

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Electrochemical Polymerization of Aniline

Milica M. Gvozdenović^{1,*}, Branimir Z. Jugović², Jasmina S. Stevanović³,
Tomislav Lj. Trišović² and Branimir N. Grgur¹

¹*Department of Physical Chemistry and Electrochemistry,
Faculty of Technology and Metallurgy, University of Belgrade, Belgrade,*

²*Institute of Technical Sciences, Serbian Academy of Science and Arts,*

³*Center for Electrochemistry, Institute of Technology and Metallurgy, Belgrade
Serbia*

1. Introduction

From its revolutionary discovery, up to day electroconducting polymers attracts attention of researchers along scientific community. Among numerous known electroconducting polymers, polyaniline and its derivatives are probably the most investigated. Such popularity, in both theoretical and practical aspects, is a consequence of its unique properties: existence of various oxidation states, electrical and optical activity, low cost monomer, red/ox reversibility, environmental stability etc. (Inzelt, 2008; Horvat-Radošević & Kvastek, 2006; Gospodinova & Terlemezyan, 1998). These diverse and important features seem to be promising in wide area of practical applications in: rechargeable power sources (Gvozdenović et al., 2011; Jugović et al., 2006; Jugović et al., 2009), sensors (Bezbradica et al., 2011; Dhaoui, 2008; Grummt et al. 1997, Gvozdenović et al., 2011; Mu & Xue, 1996), magnetic shielding, electrochemical capacitors (Xu et al., 2009), electrochromic devices (Kobayashi et al. as cited in Mu, 2004; Wallace et al., 2009), corrosion protection etc. (Biallozor & Kupniewska, 2005; Camalet et al., 1996, 1998, 2000a, 2000b; Gvozdenović & Grgur, 2009; Gvozdenović et al., 2011; Kraljić et al., 2003; Popović & Grgur, 2004; Popović et al. 2005, Grgur et al., 2006; Özyilmaz et al., 2006). Polyaniline is commonly obtained by chemical or electrochemical oxidative polymerization of aniline (Elkais et al., 2011; Jugović et al., 2009; Lapkowski, 1990; Stejskal & Gilbert, 2002; Stejskal et al., 2010) although photochemically initiated polymerization (Kim et al., 2001 as cited in Wallace et al., 2009; Teshima et al., 1998) and enzyme catalyzed polymerization were also reported (Bhadra et al., 2009; Nagarajan et al., 2000).

Polyaniline obtained by electrochemical polymerization is usually deposited on the electrode, however electrohydrodynamic route was also developed resulting in polyaniline colloids of specific functionalities (Wallace et al., 2009). Electrochemical polymerization of aniline is routinely carried out in strongly acidic aqueous electrolytes, through generally accepted mechanism which involves formation of anilinium radical cation by aniline oxidation on the electrode (Hussain & Kumar, 2003). Electrochemical polymerization of aniline is proved to be auto-catalyzed (Mu & Kan, 1995; Mu et al., 1997). The experimental conditions, such as: electrode material, electrolyte composition, dopant anions, pH of the

* Corresponding Author

electrolyte etc., all have strong influence on the nature of the polymerization process (Camalet et al., 2000; Ćirić Marjanović et al., 2006; Córdova et al., 1994; Duić & Mandić, 1992; Giz et al., 2000; Gvozdenović & Grgur, 2009; Inzlet, 2008; Lippe & Holze, 1992; Mu & Kan, 1998; Mun & Kan, 1998; Nunziante & Pistoia, 1989; Okamoto & Kotaka, 1998a, 1998b, 1999; Popović & Grgur, 2004; Pron et al., 1993; Pron & Rannou, 2010; Wallace et al., 2009). The low pH is almost always needed for preparation of the conductive polyaniline in the form of emeraldine salt, since it is evidenced that at higher pH, the deposited film is consisted of low chain oligomeric material (Stejskal et al., 2010). The doping anion incorporated into polymer usually determines the morphology, conductivity, rate of the polyaniline growth during electrochemical polymerization, and has influence on degradation process (Córdova et al., 1994; Lippe & Holze, 1992; Mandić et al., 1997; Okamoto & Kotaka, 1999, Pron & Rannou, 2010). The electrochemical polymerization of aniline is practically always carried out in aqueous electrolytes, although polymerization in organic solvents such as acetonitrile was also reported. Recently it was observed that ionic liquids electrolytes might be used for successful preparation of conductive polyaniline (Heinze et al., 2010; Wallace et al., 2009). Finally, electrochemical polymerization and co-polymerization of numerous substituted aniline derivatives, resulted in polymer materials with properties different from the parent polymer, were also investigated (Karyakin et al. 1994; Kumar, 2000; Mattoso & Bulhões, 1992; Mu, 2011; Zhang, 2006).

Since there is a still growing interest for the research in the field of conducting polymers with polyaniline as the most representative, the aim of this paper is to review the extremely rich literature attempting to describe all important aspects of electrochemical polymerization of aniline.

2. Polyaniline

Polyaniline is probably the eldest known electroconducting polymer, since it was used for textile coloring one century ago (Sayed & Dinesan, 1991; Wallace et al., 2009). The great interest in research of polyaniline is connected to discovery of its conductivity in the form of emeraldine salt and existence of different oxidation forms (Inzelt, 2008; MacDiarmid et al., as cited in Wallace et al., 2009; Syed & Dinesan, 1991).

2.1 Different oxidation states of polyaniline

Unlike other known electroconducting polymers, polyaniline can exist, depending on degree of oxidation, in different forms, known as: leucoemeraldine, emeraldine and pernigraniline. Leucoemeraldine, eg. leucoemeraldine base, refers to fully reduced form; emeraldine, eg. emeraldine base, is half-oxidized, while pernigraniline, eg. pernigraniline base, is completely oxidized form of polyaniline. The only conducting form of polyaniline is emeraldine salt, obtained by doping or protonation of emeraldine base (Fedorko et al., 2010; MacDiarmid et al., 1987, Pron & Rannou, 2002).

The unique feature of mentioned polyaniline forms is ease of its mutual conversions by both chemical and electrochemical reactions as it can be seen in Fig.1. (Gospodinova & Terlemezyan, 1998; Kang et al., 1998; Stejskal et al., 1996).

Apart from the changes in oxidation levels, all the transitions among polyaniline forms are manifested by color and conductivity changes (Stejskal et al., 1996). The conducting protonated emeraldine in the form of green emeraldine salt, obtained as a product of

electrochemical polymerization of aniline in acidic electrolytes, can be easily transformed by further oxidation to fully oxidized dark blue pernigraniline salt, which can be treated by alkali to form violet pernigraniline. Emeraldine salt can also be reduced to transparent leucoemeraldine, or can be transformed by alkali to blue non conducting emeraldine. The two blue forms of polyaniline, pernigraniline salt and emeraldine have different shades of blue (Stejskal et al., 1996). Both reduction of emeraldine salt to leucoemeraldine and oxidation to pernigraniline states are followed by decrease in conductivity (Stejskal et al., 2010).

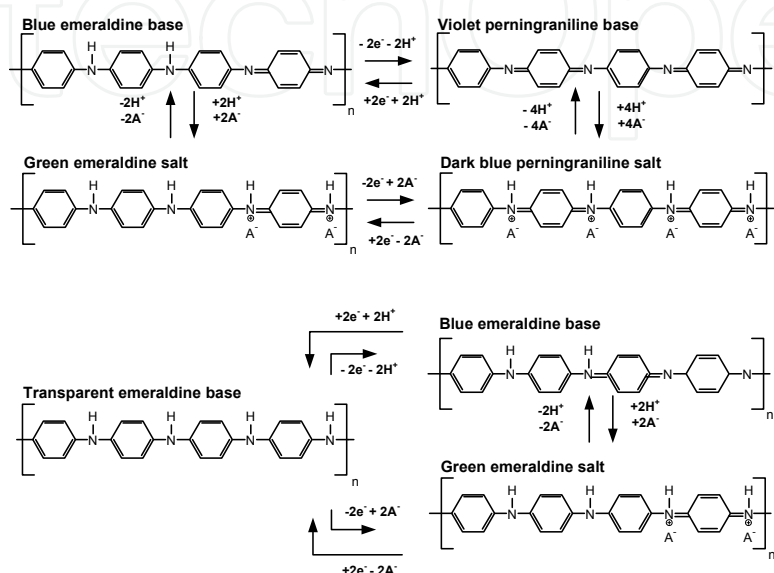


Fig. 1. Different forms of polyaniline

2.2 Polyaniline conductivity

The mechanism of polyaniline conductivity differs from other electroconducting polymers, owing to the fact that nitrogen atom is involved in the formation of radical cation, unlike most of the electroconducting polymers whose radical cation is formed at carbon. On the other hand, nitrogen is also involved in the conjugated double bonds system. Therefore, electrical conductivity of polyaniline is dependent both on the oxidation and protonation degrees (Fedorko et al., 2010; Genies et al., 1990; Pron & Rannou, 2002; Wallace et al., 2009).

