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Electrocatalysis on polymer-modified electrodes

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Abstract. The procedures for applying polymeric films onto conductive supports and doping them with active microparticles of metal-catalysts or functional redox groups are considered. General principles of the electrocatalytic action of these systems are discussed. Experimental results on the electrocatalysis on electrodes modified by polymeric films are analysed. Attention is drawn to systems involving particles of platinum-group metals incorporated into polymeric matrices. The properties of electrodes modified by ion-conducting and electron-conducting polymers are compared. Certain problems to be solved in future studies of the electrode systems under discussion are formulated. The bibliography includes 265 references.

I. Introduction

The development of new types of electrode materials pertains to important problems of electrochemistry. The electrodes the surfaces of which have been formed with involvement of polymeric films are the promising subject of studies aimed at solving this problem.† The attention of scientists to these electrode materials is determined by the fact that their adsorption, electrochemical, photoelectrochemical, corrosion and electrocatalytic properties can be changed by varying their surface composition and structure. The progress in solving this problem requires the knowledge of the structure and electrochemical properties of the support – modifying layer system and an insight into the mechanisms of the processes in this system.

Polymers used in electrochemical systems may be divided into two groups, *viz*., ion-exchange (without electron conduction) and electron-conducting polymers. The polymeric films with solely ionic conduction applied onto conductive supports should be, as a rule, functionalised by redox groups to find catalytic (electrocatalytic) applications (this is the reason for the frequently used term 'redox polymers'). The latter act as mediators, so that the polymer – support system can accelerate certain electrode processes.

The structures of electron-conducting organic polymers are characterised by the presence of conjugated bonds between electroactive groups in the chains, which is the reason for their high electron conductance in a certain potential range. The possibilities of the mediator catalysis by electron-conducting polymers can substantially be widened by additional introduction in them of functional groups through chemical bonding or Coulomb interaction between multicharge ions sorbed from a solution and charges of the polymeric matrix.

The use of polymeric films as the matrices for classical electrocatalysts, *viz*., platinum-group metals, opens up wide prospects. The development of such systems increases substantially the number of electrode processes where the use of polymers can be very effective. Particularly, this will allow the use of M – polymer – support systems (M is the metal-catalyst) in the electrooxidation of hydrogen and simple organic compounds, electroreduction of oxygen, *etc*., which attracts the keenest attention in the context of the fuel cell problem. It is those chemical reactions, which are accompanied by strong adsorption (chemisorption) of initial and/or intermediate species, that are frequently called 'electrocatalytic' in the electrochemical literature.[1,2] At the same time, in many studies, the term 'electrocatalysis' is used in a more broad sense, embracing acceleration of electrode reactions and/or enhancement of their selectivity due to the mediator catalysis.

This review surveys the current directions of research in the field of using polymers for fabricating highly active electrodes. The main advances and problems in this field of electrochemistry are considered. Despite the abundance of reviews on electrochemistry of polymers (*e.g*., see Refs 3 – 16), quite a limited number of publications generalising the results on electrocatalysis on polymer-coated electrodes are available: certain reports comprehensively discussed the problems of synthesis, structure and physicochemical and electrocatalytic properties of a single polymer or a group of polymers similar in composition (*e.g*., Refs 9, 11, 12), other reviews delving deeply into the theory of electrochemistry of polymers and the principles of their use for electrocatalysis merely listed the electrode systems and electrocatalytic processes studied (*e.g*., see Refs 6, 13, 16).

† In the scientific literature, these electrode systems are shortly called the polymer-modified electrodes, because it is by the polymeric coatings that their electrochemical behaviour is often determined virtually totally. It is not without purpose that along with the term 'polyaniline-modified electrodes', the term 'polyaniline electrode' is frequently used.

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This review cannot also pretend to comprehensively cover all the problems on the subject and give an exhaustive bibliography, otherwise this would contain over thousand references. The questions concerned with the main procedures of the preparation of electrodes with polymeric coatings, the principles of using them for the catalysis of electrochemical processes, the specific and/or general features of the behaviour of systems with ion-exchange and electron-conducting coatings, the main developments and problems in the promotion of a number of important electrode reactions are considered. Among the latter reactions, preference is given to the processes occurring in aqueous solutions and vital for the development of fuel cells and electrosynthesis. Nafion and poly(vinylpyridine) are chosen as the typical representatives of ion-exchange polymers, and polyaniline and polypyrrole represent the electron-conducting polymers. Attention is drawn to the systems with electrocatalytically active surfaces formed by incorporation of microparticles of noble metals into polymeric matrices. An attempt is undertaken to analyse the reasons for such a wide scatter and discrepancy in the experimental results on the electrocatalytic activity of these systems.

