Electrochemical synthesis of electroconducting polymers

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Abstract

Electroconducting polymers from the group of synthetic metals are extensively investigated due to numerous properties perspective in practical application. These materials may be synthesized by both chemical and electrochemical procedures. Chemical synthesis is suitable when bulk quantities of the polymer are necessary and up to date it presents dominant commercial method of producing electroconducting polymers. Nevertheless, the electrochemical synthesis has its advantages; it avoids usage of oxidants since conducting polymeric material is obtained at anode upon application of positive potential, leading to increased purity. On the other hand, since the polymer is deposited onto electrode, further electrochemical characterization is facilitated. Owing to actuality of the research in the field, this text aims to describe important aspects of electrochemical synthesis of electroconducting polymers, with special emphasis to polyaniline and polypyrrole.

Keywords: electrochemical synthesis, anode, polyaniline, polypyrrole.

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From an unexpected discovery of polyacetylene conductivity in the late seventies, later awarded by the Nobel Prize in Chemistry in 2000, the field of electroconducting polymers is still expanding. Although the term "electroconducting polymers" nowadays covers a large group of polymeric materials, with both ionic and electronic conductivity, commonly this term refers to polymeric materials with electronic conductivity originated from the specificity of the molecular structure [1,2], often called "synthetic metals" and the following text will be dedicated exclusively to this group of electroconducting polymers. By studying the mechanism of electrical conductivity it was soon realized that the basic request for macroscopic electrical conductivity was existence of conjugated double bounds, while necessary condition was doping [3]. Although the term doping was taken from traditional semiconductors terminology and it refers to a completely different process, *i.e.*, oxidation (rarely reduction) during which the stoichiometric amount ions (dopants) are introduced into polymer backbone [4]. Moreover, doping often refers to a process in which polyaniline polymer chain is protonated and recent studies indicate that protonation of polypyrrole is also possible [5]. The presence of a large quantity of ions in the polymer alters its structure bringing completely new and unique properties such as: controllable electrical conductivity, reversible doping/dedoping (oxidation/reduction) process, optical

activity, corrosion stability etc. [6]. Mentioned properties are considered in the field of: rechargeable power sources [7–9], electrochemical capacitors [10–12], electrochromic devices [13–15], sensors [16–18], magnetic shielding materials [19–21], corrosion protection [22–26], etc.

Although, at the very beginning, the electroconducting polymers were synthesized chemically [3], with deeper insight into the polymerization mechanism, it became clear that electroconducting polymers can also be obtained by electrochemical methods. Both chemical and electrochemical synthesis refers to oxidative polymerization however, other alternative approaches such as: photochemically initiated or enzyme catalyzed polymerization were also reported [4,27].

Although suitable for smaller quantity of the desired electroconducting polymer, the electrochemical synthesis has some advantages. The electrochemical synthesis involves the direct oxidation of the monomer at the anode, so there is no need of an oxidizing agent. On the other hand, in most cases, the polymer is deposited on electrode facilitating further analysis. Having in mind the popularity of polyaniline and polypyrrole in both theoretical and practical aspects, the following text, apart from the general discussion, will be dedicated to the principles of electrochemical synthesis of polyaniline and polypyrrole.

The complexity of electrochemical synthesis

As stated before, the electrochemical synthesis refers to the oxidation of the monomer and growth of the polymer chain onto anode. Since the oxidation is carried out by applying a positive potential or current, the electrochemical polymerization avoids application

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of the oxidant, thus achieving greater purity of the desired polymer. On the other hand, growth of the polymers occurs simultaneously with insertion of dopant anions in accordance to generalized stoichiometric equation:

$$nM + nyA^- \xrightarrow{\text{oxidation}} [M^{y+}(A^-)^{y-}]_n + n(2+y)e^-$$
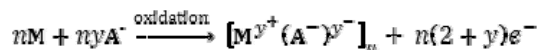
where, M refers to monomer and A refers to dopant anion whose role is to compensate the positive charge at anode, while y is doping degree defined as ratio between the number of charges in the polymer and the number of monomer units [28]. Although the experimental demands for electrochemical formation of electroconducting polymers are simple, the mechanism itself is quite complicated.

Relying on the knowledge of the mechanism of chemical synthesis, it is generally accepted that the first step of the mechanism of electrochemical polymerization is formation of the primary cation-radicals by monomer oxidation at the anode [4,29–32]. These species have essential role in the outcome of the electrochemical polymerization. If being too reactive, they can react with other compounds in the electrolyte, or react with monomers at the "wrong" positions. If, on the other hand being too stable, they may diffuse from the anode before it comes to the further reaction so there will be no formation of electroconductive polymer film [30]. After the primary cation-radicals were formed, the further formation of dimers occurs trough deprotonation and rearomatization [4,32]. The growth of the polymer is achieved by further oxidation and reactions of cation-radicals or cation-radicals and monomers [4]. In order to obtain electroconductive polymer film on the electrode, it is necessary that radical coupling and the continual growth of the polymer occur in the vicinity of the electrode, otherwise, it is possible that cation-radicals and dimers diffuse from the electrode surface (intensive mixing reduces polymerization yield) [4]. The yield can also be reduced by the possible undesired side reactions of cation-radicals and nucleophilic species present in the electrolyte [34].

Once the polymer layer is formed, further polymerization will take place on the modified electrode. This explains the fact that the potential required for the oxidation of the already formed polymer is lower than the potential required for the oxidation of the monomer and the formation of radical cations [6]. Explanation of the kinetics of nucleation and growth processes during electrochemical synthesis of electroconducting polymers relies on the theory of electrochemical metal deposition [6,34]. According to the theory, two types of nucleation are possible, instantaneous and progressive with three types of the growth process: one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D). Instantaneous nucleation refers to constant number of nuclei growing without further formation, while progressive nucleation refers to constant generation of the nuclei [35]. Growth in only one direction refers to 1D growth, perpendicular to the electrode surface, 2D growth is characterized by nuclei with preferences to growth parallel to the electrode surface, while 3D growth implies similar rates of growth in both perpendicular and parallel directions [6].

Factors influencing electrochemical synthesis of electroconducting polymers

Bearing in mind the similarity of the proposed mechanisms of chemical and electrochemical synthesis of electroconducting polymers, it is reasonable to expect that similar factors influencing chemical would exhibit influence on electrochemical synthesis of electroconducting polymers [36]. Beside composition of reaction solution, *i.e.*, electrolyte, and temperature, the electrochemical synthesis is subjected to the influence of the electrode material and selected electrochemical technique [37–40].

Electrode material

Although, as mentioned previously, the electrochemical synthesis proceeds without use of oxidants, the nature of the electrode influences the ease of the monomer oxidation and on the other hand deposition of the polymer is dependent on the surface energy of the electrode and its hydrophobic/hydrophilic nature. The major limitations of electrochemical synthesis of electroconductive polymers on numerous metals and alloys are relatively high potentials required for monomer oxidation. At these potentials most metals are either dissolved (iron, steel, copper,…), or form low or even nonconductive passive layers (aluminum and its alloys). This problem is of particular importance when electrochemical synthesis is performed for the purpose of corrosion protection [22,23,25,41,42].

However, the electrochemical synthesis can be easily, by proper design of experimental set-up, performed on so called inert electrodes, such as: Pt, Au, graphite, glassy carbon, ITO glass, etc. [7,43–45].

Electrochemical techniques

Some of the properties of electroconducting polymers obtained electrochemically are dependent on the choice of electrochemical polymerization techniques [4]. Generally, electrochemical techniques used for synthesis of electroconducting polymers can be classified in: galvanostatic, potentiostatic, potentiodynamic.

