Review

Self-doped polyanilines

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Abstract

Self-doped polyanilines (PANIs) are polyaniline derivatives that bear negatively charged functional groups. These novel materials have many properties different from those of the parent polyaniline, and some specific fields for their use are expected. The present paper reviews some aspects of polymerization, electropolymerization, and properties of these materials.
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1. Introduction

Among many derivatives of polyaniline (PANI), self-doped polyanilines possess some distinct properties, making them promising in a broad field of applications. For the parent PANI, it is well known that its reversible oxidation and reduction is accomplished with the movement of anions into or from the bulk of polymer. Particularly, the oxidation of a fully reduced, electrically insulating leucoemeraldine form of PANI to its half oxidised conducting emeraldine form is followed in an acidic solution by the penetration of anions from the solution into the polymer layer, so that the electroneutrality of polymer is retained. In the second-oxidation step, leading to a fully oxidised non-conducting pernigraniline form, the anions are expelled from the polymer along with protons into a surrounding solution. Under certain conditions, the anion exchange between PANI and solution can be a rate-determining step that limits an entire redox process.

In contrast to PANI, its self-doped derivatives contain in their structure an ionisable, negatively charged functional group, which acts as an inner dopant anion, bound to the polymer backbone. Thus, no anion exchange between the polymer and surroundings take place during oxidation or reduction. The charge compensation occurs in this case at the expense of cation (usually a proton) exchange, that occurs much more faster and do not limit the rate of the charging (redox) process.

Two major potential fields of application seem to be responsible for the continuing interest since early 1990s in synthesis and study of self-doped conducting polymers. One of them relates to batteries, especially to the secondary rechargeable lithium batteries. In the discharging cycle of these batteries, the electrons flowing from the lithium anode (negative pole) through an external electric circuit must be consumed at the cathode (positive pole). When used as an active mass of a positive electrode, conducting polymers ensure an efficient utilization of electrons by converting the oxidised form of a conducting polymer into its reduced form. Adversely. electrochemical oxidation of a reduced form takes place in the reverse charging cycle. For the conventional conducting polymers like PANI or polypyrrole, the reversible charging–discharging process requires the movement of anions into or from the polymer. The reversible exchange of anions between the active polymer mass and electrolyte limits many important characteristics of such batteries like the electric charge density (relative to the mass of a polymer), the maximum electric current available (due to limited rate of electrochemical process including anion exchange), cycleability of battery, storage characteristics, etc. In opposite, the use of self-doped conducting polymers exclude the participation of anions in charging–discharging process. Instead, the charge compensation for self-doped polymers occurs at the expense of lithium cation insertion or expulsion, and a great efficiency of this process leads to a significant improvement of some characteristics of rechargeable lithium batteries.

Another promising field of application for self-doped conducting polymers is their use for sensors and biosensors. PANI shows its electric conductivity only in its protonated (proton doped) form, or, in terms of solution chemistry, at low pH values. At pH above 3 or 4, PANI does not show

neither conductivity, nor electrochemical redox processes. For biosensor applications however, nearly pH-neutral solutions must be used, since most of biocatalysts (enzymes) operate in neutral or slightly acidic or alkaline solutions only. Therefore, it is difficult or impossible to couple enzyme-catalysed electron transfer processes of solution species with electron transport or electrochemical redox reactions of PANI or related conducting polymers. Fortunately, it has been found that self-doped PANI has an extended pH range of electric conductivity and electrochemical activity, covering that of many biocatalysts. Thus, the use of self-doped PANI or its derivatives could in principle ensure the direct or mediated electron exchange between the polymer matrix and active centers of biocatalyst molecules.

In addition to these two major areas of application, which are intensely discussed at present, some new areas are expected to appear shortly, taking into account some specific properties of self-doped polymers that differ them from the corresponding parent polymers. For instance, a distinctive property of self-doped PANI is its solubility in alkaline aqueous solutions. So, conductive and electroactive layers could be deposited onto any, even non-conducting, surface by a simple casting of a self-doped PANI solution, followed by the solvent evaporation. Such layers could find numerous applications in diverse areas of technology.

