Russian Chemical Reviews **85** (1) 14 – 37 (2016) © 2016 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RCR4509

Composite electrode materials based on conducting polymers loaded with metal nanostructures

V V Kondratiev, V V Malev, S N Eliseeva

Saint Petersburg State University
Universitetskaya nab. 7/9, 199034 St Petersburg, Russian Federation

The electrochemical and chemical methods for synthesizing conducting polymer-metal nanocomposite materials are considered as well as the main factors affecting the structure and electrochemical properties of these composites. The experimental data on the catalytic activity of conducting polymer – metal electrodes are analyzed in respect to several electrochemical reactions. The approaches to theoretical description of electrochemical processes on heterogeneous conducting polymer – metal electrodes are discussed and examples of experimental testing of applicability of the proposed the theoretical models are shown.
The bibliography includes 335 references.

Contents

I. Introduction 14
II. Methods of synthesis of conducting polymer – metal nanocomposites 16
III. Electrochemical reactions on conducting polymer – metal nanocomposite electrodes. Electrocatalysis 23
IV. Conclusion 31

I. Introduction

Organic polymers are traditionally considered as insulating materials and, in this role, their conductivity is obviously undesired. However, attempts to develop polymer materials with high electrical conductivity have been undertaken for a long time. For this purpose, polymers were proposed to be mixed with conducting fillers, for instance, powders and fibres of metals or various carbon materials.

The discovery by Shirakawa [1, 2] of the possibility of sharply enhance the electronic conductivity of iodine-doped polyethylene made in the late 1970s gave a powerful impetus to the development of studies in the field of conducting polymers. This discovery stimulated the active studies of properties of a new class of compounds, electronically conducting organic polymers with conjugated bonds. The rapid development of the electrochemistry of conducting organic polymers traces back to the first electrochemical synthesis of polypyrrole [3] and, later, polyaniline [4] and other polymers. The Nobel Prize of 2000 in chemistry was given to A Heeger, A MacDiarmid and H Shirakawa for their great contribution to the studies of conducting organic polymers with conjugated bonds.

In the conducting polymers, it is macromolecules themselves and their compositions with other compounds that conduct electricity. For conducting polymers with conjugated π-bonds, a special name was invented: intrinsically conducting polymers (ICPs), which was later shortened to conducting polymers. In the modern English-language literature the term 'conducting polymers' is also widely used for an absolutely different class of materials, polymer electrolytes, *i.e.*, polymers with high ionic conductivity. In connection with this, it deserves mention that the objects considered in this review pertain only to conducting organic polymers with conjugated π-bonds.

The keen interest in such polymers is associated first of all with their high electronic conductivity (up to 10^3 S cm^{-1}), close to that of metals. For this very reason, the class of conducting organic polymers was named 'synthetic metals' and even a journal with the same name, *Synthetic Metals* which publishes results of investigations in this field was initiated in 1979. However, it deserves mention that conducting organic polymers are not always good conductors; in their neutral state, they usually behave as poorly conducting materials. The conductivity of p-doped polymers can vary in a very wide range.

The materials under consideration were actively and widely studied so that a special line of research in electrochemistry appeared, namely, the electrochemistry of conducting polymers with conjugated bonds. The results of

V V Kondratiev Doctor of Chemical Sciences, Professor of the Department of Electrochemistry at the Institute of Chemistry, SPbSU.
Telephone: +7(812)428 – 6900, e-mail: vkondratiev@mail.ru
V V Malev Doctor of Chemical Sciences, Professor of the same Department.
Telephone: +7(812)428 – 6900, e-mail: valery.malev@gmail.com
S N Eliseeva Candidate of Chemical Sciences, Senior Teacher of the same Department.
Telephone: +7(812)428 – 6900, e-mail: eliseeva_s@rbcmail.ru
Current research interests of the authors: electrochemistry of conducting polymers, redox polymers and conducting polymer – metal composite materials based on them.

Received 24 September 2014
Uspekhi Khimii **85** (1) 14 – 37 (2016); translated by T Ya Safonova

these studies were summarized in several reviews and monographs (*e.g.*, see Refs 5–22). Recently, this area was considerably extended due to the development of composite electrode materials with incorporated metal or carbon nanostructures, containing also organic or inorganic modifiers (see, for example, Refs 23–31).

The steady interest in studying the properties of conducting polymers and their composites is stimulated by numerous practical applications of these materials in various fields such as electrocatalysis, development of electrochemical sensors and biosensors, molecular electronics, development of electroluminescent and electrochromic devices, solar cells, chemical power sources, corrosion protection of metals.[5–19,22–30] The quest for new electrode materials meeting the requirements of practice favoured the production of conducting polymer–metal composite electrode materials based on the polymers that serve as the conducting matrices for bulk-incorporated micro- and nanosized metal structures. The interest in the development of these hybrid organic-inorganic materials is explained by the advantages of nanostructuring and formation of the highly dispersed state of metals within a conducting matrix and also by appearance of new new functional characteristics of materials. Conducting polymer–metal nanocomposites form a promising class of electrode materials which combine the electrocatalytic properties of metal nanoparticles (NP) and conducting polymers.

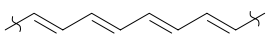
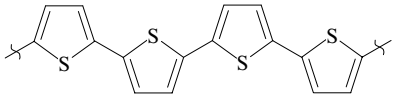
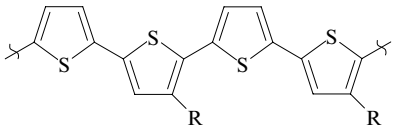
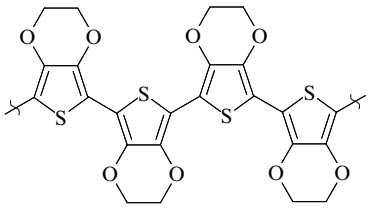
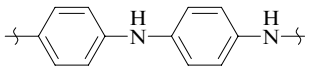
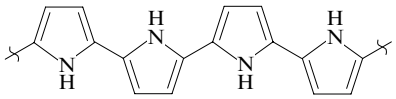
Among the most important groups of conducting organic polymers are those based on aromatic amines, namely, polyaniline (PANI) and its derivatives, poly(*o*-aminophenol) and poly(*o*-phenylenediamine), polymers based on unsubstituted and substituted five-membered heterocyclic compounds, namely, polythiophenes (PT) including substituted polythiophenes such as polymethylthiophene (PMT), poly(3,4-ethylenedioxythiophene) (PEDOT), polypyrrole (PPY), and also on other organic polymers containing systems of conjugated bonds, for instance, polycarbazole and polyphenylenevinylene. Table 1 shows the values of conductivity for some conducting polymers in their p-doped state.

A characteristic feature of conducting polymers is the ability to undergo reversible redox transformations which involve also the so-called dopant species, *i.e.*, charge-compensating ions. Such transformations induce drastic changes in the polymer conductivity from its values typical of the well-conducting quasimetallic state to the values typical of the semiconducting state.

A breakthrough in understanding of the mechanism of charge-transfer processes in conducting polymers was made resorting to the polaron-bipolaron concept of conduction.[32–34] The concept of polaron borrowed from condensed-state physics was applied to conducting organic polymers, where polaron was defined as a charged quasiparticle. At present, the polaron theory of conduction is widely accepted as the main model explaining the electronic conduction of polymers with conjugated bonds. According to this theory, the electronic conduction is provided by motion of polarons and bipolarons along polymer chains under the action of electric field *via* reorganization of double and single bonds and also due to jumps of electrons between the chains.

The electrochemically active fragment in a conducting polymer is a double bond the electrons of which can be eliminated rather easily upon polymer oxidation. In the initial state, this yields a radical cation. The existence of unpaired electrons in conducting polymer films was confirmed experimentally by electron paramagnetic resonance spectroscopy.[35,36] The elimination of electrons immediately leads to delocalization of orbitals in the charged polymer (within several, usually three to six monomer units), which sharply decreases the energy of the final oxidized polymer. This induces structural deformation of this polymer segment and polarization of the environment (which justifies the use of the name 'polaron' for the chain fragment with radical cation). Environment polarization and interaction with counter-ions stabilize the radical cation. The polaron chain fragment can undergo further oxidation giving off an unpaired electron to yield a bipolaron, *i.e.*, a dication carrying the double positive charge.

Table 1. Examples of conducting polymers.

Polymer	Structural formula of polymer fragment	Conductivity /S cm^{-1}
Polyacetylene		10^4
Polythiophene		10^3
Poly-3-alkylthiophene (R = Alk)		10^2
Poly-3,4-ethylenedioxythiophene		3×10^2
Polyaniline		10^2
Polypyrrole		10^3

The polymer reduction (n-doping) generates an extra electron on the chain fragment (radical anion). In the majority of studies, attention was focused on the p-doping giving more stable polymer states. This is why this review considers mainly the p-doping processes. The mixed electronic-ionic mechanism of conduction in conducting polymers is provided by the motion of delocalized electrons or holes along polymer chains and between them, which is accompanied by transfer of charge-compensating dopant ions.

Various kinetic aspects of electrode processes on polymer–metal films involving species of external redox systems present in the electrolyte solution were considered in quite a number of studies; however, the detailed elucidation of the mechanism of such processes and their modelling including the quantitative description of the kinetics still remain topical tasks. This is associated with both the occurrence of complex intrinsic electrochemical processes in polymer

films and with the wide diversity of mechanisms of electrode processes involving species of external redox systems present in the electrolyte solution. These factors complicate analysis and interpretation of the results. Even when considering simple films of conducting polymers, the vast majority of authors use relationships derived for the electrode/solution interface (*i.e.*, without the intermediate film); moreover, it is usually unclear which interface is considered, the electrode/film or film/solution one. However, account must be taken of the fact that the total potential drop between the electrode and the solution is the sum of two potential drops on these interfaces; moreover, strictly speaking, both potential drops depend on the electrode potential. These issues were considered in detail in a series of studies.[37–47]

The present review analyzes the achievements and the unsolved problems in the field of electrochemistry of conducting polymer–metal composite electrode materials, considers new methods of their synthesis and the results of studies of their structure and electrochemical properties and also discusses the theoretical aspects of describing processes on heterogeneous electrodes with inclusions of catalytically active metals.

The limited size of the review precludes covering all the problems on this subject; this is why, here we consider the most important aspects of electrochemistry of conducting polymer–metal composites and only fundamental studies. Among the vast number of original publications of the past decades on the compositions of conducting polymers with metal NP, most were devoted to synthetic methods and structural studies as well as to certain applied aspects of using these materials.

These very questions were addressed in several recent reviews.[19,23–25,27,28,31,48] Mention should be made of the study by Tsakova,[23] who analyzed the literature up to 2010 on the synthetic methods and investigations in the field of sensors preferentially based on conducting polymer–metal composites and also of the review by Podlovchenko and Andreev [19] in which one section was devoted to the catalysis of electrochemical reactions on composite films of conducting polymers loaded with metal particles. Much less attention was paid to studying the kinetics of electrode processes on such electrodes, assessing the reactivity of these composites. For this reason, in the present review, we address the experimental and theoretical aspects of studying the polymer–metal composite electrode materials based on conducting polymers with inclusions of noble metal particles, which exhibit pronounced catalytic activity towards several electrochemical processes. Special attention is drawn to heterogeneity of properties of conducting polymer–metal composite electrodes and also to explanation of the results of theoretical modelling of electrode processes in such systems.

The conducting polythiophenes and polyanilines widely used in studying the conducting polymer–metal composites are mainly considered here as examples, because the authors of this review had long experience in studying precisely these groups of polymers.

II. Methods of synthesis of conducting polymer–metal nanocomposites

The porous structure of conducting polymers makes it possible to use them as matrices loaded with metal particles serving as the reaction centres. The conducting polymer–metal composites formed by loading the conducting polymers with metal nanoparticles are of special interest because they combine the properties of both components. As compared with compact metals, the activity of polymer–incorporated noble metal particles is higher due to higher surface area-to-volume ratio and unique surface properties.

An attractive feature of materials based on conducting polymers is that nitrogen-, oxygen- or sulfur-containing groups present in polymer molecules can stabilize nanosized clusters by interacting with metal atoms and thus limit the cluster aggregation. Hence, besides serving as the support for metal particles and providing their electric integration, the polymer matrix also acts as the stabilizing medium that prevents agglomeration of metal particles during the synthesis and operation of the catalyst.

Due to porosity and high electronic conductivity of the polymer, the composite materials exhibit good electron-ion transport properties in the material bulk. The incorporation of metal particles into polymers yields nanostructured polymer–metal materials with properties promising for various fields of science and technology. Polymer matrices contain pores of different size determined by the method of their synthesis and their physical state. The chemical nature of the matrix and the method of its loading with metal determine the stability of metal dispersions and their size characteristics. The development of new electrode materials based on conducting polymers often involves incorporating noble metals known for their high catalytic activity (platinum, palladium, gold, *etc.*). The literature contains numerous descriptions of synthetic procedures for preparation of conducting polymer–metal composites. These methods were surveyed in several reviews (see Refs 19, 23 and 28).

The methods of preparation of conducting polymer–metal composite films on electrodes can be conditionally divided into four main groups:

— electrochemical or electroless deposition of metal NP into pre-synthesized films of conducting polymers;

— incorporation of pre-synthesized metal NP during the electrochemical or electroless synthesis of conducting polymers;

— synthesis of polymer–metal composite films from colloid dispersions of polymers and metal NP;

— one-step synthesis of polymer–metal composites from mixed solutions containing the monomer and metal ions.

Each of the above synthetic methods has its own advantages and drawbacks and the use of one or another method depends on whether the chosen method yields nanocomposite materials that comply with the solution of the particular scientific or applied problem. Below we consider some features of the methods of synthesis of nanocomposite materials.

II.1. Methods based on deposition of metal nanoparticles into pre-synthesized polymer films

At present, polymer–metal composites are synthesized most often by deposition of metal nanoparticles into polymer films. Metal nanostructures are formed in the bulk or on the surface of the pre-synthesized conducting polymer. Metal NP can be deposited into the polymer film by either electrochemical or electroless plating methods from solutions of their salts. Moreover, the particles are stabilized by the matrix itself, whereas the incorporation of pre-synthesized metal NP requires the use of stabilizers to prevent their aggregation.

II.1.a. Electrochemical deposition of metal nanoparticles into polymer films from solutions of metal salts

Taking into account the conducting nature of polymers, the electrodeposition of metals into films was used as the most suitable and convenient method for preparation of conducting polymer–metal composites. For the first time, this method was used to produce PMT/Ag, Pt (Ref. 49) and PPY/Pd, Pt (Ref. 50) composites. Later, the electrodeposition of metals was widely used to synthesize the catalytic conducting polymer–metal materials with inclusions of gold,[51–64] palladium,[65–77] platinum,[65,67,71,72,78–111] silver[112–114] and other metals and also bimetallic compositions.[89,98,102,106,115–117]

When carrying out electrodeposition of metal NP on electrodes modified with a conducting polymer film, one has to take account of film properties, namely, its original oxidation state, the morphology and chemical state of its surface and also its bulk characteristics such as porosity and metal–polymer chemical interactions. These factors are interrelated; hence, it is difficult to precisely separate their effects on the characteristics of a metal incorporated into a conducting polymer.

The electrodeposition of nanoparticles into conducting polymers can be carried out from solutions containing metal or metal complex ions. The use of metal complexes of different nature makes it possible to additionally control the range of electrodeposition potentials. The deposition rate and the amount of incorporated metal can be controlled by varying the potential (or current) in the course of deposition. For the reduction of metal ions, electrochemical methods are used, namely, cyclic voltammetry (CV), galvanostatic reduction, potentiostatic pulse method and methods employing asymmetrical current pulses. The use of various electrochemical modes of deposition may substantially affect the size of metal clusters, their localization and the density of their distribution in the polymer film.[24]

In the case of methods involving loading of pre-synthesized polymer film with metal nanoparticles, the structure and surface morphology of the resulting nanocomposite materials are determined, first of all, by the structure and properties of the polymer. The nanocomposite films are typical microheterogeneous systems that contain micro- and nano-sized phases with different properties and chemical compositions.

The role played by the polymer morphology was demonstrated in several papers.[70,110,118,119] The appearance of metal clusters of different size was attributed to different structure of the polymer and topographic and energetic heterogeneity of its surface including the surface of pores accessible for the electrolyte in the polymer bilk.[70,118,119] The presence of microdefects in the polymer structure such as large pores in a thin film which provide the access of electrodeposited metal to the substrate surface may give rise to abnormlly large metal clusters.[118]

Depending on the polymer porosity and conductivity at metal electrodeposition potentials, the deposited metal can have different preferential location and different distribution throughout the film.[24,120,121] In the general case, one can expect that the low polymer conductivity in the metal deposition potential region chosen and high through porosity of the polymer film may induce metal deposition on the internal substrate/polymer interface. The high conductivity of the polymer film should favour the electrodeposition on the external polymer/electrolyte solution interface. These trends were experimentally confirmed in several studies[119,122,123] devoted to nucleation and growth of deposits.

The preliminary impregnation of the polymer film with the electrolyte solution and the use of pulse modes of potential or current application produced more uniform metal deposition throughout the polymer pore bulk.[24,95,105,124–126]

A detailed study of the potentiostatic deposition of palladium into a poly-PEDOT film has demonstrated[68] that the growth of Pd clusters is initially controlled by the charge transfer, and this is followed by sharp transition to the diffusion control over the deposition process. Presumably, the nucleation of Pd particles occurred at the substrate/polymer interface and the further growth of clusters took place inside the microporous polymer structure. The scanning electron microscopy (SEM) images of the composite film confirmed the absence of palladium clusters on its surface. It was shown[127] that the metal can be deposited directly on a polymer; thus, atomic force microscopic (AFM) studies revealed palladium particles on the surface of a PANI film at the potential of palladium deposition of 0.14 V (the region of the absence of PANI conductivity).

