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THE EFFECT OF ELECTROACTIVE ANIONS ON SYNTHESIS AND ELECTROCHEMICAL BEHAVIOR OF POLYANILINE. APPLICATION PERSPECTIVES

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The article discusses the features of electrochemical synthesis and behavior of polyaniline and polyaniline based composites doped by electroactive anions (EAA). It has been found that in some cases electroactive anion forms complex with the aniline molecule in electrolyte, which performs as initiator of polymerization. This provides acceleration of the initial stage of aniline electropolymerization. As a result, it becomes possible to prepare high-quality corrosion resistant polyaniline coatings on non-noble metal electrodes. The composites based on polyaniline and nanocarbon materials (carbon nanotubes, graphene oxide) have been prepared, which are promising for use in supercapacitors. Using EAA we developed electrochemical sensors to hydrogen and total content of antioxidants in food.

Keywords: polyaniline, electroactive anions, doping, electrochemical behavior, applications.

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1. Introduction.
The role of anions in the formation of spatial structure of polymer matrices

Various electroactive polymers have been intensely investigated over the two past decades; moreover, polyaniline (PANI) is one of the most analyzed polymers. PANI is a ‘workhorse’ for researchers for several reasons, namely, because PANI is easily available and well-studied polymer stable in air, which can be a conductor and an isolator depending on oxidation state. In reduced state, PANI is soluble in several organic solvents and easily forms coatings on various materials. Therefore, it became possible to use PANI in different fields of engineering such as electrochemical energy storage systems (batteries and supercapacitors), electrochromic devices, optical and pH sensors, heterogeneous catalysis, gas-separating membranes, corrosion-resistant coatings and etc.) [1, 2]. Thus, it became necessary to analyze the possibility of PANI modification for the development of desirable technological properties such as conductivity, solubility, morphology, ability to form films, adhesion to other materials (metals and polymers), electrochemical capacity, charge-discharge characteristics, stability and reproducibility of experimental data.

In aqueous and organic solvents, PANI shows electroactivity in the presence of protic acid in electrolyte. It is well known that at reversible electrochemical oxidation of leucoemeraldine form of PANI in acidic media (Fig. 1), anions X^- are intercalated in a polymer matrix. Such intercalation is called the anionic doping of PANI. When PANI is doped by small and mobile anions, diffusion does not prevent the anions from leaving polymer while it is reduced and entering it while oxidized. Redox conversion in such systems is accompanied by structural changes in a polymer matrix.

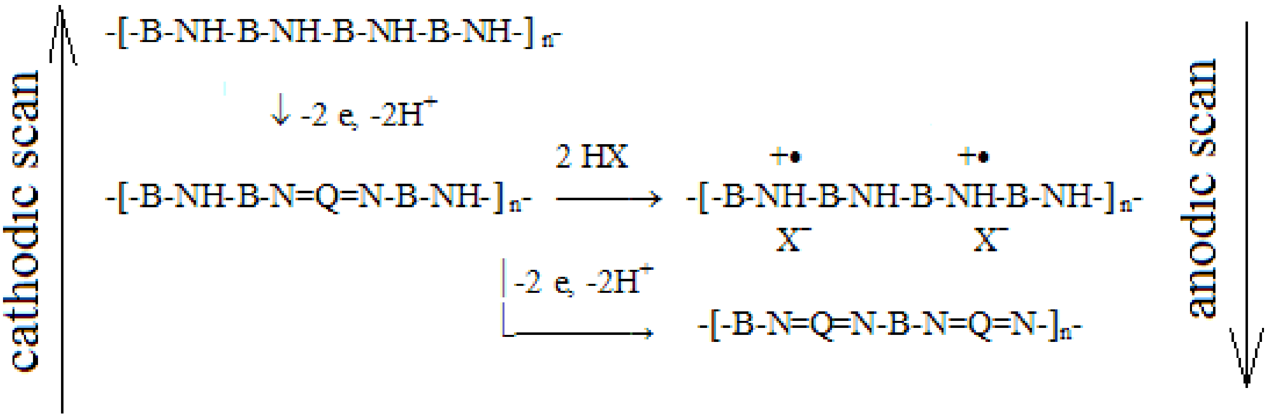

Fig. 1. The reversible acid/base doping/dedoping and redox chemistry of polyaniline

The nature of anions which compensate charge in a conducting polymer matrix affects strongly its properties. Therefore, the choice of electrolyte for chemical or electrochemical synthesis allows one to modify polymer properties and, hence, widen the field of application [3–5]. Routine electrosynthesis (ES) of PANI is performed in aqueous H_2SO_4. Nevertheless, other strong acids such as HNO_3, HCl, HBF_4, $HClO_4$, and CF_3COOH are used as well. It was found that the type of anion defines morphology of PANI and stimulates formation of either compact (HBF_4, $HClO_4$, CF_3COOH – the 1st class) or loose (H_2SO_4, HNO_3, HCl – the 2nd class) polymer structure [6]. It is reported in [7, 8] that similarly, albeit weaker, to anions, alkali metal cations affect electropolymerization rate and properties of PANI with the effect decreasing in the row: $Cs^+ \geq K^+ > Li^+ > Na^+$. The effect of anion on porosity and swelling of PANI was investigated by standard porosimetry [9]. Calculation showed that the use of Cl^-, $H_2SO_4^-$, $H_2PO_4^-$, BF_4^- and $HCOO^-$ in ES provides the formation of matrices with larger pore size upon swelling, while polymer matrices with organic CF_3COO^-, $CH_3-C_6H_4-SO_3^-$ anions are hydrophobic, in some cases being close to Teflon in hydrophobicity. PANI doping by more complex organic acids was investigated for improving of film formation. ES of PANI was carried out in the presence of camphor sulfonic acid [10], *p*-toluenesulfonic acid [11], substituted fluorosulfonic acids [12, 13], polystyrene sulfonic acid [14], and polyvinyl sulfonic acid [15]. Matrix oxidative polymerization of aniline in aqueous solution in the presence of poly(2-acrylamido-2-methyl-1-propane) sulfonic acid (PAPSA) provides the formation of a water soluble complex of polyaniline and PAPSA [16]. Substituted poly(styrene sulfonic) and various substituted polyacrylic acids were used as polyanions [17]. A molecular model of the complex formation between partially doped polyaniline (polycation) chains and negatively charged polyanion chains was suggested. It is a so-called double-stranded structure in which polyaniline macromolecules arranged along a polyanion macromolecule are held in such configuration due to electrostatic interaction forming twisted threads [17–21]. The syntheses afforded a series of water- and methanol-soluble matrix complex polyanilines that showed electroactivity at noticeably higher pH values which are important for the development of biosensors and other diagnostic devices for biological systems.

The search for new anions as dopants can reveal unexpected properties in the systems as it was shown, for example, in the synthesis of PANI in the presence of (+) – or (–)camphor-10-sulfonic acid. The synthesis afforded optically active chiral PANI, which retained its optically active configuration even after dopants had been removed from the polymer. The polymer ‘remembered’ its history after doping by hydrochloric acid as well [22–24].

The insertion of polyacid based polyanions into a polyaniline matrix allows polyanion to remain in polymer to prevent deprotonation in electrolytes with pH >4. As a result, redox activity and electric conductivity are retained [25]. Anion migration from polymer can also be lowered due to anions capable of forming chemical and coordination bonds with the PANI matrix, saving the polymer matrix.

2. Electroactive anions in PANI

All the above mentioned examples of the effect of anion on properties of PANI do not consider, in essence, electrochemical activity of anions. One of numerous classes of investigated anions is, in fact, a class of electroactive anions (EAA) or electroactive compounds bearing negatively charged groups. When inserted in PANI upon anionic doping, these compounds are able to increase electroactivity of polymer by their own electrochemical activity. New formed composite materials can show noticeably higher redox capacity as compared with PANI itself. One can also expect that within potential range of electro-inactivity of PANI, the composite will retain electroactivity due to EAA inserted in the polymer.