Galvanostatic technique refers to formation of electroconducting polymer at constant rate (current density). The polymer film, obtained at the end of the polymerization is in doped, *i.e.*, conductive form [6]. This technique allows control of the polymer film thickness by adjusting the duration of the polymerization pro-

cess. For its simplicity, galvanostatic technique is the suitable for practical application. Implementation of galvanostatic technique requires proper selection of the polymerization current density, since potential increases during polymerization, as a consequence of resistance increase due to the growth of the polymer film at the electrode. Increase of the potential favors side reactions thus reducing the polymerization efficiency [28].

Potentiostatic polymerization technique refers to application of a constant positive (for oxidative polymerization) potential. It is necessary to choose the potential high enough for polymerization to proceed. On the other hand, potential has to be low enough to avoid undesired secondary reactions and over oxidation of the polymer [6,28,46]. Similar to galvanostatic polymerization, the obtained polymer is in doped state. It is also possible to use a modified pulse potentiostatic technique [46]. This technique involves application of alternating anodic and cathodic pulses of constant potential. During the duration of anodic pulse, the electrochemical polymerization and deposition of the polymer are occurred, while dedoping of the polymer occurs during cathodic pulse. The parameters of the pulse potentiostatic technique, namely: lower (cathodic) and upper (anodic) limit potentials with additional cathodic and anodic pulse times, have influence on the morphology of the formed polymer [48].

Potentiodynamic technique refers to the application of cyclic voltammetry technique for electrochemical polymerization. In this case, the electrode is subjected to cyclic regular change of the potential during which electroconducting polymer changes between its non-conducting (dedoped) and conducting (doped) form [6]. It was shown that nanostructured electroconducting polymers can be obtained by potentiodynamic electrochemical synthesis [49].

Electrochemical synthesis of electroconducting polymers are usually performed in three-electrode cell arrangement, although galvanostatic synthesis can be performed in two electrode system [4]. In three electrode cell, working electrode operates as anode on which polymerization and deposition of the polymer occur. Reduction of solvent, dissolved oxygen or other compound of the electrolyte occurs at counter electrode, while reference electrode serves for the potential control. Three electrodes can all share the same compartment (one compartment cell) or they can be organized in two compartments (one for counter and working electrodes and one for reference electrode) or three compartments (each electrode has its compartment). If working and counter electrodes are in the same compartment, the reactions occurring on the counter electrode cannot be neglected. The most common reaction at counter electrode is the reduction of

water (if aqueous electrolytes are used) or other additives from electrolyte, and this problem might be overcome by intentional addition of auxiliary reagent such as electroactive metal ion or ferricyanide or by use of three compartments of electrochemical cell, which are common for laboratory investigations [4]. The cell geometry also plays important role, especially for practical purposes.

Apart from standard electrochemical cells, Wallace *et al*. developed new electrochemical flow cell for potentiodynamic synthesis of colloids or water soluble electroconducting polymers. In this cell the anode was separated from two cathodes by ion exchange membrane, with anodic and cathodic electrolytes passed through these separated compartments [39,50,51]. Anode is made of porous material with developed surface area while flowing electrolyte prevents deposition of the polymer. Anolite, beside monomer, contains stabilizer polyethylene or polyvinyl alcohol, which favors formation of colloids.

Electrolyte

Composition of electrolytes used for electrochemical synthesis of electroconducting polymers involves, beside selected monomer, solvent and acid which serves as source of dopants ion and in some cases may contain some additional compounds [1,2,28,40,51,52].

Apart from being capable to dissolve monomer, the solvent has to be as pure as possible, and stable at potentials of interest for the polymerization. For example, the presence of dissolved oxygen may be problematic due to reaction with radical intermediates and it can be also reduced at counter electrode and forms hydroxide [4]. Interaction of the solvent, monomers and electrode materials cannot be neglected even before the polymerization is initiated since they will all have impact on monomer adsorption onto electrode. Once the polymerization is started, the properties of solvent will have influence on solubility of the polymer. On the other hand, as stated before, nucleophilicity of the solvent should be also considered, the nucleophilic solvent would react with radicals and thus preventing the normal course of the electrochemical polymerization [4,36].

Most of the electrochemical syntheses of electroconducting polymers are performed in aqueous electrolytes bearing in mind the price, easy handling, environmental concerns, and the fact that various dopants may be used. However, various organic solvents were also investigated, such as: acetonitile, dichlormethane, nitrobenzene, propylene carbonate and recently the application of ionic liquids was also considered [4,38,53–55].

Dopants or counter ions are incorporated into polymer structure during electrochemical polymerization fulfilling the request of electroneutrality by compen-

sating positive charge on anode. Since their amount is on stoichiometric levels, it is reasonable to expect that their presence and properties would dramatically influence the morphology, conductivity, electrochemical activity and the polymerization process as well [4,56,57]. As expected, dopants have to be both chemically and electrochemically stable. If dopant is electroactive at potentials lower than those required for polymerization of the monomer, than they can be only used for potentiostatic synthesis [4].

Temperature has also impact on electrochemical synthesis of electroconducting polymers, not only influencing the kinetics of the process, but also influencing the extent of undesired side reactions. Free radicals obtained in anodic process react with oxygen in reaction that is highly sensitive to temperature; therefore the increase in temperature has adverse impact on electrochemical syntheses through decrease of the polymerization efficiency [4].

Electrochemical synthesis of polyaniline

It is believed that polyaniline is the oldest known electroconducting polymer since it was used in textile industry as a cotton dye over a century ago [58]. The increased interest in polyaniline dates from the discovery of its conductivity in the form of emeraldine salt and existence of different oxidation forms, as given in general scheme in Fig. 1 [40,59–62].
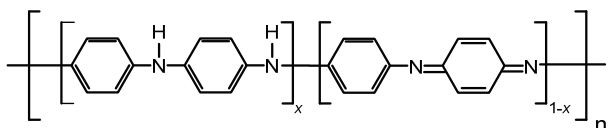

Figure 1. General scheme of polyaniline.

Fully reduced form refers to leucoemeraldine base ($x = 1$), half-oxidized form refers to emeraldine base ($x = 0.5$), while fully oxidized form is pernigraniline base ($x = 0$). None of these forms is conductive [42,63,64]. The only conductive form of polyaniline, the emeraldine salt, can be obtained by doping or protonation of emeraldine base [65]. The unique property of polyaniline forms is mutual conversion by both chemical and electrochemical reactions, which are followed by color and conductivity changes [64].

Electrochemical polymerization of aniline in acidic electrolytes leads to formation of green conductive emeraldine salt. Emeraldine salt can be easily oxidized to dark blue perninganiline salt or be transformed in reaction with alkali to violet pernigraniline base. Emeraldine salt can also be reduced to transparent leucoemeraldine base, or transformed in reaction with alkali to blue emeraldine base. Both the reduction and oxidation of conductive emeraldine salt are followed by decrease of conductivity [64].

The mechanism of electrochemical polymerization of aniline

As in case of chemical, the electrochemical synthesis of polyaniline is always carried out in strong acidic solutions (pH < 2), since increase in pH would lead to formation of short conjugation oligomers [4,65,66].

The generally accepted mechanism of electrochemical synthesis of polyaniline [4,30,68,69] is given in Fig. 2.

As mentioned before, first step of the polymerization process refers to formation of radical cation by oxidation of monomers at anode. Formation of primary radical cation (aniline radical cation), is believed to be the rate-determining step [68–70]. The existence of aniline radical cation was experimentally confirmed when substances capable of retarding the process were added which supported the radical mechanism. The oxidation of aniline monomer is irreversible process, occurring at potential of about 0.9 V (*vs.* standard calomel electrode), which is higher than polyaniline redox potential [30]. Formation of the radical cation is than followed by coupling of the radicals at *N*- and *p*- positions with elimination of two protons. The formed dimers and lately oligomers are than subjected to further oxidation along with aniline. Oxidation potential of dimers and oligomers are lower than oxidation potential of aniline [62]. Radical cations, formed from oligomers and aniline radical cations, are than coupled leading to chain propagation. Polyaniline is doped by anions from electrolyte. The unique feature of electrochemical formation of polyaniline is the fact that nitrogen atom is involved in formation of radical cation, unlike most of others electroconducting polymers whose radical cation is formed on carbon atom. Nitrogen is also present in conjugated system of double bonds explaining the fact that electrical conductivity of polyaniline depends both on oxidation and protonation levels [4,59,65].