In order to load a PANI film with Pd particles, the electrodeposition was carried out in the CV and pulsed-potential modes.[77] The amounts of PANI (4–86 nmol litre^{-1} cm^{-2}) and palladium metal (0.2–2.1 μmol litre^{-1} cm^{-2}) deposited and their ratio were controlled by coulometry. The average size of single palladium clusters that formed aggregates on the film surface was ~ 5 nm. Hydrogen sorption on the the composite films was studied. The hydrogen-to-palladium (H : Pd) ratio was shown to be higher in the composite film, which was explained by partial shielding of palladium particles by the poorly conducting PANI film.

The factors that determine the distribution, the size and the number per unit surface of particles incorporated upon metal electrodeposition are of special note. These issues are closely connected with the kinetics of crystallization of metals on the polymer surface and depend on the method used for the deposition of particles. Generally, as expected, the general trends are the same as found earlier for the electroless and electrochemical deposition of metals from solutions onto the metal or carbon substrate.

There are two main models of nucleation during the metal electrodeposition, namely, instantaneous and progressive nucleations. However, the analysis of current transients, *i.e.*, the comparison of experimental curves with the theoretical curves plotted in terms of either instantaneous or progressive nucleation model, which is traditionally used for elucidation of the nucleation mechanism, is in this case complicated. This is due to the fact that during metal deposition into conducting polymers, the current response to a potential pulse includes an additional contribution associated with the simultaneous polymer recharging process. Additional experiments on measuring the current transients in solutions in the absence of metal ions make it possible to take account of this contribution to some extent but produces additional errors and, hence, complicates the analysis.[113,128,129]

It was shown experimentally that to obtain single particles on the surface and in the bulk of a polymer, electrodeposition should be carried out from dilute solutions of metal salts. However, unlike smooth uniform substrates made of metals or carbon materials, in polymers,

the energetic heterogeneity of primary nucleation centres is expected to be much more pronounced which can be attributed to donor–acceptor interactions with metal precursors (ions) and also to the local conductivity of polymer structures. When the electrodeposition is carried out from dilute salt solutions, the single nuclei formed in the initial instant start growing as the time of their contact with the electrolyte solution increases. Naturally, in this case, the energy of metal–metal interaction is considerably higher than the energy of metal interaction with the polymer nucleation centre, which favours the growth of three-dimensional clusters.

For electroless deposition upon redox interaction of the reduced polymer with metal ions, similar relationships were observed. When the deposition is carried out in dilute solutions, the number of particles is small; in more concentrated solutions, a much larger number of nuclei is formed in the initial instant of polymer contact with the metal salt solution.[130]

The original methods of deposition of metal nanostructures into conducting polymers were demonstrated using the SEM method. The metal nanostructures on the surface were prepared by using a gold (or silver) microelectrode, which was dissolved in the electrolyte on positive polarization to yield gold (or silver) ions, which were locally deposited on the polymer film surface. It was concluded[131–133] that the size of metal particles formed depended on the lateral surface conductivity of polymers.

An interesting method for the synthesis of composites with controlled distribution of the primary gold nuclei along the polyaniline chain was proposed.[52,134–136] By controlling the potential of a polyaniline electrode in a solution containing $AuCl_4^-$ ions, in order to exclude the chemical oxidation of these ions, their complexes or $PANI \cdot AuCl_4^-$ associates were formed on polymer molecules. Presumably, these complexes are formed upon interaction of gold ions with the imine groups of PANI. The applied negative potential pulses led to the reduction of the precursor gold complexes to yield regularly arranged gold nuclei. Then the potential variation cycle was repeated, which led, in the authors' opinion, to the growth of gold clusters.

Of great interest are the studies on incorporation of metal nanostructures of a desired geometry, particularly, nanorods and nanofibres, into conducting polymers.[137,138] This is done using various methods of template-assisted synthesis, which employ both rigid (*e.g.*, anodized aluminium)[139–141] and flexible (polymers and other substances) matrices.[142–144] The use of templates for the synthesis of metal nanostructures within conducting polymers seems to be a promising method for obtaining systems with desired properties. In particular, D-camphor-10-sulfonic acid, which served both as dopant and as surfactant, was used as the flexible template in the synthesis of PANI/Au nanowires;[145] this gave nanowires with the average diameter of 50–60 nm and the length of $>1-2$ μm. The size of nanowires depended on the concentration ratio of aniline, gold chloride and surfactant. Polyaniline nanotubes were prepared by dissolving gold from the composite structure.

Promising new trends include the synthesis of core–shell type polymer–metal nanocomposites, segmented nanocomposites such as PANI/Au and Au–PANI–Ni–Au–PANI,[146] the Au–PPY–Ni–Au nanowires[147] and PT–metal oxide nanostructures.[148] These materials exhibit new interesting properties, which extend the scope of their applications.

II.1.b. Electroless deposition of metal nanoparticles from their salt solutions

The following two methods are used for the electroless deposition of metal NP into conducting polymer films:

— spontaneous redox reaction between the reduced form of the polymer and electropositive metal ions in solution;

— saturation of the polymer film with the precursor (metal salt) followed by the introduction of a reducing agent (borohydride, hydrazine, lower alcohols or other compounds) into solution.

A drawback of above methods of formation of nanocomposites is that it is difficult to control the particle size and distribution.

The spontaneous reduction of metal ions by conducting polymers to yield metal atoms is possible for ions of electropositive metals with high oxidative capacity such as Pd^{2+}, Au^{3+} or Ag^+. This method opens up additional attractive applications for conducting polymers, namely, in extraction of noble metals from their solutions,[149,150] development of potentiometric sensors for noble metals,[151,152] and also for metallization of contact areas covered with a conducting polymer supported on a non-conducting material.[153] The simultaneous reduction of metal ions by polymers is a simple and convenient method of loading the polymers with metal nanoparticles. This method of synthesizing conducting polymer–metal composites was used for loading polymers with nanoparticles of gold,[56,112,149,150,154–159] palladium,[69,70,151,152,160–173] silver,[153,174–183] platinum[184,185] and bimetallic compositions.[69,117,186]

A study of PPY/Pd systems was reported.[173] The reactions of doped polypyrrole were shown to strongly depend on the acidity of the $PdCl_2$ solutions and the type of palladium(II) chloride complexes. From palladium chloride solutions with low acidity, two forms of palladium species, Pd^0 and Pd^{2+}, were incorporated into the PPY matrix. The samples were shown to contain palladium aggregates of different size, from 0.5 to 2 μm.

Particular attention was given to processes of electroless reduction of electropositive metal ions on poly(3,4-ethylenedioxythiophene) and polyaniline films.[112,114–119] By using the quartz crystal microbalance and coulometry methods, the specific features of electroless deposition of palladium and gold particles into PEDOT films were studied in detail.[170,172,187] Let us consider the features most important for the PEDOT/Pd system. The initial oxidation state of the polymer film and its thickness were shown to determine the total reductive capacity of the film and, hence, the total mass of incorporated metal. Similar correlations were also found for other systems.[69,170,172,187] For films with specified initial parameters, the amount of incorporated metal increased with the increase in the concentration of metal ions in solution and the deposition time. Figure 1 shows a typical microbalance response for composite films synthesized in successive 30-s deposition events of palladium particles into the PEDOT film. The dependences of the frequency of the quartz crystal resonator (f) and, correspondingly, of the film mass on the potential (E) are parallel to one another; the film mass is proportional to the number of palladium deposition events (the deposition

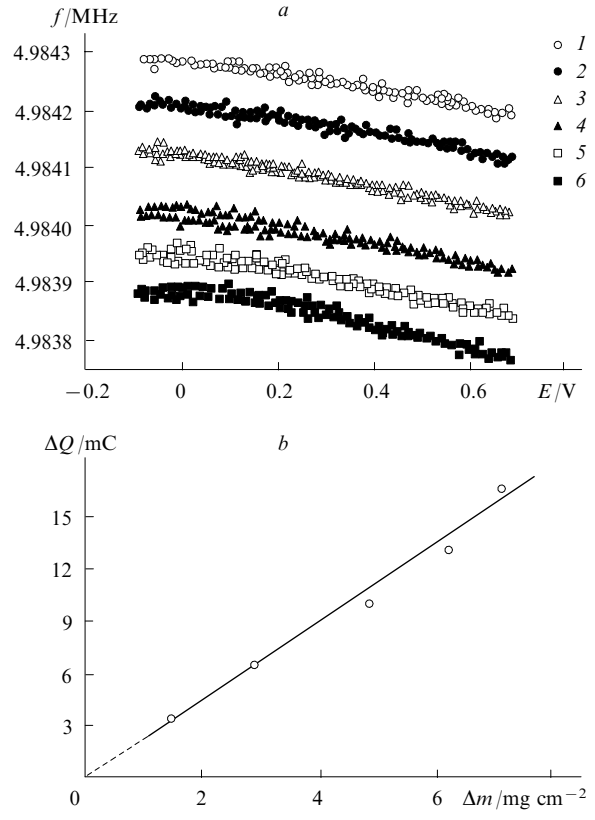


Figure 1. Dependences of $f(E)$ in 0.1 M H_2SO_4 solution for PEDOT (*1*) and composite films (*2–6*) synthesized in successive steps of electroless deposition by exposure in 5×10^{-4} M $PdCl_2$ solution (*a*) and dependence of the palladium mass found by microgravimetry on the quantity of electricity consumed in film oxidation by palladium (*b*).[170]
Time of a single deposition step was 30 s; total time of deposition varied from curve *2* to curve *6* from 30 to 150 s; the electrode surface area was 1.37 cm^2.

time). The electroless deposition of palladium into the PEDOT film (redox process) includes two conjugated reactions [170]

$$Pd^{2+} + 2e \longrightarrow Pd^0 \quad (1)$$

$$2\,PEDOT - 2e \longrightarrow 2\,PEDOT^+ \quad (2)$$

The second reaction is shown schematically, because oxidation to different states and participation of different dopant anions are possible. In view of the stoichiometry of reaction (1), the mass of the metal incorporated into the film can be assessed by the Faraday law.[29, 188] The quantity of electricity consumed in the reduction of ions to palladium metal (Q_1) is related to the palladium mass deposited into the film as

$$Q_1 = 2F\frac{\Delta m_{Pd}}{M_{Pd}} \quad (3)$$

where F is the Faraday constant, Δm_{Pd} is the mass of palladium deposited in the polymer film, M_{Pd} is the molar mass of palladium. Also, the same quantity of electricity (Q_1) is equal to the charge consumed in the respective process of PEDOT film charging (Q_2) from a certain initial potential (E_i) to the final potential (E_f) corresponding to the termination of the deposition processes

$$Q_2 = \int_{E_i}^{E_f}\frac{J}{v}dE = \int_{E_i}^{E_f} C_{lf}\,dE \quad (4)$$

where J is the current, C_{lf} is the low-frequency capacitance. The quantity Q_2 was determined by integrating the anodic segment of the voltammogram from the potential E_i of the reduced film to E_f reached during the synthesis when the polymer film is kept in the palladium solution.

Thus, the mass of palladium metal incorporated into the film in the course of electroless deposition can be calculated using the relationship

$$\Delta m_{Pd} = \frac{M_{Pd}}{2F}\int_{E_i}^{E_f} C_{lf}\,dE \approx \frac{M_{Pd}\,C_{lf}}{2F}(E_i - E_f) \quad (5)$$

Table 2 shows the masses of palladium in the film, both calculated from the quantity of electricity and determined by the microbalance method.

The palladium masses determined by the microbalance method are somewhat higher that those calculated from the quantity of electricity (from CV data). This is attributable to the additional transfer of water and electrolyte components during metal deposition into the film. Similar relationships for the electroless deposition of gold and silver were found for systems PEDOT/Au (see Ref. 187) and PEDOT/Ag.[153, 183]

The morphology of the PEDOT/Pd (Refs 170 and 171) and PEDOT/Au (Ref. 187) composite films synthesized by electroless deposition of metals was studied as a function of synthetic conditions (deposition time, concentration of the metal salt solution). It was shown that after the immersion of a PEDOT film into a dilute solution of palladium chloride, the initial film morphology changes: nanosized (10–30 nm), mainly spherical palladium particles appear on the surface of the porous polymer structure (Fig. 2). The transmission electron microscope (TEM) images of the PEDOT/Pd composite film reveal that the size of particles formed from the 5×10^{-3} M $PdCl_2$ solution increase from 6–10 to 20–30 nm as the deposition time increases from 30 to 120 s. Analysis of the TEM image (Fig. 3) shows that metal nucleation occurs directly on the polymer compact structures and also confirms a bulk distribution of palladium NP (at least in the near-surface layers).

It can be assumed that in this method of metal deposition into polymers, metal nuclei are formed upon the

Table 2. Experimental values of the average mass of palladium in the PEDOT/Pd composite film found from CV data [170] and by the electrochemical quartz crystal microbalance (EQCM) method.

Deposition time /s	Δm_{Pd} /μg cm^{-2}	
	EQCM	CV
30	1.41	1.30
60	2.83	2.61
90	4.77	4.46
120	6.18	5.90
180	7.17	6.82

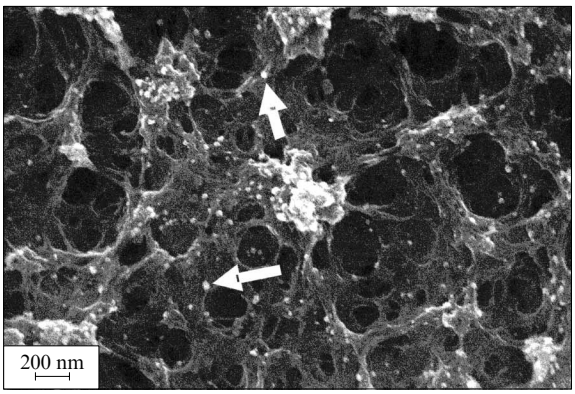


Figure 2. SEM image of a PEDOT/Pd film.[172]
Deposition for 60 s from a 5×10^{-3} M $PdCl_2$ solution in 0.1 M H_2SO_4; single palladium clusters are marked with arrows.

primary interaction of precursors (metal ions) with the polymer functional groups (*e.g.*, amino groups in polyaniline). Increasing the metal ion concentration in solution for the synthesis leads to an increase in the number of primary nuclei (particle distribution density) and the cluster size. Thus, the particle size can be controlled by varying the salt concentration during the synthesis, the thickness of the conducting polymer film and the deposition time.

The active sites of primary activation are probably the best-ordered polymer structures with high conductivity, which are capable of being oxidized by metal ions.[24] The nucleus growth should also be determined by the polymer local conductivity associated with polymer morphology and, hence, should depend not only on the processes of metal ion diffusion in solution but also on the charge transfer in the polymer film. It was assumed[10] that at the electroless deposition of gold into films, the thiophene sulfur atoms in the polymer molecules or nitrogen atoms in polyaniline can interact first with metal ions and then with metal clusters formed on the polymer surface and in its pores. These interactions favour stabilization of nanosized gold clusters. Analogous interactions are also possible for other metals.[58, 59, 189]

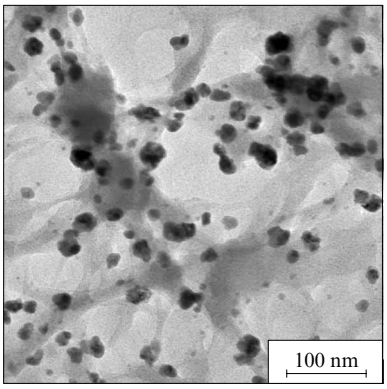


Figure 3. TEM images of a PEDOT/Pd film.[117]
Deposition for 120 s from a 5×10^{-3} M $PdCl_2$ solution in 0.1 M H_2SO_4.

The electroless reduction of silver ions was shown[153] to be located preferentially in the surface layers of the polymer film, which are in contact with the metal salt solution. An increase in the silver ion concentration in the solution leads to a higher rate of silver incorporation into the film. The formation of the PEDOT/Ag composite and the mass variations during the electroless deposition of silver into the polymer structure were studied using quartz-crystal microbalance and electron microscopy.[183]

The use of electroless deposition of palladium as an alternative to electrochemical deposition was shown[69] to produce Pd nanocrystals uniformly distributed over the polymer surface with the distribution density $>10^9$ cm^{-2}. The successive deposition of, first, palladium and, then, copper produced the bimetallic system PEDOT/Pd–Cu. In the presence of Pd nanocrystals, the potential of initiation of copper crystallization decreases due to the appearance of new sites, *i.e.*, the copper nucleation can proceed on primarily incorporated palladium.

For the electroless deposition of gold and palladium, the opportunities for the synthesis of bimetallic composite materials were explored. Thus bimetallic catalysts based on gold nanoparticles decorated with palladium particles were obtained on a PEDOT film.[117] The synthesis of these PEDOT/Au–Pd composite films included three stages:

— synthesis of a PEDOT polymer film on the electrode surface;

— reduction of the polymer film, followed by electroless deposition of metal particles into the polymer matrix from a solution of gold(III) chloride complexes;

— subsequent reduction of the composite film and electroless deposition of palladium metal particles into the polymer matrix from a palladium(II) chloride solution.