As mentioned before, polyaniline is characterized by existence of various oxidation forms. Polyaniline in the form of emeraldine base can be doped (protonated) to conducting form of emeraldine salt. Emeraldine base, half oxidized form, is consisted of equal amount of amine ($-NH-$) and imine ($=NH-$) sites. Imine sites are subjected to protonation to form bipolarone or dication (emeraldine salt form). Bipolarone is further dissociated by injection of two electrons both from electron pairs of two imine nitrogen, into quinodimine ring, and the third double bond of benzenoid ring is formed (Stejskal, 2010).

Unpaired electrons at nitrogen atoms are cation radicals, but essentially they represent polarons. The polaron lattice, responsible for high conductivity of polyaniline in the form of emeraldine salt is formed by redistribution of polarons along polymer chain, according to schematic representation given in Fig. 2. (Wallace et al., 2009)

Although both bipolaron and polaron theoretical models of emeraldine salt conductivity were proposed (Angelopoulos et al., as cited in Wallace et al., 2009; Tanaka et al., 1990), it was lately confirmed that, beside from the fact that few of spineless bipolarons exist in

polyaniline, formation of polarons as charge carriers explained high conductivity of polyaniline (Mu et al., 1998; Patil et al., 2002). As mentioned, unique property of polyaniline is conductivity dependence on the doping (proton) level (Chiang et al., 1986; Wallace et al., 2009). The maximal conductivity of polyaniline is achieved at doping degree of 50%, which corresponds to polyaniline in the form of emeraldine salt (Tanaka et al., 1989). For higher doping degrees some of the amine sites are protonated, while lower doping degrees means that some of the imine sites were left unprotonated (Wallace et al., 2009), explaining why, in the light of the polaron conductivity model, reduction of emeraldine salt to leucoemeraldine and oxidation to pernigraniline states decrease the conductivity. The order of magnitude for conductivity varies from $10^{-2} \text{ S cm}^{-1}$, for undoped emeraldine, up to 10^3 S cm^{-1} for doped emeraldine salt (Inzelt, 2008; Wallace et al., 2009).

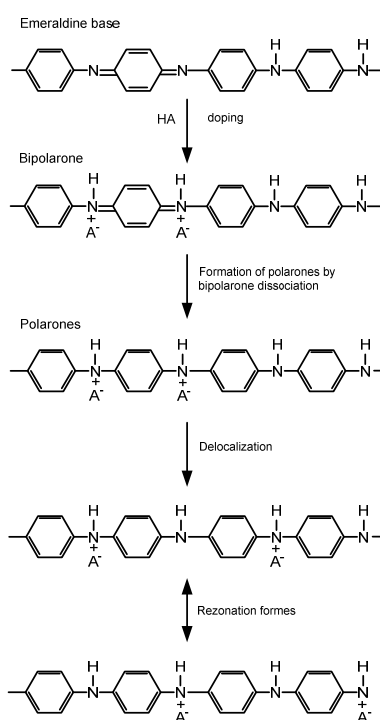


Fig. 2. Schematic presentation of polyaniline conductivity

Beside the fact that doping degree has the pronounced effect on the conductivity, various other factors such as: moisture amount (Kahol et al., 1997; Patil et al., 2002), morphology (Monkman & Adams, 1991; Zhou et al., 2007), temperature (Probst & Holze, 1995) etc. were also found to have influence on the polyaniline conductivity.

3. Mechanism and kinetics of the electrochemical polymerization of aniline

Generally, electroconducting polymers are obtained by either chemical or electrochemical oxidative polymerization, although reductive polymerization was also reported (Heinze et al., 2010; Inzelt et al., 2000; Yamamoto & Okida, 1999; Yamamoto, 2003, as cited in Inzelt, 2008). Chemical polymerization is used when large quantity of polymer is requested. Electrochemical polymerization is favorable, since in the most cases the polymer is directly deposited on the electrode facilitating analysis. On the other hand, electrochemical polymerization is especially useful if polymer film electrode is needed. By proper design of

the electrochemical experiment, polymer thickness and conductivity can be easily controlled. It is believed that electrochemical polymerization is consisted of three different steps, in first, oxidation of the monomer at anode lead to formation of soluble oligomers in the diffusion layer, in the second, deposition of oligomers occurs through nucleation and growth process, and finally, the third step is responsible for chain propagation by solid state polymerization (Heinze et al., 2010). Unfortunately, a general mechanism of electrochemical polymerization could not be established, since it was evidenced that various factors had influence. However, it was observed that first step of the electrochemical polymerization was formation of reactive cation radicals (Heinze et al., 2010; Kankare, 1998). The next step, strongly dependent on the experimental conditions, is believed to be essential for the polymer growth (Inzelt, 2008). The knowledge on the kinetics of the nucleation and growth process during electrochemical synthesis of electroconducting polymers is also of great interest, since it would be useful in control of the morphology, density, crystallinity etc. of the desired polymer.

3.1 Mechanism

Both the mechanism and the kinetics of the electrochemical polymerization of aniline were extensively investigated (Andrade et al. 1998; Arsov et al. 1998; Carlos et al. 1997; Hussain & Kumar, 2003; Inzelt et al., 2000, Bade et al. 1992; Lapkowski, 1990; Malinauskas et Holze, 1998; Mandić et al., 1997; Mu & Kan, 1995; Mu et al., 1997). Electrochemical, similarly to chemical, polymerization of aniline is carried out only in acidic electrolyte, since higher pH leads to formation of short conjugation oligomeric material, with different nature (Wallace et al., 2009). As stated before, it is generally accepted that the first step of the polymerization process of aniline involves formation of aniline cation radicals, by anodic oxidation on the electrode surface, which is considered to be the rate-determining step (Zotti et al., 1987, 1988). The existence of aniline radical cation was experimentally confirmed, by introducing molecules, (resorcinol, hydroquinone, benzoquinine etc.), capable of retarding or even stopping the reaction, which evidenced a radical mechanism (Mu et al., 1997). The oxidation of the aniline monomer is an irreversible process, occurring at higher positive potentials than redox potential of the polyaniline (Inzelt, 2008).

The following step is dependent on numerous factors such as: electrolyte composition, deposition current density, or potential scan rate, nature and state of the anode material, temperature etc. (Inzelt, 2008). There is a request for relatively high concentration of radical cations near the electrode surface. Radical cations can be involved, depending on reactivity, in different reactions. If it is quite stable, it may diffuse into the solution and react to form soluble products of low molecular weights. On the other hand, if is very unstable, it can react rapidly with anion or the solvent, in the vicinity of the electrode and form soluble products with low molecular weights (Park & Joong, 2005). In favorable case, coupling of the anilinium radicals would occur, followed by elimination of two protons and rearomatization leading to formation of dimer (lately oligomer). The aniline dimer, or oligomer, is further oxidized on the anode together with aniline. The chain propagation is achieved by coupling radical cations of the oligomer with anilinium radical cation. Finally, the counter anion originating from the acid, normally present in the electrolyte, dopes the polymer, meeting the request of electroneutrality. The mentioned mechanism of aniline electrochemical polymerization is schematically presented in Fig. 3 (Hussain & Kumar 2003, Wallace et al. 2009).

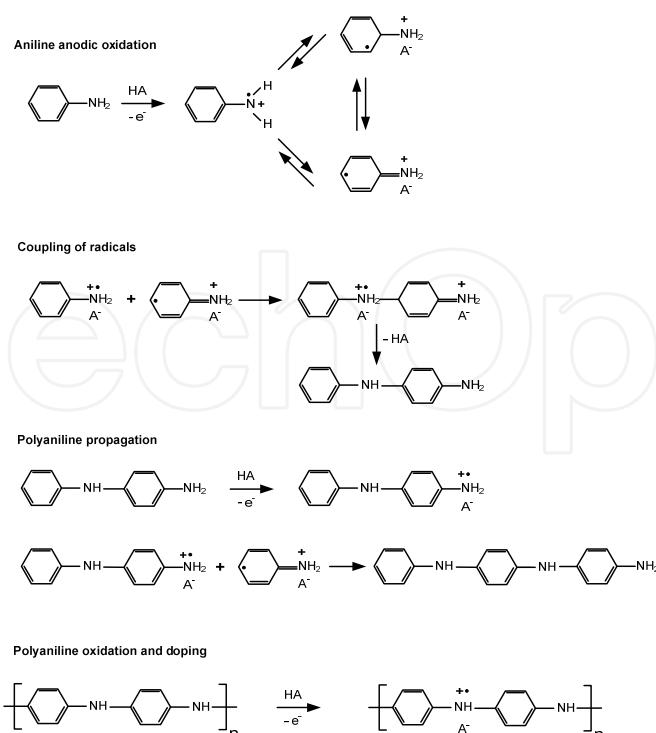


Fig. 3. Schematic presentation of mechanism of electrochemical polymerization of aniline.