It was claimed that electrochemical synthesis of polyaniline is an autocatalytic process, meaning that further formation of the polymer on already deposited polymer proceeds faster than on the bare electrode, *i.e.*, the more polyaniline is formed on anode, the higher is the rate of the polymerization process [4,30,40,70–72]. The autocatalytic synthesis of aniline was experimentally confirmed during electrochemical polymerization of aniline by cyclic voltammetry technique. It was evidenced that current increased over time for potentials higher than 0.8 V (*vs.* saturated Calomel Electrode) and that anodic peak potentials decreased. The increased intensity of the anodic peak currents was connected to increased polymerization rate, while decrease of the anodic peak potentials was
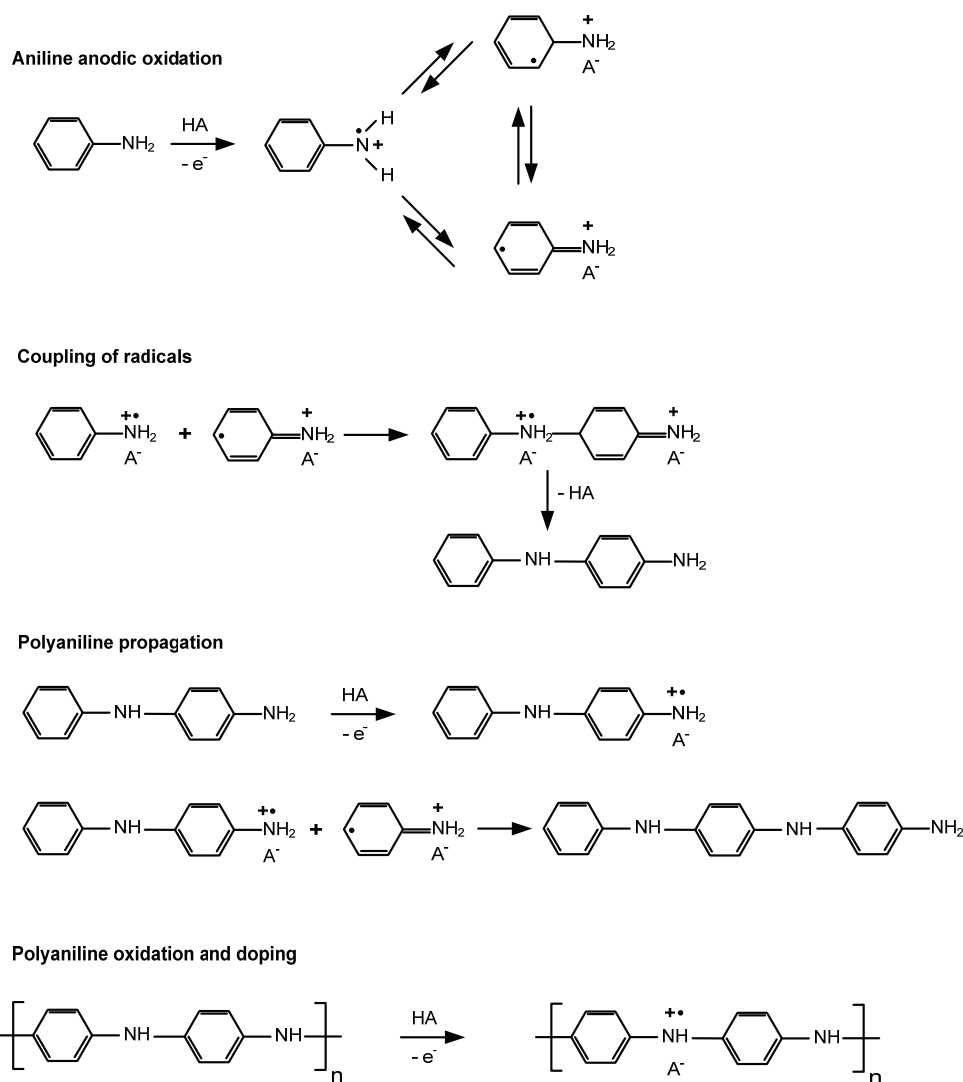
Figure 2. Mechanism of electrochemical synthesis of polyaniline.

assigned to facilitated electrochemical polymerization [70].

Factors influencing electrochemical synthesis of polyaniline

Electrochemical synthesis of polyaniline proceeds easily on inert electrodes in strong acidic aqueous electrolytes containing aniline, according to described mechanism. As expected, parameters such as: electrode (anode) materials, choice of solvent, composition of electrolyte, temperature, have influence on properties of obtained polyaniline [4,6,30,45,58].

If potentiodynamic technique is used for electrochemical synthesis of polyaniline, the several characteristic peaks appear on cyclic voltammograms, as it can be seen in Fig. 3.

First anodic peak at potential of ~0.2 V refers to doping characterizing transformation of leucoemeraldine base to emeraldine salt, further increase of potential leads to appearance of another anodic peak at

0.8 V characteristic to formation of fully oxidized pernigraniline salt [7,62,73]. Between mentioned well defined anodic peaks, small peaks at potentials ~0.4 V refer to formation of degradation and hydrolysis products [62]. If galvanostatic polymerization is used for electrochemical formation of polyaniline (insert of Fig. 3), chronopotentiograms are characterized by fast potential increase during which electrode surface is covered by polyaniline film and potential plateau at which polymerization proceeds on already formed polymer [7,45].

If polyaniline has to be obtained electrochemically as protective coating on active metals and their alloys, dissolution or passivation by nonconductive oxides would occur, since aniline polymerization potential is quite high, laying in potential region of either active metal dissolution, (iron, mild steels, copper,…) or formation of non-conductive oxides (aluminum) [22,23,25,26,42,74,75]. Two approaches were pro-
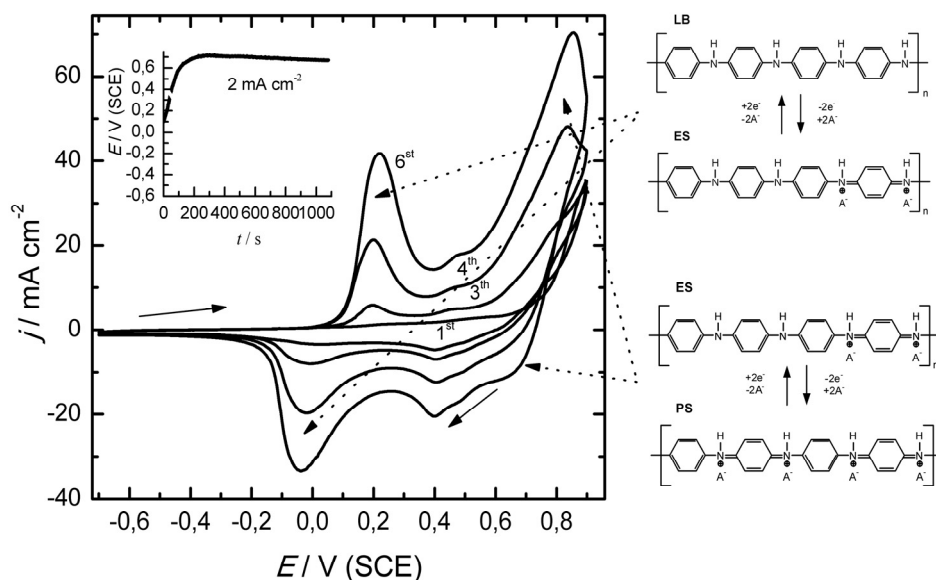
Figure 3. Electrochemical synthesis of polyaniline at graphite electrode by cyclic voltammetry (v = 20 mV s^{-1}) from 1.0 mol dm^{-3} HCl containing 0.25 mol dm^{-3} aniline. Inset: chronopotentiometric curve (j = 2.5 mA cm^{-2}) of electrochemical synthesis of polyaniline from the same electrolyte. (Reprinted from Materials Chemistry and Physics, vol. 125, Issue 3, M. M. Gvozdenović , B. Z. Jugović, T. Lj. Trišović, J.S. Stevanović and B. N. Grgur, "Electrochemical characterization of polyaniline electrode in ammonium citrate containing electrolyte", pp. 601–605, Copyright 2004, with permission from Elsevier).