Doping anions can be inserted into the polymer during either synthesis of polymer or subsequent cycling in the electrolyte containing them. Tetrasulfo anions of phthalocyanines of Fe and Co were one of the first electroactive polymers inserted in PANI. Thus prepared composites were tested to catalytic activity in reaction of reduction of O_2 and showed low stability in time [26–28]. The doping of PANI by $[Fe(CN)_6]^{3-/4-}$ anions was accompanied by polymer degradation [29]. The insertion into PANI of electroactive anions based on quinoid derivatives provided better electrochromic properties of new composites [30]. The corresponding increase in redox capacity was reported [31], though the authors observed lower conductivity of polymer as a result of cross-linkage between PANI chains. The design, synthesis, and applications of polyoxometalate doped with the conductive polymer composites are critically discussed and future directions for their use in energy materials, sensors and electrocatalysis are envisioned [32–35].

The use of quinones as EAA allowed broadening the range and intensity of electrochromic properties of starting PANI [30]. Heteropolyanions containing various metals [36, 37], copper phthalocyanines [38], ferricyanides [39], representatives of *o*- and *p*-quinones and heterocyclic compounds, for example, indigo tetrasulfonate [31] tested as EAA allowed the development of a new class of high efficient biosensors. It was found that EAA which do not form strong chemical bonds with PANI substitute a part of major doping sulfo anions when cycled electrochemically in sulfuric acid. Such EAA can enter or leave reversibly polymer. Nevertheless, they can remain partially linked with a PANI matrix as counter ions thus increasing specific capacity of modified composite material.

Of considerable importance is the effect of EAA on synthesis reaction rate and electrochemical behavior of PANI. It is known [40] that the limiting stage of electrochemical and chemical synthesis of PANI is oxidation of aniline An to radical cation (Fig. 2) followed by dehydrodimerization and the formation of *p*-aminodiphenylamine. Then the reaction observed is an autocatalytic one.

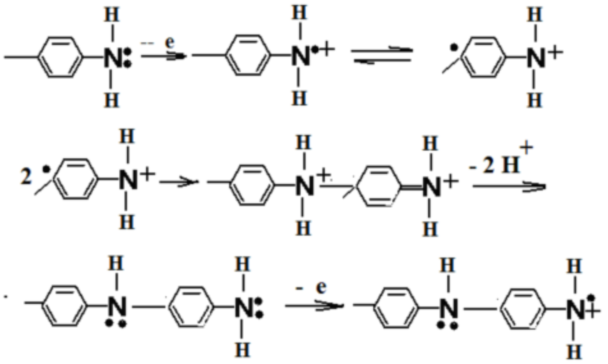

Fig. 2. Scheme of electrocatalytic oxidative mechanism of PANI synthesis

It was found that in the presence of EAA in electrolyte, ES is carried out at lower oxidation potentials and shorter induction period. Independently of electrode material and method of ES, $IrCl_6^{2-}$ was discovered to be the most efficient [41–53]. It is assumed, that strong oxidative properties of $IrCl_6^{2-}$ provide easy oxidation of several aliphatic and aromatic amines and diamines. Depending on concentration of electrolyte and acidity of solution, formal potential of $IrCl_6^{2-}$ / $IrCl_6^{3-}$ is within 0.7–0.8 V vs. SCE [54, 55], and the start of oxidation of aniline on Pt electrode in 1 M HCl is observed at 0.45–0.65 V vs. SCE. One can assume from the analysis of the experimental data that $IrCl_6^{2-}$ easily oxidizes coordinated aniline and performs as oxidant regenerated on electrode upon electrochemical cycling.

It was possible to isolate a complex from solution with An: $IrCl_6^{2-}$ = 2 molar ratio. It was found from elemental analysis that complex composition is An: $IrCl_6^{2-}$ = 2 as well [46]. Considering that $IrCl_6^{2-}$ is one-electron oxidant, one could assume two modes for the state of aniline molecules in the complex: i) one aniline molecule is in oxidized radical state and the other one is in neutral state; ii) both aniline molecules form a dimeric radical. The study of the interaction of EAA with An by IR-Vis and ESR spectroscopy [46] allowed of certain conclusion on formation pathways and possible structure of the initial complex. Most probably, the first stage consists in the formation of an ionic pair $IrCl_6^{2-} \cdot C_6H_5NH_3^+$, which converts to $[IrCl_6^{3-}(C_6H_5NH_2^{+\cdot})]^-$ (I) and electron transfer from An to Ir(IV). Then a neutral An molecule is captured which results in the formation of a final Ir(III) complex containing paramagnetic dimer $[IrCl_5(C_6H_5NH_2)_2]^{+\cdot}$. In this way $IrCl_6^{2-}$ speeds up the formation of *p*-aminodiphenylamine and reduces or eliminates the induction period.

The organic radical anion containing negatively charged groups can perform as EAA as well. The 2,2-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS) bears a bulky $ABTS^{2-}$ dianion (Fig. 3), which is well retained in the PANI matrix due to electrostatic interaction and steric factors.

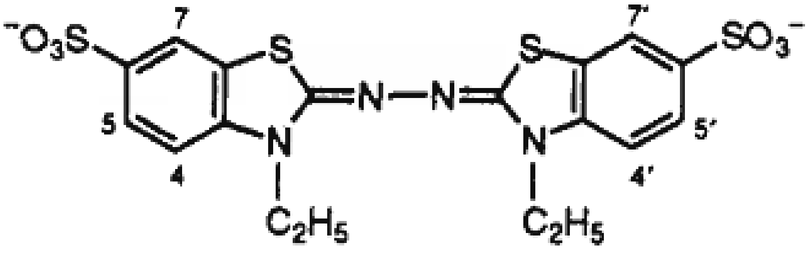

Fig. 3. Structural formula of 2,2-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) dianion ($ABTS^{-2}$)

As for $IrCl_6^{2-}$, an $An \cdot ABTS^{2-}$ = 2 complex can be isolated from solution containing 1M H_2SO_4 and aniline [51]. In water solution with pH<3, $ABTS^{2-}$ exists as $HABTS^-$, and electrode potential for the $ABTS^{\cdot-}$+e +H^+=HABTS- reaction determined from CVA [50] is $E_{1/2}$= 0.53V (SCE). Thus, $ABTS^{\cdot-}$ is a weaker oxidant than $IrCl_6^{2-}$ and most probably its effect on ES is stipulated by adsorption of a uncharged $[An_2\ ABTS^{2-}]^0$ complex on the electrode that results in shorter induction period in ES. However, in contrast to the effect of $IrCl_6^{2-}$, the growth of a PANI coating is slower. The prepared samples of PANI showed noticeably better electrochemical parameters upon cycling (electrochemical capacity and Coulombic efficiency) [51]. One can assume that the improvement is due to looser structure of PANI (Fig. 4a, 4b, 4c) formed during ES, which remains upon cycling in another EAA free electrolyte. Thus, initially formed structure of PANI shows 'memory' effect. After doping PANI with other anions, it is still possible to re-dope PANI with 'parent' EAA [59].