It was evidenced that electrochemical polymerization of aniline is an autocatalytic process (Inzelt, 2008; Mu & Kan, 1996; Mu et al., 1997; Stilwell & Park, 1996; Wallace et al., 2009). It was observed that current increased over time, at constant potentials higher than 0.80 V and that anodic peak potentials shifted to more negative values upon increasing cycle number (Mu et al., 1997). Generally, it means that the more polymer formed on the anode, the higher the rate of the electrochemical polymerization.

3.2 Nucleation and growth of polyaniline

Explanation of the kinetics of the nucleation and growth process during electrochemical synthesis of electroconducting polymers is usually relaying on the metal deposition theory (Heinze et al., 2010; Kankare, 1998). According to the theory, two kinds of nucleation process exist, instantaneous and progressive, with three types of growth referring to: one- (1D), two- (2D), and three- (3D) dimensional processes. Instantaneous nucleation implies constant number of nuclei, growing without the further formation of nuclei. In the case of progressive nucleation, nuclei are constantly generated. 1D growth implies growth in only one direction, e.g. perpendicular to the electrode surface. In the 2D growth, the nuclei has preference to grow parallel to the electrode surface, while the 3D growth is characterized by the similar rates for these processes perpendicular and parallel to the electrode are quite similar (Heinze et al., 2010).

It was shown, mostly base on potentiostatic experiments, that several stages of polyaniline growth during electrochemical polymerization of aniline were involved, proceeding through different mechanism (Mandić et al., 1997). Cyclic voltammetry studies indicated that polyaniline growth was strongly dependent on type and concentration of anion in the electrolyte (Zotti et al., 1988). Studies on the early stages of the polyaniline growth indicate progressive nucleation of the polyaniline film, with 2D or 3D growth mechanism or 3D

instantaneous nucleation, depending on electrolyte concentration and composition (Bade et al., 1992; Córdova et al., 1994; Mandić et al., 1997). The mass transfer controlled early stage of the polyaniline growth leads to formation of a compact layer (Inzelt 2010). In the case of perchloric acid, depending on monomer concentration, the nucleation process proceeds from progressive, at lower, to instantaneous nucleation at higher concentration (Mandić et al., 1997). At advanced stage, characterized by exponential current increase, 1D growth was assumed, resulted in continual branching and formation of the open structure (Cruz & Ticianelli, 1997).

3.3 Factors affecting electrochemical polymerization of aniline

Electrochemical synthesis of electroconducting polymers is strongly dependent on numerous parameters involved, such as: nature of the doping anion (affecting morphology, order of the polymer rate growth, nature and the composition of the solvent (to nucleophilic solvent would react with cation radicals formed by monomer oxidation on the anode) electrode material (depending on its surface energy controls the ease of the desired polymer deposition), temperature of the electrochemical polymerization etc. (Heinze et al., 2010; Inzelt, 2008; Pron & Rannou, 2002; Pruneanu et al., 1998; Wallace et al., 2009).

3.3.1 Doping anions

Electrochemical polymerization of aniline, as mentioned before, is practically always carried out in strong acidic aqueous electrolytes. Doping anions incorporated in polyaniline originate from the acid, and represent its conjugated base. The dopant anions are inserted during electrochemical polymerization fulfilling the request of electroneutrality, and therefore their concentrations are on the stoichiometric levels, for its reasonable that their presence have strong influence on, polyaniline morphology, conductivity, and electrochemical activity and the polymerization process itself (Arsov et al., 1998; Cordova et al., 1994; Dhaoui et al., 2008; Koziel, 1993, 1995; Lapkowski, 1990, 1993; Lippe & Holze, 1992; Okamoto & Kotaka, 1998; Pron et al., 1992; Pron & Rannou, 2002).

It was experimentally confirmed that polyaniline obtained in the presence of so called “large dopant anions”, originated from hydrochloride acid, sulfuric acid, nitric acid, *p*-toluensulfonic acid, and sulfosalicylic acid promoted formation of more swollen and open structured film, while the presence of “small ions” such is ClO_4^- or BF_4^- , resulted in formation of a more compact structure (Nunziante & Pistoria, 1989; Pruneanu et al., 1998; Zotti et al., 1988). The order of the polyaniline growth was also proved to increase with the size of the dopant anion (Inzelt et al., 2000). It was shown that addition of polyelectrolytes in polymerization electrolyte resulted in insertion of these molecules as dopants (Hyodo & Nozaki 1988, as cited in Wallace et al. 2009). It was also possible to obtain optically active polyaniline by electrochemical polymerization in the presence of (+) or (-) camphorsulfonic acid, leading to insertion of chiral dopants (Majidi et al., 2009).

3.3.2 Electrolyte composition

As mentioned previously, electrochemical polymerization of aniline is usually performed in aqueous electrolytes. There is limited number of studies referred to electrochemical polymerization in non-aqueous solvents (Genies & Lapkowski, 1987; Lapkowski, 1990; Pandey & Singh, 2002; Şahin et al., 2003). In the early studies acetonitrile was mostly used as solvent, for example Watambe et al. (Miras et al. 1991; Watambe et al. 1989, as cited in

Wallace et al., 2009) made first electrochemical polymerization of aniline in acetonitrile solution containing lithium perchlorate, the resulted polymer exhibited similar redox properties as “ordinary” prepared polyaniline.

Lately, apart from acetonitrile, the studies involved use of: dichlormethane, nitrobenzene with various electrolytes such as: sodium tetraphenylborate, tetraethylammonium tetrafluoroborate and tetraethylammoniumperchlorate and resulted films showed different microstructures and electrochemical activity (Pandey & Singh, 2002). Other studies referred to electrochemical polymerization of aniline and fluoro- and chloro- substituted anilines and their copolymers with aniline in acetonitrile containing tetrabutylammonium perchlorate and perchloric acid. The obtained polymers exhibited similar electrochemical and UV-behavior to “ordinary” polyaniline, but their conductivities were remarkably lower, explained by the steric effects of the substituent (Şahin et al. 2003). Various alkyl substituted anilines were electrochemically polymerized in both acetonitrile and dimethylsulfoxide, their conductivities were also very low suggested that there were not in the typical state of the emeraldine salt (Yano et al., 2004). Successful electrochemical co-polymerization of aniline and pyrrole was also carried out in acetonitrile.

Finally, electrochemical polymerization of aniline was performed in various ionic liquids (Heinze et al., 2010; Innis et al., 2004; Li et al., 2005; Mu, 2007). For example, using IR and NMR spectroscopy Mu showed that the ionic liquid, namely 1-ethyl-3-methylimidazolium ethyl sulfate was incorporated in polyaniline during electrochemical polymerization. It was also observed that resulted polyaniline had exhibited good electrochemical activity in solutions with pH 12, and also considerably wider window of the detectable color changes at higher pH values, this effect was explained by the fact that used ionic liquid possessed high buffer capacity, which improved the redox activity and the electrochemical activity in broader pH range (Mu, 2007). Apart from the strong influence of the solvent, the presence of other components in the electrolyte solution, used for electrochemical polymerization of aniline, also had influence, primarily, on the morphology of the deposit (Inzelt, 2008). It was shown that presence of alcohols in the electrolyte would lead to polyaniline in the form of nanofibres agglomerated into interconnected network, FTIR spectra of the resulted polymer revealed strong interactions between alcohol and polyaniline molecules (Zhou et al., 2008).

3.3.3 Electrode material

Electrochemical polymerization of aniline is easily performed at so called inert electrodes, such as: platinum, gold, various graphite, carbons or indium-tin-oxide glasses, according to previously described mechanism. But the fact that relatively high electrode potential is required for oxidation of aniline, restricts the usage of other materials. The electrochemical polymerization of aniline on active metals is usually considered for application in corrosion protection (Biallozor & Kupniewska, 2005; Tallman et al., 2002). The problem connected to electrochemical polymerization onto active metals is either dissolution, or formation of non-conducting passive layer, on the potentials necessary for oxidation of aniline.