posed, the application of electrode surface pre-treatments or electrolytes capable of formation of passive, but still conductive layers on which undisturbed polymerization would occur [4,22,75].

As in case with chemical synthesis the electrochemical synthesis is practically always carried out in very acidic electrolytes (pH < 2) [42,64,67]. Okamoto and Kotaka were investigated galvanostatic electrochemical synthesis of polyaniline in pH range between 0.2 and 3.7, using UV spectroscopy for determination of existence of emeraldine salt and occurrence of oligomers. They pointed out that emeraldine salt was formed at pH lower than 1.7, while increase of pH resulted in formation of films with spectra characteristic for oligomers [56].

Anions inserted during electropolymerization of aniline usually originate from acid, present their conjugated base, and exhibit influence on morphology, conductivity and redox properties of obtained polyaniline [35,57,76–78]. It was experimentally evidenced that polyaniline doped by highly hydrated ions originating from hydrochloric acid, sulfuric acid, nitric acid, *p*-toluenesulfonic acid, sulfosalicylic acid exhibited more open and swollen structures, while small ions, for example ClO$_4^-$ or BF$_4^-$ are responsible for more compact structures [79]. It was showed that doping of polyaniline with chiral dopants was also possible, resulted in emeraldine salt film with strong circular dichroism, meaning that chirality was introduced into polyaniline by the use of specific types of dopants [5,50]. Addition of polyelectrolytes can lead to incorporation of their polyanions as dopants into electroconducting polymer

matrix [4]. Some of the researches have shown that addition of inert salts into electrolyte resulted in polyaniline with increased molecular weight [4,80]. Addition of alcohols into electrolyte also exhibited influence on morphology of obtained polyaniline leading to one dimensional growth, this effect was explained by solvation of polyaniline by alcohol molecules due to intermolecular bonding by hydrogen bonds [81].

Electrochemical synthesis of polypyrrole

Besides polyaniline, polypyrrole is certainly one of the most extensively investigated electroconducting polymer. Both electrical conductivity and chemical stability of polypyrrole originate from heteroatomic and extended π-conjugated backbone structure. This structure is not sufficient for conductivity on its own. However, conductivity achieved by doping largely exceeds those of other electroconducting polymers, which is a good prerequisite for practical application [82]. Unlike polymerization of aniline, polymerization of pyrrole can be successfully performed in neutral aqueous environment and variety of organic solvents can be also used [83].

The mechanism of electrochemical polymerization of pyrrole

According to generally accepted mechanism of electrochemical polymerization of pyrrole, the first step refers to formation of the primary radical cation, as seen in Fig. 4 [36].

Unpaired electron and positive charge are delocalized and quantum mechanical calculations reveal that
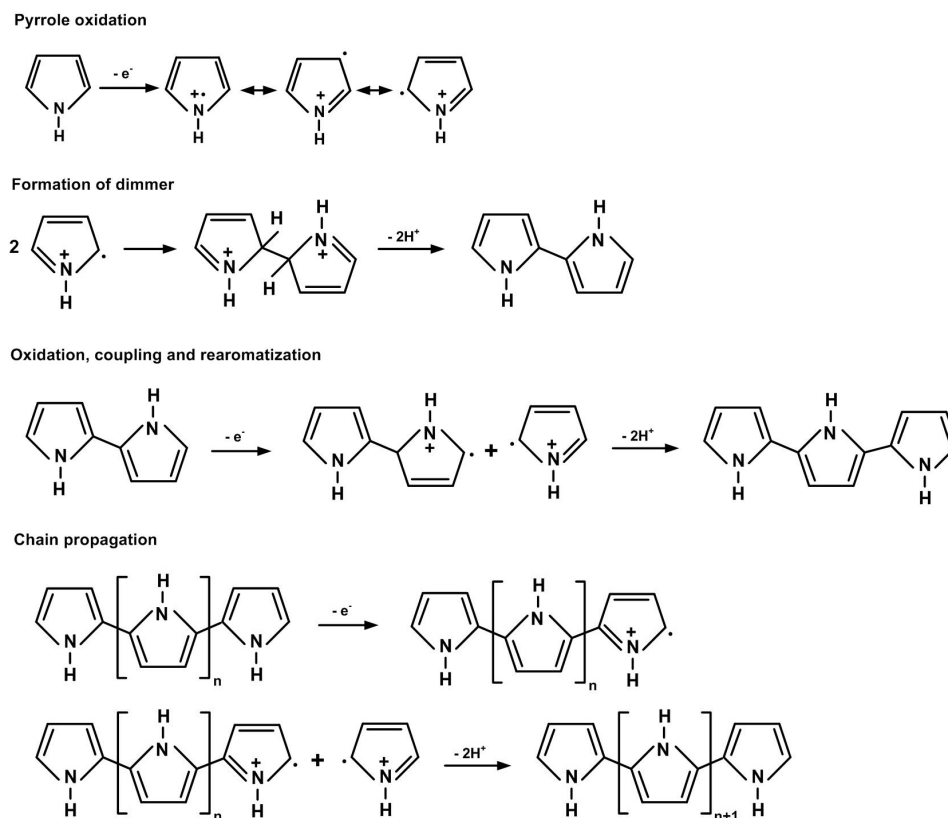
Pyrrole oxidation

Formation of dimmer

Oxidation, coupling and rearomatization

Chain propagation

Fig. 4. Mechanism of polypyrrole electrochemical synthesis.

electron spin density is the greatest at *o*-positions, therefore they are the most reactive, so radical coupling takes place at these positions [28].

By coupling of two primary radical cations, positively charged dimer is formed. Since two protons of the positively charged dimer distort the conjugation, rearomatization is likely to occur through deprotonation leading to formation of energetically favorable neutral dimer [4]. According to alternative, but not accepted mechanism, radical cation can react with neutral pyrrole molecules leading to formation of a new radical cation [4]. Neutral dimer is, in further step, oxidized at anode giving new radical cation. As expected, oxidation of the dimer is easier comparing to neutral pyrrole, therefore occurring at the lower potential. In the forthcoming steps coupling of dimer radical cations (lately, oligomer radical cations) and primary radical cations occur, followed by a release of protons and rearomatization. Oxidation, coupling and rearomatization are repeated leading to formation of polypyrrole. Although the electron spin density is the largest at *o*-position, by development of the conjugation length, spin density is spreading over conjugating system, so the radicals might be coupled in other positions, resulting in disturbing of the linearity and branching [4].

Factors influencing electrochemical synthesis of polypyrrole

Nature of the electrochemical synthesis of polypyrole is affected by similar factors as in the case of electrochemical synthesis of polyaniline.

