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Electrochemical Polymerization of Aniline

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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 derivates 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 vide 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; Özylimaz 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; Steiskal at 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).

Polyanilne obtained by electrochemical polymerization is usually deposited on the electrode, however electrochydrodinamic 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

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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 is 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 derivates, 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 know electroconducting polymers, polyaniline can exist, depending on degree of oxidation, in different forms, known as: leuoemeraldine, emeraldine and perningraniline. Leucoemeraldine, eg. leucoemeraldine base, refers to fully reduced form; emeraldine, eg. emeraldine base, is half-oxidized, while perningraniline, eg. perningraniline base, is completely oxidized form of polyaniline. The only conducting form of polyaniline is emeraldin 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 perningraniline salt, which can be treated by alkali to form violet perningraniline. 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 polyanilne, perningranilne salt and emeraldine have different shades of blue (Stejskal et al., 1996). Both reduction of emeraldine salt to leucoemeraldine and oxidation to perningraniline states are followed by decrease in conductivity (Stejskal et al., 2010).

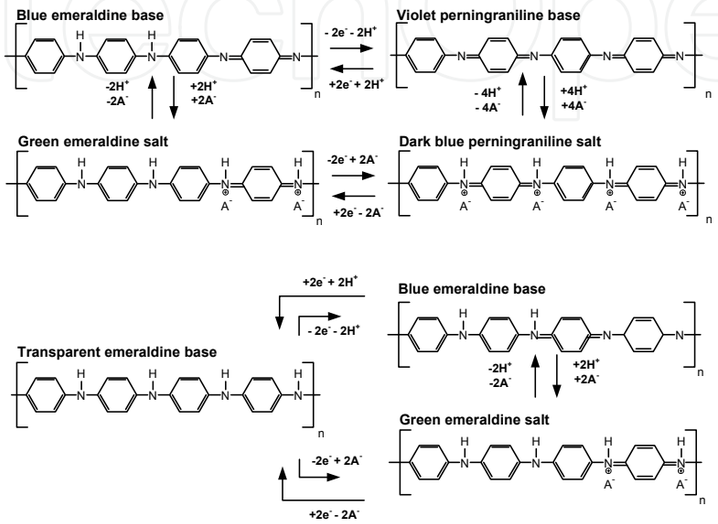


Fig. 1. Different forms of polyaniline

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 at 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 dicatione (emeraldine salt form). Bipolarone is further dissociated by injection of two electrons both from electron pairs of two imine nitrogen, into quinodiimine ring, and the third double bond of benzenoid ring is formed (Stejskal, 2010).

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

Although both bipolaron and polaron theoretical models of emeraldine salt conductivity were proposed (Angelopulus 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 perningraniline states decrease the conductivity. The order of magnitude for conductivity varies from 10^{-2} S cm^{-1}, for undoped emeraldine, up to 10^{3} S cm^{-1} for doped emeraldine salt (Inzelt, 2008; Wallace et al., 2009).

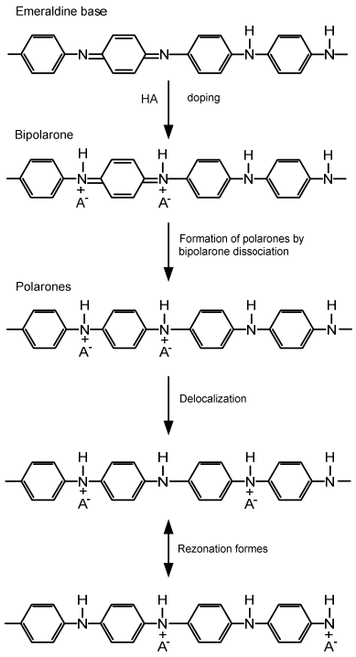


Fig. 2. Schematic presentation of polyaniline conductivity

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 had 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; Inzlet 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).