It was shown that under similar conditions, the rate of palladium deposition into the PEDOT/Au film is considerably higher as compared with the PEDOT film. The preferential deposition of palladium on gold was favoured by two factors: the advantageous palladium nucleation on the surface of gold clusters and the pronounced chemical reaction between palladium and gold atoms. The latter factor, including the interaction of precursors, *i.e.*, palladium ions, with gold surface atoms was particularly noted in the studies dealing with Pd–Au catalysts.[190, 191]

For the synthesis of mono- and bimetallic catalysts on polymer–carbon substrates, PANI was successfully used as the reducing agent for noble-metal ions (Pt, Pd, Au). The PANI powder or PANI composites with carbon materials were reduced to the leucoemeraldine form in a hydrogen flow, then the metal was immersed into a solution of a noble metal salt (or mixed salts) where the ions were spontaneously reduced to metal atoms.[192, 193] Apparently, the reduction of metal ions is related to the possibility of stabilization of the reaction product, metal NP, due to the precursor interaction with nitrogen-containing functional groups of polymers. The complexation of such metals with aromatic amines is well known and widely used in the synthesis of metal NP. For example, dopamine, a low-molecular aromatic amine containing an analogous functional group, serves as the stabilizer for the formation of catalytic dispersions of platinum and platinum group metals.

The use of external chemical reducing agents for the metal deposition into films of conducting polymers can also be considered as a method for formation of conducting polymer–metal composites.[23] The synthesized polymer film

is saturated with metal ions, which is followed by their chemical reduction (due to the addition of a reducing agent, *e.g.*, sodium borohydride, hydrazine, *etc.*). This method extends the range of elements that can be deposited into films beyond electropositive metals.

II.2. Incorporation of pre-synthesized metal nanoparticles into conducting polymers

The group of methods of incorporation of pre-synthesized NP into conducting polymers includes co-deposition of polymers with metal NP prepared beforehand as colloid solutions or capture of NP from colloid solutions by polymers. Nanoparticles can be incorporated into a polymer during monomer electropolymerization from its solution additionally containing metal colloid particles.[58, 59, 95, 99, 140, 194–203] Yet another method of incorporating preliminarily prepared NP consists of saturating the porous matrix with a solution of metal colloid particles followed by the removal of solvent.[204] Also, metal NP can be incorporated into a polymer by chemical oxidation of the monomer in the presence of ready nanoparticles.[205–213]

An advantage of this group of methods for the synthesis of nanocomposites lies in the possibility of incorporation of nanoparticles of a given size into the polymer and their uniform distribution over the film bulk; their drawback is the necessity of using stabilizing agents which are introduced as a rule into solution during the synthesis of NP. The stabilizers are required to prevent aggregation and sedimentation of metal particles. In the majority of cases, the used surfactants or complexing agents interact with the metal particles to form shells shielding their surface. The stabilized metal NP are either completely incorporated into the polymer matrix or this is accompanied by the partial decomposition of the associates. However, in the presence of stabilizer molecules, the activity of particles as regards their other interactions may decrease, which entails a lower total catalytic activity of the incorporated metal NP. Hence, among the important problems associated with the use of this synthetic method is the preparation of sufficiently stable NP of a desired size satisfying the requirements of one or another scientific or applied problem. Thanks to the recent success achieved in the field of synthesizing metal NP with different structure and in different stabilizing media, the method under consideration is widely used for synthesizing conducting polymer–metal composites.

The most popular method is the synthesis of colloids through the reduction of metal cations in the presence of bulky anions (*e.g.*, citrate ions), polymers and quaternary ammonium salts as the stabilizers.

Electrochemical polymerization in the presence of platinum colloids was studied for PPY.[194, 214] Later, various metal-containing colloids were incorporated during electropolymerization of aniline,[140, 186, 197] thiophene,[200] pyrrole[95, 142, 195, 198, 199, 201] and EDOT.[202, 203] The electrochemical polymerization was carried out under potentiostatic or potentiodynamic conditions in the presence of metal colloids. A PEDOT/Au composite film (with the average NP size of 10 nm) was electrodeposited onto the surface of a PEDOT electrode from an aqueous solution containing the EDOT monomer and the pre-synthesized gold NP in the presence of stabilizing agents.[202, 203] It was shown[120] that the average size of gold NP and their size distribution can be varied over wide ranges by changing the nature of stabilizing agents. Using the potentiodynamic method, a PEDOT/Au film was electrodeposited on a glassy carbon (GC) electrode from a solution containing gold NP stabilized by EDOT molecules.[58, 59] Spherical gold clusters measuring 50–100 nm on PEDOT fibres were uniformly distributed over the whole polymers surface.[58]

The majority of procedures for stabilizing gold NP are based on the formation of a covalent bond between the gold atoms on the surface of particles and the sulfur atoms of sulfur-containing ligands (di-, tri- and tetrathiols, disulfides, thioethers, *etc.*).[203, 215–221] However, long thiol molecules used to stabilize gold NP are not always efficient,[222–225] because they form an insulating shell around the NP, which hinders the transport of electrons and species.

The majority of studies of metal NP and methods of their synthesis are devoted to gold particles rightly considered as the model objects with interesting properties. The active studies and the advances in the field of synthesis of gold NP† could not but be reflected in attempts to use them in conducting polymers. Among composites of various conducting polymers, those loaded with gold NP are the leaders.

Literature describes many methods of synthesizing gold nanoparticles from 1 nm to several micrometres in diameter and also NP of silver[212] and platinum[95] which employ various physical and chemical techniques.[226–232] It should be noted that in the majority of cases, the reduction of metal ions to atoms proceeds in the presence of a stabilizing polymer, because the interaction of metal cations with polymer functional groups prior to the reduction restricts the size of formed particles. Another method of stabilization used more rarely consists of monomer polymerization around the nanoparticles. Aniline, thiophene[233] and EDOT can be used as such monomers.[234–237] For example, a colloid solution of the PT/Au composite synthesized by thiophene polymerization in the presence of $HAuCl_4$ and containing no additional agents was stable for several weeks.[233]

The monomer molecules of aniline[205] and thiophene[233, 238] were also used in the preliminary synthesis of metal NP. The redox reactions of these molecules with electropositive metal ions yielded nanoparticles stabilized by polymer shells. In the latter case, the concentration of metal ions in solution was selected to be sufficiently low as compared with the monomer concentration so that the resulting metal NP could form a stable colloid solution. This was followed by the electrochemical polymerization to yield composite films on the electrode. Thus gold nanocomposites with polyaniline,[205] polythiophene[239] and poly(3,4-ethylenedioxythiophene)[234–236, 240, 241] were synthesized.

II.3. Synthesis of conducting polymer–metal composite films from colloid dispersions of polymer and metal nanoparticles

Recently, methods of synthesizing composite films based on preparation of mixed colloid solutions of polymers and metal NP have been actively developed. Colloid dispersions of composites can be prepared by mixing the initial colloid solutions of polymer and metal NP or by direct formation of metal NP in polymer dispersions upon the addition of salt solutions of electropositive metals such as gold, palla-

† Please, refer to publications on the synthesis and use of metal NP, including gold NP (*e.g.*, see review[215]).

dium or silver. The formation of composite films on electrodes from colloid dispersions can be accomplished by their dropwise application on the substrate, by spreading a uniform coating of a liquid layer over a horizontal substrate rotating at a high velocity (spin-coating) or also by the jet printing technology with subsequent drying.[242–245] Furthermore, layer-by-layer deposition of separate solutions containing polymer and metal NP can be used.[56, 157–159] The adsorption method of successive application of layers of metal nanoparticles and conducting polymers onto substrates was considered in several publications.[54, 204, 246–248]

The methods listed above can be used in the large-scale syntheses of films of composite materials; this is done using both simple and high-tech methods for applying solutions onto even large surfaces. Also, it is possible to form specified structures on the surface of conducting and non-conducting substrates, in particular, the methods using jet printers. The method of printing of electrochemical sensors by means of special jet printers with heated platforms in which metal composite dispersions are used as the ink is of particularly wide application.

For solving practical problems, adhesion of the applied material to the substrate surface is a very important parameter. To increase the adhesion and stabilize the coating, additional stabilizers are used which prevent dissolution of composite materials on their long-term operation in electrolyte.[249] New methods were also proposed for synthesizing aqueous dispersions of PEDOT/PSS/Pd, PEDOT/PSS/Au and PEDOT/PSS/Au/Pd composites (PSS is polystyrene sulfonate). The synthesis of colloid solutions of conducting polymer–metal composites is very important because this opens up wide opportunities for applying catalyst particles on various substrates (including non-conducting ones) *via* their dropwise application or printing with a jet printer. Simple mixing of PANI with suspensions of Pd nanoparticles[250, 251] and also mixing of PEDOT–PSS with dispersions of Au and Ag (Ref. 252) yielded the corresponding metal nanocomposites in solution. It was found[253] that encapsulation of pre-synthesized gold NP into pre-synthesized water-soluble polyaniline-2-carboxylic acid provides composite nanocolloids which are stable in aqueous solutions.

To develop multilayer structures of PANI and gold nanoparticles, the electrode was re-immersed into a solution containing polyaniline and colloids of Au or Ag (layer-by-layer).[42, 165–167] This approach turned out to be very convenient for deposition of ultrathin composite layers with a uniform distribution of metal NP.[254]

II.4. One-step synthesis of conducting polymer–metal composites from mixed solutions of monomers and metal salts

II.4.a. Chemical synthesis of conducting polymer–metal composites by direct redox reactions between the monomer and metal ions in solution

One of the methods of one-step synthesis of conducting polymer–metal composites is based on the redox reaction between molecular components of the mixed solution, *i.e.*, the precursors of composite components. Conducting polymer–metal composites are obtained by oxidizing the conjugated monomer (*e.g.*, pyrrole, aniline) by transition metal cations (*e.g.*, palladium, platinum), which induces the simultaneous formation of both the polymer matrix and the metal nanoparticles dispersed in polymer globules.

In essence, this method is close to those described above in Sections II.2 and II.3, special cases of which also employ monomer molecules for synthesizing nanoparticles of electropositive metals. However, the main argument for its recognition as an individual method is that the precipitate is formed in a single step to be used later in electrode preparation.

To date, several papers were published devoted to the use of this method for preparation of nanocomposites with Au, Pd, Ag and Pt nanoparticles.[51, 64, 11, 137, 145, 234, 255–279] In the one-step electroless synthesis, the bulky anions such as PSS, dodecyl sulfate (SDS), polyvinylpyrrolidone (PVP), *etc*. were used as NP stabilizers.[234, 274] The EDOT monomer was simultaneously used to reduce $HAuCl_4$ and stabilize the gold NP thus formed.[234, 236] The SEM and TEM images acquired in these studies demonstrated gold nanowires with the diameter of $\sim$20–30 nm and the length of 0.5–1 μm covered with the polymer (PEDOT). The effect of the reducing agent (EDOT) concentration and the synthesis time on the morphology and conductivity of PEDOT/Au composites was considered. In several studies, other stabilizers were used together with PEDOT, such as trioctylamine,[241] PSS,[234, 280] SDS,[234] PVP,[234] *etc*. It was shown that PEDOT/Au particles stabilized by polystyrene sulfonate became water-soluble, in contrast to gold particles covered only by the PEDOT film.[234] The effect of the EDOT : PSS/$HAuCl_4$ reactant ratio on the morphology of gold particles was studied.[280] When trioctylamine was used as the stabilizer, the formation of spherical gold aggregates with the diameter of $\sim$230 nm built of 10 nm gold NP was observed.[241] The NP size was controlled by varying the deposition time and concentrations of stabilizing and reducing agents. Several publications were devoted to studies of colloid solutions of composites by optical and IR spectroscopy.[241, 280]

For studying the electrochemical properties of deposits of conducting polymer–metal composites synthesized in a single step, they were fixed by various methods on electrode substrates. Particularly, the filtered and dried precipitates of conducting polymer–metal composites were introduced into carbon pastes, mixed with additional binding materials and then applied onto various substrates.[111, 281] For example,[111] the composite obtained as a powder was filtered, dried, and then applied on a GC electrode within a paraffin film. In another study,[282] PPY/Pd composites synthesized by colloid solution sedimentation were successfully used both as powders and deposits on a carbon substrate for catalyzing the organic reactions of cross-coupling of aryl and(or) hetaryl substrates. For deposition on substrates, suspensions of composite powders in organic solutions (acetonitrile, *N*-methylpyrrolidone, *etc*.) were used.[275, 282–284]

In addition to the methods of extraction of composite deposits and their subsequent application on electrode surfaces, a method of direct application of liquid colloid dispersions onto substrate surface followed by their drying to yield a solid film was also used. This version of preparation of composite electrode is similar to those discussed above in Section II.3.

II.4.b. One-step electrochemical synthesis of conducting polymer–metal composites from monomer and metal salt solutions

The electrochemical synthesis of conducting polymer–metal composite films on electrodes from solutions containing

a metal salt and the monomer can be carried out in a single step by cycling the electrode potential in a wide range or by applying potential pulses of different polarity. The potential variation region involves potentials of polymer–film electrodeposition on the electrode surface and the potentials of electrodeposition of metal particles on the film surface. The conducting polymer film is formed in the positive potential region, whereas the metal electrodeposition occurs in the negative potential region. Both processes occur in the same mixed solution but are time-spaced. By selecting the potential region and the potential scan rate or the time of potential pulses, one can control the ratio of composite components and the size of metal particles. These synthetic methods were discussed in several studies dealing with Pt-, Pd-, Au- and Ag-containing composites based on PANI, PEDOT, PPY and some other polymers.[67, 76, 254]

The features of formation and electrochemical behaviour of PANI/Pt and PANI/Pd systems formed on the surface of a GC electrode in the course of its potential cycling in solutions containing aniline, a metal salt and a supporting electrolyte were studied.[67] It was assumed that the deposits grew mainly in the direction away from the substrate within polymer pores. It was also shown[67] that the real surface area of platinum and palladium deposits incorporated into PANI can be found by considering the adsorption of copper atoms (the specific surface area of the Pd deposit was found to be $35-45\ m^2\ g^{-1}$). The PANI matrix favoured the formation of highly dispersed palladium deposits (particles of 8–10 nm) in contrast to platinum deposits (particles of ~ 40 nm). The SEM studies revealed considerable differences in the morphology of PANI/Pt and PANI/Pd films. The microparticles of catalytic metals have a substantial effect on the redox properties of the film and accelerate its degradation.

The PANI/Ni films containing up to 4% of nickel have been prepared by electrodeposition.[285] It was shown that the size and content of nickel particles can be varied by varying the metal concentration in solution and the potential scan rate. The PANI/Ni films exhibited well pronounced ferromagnetic properties.

III. Electrochemical reactions on conducting polymer–metal nanocomposite electrodes. Electrocatalysis

Figure 4 shows the general scheme of electrode processes observed on a conducting polymer–metal composite film. Localization of electrochemical reactions involving species of an external redox system is an issue deserving special discussion. The electrode processes involving such species contained in the electrolyte solution may in principle proceed at the following interfaces:

(*1*) conducting substrate/polymer film;

(*2*) polymer film/electrolyte solution;

(*3*) metal cluster/electrolyte solution.

The first case is likely only for films with sufficiently high porosity, *i.e.*, in the presence of pores of different size, which make easier the access of reacting species through electrolyte to the substrate. The porous structure of films also provides for the processes at interfaces *2* and *3*. In particular, they can occur both on the visible external polymer surface and metal clusters located on it and on the internal surface of film pores and metal clusters in them. Indeed, studying the structure of such films revealed the

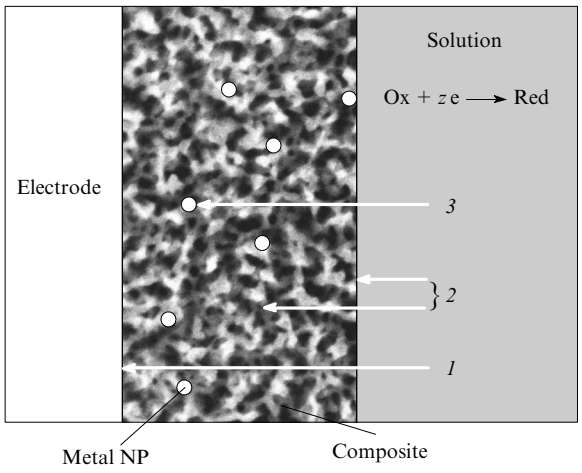


Figure 4. Scheme of the electrode processes on a composite film. (*1–3*) Interfaces (see the text). Ox is the oxidant, Red is the reductant.

presence of metal particle inclusions both on the surface and in the pores.[286, 287] Moreover, it should be noted that the position of a metal cluster in contact with electrolyte solution, either inside the film or near the film/electrolyte interface, has a substantial effect on the kinetics of the process: in the former case, an additional stage of ion transport in the film appears, whereas in the latter case, this stage is absent.

The porosity of the material and the presence of reaction surfaces with different electrochemical activity and different structure of the electric double layer may give rise to complex kinetic behaviour not obeying the classical equations of electrochemical kinetics for homogeneous metal electrodes. The kinetics of electrode processes in such systems can be complicated and its details often remain unclear.