Pyrrole, similarly to aniline, is easily electrochemically polymerized in both aqueous and organic based electrolytes containing pyrrole on inert anodes, including graphite, gold or platinum, according to above given mechanism. Figure 5 shows galvanostatic polymerization of pyrrole from aqueous electrolyte together with cyclic voltammogram obtained after galvanostatic synthsis in the same electrolyte in order to show characteristic doping/dedoping processes occurring during potentiodynamic synthesis (inset of Fig.5).

As seen in Fig. 5, chronoamperometric curve is characterized, by fast increase of the potential during which the electrode is covered with a layer of polypyrrole, the succeeding plateau of the potential although lower than in the case of polyniline, refers to further polymerization on already formed polymer. It can be noticed that after galvanostatic synthesis the polypyrrole is almost completely in its doped state which is reflected in rapid increase of the potential [6]. Cathodic part of the voltammogram is characterized by wide peak attributed to dedoping of ions from polypyrrole, after which anodic part of the voltammogram refers to

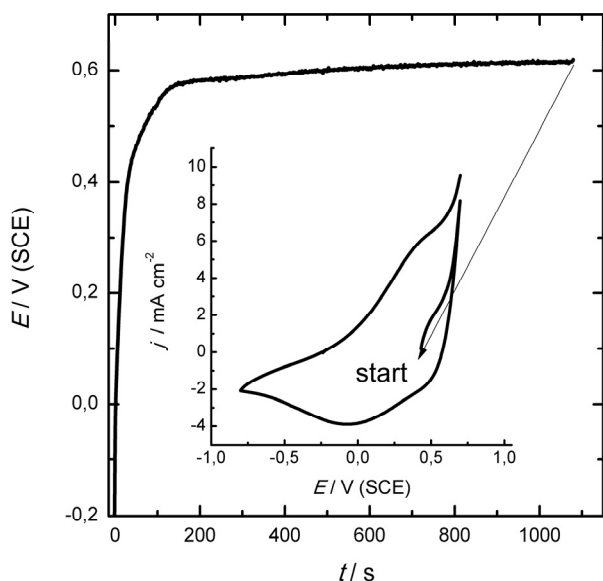doping and further polymerization of pyrrole occurring simultaneously [84].

Figure 5. Chronoamperometric curve of electrochemical polymerization of pyrrole at graphite electrode (j = 2.0 mA cm⁻²) from 0.1 mol dm⁻³ HCl and 0.2 mol dm⁻³ pyrrole. Inset: cyclic voltammogram (v = 20 mV s⁻¹) recorded after 1100 s of galvanostatic synthesis of polypyrrole from the same electrolyte.

Electrochemical synthesis of polypyrrole on active metals is faced to expected problems of the substrate dissolution owing to the high potential required for oxidation of the monomer [4,22,85–88].

Lot of efforts have been taken in order to find suitable conditions to passivate metal without hindering electrochemical synthesis of polypyrrole. Smooth and uniform polypyrrole coatings were deposited using lower current densities on low carbon steel and mild steel using oxalic acid based aqueous electrolyte [41,86,88,89]. In these cases, metal surface was shown to be firstly passivated by conductive interlayer of iron oxalate, on which uniform and protective film of polypyrrole was formed [90]. There are also evidence in literature that adherent polypyrrole might be formed on different oxidizable metals in aqueous electrolyte containing sodium salycilate. Sodium salycilate is capable of producing, together with metal ions, thin protective layer slowing substrate dissolution without impeding polymerization of pyrrole [86].

Beside oxalate based electrolytes, electrochemical synthesis of polypyrrole on aluminum was achieved in molybdate containing electrolytes [85,91,92].

Electrochemical polymerization of pyrrole was intensively studied in non-aqueous solutions, primarily in acetonitrile [4]. When polymerization is carried out in aqueous electrolytes it was assumed that water had role in the polymerization process. It was experimentally confirmed that polypyrrole maintained 2–4% of

water which was impossible to remove [5,93]. When acetonitrile was used as solvent for electrochemical polymerization of pyrrole, obtained polypyrrole had lower porosity as a consequence of impossibility of hydratation of dopants (counter-ions), unlike aqueous solutions in which the dopants are hydrated resulting in increased porosity of the obtained polypyrrole. On the other hand, it was also observed that polypyrrole electrochemically synthesized from either acetonitrile or propylene carbonate, exhibited higher conductivity comparing to those obtained from aqueous electrolytes [4]. Recently ionic liquids were also used as both solvents and source of dopants in electrochemical synthesis of electroconducting polymers. It was shown that polypyrrole grown from ionic liquids had different morphology and conductivity [38,94].

The nature and concentration of dopants, *i.e.*, counter ions, has influence on conductivity and polymerization rate of pyrrole, this effect was observed in both aqueous and non-aqueous solvents [4,82]. It was confirmed that doping by sulfonated aromatic ions, such as *p*-toulensulfonate led to higher conductivity of polypyrrole due to formation of crystalline structure [95,96]. Proteins and polyelectrolytes can also be incurporated as dopants during electrochemical formation of polypyrrole [4,97,98]. Besides pyrrole, the electrochemical polymerization of substituted pyrroles was also investigated, although these polymers were shown to be less conductive comparing to polypyrrole.

CONCLUSIONS

The existence of specific molecular structure that involves the system of conjugated double bonds leading to delocalization of electronic states is a key feature of electroconducting polymers, important representatives of synthetic metals. Electrical conductivity achieved by specific doping on stoichiometric level is, beside of the polymer type, dependent on the nature and amount of dopants, covering practically whole range from insulator, semiconductor to conductor regime. Since the presence of different amount of dopants makes conductivity adjustable, and bearing in mind that doping (oxidation) and dedoping (reduction) are reversible processes, electroconductive polymers are very promising materials for practical applications in various fields. Therefore not surprisingly, electroconducting polymers are still important subject of numerous researches. The application of electrochemical techniques of both synthesis and characterization has very important role in the science of electroconducting polymers, since it enables relatively simple and reproductive approach. From the very beginning and up to now, synthesis and characterization of polyaniline and polypyrrole are certainly the most investigated.

REFERENCES

[1] S. Jovanović, G. Nestorović, K. Jeremić, Elektroporovodni polimerni materijali, Hem. Ind. **57** (2003) 511–525.

[2] Conducting Polymers-Theory, Sinthesis, Properties and Characterization, T.A. Skotheim, J. Reynolds, Eds., CRC-Press, Teyor & Francis Group, New York, 2007.

[3] A.G. Macdiarmid, Synthetic Metals: A Novel Role for Organic Polymers, Nobel Lecture, 2001.

[4] G.G. Wallace, P.R. Teasdale, G.M. Spinks, L.A.P. Kane--Maguire, Conductive Electroactive Polymers, 3rd. ed. Telyor & Francis Group, Boca Raton, FL, 2009.

[5] J. Škodova, D. Kopecký. M. Vrňata, M. Varga,J. Prokeš, M. Cieslar, P. Bober, J. Stejskal, Polypyrrole-silver composites prepared by the reduction of silver ions with polypyrrole nanotubes, Polym. Chem. **4** (2014) 3610––3616.

[6] J. Heinze, B. Frontana-Uribe, S. Ludwigs, Electrochemistry of conducting polymers-persistent models and new concepts. Chem. Rev. **110** (2010) 4724–4771.

[7] B. Jugović, M. Gvozdenović, J. Stevanović, T. Trišović, B. Grgur, Characterization of electrochemically synthesized PANI on graphite electrode for potential use in electrochemical power sources, Mater. Chem. Phys. **114** (2009) 939–942.

[8] M.M. Gvozdenović, B.Z. Jugović, T.L. Trišović, J.S. Stevanović, B.N. Grgur, Electrochemical characterization of polyaniline electrode in ammonium citrate containing electrolyte, Mater. Chem. Phys. **125** (2011) 601–605.