In 1990, Yue and Epstein [1], and Bergeron et al. [2] reported first syntheses of self-doped conducting PANI derivatives. Since these reports, many papers have been published, dealing with synthesis and properties of self-doped conducting polymers. The present review has been aimed to summarize and overview the most important achievements in the field.

2. Chemical synthesis and properties of self-doped polyanilines

Self-doped PANI and its derivatives can be obtained either by chemical, or by electrochemical synthesis. In this chapter, chemical synthesis will be considered. Following this way, self-doped PANI can be obtained either by the chemical modification of PANI itself or by polymerization of appropriate monomers. In both cases, two kinds of self-doped PANI derivatives have been prepared. One of them contains ionizable negatively charged functional groups (usually sulfonate groups), attached directly to the aromatic rings of the polymer backbone. Another kind contains sulfonate groups, bound through a spacer consisting of 3–5 methylene groups to the nitrogen atoms of PANI.

2.1. Chemical modification of polyaniline

Yue and Epstein obtained ring-sulfonated PANI (SPAN) by the sulfonation of the emeraldine base of PANI with fuming sulfuric acid for 2 h at room temperature followed by precipitation of the reaction product with methanol and acetone [1]. In the structure of the resulting SPAN, a half of aromatic rings of polymer backbone contain sulfonate groups. The 50% degree of sulfonation is enough to compensate all positive charges of the protonated nitrogen atoms in the emeraldine salt form of this polymer. The polymer thus obtained has a significantly lower electric conductivity compared to PANI of about 0.1 S/cm, however, this value is independent on pH up to 7. A high local concentration of protons due to the presence of ring-bound sulfonate groups has been claimed to be responsible for the retention of doping at neutral pH. In contrast to the parent PANI, self-doped SPAN was found to be well soluble in diluted aqueous base [1]. The degree of sulfonation for SPAN has been confirmed by elemental analysis. FTIR spectroscopy [1], and XPS analysis [3].

Somewhat later, Wei and Epstein obtained ring-sulfonated SPAN with a higher degree of sulfonation, reaching 75%, i.e. three-fourth of aniline monomer units in the polymer backbone contain sulfonate groups [4]. This has been achieved by treatment of the reduced leucoemeraldine base form of PANI with fuming sulfuric acid. The product thus prepared has about 1.5-fold increased solubility in aqueous alkaline solution (about 38 mg/ml, compared to 23 mg/ml for 50% sulfonated SPAN). The conductivity for 75% sulfonated SPAN was found to be approximately one order of magnitude higher (1 S/cm), compared to 50% sulfonated SPAN, and independent on pH within a broad range of 0–14.

In cyclic voltammograms, this SPAN shows two distinct anodic peaks of oxidation at 0.32 and 0.67 V versus Ag/AgCl in 1 M HCl. Thus, 75% sulfonated SPAN has an electrode potential window of 0.35 V, where its conducting protonated emeraldine form exists [4]. Unfortunately. this window is about two-fold narrower compared to that of PANI, known from literature. Both electrochemical redox processes were found to depend on solution pH. The slope of midpoint potential on pH was found to be −0.059 V per pH unit within the pH limits of 1–5, while that from pH 5 to 7 is −0.118 V per pH unit [5].

The variation of sulfonation degree for SPAN has been achieved by treating the undoped PANI with 96% sulfuric acid and Ag_2SO_4 [6]. The conductivity of SPAN prepared decreased continuously with increasing sulfonation degree from 5 S/cm for PANI (i.e. zero sulfonation degree) to 0.023 S/cm for the maximum sulfonation degree of 0.45. In cyclic voltammograms, SPAN has two pairs of anodic and cathodic peaks, characterised by the midpoint potential values of 0.21 and 0.56 V versus SCE, corresponding to 0.35 V wide potential window for the conducting emeraldine form.

