eliminates the problem of the changes in the electrodes' shape in the solution–deposition cycles. The flat discharge that usually destroys conventional batteries is not dangerous in the case of conducting polymers. However, there are certain problems associated with the use of conducting polymers in batteries. First, in the course of charge–discharge, the bulky ions enter and leave the polymer film giving rise to mechanical stresses; this brings about the problem of mechanical integrity of the polymeric electrodes during their operational life. Second, the use of a lithium electrode requires high purity of the electrolyte and perfect sealing of the battery in order to prevent penetration of water or oxygen into it. A battery with PPy/Cl^- cathode and PPy/polyvinylsulfate anode was developed;[152] the discharge of the battery is accompanied by removal of Li^+ ions from the anode and Cl^- anions from the cathode. Upon charging, these ions again are inserted into the electrodes. An all-solid rechargeable lithium battery with electrolyte based on polyacrylonitrile extended with organic solvent has been proposed.[230]

Amorphous MoS_3 is often used as a cathodic material in lithium batteries.[232] Yet, its conductivity is exceedingly low, 5.2×10^{-4} S cm^{-1}, and a conductive carbonaceous additive must be used. Introduction of MoS_3 into the PPy matrix in the course of EP of pyrrole in the presence of ammonium tetrathiomolybdate provided a possibility of enhancing the conductivity of thin-film MoS_3 electrodes to 2.6 S cm^{-1} (see Refs 195, 196). The VA of PPy/MoS_4^{2-} film shows a shift of ΔE_p by 200 mV to the cathodic region; this is a typical feature of immobilised anions. The capacitive currents are low, cations take part in the charge transport. The EP of pyrrole from aqueous KCl solution on the substrate matrix Pt/MoS_3 results in the formation[197] of a film having electrochemical behaviour typical of the polymers doped with small anions and with a higher ionic conductivity than that of PPy/MoS_4^{2-}. Apart from MoS_3, for rechargeable lithium batteries, the PPy/V_2O_5 [224] and PPy/MnO_2 [223,225] composites were used as cathodic materials.

PPy doped with alkylnaphthalenesulfonates was used in an all-solid electrolytic capacitor with aluminium electrodes.[233] The PPy was prepared by EP on the surface of anodised aluminium foil that was preliminarily covered with a thin layer of pyrolytic MnO_2. Substantially improved thermostability of the capacitor (1000 h at 120 °C) was achieved by means of introduction of nitrophenol in the electrolyte at the stage of pyrrole EP. The properties of this capacitor were superior compared to the common aluminium electrolytic, multilayered ceramic and tantalum capacitors with solid electrolyte and the thin-film organic ones.

The electric conductivity of the conducting polymers is sensitive to chemical agents; this provides a possibility of developing various sensors based on them. It was reported that PPy can be used as a sensor for certain components in gas mixtures, including both inorganic (NO, CO_2, CO, NH_3, H_2S)[234,235] and organic (acetone, methanol, ethanol)[236] compounds.

The amperometric biosensors based on PPy with incorporated enzymes such as glucose oxidase,[237,238] alcohol dehydrogenase,[239] glutamate oxidase and peroxidase[240] can find extensive applications. The electrocatalytic activity of the glucose oxidase was enhanced by the introduction of a redox mediator, tiron, and a polymeric dopant, altion (a water-soluble analogue of Nafion).[238] The latter, owing to the high content of fluorine in the polymer, enhances solubility of oxygen and thus promotes oxidation of glucose. In the near future, one might anticipate development of preparations on the basis of PPy, by EP of monomers with grafted enzymes or drugs.[241] Since PPy is biocompatible and non-toxic, it is possible, by electrochemical reduction of oxidatively doped polymer, to controllably supply an organism (cell) with microscopic doses of a drug that has been immobilised in ionic form, *e.g.*, glutamate, aspartate, dopamine.[242,243] Separation of some drugs using PPy was reported;[244] caffeine and theophylline are selectively absorbed by PPy, whereas protein molecules are not. PPy can be used as an efficient conductor in biological media (*e.g.*, for regeneration of a nerve tissue).[245]

A promising field is the application of PPy as a protective coating for semiconducting anodes in photoelectrochemical cells. Usually, when photochemical reactions on inorganic semiconductors are carried out in humid media, the surface of semiconductor rapidly oxidises and electrodes become inoperative. The PPy film covering semiconductor prevents passivation of its surface and simultaneously allows formation of the electron holes, which pass to the polymer (in other words, the electrochemical reaction will now occur on the polymer surface). Such systems were studied for GaAs,[246] CdS,[56,57] CdSe.[57] Photochemical cells with solid poly-

electrolytes were developed.[247] The photoelectrochemical oxidation of water could be performed by combining the photoeffect on PPy-film-protected CdS[56, 57] and CdSe[57] with electrocatalysis on RuO_2, Pt, Rh particles dispersed in the polymer.

Flexible films of conducting polymers can be used as protective electromagnetic shields.[3, 248] For example, 50-μm-thick PPy films provide 30-dB attenuation; in many cases, this is sufficient for practical applications.[249]

The PPy films electrochemically deposited onto a surface of porous silicon were used as electrical contacts in the structure of an electroluminescent diode.[250]

The PPy antistatic coatings on synthetic polymer fibres (polyethylene,[251, 252] nylon[253]) were produced by polymerisation from gas with the oxidants (iron and copper salts) applied onto the fibre surface.

Microscopic electrochemical transistors were prepared [243] by means of electrocopolymerisation of pyrrole and *N*-methylpyrrole between microelectrodes (emitter and collector) separated with a narrow slit. The conductivity of the polymer channel can be controlled by varying the voltage applied to the auxiliary control electrode. The latter was embedded in a solid or fluid polymeric electrolyte placed over the conducting polymer coating.

The capability of the polymer to reversibly change its volume in the range from 1% to 100% upon electrochemical doping was used [254] to make 'electrochemical muscles' based on bilayered strips comprising PPy and polyethylene layers. Upon doping, the free end of the strip strongly deflected from its initial position and returned back upon dedoping.

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