[9] B.N. Grgur, M.M. Gvozdenović, J. Stevanović, B.Z. Jugović, V.M. Marinović, Polypyrrole as possible electrode materials for the aqueous-based rechargeable zinc batteries, Electrochim. Acta **53** (2008) 4627–4632.

[10] Y. Zhang, H. Feng, X. Wu, L. Wang, A. Zhang, T. Xia, H. Dong, X. Li, L. Zhang, Progress of electrochemical capacitor electrode materials: A review, Int. J. Hydrogen Energy **34** (2009) 4889–4899.

[11] H.R. Ghenaatian, M.F. Mousavi, S.H. Kazemi, M. Shamsipur, Electrochemical investigations of self-doped polyaniline nanofibers as a new electroactive material for high performance redox supercapacitor, Synth. Met. **159** (2009) 1717–1722.

[12] L. Zhang, G. Zhao, Y. Wang, Polyaniline nanowire electrodes with high capacitance synthesized by a simple approach, Mater. Sci. Eng., C **33** (2003) 2013.

[13] E.D.C. Rios, A. Viana Rosario, A. Flávia Nogueira, L. Micaroni, Electrochromic devices based on poly(3--methylthiophene) and various secondary electrochromic materials, Sol. Energy Mater. Sol. Cells **94** (2010) 1338–1345.

[14] P. Camurlu, C. Gültekin, A comprehensive study on utilization of *N*-substituted poly(2,5-dithienylpyrrole) derivatives in electrochromic devices, Sol. Energy Mater. Sol. Cells **107** (2012) 142–147.

[15] A.J.C. da Silva, F.A. Ribeiro Nogueira, J. Tonholo, A.S. Ribeiro, Dual-type electrochromic device based on polypyrrole and polythiophene derivatives, Sol. Energy Mater. Sol. Cells **95** (2011) 2255–2259.

[16] M.M. Gvozdenović, B.Z. Jugović, D.I. Bezbradica, M.G. Antov, Z.D. Knežević-Jugović, B.N. Grgur, Electrochemical determination of glucose using polyaniline electrode modified by glucose oxidase, Food Chem. **124** (2011) 396–400.

[17] D. Bezbradica, B. Jugović, M. Gvozdenović, S. Jakovetić, Z. Knežević-Jugović, Electrochemically synthesized polyaniline as support for lipase immobilization, J. Mol. Catal., B **70** (2011) 55–60.

[18] D. Jambrec, M. Gvozdenović, M. Antov, B. Jokić, J. Stevanović, B. Jugović, B. Grgur, Electrochemically deposited nanofibrous polyaniline for amperometric determination of glucose, Dig. J. Nanomater. Biostructures **7** (2012) 785–794.

[19] Ö. Yavuz, M.K. Ram, M. Aldissi, P. Poddar, H. Srikanth, Polypyrrole composites for shielding applications, Synth. Met. **151** (2005) 211–217.

[20] J.D. Sudha, S. Sivakala, R. Prasanth, V.L. Reena, P. Radhakrishnan Nair, Development of electromagnetic shielding materials from the conductive blends of polyaniline and polyaniline-clay nanocomposite-EVA: Preparation and properties, Compos. Sci. Technol. **69** (2009) 358–364.

[21] A. Kaur, S.K. Dhawan, Tuning of EMI shielding properties of polypyrrole nanoparticles with surfactant concentration, Synth. Met. **162** (2012) 1471–1477.

[22] S. Biallozor, A. Kupniewska, Conducting polymers electrodeposited on active metals, Synth. Met. **155** (2005) 443–449.

[23] M.M. Gvozdenović, B.N. Grgur, Electrochemical polymerization and initial corrosion properties of polyaniline-benzoate film on aluminum, Prog. Org. Coat. **65** (2009) 401–404.

[24] A. Elkais, M. Gvozdenović, B. Jugović, T. Trišović, M. Maksimović, B. Grgur, Electrochemical synthesis and corrosion behavior of thin polyaniline film on mild steel, copper and aluminum, Hem. Ind. **65** (2011) 15–21.

[25] M.M. Popović, B.N. Grgur, Electrochemical synthesis and corrosion behavior of thin polyaniline-benzoate film on mild steel, Synth. Met. **143** (2004) 191–195.

[26] M.M. Gvozdenović, B.Z. Jugović, J.S. Stevanović, B. Grgur, T.L. Trišović, Z.S. Jugović, Electrochemical synthesis and corrosion behavior of polyaniline-benzoate coating on copper, Synth. Met. **161** (2011) 1313–1318.

[27] S. Bhadra, D. Khastgir, N.K. Singha, J.H. Lee, Progress in preparation, processing and applications of polyaniline, Prog. Polym. Sci. **34** (2009) 783–810.

[28] J. Kankare, Conducting polymers: Basic Methods of Synthesis and Characterization, in: Electrical and Optical Polymer Systems: Fundamentals, Methods and Applications, D. Wise, G. Wnek D. Trantolo, J.Cooper, D. Gresser, Eds., CRC Press, New York, 1998, pp. 167–199.

[29] G. Inzelt, Temperature dependence of the voltammetric response of polyaniline film electrodes, J. Electroanal. Chem. Interfacial Electrochem. **279** (1990) 169–178.

[30] G. Inzelt, Conducting Polymers-A New Era in Eelctro-chemistry, Springer-Verlag Berlin, 2008.

[31] H. Daifuku, T. Kawagoe, T. Matsunaga, N. Yamamoto, T. Ohsaka, N. Oyama, Quartz crystal microbalance study on redox reaction mechanism of polyaniline, Synth. Met. **43** (1991) 2897–2900.

[32] L. Arsov, W. Plieth, G. Koßmehl, Electrochemical and Raman spectroscopic study of polyaniline; influence of the potential on the degradation of polyaniline, J. Solid State Electrochem. **2** (1998) 355–361.

[33] A. Diaz, J. Crowley, J. Bargon, G. Gardini, J. Torrance, Electrooxidation of aromatic oligomers and conducting polymers, J. Electroanal. Chem. Interfacial Electrochem. **121** (1981) 355–361.

[34] R. Mažeikienè, A. Malinauskas, Electrochemical behaviour of polyaniline film polymerized by the use of a chemical oxidation step, Electrochim. Acta **41** (1996) 1587–1591.

[35] Z. Mandić, L. Dujić, F. Kovačiček, The influence of counter-ions on nucleation and growth of electroche-mically synthesized polyaniline film, Electrochim. Acta **42** (1997) 389–1402.

[36] Handbook of Radical Polymerization, K. Matyjaszewski, T. Davys, Eds., John Wiley & Sons, Hoboken, NJ, 2002.

[37] P.C. Innis, Y.C. Chen, S. Ashraf, G.G. Wallace, Electro-hydrodynamic polymerisation of water-soluble poly ((4--(3-pyrrolyl)) butane sulfonate), Polymer **41** (2000) 4065–4076.

[38] J.M. Pringle, J. Efthimiadis, P.C. Howlett, J. Efthimiadis, D.R. MacFarlane, A.B. Chaplin, S.B. Hall, D.L. Officer, G.G. Wallace, M. Forsyth, Electrochemical synthesis of polypyrrole in ionic liquids, Polymer **45** (2004) 1447–1453.

[39] Y. Pornputtkul, L.A.P. Kane-Maguire, G.G. Wallace, Inf-luence of Electrochemical Polymerization Temperature on the Chiroptical Properties of (+)-Camphorsulfonic Acid-Doped Polyaniline, Macromolecules **39** (2006) 5604–5610.

[40] G. Inzelt, M. Pineri, J. Schultze, M. Vorotyntsev, Electron and proton conducting polymers: recent developments and prospects, Electrochim. Acta **45** (2000) 2403–2421.