SPAN of different sulfonation degree has been also prepared by treating of PANI with chlorosulfonic acid in dichloroethane at elevated temperature [7]. With increasing sulfur to nitrogen ratio in the resulting SPAN from 0.65 to 1.3, the solubility in water increases from 22 to 88 g/l, and the conductivity decreases from 0.02 to 1.7×10^{-5} S/cm [7]. Commercially available SPAN with sulfonation degree of 100% has been reported to have the conductivity of

0.02 S/cm [8], which is lower than for SPAN with sulfonation degree of 50 [9] and 75% [5]. The decrease in electric conductivity with increasing degree of sulfonation has been explained by the higher twist of the phenyl rings relative to one another and increased interchain separation due to increasing density of sulfonate groups [8]. The shift of a polaron band in near IR spectra for SPAN to higher energies, as compared to PANI, is in accordance with lower electric conductivity [10]. The benefits of a direct sulfonation of PANI over other sulfonation agents has been discussed [11].

Few uses for SPAN have been proposed. When used as a positive electrode for lithium batteries, SPAN showed an increased capacity for electric charge storage. For 50% sulfonated SPAN, specific charge of 37 Ah/kg was reported in aqueous electrolytes for the first-oxidation step, whereas an increased specific charge of 68 Ah/kg was reported in non-aqueous electrolytes for both two consecutive oxidation steps, thus, the SPAN-Li battery could have some 50% more specific energy than a PANI-Li battery [10].

SPAN films have been also used as semiconducting layers for the field-effect transistors [12]. The devices prepared have good source current-drain versus voltage characteristics, and their field-effect mobilities were closely related to those of the amorphous silicon transistors. A multilayered structure consisting of SPAN and poly(p-phenylene vinylene) was prepared by the electrostatic self-assembly technique and used for light-emitting diodes [13,14]. Electrochemical modulation of solution pH and enzyme activity at SPAN-coated electrodes was demonstrated [15].

The mechanism of thermal degradation for SPAN has been investigated by thermal gravimetric analysis, and has been found different from that of PANI, doped by hydrochloric acid [16]. The conductivity of SPAN was also found to depend on temperature. For the cast SPAN films, the conductivity increases with temperature from 0.002 S/cm at $-10\,^\circ$C to 0.01 S/cm at $25\,^\circ$C, and to 0.09 S/cm at $190\,^\circ$C, and decreases up to 0.06 S/cm at $225\,^\circ$C due to thermal undoping [17]. This thermal undoping proceeds irreversibly, since, after the heating scan, the conductivity at room temperature drops by a factor of 1000. A relatively high temperature of thermal undoping for SPAN of $190\,^\circ$C was found to decrease up to $110\,^\circ$C in the blends of SPAN with poly(vinyl alcohol) due to the occurrence of dehydration at this temperature [18]. The presence of covalently bonded sulfonic groups in PANI structure has been claimed to increase the thermal stability of the polymer [19].

A distinct route for the preparation of self-doped PANI by its chemical modification is a treatment of emeraldine base of PANI with the sulfopropylation agent 1,3-propanesultone [2]. Following this way, nitrogen-substituted sulfopropylated derivatives of PANI can be prepared, different from ring-sulfonated derivatives. Chen and Hwang prepared a water soluble self-doped PANI derivative, poly(aniline-co-N-propanesulfonic acid-aniline) (PAPSA) by the treatment of emeraldine base of PANI with 1,3-propanesultone [20]. Based on elemental analysis, the degree of sulfonation of

about 50% was obtained. The polymer has the conductivity of 0.015 S/cm, and has been well characterised with IR and XPS spectroscopy [21]. In 0.1 M HCl solution, PAPSA film shows two electrochemical redox processes, characterised by the midpiont potentials of 0.19 and 0.72 V versus SCE [21]. These potentials depend on the solution acidity, and a slope of $E_{1/2}$ versus pH of -0.059 V per pH, and $-0.1\,18$ V per pH has been obtained for the first and second redox processes, respectively, within the pH window between 0 and 2.

2.2. Polymerization of sulfonated monomers

Next to sulfonation of a separately prepared PANI, self-doped derivatives can be obtained by the polymerization of aniline monomers, containing sulfonate or other ionizable negatively charged group. For this polymerization, usual methods can be employed, used in aniline polymerization. The polymerization can be provided with the use of relatively strong oxidising agents, leading to chemically active cation radicals or related species, derived from the monomers [22–24].