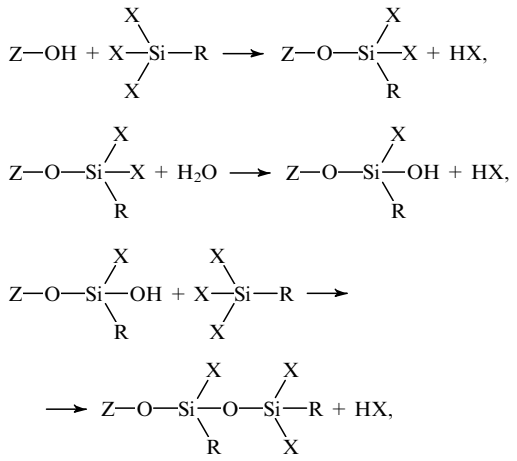
II. Modification of electrode surfaces by polymers

Of the various methods for applying polymeric coatings onto conductive supports, here we consider only those used most frequently in fundamental studies for fabricating the support–polymeric matrix systems. As a rule, films of ion-exchange polymers are 'attached' to the surface by chemical bonding or through adsorption interaction.[17–32] Both chemical and electrochemical methods are used for synthesising conducting polymeric films on the surfaces of solid supports.[3, 7, 9, 14, 33] Solubility of the polymer is the important factor determining the adhesion of the film.

1. Methods of application of modifying polymeric coatings

a. The immersion method

The immersion method is based on the exposure of an electrode (support) to a polymer solution for a certain time sufficient for the adsorption of molecules and the formation of a film on the surface.[17–21] Due to chemisorption and low solubility of coatings formed in the solutions used, the films obtained by this method well adhere to the surface. The formation of coatings can proceed as a result of chemical reactions of the polycondensation type. A typical example is the formation of polymeric layers from organosilanes X_3SiR (X = Cl, OCH_3, *etc*., R is the substituent involving a certain functional group) on oxidised surfaces.[14, 20, 21] The formation of molecular networks occurs due to a sequence of reactions presented by the following scheme:



where Z is the supporting surface.

b. 'Drop evaporation'

The method of drop evaporation was used for modifying electrodes of small areas. Dropwise application of several microlitres of a polymer solution of a given concentration followed by evaporation of the solvent allowed one to obtain films well characterised with respect to both the amount of the polymer and its composition.[22–25] The structural uniformity of the films depended to the greater extent on the evaporation procedure, namely, the latter should occur sufficiently slowly. The composition of the original film (including its functional groups) can be changed by treating it with the corresponding reagent using the same method of 'drop evaporation'. Thus the stability of a poly(ethylene imine) film in acidic solutions is increased upon treatment with a solution of dibromobutane in propan-2-ol, which resulted in cross-linking of the polymer [26–28] and a decrease in its solubility in aqueous solutions with low pH.

c. Oxidative and reductive deposition

Solubilities of certain compounds in their oxidised and reduced forms are different. This can be used for the deposition of modifying (including polymeric) films on electrodes.[29–32] For example, it was found [29, 30] that viologens with more than four carbon atoms in the alkyl substituent and certain polymeric viologens form stable films of radical cations upon their chemical or electrochemical reduction. The same principle was also applied for the deposition of poly(vinylferrocene) films.[31, 32]

The methods discussed of deposition of polymeric coatings and their versions were used for the deposition of redox polymers and, in certain cases, for modifying electrodes by electron-conducting polymers. However, the common practice for the preparation of electron-conducting polymeric films is electrochemical polymerisation.

2. Redox polymers as the mediators of redox processes

Ion-conducting polymeric films with incorporated redox groups were used as the charge carriers from the substrates in a solution to the support.[7, 10, 14, 17–20] If the substrate is oxidised or reduced faster on electrodes modified by redox polymers as compared with unmodified electrodes (support), one can speak of the catalytic effect of the film. A scheme in Fig. 1 illustrates the process of charge transfer in the reduction of species A to species B ($A + e^- \rightarrow B$) through redox centres (Red/Ox) in the polymeric film.

In the general case, the reduction rate is determined by the rates of the following processes: diffusion of species A from the solution bulk to the film surface, the reaction

$$A + Red \longrightarrow B + Ox$$

in the film surface layer, the charge transfer in the film and the reaction

$$Ox + e^- \longrightarrow Red.$$

A specific and the most important process in the systems of the type discussed above is the charge transport in the film, which is characterised by the formal diffusion coefficient D_t. Despite the absence of the self-conduction of the polymer, the charge transfer through the film is possible by either physical diffusion of Red and/or Ox in the film or the step-by-step electron exchange between neighbouring redox centres (see Fig. 1).[34–41] These processes are accompanied by the motion of polymeric chains, the solvent and counter-ions. The redox centres frequently represented polycharge ions [$Fe(CN)_6^{3-/4-}$, $Mo(CN)_8^{3-/4-}$, $IrCl_6^{2-/3-}$, *etc*.] which are strongly bound to ion-exchange polymers due to the Coulomb interaction.