[41] B.N. Grgur, P. Živković, M.M. Gvozdenović, Kinetics of the mild steel corrosion protection by polypyrrole-oxalate coating in sulfuric acid solution, Prog. Org. Coatings **56** (2006) 240–247.

[42] G. Ćirić-Marjanović, Recent advances in polyaniline research: Polymerization mechanisms, structural aspects, properties and applications, Synth. Met. **177** (2013) 1–47.

[43] B.N. Grgur, A. Žeradjanin, M.M. Gvozdenović, M.D. Maksimović, T.L. Trišović, B.Z. Jugović, Electrochemical characteristics of rechargeable polyaniline/lead dioxide cell, J. Power Sources **217** (2012) 193–198.

[44] D. Bhattacharjya, I. Mukhopadhyay, Controlled Growth of Polyaniline Fractals on HOPG through Potentio-dynamic Electropolymerization, Langmir **28** (2012) 5893–5899.

[45] M.M. Gvozdenović, B.Z. Jugović, J.S. Stevanović, T.Lj. Trišović, B.N. Grgur, Electrochemical Polymerization of Aniline, in Electropolzmeriyation, E. Schab-Balcerzak, Ed., InTech, Rijeka, 2011.

[46] V. Gupta, N. Miura, Large-area network of polyaniline nanowires prepared by potentiostatic deposition pro-cess, Electrochem. Commun. **7** (2005) 995–999.

[47] Z. Tang, S. Liu, Z. Wang, S. Dong, E. Wang, Electro-chemical synthesis of polyaniline nanoparticles, Electro-chem. Commun. **2** (2000) 32–35.

[48] V. Tsakova, A. Milchev, J. Schulze, Growth of polyaniline films under pulse potentiostatic conditions, J. Electro-anal. Chem. **346** (1993) 85–97.

[49] S. Mu, Y. Yang, Spectral characteristics of polyaniline nanostructures synthesized by using cyclic voltammetry at different scan rates, J. Phys. Chem., B **112** (2008) 11558–11563.

[50] V. Aboutanos, L.A.P. Kane-Maguire, G.G. Wallace, Elec-trosynthesis of polyurethane-based core-shell PAn (+)/-HCSA colloids, Synth. Met. **114** (2000) 313–320.

[51] P.C. Innis, I.D. Norris, L.A.P. Kane-Maguire, G.G. Wallace, Electrochemical Formation of Chiral Polyaniline Colloids Codoped with (+)- or (−)-10-Camphorsulfonic Acid and Polystyrene Sulfonate, Macromolecules **92** (1998) 6521––6528.

[52] A. Diaz, J. Crowley, J. Bargon, G. Gardini, J. Torrence, Electrooxidation of aromatic oligomers and conducting polymers, J. Electroanal. Chem. Interfacial Electrochem. **121** (1981) 355–361.

[53] S. Mu, Pronounced effect of the ionic liquid on the electrochromic property of the polyaniline film: Color changes in the wide wavelength range, Electrochim. Acta. **52** (2007) 7827–7834.

[54] Y. Sahin, A. Aydin, Y.A. Udum, K. Pekmez, A. Yildiz, Electrochemical synthesis of sulfonated polypyrrole in FSO3H/acetonitrile solution, J. Appl. Polym. Sci. (2004) 526–533.

[55] S. Perc, Electrochemical Synthesis of Poly(2-iodoaniline) and Poly(aniline-co-2-iodoaniline) in Acetonitrile, J. Appl. Polym. Sci. **89** (2003) 1652–1658.

[56] H. Okamoto, T. Kotaka, Structure and properties of poly-aniline films prepared via electrochemical polymeriz-ation. I: Effect of pH in electrochemical polymerization media on the primary structure and acid dissociation constant of product polyaniline films, Polymer **39** (1998) 4349–4358.

[57] [H. Okamoto, T. Kotaka, Effect of counter ions in elec-trochemical polymerization media on the structure and responses of the product polyaniline films III . Structure and properties of polyaniline films prepared via electrochemical polymerization, Polymer **40** (1998) 407––417.

[58] A. Syed, M. Dinesan, Polyaniline—A novel polymeric material,Talanta **38** (1991) 815–837.

[59] A. Pron, P. Rannou, Processible conjugated polymers : from organic semiconductors to organic metals and superconductors, Prog. Polym. Sci. **27** (2002) 135–190.

[60] A. McDiarmid, J. Chiang, M. Halpern, W. Huang, S. Mu, N. Somasiri, W. Wu, S. Yaniger, Polyaniline: Interconversion of Metallic and Insulating Forms, Mol. Cryst. Liq. Cryst. **121** (1985) 173–180.

[61] H. Javadi, F. Zuo, M. Angelopoulus, A. McDiarmid, A. Epstein, Frequency Dependent Conductivity of Emeraldine: Absence of Protonic Conductivity, Mol. Cryst. Liq. Cryst. Inc. Nonlinear Opt. **160** (1988) 225–233.

[62] N. Gospodinova, L. Terlemezyan, Conducting polymers prepared by oxidative polymerization: polyaniline, Prog. Polym. Sci. **23** (1998) 1443–1484.

[63] J. Stejskal, I. Sapurina, Polyaniline: Thin films and colloidal dispersions (IUPAC Technical Report), Pure Appl. Chem. **77** (2005) 815–826.

[64] J. Stejskal, P. Kratochvíl, A. Jenkins, The formation of polyaniline and the nature of its structures, Polymer **37** (1996) 1420–1481.

[65] P. Fedorko, M. Trznadel, A. Pron, D. Djurado, J. Planès, J. P. Travers, New analytical approach to the insulator–metal transition in conductive polyaniline, Synth. Met. **160** (2010) 1668–1671.

[66] N.V. Blinova, J. Stejskal, M. Trchová, J. Prokeš, M. Omastová, Polyaniline and polypyrrole: A comparative study of the preparation, Eur. Polym. J. **43** (2007) 2331––2341.

[67] J. Stejskal, I. Sapurina, M. Trchová, Polyaniline nanostructures and the role of aniline oligomers in their formation, Prog. Polym. Sci. **35** (2010) 1420–1481.

[68] G. Zotti, S. Cattarin, N. Comisso, Electrodeposition of polythiophene, polypyrrole and polyaniline by the cyclic potential sweep method, J. Electroanal. Chem. Interfacial Electrochem. **235** (1987) 259–273.

[69] A. Hussain, A. Kumar, Electrochemical synthesis and characterization of chloride doped polyaniline, Bulettin Mater. Sci. **26** (2003) 329–334.

[70] G. Zotti, S. Cattarin, N. Comisso, Cyclic potential sweep electropolymerization of aniline: The role of anions in the polymerization mechanism, J. Electroanal. Chem. Interfacial Electrochem. **239** (1988) 387–396.

[71] S. Mu, J. Kan, Evidence for the autocatalytic polymerization of aniline, Electrochim. Acta **41** (1996) 1593––1599.

[72] S. Mu, C. Chen, J. Wan, The kinetic behavior for the electrochemical polymerization of aniline in aqueous solution, Synth. Met. **88** (1997) 249–254.

[73] L. Arsov, W. Plieth, G. Koßmehl, Electrochemical and Raman spectroscopic study of polyaniline; influence of the potential on the degradation of polyaniline, J. Solid State Electrochem. **2** (1998) 355–361.

[74] A.R. Elkais, M.M. Gvozdenović, B.Z. Jugović, B.N. Grgur, The influence of thin benzoate-doped polyaniline coatings on corrosion protection of mild steel in different environments, Prog. Org. Coat. **76** (2013) 670–676.

[75] D.E. Tallman, G. Spinks, A. Dominis, G.G. Wallace, Electroactive conducting polymers for corrosion control, J. Solid State Electrochem. **6** (2002) 73–84.