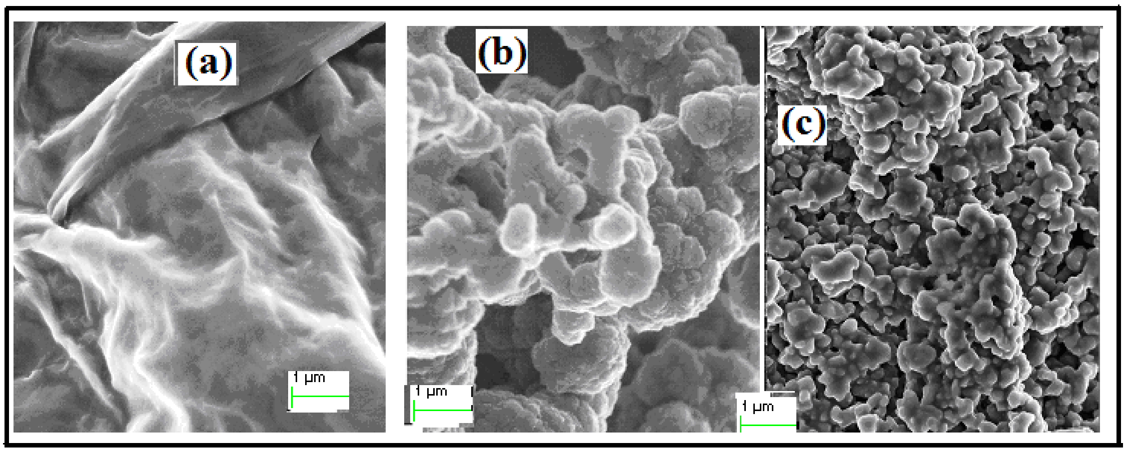

Fig. 4. SEM images of PANI samples obtained in potentiostatic mode of (a) 0.1M AS in 0.1M H_2SO_4, (b) from the same in the presence of electrolyte $IrCl_6^{2-}$ (An: $IrCl_6^{2-}$ = 10^3), (c) of the same electrolyte in the presence of ABTS (An: $ABTS^{2-}$ = 10^3)

Interesting catalytic properties are illustrated by electroactive MnO_4^{-1} anion [45, 56, 57]. It was shown by using spectrophotometry that aniline oxidized by electroactive MnO_4^{-1} anion forms blue solutions which most probably contain dimers of aniline formed after dimerization of radical or radical cation particles of aniline. The most favorable conditions for preparing polymers containing minimal number of defects are potential scanning synthesis and concentration of EAA of 10^{-4}–10^{-5} M. The role of $KMnO_4$ is the most demonstrative in the synthesis of PANI on Ta and Si electrodes [57], where polymer coatings were prepared at potentials of 0.4 and 0.6 V. In the absence of $KMnO_4$ the polymer can be prepared on these electrodes at potentials >1 V only.

3. Electrochemical synthesis of PANI coating on non-noble metals passivated by oxide films

The interest to metal protection from corrosion through deposition of conducting polymer coatings and, namely, PANI arose in the early 80-s of the 20th century [60]. ORMECON Chemie GmbH (Germany) used PANI based coatings deposited from dispersions in organic solvents on non-noble metal surface (carbon and stainless steel, copper). The group of researchers from Los Alamos and NASA showed the possibility of protection of metal structures from corrosion by acidic gases evolved at spaceship launch. They suppose that the corrosion-inhibiting effect is stipulated by the shift of corrosion potential to positive values up to that of noble metals. Corrosion current decreased or even vanished. High corrosion stability of PANI is a result of the formation of a stable composite layer formed by oxide and conducting polymer on metal surface. The formation of transition metal complexes with PANI is discussed in detail in [61]. In general, the term 'composite' is used to describe systems containing components able to form own phases. If one of the components is distributed uniformly in a polymer matrix of another one, the component can be considered as a bulky one. However, when a polymer coating is formed on the surface of another material, an intermediate layer formed at the interface contains phase components as well. Such layers can be called surface composites. Most often, surface composites form upon applying a conducting polymer coating by electrochemical polymerization of monomer. Below there are some examples which show that EAA play an important role in ES of coatings on various metallic supports.

PANI films can protect surface of various materials such as non-noble metals, electroconducting oxides, semiconductors and others [41, 45, 47, 51, 62–67]. Polymer coating is synthesized on the surface of a passivating oxide layer formed on protected metallic supports. Such a layer is formed by either normally or by protecting surface passivation. If an oxide film is stable enough in acidic solution used in synthesis of PANI, cell voltage should be increased essentially to compensate high resistance of an oxide layer that, in turn, results in essential overoxidation of PANI and the formation of defect island PANI coating. Of great importance is higher adhesion of polymer coating due to the formation of chemical bonds of PANI with oxidized metal surface.

We investigated corrosion-resistant coatings for surface of Ti [42], Ta [41], Pb [43], Al[44], p- and *n*-Si [47, 68], and stainless steel [41]. Electrodeposition of PANI onto non-noble metals is hindered by that some metals dissolve and others are passivated to form low-conducting oxide films in acidic medium at positive potentials of ES of PANI. Electrooxidation of monomer is impossible on the surface of dissolving metal because of its reductive properties. Generally, ES of PANI on metal surface covered by oxide film requires a special synthetic procedure which involves thorough mechanical treatment of the electrode surface. Generally, ES is carried out in inert atmosphere.

In case of the formation of a passivated oxide film, ES is realized in conditions unfavorable for the formation of high-quality coating because of isolating properties of an oxide film. It was shown [41, 42] that the addition of initiators, namely, catalytic quantities of transition metal salts to the reaction medium facilitates noticeably ES of PANI on Ta, Ti and stainless steel electrodes. Then this technique was tested on various surfaces. Potentiostatic, galvanostatic and potential pulse conditions were used for ES. It was found that pulse conditions provide higher quality of coatings. However, a key role is played by EAA in electrolyte that allows very homogeneous, dense, uniformly distributed and well-adhered electrode coatings to be prepared. In the absence of initiator, non-uniform island growth of polymer coating is usually observed, which most probably starts on either defects or places of the smallest thickness of an oxide film.

The insertion of transition metal anions in an oxide film during growth provides a uniform distribution of polymer coating nuclei. All tested non-noble metals were covered by intrinsic oxide films, which protected active metal surface and provided stability in air. However, such films show different stability in acidic media. For Ti, Ta and Pb, ES of PANI was possible in sulfuric acid without extra oxidation. Fig. 5a shows the examples noticeably lower voltage in galvanostatic synthesis and Fig. 5b shows shorter induction period in potentiostatic synthesis on these metal surfaces. The use of Al required special pre-passivation of the electrode surface since intrinsic oxide coating did not protect metal from corrosion in conditions of ES of PANI (anodic potential and acidic medium). The highest quality PANI coatings were prepared in potential pulse conditions on the electrode passivated using technique reported in [44]. This method consists in pre-treatment of an Al electrode by the salt of K_2IrCl_6 dissolved in water-alcohol mixture, washing-off and annealing at 400^{0}C. Iridium inserted in an oxide layer and at positive potential was most probably in oxidation state +4.

Fig. 5c and 5d illustrate the first moment of oxidation of An on Pt, Ti, and Ta electrodes in $IrCl_6^{2-}$ free 1 M H_2SO_4 (Fig. 5c) and in the presence of $IrCl_6^{2-}$ (Fig. 5d). In chloroiridate free solution An starts oxidizing at potential higher than +0.7 V on Pt electrode, +0.8 V on Ti electrode and +1.0 V on Ta electrode, and An does not oxidize on Pb and Al electrodes within this potential range. It is seen from Fig. 5 that the addition of catalytic quantities of $IrCl_6^{2-}$ (An: $IrCl_6^{2-}$ = $10^2 – 10^3$) noticeably shifts oxidation potentials of An to the cathodic range for Ti and Ta electrodes. After several cycles of passivation, An starts oxidizing in the presence of catalysts on at +06 V on Pb electrode and +0.75-0.8 V on Al electrode.