In the case of iron and steel the potential at which polymerization starts is in the region of active dissolution, leading to lost of the metal and contamination of the electrolyte, therefore it necessary to find a suitable electrolyte that would enable strong passivation of the metal without suppressing further electrochemical polymerization. The most common electrolyte used to electrochemical deposition of polyaniline on steel and aluminum is oxalic acid (Camalet et al., 1996, 2000a, 2000b; Martyak et al., 2002). The use of oxalic acid permitted

formation of passive layer consisted of iron oxalate, on which aniline polymerize. It was also showed that *p*-toluen sulfonic acid can be used for electrochemical polymerization of aniline, the deposition occurred after passivation. The passive film, in contrast to oxalic acid, was consisted mainly of iron oxide (Camalet et al., 1998). Other approach involves the pretreatment of the steel surface by polypyrrole, which can be easily formed electrochemically on iron and steel, with low extent of the metal dissolution, after this treatment aniline is easily electrochemically polymerized (Lacroix et al., 2000). The problem with electrochemical polymerization of aniline on aluminum is occurrence of two simultaneous processes electrochemical polymerization and passivation of the electrode by very stable protective oxide (Biallozor & Kupniewska, 2005). The studies of electrochemical polymerization on aluminum and its alloys involved pretreatment of the metal, and further polymerization (Huerta-Vilca et al., 2005; Wang & Tan, 2006). Similarly to steel, oxalic acid and *p*-toluen sulfonic acid electrolytes were used to grow polyaniline on aluminum (Conroy & Breslin, 2005; Karpagam et al., 2008). It was shown that sodium benzoate could be used to electrochemically polymerize aniline, without need for pretreatment, on steel, copper and aluminum (Gvozdenović & Grgur, 2009; Gvozdenović et al. 2011; Popović & Grgur, 2004). Electrochemical polymerization of substituted anilines on various metals and alloys were also carried out (Chaudhari & Patil 2007; Chaudhari et al., 2009; Pawar et al., 2007).

3.4 Experimental performance

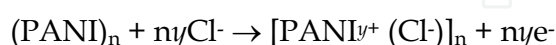
Generally, experimental set-up for electrochemical synthesis of electroconducting polymers in laboratory conditions is simple. It involves, in majority of cases, standard three-electrode electrochemical cell, although in some cases of galvanostatic polymerization, two electrode cell can be used (Wallace et al., 2009). The polymer obtained by this procedure is deposited directly on the electrode. Novel experimental set-up, enabling electrochemical generation of polyaniline colloids, using flow-through electrochemical cell, was also reported (Aboutanos et al., 1999; Innis et al., 1998). In this novel electrochemical cell, anode was separated from two and cathodes by ion exchange membrane. The anodic and cathodic electrolytes were passed through electrode compartments at specified flow, while polymerization was achieved at constant potential.

The most common experimental techniques used for electrochemical polymerization of aniline are: cyclic voltammetry (potentiodynamic), galvanostatic and potentiostatic techniques. Polymerization using cyclic voltammetry is characterized by cyclic regular change of the electrode potential and the deposited polymer is, throughout the experiment, changing between its non-conducting and conducting (doped) state, followed by exchange of the electrolyte through polymer (Heinze et al., 2010). At the end of polymerization the obtained polymer is in its non-conducting form, moreover, cyclic voltammetry favors formation of disordered chains and open structure (Heinze et al., 2010) As stated before, relatively high potential is required for electrochemical oxidation of aniline monomer, therefore at first 2 – 10 cycles, the upper potential limit is high, but owing to autocatalytic nature of aniline electropolymerization, the upper potential limit can be decreased to avoid degradation resulted from over oxidation of pernigranilin form of polyaniline (Inzelt, 2008). Recently, it was shown that cyclic voltammetry can even be useful for formation of nanostructure polyaniline. It was shown that different sized polyaniline nanofibres were electrochemically polymerized, by different scan rates, in the presence of ferrocensulfonic acid (Mu & Yang, 2008).

Galvanostatic polymerization, owing to current control, enables reaction to proceed at constant rate. Galvanostatic synthesis permits estimation of the polymer mass deposited on the electrode (Kankare, 1998). On the other hand, galvanostatic polymerization leads to formation of polyaniline in its conductive form.

Electrochemical polymerization of aniline on graphite electrode from hydrochloride acid electrolyte, obtained by cyclic voltammetry (numbers on the figure refers to cycle number) given in Fig. 4., while in the insert of the Fig.4, chronopotentiometric curve of galvanostatic polymerization from the same electrolyte is shown (Gvozdenović et al., 2011; Jugović, PhD thesis, 2009; Jugović et al., 2009)

Electrochemical polymerization of aniline proceeds together with insertion of chloride anions (dopant) from the electrolyte, according to:



Where γ refers to doping degree, ration between the number of charges in the polymer and the number of monomer units (Kankare, 1998).

As seen on cyclic voltammograms in Fig.4., doping of chloride ions started at potential of ~ -0.1 V (SCE), the first well defined anodic peak, situated at potential of 0.2 V (SCE) indicate transition of leucoemeraldine form of polyaniline to emeraldine salt, followed by the changes of γ between 0 and 0.5.

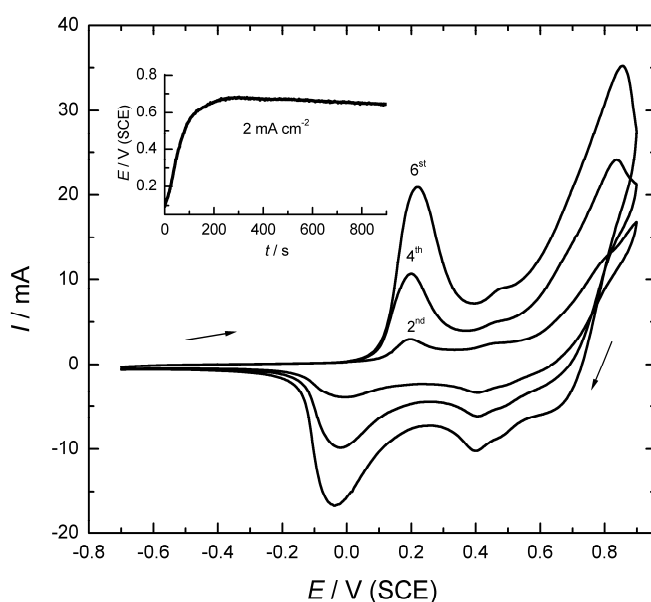


Fig. 4. Cyclic voltammograms of electrochemical polymerization of aniline on graphite electrode from aqueous solution of 1.0 mol dm^{-3} HCl and 0.25 mol dm^{-3} aniline, at scan rate of 20 mV s^{-1} . Insert: Chronopotentiometric curves of aniline polymerization at constant current density of 2.0 mA cm^{-2} .

Second anodic peak, occurred at potential of ~ 0.5 V (SCE) denotes formation of fully doped pernigraniline salt ($\gamma = 1$).

The potentiostatic technique of electrochemical polymerization is characterized by pronounced changes in the current i.e. polymerization rate, and similarly to galvanostatic polymerization obtained polymer is in its doped form (Heinze et al., 2010). It was observed

that potentiostatic method could be useful in obtaining polyaniline nanowires (Gupta & Miura, 2007). Modified potentiostatic techniques were also reported.

Some of the researches used pulse potentiostatic technique to obtain polyaniline electrochemically (Tang et al., 2000; Tsakova et al., 1993; Zhou et al., 2007). The potentiostatic pulse technique implies application of periodic cathodic and anodic pulses, with important parameters, lower (cathodic) and upper (anodic) limit potentials with additional cathodic and anodic pulses duration, during given time. It was observed (Zhou et al., 2007) that mentioned parameters had strong influence on the morphology of polyaniline, thus on its electrochemical activity.

3.5 Electrochemical co-polymerization of aniline and aniline derivatives

Owing to its conductivity and redox activity, polyaniline is considered for practical application in various fields. Unfortunately, beside its unique properties, application of polyaniline in biochemical systems is limited as a consequence of the loss of activity at pH above 4 (Karyakin et al., 1994; Malinauskas, 1999; Mu 2011). This problem might be overcome by introduction of so-called pH functional groups into polyaniline chain (Mu, 2011). This could be achieved either by sulfonation (Wei et al., 1996) or by co-polymerization, which is more efficient way to alter the properties of parent polymer. Electrochemical polymerization of aniline and aniline derivatives with pH functional groups, sulpho, carboxyl or hydroxyl was reported. It was observed that self-doped polyanilines, obtained by electrochemical co-polymerization of aniline with: *o*-aminobenzoic acid, *m*-aminobenzoic acid, or *m*-aminobenzenesulfonic acid had exhibited redox activity at high pH (Karyakin et al., 1996).

Apart from aniline and aniline derivative, electrolyte solution also contains acid necessary for protonation of nitrogen atom. The obtained co-polymers are often called self-doped polyanilines, since the introduced negatively charged functional groups play a role of an intermolecular dopant which is able to compensate the charge on positively charged nitrogen atoms of the polymer. The presence of intermolecular anion alters properties of "ordinary" polyaniline, and has influence on the polymerization process as well. It was shown that upper switching potential limit had important influence on self-doping, the limit of 0.9 V was proven to be optimal, and while in the case of unsubstituted aniline, upper limit was lower.

The problem related to electrochemical activity of self-doped polyaniline is its rapid loss. Recently, it was shown that electrochemical polymerization of aniline and 5-aminosalicylic acid, which has two acidic functional groups, had led to co-polymer with satisfactory redox activity (Mu, 2011).