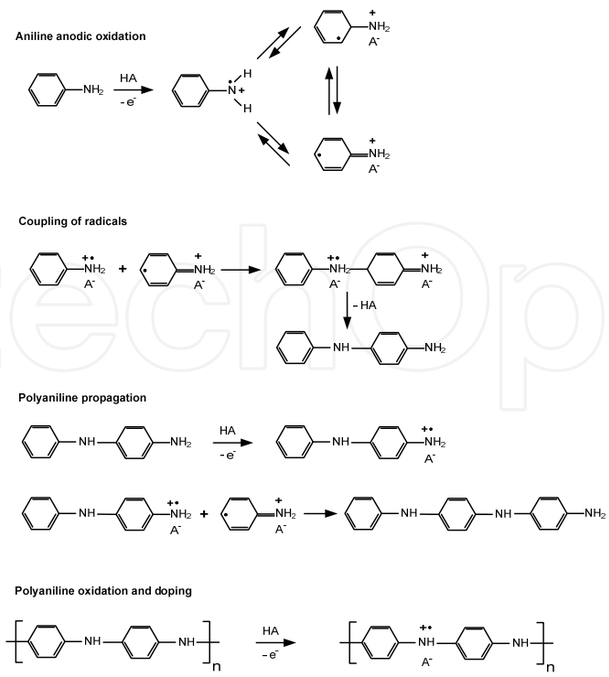


Fig. 3. Schematic presentation of mechanism of electrochemical polymerization of aniline.

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 refering 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 (Inzlet 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 nucleofilic 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; Wallce 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, polyanilne 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 polyanilne 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 acetronitrlie 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, tetraethilammonium tetrafluoroborate and tetraetilammoniumperchlorate 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 coopolymers with aniline in acetonitrile containing tetrabutilammonium 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 acetonytrile and dimethiylsulfoxide, 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 potetntiostatic 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 perningranilin 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 electrochemicaly 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, hronopotnetiometric 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:

$$(PANI)_n + ny Cl^- \rightarrow [PANI^{y+} (Cl^-)]_n + nye^-$$

Where y 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 y between 0 and 0.5.

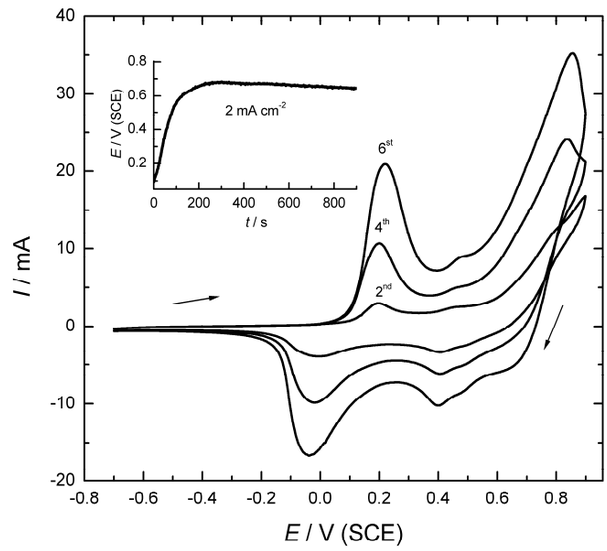


Fig. 4. Cyclic voltammograms of electrochemical polymerization of aniline on graphite electrode from aqueous solution of 1.0 mol dm^{-3} HCl and 0.25 mol dm^{-3} aniline, at scan rate of 20 mV s^{-1}. Insert: Chronopotentiometric curves of aniline polymerization at constant current density of 2.0 mA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

Second anodic peak, occurred at potenial of ~ 0.5 V (SCE) denotes formation of fully doped perningraniline salt (y = 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 nanowiers (Gupta & Miura, 2007). Modified potentiostatic techniques were also reported.
Some of the researches used pulse potentiostatic technique to obtained 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 derivates

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 lost 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 derivates 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* – aminobenzensulfonic acid had exhibited redox activity at high pH (Karyakin et al., 1996).
Apart from aniline and aniline derivate, 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 plays 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 un- substituted aniline, upper limit was lower.
The problem related to electrochemical activity of self-doped polyaniline is its rapid lost. Recently, it was showed that electrochemical polymerization of aniline and 5-aminosalycylic acid, which nears two acidic functional groups, had lead to co-polymer with satisfactory redox activity (Mu, 2011).

4. Conclusion

Although polyaniline is among the first know electroconductive polymers, the interest in this field of study still exist, since its diverse and unique properties can be useful in various practical applications. Electrochemical polymerization of aniline and aniline derivates 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 derivates 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

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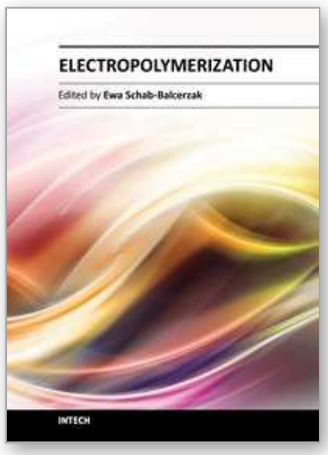
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Electropolymerization

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

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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

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