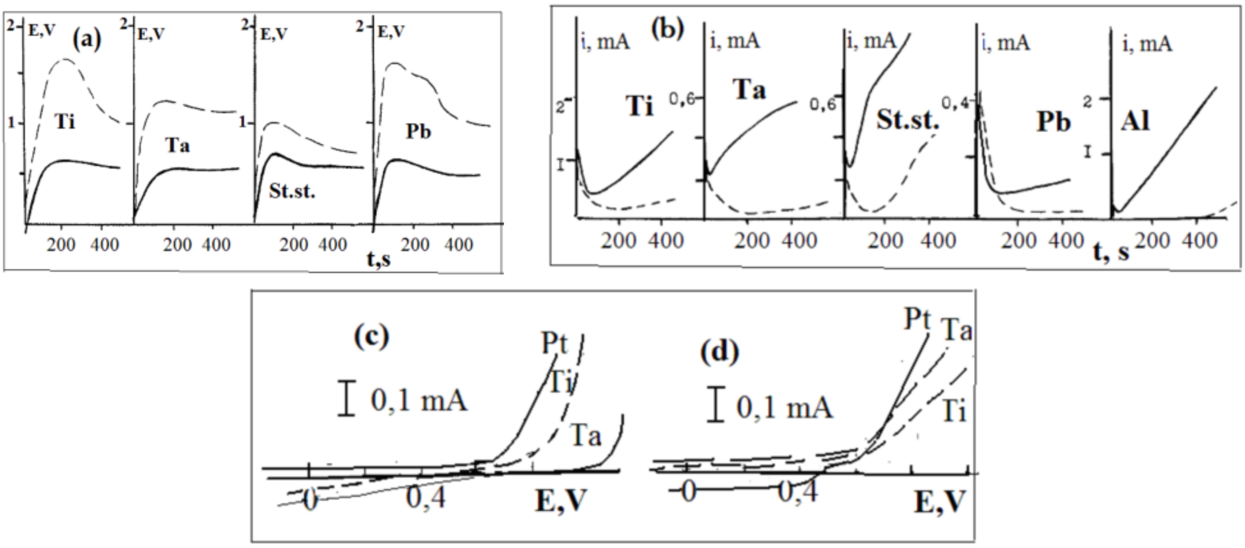

Fig. 5. (a) Galvanostatic synthesis of PANI at i = 0.2 mA/cm ^{2} at Ti, Ta, Pb and stainless steel electrodes; without a catalyst (– – –); that in the presence of $IrCl_6^{2-}$ (——), (b) potentiostatic synthesis of PANI at E = +0.8 V without a catalyst (– – –); that in the presence of $IrCl_6^{2-}$ (——). In 0.1 M aniline solution in 0.1 M H_2SO_4; [$IrCl_6^{2-}$] = 10^{-3} M.
(c, d) Starting the oxidation An from 0.1M AS in 0.1M H_2SO_4 (c) without a catalyst;
(d) in the presence of electrolyte $IrCl_6^{2-}$ (An: $IrCl_6^{2-}$ = 10^3)

Similarly, technique for ES of PANI on *p*- and *n*-Si was developed. Anodic etching of silicon surface covered by a thin layer of silicon dioxide in aqueous hydrofluoric acid provides high developed surface of porous silicon (PS). The conditions for preparation of PS affect both surface conductivity of PS layers and size of pitting pores which determine ES of PANI on pore surface. Conducting material inserted in pores would provide electrical contacts with PS layers and has own developed conducting surface. Potentiostatic, potential pulse and galvanostatic methods for ES of PANI on the surface of *p*- and *n*-Si were tested [47, 68]. It was shown that the use of catalytic quantities of initiator $IrCl_6^{2-}$ in ES (An: $IrCl_6^{2-}$ = 1000) accelerates ES of PANI and decreases working potential down to 0.65–0.7 V (Fig. 6).

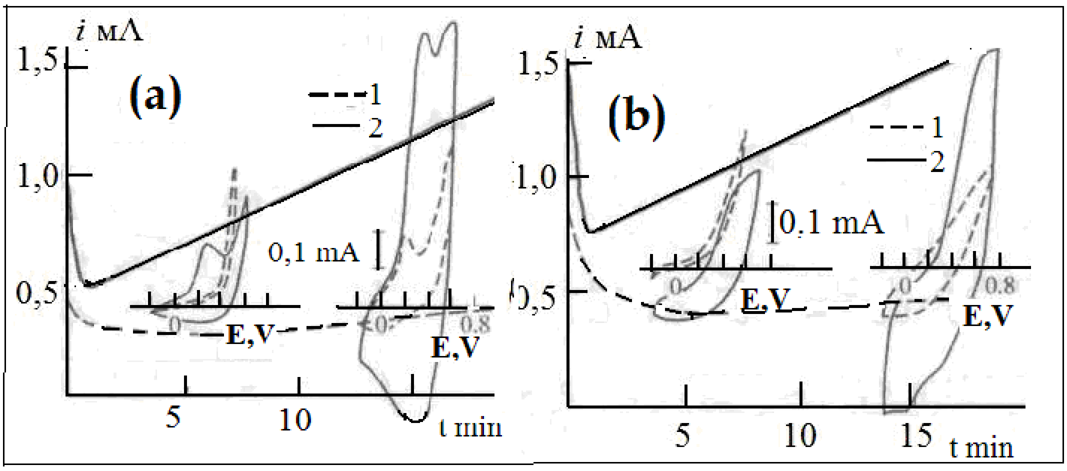

Fig. 6. Current change with time under potentiostatic synthesis of PANI and CVA PANI ES on the *p*-Si (a) and *n*-Si (b): (1) at 0.8 V; (2) - at 0.7V with the addition of the electrolyte H_2IrCl_6.

An: $IrCl_6^{2-}$ = 10^3. CVA dropped in the reaction solution after 5 and 15 minutes of synthesis. V = 20mV/s

It was shown that stability of a polymer coating depends strongly on method of preparation of PANI and type of Si electrode. The highest stability till 7.5 M H_2SO_4 displayed PANI coatings prepared on *p*-Si in the presence of $IrCl_6^{2-}$ at 0.65 V in potentiostatic conditions. It should be noted that such behavior of *p*-Si is due to the fact that holes are major current carriers and their concentration in the anodic range of ES of PANI is always high. Anodic behavior of *n*-Si is governed by the behavior of oxidant ($IrCl_6^{2-}$) as a source of additional valence electrons. For *n*-Si, noticeable dissolution of PANI coating starts even in 5 M H_2SO_4. Possibly, the presence of oxidant provides extra oxidation of *n*-Si surface, and adhesion of a polymer film to electrode surface is not strong.

4. PANI based nanocarbon composite materials

Recently, the development of electrode materials for electrochemical supercapacitors based on PANI composite and carbon nanotubes or graphene as carbon filler has attracted great interest. Depending on synthetic procedure, PANI shows high specific capacity ranging from 500 to 1400 F/g, which consists of double-layer capacity and Faraday capacity (pseudo-capacity), but mechanical properties of polymer are unsatisfactory upon cycling as a result of changes in electrode volume upon doping/dedoping by anions. As a result, >50% loss of capacity is observed after 1000 cycles. Moreover, reduced PANI shows insulating properties. Carbon nanotubes (CNT) represent the good mechanical properties and repeated charge-discharge cycles do not affect their specific capacity, which is not high enough [69].

One could expect that the design of composites based on conducting polymers and nanotubes allows best properties of these materials to be combined. Indeed, it was shown that the insertion of carbon nanotubes (CNT) in PANI provides the formation of cage of reinforcement in a polymer matrix, which increases mechanical strength of polymer and conductivity of a composite electrode [69, 70]. The composite is formed as a result of chemical synthesis of PANI in the presence of oxidants and CNT and electrochemical synthesis of PANI in the presence of CNT in electrolyte. PANI composites containing from 0.1 wt.% to 65 wt.% of CNT were prepared and characterized [69].

Very high values of specific capacity for PANI based composite electrodes containing different carbon fillers are reported: 500 F/g for nanofibers (0,8 wt.%) [71], 350–606 F/g with CNT [72–75]. PANI composite with graphene oxide or reduced graphene oxide shows specific capacity [72, 76–88] from 210 to 1130 F/g [82, 84, 86]. However, it should be noted that the discrepancy of experimental data can be interpreted by different synthetic procedures and methods of investigation.

The basic method for preparation of PANI composites with carbon nanofillers is chemical oxidative polymerization of aniline *in situ*, i.e. polymerization in the presence of nanofiller dispersion in reaction medium [89]. The advantages of such approach are simplicity, possibility of scaling up the process, possibility of varying polymerization conditions, and uniform distribution of nanofiller particles in a polymer matrix.