4. Conclusion

Although polyaniline is among the first known electroconductive polymers, the interest in this field of study still exists, since its diverse and unique properties can be useful in various practical applications. Electrochemical polymerization of aniline and aniline derivatives were intensively investigated. Various factors such as: electrode material, dopant anions, electrolyte composition, monomer type, pH etc. were proven to exhibit influence in the electropolymerization process and properties of the desired polymer. The electrochemical synthesis of polyaniline, similar to chemical, is practically always performed in strong acidic

electrolytes, according to radical mechanism, and the polymer is deposited on anode, permitting easy way for further analysis. It was also proved that, using inconvenient experimental setup, polyaniline colloids can also be obtained electrochemically. Finally, studies of electrochemical co-polymerization of aniline and its derivatives with acidic functional groups were also performed, leading to so called self-doped polyanilines, with benefit of being electrochemically active even in high pH solutions.

5. Acknowledgment

This work was supported by the Ministry of Education and Science, Republic of Serbia, under Contract No. 172046

6. References

- Aboutanos V.; Barisci J.; Kane-Maguire L. & Wallace G. (1999). Electrochemical preparation of chiral polyaniline nanocomposites. *Synthetic Metals*, Vol. 106, No. 2, (October 1999), pp. 89-95, ISSN0379-6779
- Andrade G.; Aguirre M. & Biaggi S.(1998). Influence of the first potential scan on the morphology and electrical properties of potentiodynamically grown polyaniline films. *Electrochimica Acta*, Vol. 44, No. 4, (September 1998), pp. 633-642, ISSN0013-4686
- Arsov Lj.; Plieth W. & Koßmehl. (1998). Electrochemical and Raman spectroscopic study of polyaniline; influence of the potential on the degradation of polyaniline. *Journal of Solid State Electrochemistry*, Vol. 2, No. 5, (August 1998), pp. 355-361, ISSN1432-8488
- Bade K.; Tsakova V. & Schultze J. (1992). Nucleation, growth and branching of polyaniline from microelectrode experiments. *Electrochimica Acta*, Vol. 37, No. 12, (September 1992), pp. 2255-2261, ISSN0013-4686
- Bernard M.-C.; Cordoba de Torresi S. & Hugot-Le Goff A.(1999). In situ Raman study of sulfonate-doped polyaniline. *Electrochimica Acta*, Vol. 44, No. 12, (January 1999), pp. 1989-1997, ISSN0013-4686
- Bezbradica D.; Jugović B.; Gvozdenović M.; Jakovetić S. & Knežević-Jugović Z. (2011). Electrochemically synthesized polyaniline as support for lipase immobilization. *Journal of Molecular Catalysis B: Enzymatic*, Vol. 70, No. 1-2, (June 2011), pp. 55-60, ISSN1381-1177
- Bhadani, S.; Gupta M. & Sen Gupta S. Cyclic Voltammetry and Conductivity Investigations of Polyaniline. (1993), *Journal of Applied Polymer Science*, Vol. 49, No. 3 (July 1993), pp. 397-403, ISSN0021-8995
- Bhadra S.; Khastgir D.; Singha N. & Lee J. (2009). Progress in preparation, processing and applications of polyaniline. *Progress in Polymer Science*, Vol. 34, No. 8, (August 2009), pp. 783-810, ISSN0079-6700
- Biallozor S. & Kupniewska A. (2005). Conducting polymers electrodeposited on active metals. *Synthetic Metals*, Vol. 155, No. 3, (December 2005), pp. 443-449, ISSN0379-6779
- Camalet J.; Lacroix J.; Aeiya S. & Lacaze P.(1998). Characterization of polyaniline films electrodeposited on mild steel in aqueous *p*-toluenesulfonic acid solution. *Journal of Electroanalytical Chemistry*, Vol. 445, No.1-2 (March 1998) pp. 117-129, ISSN1572-6657

- Camalet J.; Lacroix J.; Aeiyaich S.; Chane-Ching K. & Lacaze P. Electrodeposition of protective polyaniline films on mild steel. *Journal of Electroanalytical Chemistry*, Vol. 416, No. 1-2, (November 1996), pp. 179-182, ISSN1572-6657
- Camalet J.; Lacroix J.; Aeiyaich S.; Chane-Ching K.; Petit Jean J.; Chauveau E. & Lacaze P. (2000). Aniline electropolymerization on mild steel and zinc in a two-step process. *Journal of Electroanalytical Chemistry*, Vol. 481, No.1 (January 2000) pp. 76-81 ISSN1572-6657
- Camalet J.; Lacroix J.; Ngyen T.; Aeiyaich S.; Pham M.; Petit Jean J. & Lacaze P.-C. (2000). Aniline electropolymerization on platinum and mild steel from neutral aqueous media. *Journal of Electroanalytical Chemistry*, Vol. 485, No.1 (May 2000) pp. 13-20, ISSN1572-6657
- Chaudhari S. & Patil P. (2007). Corrosion protective poly(*o*-ethoxyaniline) coatings on copper. *Electrochimica Acta*, Vol. 53, No. 2, (December 2007), pp. 927-933, ISSN0013-4686
- Chaudhari S.; Gaikwad A. & Patil P.(2009). Poly(*o*-anisidine) coatings on brass: Synthesis, characterization and corrosion protection. *Current Applied Physics*, Vol. 9, No. 1, (January 2009), pp. 206-218, ISSN1567-1739
- Chiang J. & MacDiarmid A. (1986). Polyaniline: Protonic acid doping of the emeraldine form to the metallic regime. *Synthetic Metals*, Vol. 13, No. 1-3, (January 1986), pp. 193-205, ISSN0379-6779
- Ćiric-Marjanović G.; Marjanović N., Popović M.; Panić V.& Mišković-Stanković V. (2006). Anilinium 5-sulfosalicylate electropolymerization on mild steel from an aqueous solution of sodium 5-sulfosalicylate/disodium 5-sulfosalicylate. *Russian Journal of Electrochemistry*, Vol. 42, No. 12, (December 2006), pp. 1358-1364, ISSN1023-1935
- Conroy K. & Breslin C.(2003).The electrochemical deposition of polyaniline at pure aluminium: electrochemical activity and corrosion protection properties. *Electrochimica Acta*, Vol. 48, No. 6, (February 2003), pp. 721-732, ISSN0013-4686
- Córdova R.; del Valle M.; Arratia A.; Gómez H. Schrelber R. (1994). Effects of anions on the nucleation and growth mechanism of polyaniline. *Journal of Electroanalytical Chemistry*, Vol. 377, No. 1-2, (October 1994), pp. 75-83, ISSN1572-6657
- Cruz C. & Ticianelli E. (1997).Electrochemical and ellipsometric studies of polyaniline films grown under cycling conditions. *Journal of Electroanalytical Chemistry*, Vol. 428, No. 1-2, (May 1997), pp. 185-192, ISSN1572-6657
- Dalmolin C.; Canobre S.; Biaggio S.; Rocha-Filho R.; Bocchi N. Electropolymerization of polyaniline on high surface area carbon substrates. *Journal of Electroanalytical Chemistry*, Vol. 578, No. 1, (April 2005), pp. 9-15, ISSN1572-6657
- Dhaoui W.; Bouzitoun M.; Zarrouk H.; Ouada H. & Pron A. (2008). Electrochemical sensor for nitrite determination based on thin films of sulfamic acid doped polyaniline deposited on Si/SiO₂ structures in electrolyte/insulator/semiconductor (E.I.S.) configuration. *Synthetic Metals*, Vol. 158, No.17-18, (October 2008), pp. 722-726, ISSN0379-6779
- Duić Lj. & Mandić Z. (1992). Counter-ion and pH effect on the electrochemical synthesis of polyaniline. *Journal of Electroanalytical Chemistry*, Vol. 335, No. 1-2, (September 1992), pp. 207-221, ISSN1572-6657
- Elkais A.; Gvozdenović M.; Jugović B.; Stevanović J.; Nikolić N.; Grgur B. (2011). Electrochemical synthesis and characterization of polyaniline thin film and