[76] L. Duić, Z. Mandić, Counter-ion and pH effect on the electrochemical synthesis of polyaniline, J. Electroanal. Chem. **335** (1992) 207–221.

[77] H. Tang, A. Kitani, M. Shiotani, Effects of anions on electrochemical formation and overoxidation of polyaniline, Electrochim. Acta **41** (1996) 1561–1567.

[78] J. Lippe, R. Holze, The anion-specific effect in the overoxidation of polyaniline and polyindoline, J. Electroanal. Chem. **339** (1992) 411–422.

[79] V. Kertez, G. Inzelt, S. Pruneanu, E. Csaho, È. Lora, Electrochemical quartz crystal microbalance study of the influence of the solution composition on the behaviour of poly(aniline) electrodes, Electrochem. Commun. **43** (1998) 2305–2323.

[80] L. Mattoso, R. Faria, L. Bulhoes, A. MacDiarmid, Influence of electropolymerization conditions on the molecular weight of polyaniline, Polymer **35** (1994) 5104––5108.

[81] S. Zhou, T. Wu, J. Kan, Effect of methanol on morphology of polyaniline, Eur. Polym. J. **43** (2007) 395–402.

[82] S.H. Cho, S.K. Tae, L.J. Ypoung, Recent Advances in Polypyrrole, in: Conducting Polymers-Theory, Synthesis, Properties and Characterization, T. Skotheim, J. Reynolds, Eds., Teyor & Francis Group, 2007, pp. 1–87.

[83] T. Vernitskaya, O. Efimov, Polypyrrole: a conducting polymer; its synthesis, properties and applications, Russ. Chem. Rev. **66** (1997) 443–457.

[84] S. Carquigny, O. Segut, B. Lakard, F. Lallemand, P. Fievet, Effect of electrolyte solvent on the morphology of polypyrrole films: Application to the use of polypyrrole in pH sensors, Synth. Met. **158** (2008) 453–461.

[85] G.S. Akundy, J.O. Iroh, Polypyrrole coatings on aluminum – synthesis and characterization, Polymer **42** (2001) 9665–9669.

[86] N. Krstajić, B. Grgur, S. Jovanović, M. Vojinović, Corrosion protection of mild steel by polypyrrole coatings in acid sulfate solutions, Electrochim. Acta **42** (1997) 1685–1691.

[87] J. Nie, D.E. Tallman, G.P. Bierwagen, The electrodeposition of polypyrrole on Al alloy from room temperature ionic liquids, J. Coatings Technol. Res. **5** (2008) 327–334.

[88] S. Jovanović, R. Stanković, V. Laninović, G. Nestorović, M. M. Popović, B. Vidić, O. Pavlović, N. Krstajić, B.N. Grgur, S. Stanković, Synthesis and electrochemical properties of polypyrrole, polyaniline and poly-3-methyl thiophene, Hem. Ind. **54** (2000) 417–427.

[89] W. Su, J.O. Iroh, Electropolymerization of pyrrole on steel substrate in the presence of oxalic acid and amines, Electrochim. Acta **44** (1999) 2173–2184.

[90] C. Ferreira, S. Aeiyach, J. Aaron, P.C. Lacaze, Electrosynthesis of strongly adherent polypyrrole coatings on iron and mild steel in aqueous media, Electrochim. Acta **41** (1996) 1801–1809.

[91] I.L. Lehr, S.B. Saidman, Characterisation and corrosion protection properties of polypyrrole electropolymerised onto aluminium in the presence of molybdate and nitrate, Electrochim. Acta **51** (2006) 3249–3255.

[92] S. Dong, J. Ding, Study on polypyrrole film by electrochemical polymerization in aqueous solution, Synth. Met. **20** (1987) 119–124.

[93] M. Deepa, S. Ahmad, Polypyrrole films electropolymerized from ionic liquids and in a traditional liquid elec-

trolyte: A comparison of morphology and electro–optical properties, Eur. Polym. J. **44** (2008) 3288–3299.

[94] M. Kiani, G. Mitchell, The role of the counter-ion in the preparation of polypyrrole films with enhanced properties using a pulsed electrochemical potential, Synth. Met. **48** (1992) 203–218.

[95] M. Kiani, N. Bhatt, F. Davis, G. Mitchell, Highly anisotropic electrically conducting films based on polypyrrole, Polymer **33** (1992) 4113–4120.

[96] T. Shimadzu, A. Ohtani, K. Honda, Charge-controllable poly pyrrole/poly electrolyte composite membranes: Part III. Electrochemical deionization system constructed by anion-exchangeable and cation-exchangeable polypyrrole electrodes, J. Electroanal. Chem. **251** (1988) 323-337.

[97] K. Zhong, K. Doblhofer, Polypyrrole-based electrode coatings switchable electrochemically between the anion- and cation-exchanger states, Electrochim. Acta **35** (1990) 1971–1976.

IZVOD

ELEKTROHEMIJSKA SINTEZA ELEKTROPROVODNIH POLIMERA

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(Pregledni rad)

Tradicionalno shvatanje o polimerima kao odličnim izolatorima izmenjeno je sedamdesetih godina prošlog veka kada su naučnici uspeli da sintetizuju poiliacetilen čija je provodljivost bila bliska metalnoj. Ova činjenica ukazala je na novo svojstvo polimernih materijala i lansirala potpuno novo multidisciplinarno naučno polje, popularno nazvano, sintetički metali. Iako je danas pojmom elektroprovodnih polimera obuhvaćena velika grupa jedinjenja koja su klasifikovana prema prirodi prenosioca naelektrisanja, naziv elektroprovodni polimeri se najčešće koristi u literaturi upravo za polimerne materijala iz grupe sintetičkih metala koji poseduju elektronsku provodljivost kao posledicu specifičnosti molekulske strukture. Pored zahteva molekulske structure, koja podrazumeva konjugovani sistem dvostrukih veza, za provodljivost elektroprovodnih polimera neophodno je dopovanje. Termin dopovanje, iako preuzet iz terminologije klasičnih neorganskih poluprovodnika, podrazumeva u mnogome drugačiji proces. Dopovanje elektroprovodnih polimera podrazumeva oksidaciju tokom koje se, u cilju održavanja elektroneutralnosti polimernog lanca, uvodi stehiometrijska količina jona (anjona). Terminom dopovanje obuhvaćena je i protonacija polimernog lanca kiselinom, u slučaju polianilina, a nedavno je potvrđena i u slučaju polipirola. Kako je, na ovaj način, uvedena velika količina jona izmenjenja je polazna struktura elektroprovodnog polimera, tako da svojstva nastalog materijala zavise u velikoj meri od svojstava dopanta. Iako su na početku razvoja ove oblasti, elektroprovodni polimeri bili sintetizovani hemijskim postupcima, sticanjem uvida u mehanizam hemijske sinteze koja podrazumeva oksidativnu radikalnu polimerizaciju, postalo je jasno da se ovi materijali mogu dobiti i elektrohemijskim postupcima. Elektrohemijska sinteza ima prednosti, pošto se polimer dobija oksidacijom na elektrodama (anodama), čime je izbegnuta upotreba oksidacinog sredstva i omogućena veća čistoća proizvoda. Sa druge strane, elektroprovodni polimer je u većini slučajeva dobijen u obliku prevlake na elektrodi, pa je njegova dalja karakterizacija elektrohemijskim tenikama olakšana. Interesovanje za oblst sinteze elektroprovodnih polimera ne jenjava, pa je ovaj tekst posvećen osnovnim principima elektrohemijskih postupaka sinteze sa posebnim osvrtom na najpopularnije elektroprovodne polimere, polianilin i polipirol.

Ključne reči: elektrohemijska sinteza • anoda • polanilin • polipirol