An attempt to polymerize m-anilinesulfonic acid (metanilic acid) with the use of ammonium peroxydisulfate as an oxidising agent yielded a low molecular mass polymer (M_W of 3000) with low electric conductivity, not exceeding 3×10^{-6} S/cm [25]. A probable reason for this is a low reactivity of metanilic acid as a monomer due to the presence of electron withdrawing sulfonate group. Fortunately, a similar monomer containing in addition the methoxy substituent, which is known to be an electron donating group, yielded upon polymerization with the use of ammonium peroxydisulfate a fully sulfonated self-doped poly(2-methoxyaniline 5-sulfonic acid) with M_W of 10000 and a conductivity of 0.04 S/cm [25]. The use of this self-doped polymer as overcoated film for resists for the charge prevention for e-beam lithography, and as a conductive bottom layer of multilevel resists for the reduction of gate oxide damage in metal etching, was demonstrated [25].

Self-doped PANI has been obtained by polymerization of 4-aminodiphenylamine-2-sulfonic acid with ammonium peroxodisulfate [26]. The resulting polymer is soluble in aqueous base solution, it has a conductivity of 1.3×10^{-5} S/cm, and shows two redox peaks in cyclic voltammograms with midpoint potentials of 0.50 and 0.68 V versus Ag/AgCl in 1 M HCl solution [26]. Similarly, a soluble self-doped polymer poly(diphenylamine-4-sulfonic acid) has been obtained by oxidation of the corresponding monomer in an aqueous acidic solution with potassium peroxodisulfate [27]. Oxidative polymerization of 5- or 8-aminonaphthalene-2-sulfonic acids with sodium peroxodisulfate or potassium periodate yields water soluble conducting self-doped polymers [28].

Similarly to sulfonate-containing monomers, a carboxy-containing monomer 2,3-dicarboxyaniline has been oxidatively polymerized in an aqueous solution by sodium peroxodisulfate to yield oligo(2,3-dicarboxyaniline) [29].

The resulting oligomer has ca. 21% self-doping degree, and shows two stable electrochemical redox couples over a wide pH range.

Next to homopolymerization, self-doped PANI derivatives can be obtained by the oxidative copolymerization of two monomers, at least one of which contains a sulfonate group. Copolymerization of aniline with metanilic acid using either ammonium peroxodisulfate or iron(III) perchlorate as oxidising agents has been reported yielding a copolymer with 50% sulfonation degree [30]. The copolymer obtained is thermally more stable than perchlorate doped PANI.

Copolymers of aniline and metanilic acid with sulfur-to-nitrogen ratio of 0.05 to 0.40 have been obtained with the use of ammonium peroxodisulfate in 1 M HCl at varying molar ratio of both comonomers and varying polymerization temperature [31,32]. The conductivity of copolymers thus prepared was lower than that of PANI. Similarly, copolymers of 2-methoxyaniline and metanilic acid have been prepared [33,34]. Due to a great difference in the reactivity of both comonomers used, the content of 2-methoxyaniline in the resulting copolymer is much higher than in the polymerization mixture. In opposite, one-to-one structure for copolymers derived from p-aminodiphenylamine and o-aminobenzenesulfonic acid was obtained by copolymerization of the corresponding comonomers, even though the feed ratio is varied [35]. The resulting self-doped copolymer has a lower conductivity compared to PANI, however, the conductivity does not depend on pH.

Nanocomposite materials based on 3-anilinopropanesulfonic acid (APSA), polymerized onto V_2O_5 xerogel, were reported [36,37]. Oxidative polymerization proceeded either with the addition of hydrogen peroxide [36], or even without the addition of any oxidising agent, at the expense of reduction of V(V) species, which are then reoxidised by the stream of oxygen [37]. The use of this composite material for lithium secondary batteries has been discussed.