The investigation of polymerization products prepared in the presence of CNT by transmission electron microscopy (TEM) showed that growing polymer forms two phases, one of which forms a closed shell round CNT (‘surface polymerization’), while the other one is free polymer with granular morphology in the space between CNT. The ratio between these phases can be varied depending on reaction conditions. Surface polymerization can be realized by optimizing reaction conditions [90] and/or changing surface properties by functionalization [91].

The most effective method for preparation of structurally uniform PANI–CNT composite is pre-modification of nanotube surface using polymerization initiators – electroactive anions.

CNT were modified using surface adsorption of polymerization initiators $IrCl_6^{2-}$ and ABTS from solution (Fig. 7).

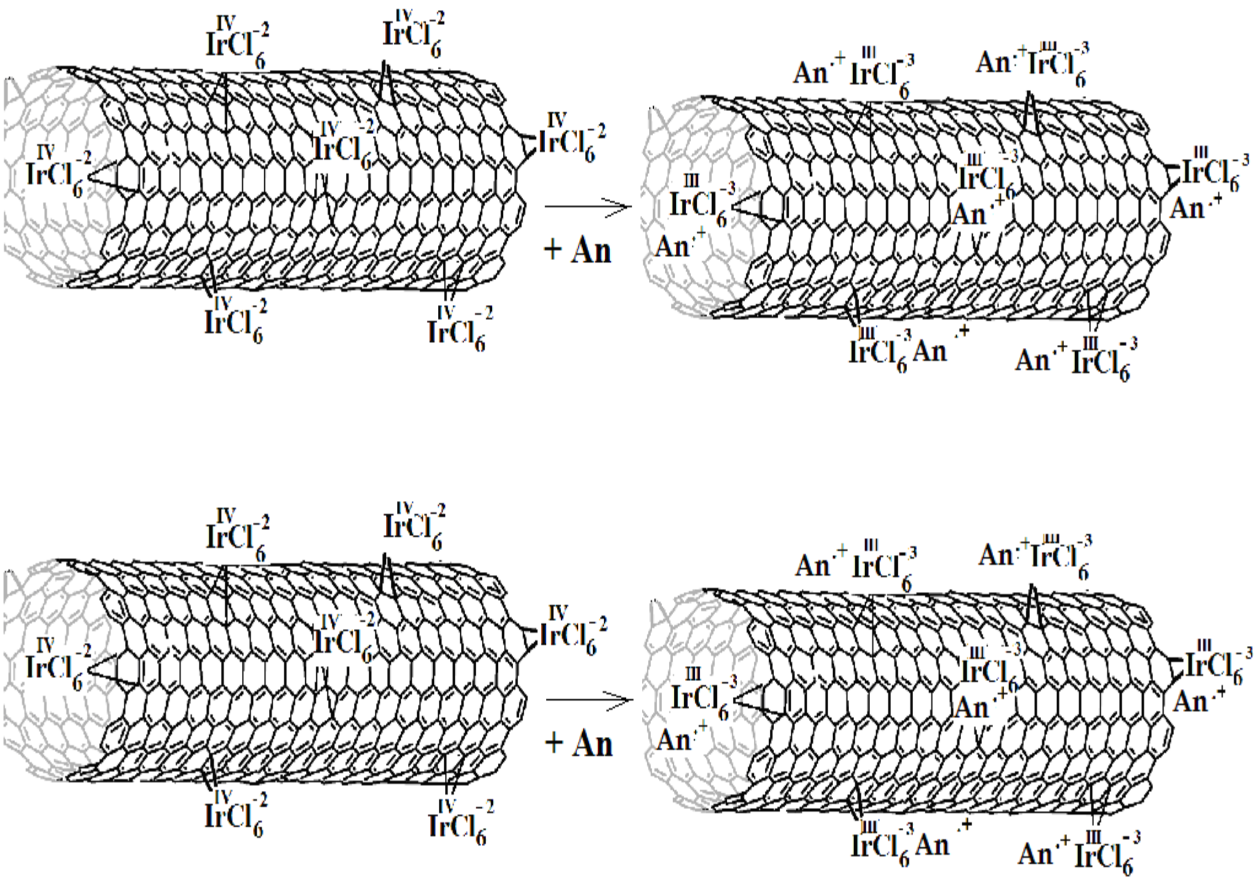

Fig. 7. The schematic arrangement of the $IrCl_6^{2-}$ catalyst and An on carbon nanotubes

Percentage of adsorbed $IrCl_6^{2-}$ и ABTS determined from maximal changes in optical density of solution was 8 and 14 wt.%. After chemical synthesis of PANI on modified surface of CNT, the samples were tested by TEM (Fig. 8).

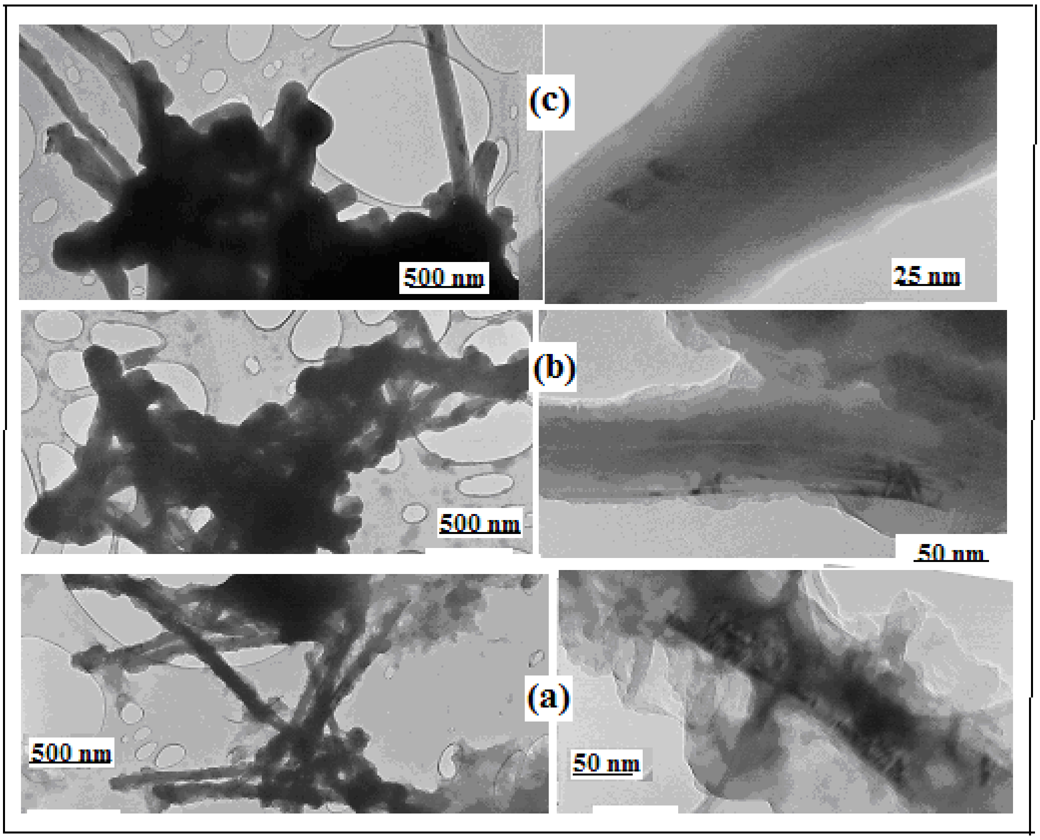

Fig. 8. Micrographs of the composites obtained by transmission electron microscopy: (a)PANI / CNT; $^{-}$ (b) PANI / CNT / $IrCl_6^{2-}$ and (c) PANI / CNT / ABTS

A weakly pronounced polymer coating non-uniform in thickness forms on the surface of unmodified CNT (Fig. 8a) along nanotubes (1–30 nm). The coating has irregular diffusion boundary. On the contrary, a polymer coating of composites with modified nanotubes along nanotubes is of essentially larger size (40–100 nm) and has smooth boundary (Fig. 8b, 8c). The most obvious example is a composite with ABTS, where polymer forms an amorphous uniform in thickness and density coaxial shell round nanotubes. The coating boundary is well-pronounced and smooth. Thus, adsorbed initiator accelerates polymerization of aniline on the surface of nanotubes, i.e. at the interface as described in [92–93]. A similar transition of polymerization from substrate surface to the bulk of reaction medium was found by IR Fourier spectroscopy [94].