Primarily, in studying the redox processes on conducting polymers, it was assumed that their occurrence is limited to the potential region of electrochemical activity of the polymer film; and, hence, when the film is transferred into its non-conducting (or poorly conducting) state, the processes on the outer interface polymer film/electrolyte should be inhibited, which can serve as an indication of electronic conduction of the film.[288] This statement was confirmed experimentally[289, 290] for redox processes of iron(II) aqua ions on PPY films. For several non-polar gases (H_2, O_2) and uncharged compounds, it was found[291] that when the potential of a conducting polymer film is in the region of its non-conducting state, the reaction occurs on the inner conducting substrate/polymer interface; furthermore, the effect of the substrate material on the reaction kinetics was found for gas molecules.[292] The latter fact points most convincingly to the presence of the reaction at the inner interface.

To date, a large number of studies devoted to catalytic activity of conducting polymer–metal composite films have appeared. As a rule, these studies were associated with the prospects for the design of materials for low-temperature fuel cells[293] and electrochemical sensors.[294] In addition to its practical importance, studying the electrode reactions on

conducting polymer–metal composite films makes it possible to assess the electrochemical properties of the latter and compare them with the properties of polycrystalline electrodes. This is of special interest when the processes under consideration occur preferentially on metal particles, *i.e.*, microelectrodes, and the polymer matrix serves as the integrating conducting medium.

However, as was noted in a review,[19] the results of numerous studies of catalytic processes on conducting polymer–metal composites are often conflicting and their comparison is difficult due to the difference in experimental conditions, low reproducibility of results and, in the majority of cases, the absence of data on the specific current calculated per unit real surface area of the catalytic metal (provided that catalysis occurs preferentially due to metal inclusions).

Thus, highly important is the correct choice of experimental conditions under which the reactions of the system studied can be reliably separated (for polymer and metal inclusions) in order to find and analyze the partial currents of electrochemical reactions separately for metal inclusions. Another important problem to be solved for reliable elucidation of kinetics of electrochemical processes on polymer–metal electrodes is finding the real surface area of metal particles. In most publications, this information is absent, which complicates more profound analysis of the material. Despite the mentioned complications, certain success was achieved recently both in the mathematical description of electrochemical processes on heterogeneous conducting polymer–metal electrodes and in experimental testing of applicability of theoretical results obtained.

III.1. Theoretical aspects of the description of electrochemical processes on conducting polymer–metal electrodes

Above, it was mentioned that real conducting polymer–metal films are porous systems heterogeneous in their properties and can serve as attractive candidates in studying and modelling electrode processes. Theoretically, polymer films in which redox processes proceed mainly on catalytic metal inclusions distributed both over the film surface and in the internal pore bulk are most interesting in this respect. The theoretical aspects of electrode processes on electrodes heterogeneous in their properties were published earlier only for simple systems, *e.g.*, for an ensemble of metal NP distributed over the electrode substrate surface that functon as separate microelectrodes.[295–297]

In terms of theoretical models, this system is considered as a monolayer of metal particles in a polymer film, to which the concepts developed for microelectrodes and their ensembles can be applied.[296, 297] The size of microelectrodes determines the character of diffusion to their surface, which is reflected in kinetics. The effect of the microelectrode size is determined by the ratio of thickness of diffusion layers on metal particles to the linear size of the latter and also depends on the distribution of microelectrodes over the film surface.

The mechanisms of electrode processes on conducting polymer–metal composite films were analyzed in detail.[29, 286, 287, 298] The composite films were considered as the systems consisting of a multitude of metal cluster microelectrodes distributed over the surface and throughout the bulk of the conducting polymer matrix. The electrochemical reactions involving species of the external redox system and occurring on these films were analyzed for the case of random distribution of microelectrodes in the film bulk and the distance (R_{ij}) between the clusters comparable with the size of clusters (r_n) and also for the case of $R_{ij} \gg r_n$. As follows from the foregoing (Section II.1), this model complies with experimental data on the structure of conducting polymer–metal composite films.

For the sake of simplicity, the reacting species of the external redox system in electrolyte solution will be called below the test species. It was assumed that the electrode reaction that involves the test species and proceeds on the surface of clusters is irreversible and its rate is described by first-order kinetics. At the same time, the transfer of electrons between the substrate and clusters (*i.e.*, through film parts separating them) occurs under reversible conditions.

The main assumption made in the subsequent analysis is that the clusters are small compared with the thickness of the accommodating conducting polymer film. Insofar as the thickness of diffusion layers that appear as a result of reactions of test species on the surface of cluster microelectrodes is of the order of magnitude of the cluster radius, the above assumption allows us to use two scales of distance. The first scale (microscopic) serves for characterizing the local distribution of test species around the clusters, whereas the second scale (macroscopic) is used for describing variations in the averaged concentration of the same species on the scale of distances comparable with the film thickness. It is evident that on the macroscopic level, the description is reduced to the diffusion problem complicated by the presence of the bulk electrochemical reaction of test species on point-like clusters. Particularly, to describe the distribution of the concentration of reacting species $c_k(z, t)$ inside the film, *i.e.*, on the macroscopic scale of distance $0 \leqslant z \leqslant L_0$, where L_0 is the film thickness, the differential equation was derived

$$\frac{\partial c_k(z,t)}{\partial t} = \frac{D_k \partial^2 c_k(z,t)}{\partial z^2} - K(z,E)\, c_k(z,t) \qquad (6)$$

where D_k is the diffusion coefficient of test species, $K(z, E)\, c_k(z, t)$ is the rate of the bulk transformation of test species. This quantity was calculated with the use of the microscopic scale of distances as a flow of substance to the cluster surface (or to certain parts of the surface) accommodated in a macroscopically narrow film layer with the thickness equal to the average diameter of clusters located at a fixed distance z from the electrode substrate surface. In this case, the effective rate constant for the bulk reaction $K(z, E)$ turns out to depend not only on the electrode potential E (due to contact between clusters and the substrate through the conducting polymer film) but also on the distance z when the clusters are distributed nonuniformly in the film bulk. This constant implicitly depends on the cluster size. Thus, we have considered a fairly general case of composite films with the only (but justified, as noted above) assumption of smallness of clusters as compared with the film thickness. Without dwelling into details of solution of this problem (they were fully considered before[29, 298]), we consider the final results which can be tested experimentally.

Thus, summarizing the results of the theoretical analysis and numerical calculations carried out for the case of uniform distribution of identical clusters throughout the

film thickness, it should be pointed out that the electrode modified with a composite film behaves as a compact electrode made of the material of particles incorporated into the film. It deserves mention that this conclusion proved to be true for electrochemical measurements carried out both under steady-state and non-steady-state conditions. Particularly, on such composite electrode, the steady-state voltammetric curve of oxidation/reduction of test species was described by an irreversible-wave equation the same as for the macroscopic metal electrode,[298] namely,

$$J_k - A\rho c_k^{(0)}\left(1 - \frac{J_k}{J_k^{\lim}}\right)k_0' \exp\left(-\frac{\alpha \mathrm{F}E}{RT}\right) \qquad (7)$$

with some effective rate constant k_0' determined by the relationship

$$k_0' = \frac{\rho n a_0(r_0) L_0 k_0}{2\sigma A r_0} \qquad (8)$$

Parameters involved in these expressions are defined as follows: J_k is the current; A is the visible surface of the film; ρ and σ are the rate constants for the injection of test species into the film and their escape from the film ($\rho = \sigma$ [cm s^{-1}] for clusters in direct contact with film-surrounding solution); $c_k^{(0)}$ is the concentration of test species in the solution surrounding the electrode; $J_k^{\lim}$ is the limiting current observed on a composite electrode with the visible film surface and determined by both the size and the number of particles incorporated into the film and the conditions of solution stirring; α is the apparent transfer coefficient; E is the electrode potential; $na_0(r_0)$ is the overall surface of clusters accommodated in a microscopic film layer with the thickness of $2r_0$ (*i.e.*, the cluster diameter); L_0 is the film thickness; k_0 is the real rate constant for the electrode process.

Thus, the effective rate constant k_0' can be changed not only by varying the temperature as for metallic electrodes but also by varying the content of inclusions in the film [*i.e.*, the factor $na_0(r_0)$, the radius of incorporated particles r_0 and the film thickness L_0]. In fact, this forms the specific character of composite films as compared with macroscopic electrodes made of the material of the inclusions present in the film.

It should be noted that Eqn (8) holds for films containing identical clusters (with the radius r_0). In the general case, the radii of clusters are different and the corresponding expression for this constant is more complicated due to the use of averaging over the cluster size. However, the equation for the voltammetric characteristic, *i.e.*, Eqn (7), remains unchanged. It should be added that this equation also remains unchanged when clusters of identical size are distributed randomly throughout the film bulk but their overall surface area within the film remains specified. Moreover, the form of Eqn (8) is also retained with the only difference that the product $na_0(r_0)$ should be considered as a certain arbitrary function of the distance to the electrode substrate.

These results, unexpected at first glance, have a simple explanation if one assumes additionally[298] that the film thickness (L_0) far exceeds the thickness of the diffusion layer (δ) formed in the electrode-surrounding electrolyte solution in the presence of redox reactions of test species. Taking into account that the values L_0 for conducting polymer films usually do not exceed one micrometre and δ lies in the range of 10^{-3}–10^{-2} cm if the stirring intensity is moderate, then this assumption can be considered as justified in the majority of cases. Under these conditions (*i.e.*, for the low L_0/δ ratio), the concentration gradients of test species inside the film should be virtually absent if the currents are not too close to the limiting value [$J_k^{\lim}$, see Eqn (7)]. Hence, all the clusters incorporated into the film are under virtually the same conditions so that the governing factor is their total surface area and not the way they are distributed in the film bulk. In connection with this, the above conclusion that the form of voltammetric (polarization) curve is independent of the particular type of distribution of identical clusters throughout the film bulk can be extended, with sufficient confidence, to the case of clusters of different size.

As an illustration to these briefly described consequences of the theory, we consider the results of studies in which experiments implied both the analysis of the currents of test species with distinguishing the partial reaction currents on metal inclusions and estimation of the real surface area of such inclusions. Certain examples of experimental verification of the theoretical relationships are shown below for the reactions of hydrogen peroxide reduction on PEDOT/Au composites films[299] and hydrazine oxidation on PEDOT/Pd film.[171, 300]

The wave of hydrogen peroxide reduction on the polymer surface is located at considerably more negative potentials (by up to 200 mV) than the reduction wave on gold clusters, which points to the electrocatalytic reduction of hydrogen peroxide on gold clusters. The noticeable separation of these waves on the potential scale allowed the authors[299] to isolate and analyze the partial current of hydrogen peroxide reduction on gold as a function of the time of gold deposition into the film. It was demonstrated that for all times of gold deposition into PEDOT films and the corresponding variations in the size and distribution of Au particles, the measured partial voltammetric curves of the reduction on gold clusters really satisfied Eqn (7) so that the curves could be linearized on the semi-logarithmic (Tafel) coordinates E *vs.* $\log[j/(j_\mathrm{d} - j)]$ (j is the current; j_d is the diffusion current). The analysis of partial voltammograms on the mentioned coordinates yields the slope of 0.21–0.24 V for their linear segments, which points to the presence of an irreversible two-electron process with the apparent transfer coefficient of 0.24–0.28. The resulting transfer coefficient suggests that the slow stage of the overall two-electron process is the transfer of the first electron. The above data agree with the mechanism proposed[301] for hydrogen peroxide reduction on gold.

The increase in the observed rate constant with the increase in the amount of gold loaded into the film shifts the cathodic wave of the reduction of test species to more positive electrode potential, which means acceleration of the process. Obviously, this is associated with the increase in the total surface area of gold clusters [$na_0(r_0)$] as the amount of gold loaded into the PEDOT film increases; however, the rigorous consideration requires taking into account additional data (see below). This preliminary conclusion was confirmed experimentally for hydrogen peroxide reduction on PEDOT/Au films[299] and hydrazine oxidation on PEDOT/Pd films.[171, 300]

It should be added that for long times of gold loading into the polymer film, the position of the voltammogram

virtually coincides with that for hydrogen peroxide reduction on polycrystalline gold. A shift of the hydrazine oxidation wave with increase in the time of PEDOT-film loading with palladium particles was also observed in another study.[171]

The limiting currents of hydrogen peroxide reduction and hydrazine oxidation measured on rotating disk electrodes modified with PEDOT/Au (Ref. 299) and PEDOT/Pd (Ref. 171) films turned out to be lower than the corresponding limiting diffusion currents to the unmodified electrode; the currents coincided only in the case of long-term metal loading into the films. This is associated with the fact that at relatively short times of gold and palladium deposition, nanosized clusters of these metals are formed. The density of distribution of such clusters is low so that the distance between them far exceeds their diameter; hence, the diffusion of test species to clusters proceeds independently (on the scale of microscopic distances; see above). The currents corresponding to reactions of test species on the surfaces of clusters are independent of one another, which corresponds to the monotonic increase in the observed overall current (including the observed limiting current $J_k^{\lim}$) with the time of metal deposition. With the increase in the density of distribution of metal clusters in the film, the diffusion layers around the clusters begin to overlap, and the spherical diffusion of test species towards particular clusters is gradually replaced by their one-dimensional diffusion to all clusters in the film. Ultimately, this leads to independence of the recorded current of further increase in the metal deposition time, as was confirmed theoretically.[298]

The described features were confirmed experimentally. Indeed, as the gold deposition time and amount loaded into the PEDOT film increased, the limiting current of hydrogen peroxide reduction also increased.[299] The analogous effect was observed also for hydrazine oxidation on palladium particles loaded into a PEDOT/Pd composite film.[171] For sufficiently long times of metal (gold, palladium) deposition, the increase in the limiting current slows down to reach virtually constant values corresponding to the limiting diffusion current of hydrogen peroxide reduction and hydrazine oxidation controlled by the diffusion mass transfer of test species in the surrounding solution.

Now, we consider how the limiting currents in films loaded with different amounts of metal (*e.g.*, gold) change with the intensity of solution stirring [in the studies cited,[171,299] rotating disk electrodes (RDE) were used]. As was mentioned above, the limiting current for long-term loading of gold is independent of the loading time so that the recorded overall limiting current is of the diffusion nature. Thus, the dependence of this current on $\omega^{1/2}$ (where ω is the angular rotation rate of the corresponding disk electrode) is linear and can be extrapolated to the origin, which points to its compliance with the Levich equation, *i.e.*, the presence of diffusion limitations on the transfer of H_2O_2 molecules to the visible electrode surface. For short times of gold loading, the dependences of the overall and partial (on metal clusters) currents of hydrogen peroxide reduction have a more complicated form. Figure 5 shows the corresponding dependences plotted on the Koutecky–Levich coordinates. When extrapolated to $\omega^{-1/2} = 0$, the linear dependences $1/I_d$ *vs.* $\omega^{-1/2}$ substantially deviate from the coordinate origin for short times of gold loading (see curves *2*, *3*).

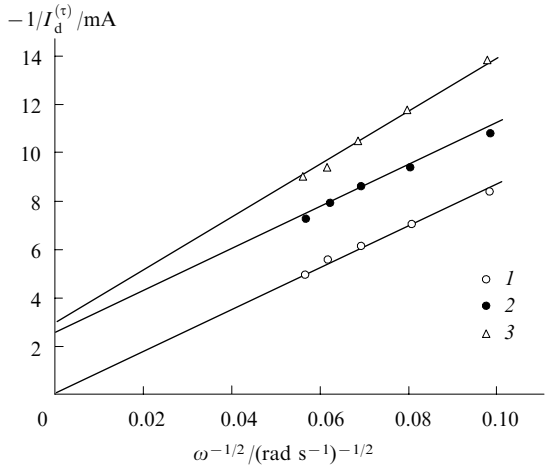


Figure 5. Dependences of $1/I_d^{(\tau)}$ [$I_d^{(\tau)}$ is the limiting diffusion current at a specified gold deposition time τ] on $\omega^{-1/2}$ for electroreduction of hydrogen peroxide on the PEDOT/Au composite film.[299]
The dependences were obtained in 0.2 M phosphate buffer containing 10^{-3} M H_2O_2 on electrodes with different gold amounts loaded from 10^{-3} M $HAuCl_4$; deposition time/s: (*1*) 720; (*2*) 60, overall current; (*3*) 60, partial reduction current on gold clusters.

According to the concepts briefly described below, the *y*-intercepts should be considered as the kinetic components of the overall (curve *2*) and partial (curve *3*) currents realizable only for the infinitely high electrode rotation rate. The appearance of such kinetic currents is associated with the parallel processes of H_2O_2 reduction on the ensemble of microelectrodes (gold clusters) and on the film surface free of these clusters.

This type of analysis was described in the supplement to the aforementioned publication.[299] In particular, it was shown that the limiting current reached on a modified electrode $I_d^{(\tau)}$ [in Eqn (7), $J_k^{\lim}$] should not exceed the limiting diffusion current and can coincide with the latter only at sufficiently high densities of particle distribution in the film. In fact, this means that for low limiting currents (as compared with the limiting diffusion current), the amount of metal loaded into the film is insufficient for the purely diffusion mode of the supply of species that react on the composite electrode. Insofar as another conclusion of the study under consideration was the virtual independence of the observed current of the pattern of cluster distribution in the film, then it can be formally assumed that the number of clusters is insufficient even if all clusters present in the film are concentrated on the electrode/solution interface. This is why the analysis is carried out for an imaginary system with the clusters located on the film/solution interface. In this case, the problem is reduced to the description of parallel reactions of test species which proceed on the film areas covered with clusters (corrected for the surface curvature) and free of them with allowance made for the convective-diffusion nature of the supply of species to this surface.