- polyaniline powder, *Progress in Organic Coatings*, Vol. 71, No. 1, (May 2011) pp. 32-35, ISSN0300-9440
- Fedorko P.; Trznadel M.; Pron A.; Djurado D.; Planès J. & Travers J. (2010). New analytical approach to the insulator-metal transition in conductive polyaniline. *Synthetic Metals*, Vol. 160, No. 15-16, (August 2010), pp. 1668-1671, ISSN0379-6779
- Ferreira V.; Cascalheira A. & Abrantes L. (2008). Electrochemical preparation and characterisation of Poly(Luminol-Aniline) films. *Thin Solid Films*, Vol. 516, No. 12, (April 2008), pp. 3996-4001 ISSN0040-6090
- Genies E.; Boyle A.; Lapkowski M. & Tsintavis. (1990). Polyaniline: A historical survey. *Synthetic Metals*, Vol. 36, No. 2, (June 1990), pp. 139-182, ISSN0379-6779
- Giz M.; de Albuquerque Maranhão S. & Torresi R. (2000). AFM morphological study of electropolymerized polyaniline films modified by surfactant and large anions. *Electrochemistry Communications*, Vol.2, No. 6, (June 2000), pp. 377-381, ISSN1388-2481
- Gospodinova N. & Terlemezyan L. Conducting polymers prepared by oxidative polymerization: polyaniline. (1998). *Progress in Polymer Science*, Vol. 23, No. 8, (December 1998), pp. 1443-1484, ISSN0079-6700
- Grgur B.; Gvozdenović M.; Mišković-Stanković V. & Kačarević-Popović Z. (2006). Corrosion behavior and thermal stability of electrodeposited PANI/epoxy coating system on mild steel in sodium chloride solution. *Progress in Organic Coatings*, Vol. 56, No. 2-3, (July 2006), pp. 214-219, ISSN0300-9440
- Grummt U.; Pron A.; Zagorska M. & Lefrant S. (1997). Polyaniline based optical pH sensor. *Analytica Chimica Acta*, Vol. 357, No. 3, (December 1997), pp. 253-259, ISSN0003-2670
- Gupta V. & Miura N. (2005). Large-area network of polyaniline nanowires prepared by potentiostatic deposition process. *Electrochemistry Communications*, Vol. 7, No. 10, (October 2005), pp. 995-999, ISSN1388-2481
- Gvozdenović M. & Grgur B. (2009). Electrochemical polymerization and initial corrosion properties of polyaniline-benzoate film on aluminum. *Progress in Organic Coatings*, Vol. 65, No. 3, (July 2009), pp. 401-404, ISSN0300-9440
- Gvozdenović M.; Jugović B.; Stevanović J.; Grgur B.; Trišović T. & Jugović Z. (2011). Electrochemical synthesis and corrosion behavior of polyaniline-benzoate coating on copper, *Synthetic Metals*, Vol. 161, No. 13-14, July 2011, pp 1313-1318, ISSN0379-6779
- Gvozdenović M.; Jugović B.; Bezbradica D.; Antov M. Knežević-Jugović Z. & Grgur B. (2011). Electrochemical determination of glucose using polyaniline electrode modified by glucose oxidase. *Food Chemistry*, Vol. 124, No.1, (January 2011), pp. 396-400, ISSN0308-8146
- Gvozdenović M.; Jugović B.; Trišović T.; Stevanović J. & Grgur B. (2011). Electrochemical characterization of polyaniline electrode in ammonium citrate containing electrolyte. *Materials Chemistry and Physics*, Vol. 125, No. 3, (February 2011), pp. 601-605, ISSN0254-0584
- Heinze J.; Frontana-Urbe B. & Ludwigs S. (2010). Electrochemistry of Conducting Polymers- Persistent Models and New Concepts. *Chemical Reviews*, Vol.110, No.8, (June 2010), pp. 4724-4771 ISSN0009-2665

- Horvat-Radošević V. & Kvastek K. Role of Pt-probe pseudo-reference electrode in impedance measurements of Pt and polyaniline (PANI) modified Pt electrodes. (2006). *Journal of Electroanalytical Chemistry*, Vol. 591, No. 2, (June 2006), pp. 217-222, ISSN1572-6657
- Huerta-Vilca D.; de Moraes S. & de Jesus Motheo A. (2005). Aspects of polyaniline electrodeposition on aluminium. *Journal of Solid State electrochemistry*, Vol. 9, No. 6 (June 2005), pp. 416-420, ISSN1432-8488
- Hussain A. & Kumar A. (2003). Electrochemical synthesis and characterization of chloride doped polyaniline. *Bulletin of Material Science*, Vol. 26, No. 3, (April 2003), pp. 329-334 ISSN0250-4707
- Innis P.; J. Mazurkiewicz J.; Nguyen T.; Wallace G. & MacFarlane D. (2004). Enhanced electrochemical stability of polyaniline in ionic liquids. *Current Applied Physics*, Vol. 4, No. 2-4, (April 2004), pp. 389-393, ISSN1567-1739
- Innis P.; Norris I.; Kane-Maguire L. & Wallace G. (1998). Electrochemical Formation of Chiral Polyaniline Colloids Codoped with (+)- or (-)-10-Camphorsulfonic Acid and Polystyrene Sulfonate. *Macromolecules*, Volume 31, No. 19, (September 1998), pp 6521-6528 ISSN0024-9297
- Inzelt G.; Pineri M.; Schultze J. & Vorotyntsev M. Electron and proton conducting polymers: recent developments and prospects. *Electrochimica Acta*, Vol. 45, No. 15-16, (May 2000), pp. 2403-2421 ISSN0013-4686
- Inzelt G. (2008). *Conducting Polymers – A New Era in Electrochemistry*, Springer-Verlag, ISBN 978-3-540-75929-4, Berlin, Heidelberg
- Jugović B.; Trišović T.; Stevanović J.; Maksimović M. & Grgur B. (2006). Novel electrolyte for zinc-polyaniline batteries, *Journal of Power Sources*, Vol. 160, No. 2, (October 2006), pp. 1447-1450 ISSN0378-7753
- Jugović B.; Gvozdenović M.; Stevanović J.; Trišović T. & Grgur B. (2009). Characterization of electrochemically synthesized PANI on graphite electrode for potential use in electrochemical power sources. *Materials Chemistry and Physics*, Vol. 114, No. 2-3, (April 2009), pp. 939-942, ISSN0254-0584
- Kahol P.; Dyakonov A.; & McCormick B. (1997). An electron-spin-resonance study of polymer interactions with moisture in polyaniline and its derivatives. *Synthetic Metals*, Vol. 89, No. 1, (July 1997), pp. 17-28, ISSN0379-6779
- Kang E; Neoh K. & Tan K. Polyaniline: A polymer with many interesting intrinsic redox states, *Progress in Polymer Science*, Vol. 23, No. 2, (1998), pp. 277-324, ISSN0079-6700
- Kankare J. (1998). Electronically Conducting Polymers: Basic Methods of Synthesis and Characterization, In: *Electrical and Optical Polymer Systems: Fundamentals: Methods, and Applications*, Ed. by: Wise D.; Wnek G.; Trantolo D.; Cooper J. & Gresser D., pp. 167-199, Marcel Dekker, ISBN 0824701186, New York
- Karpagam V.; Sathiyarayanan S. & Venkatachari G. (2008). Studies on corrosion protection of Al2024 T6 alloy by electropolymerized polyaniline coating *Current Applied Physics*, Vol. 8, No. 1, (January 2008), pp. 93-98, ISSN1567-1739
- Karyakin A.; Strakhova A. & Yatsimirsky A. (1994). Self-doped polyanilines electrochemically active in neutral and basic aqueous solutions.: Electropolymerization of substituted anilines. *Journal of Electroanalytical Chemistry*, Vol. 371, No. 1-2, (June 1994), pp. 259-265, ISSN1572-6657