3. Electrochemical synthesis of self-doped polyanilines

During the past decade, a number of publications has been devoted to electrochemical synthesis of self-doped polyanilines (electropolymerization). At a high positive (anodic) potential, the electrochemical oxidation of aniline type monomers proceeds, yielding highly reactive intermediate species like cation radicals. Electrochemically generated species react in the next following step with solute monomers, yielding either oligomers or polymers, depending on reaction variables. The reactivity of diverse intermediate species in the polymerization reaction can vary over a broad range, as evidenced with the use of simultaneous electrochemical–spectroscopic techniques [38,39]. The oligomers or polymers thus formed can either dissolve in the electrolyte used, or deposit onto the electrode surface as a compact layer, depending on their molar mass and solubility. With the use of electrochemical thermospray

mass spectrometry, it has been shown that, for electropolymerization of aniline and N-alkylanilines, the oligomers containing up to three monomer units diffuse into the surrounding solution, whereas oligomers of higher degree of polymerization deposit on the electrode [40]. The presence of sulfonate group in a monomer molecule increases the solubility of the resulting polymer, so, it is possible to obtain soluble self-doped polymers of a relatively high degree of polymerization by electrochemical means. This chapter reviews electrochemical polymerization and copolymerization, leading to either soluble, or deposited self-doped polyanilines.

3.1. Self-doped homopolymers

In the regular half-oxidised protonated (emeraldine salt) form of PANI, a half of all nitrogen atoms are protonated, i.e. bear the positive charge. Thus, the homopolymerization of one kind of monomer containing sulfonate or related group leads to a polymer that contains an excess of negatively charged groups, relative to positively charged nitrogen atoms. Therefore, such homopolymers appear highly soluble in water, and hardly could be deposited on electrode during electropolymerization.

No deposition was observed during electrochemical oxidation of o-, m-, and p-aminobenzenesulfonic acids in an acidic aqueous solution, performed at a constant anodic current density of 0.3 mA/cm^2 [41]. The soluble products were precipitated from electrolyte with methanol, and identified as water soluble self-doped polymers with molar mass ranging from 5.1×10^4 for poly(p-aminobenzenesulfonic acid) to 1.6×10^5 for poly(m-aminobenzenesulfonic acid). The solubility of these polymers in water ranges from 26 to 46 mg/ml regardless of the solution pH, and the conductivity was reported to vary from 10^{-3} S/cm for as prepared samples to 10^{-2} to 10^{-1} S/cm for samples, doped with Fe(ClO$_4$)$_3$ [41].

Similarly, water soluble polymers were obtained by electropolymerization of 2-methoxyaniline-5-sulfonic acid [42]. Both the conversion of monomer, and molar mass of the resulting polymer can be controlled by choosing the solution pH, whereas two molar mass fractions were found in the resulting product, characterized by molar mass of 2200 and 15,000. The resulting self-doped polymer has a conductivity of 0.01 S/cm, and is highly soluble in water (30 wt.%) [42]. Similarly, poly(2-methoxyaniline-5-sulfonic acid) has been prepared by the use of electrohydrodynamic processing method [43].

Apart from sulfonic acid derivatives of aniline, its carboxylic acids have been also polymerized electrochemically. Polymers derived from o-, m-, and p-aminobenzoic acids have been obtained and characterised as being short-chain conducting polymers [44]. The rate of electropolymerization for all three isomers was found to be much lower than for aniline, whereas electropolymerization of p-substituted isomer proceed to a similar extent as for o- and m-isomers.

Poly(2,3-dicarboxyaniline) was obtained by electropolymerization on glassy carbon electrode, showing stable redox activity over a wide pH range [45].

Next to ring-substituted aniline monomers, *N*-alkylsulfonate derivatives have been also involved in electropolymerization. The most frequently used monomer of this kind is 3-anilino-1-propanesulfonic acid (APSA), that can be easily obtained by the alkylation of aniline with 1,3-propanesultone [46,47]. A similar monomer 4-anilino-1-butanesulfonic acid (ABSA) can be prepared very similar by treating of aniline with 1,4-butanesultone [48]. An attempt to electropolymerize APSA on a transparent ITO glass electrode gave no stable film, although both an intermediate and a final reaction product, presumably an oligomer or polymer of APSA, could be well detected by UV-Vis spectroscopy [38]. Both polyAPSA and polyABSA were shown to form liquid crystalline assemblies in aqueous solution upon the electropolymerization of appropriate monomers [49]. By the use of X-ray diffractometry, it has been shown that aqueous solutions of both these self-doped polymers possess high orientational and positional order [49]. Upon electropolymerization on platinum electrode, ABSA yielded an adherent polymer film that shows well-defined electrochromic properties by electrode potential cycling [48]. With the use of polyABSA as anodically coloring material, and tungsten trioxide as cathodic coloring material an all solid-state electrochromic window has been reported that could support 2000 switch-on–off cycles of 60 s duration [50].