The consequences of such consideration are as follows:

— the slopes of dependences of the reciprocal values of overall and partial currents on the rotation rate (on the Koutecky–Levich coordinates) considerably differ;

— the y-intercepts obtained upon extrapolation of the corresponding linear dependences $1/I_d$ *vs.* $\omega^{-1/2}$ to $\omega^{-1/2} = 0$ are also different;

— the slopes of the plots for reciprocal overall limiting diffusion current coincide at long times of gold loading into the PEDOT film.

As can be judged from the data shown in Fig. 5, all these factors are present in the experiment. Thus, the experimental results on the hydrogen peroxide reduction on composite PEDOT/Pd films are in good agreement with the theoretical description of electrode reactions in such systems.

An important consequence of the theoretical analysis carried out by Malev *et al.*[29,286,287,298] is the conclusion that the volume distribution of metal NP in contact with electrolyte components (the components of external redox systems) plays a significant role only for currents very close to the limiting current of the total composite electrode. Then the concentration of test species in the film pores becomes so small that its relative changes $[\Delta c_k(z,t)/c_k(z,t)]$ start to depend substantially on the distance z to the substrate surface. This factor makes unequal the conditions of transport to clusters located at different distances z in the film, so that the diffusion of test species to such clusters becomes dependent both on the character of their distribution and the possible deviations in their size. Unfortunately, this phenomenon can hardly be reliably detected and used for estimating the cluster distribution under the conditions of electrochemical measurements. Indeed, according to calculations,[298] the deviations of polarization curves of composite electrodes from the dependences set by equation (7) are noticeable only for currents differing from the limiting values by no more than 5%.

One can also mention the effect of the first cycle (or the first pulse) when the electrode saturated with redox-system components produces its first current response, which is considerably higher than in the subsequent cycles (or potential pulses). This is attributable to saturation of the film with active components, which disappears in subsequent cycles. The first-cycle effect can be used for enhancing the sensitivity of electrochemical sensors. However, under the steady-state (or quasi-steady-state) conditions of measuring voltammetric curves, the effect of volume distribution of catalyst nanoparticles disappears and the catalyst efficiency is determined first of all by the density of particle distribution and their effective surface area.

III.2. Electrocatalysis or the effect of the surface area. Determination of the surface area of metal particles in conducting polymer–metal composites

The electrocatalytic processes on different conducting polymer–metal composite electrodes remain at the centre of attention of scientists,[302–335] which is associated with the development of low-temperature fuel cells and sensors.[293,294,302] Of particular importance is the electrocatalysis of the processes of hydrogen, formic acid, hydrazine, methanol and ethanol oxidation and oxygen reduction. The oxidation of methanol and other small molecules is known to proceed *via* several parallel reactions, particularly, those giving intermediates that can poison the catalytic metal particles. These intermediates include, for instance, carbon monoxide and formaldehyde, which can be adsorbed strongly on the catalyst thus hampering its operation; this is why attention is focused on the options of further oxidation of these products.

Table 3 shows the data obtained for various catalytic reactions on polymer–metal composite materials. It deserves mention once again that among the overwhelming majority of studies, little attention was paid to determination of the real size effect, *i.e.*, to measuring the catalytic activity per unit real surface area of the catalytic metal. For a part, this is associated with the difficulty in finding the real surface area of metal nanostructures contained in a polymer and also with its possible changes during electrochemical experiments under different conditions.[19] The determination of the real active surface area of particles by the direct experimental methods is a difficult task. The estimates can be made based on indirect data on the adsorption of certain molecules on the surface of particles and also based on model calculations of the particle size distribution and density.

The use of the known methods of assessing the real surface area of metal electrodes, well-developed for platinum group noble metals, is often complicated by the peculiar properties of both the conducting polymer–metal systems and of the metal in its dispersed state. Thus, the determination of the platinum real surface area based on hydrogen adsorption can be incorrect because of the adsorption interaction of NP with the polymer and the changes in the substrate pseudo-capacity.[78,303,304] The processes of hydrogen sorption/desorption on palladium particles are complicated by the absorption of hydrogen in the bulk of this metal, which gives no way of estimating the palladium real surface area based on hydrogen peaks in voltammograms.[305,306] It was recommended[65,67,79,305–307] to determine the real surface area of inclusions of platinum metals (Pt, Pd) from the adsorption of copper on their surface. Good reproducibility of values of the real surface area of platinum particles incorporated into PANI estimated from the adsorption of copper atoms has been pointed out.[67] However, this method cannot be used for some conducting polymers due to the possible specific interaction of copper ions with polymer functional groups (*e.g.*, with sulfur atom in the thiophene ring) and also due to redox interactions of copper ions with the polymer.[261]

A method that can be considered as promising for assessing the real surface area of platinum group metal and gold particles is the electrochemical adsorption of oxygen. It was noted[79,308–311] that this method can be incorrect for polymers that are easily oxidized at relatively high anodic potentials of oxygen adsorption. However, many conducting polymers, for instance, thiophenes, exhibit fairly high resistance to oxidation in the mentioned potential range. The data for the PEDOT/Pd composite[170,172] can serve as an example of such estimates. In dilute acid solutions (0.1 M H_2SO_4, 0.1 M $HClO_4$), the oxygen desorption peaks in voltammograms are well reproducible, so that their clear dependence on the time of film loading with palladium particles is evident. The charge (Q_{Pd}) consumed in the reduction of palladium surface oxide can be considered as a measure of the palladium surface area. The Q_{Pd} value was found by integrating the current under the cathodic peak of oxygen desorption from the palladium surface, with a correction made for the charging current. The currents of palladium oxide reduction on the PEDOT/Pd film are easily separated from the charging currents of the PEDOT film. This provides for reliable calculations of the real surface area of palladium particles under the assumption of closeness of the specific

Table 3. Catalytic reactions on polymer-metal composite materials.

Polymer	Metal NP	NP size /nm	Specific content of metal catalyst /μg cm^{-2}	Comments (investigation method; catalytic effect; real surface area estimates)	Ref.
			Methanol oxidation		
PANI	Pt	20 – 100	10 – 30	Three different methods of Pt NP incorporation were tested; method of steady-state polarization curves	81
PANI	Pt	10 – 30	25 – 750	CV method; methanol adsorption isotherms at different concentrations were studied; the real surface area of platinum particles was assessed	94
PANI	Pt	–	62 – 76	Method of steady-state polarization curves; the real surface area of platinum particles was assessed	127
PANI	Pt	100 – 400	200	CV method; catalytic currents at different Pt contents in PANI were measured	109
PANI	Pt	–	112 – 260	CV method; electrocatalytic activity of platinum particles in PANI was noted; synergistic effect between dispersed Pt particles and PANI; the real surface area of platinum particles was assessed	108
PANI	Pt, Pt/Pd	~3	–	CV and chronoamperometry; PANI – nanofibres (60 – 100 nm diameter)	316
Pt/C and PANI/Pt/C	Pt	–	0.051	CV, chronoamperometry and electrochemical impedance spectroscopy; methanol oxidation on two modifiers, Pt/C and PANI/Pt/C, was compared	317
PANI/SWCNT [a]	Pt	20 – 80	30 – 100	Method of steady-state polarization curves; methanol oxidation current was studied as a function of the mass of incorporated Pt particles	318
PANI	Pt	210	–	CV method; layer-by-layer composite synthesis; methanol oxidation depends on the number of layers and the nature of the external layer (PANI or Pt)	319
PANI	Pd	150	–	Methods of steady-state polarization curves and CV; methanol oxidation current was studied as a function of the method of Pd synthesis (from $PdCl_4^{2-}$ or $PdCl_6^{2-}$), comparison with a plane Pd electrode was made	312
PANI – PSS	Pt	–	–	Methods of CV and chronoamperometry; synthesis with different PANI : PSS ratios was tested; electrochemical deposition	313
PEDOT	Pt – Ru	123	12 – 13	Methods of CV and chronoampermetry; electrodeposition of bimetallic Pt – Ru clusters into PEDOT; methanol oxidation current on the PEDOT/Pt – Ru electrode was several times higher than on the Pt – Ru electrode in the absence of PEDOT	314
PEDOT	Pt	4 – 25	–	Methods of CV and chronoamperometry; PEDOT was shown to noticeably improve the catalytic reactions on Pt particles (no considerable poisoning by CO species was observed)	322
PPY	Pt	3.5	–	Methods of CV and chronoamperometry; one-step synthesis of composites; composites were more active than commercial Pt/C catalysts	320
			Ethanol oxidation		
PEDOT/ ER-GO [b]	Pt	–	~80	Methods of CV, inversion voltammetry, chronoamperometry and electrochemical impedance spectroscopy; real surface area was assessed (47.1 m^2 g^{-1})	321
PANI	Pd	–	–	CV method (repeated cycling, 1st and 200th cycles)	323
Carbnano/ [c] PANI	Pt	9	–	CV and thermogravimetry; composite activity was comparable with that of Pt/C NP	324
			Oxygen reduction		
PPY	Pt	–	–	CV method	325
PPY	Pt	–	–	Method of steady-state polarization curves	214
Carbnano/ [c] PANI	Pt	9	–	CV method; Koutecky – Levich dependences for O_2 reduction were plotted on Tafel coordinates; thermogravimetry	326

Table 3 (continued).

Polymer	Metal NP	NP size /nm	Specific content of metal catalyst /μg cm^{-2}	Comments (investigation method; catalytic effect; real surface area estimates)	Ref.
			Oxygen reduction		
PANI	Pt	–	–	Electrodeposition of Pt particles; composite was covered with Nafion; non-steady-state curves	327
PPY	Pt–Cu	–	–	Methods of steady-state curves on RDE and electrochemical impedance spectroscopy; four-electron mechanism and catalytic effect were established	328
			Hydrazine oxidation		
PANI	Pt	1–2	–	CV method; hydrazine oxidation was studied as a function of the method of composite synthesis	185
PEDOT	Pd	6–30	1.4–7.07	Methods of CV and steady-state polarization curves on RDE; electroless deposition of metal; the catalytic effect was mainly due to the increase in the surface area of metal particles in the composite	171
PANI	Pd	–	–	Methods of CV and amperometry; layer-by-layer deposition	329
PANI	Pd	2–22	–	Methods of CV and electrochemical impedance spectroscopy; layer-by-layer deposition	330
			Formic acid oxidation		
PANI	Pt	–	62–76	Method of steady-state polarization curves; the real surface area of platinum particles was estimated	334
Polycarbazole	Pt, Pt–Ru	–	0.30	CV method; the formic acid oxidation current was studied as a function of the mass of incorporated platinum	332
PANI	Pd	–	–	Method of steady-state polarization curves; the effect of synthetic conditions and the PANI amount in the composite on the formic acid oxidation was studied	127
PPY, PANI, polycarbazole, polyindole	Pt	–	–	CV methods; the effect of the nature of polymer support (polyaniline, polypyrrole, polycarbazole, polyindole) on the formic acid oxidation on Pt particles was studied	333
Poly(*o*-toluidine)	Pt	–	4.2–46	CV method; electrodeposition of palladium nanoparticles by various deposition modes	331
PT	Pt, Pt–Pd	–	–	CV method; metal NP in the polythiophene film were electrodeposited on the ITO [d] substrate	200
PANI	Pd	–	–	CV method (repeated cycling, 1st and 200th cycles); the catalytic properties were found to be more stable for palladium NP incorporated in the polymer	323
			Hydrogen oxidation		
PANI	Pt	–	5–300	Method of steady-state polarization curves on RDE; the exchange current was observed to increase with increasing platinum loading in the range of 5–150 μg cm^{-2}; for high loadings, the exchange current remained unchanged	30
PPY	Pt	44000	16–36	Method of steady-state polarization curves; the limiting current of hydrogen oxidation increased with increasing platinum loading (up to 50 μg cm^{-2})	335

[a] Single-walled carbon nanotubes. [b] Electroreduced graphene oxide. [c] Carbon nanotubes. [d] Indium tin oxide.

charge density consumed for oxygen desorption from palladium particles and the corresponding value for the polycrystalline palladium electrode. Table 4 shows the experimental surface areas of palladium particles (S_{Pd}) incorporated into the PEDOT film during different loading times.

The impedace spectra of PEDOT/Pd films in 0.1 M H_2SO_4 in the potential regions of electrochemical sorption/desorption of hydrogen on the surface of incorporated palladium particles demonstrated clear-cut semicircles with the diameter (determining the resistance to charge transfer and inversely proportional to the surface area of these particles) decreasing with the increase in the palladium amount in the film. Apparently, the latter is associated with the increase in the surface area of palladium particles accessible to hydrogen sorption/desorption under the mentioned conditions. Under the assumption that the specific resistance to charge transfer is the same for smooth palladium and palladium particles embedded into a film, the real surface area of palladium particles within the composite

Table 4. Experimental values of the surface area of palladium metal incorporated into a PEDOT film at different times of deposition.

Pd deposition time /s	$Q_{Pd} \times 10^{-5}$ /C	S_{Pd} /cm^2
400	13.95	0.332
240	7.575	0.180
120	5.467	0.130
60	4.116	0.098
30	2.176	0.052

film has been found.[170] For the palladium loading used, based on the real surface area of Pd particles, their specific surface area was determined to be 36 m^2 g^{-1}, whereas the average size of palladium particles calculated in terms of the model of spheres was found to be close to 14 nm. Note that a similar size of palladium NP (10–20 nm) was also found under the same conditions by the SEM method.[172]

Actually, the data in Table 3 show that the authors of the majority of studies consider the electrocatalytic activity of such composites only based on the gain in the rate of some process taking place in these objects compared with the rate (current) observed on the electrode chosen for comparison (polymer film, electrode substrate, *etc.*), *i.e.*, in fact, the possible changes in the real surface area of the catalytic metal on going from test system to reference system are virtually ignored. The most reliably established and important benefits observed upon dispersing the catalytic metal throughout the polymer matrix include the increase in both the active surface area of the catalytic metal and the stability of its particles in the nanosized state, providing the long-term stability of electrode characteristics. These conclusions were drawn in the majority of studies with different degrees of reliability. However, more profound generalization of results of various studies, even those obtained for similar systems, is often complicated by different conditions of synthesis of conducting polymer–metal composites, dissimilar characteristics of metal inclusions and ambiguities in electrochemical response acquisition.

Below, we consider in more detail some of the important conclusions made in the studies presented in Table 3.

Oxidation of alcohols.[81, 94, 108, 109, 124, 127, 312–324] The PANI/Pd composite films were studied as electrode material to be used in sensors for methanol. The pronounced adsorption interaction of methanol with palladium particles was revealed and it was shown that the electric resistance of the PANI/Pd composite film is very sensitive to methanol adsorption on Pd particles.[315] However, the developed [315] impedance-metric sensor had a narrow dynamic range of determination (up to 10 ppm) because of fast saturation of methanol adsorption on palladium particles.

The catalytic activity of compact platinum and platinum dispersed in PANI was compared [81] by varying the amount of deposited Pt nanoparticles in the range of 10–30 μg cm^{-2} to catalyze methanol oxidation in sulfuric acid. The advantages of the PANI/Pt composite material over compact platinum were caused by its weaker poisoning by CO_{ads} and COH_{ads} groups formed on the platinum surface. The weaker catalyst poisoning in PANI/Pt was observed also for oxidation of other simple molecules.[87, 96, 316–319] Potentiostatic pulsed studies of methanol oxidation on the PPY/Pt electrode have also confirmed its weaker tendency to poisoning and revealed the enhanced catalytic activity of platinum within the composite compared with the compact platinum electrode.[124]

A more reliable comparison of the catalytic activity of platinum in a compact electrode and as Pt particles within PANI was carried out for the case of methanol oxidation in acidic solutions.[94, 127] The methanol oxidation currents were compared by taking into account the real surface area of the platinum catalyst. A noticeable catalytic effect in methanol oxidation was observed on PANI/Pt composite films synthesized by the electrodeposition method.[94, 127] The observed catalytic effect was shown [79] to increase with the increase in the amount of metal loaded into the polymer and depend on the distribution of Pt particles throughout the polymer. For the mass of deposited platinum of $<25–35$ μg cm^{-2}, the reaction mechanism was found to differ from mechanisms observed for both the deposited mass of $>60–750$ μg cm^{-2} and a smooth platinum electrode. For small amounts of platinum in PANI, methanol adsorption was the rate-limiting step of oxidation.

The calculated [94] specific currents of methanol electrooxidation on a composite film proved to considerably exceed the oxidation current on platinized platinum (Pt/Pt_{nano}). It was noted that this effect may be associated with the peculiar structure of the platinum deposit in thin PANI films. A similar conclusion was drawn for the case of formic acid electrooxidation on PANI/Pt films.[127] In the latter study, a noticeable increase in the catalytic activity of platinum particles as compared with Pt/Pt_{nano} was observed.

The majority of publications on the reduction of alcohols on platinum-group metals revealed a general feature, namely, the increase in the current density on polymer electrodes with the increase in the time of metal loading for small and medium times and the attainment of saturation (for platinum, usually at 150–200 μg cm^{-2}) for long-term metal loading.

In a review,[302] it was noted that among various conducting polymer–metal catalysts of alcohol oxidation, the best catalysts were nanoparticles of platinum and its bimetallic compositions, particularly, Pt–Ru. For more efficient operation of such catalysts, it is the practice to use substrates of the combined carbon and polymer materials, which are most stable against poisoning and satisfy the conditions of long-term operation.