- Koziel K. & Lapkowski M.(1993). Studies on the influence of the synthesis parameters on the doping process of polyaniline. *Synthetic Metals*, Vol. 55, No. 2-3, (March 1993), pp. 1011-1016, ISSN0379-6779
- Koziel K.; Lapkowski M. & Lefrant S. (1995). Spectroelectrochemistry of polyaniline at low concentrations of doping anions. *Synthetic Metals*, Vol. 69, No. 1-3, (March 1995), pp. 137-138, ISSN0379-6779
- Kraljić M.; Mandić Z. & Duić Lj. (2003). Inhibition of steel corrosion by polyaniline coatings. *Corrosion Science*, Vol. 45, No. 1, (January 2003), pp. 181-198, ISSN0010-938X
- Kumar D.(2000). Synthesis and characterization of poly(aniline-co-o-toluidine) copolymer *Synthetic Metals*, Vol. 114, No. 3, (September 2000), pp. 369-372 ISSN0379-6779
- Lacroix J.; Camalet J.; Aeiya S.; Chane-Ching K.; Petitjean J.; Chauveau E. & Lacaze P. (2000). Aniline electropolymerization on mild steel and zinc in a two-step process. *Journal of Electroanalytical Chemistry*, Vol. 481, No.1, (January 2000), pp. 76-81, ISSN1572-6657
- Lapkowski M. (1990). Electrochemical synthesis of linear polyaniline in aqueous solutions. *Synthetic Metals*, Vol. 35, No. 1-2, (February-March 1990), pp. 169-182 ISSN0379-6779
- Li M.; Ma C.; Liu B. & Jin Z. (2005). A novel electrolyte 1-ethylimidazolium trifluoroacetate used for electropolymerization of aniline. *Electrochemistry Communications*, Vol. 7, No. 2, (February 2005), pp. 209-212, ISSN1388-2481
- Macdiarmid A.; Chiang J.; Richter A. & Epstein A. (1987). Polyaniline: a new concept in conducting polymers. *Synthetic Metals*, Vol. 18, N. 1-3, (February 1987), pp. 285-290, ISSN0379-6779
- Majidi M.; Kane-Maguire L. & Wallace G. (1994). Enantioselective electropolymerization of aniline in the presence of (+)- or (-)-camphorsulfonate ion: a facile route to conducting polymers with preferred one-screw-sense helicity. *Polymer*, Vol. 35, No. 14, (July 1994), pp. 3113-3115, ISSN0032-3861
- Malinauskas A. & Holze R. (1997). Suppression of the "first cycle effect" in self-doped polyaniline. *Electrochimica Acta*, Vol. 43, No. 5-6, (November 1997), pp. 515-520, ISSN0013-4686
- Malinauskas A. (1999). Electrocatalysis at conducting polymers. *Synthetic Metals*, Vol. 107, No. 2, (November 1999), pp. 75-83 ISSN0379-6779
- Mandić Z.; Duić Lj. & Kovačiček F. (1997). The influence of counter-ions on nucleation and growth of electrochemically synthesized polyaniline film. *Electrochimica Acta*, Vol. 42, No. 9, (1997), pp. 1389-1402, ISSN0013-4686
- Martyak N.; McAndrew P.; McCaskie J. & Dijon J. (2002). Electrochemical polymerization of aniline from an oxalic acid medium. *Progress in Organic Coatings*, Vol. 45, No. 1, (September 2002), pp. 23-32, ISSN0300-9440
- Mattoso L. & Bulhões L. (1992). Synthesis and characterization of poly(o-anisidine) films. *Synthetic Metals*, Vol. 52, No. 2, (October 1992), pp. 171-181, ISSN0379-6779
- Mažeikienė R.; Niaura G. & Malinauskas A. (2003). Voltammetric study of the redox processes of self-doped sulfonated polyaniline. *Synthetic Metals*, Vol. 139, No. 1, (August 2003), pp. 89-94, ISSN0379-6779
- Miras M.; C. Barbero C. & Haas O. (1991). Preparation of polyaniline by electrochemical polymerization of aniline in acetonitrile solution. *Synthetic Metals*, Vol. 43, No. 1-2, (June 1991), pp. 3081-3084, ISSN0379-6779

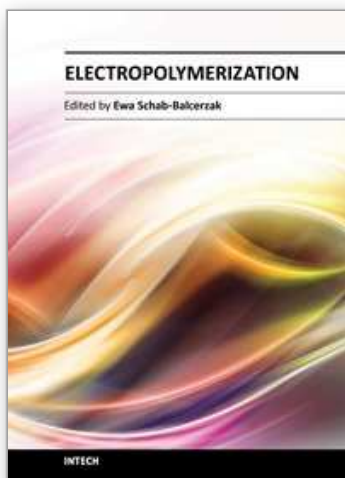
- Monkman A. & Adams P. (1991). Optical and electronic properties of stretch-oriented solution-cast polyaniline films. *Synthetic Metals*, Vol. 40, No.1, (March 1991), pp. 87-96, ISSN0379-6779
- Mu S. & Kan J. (1996). Evidence for the autocatalytic polymerization of aniline, *Electrochimica Acta*, Vol.4, No.10, (November 1996), pp. 1593-1599, ISSN0013-4686
- Mu S. & Kan J. The effect of salts on the electrochemical polymerization of aniline. *Synthetic Metals*, Vol. 92, No. 2, (January 1998), pp. 149-155, ISSN0379-6779
- Mu S. & Xue H. (1996). film. *Sensors and Actuators B: Chemical*, Vol. 31, No. 3, (March 1996), pp.155-160 ISSN0925-4005
- Mu S. & Yang Y. (2008). Spectral Characteristics of Polyaniline Nanostructures Synthesized by Using Cyclic Voltammetry. *Journal of Physical Chemistry B*. Vol. 112, No. 37, (September 2008), pp. 11558-11563 ISSN1520-6106
- Mu S. & Kan J. (1998). The effect of salts on the electrochemical polymerization of aniline. *Synthetic Metals*, Vol. 92, No. 2 (January 1998), pp.149-155, ISSN0379-6779
- Mu S. (2004). Electrochemical copolymerization of aniline and *o*-aminophenol. *Synthetic Metals*, Vol.143, No. 3, (June 2004), pp. 259-268, ISSN0379-6779
- Mu S. (2007). Pronounced effect of the ionic liquid on the electrochromic property of the polyaniline film: Color changes in the wide wavelength range. *Electrochimica Acta*, Vol. 52, No. 28, (November 2007), pp. 7827-7834, ISSN0013-4686
- Mu S. (2011). Synthesis of poly(aniline-co-5-aminosalicylic acid) and its properties. *Synthetic Metals*, Vol. 161, No. 13-14, (July 2011), pp. 1306-1312, ISSN0379-6779
- Mu S. (2011). Synthesis of poly(aniline-co-5-aminosalicylic acid) and its properties. *Synthetic Metals*, Vol. 161, No. 13-14, (July 2011), pp. 1306-1312, ISSN0379-6779
- Mu S.; Chen C. & Wan J. (1997). The kinetic behavior for the electrochemical polymerization of aniline in aqueous solution, *Synthetic Metals*, Vol.88, (April 1997), pp. 249-254, ISSN0379-6779
- Mu S.; Kan J.; Lu J. & Zhuang L. (1998). Interconversion of polarons and bipolarons of polyaniline during the electrochemical polymerization of aniline. *Journal of Electroanalytical Chemistry*, Vol. 446, No. 1-2, (April1998), pp.107- 112, ISSN1572-6657
- Nagarajan R.; Tripathy S; Kumar J.; Bruno F. & Samuelson L. (2000). An Enzymatically Synthesized Conducting Molecular Complex of Polyaniline and Poly(vinylphosphonic acid). *Macromolecules*, Vol. 33, No. 262, (November 2000), pp. 9542-9547 ISSN0024-9297
- Nunziante P. & Pistoia G. (1989). Factors affecting the growth of thick polyaniline films by the cyclic voltmmetry technique. *Electrochimica Acta*, Vol. 34, No. 2, (February 1989), pp. 223-228, ISSN0013-4686
- Okamoto H. Okamoto M. & Kotaka T. (1998). Structure and properties of polyaniline films prepared via electrochemical polymerization. II: Structure and properties of polyaniline films prepared via electrochemical polymerization. *Polymer*, Vol. 39, No. 18, (1998), pp. 4359-4367 ISSN0032-3861
- Okamoto H. & Kotaka T. (1998). Structure and properties of polyaniline films prepared via electrochemical polymerization. I: Effect of pH in electrochemical polymerization media on the primary structure and acid dissociation constant of product polyaniline films. *Polymer*, Vol. 39, No. 18, pp. 4349-4358, ISSN0032-3861