3.2. Self-doped copolymers

A better route to obtain self-doped PANI derivatives, both soluble and insoluble, presents the electrochemical copolymerization of aniline with its sulfonate- or carboxylate group-pendant comonomers. While homopolymers, derived from sulfonate-containing monomers, possess an excess of negatively charged sulfonate groups, the composition of copolymers can be varied in a broad range by a simple change of comonomer ratio in a feed solution, and electropolymerization conditions as well.

Most of the works published are dealing with the electrochemical copolymerization of aniline with its sulfonate-substituted derivatives. For the first time, Lee et al. copolymerized electrochemically aniline and metanilic acid in an aqueous perchloric acid solution, and obtained a 40% self-doped copolymer, which had additionally a 20% doping level by perchlorate [51]. The copolymer had a lower electric conductivity, but better solubility in alkaline solvents, compared to PANI. The total self-doping level was reported to be limited to 50%, but the extent of intramolecular doping versus intermolecular by solution anions could be changed by adjusting the comonomer ratio in the electropolymerization solution [52]. The presence or absence of specific anions in electropolymerization solution could also influence the extent of self-doping and intermolecular doping. So, electrochemical copolymerization without a supporting electrolyte of aniline and *o*-aminobenzenesulfonic acid leads to formation of an electroactive copolymer film [53].

Karyakin et al. compared the electrocopolymerization of aniline with metanilic, anthranilic (*o*-aminobenzoic), and *m*-aminobenzoic acids under same experimental conditions [54]. The molar ratio of aniline and substituted aniline comonomers has been varied between 1:3 and 3:1, and a ratio of 1:1 was found to be optimal. Regarding the pH-dependence of the electroactivity, a copolymer of aniline with metanillic acid was found to be the best copolymer, showing activity up to pH 10. Both redox processes for the electrodeposited copolymer films have been found to shift on the potential scale to lower values with increasing pH, and overlapping at pH exceeding 5 [54]. Some later, electrosynthesis of this copolymer has been optimised by choosing appropriate synthesis conditions and a 3:1 aniline to metanilic acid ratio [55].

In a detailed study on the electropolymerization of aniline and metanilic acid [56], a limited involvement of metanilic acid in copolymerization has been claimed. The content of metanilic acid units in the copolymer, and thus the degree of self-doping, depend greatly on the molar ratio of both components. Self-doped copolymers can be obtained only at a higher content of metanilic acid compared to aniline, whereas no metanilic acid residues were detected in the copolymer at equal concentrations of both comonomers. Also, the degree of self-doping decreases with the film thickness, and with increasing acidity of electrolyte [56]. Similarly, an optimum concentration ratio of 9:1 was found for electrocopolymerization of aniline and *o*-aminobenzenesulfonic acid [57]. The resulting self-doped copolymer is soluble in pH-neutral solutions. and electrodeposited film of a copolymer shows a shift of both redox boundaries by 60 mV per pH unit. The copolymer of *m*-methylaniline (*m*-toluidine) and *o*-aminobenzenesulfonic acid was similarly prepared by electrocopolymerization at a relative excess of sulfonated comonomer, whereas only a thin insulating layer was obtained by copolymerization of the same sulfonated comonomer with either *o*-methoxyaniline or *o*-ethoxyaniline [58].

Recently, the need in a relative excess of sulfonated comonomer for its electropolymerization with aniline was confirmed for metanilic acid [59]. The optimum ratio of aniline and metanilic of 1:10 was found in preparing of a copolymer with 25% sulfonation degree [59]. The specific resistivity for this copolymer (530 Ω m) was found to be higher than for PANI, sulfonated with fuming sulfuric acid (166 Ω m) [60].