The modified samples showed better electrochemical parameters [49]. The most noticeable is electrochemical reversibility of electrode reactions, namely, the difference of potentials of anodic and cathodic peaks $\Delta E = E_{pa} - E_{pc}$ is lower in a composite containing modified CNT. Another very important peculiarity for the use in supercapacitors is retention of electrochemical capacity in composite upon repeated cycling. After 100,000 cycles in potential pulse conditions, the loss of capacity for the ABTS containing composite was 5% against 20% for non-modified samples. These experimental data allow one to conclude on that the formation of individual polymer shells around modified CNT provides the conditions for higher reversibility of electrode reactions, which is most probably due to increased charge transfer rate in the CNT–PANi shell system. Fast charge transfer from one electroactive center to another (redox conductivity) inside a polymer shell is accelerated additionally by the participation of a conducting framework of CNT. Obviously, charge transport is more efficient as compared with parent polyaniline and composites containing non-modified CNT specified by the presence of a phase of PANI unbound from the surface.

Interest to commercial application of nanocarbon materials has grown especially after the discovery of graphene by Nobel Prize winners A. Geim and K. Novoselov [95]. Graphene is a honeycomb-like monolayer formed by sp^2-carbon atoms. Though monolayered graphene can be used in electronic devices, most interest of developers of carbon nanomaterial composites is attracted to quite accessible graphene oxide stacks or nanosheets, which can exist as stable dispersion in solvent (water, alcohols, dimethylformamide and others). Generally, graphene oxide nanosheets (GONS) are original carbon nanomaterial as fine powder. To distinguish it from monolayered graphene, term '3D-graphene' is used. In comparison with monolayered graphene, GONS show certain disadvantages including low specific surface and electroconductivity. The disadvantages are stipulated by the presence of oxygen bearing epoxy and hydroxyl groups on the surface, and carbonyl and carboxyl on the edges of nanosheets. These groups prevent aggregation of GONS and are useful for preparing composites with, for example, PANI due to the ability to form hydrogen bonds. Polarity of functional groups provides higher wettability of electrode material [96–100]. Below are the results of syntheses and analysis of properties of PANI-GONS and PANI – reduced GONS (RGONS) composites. Methods for chemical synthesis of composites of PANI in the presence of fine dispersion of GONS reduced at 1200 mV (SCE) (RGONS) were developed [52]. Composites with different percentage of PANI were tested as electrode materials for supercapacitors.

A detailed examination of this material shows that interaction is generated between a polymer matrix and GONS in polymerization, which is accompanied by partial reduction of GONS. One can assume that this provides higher conductivity of partially reduced graphene oxide. In general, a nanocarbon component can be considered as extended surface current-carrying network (Fig. 9), which provides higher electron conductivity as compared with pristine polyaniline. Specific capacity of a GONS- PANI composite electrode was 547 F/g upon cycling within the 0.7–0.05 V range in 1M H_2SO_4. GONS are uniformly distributed in PANI matrix of the above described composites. Nevertheless, it was possible to synthesize electrochemically composites in which the RGONS layer was applied directly on surface of electrode (glassy carbon or metallic plate) and covered by the PANI layer on top. For this purpose, water dispersion of GONS (3 mg/ml) was reduced electrochemically at –1.2 V in 0,15 M $LiClO_4$ on a glassy carbon (GC) electrode, which was a bar (S = 0.2 cm^2) sealed in a glass tube or a plate 1x4 cm in size. To prepare RGONS coatings of different thickness, electrolysis was carried out for 500, 750, 1000, 1250, 1500 and 2000 seconds. To prevent agglomeration of RGONS, the electrode was washed repeatedly with distilled water and stored in 1M H_2SO_4.

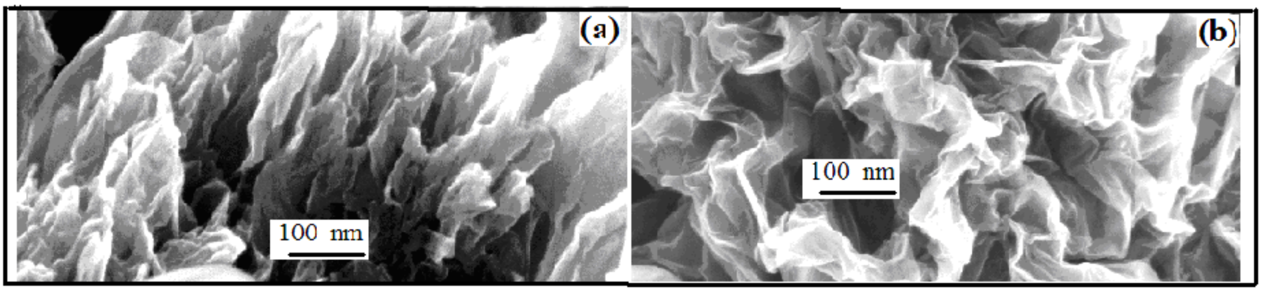

Fig. 9. Electron micrographs of the resulting coatings RGONS with the times of electroreduction GONS (–1200mV): (a) 500s, (b) 1000s

In addition before ES of PANI anions $IrCl_6^{2-}$ were adsorbed on RGONS coating. This allowed one to obtain developed interface since the participation of initiator $IrCl_6^{2-}$ provided polymer growth even in almost inaccessible area of RGONS coating such as folds and pores. The main task is to preserve to maximal extent the developed surface of the electrode coating which appears as separate nanosheets as evidenced from TEM [52, 99].

To control adsorption of $IrCl_6^{2-}$, the GC electrode covered by RGONS was immersed into a cell filled with solution of desired concentration of $IrCl_6^{2-}$, and the changes in absorption spectra were monitored. It is seen from Fig. 10a (curve 2) that almost 70% of $IrCl_6^{2}$ was adsorbed on RGONS for 90 minutes: 0.84–0.88 wt.% of Ir according to the energy dispersive spectra. However, the adsorption of $IrCl_6^{2-}$ on the surface covered by non-reduced GONS(S = 0.2 cm^2) is noticeably slower (Fig. 10, curve 1). For comparison, ~10% of $IrCl_6^{2-}$ (0.06 wt.%) was adsorbed from solution on non-reduced GONS. The growth of PANI coating is going on more active on the RGONS surface treated by $IrCl_6^{2-}$ than on untreated GONS surface. This fact is justified by the CVA data (Fig. 10b).