- Okamoto H. & Kotaka T. (1998). Structure and properties of polyaniline films prepared via electrochemical polymerization. III: Effect of counter ions in electrochemical polymerization media on the structure responses of the product polyaniline films. *Polymer*, Vol. 40, No. 2, (1989), pp. 407-417, ISSN0032-3861
- Özyılmaz A.; Erbil M. & Yazıcı B. (2006). The electrochemical synthesis of polyaniline on stainless steel and its corrosion performance. *Current Applied Physics*, Vol. 6, No. 1, (January 2006), pp. 1-9, ISSN1567-1739
- Pandey P. & Singh G. (2002). Electrochemical Polymerization of Aniline in Proton-Free Nonaqueous Media, Dependence of Microstructure and Electrochemical Properties of Polyaniline on Solvent and Dopant. *Journal of Electrochemical Society*, Vol. 149, No. 4, (April 2002) pp. D51-D56, ISSN0013-4651
- Park S. & Joong H. (2005). Recent Advances in Electrochemical Studies of π -Conjugated Polymers. *Buillten of the Korean Chemical Society*, Vol. 26, No. 5, (May 2005), pp. 697-706 ISSN0253-2964
- Patil R.; Harima Y.; Yamashita K.; Komaguchi K.; Itagaki Y. & Shiotani M. (2002). Charge carriers in polyaniline film: a correlation between mobility and in-situ ESR measurements. *Journal of Electroanalytical Chemistry*, Vol. 518, No. 1, (January 2002), pp. 13-19, ISSN1572-6657
- Pawar P.; Gaikwad A. & Patil P. (2007). Corrosion protection aspects of electrochemically synthesized poly(o-anisidine-co-o-toluidine) coatings on copper. *Electrochimica Acta*, Vol. 52, No. 19, (May 2007), pp. 5958-5967, ISSN0013-4686
- Popović & Grgur B. (2004). Electrochemical synthesis and corrosion behavior of thin polyaniline-benzoate film on mild steel. *Synthetic Metals*, Vol. 143, No. 2, (June 2004), pp. 191-195, ISSN0379-6779
- Popović M.; Grgur B. & Mišković-Stanković V. (2005). Corrosion studies on electrochemically deposited PANI and PANI/epoxy coatings on mild steel in acid sulfate solution. *Progress in Organic Coatings*, Vol. 52, No. 4, (April 2005), pp. 359-365, ISSN0300-9440
- Probst M. & Holze R. (1995). Time- and temperature-dependent changes of the *in situ* conductivity of polyaniline and polyindoline. *Electrochimica Acta*, Vol. 40, No. 2, (February 1995), pp. 213-219, ISSN0013-4686
- Proń A.; Laska J.; Österholm J-E. & Smith P. (1993). Processable conducting polymers obtained via protonation of polyaniline with phosphoric acid esters. *Polymer*, Vol. 34, No. 20, (October 1993), pp. 4235-4240 ISSN0032-3861
- Pron A. & Rannou P. (2002). Processable conjugated polymers: from organic semiconductors to organic metals and superconductors. *Progress in Polymer Science*, Vol. 27, No. 1, (February 2002), pp. 135-190, ISSN0079-6700
- Pruneanu S.; Csahók E.; Kertész V. & Inzelt G. (1998). Electrochemical quartz crystal microbalance study of the influence of the solution composition on the behaviour of poly(aniline) electrodes. *Electrochimica Acta*, Vol 43. No. 16-17, (May 1998), pp. 2305-2323, ISSN0013-4686
- Şahin Y.; Perçin P.; Şahin M. & Özkan G. (2003). Electrochemical preparation of poly (2-bromoaniline) and poly (aniline-co-2-bromoaniline) in acetonitrile. *Journal of Applied Polymer Science*, Vol. 90, No. 9, (November 2003), pages 2460-2468, ISSN0021-8995

- Spinks G.; Dominis A. Wallace G. & Tallman D (2002). Electroactive conducting polymers for corrosion control. Part 2. Ferrous metals. *Journal of Solid State Electrochemistry*, Vol. 6, No. 2, (February 2002), pp. 85-100, ISSN1432-8488
- Stejskal J. & Gilbert R. (2002). Polyaniline. Preparation of a conducting polymer (IUPAC Technical Report). *Pure and Applied Chemistry*, Vol. 74, No. 5, (2002), pp. 857-867 doi:10.1351/pac200274050857
- Stejskal J.; Kratochvíl & Jenkins A. (1996). The formation of polyaniline and nature of its structures. *Polymer*, Vol. 37, No. 2, pp. 367-369, (February 1996), ISSN0032-3861
- Stejskal J.; Sapurina I. & Trchová M. (2010). Polyaniline nanostructures and the role of aniline oligomers in their formation. *Progress in Polymer Science*, Vol. 35, No. 12, (December 2010), pp. 1420-1481, ISSN0079-6700
- Syed A. & Dinesan M. (1991). Polyaniline – A novel polymeric material, *Talanta*, Vol. 38, No. 8, (August 1991), pp. 815-837 ISSN0039-9140
- Tallman D.; Spinks G.; Dominis A. & Wallace G. (2002). Electroactive conducting polymers for corrosion control. Part1. General introduction and review of non-ferrous metals. *Journal of Solid State Electrochemistry*, Vol. 6, No. 2, (February 2000), pp. 73-84, ISSN1432-8488
- Tanaka J.; Mashita N.; Mizoguchi K. & Kume K. (1989). Molecular and electronic structures of doped polyaniline. *Synthetic Metals*, Vol. 29, No. 1, (March 1989), pp. 175-184, ISSN0379-6779
- Tanaka K.; Wang S. & Yamabe T. (1990). Will bipolarons be formed in heavily oxidized polyaniline? *Synthetic Metals*, Vol. 36, No.1, (May 1990), pp. 129-135, ISSN0379-6779
- Tang H.; Kitani A. & Shiotani M. (1996). Factors of anions on electrochemical formation and overoxidation of polyaniline. *Electrochimica Acta*, Vol. 41, No. 9, (June 1996) pp. 1561-1567 ISSN0013-4686
- Tang Z.; Liu S.; Wang Z.; Dong S. & Wang E. (2000). Electrochemical synthesis of polyaniline nanoparticles. *Electrochemistry Communications*, Vol. 2, No.1, (January 2000), pp. 32-35, ISSN1388-2481
- Tsakova V.; Milchev A. & Schultze J. (1993). Growth of polyaniline films under pulse potentiostatic conditions. *Journal of Electroanalytical Chemistry*, Vol. 346, No. 1-2, (March 1993), pp. 85-97, ISSN1572-6657
- Wallace G.; Spinks G.; Kane-Maguire L. & Teasdale P. (2009). *Conductive Electroactive Polymers*, CRC Press, Taylor & Francis Group, ISBN 978-1-4200-6709-5, Boca Raton
- Wang T. & Tan Y. (2006). Understanding electrodeposition of polyaniline coatings for corrosion prevention applications using the wire beam electrode method. *Corrosion Science*, Vol. 48, No. 8, (August 2006), pp. 2274-2290, ISSN0010-938X
- Xu G.; Wang W.; Qu X.; Yin Y.; Chu L.; He B.; Wu H.; Fang L.; Bao Y. & Liang L. (2009). Electrochemical properties of polyaniline in *p*-toluene sulfonic acid solution. *European Polymer Journal*, Vol. 45, No. 9, (September 2009), pp. 2701-2707, ISSN0014-3057
- Yano J.; Ota Y. & Kitani A. (2004). Electrochemical preparation of conductive poly(*N*-alkylaniline)s with long *N*-alkyl chains using appropriate dopant anions and organic solvents. *Materials Letters*, Vol. 58, No. 12-13, (May 2004), pp. 1934-1937 ISSN0167-577X
- Zhang J.; Shan D. & Shaolin M. (2006). Electrochemical copolymerization of aniline with *m*-aminophenol and novel electrical properties of the copolymer in the wide pH

- range. *Electrochimica Acta*, Vol. 51, No. 20, (May 2006), pp. 4262-4270, ISSN0013-4686
- Zhou H.; Wen J.; Ning X.; Fu C.; Chen J. & Kuang Y. (2007). Electrosynthesis of polyaniline films on titanium by pulse potentiostatic method. *Synthetic Metals*, Vol. 157, No. 2-3, (February 2007), pp. 98-103, ISSN0379-6779
- Zhou S.; Wu T.; Kan J. Effect of methanol on morphology of polyaniline.(2007). *European Polymer Journal*, Vol. 43, No. 2, (February 2007), pp. 395-402, ISSN0014-3057
- Zotti G; Cattarin S. & Comiss N. (1987). Electrodeposition of polythiophene, polypyrrole and polyaniline by the cyclic potential sweep method. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, Vol. 235, No. 1-2, (October 1987), pp. 259-273, ISSN1572-6657
- Zotti G; Cattarin S. & Comiss N. (1988). Cyclic potential sweep electropolymerization of aniline: The role of anions in the polymerization mechanism. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, Vol. 239, No. 1-2, (January 1988). pp. 387-396, ISSN1572-6657

IntechOpen



Electropolymerization

Edited by Dr. Ewa Schab-Balcerzak

ISBN 978-953-307-693-5

Hard cover, 214 pages

Publisher InTech

Published online 22, December, 2011

Published in print edition December, 2011

In recent years, great focus has been placed upon polymer thin films. These polymer thin films are important in many technological applications, ranging from coatings and adhesives to organic electronic devices, including sensors and detectors. Electrochemical polymerization is preferable, especially if the polymeric product is intended for use as polymer thin films, because electrogeneration allows fine control over the film thickness, an important parameter for fabrication of devices. Moreover, it was demonstrated that it is possible to modify the material properties by parameter control of the electrodeposition process. Electrochemistry is an excellent tool, not only for synthesis, but also for characterization and application of various types of materials. This book provides a timely overview of a current state of knowledge regarding the use of electropolymerization for new materials preparation, including conducting polymers and various possibilities of applications.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Milica M. Gvozdenović, Branimir Z. Jugović, Jasmina S. Stevanović, Tomislav Lj. Trišović and Branimir N. Grgur (2011). Electrochemical Polymerization of Aniline, *Electropolymerization*, Dr. Ewa Schab-Balcerzak (Ed.), ISBN: 978-953-307-693-5, InTech, Available from:

<http://www.intechopen.com/books/electropolymerization/electrochemical-polymerization-of-aniline>

INTECH
open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2011 The Author(s). Licensee IntechOpen. This is an open access article distributed under the terms of the [Creative Commons Attribution 3.0 License](https://creativecommons.org/licenses/by/3.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

IntechOpen

IntechOpen