Apart from monosulfonates of aniline, its polysubstituted derivatives were also employed in electrocopolymerization. It was found that with increasing concentration of aniline-2,5-disulfonic acid (ADSA) comonomer in a feed solution containing aniline, the electrodeposition rate for copolymer decreases, and no solid copolymer film was deposited at a high content of ADSA [61]. Thus, the S/N ratio in the resulting copolymer could be varied between 0,

corresponding to PANI homopolymer, and 1.66, corresponding to polyADSA. In the latter case, the polymer shows a high solubility in water up to 109 g/l, and high conductivity of 0.34 S/cm independent on pH [62]. Initial stages of electrocopolymerization of aniline with diphenylamine-4-sulfonic acid [63,64], and of aniline, *o*-toluidine, and *N*-methylaniline with diaminobenzenesulfonic acid [65] has been investigated with in situ UV-Vis spectroelectrochemistry. The results revealed the formation of a head-to-tail type intermediate at initial stage of electrooxidation [63,64].

Electrochemical copolymerization of aniline and APSA was studied with UV-Vis spectrometry, and a film of the copolymer has been obtained at ITO glass electrode [38]. Copolymers of *N*-methylaniline and APSA were obtained by electropolymerization at platinum electrode, and it was shown that the properties of copolymer films obtained depend on the comonomer ratio in the electropolymerization solution [66]. Following the same way, copolymers of aniline and APSA were deposited on the electrode, and some known phenomena like the "first cycle effect" were investigated with the copolymers prepared [67].

4. Redox processes of self-doped polyanilines

The oxidation and reduction of PANI and its analogues is accompanied by the solution anion transport. For self-doped polyanilines, the presence of anionic group in their structure has a crucial effect on the anion binding or release upon the electron transfer. Thus, some attempts have been drawn to study the differences in anion movement between the parent PANI and its self-doped derivatives.

The ion exchange mechanism for PANI and SPAN, prepared by the direct sulfonation of PANI, has been studied by the probe beam deflection, and electrochemical quartz crystal microgravimetry [68,69]. It has been found that for electrochemical oxidation of PANI at pH > 2, the anions move into the polymer film in the first-oxidation process, whereas both anions and protons are expelled from the film in the second step. Contrary to this, only protons are expelled both in the first and the second-oxidation step [68]. By the use of the same techniques, it was later found that protons are expelled in both oxidation processes, followed by a counterflux of water into SPAN film at pH 1 [69]. No exchange of alkali metal cations has been found in a pH 1 solution whereas expulsion of Li^+ cations proceeds during electrooxidation of SPAN film in non-aqueous electrolyte [69].

An ellipsometric study of electrochemically deposited copolymers of aniline and metanilic acid show a small variation of a copolymer film thickness of about 2% between the reduced and oxidised states, in contrast to a high degree of variation, reaching 10–30% for PANI [59]. This indicate probably that the anion/water insertion during the first-oxidation step for copolymer is smaller than for PANI, but it increases with the decrease of the sulfonation degree.

Based on quartz crystal microgravimetric study, it has been concluded that, at pH 1, protons are mainly involved in the charge compensation process. At higher solution pH, an increase of anion and cation fluxes was observed, and a higher degree of participation of Li^+ compared to Cs^+ in this process was found [59]. The results reported in [59] could be summarized by the following equations.

In an acidic solution, the proton expulsion in the first-oxidation step proceeds:

$$(PANI \cdot H^+ - SO_3^-)_n - ne^- - nH^+ \rightarrow (PANI^+ - SO_3^-)_n.$$
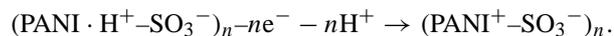
At higher pH, where an increased number of PANI–SO_3^- · M^+ groups is present in the polymer structure, both alkali metal cation (M^+) expulsion, and anion (A^-) insertion are possible, depending on the cation size and other variables:

$$(PANI - SO_3^- \cdot M^+)_n - ne^- - nM^+ \rightarrow (PANI^+ - SO_3^-)_n$$

$$(PANI - SO_3^- \cdot M^+)_n - ne^- + nA^-$$
$$\rightarrow (PANI^+ \cdot A^- - SO_3^- \cdot M^+)_n.$$
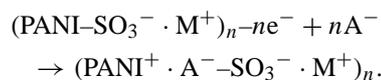
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