For PANI/Pd composites synthesized by deposition of palladium from a solution containing $PdCl_4^{2-}$, the rate of methanol oxidation was found to be higher and the palladium surface poisoning was shown to be stronger as compared with a plane platinum electrode.[312]

The catalytic activity of a PPY/Pt electrode in methanol oxidation was found [320] to increase with the increase in the platinum content and reach saturation at a considerably high platinum content, namely, up to 150–180 μg cm^{-2}. As the PPY/Pt film thickness increased from 0.4 to 1.2 μg, the methanol oxidation current passed through a maximum.

A high (390 A g^{-1}) current density of ethanol electrooxidation was observed [321] on a composite material, Pt–PEDOT/ER-GO, and the high stability of platinum particles within this composite to poisoning with ethanol oxidation products was revealed. The high current densities of ethanol oxidation were associated with the higher active surface area of platinum nanoparticles (47 m^2 g^{-1}).

The activity of bimetallic nanoclusters Pt–Ru electrodeposited into a PEDOT film supported by carbon paper

was studied.[314] The average diameter of Pt–Ru nanoclusters was ~ 123 nm. In the absence of PEDOT, the size of clusters was ~ 251 nm and they were distributed less uniformly over the carbon paper. Studies by the CV method have shown that the methanol oxidation current was several times higher on the Pt–Ru/PEDOT electrode as compared with the Pt–Ru electrode in the absence of PEDOT.

Oxygen reduction.[214, 325–328] The reduction of molecular oxygen in PPY/Pt composites was found to proceed predominantly on platinum inclusions.[325] The reduction mechanism was shown[325] to depend on the method of platinum loading into the polymer. When the process occurred preferentially on the platinum deposit located on the polymers surface, selective oxygen reduction by a four-electron mechanism took place to yield water molecules. When the proportion of Pt particles located in the polymer bulk was considerable, the amount of the intermediate reduction product, hydrogen peroxide, was observed to increase. The effect of Pt particles incorporated into the polymer bulk on the catalytic characteristics of deposits was also considered in several other publications (see Refs 124, 194, 214, 320 and 328). The author of one of these studies[214] concluded that the oxygen reduction current on a 3D PPY/Pt electrode increases as compared with a 2D PPY/Pt electrode.

Hydrazine oxidation.[171, 185] The PANI/Pd nanocomposites were synthesized by loading polymer films with palladium by the method of layer-by-layer deposition *via* the adsorption of $PdCl_6^{2-}$ or $PdCl_4^{2-}$ ions followed by their electroreduction.[329] A similar method was also used in another study.[330] The size of Pd particles varied in the range from 2 to 22 nm depending on the concentration of palladium chloride used. The electrocatalytic and sensor properties of composites were studied by the CV method.[329, 330] The hydrazine reduction current increased with the increase in the number of deposited layers, which is equivalent to the increase in the number of palladium particles loaded into composite films.

Formic acid oxidation.[127, 200, 322, 331–334] The electrocatalytic activity of Pt nanoparticles and bimetallic Pt–Ru nanoparticles loaded into polycarbazole towards formic acid oxidation was studied by CV and chronoamperometry.[332] In the presence of polycarbazole, the synergistic effect was observed in the catalysis of this reaction, which was presumably due to weakening of the adsorption of intermediate products of formic acid oxidation, particularly, to poisoning of platinum by carbon monoxide. As the metal loading increased (up to 0.30 mg cm^{-2} of Pt or Pt–Ru nanoparticles), the formic acid oxidation current was observed to increase.

The currents of formic acid oxidation observed on compact platinum and platinum particles electrodeposited on poly(*o*-toluidine) were compared.[331] A considerable catalytic effect was concluded for the composite film; however, the authors did not compare the steady-state currents of this process calculated per unit real surface area of platinum catalysts.

The more reliable conclusions on the considerable catalytic effect of the PANI/Pt composite in formic acid oxidation were drawn[127] by comparing the specific currents observed on platinum particles loaded into polyaniline and platinized platinum. The catalytic efficiency towards formic acid oxidation was shown to be higher for palladium particles dispersed in the polyaniline matrix. This conclusion was made based on the comparison of steady-state oxidation currents per unit surface area of metal particles.

The electrocatalytic activity of PT/Pt and Pt–Pd films (electrochemically deposited NP) was studied in the reaction of formic acid electrooxidation.[200] The observed high activity of composites was attributed to uniformity of NP dispersion in the PT film and also to the effect of palladium in the bimetallic Pt–Pd system.

Recently, reseachers have paid increasing attention to the role of the supporting polymer used for deposition of particles of catalytically active metals and estimated the efficiency of the catalytic site comprising not only metal clusters but also surface groups and atoms of the supporting polymer, which interact with metal atoms.

An attempt to explain the effect of the nature of the polymer support was undertaken[334] in which the films of several polymers (polyaniline, polycarbazole, polyindole) of equal thickness coated with a monolayer of platinum nanoparticles pre-synthesized under the same conditions were studied. Systematic investigations of formic acid oxidation on these polymer–metal composites made it possible to conclude that polycarbazole is the most suitable support for catalysts with Pt particles. This is attributable to the particular set of chemical properties of the donor nitrogen atoms, which provide the optimal functioning of the catalytic site. The effect of the conducting polymer support on the catalytic properties of platinum particles in methanol and formic acid oxidation was also studied in another work.[322]

Hydrogen oxidation on the platinum catalyst incorporated into a conducting polymer.[30, 335] The electrooxidation of hydrogen on a catalyst in the form of platinum dispersed in the polymer matrix (polyaniline) was studied[30] for the platinum loading varying from 5 to 300 μg cm^{-2}. It was shown that as the platinum loading in the composite film increased to 150 μg cm^{-2}, the exchange current of the mentioned process increased. The further increase in the platinum loading into the film resulted in attainment of the maximum constant exchange current typical of smooth platinum electrodes. The similar effect was observed also for hydrogen electrooxidation on PPY/Pt films.[335] As the amount of platinum electrodeposited into a polypyrrole film increased to 50 μg cm^{-2}, the current density increased to reach its limiting (saturation) value typical of a compact Pt electrode.

The redox reactions of substances on composite electrodes can be complicated in the potential region in which the electronic conductivity of the polymer matrix is considerably lower, which leads to the loss of the effective conductivity of the whole composite. In such cases, the problem of unstable conductivity is solved by using the complex compositions of conducting polymer with stable electron-conducting components, for instance, carbon substances of various modifications.[302]

IV. Conclusion

The material discussed above reflects the recent advantages and unsolved problems in the field of electrochemistry of conducting polymer–metal materials. Considerable progress was observed in the development of methods for synthesizing these materials with different distribution of metal-containing nanostructures throughout the conducting polymer matrix and also of methods for studying the

morphology of materials. In the literature, considerable attention was given to analysys of how different factors affect the reactivity of composite materials, particularly, the role of the size of metal nanoparticles and the character of their distribution throughout the bulk and over the surface of polymer electrodes. However, as follows from the analysis of experimental data, the systematic investigation of these factors taking into account not only the total content of catalytic metal but also the real surface area of metal clusters accessible for the reaction and the way they are distributed in the polymer still remains a topical problem. Such studies make it possible to relate the structure chemical parameters of the complex conducting polymer–metal electrodes to their intensive parameters (rates of electrochemical reactions) and draw more reliable conclusions on the factors responsible for their catalytic effect.

Many of results explain the catalysis as merely the effect of the higher catalyst surface area in metal dispersions, whereas the studies of the real size effect (the increase in specific activity of catalytic metal particles) are few. Comparable catalytic activities of metal NP and the compact metal were noted in several studies with the exception of composites containing small platinum clusters for which the size effect was revealed. However, for metals dispersed throughout polymer matrices, the economy of noble metals as catalysts as compared with compact electrodes is noticeable.

In several recent publications on catalysis of electrooxidation of alcohols and other organic compounds, it was noted that despite the well-known higher stability of catalytic metal dispersions in polymer matrices, research into these materials is still in the very beginning. This is associated with the complexity of these systems, the wide diversity of methods and materials used for their synthesis and the small number of investigations in which these problems are considered systematically. The evident progress was achieved in the development of theoretical concepts on the charge transfer processes, which made possible the more comprehensive interpretation and verification of the parameters found.

This review was prepared with the financial support from the Russian Foundation for Basic Research (Project Nos 16-03-00457 and 14-29-04043). The authors are grateful to the Interdisciplinary Resource Centre for Nanotechnology of the Saint Petersburg State University for its help in studying nanostructural conducting polymer–metal materials.

References

1. H Shirakawa, E J Louis, A G Macdiarmid, C K Chiang, A J Heeger *J. Chem. Soc., Chem. Commun*. 578 (1977)
2. C K Chiang, C R Fincher, Y W Park, A J Heeger, H Shirakawa, E J Louis, S C Gau, A G Macdiarmid *Phys. Rev. Lett*. **39** 1098 (1977)
3. K K Kanazawa, A F Diaz, R H Geiss, W D Gill, J F Kwak, J A Logan, J F Rabolt, G B Street *J. Chem. Soc., Chem. Commun*. 854 (1979)
4. P J Nigrey, A G Macdiarmid, A J Heeger *J. Chem. Soc., Chem. Commun*. 594 (1979)
5. G Tourillon, in *Handbook of Conducting Polymers* Vol. 2 (Ed. T A Skotheim) (New York: Marcel Dekker, 1986) p. 293
6. J Heinze *Top. Curr. Chem*. **152** 1 (1990)
7. J Roncali *Chem. Rev*. **92** 711 (1992)
8. G Schopf, G Kossmehl *Polythiophenes: Electrically Conductive Polymers* (Berlin: Springer-Verlag, 1997)
9. *Handbook of Conducting Polymers* (2nd Ed.) (Eds T A Skotheim, R L Elsenbaumer, J R Reynolds) (New York: Marcel Dekker, 1997)
10. G Inzelt, M Pineri, J W Schultze, M A Vorotyntsev *Electrochim. Acta* **45** 2403 (2000)
11. P Novak, K Muller, K S V Santhanam, O Haas *Chem. Rev*. **97** 207 (1997)
12. G Inzelt, in *Electroanalytical Chemistry* Vol. 18 (Ed. A J Bard) (New York: Marcel Dekker, 1994) p. 89
13. R W Murray, in *Electroanalytical Chemistry* Vol. 13 (Ed. A J Bard) (New York: Marcel Dekker, 1984) p. 20
14. P Chandrasekhar *Conducting Polymers. Fundamental and Applications* (Boston: Kluwer Academic, 1999)
15. B L Groenendaal, F Jonas, D Freitag, H Pielartzik, J R Reynolds *Adv. Mater*. **12** 481 (2000)
16. L Groenendaal, G Zotti, P H Aubert, S M Waybright, J R Reynolds *Adv. Mater*. **15** 855 (2003)
17. V V Malev, V V Kondratiev *Russ. Chem. Rev*. **75** 147 (2006)
18. G Inzelt *Conducting Polymers: a New Era in Electrochemistry* (Berlin: Springer, 2008)
19. B I Podlovchenko, V N Andreev *Russ. Chem. Rev*. **71** 837 (2002)
20. G Inzelt *J. Solid State Electrochem*. **15** 1711 (2011)
21. *Handbook of Organic Conductive Molecules and Polymers*. (Ed. H S Nalwa) (New York: Wiley, 1997)
22. M A Vorotyntsev, S V Vasilyeva *Adv. Colloid Interface Sci*. **139** 97 (2008)
23. V Tsakova, in *Nanostructured Conductive Polymers* (Ed. A Eftekhari) (Chippenham: Wiley, 2010) p. 289
24. V Tsakova *J. Solid State Electrochem*. **12** 1421 (2008)
25. D W Hatchett, M Josowicz *Chem. Rev*. **108** 746 (2008)
26. R Gangopadhyay, A De *Chem. Mater*. **12** 2064 (2000)
27. A Malinauskas, J Malinauskiene, A Ramanavicius *Nanotechnology* **16** R51 (2005)
28. B C Sih, M O Wolf *Chem. Commun*. 3375 (2005)
29. V V Malev, V V Kondrat'ev, A M Timonov *Polimer-modifitsirovannye Elektrody* (Polymer-Modified Electrodes) (St Petersburg: Nestor-istoriya, 2012)
30. M J Croissant, T Napporn, J M Leger, C Lamy *Electrochim. Acta* **43** 2447 (1998)
31. K Jackowska, A T Biegunski, M Tagowska *J. Solid State Electrochem*. **12** 437 (2008)
32. R R Chance, D S Boudreaux, J L Bredas, R Silbey, in *Handbook of Conducting Polymers* Vol. 2 (Ed. T A Skotheim) (New York: Marcel Dekker, 1986) p. 825
33. J L Bredas, G B Street *Acc. Chem. Res*. **18** 309 (1985)
34. S Roth *One-Dimensional Metals* (Weinheim: VCH, 1995)
35. K Mizoguchi, in *Handbook of Organic Conducting Molecules and Polymers* Vol. 3 (Ed. H S Nalwa) (New York: Wiley, 1997) p. 251
36. M Nechtschein, F Devreux, F Genoud, E Vieil, J M Pernaut, E Genies *Synth. Met*. **15** 59 (1986)
37. V E Kazarinov, M D Levi, A M Skundin, M A Vorotyntsev *J. Electroanal. Chem*. **271** 193 (1989)
38. M D Levi, M A Vorotyntsev, A M Skundin, V E Kazarinov *J. Electroanal. Chem*. **319** 243 (1991)
39. M A Vorotyntsev, L I Daikhin, M D Levi *J. Electroanal. Chem*. **332** 213 (1992)
40. M D Levi, N M Alpatova, E V Ovsyannikova, M A Vorotyntsev *J. Electroanal. Chem*. **351** 271 (1993)
41. M A Vorotyntsev *Synth. Met*. **57** 4556 (1993)