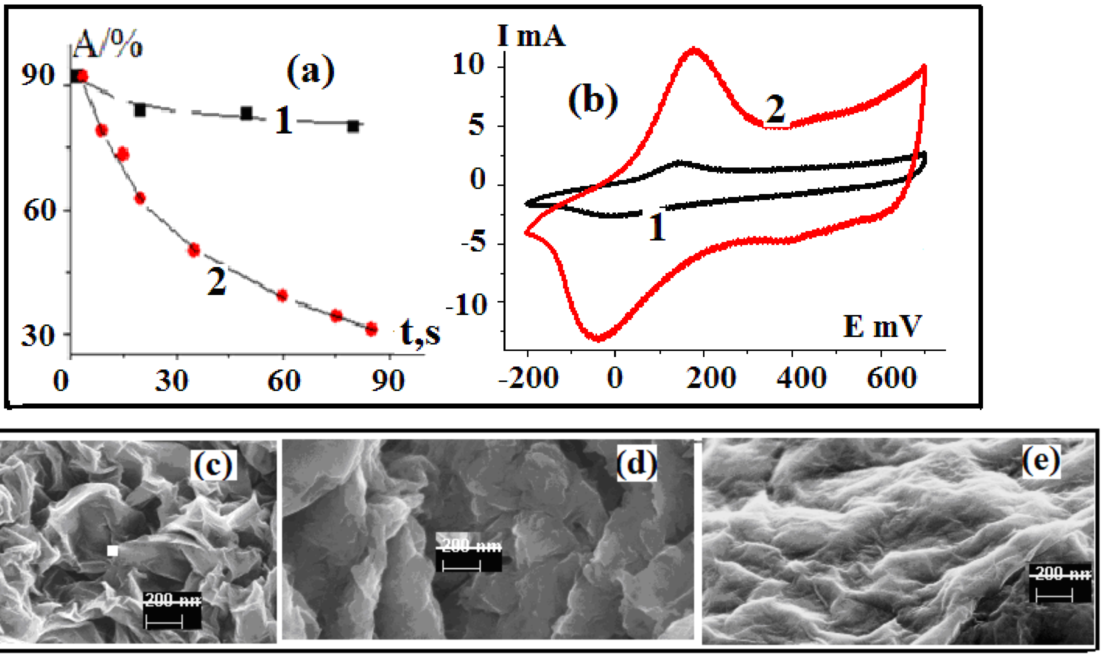

Fig. 10. (a) The absorption curves $IrCl_6^{2-}$ solution of [0,25.10^{-6} M/ ml] GONS surfaces (curve 1) and RGONS (curve 2) with time; (b) the amount of PANI on surfaces GONS (1) and RGONS (2) in potentiodynamic ES from 0.1 M solution of the AS in 0.1 M H_2SO_4 for 100 cycles. SEM image surfaces of composites of PANI-RGONS with the content of PANI; (c) 15 wt.%, (d) 30 wt.%, and (e) 60 wt.%

Of considerable importance for electrochemical properties of layered PANI-RGONS composite is mass ratio of components. Maximal specific capacity and especially upon repeated cycling is provided by the content of PANI higher than 50%. Critical changes in conductivity and electrochemical capacity are observed at 30–75% percentage of PANI /RGNOS (Fig. 11).

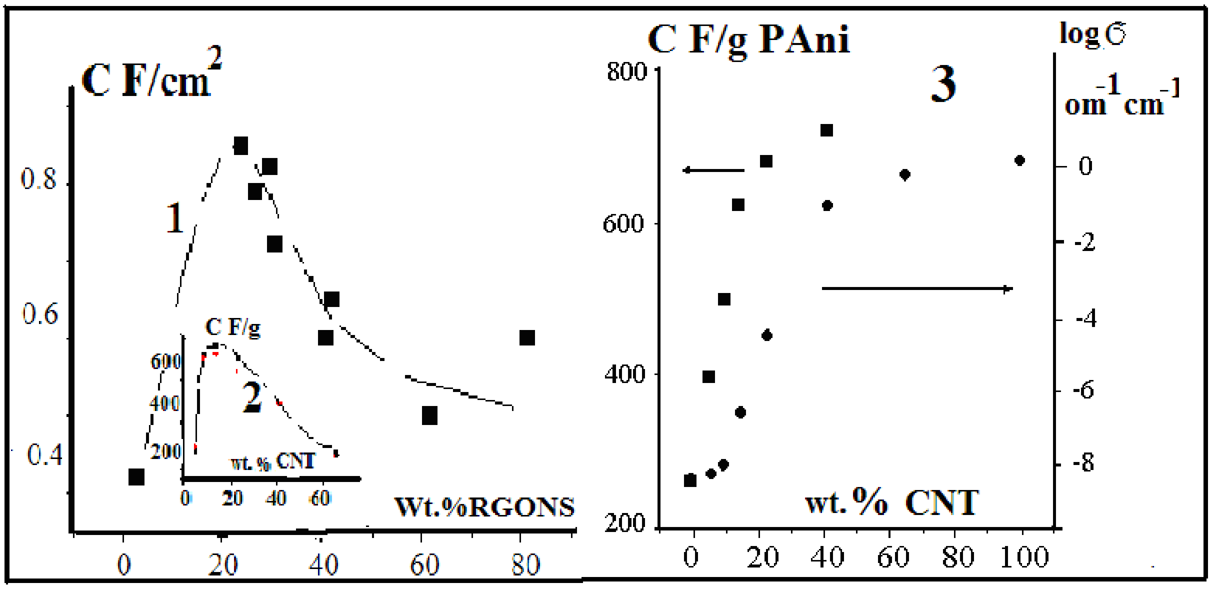

Fig. 11. Calculated C for PANI composite carbon component: for PANI-RGONS (1); for PANI-CNT (2). Critical changes in conductivity and electrochemical capacitance as a function of wt.% carbon content in the composite material for the PANI-CNT (3)

It was shown by TEM that the surface of RGNOS is almost filled by polymer. Further increase in the amount of deposited PANI provides the formation of compact coating which complicates access counter ions in material (Fig. 10 c and d).

5. Development of electrochemical sensors to hydrogen and antioxidants

5.1. Study of electrocatalytic properties of Pd, Pt, Rh, Ir, dispersed in PANI matrix and on carbon nanomaterial surface

An urgent task for hydrogen power engineering is now the development of amperometric sensors to hydrogen able to work in air, dry inert atmosphere and vacuum. In hydrogen sensors, the catalysts in indicator electrodes are platinum metals in high dispersed state applied to polymeric or carbon supports. We suggested that material based on PANI and CNT should be used as support [101–102]. One can use proton conducting polymer electrolyte, for example, polyvinyl alcohol – orthophosphate acid – water in which cell electrochemical reaction:

$H_2 - 2e^- > 2H^+$ proceeds, or solid fluorine-conducting electrolyte, for example, $Pb_{0,9}Al_{0,05}Ti_{0,05}F_{2,1}$ in which reaction: $H_2 + 2F - 2e^- > 2HF$ proceeds. As conducting polymer, PANI does not manifest sensitivity to hydrogen. Catalytic activity of platinum metal is affected by the choice of metal, its quantity and method of insertion in a conducting polymer matrix. It was shown [103] that the use of reduced PANI when applied to catalysts surface allows one to prepare more active electrodes than the use of oxidized PANI. Two types of catalysts were tested, namely, PANI and PANI-CNT composite based ones. Two methods were used to insert catalysts in a polymer matrix. In the former method, $PdCl_2$, H_2PtCI_6, K_2IrCI_6 or $RhCI_3$ were introduced in electrolyte containing controlled amount of aniline sulfate and 0.1 M H_2SO_4, and ES was performed in potential scanning conditions at –0.2+0.7 V (SCE). When potential was scanned to the positive potential range, PANI film grew on the electrode surface, and anions of platinum metal salts inserted in polymer matrix as counter ions. At reverse potential scanning to the cathodic field, platinum metal salts dissolved in electrolyte were reduced to metallic state in the bulk of polymer. In the latter method, PANI was pre-synthesized in metal salt free electrolyte. Electrosynthesis was accomplished at –0.1 V and electrode kept up for several minutes to stationary current. The electrode covered by polymer was washed with distilled water and kept in solution of $0.5–4.10^{-3}$ M of metal salt in 1M H_2SO_4. Then the electrode was washed with distilled water, dried and cycled in 0.1M H_2SO_4 in the –0.2+0.7 V potential range for active centers of electropolymerization could be formed.

The electrodes were tested for catalytic sensitivity to H_2 in gas mixtures, namely, $Ar+H_2$ and N_2+H_2. The experimental study of the reaction of hydrogen oxidation: $H_2 - 2e^- > 2H^+$ with proton conducting electrolyte containing polyvinyl alcohol and phosphoric acid (PVA-$H_3PO_4 \cdot xH_2O$) in Ar–H_2 mixture showed that maximal catalytic activity and a linear dependency of current on concentration of hydrogen is demonstrated by the PANI-Pd electrode. Proton conducting electrolyte (PVA-H_3PO_4 xH_2O) and PANI-Pd can be used in the development of hydrogen gas sensors to be operate in gases containing water vapors. Linearity of the dependence of sensor current on concentration of hydrogen can be achieved in the 0–100 v.% of H_2 concentration range.

The study of the reaction: $H_2+2F^- +2e^- \rightleftarrows 2$ HF showed linearity of the dependency of reaction on concentration of hydrogen in gas phase. The dependency is linear in the H_2 concentration range 0–1 vol.% for the PANI-Pd electrode and 0–0.1 vol.% for MWNT-Pd. Fluorine conducting electrolytes can be used in the development of gas sensors of amperometric type for detection of hydrogen in inert gas media in the absence of water vapors in contrast to proton conducting electrolytes.

5.2. Chemically modified PANI based electrode as an amperometric sensor for determination of total antioxidants content

EAA has been used to develop a sensor based on chemically modified electrode (CME) for determination of total antioxidants capacity (TAC) in fruits, vegetables, vines, etc. Antioxidants are 'sacrificial' agents which efficiently scavenge free radicals thus protecting cells from oxidative damage. The principle of operation of such CME is based on the reaction of mediator (oxidant) present in electrode coating with antioxidant (reductant) at the CME/electrolyte interface. The oxidized form of mediator will react again with antioxidant resulting in an increase of the current from the bulk of polymer to an electrode (Fig. 12).

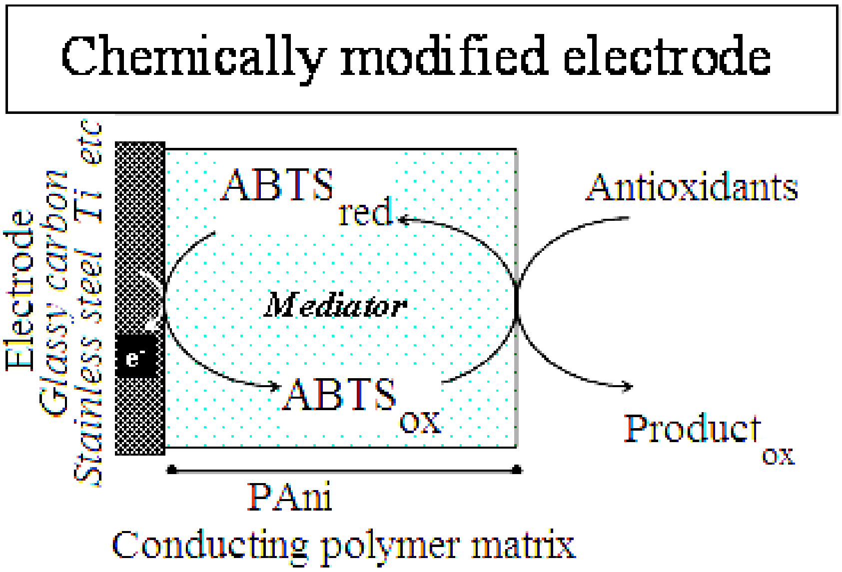

Fig. 12. The scheme of the electrochemical biosensors as high-organized catalytic system

The impetus to this work was chemical methods of analysis [58, 104] based on the rapid reduction of stable radical anion of azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) ($ABTS^{\bullet}$) with antioxidants. The electrochemical reduction-oxidation of $ABTS^{2-}$ is a quasi-reversible reaction, $ABTS^{-\bullet} + e \rightarrow ABTS^{2-}$. Therefore, $ABTS^{2-}$ can be used a redox catalyst (mediator) in the amperometric sensor for determination of TAC with PANI to immobilize $ABTS^{2-}$ on electrode. The dependences of current on concentration of model antioxidants are proportional to the antioxidant concentrations at electrode potential sufficiently high to oxidize $ABTS^{2-}$ to $ABTS^{\bullet}$ [58].

It was shown that $IrCl_6^{2-}$ can be also used as a mediator [48, 58]. We demonstrated that the PANI modified glassy carbon, tantalum or titanium electrodes well respond to the presence of such antioxidants as Trolox, ascorbic uric and gallic acids in solution. The mediator was introduced in PANI either during electrosynthesis or by impregnation of the prepared polymer in solution of mediator. An important condition for stable work of CME is a constant content of immobilized mediators. This is achieved by a strong electrostatic and steric interaction between mediator and polymer. All obtained CME were used for determination of concentration of antioxidants at electrode potential of +0.68V (SCE). It should be noted that mediator free PANI is demonstrated very weak amperometric response to different concentration of antioxidants.

The role of mediator in sensor was analyzed for three types of sensors: i) PANI; ii) PANI- $ABTS^{2-}$; iii) PANI - $IrCl_6^{2-}$. The sensors were stored in air for one year, and their activity was tested periodically. Ascorbic acid was used as reference compound. Freshly prepared $6x10^{-3}$ M solution of ascorbic acid was used in each test, and sensor activity was measured (Fig. 13).

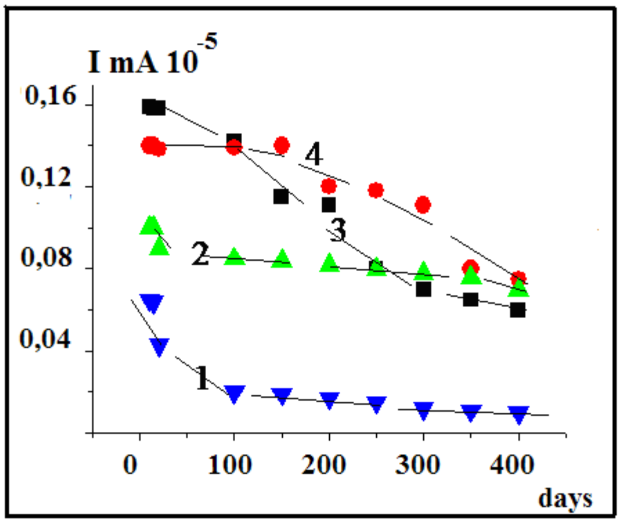

Fig. 13. Calculated for 400 days of activity sensors antioxidants:
1. PANI; 2. PANI with the contents of $ABTS^{2-}$ 0.14 wt.%;
3. PANI with the content of $IrCl_6^{2-}$ 0.15 wt.%;
4. PANI with the content of $IrCl_6^{2-}$ 0.08 wt.%

A PANI-$ABTS^{2-}$ based sensor was found to be the most stable. Its activity remained almost unchanged for 400 days (Fig.13, curve 2). The sensor was less active than the PANI-$IrCl_6^{2-}$ one (Fig. 13, curves 3, 4). However, the activity of the latter was less stable. The PANI based sensor showed the lowest activity and stability (Fig. 13, curve 1). These data are evidence of that the mediator in the sensor can perform as an active component and stabilizes noticeably long-duration work of the sensor.

Conclusion

The introduction of electroactive anions into matrices of conducting polymers affects their electrochemical behavior and opens new possibilities for commercial application for instance corrosion resistant coatings, electrode materials for supercapacitors, Li-ion batteries, sensors for hydrogen and antioxidants. In any case at initial stage of synthesis of such materials EAA performs as initiator of polymerization of aniline which provides fast and uniform growth of a polymer coating regardless of state of support surface. Growing PANI coating shows high electrical conductivity, possibly due to the participation of EAA in electron transport, high conductivity being combined with optimal porous structure for counter ion transport. This raises the prospects of finding new electrocatalysts, sensor, electrochromic and energy storage systems. These materials are very weakly studied in nonaqueous media where one can work in a wider potential range. Here you can expect the increase of specific energy of supercapacitors and the rate of colouring in electrochromic systems. Of great interest are easily synthesized polyaniline composites with carbon nanotubes and graphene which show high electrical conductivity and good physical and mechanical properties as a result of the formation of a nanocarbon framework. Rapid progress in the ink-jet printing on 3D printers opens a wide field for the development of various devices using solubility of reduced polyaniline composites with carbon nanomaterials in organic solvents.

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