42. M A Vorotyntsev, E Vieil, J Heinze *Russ. J. Electrochem.* **31** 1027 (1995) [*Elektrokhimiya* **31** 1112 (1995)]
43. M A Vorotyntsev, A A Rubashkin, J P Badiali *Electrochim. Acta* **41** 2313 (1996)
44. V V Malev, A A Rubashkin, M A Vorotyntsev *Russ. J. Electrochem.* **33** 872 (1997) [*Elektrokhimiya* **33** 945 (1997)]
45. M A Vorotyntsev, J Heinze *Electrochim. Acta* **46** 3309 (2001)
46. V V Malev, O V Levin, M A Vorotyntsev *Electrochim. Acta* **52** 133 (2006)
47. V V Malev, O V Levin, M A Vorotyntsev *Russ. J. Electrochem.* **43** 1016 (2007) [*Elektrokhimiya* **43** 1070 (2007)]
48. J Wang *Analyst* **130** 421 (2005)
49. G Tourillon, F Garnier *J. Phys. Chem.* **88** 5281 (1984)
50. G K Chandler, D Pletcher *J. Appl. Electrochem.* **16** 62 (1986)
51. J M Kinyanjui, D W Hatchett, J A Smith, M Josowicz *Chem. Mater.* **16** 3390 (2004)
52. A Saheb, J A Smith, M Josowicz, J Janata, D R Baer, M H Engelhard *J. Electroanal. Chem.* **621** 238 (2008)
53. W Yan, X M Feng, X J Chen, W H Hou, J J Zhu *Biosens. Bioelectron.* **23** 925 (2008)
54. Y Leroux, E Eang, C Fave, G Trippe, J C Lacroix *Electrochem. Commun.* **9** 1258 (2007)
55. P Santhosh, A Gopalan, K P Lee *J. Catal.* **238** 177 (2006)
56. S J Tian, J Y Liu, T Zhu, W Knoll *Chem. Mater.* **16** 4103 (2004)
57. P R Sajanlal, T S Sreeprasad, A S Nair, T Pradeep *Langmuir* **24** 4607 (2008)
58. S S Kumar, J Mathiyarasu, K L Phani *J. Electroanal. Chem.* **578** 95 (2005)
59. J Mathiyarasu, S Senthilkumar, K L N Phani, V Yegnaraman *Mater. Lett.* **62** 571 (2008)
60. K M Manesh, P Santhosh, A Gopalan, K P Lee *Talanta* **75** 1307 (2008)
61. J Li, X Q Lin *Sens. Actuators, B* **124** 486 (2007)
62. J Li, X Q Lin *Anal. Chim. Acta* **596** 222 (2007)
63. X Huang, Y X Li, P Wang, L Wang *Anal. Sci.* **24** 1563 (2008)
64. J M Kinyanjui, J Hanks, D W Hatchett, A Smith, M Josowicz *J. Electrochem. Soc.* **151** D113 (2004)
65. A V Smolin, Y M Maksimov, B I Podlovchenko *Russ. J. Electrochem.* **31** 520 (1995) [*Elektrokhimiya* **31** 571 (1995)]
66. Y M Maksimov, E A Kolyadko, A V Shishlova, B I Podlovchenko *Russ. J. Electrochem.* **37** 777 (2001) [*Elektrokhimiya* **37** 907 (2001)]
67. Y M Maksimov, B I Podlovchenko, T D Gladysheva, E A Kolyadko *Russ. J. Electrochem.* **35** 1225 (1999) [*Elektrokhimiya* **35** 1388 (1999)]
68. V Tsakova, S Winkels, J W Schultze *J. Electroanal. Chem.* **500** 574 (2001)
69. M Ilieva, V Tsakova, W Erfurth *Electrochim. Acta* **52** 816 (2006)
70. A Mourato, J P Correia, H Siegenthaler, L M Abrantes *Electrochim. Acta* **53** 664 (2007)
71. K M Kost, D E Bartak, B Kazee, T Kuwana *Anal. Chem.* **62** 151 (1990)
72. J Wang, T Golden, Y H Lin, L Angnes *J. Electroanal. Chem.* **333** 65 (1992)
73. A Yassar, J Roncali, F Garnier *J. Electroanal. Chem.* **255** 53 (1988)
74. A Yassar, J Roncali, F Garnier *J. Chim. Phys. Phys. Chim. Biol.* **86** 241 (1989)
75. A Leone, W Marino, B R Scharifker *J. Electrochem. Soc.* **139** 438 (1992)
76. H S Li, M Josowicz, D R Baer, M H Engelhard, J Janata *J. Electrochem. Soc.* **142** 798 (1995)
77. A Frydrychewicz, S Y Vassiliev, G A Tsirlina, K Jackowska *Electrochim. Acta* **50** 1885 (2005)
78. B I Podlovchenko, Y M Maksimov, T L Azarchenko, A M Gaskov *Russ. J. Electrochem.* **30** 720 (1994) [*Elektrokhimiya* **30** 794 (1994)]
79. Y M Maksimov, O V Afanaseva, B I Podlovchenko *Russ. J. Electrochem.* **31** 133 (1995) [*Elektrokhimiya* **31** 149 (1995)]
80. Y M Maksimov, B I Podlovchenko, T L Azarchenko *Electrochim. Acta* **43** 1053 (1998)
81. K M Kost, D E Bartak, B Kazee, T Kuwana *Anal. Chem.* **60** 2379 (1988)
82. K M Kost, B Kazee, D E Bartak *Abstr. Pap. Am. Chem. Soc.* **195** 89 (1988)
83. J Langmaier, J Janata *Anal. Chem.* **64** 523 (1992)
84. D J Strike, N F Derooij, M Koudelkahep, M Ulmann, J Augustynski *J. Appl. Electrochem.* **22** 922 (1992)
85. N Georgolios, P Karabinas *J. Electroanal. Chem.* **280** 403 (1990)
86. H Laborde, J M Leger, C Lamy, F Garnier, A Yassar *J. Appl. Electrochem.* **20** 524 (1990)
87. H Laborde, J M Leger, C Lamy *J. Appl. Electrochem.* **24** 219 (1994)
88. M Gholamian, A Q Contractor *J. Electroanal. Chem.* **289** 69 (1990)
89. S Swathirajan,Y M Mikhail *J. Electrochem. Soc.* **139** 5 (1992)
90. W T Napporn, H Laborde, J M Leger, C Lamy *J. Electroanal. Chem.* **404** 153 (1996)
91. F Ficicioglu, F Kadirgan *J. Electroanal. Chem.* **430** 179 (1997)
92. W T Napporn, J M Leger, C Lamy *J. Electroanal. Chem.* **408** 141 (1996)
93. I Becerik, F Kadirgan *J. Electroanal. Chem.* **436** 189 (1997)
94. A A Mikhaylova, E B Molodkina, O A Khazova, V S Bagotzky *J. Electroanal. Chem.* **509** 119 (2001)
95. K Bouzek, K M Mangold, K Juttner *Electrochim. Acta* **46** 661 (2000)
96. P O Esteban, J M Leger, C Lamy, E Genies *J. Appl. Electrochem.* **19** 462 (1989)
97. R Kostecki, M Ulmann, J Augustynski, D J Strike, M Koudelkahep *J. Phys. Chem.* **97** 8113 (1993)
98. C T Hable, M S Wrighton *Langmuir* **9** 3284 (1993)
99. M Grzeszczuk *Electrochim. Acta* **39** 1809 (1994)
100. E K W Lai, P D Beattie, S Holdcroft *Synth. Met.* **84** 87 (1997)
101. C H Yang, T C Wen *Electrochim. Acta* **44** 207 (1998)
102. A Kelaidopoulou, E Abelidou, A Papoutsis, E K Polychroniadis, G Kokkinidis *J. Appl. Electrochem.* **28** 1101 (1998)
103. A Lima, C Coutanceau, J M Leger, C Lamy *J. Appl. Electrochem.* **31** 379 (2001)
104. A Lima, F Hahn, J M Leger *Russ. J. Electrochem.* **40** 326 (2004) [*Elektrokhimiya* **40** 369 (2004)]
105. C C Hu, E Chen, J Y Lin *Electrochim. Acta* **47** 2741 (2002)
106. T Kessler, A M C Luna *J. Appl. Electrochem.* **32** 825 (2002)
107. E C Venancio, W T Napporn, A J Motheo *Electrochim. Acta* **47** 1495 (2002)
108. L Niu, Q Li, F Wei, S Wu, P Liu, X Cao *J. Electroanal. Chem.* **578** 331 (2005)
109. H H Zhou, S Q Jiao, J H Chen, W Z Wei, Y F Kuang *J. Appl. Electrochem.* **34** 455 (2004)
110. L H Mascaro, D Goncalves, L O S Bulhoes *Thin Solid Films* **461** 243 (2004)
111. J M Kinyanjui, N R Wijeratne, J Hanks, D W Hatchett *Electrochim. Acta* **51** 2825 (2006)
112. S Ivanov, V Tsakova *Electrochim. Acta* **50** 5616 (2005)

113. N Hernandez, J M Ortega, M Choy, R Ortiz *J. Electroanal. Chem.* **515** 123 (2001)
114. J Y Lee, T C Tan *J. Electrochem. Soc.* **137** 1402 (1990)
115. R Schrebler, M A Delvalle, H Gomez, C Veas, R Cordova *J. Electroanal. Chem.* **380** 219 (1995)
116. F J Liu, L M Huang, T C Wen, C F Li, S L Huang, A Gopalan *Synth. Met.* **158** 603 (2008)
117. S N Eliseeva, E G Tolstopyatova, T A Babkova, V V Kondratiev *Russ. J. Gen. Chem.* **84** 1793 (2014) [*Zh. Obshch. Khim.* **84** 1557 (2014)]
118. V Tsakova, D Borissov, S Ivanov *Electrochem. Commun.* **3** 312 (2001)
119. V Tsakova, D Borissov, B Ranguelov, C Stromberg, J W Schultze *Electrochim. Acta* **46** 4213 (2001)
120. M D Levi, M A Vorotyntsev, V E Kazarinov, A N Frumkin *Synth. Met.* **43** 2923 (1991)
121. E Barendrecht *J. Appl. Electrochem.* **20** 175 (1990)
122. V D Jovic, T Trisovic, B M Jovic, M Vojnovic *J. Electroanal. Chem.* **408** 149 (1996)
123. M A Vorotyntsev, M Skompska, A Rajchowska, J Borysiuk, M Donten *J. Electroanal. Chem.* **662** 105 (2011)
124. M Hepel *J. Electrochem. Soc.* **145** 124 (1998)
125. M Trueba, S P Trasatti, S Trasatti *Mater. Chem. Phys.* **98** 165 (2006)
126. A Zouaoui, O Stephan, M Carrier, J C Moutet *J. Electroanal. Chem.* **474** 113 (1999)
127. B I Podlovchenko, Y M Maksimov, T D Gladysheva, E A Kolyadko *Russ. J. Electrochem.* **36** 731 (2000) [*Elektrokhimiya* **36** 825 (2000)]
128. V Tsakova, A Milchev *Electrochim. Acta* **36** 1151 (1991)
129. S Ivanov, V Tsakova *Electrochim. Acta* **49** 913 (2004)
130. S N Eliseeva, E V Ubyivovk, A S Bondarenko, O F Vyvenko, V V Kondratiev *Russ. J. Gen. Chem.* **80** 1143 (2010) [*Zh. Obshch. Khim.* **80** 973 (2010)]
131. M Sheffer, D Mandler *Electrochim. Acta* **54** 2951 (2009)
132. E Malel, J Colleran, D Mandler *Electrochim. Acta* **56** 6954 (2011)
133. T Danieli, J Colleran, D Mandler *Phys. Chem. Chem. Phys.* **13** 20345 (2011)
134. A P Jonke, J L Steeb, M Josowicz, J Janata *Catal. Lett.* **143** 531 (2013)
135. A P Jonke, M Josowicz, J Janata *Catal. Lett.* **143** 1261 (2013)
136. I T Schwartz, A P Jonke, M Josowicz, J Janata *Catal. Lett.* **143** 636 (2013)
137. F J Liu, L M Huang, T C Wen, A Gopalan, J S Hung *Mater. Lett.* **61** 4400 (2007)
138. H Yoon *Nanomaterials* **3** 524 (2013)
139. H Masuda, M Satoh *Jpn. J. Appl. Phys., Part 2* **35** L126 (1996)
140. L Kong, X Lu, E Jin, S Jiang, C Wang, W Zhang *Compos. Sci. Technol.* **69** 561 (2009)
141. K S Napolskii, I V Roslyakov, A A Eliseev, D I Petukhov, A V Lukashin, S F Chen, C P Liu, G A Tsirlina *Electrochim. Acta* **56** 2378 (2011)
142. Y Li, Y Wu, Q Xu, Y Gao, G Cao, Z Meng, C Yang *Polym. Chem.* **4** 4655 (2013)
143. C W Wang, Z Wang, M K Li, H L Li *Chem. Phys. Lett.* **341** 431 (2001)
144. M Delvaux, J Duchet, P Y Stavaux, R Legras, S Demoustier-Champagne *Synth. Met.* **113** 275 (2000)
145. K Huang, Y J Zhang, Y Z Long, J H Yuan, D X Han, Z J Wang, L Niu, Z Chen *Chem. – Eur. J.* **12** 5314 (2006)
146. M Lahav, E A Weiss, Q B Xu, G M Whitesides *Nano Lett.* **6** 2166 (2006)
147. M A Bangar, C M Hangarter, B Yoo, Y Rheem, W Chen, A Mulchandani, N V Myung *Electroanalysis* **21** 61 (2009)
148. Q T Vu, M Pavlik, N Hebestreit, J Pfleger, U Rammelt, W Plieth *Electrochim. Acta* **51** 1117 (2005)
149. E T Kang, Y P Ting, K G Neoh, K L Tan *Polymer* **34** 4994 (1993)
150. E T Kang, Y P Ting, K G Neoh, K L Tan *Synth. Met.* **69** 477 (1995)
151. M Hasik, E Wenda, C Paluszkiewicz, A Bernasik, J Camra *Synth. Met.* **143** 341 (2004)
152. A Drelinkiewicz, M Hasik, J W Sobczak, E Sobczak, A Bemasik, E Bielanska *Mater. Res. Bull.* **40** 869 (2005)
153. M Ocypa, M Ptasinska, A Michalska, K Maksymiuk, E A H Hall *J. Electroanal. Chem.* **596** 157 (2006)
154. Y P Ting, K G Neoh, E T Kang, K L Tan *J. Chem. Technol. Biotechnol.* **59** 31 (1994)
155. J G Wang, K G Neoh, E T Kang *J. Colloid Interface Sci.* **239** 78 (2001)
156. J A Smith, M Josowicz, J Janata *J. Electrochem. Soc.* **150** E384 (2003)
157. S J Tian, J Y Liu, T Zhu, W Knoll *Chem. Commun.* 2738 (2003)
158. X Q Zou, H F Bao, H W Guo, L Zhang, Q Li, J G Jiang, L Niu, S J Dong *J. Colloid Interface Sci.* **295** 401 (2006)
159. U Lange, S Ivanov, V Lyutov, V Tsakova, V M Mirsky *J. Solid State Electrochem.* **14** 1261 (2010)
160. A Mourato, S M Wong, H Siegenthaler, L M Abrantes *J. Solid State Electrochem.* **10** 140 (2006)
161. L M Abrantes, J P Correia *Mater. Sci. Forum* **191** 235 (1995)
162. M Hasik, A Drelinkiewicz, M Choczynski, S Quillard, A Pron *Synth. Met.* **84** 93 (1997)
163. A Drelinkiewicz, M Hasik, M Choczynski *Mater. Res. Bull.* **33** 739 (1998)
164. M Josowicz, H S Li, K Domansky, D R Baer *Electroanalysis* **11** 774 (1999)
165. A Drelinkiewicz, M Hasik, M Kloc *Synth. Met.* **102** 1307 (1999)
166. Z H Ma, K L Tan, E T Kang *Synth. Met.* **114** 17 (2000)
167. V W L Lim, E T Kang, K G Neoh *Synth. Met.* **123** 107 (2001)
168. M Hasik, A Drelinkiewicz, E Wenda *Synth. Met.* **119** 335 (2001)
169. A Mourato, A S Viana, J P Correia, H Siegenthaler, L M Abrantes *Electrochim. Acta* **49** 2249 (2004)
170. S N Eliseeva, V V Malev, V V Kondrat'ev *Russ. J. Electrochem.* **45** 1045 (2009) [*Elektrokhimiya* **45** 1122 (2009)]
171. V V Kondratiev, T A Babkova, E G Tolstopjatova *J. Solid State Electrochem.* **17** 1621 (2013)
172. V V Kondratiev, T A Babkova, S N Eliseeva *Russ. J. Electrochem.* **48** 205 (2012) [*Elektrokhimiya* **48** 226 (2012)]
173. M Hasik, A Bernasik, A Adamczyk, G Malata, K Kowalski, J Camra *Eur. Polym. J.* **39** 1669 (2003)
174. A Q Zhang, C Q Cui, J Y Lee, F C Loh *J. Electrochem. Soc.* **142** 1097 (1995)
175. M Y Lebedev, M V Lauritzen, A E Curzon, S Holdcroft *Chem. Mater.* **10** 156 (1998)
176. F Y Song, K K Shiu *J. Electroanal. Chem.* **498** 161 (2001)
177. C Visy, E Pinter, T Fulei, R Patakfalvi *Synth. Met.* **152** 13 (2005)
178. E Pinter, R Patakfalvi, T Fulei, Z Gingl, I Dekany, C Visy *J. Phys. Chem. B* **109** 17474 (2005)
179. V M Jovanovic, S Terzic, A Dekanski *J. Serb. Chem. Soc.* **70** 41 (2005)

180. R Dimeska, P S Murray, S F Ralph, G G Wallace *Polymer* **47** 4520 (2006)
181. E Pinter, Z A Fekete, O Berkesi, P Makra, A Patzko, C Visy *J. Phys. Chem. C* **111** 11872 (2007)
182. J Stejskal, J Prokes, I Sapurina *Mater. Lett.* **63** 709 (2009)
183. E G Tolstopyatova, N A Pogulyaichenko, V V Kondratiev *Russ. J. Electrochem.* **50** 510 (2014) [*Elektrokhimiya* **50** 570 (2014)]
184. A P O'mullane, S E Dale, J V Macpherson, P R Unwin *Chem. Commun.* 1606 (2004)
185. A P O'mullane, S E Dale, T M Day, N R Wilson, J V Macpherson, P R Unwin *J. Solid State Electrochem.* **10** 792 (2006)
186. A N Grace, K Pandian *Electrochem. Commun.* **8** 1340 (2006)
187. N A Pogulyaichenko, S Hui, V V Malev, V V Kondratiev *Russ. J. Electrochem.* **45** 1176 (2009) [*Elektrokhimiya* **45** 1267 (2009)]
188. V V Kondratiev, N A Pogulaichenko, S Hui, E G Tolstopjatova, V V Malev *J. Solid State Electrochem.* **16** 1291 (2012)
189. X Huang, Y X Li, Y L Chen, L Wang *Sens. Actuators, B* **134** 780 (2008)
190. Y Ding, F R Fan, Z Q Tian, Z L Wang *J. Am. Chem. Soc.* **132** 12480 (2010)
191. F Gao, D W Goodman *Chem. Soc. Rev.* **41** 8009 (2012)
192. C Coutanceau, S Brimaud, C Lamy, J M Leger, L Dubau, S Rousseau, F Vigier *Electrochim. Acta* **53** 6865 (2008)
193. I Sapurina, J Stejskal *Chem. Pap.* **63** 579 (2009)
194. C C Chen, C S C Bose, K Rajeshwar *J. Electroanal. Chem.* **350** 161 (1993)
195. N Cioffi, L Torsi, L Sabbatini, P G Zambonin, T Bleve-Zacheo *J. Electroanal. Chem.* **488** 42 (2000)
196. K Juttner, K M Mangold, M Lange, K Bouzek *Russ. J. Electrochem.* **40** 317 (2004) [*Elektrokhimiya* **40** 359 (2004)]
197. S Marx, A Baiker *J. Phys. Chem. C* **113** 6191 (2009)
198. V Selvaraj, M Alagar, I Hamerton *J. Power Sources* **160** 940 (2006)
199. W Chen, C M Li, P Chen, C Q Sun *Electrochim. Acta* **52** 2845 (2007)
200. V Selvaraj, M Alagar, I Hamerton *Appl. Catal. B* **73** 172 (2007)
201. M Goral-Kurbiel, A Drelinkiewicz, R Kosydar, B Dembinska, P J Kulesza, J Gurgul *Electrocatalysis* **5** 23 (2014)
202. F Terzi, C Zanardi, V Martina, L Pigani, R Seeber *J. Electroanal. Chem.* **619** 75 (2008)
203. C Zanardi, F Terzi, L Pigani, A Heras, A Colina, J Lopez-Palacios, R Seeber *Electrochim. Acta* **53** 3916 (2008)
204. P J Kulesza, K Karnicka, K Miecznikowski, M Chojak, A Kolary, P J Barczuk, G Tsirlina, W Czerwinski *Electrochim. Acta* **50** 5155 (2005)
205. T K Sarma, D Chowdhury, A Paul, A Chattopadhyay *Chem. Commun.* 1048 (2002)
206. S Sharma, C Nirkhe, S Pethkar, A A Athawale *Sens. Actuators, B* **85** 131 (2002)
207. A A Athawale, S V Bhagwat *J. Appl. Polym. Sci.* **89** 2412 (2003)
208. S K Pillalamarri, F D Blum, M F Bertino *Chem. Commun.* 4584 (2005)
209. A A Athawale, S V Bhagwat, P P Katre, A J Chandwadkar, P Karandikar *Mater. Lett.* **57** 3889 (2003)
210. A A Athawale, P P Katre *J. Metastable Nanocryst. Mater.* **23** 323 (2005)
211. P P Katre, A A Athawale *Synth. React. Inorg. Met.-Org. Chem.* **37** 363 (2007)
212. Y O Kang, S H Choi, A Gopalan, K P Lee, H D Kang, Y S Song *J. Non-Cryst. Solids* **352** 463 (2006)
213. K R Reddy, K P Lee, Y Lee, A I Gopalan *Mater. Lett.* **62** 1815 (2008)
214. C S C Bose, K Rajeshwar *J. Electroanal. Chem.* **333** 235 (1992)
215. M C Daniel, D Astruc *Chem. Rev.* **104** 293 (2004)
216. E Katz, I Willner *Angew. Chem., Int. Ed.* **43** 6042 (2004)
217. N L Rosi, C A Mirkin *Chem. Rev.* **105** 1547 (2005)
218. C J Murphy *Science* **298** 2139 (2002)
219. M E Stewart, C R Anderton, L B Thompson, J Maria, S K Gray, J A Rogers, R G Nuzzo *Chem. Rev.* **108** 494 (2008)
220. R Levy, N T K Thanh, R C Doty, I Hussain, R J Nichols, D J Schiffrin, M Brust, D G Fernig *J. Am. Chem. Soc.* **126** 10076 (2004)
221. Z Wang, R Levy, D G Fernig, M Brust *Bioconjug. Chem.* **16** 497 (2005)
222. H O Finklea, in *Electroanalytical Chemistry: a Series of Advances* Vol. 19 (Eds A J Bard, I Rubinstein) (New York: Marcel Dekker, 1996) p. 109
223. H Shen, J E Mark, C J Seliskar, H B Mark, W R Heineman *J. Solid State Electrochem.* **1** 148 (1997)
224. R P Janek, W R Fawcett, A Ulman *Langmuir* **14** 3011 (1998)
225. T Yonezawa, K Yasui, N Kimizuka *Langmuir* **17** 271 (2001)
226. J Turkevich, P C Stevenson, J Hillier *Discuss. Faraday Soc.* **11** 55 (1951)
227. M Brust, M Walker, D Bethell, D J Schiffrin, R Whyman *J. Chem. Soc., Chem. Commun.* 801 (1994)
228. M Brust, J Fink, D Bethell, D J Schiffrin, C Kiely *J. Chem. Soc., Chem. Commun.* 1655 (1995)
229. M Brust, C J Kiely *Colloid Surf. A* **202** 175 (2002)
230. R W Murray *Chem. Rev.* **108** 2688 (2008)
231. I Hussain, S Graham, Z X Wang, B Tan, D C Sherrington, S P Rannard, A I Cooper, M Brust *J. Am. Chem. Soc.* **127** 16398 (2005)
232. Z X Wang, B E Tan, I Hussain, N Schaeffer, M F Wyatt, M Brust, A I Cooper *Langmuir* **23** 885 (2007)
233. B R Panda, A Chattopadhyay *J. Colloid Interface Sci.* **316** 962 (2007)
234. S S Kumar, C S Kumar, J Mathiyarasu, K L Phani *Langmuir* **23** 3401 (2007)
235. S Harish, J Mathiyarasu, K L N Phani *Mater. Res. Bull.* **44** 1828 (2009)
236. G W Lu, C Li, J Y Shen, Z J Chen, G Q Shi *J. Phys. Chem. C* **111** 5926 (2007)
237. B Y Kim, M S Cho, Y S Kim, Y Son, Y Lee *Synth. Met.* **153** 149 (2005)
238. J H Youk, J Locklin, C J Xia, M K Park, R Advincula *Langmuir* **17** 4681 (2001)
239. Z X Wang, L N Ma *Coord. Chem. Rev.* **253** 1607 (2009)
240. S V Selvaganesh, J Mathiyarasu, K L N Phani, V Yegnaraman *Nanoscale Res. Lett.* **2** 546 (2007)
241. X H Li, Y C Li, Y W Tan, C H Yang, Y F Li *J. Phys. Chem. B* **108** 5192 (2004)
242. C J Curtis, T Kaydanova, M van Hest, A Miedaner, E Garnett, D S Ginley, L Smith, A Leenheer, R T Collins, in *Digital Fabrication: Final Program and Proceedings of the Conference Held, Baltimore, MD, 2005* p. 160
243. N Lenhart, K Crowley, A J Killard, M R Smyth, A Morrin *Thin Solid Films* **519** 4351 (2011)

244. O Ngamna, A Morrin, A J Killard, S E Moulton, M R Smyth, G G Wallace *Langmuir* **23** 8569 (2007)
245. A Morrin, O Ngamna, E O'malley, N Kent, S E Moulton, G G Wallace, M R Smyth, A J Killard *Electrochim. Acta* **53** 5092 (2008)
246. N Cioffi, L Torsi, I Losito, L Sabbatini, P G Zambonin, T Bleve-Zacheo *Electrochim. Acta* **46** 4205 (2001)
247. A Alqudami, S Annapoorni, P Sen, R S Rawat *Synth. Met.* **157** 53 (2007)
248. F N Crespilho, R M Iost, S A Travain, O N Oliveira, V Zucolotto *Biosens. Bioelectron.* **24** 3073 (2009)
249. Y Y Yao, Y P Wen, J K Xu, L Zhang, X M Duan *J. Serb. Chem. Soc.* **78** 1397 (2013)
250. J E Park, S G Park, A Koukitu, O Hatozaki, N Oyama *Synth. Met.* **140** 121 (2004)
251. J E Park, S G Park, A Koukitu, O Hatozaki, N Oyama *Synth. Met.* **141** 265 (2004)
252. M A G Namboothiry, T Zimmerman, F M Coldren, J W Liu, K Kim, D L Carroll *Synth. Met.* **157** 580 (2007)
253. P Englebienne, A Van Hoonacker *J. Colloid Interface Sci.* **292** 445 (2005)
254. L Li, G P Yan, J Y Wu, X H Yu, Q Z Guo *J. Colloid Interface Sci.* **326** 72 (2008)
255. S T Selvan, J P Spatz, H A Klok, M Moller *Adv. Mater.* **10** 132 (1998)
256. S T Selvan, M Nogami *J. Mater. Sci. Lett.* **17** 1385 (1998)
257. S T Selvan, T Hayakawa, M Nogami, M Moller *J. Phys. Chem. B* **103** 7441 (1999)
258. X H Dai, Y W Tan, J Xu *Langmuir* **18** 9010 (2002)
259. M C Henry, C C Hsueh, B P Timko, M S Freund *J. Electrochem. Soc.* **148** D155 (2001)
260. Y W Tan, Y F Li, D B Zhu *Synth. Met.* **135** 847 (2003)
261. M S Cho, S Y Kim, J D Nam, Y Lee *Synth. Met.* **158** 865 (2008)
262. M Sivakumar, A Gedanken *Synth. Met.* **148** 301 (2005)
263. K Mallick, M J Witcomb, A Dinsmore, M S Scurrell *Macromol. Rapid Commun.* **26** 232 (2005)
264. K Mallick, M J Witcomb, A Dinsmore, M S Scurrell *Langmuir* **21** 7964 (2005)
265. J E Park, M Atobe, T Fuchigami *Electrochim. Acta* **51** 849 (2005)
266. S K Pillalamarri, F D Blum, A T Tokuhiro, M F Bertino *Chem. Mater.* **17** 5941 (2005)
267. P K Khanna, N Singh, S Charan, A K Viswanath *Mater. Chem. Phys.* **92** 214 (2005)
268. Y Ma, N Li, C Yang, X R Yang *Colloid Surf. A* **269** 1 (2005)
269. L M Huang, C C Tsai, T C Wen, A Gopalan *J. Polym. Sci., A* **44** 3843 (2006)
270. Y O Kang, S H Choi, A Gopalan, K P Lee, H D Kang, Y S Song *J. Appl. Polym. Sci.* **100** 1809 (2006)
271. Z Q Peng, L M Guo, Z H Zhang, B Tesche, T Wilke, D Ogermann, S H Hu, K Kleinermanns *Langmuir* **22** 10915 (2006)
272. Z Guo, Y Zhang, L Huang, M Wang, J Wang, J Sun, L Xu, N Gu *J. Colloid Interface Sci.* **309** 518 (2007)
273. Z J Wang, J H Yuan, D X Han, L Niu, A Ivaska *Nanotechnology* **18** (2007)
274. L M Huang, T C Wen *Mater. Sci. Eng. A* **445** 7 (2007)
275. L M Guo, Z Q Peng *Langmuir* **24** 8971 (2008)
276. S V Vasilyeva, M A Vorotyntsev, I Bezverkhyy, E Lesniewska, O Heintz, R Chassagnon *J. Phys. Chem. C* **112** 19878 (2008)
277. S Harish, J Mathiyarasu, K L N Phani, V Yegnaraman *Catal. Lett.* **128** 197 (2009)
278. E V Zolotukhina, M A Vorotyntsev, V A Zinovyeva, I S Bezverkhyy, D V Konev, E M Antipov, S M Aldoshin *Dokl. Phys. Chem.* **449** 63 (2013) [*Dokl. Akad. Nauk.* **449** 434 (2013)]
279. V A Zinovyeva, M A Vorotyntsev, I Bezverkhyy, D Chaumont, J C Hierso *Adv. Funct. Mater.* **21** 1064 (2011)
280. M Salsamendi, R Marcilla, M Dobbelin, D Mecerreyes, C Pozo-Gonzalo, J A Pomposo, R Pacios *Phys. Status Solidi A* **205** 1451 (2008)
281. S Komorsky-Lovric, N Vukasinovic, R Penovski *Electroanalysis* **15** 544 (2003)
282. T V Magdesieva, O M Nikitin, O A Levitsky, V A Zinovyeva, I Bezverkhyy, E V Zolotukhina, M A Vorotyntsev *J. Mol. Catal., A: Chem.* **353** 50 (2012)
283. T V Magdesieva, O M Nikitin, E V Zolotukhina, V A Zinovieva, M A Vorotyntsev *Mendeleev Commun.* **22** 305 (2012)
284. T V Magdesieva, O M Nikitin, E V Zolotukhina, M A Vorotyntsev *Electrochim. Acta* **122** 289 (2014)
285. A N Chowdhury, M S Islam, M S Azam *J. Appl. Polym. Sci.* **103** 321 (2007)
286. V V Malev, O V Levin *Electrochim. Acta* **80** 426 (2012)
287. V V Malev, O V Levin,V V Kondratiev *Electrochim. Acta* **122** 234 (2014)
288. R J Waltman, J Bargon, A F Diaz *J. Phys. Chem.* **87** 1459 (1983)
289. K Maksymiuk, K Doblhofer *Synth. Met.* **55** 1382 (1993)
290. K Maksymiuk, K Doblhofer *Electrochim. Acta* **39** 217 (1994)
291. O V Levin, V V Kondratiev, V V Malev *Russ. J. Electrochem.* **44** 98 (2008) [*Elektrokhimiya* **44** 107 (2008)]
292. D Stockert, M M Lohrengel, J W Schultze *Synth. Met.* **55** 1323 (1993)
293. E Antolini, E R Gonzalez *Appl. Catal., A* **365** 1 (2009)
294. Z Liu, L Zhang, S Poyraz, X Y Zhang *Curr. Org. Chem.* **17** 2256 (2013)
295. X Dai, G G Wildgoose, R G Compton *Analyst* **131** 1241 (2006)
296. R G Compton, G G Wildgoose, N V Rees, I Streeter, R Baron *Chem. Phys. Lett.* **459** 1 (2008)
297. S Szunerits, L Thouin, in *Handbook of Electrochemistry*. (Ed. C G Zoski) (Amsterdam: Elsevier, 2007) p. 391
298. V V Malev, O V Levin *Electrochim. Acta* **56** 3586 (2011)
299. V V Kondratiev, N A Pogulaichenko, E G Tolstopjatova, V V Malev *J. Solid State Electrochem.* **15** 2383 (2011)
300. T A Babkova, V V Kondratiev, D I Shevaldysheva *Russ. J. Electrochem.* **49** 259 (2013) [*Elektrokhimiya* **49** 288 (2013)]
301. R Zeis, T Lei, K Sieradzki, J Snyder, J Erlebacher *J. Catal.* **253** 132 (2008)
302. E Antolini *Appl. Catal., B* **100** 413 (2010)
303. K F Blurton, D R Rutt, H G Oswin, P Greenber *J. Electrochem. Soc.* **119** 559 (1972)
304. B I Podlovchenko, A G Pshenichnikov, A M Skundin *Russ. J. Electrochem.* **29** 534 (1993) [*Elektrokhimiya* **29** 366 (1993)]
305. Y M Maksimov, A S Lapa, B I Podlovchenko *Sov. Electrochem.* **25** 634 (1989) [*Elektrokhimiya* **25** 712 (1989)]
306. B I Podlovchenko, E A Kolyadko, S G Lu *J. Electroanal. Chem.* **399** 21 (1995)
307. M W Breiter *J. Electroanal. Chem.* **81** 275 (1977)
308. D E Stilwell, S M Park *J. Electrochem. Soc.* **136** 688 (1989)
309. T Kobayashi, H Yoneyama, H Tamura *J. Electroanal. Chem.* **177** 293 (1984)
310. V E Kazarinov, V N Andreev, M A Spitsyn *Electrochim. Acta* **41** 1757 (1996)
311. G Horanyi, G Inzelt *J. Electroanal. Chem.* **264** 259 (1989)

312. D W Hatchett, N M Millick, J M Kinyanjui, S Pookpanratana, M Bar, T Hofmann, A Luinetti, C Heske *Electrochim. Acta* **56** 6060 (2011)
313. C W Kuo, S J Chen, P R Chen, T Y Wu, W T Tsai, C G Tseng *J. Taiwan Inst. Chem. Eng.* **44** 497 (2013)
314. S Patra, S Dash, V Anand, C S Nimisha, G M Rao, N Munichandraiah *Mater. Sci. Eng., B* **176** 785 (2011)
315. A A Athawale, S V Bhagwat, P P Katre *Sens. Actuators B* **114** 263 (2006)
316. S J Guo, S J Dong, E K Wang *Small* **5** 1869 (2009)
317. M Zhiani, B Rezaei, J Jalili *Int. J. Hydrogen Energy* **35** 9298 (2010)
318. G Wu, L Li, J H Li, B Q Xu *J. Power Sources* **155** 118 (2006)
319. S Palmero, A Colina, E Munoz, A Heras, V Ruiz, J Lopez-Palacios *Electrochem. Commun.* **11** 122 (2009)
320. H Yang, T H Lu, K H Xue, S G Sun, G Q Lu, S P Chen *J. Electrochem. Soc.* **144** 2302 (1997)
321. F X Jiang, Z Q Yao, R R Yue, Y K Du, J K Xu, P Yang, C Y Wang *Int. J. Hydrogen Energy* **37** 14085 (2012)
322. H V Patten, E Ventosa, A Colina, V Ruiz, J Lopez-Palacios, A J Wain, S C S Lai, J V Macpherson, P R Unwin *J. Solid State Electrochem.* **15** 2331 (2011)
323. R K Pandey, V Lakshminarayanan *J. Phys. Chem. C* **113** 21596 (2009)
324. N Gavrilov, M Vujkovic, I A Pasti, G Ciric-Marjanovic, S V Mentus *Electrochim. Acta* **56** 9197 (2011)
325. F T A Vork, E Barendrecht *Electrochim. Acta* **35** 135 (1990)
326. N Gavrilov, M Dasic-Tomic, I Pasti, G Ciric-Marjanovic, S Mentus *Mater. Lett.* **65** 962 (2011)
327. V N Andreev *Russ. J. Electrochem.* **37** 605 (2001) [*Elektrokhimiya* **37** 710 (2001)]
328. M Saremi, M Salehisaki *Electroanalysis* **26** 1606 (2014)
329. S Ivanov, U Lange, V Tsakova, V M Mirsky *Sens. Actuators, B* **150** 271 (2010)
330. H L Lin, J M Yang, J Y Liu, Y F Huang, J L Xiao, X Zhang *Electrochim. Acta* **90** 382 (2013)
331. M L Banon, V Lopez, P Ocon, P Herrasti *Synth. Met.* **48** 355 (1992)
332. W Q Zhou, J K Xu, Y K Du, P Yang *Int. J. Hydrogen Energy* **36** 1903 (2011)
333. V N Andreev *Russ. J. Electrochem.* **42** 193 (2006) [*Elektrokhimiya* **42** 224 (2006)]
334. R B Moghaddam, O Y Ali, M Javashi, P L Warburton, P G Pickup *Electrochim. Acta* **162** 230 (2015)
335. F T A Vork, L J J Janssen, E Barendrecht *Electrochim. Acta* **31** 1569 (1986)