Figure 2 exemplifies the voltammograms of a smooth platinum electrode and the electrode modified by a poly(ethylene

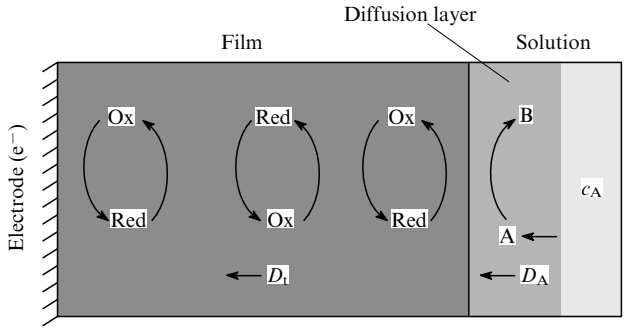


Figure 1. A scheme of reduction of a substance on the electrode modified by a redox-polymer film.
D_A is the diffusion coefficient of A particles in solution; c_A is the concentration of A in the solution bulk; D_t is the formal coefficient of charge diffusion in the polymeric film.

imine) film.‡ It is seen that before the introduction of a redox group into the ion-exchange polymer (curves *1*), the system was characterised by a very low polarisation capacity I/v (lower than that of the support, *i.e.*, smooth platinum). With the accumulation of $Fe(CN)_6^{3-/4-}$ ions in the film, the system acquires the gradually increasing redox activity due to the following reaction:

$$Fe(CN)_6^{3-} + e^- \rightleftharpoons Fe(CN)_6^{4-}.$$

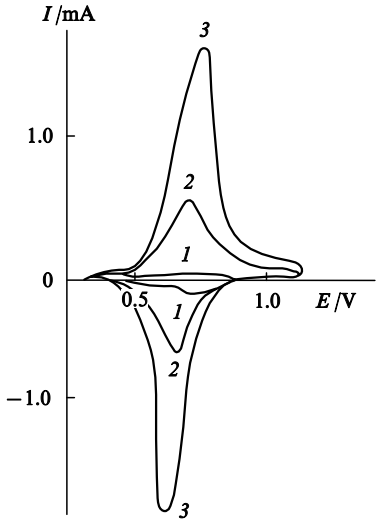


Figure 2. Cyclic voltammograms of a platinum electrode modified by a poly(ethylene imine) film.
Measured in solutions: (*1*) 0.5 M H_2SO_4; (*2*) 0.2 mM $K_3Fe(CN)_6$ + 0.5 M H_2SO_4 every 5 min (*2*) and 60 min (*3*) after the immersion of the electrode into solution. The potential scan rate $v = 50$ mV s^{-1}.

3. Electrochemical polymerisation

Synthesis of polymeric films by electrochemical polymerisation shows a number of advantages over the method of chemical polymerisation. First, the films are formed directly on the electrode surface, and the reaction product, *viz*., an electroactive film, exhibits a high conductivity. Second, the electrosynthesis provides a good current efficiency and a strict stoichiometry of the process; hence, the films of desired masses and thicknesses can be obtained. Third, the properties of the polymeric film can be controlled in the course of the synthesis. Possible electrochemical and chemical reactions occurring during the syntheses of polyaniline [3,4,42,43] and polypyrrole [11,12,43–46] were described in detail in the literature.

Electrochemical properties of the support–electron-conducting polymer system depend strongly on the conditions of the polymer synthesis. Below, we consider the effects of some of these conditions.[3–9,11,42,43,47,48]

a. The effect of the support material

In the synthesis of electron-conducting polymers, different materials were used as the supports, *viz*., platinum,[49–53] gold,[53–55] metal oxides,[49,55,56] glassy carbon,[51,52] pyrographite,[53] stainless steel[49,57] and iron[58–61] for polyaniline; noble metals,[62] conductive glass,[43,62] carbon materials,[11,63] aluminium, tantalum and copper,[62–66] steels[63–67] and semiconductors[68] for polypyrrole. From these studies, it can be concluded that the nature of the support material had virtually no effect on the synthesis and properties of conductive polymeric films with the thicknesses exceeding tens of monolayers. The exception is provided by the metals with surface oxide films.[11,45]

On the other hand, the formation of first layers initiated by the formation of radical cations[3,47] is determined largely by the nature and the structure of the support. However, in such systems the electrochemical effects caused, on the one hand, by the adsorption-induced surface modification and, on the other hand, directly by the polymeric film can hardly be separated.

The process of film formation was shown to be 'sensitive' to the solution composition (see below); hence, to obtain reproducible results, it is desirable that the synthesis (not too lengthy) is carried out in a three-electrode cell with separate anodic and cathodic compartments.

b. The effect of the polarisation mode

Films of conducting polymers used in electrocatalysis are mainly prepared by electrooxidation of monomers (the anodic synthesis). This synthesis always proceeds at a potential exceeding those of anodic doping of polymers. The anodic doping is the reversible oxidation of a polymer resulting in its transition from the state of an insulator or semiconductor into the conductive state.[3–11,13,47,69] The electroneutrality of the oxidised polymer with positive charges on certain parts of its chain is achieved by incorporation of counterions, *i.e*., anions into the polymeric matrix (P)

$$(P)_n + xA^- - xe^- \longrightarrow (P)_n^{x+}(A^-)_x,$$

where n is the degree of polymerisation. The x/n ratio characterises the degree of doping of the polymer. Dedoping (cathodic reduction) of an anodically doped polymer results in the elimination of charges in its chains and the dissociation of the anions to the solution. The doping–dedoping processes are accompanied by

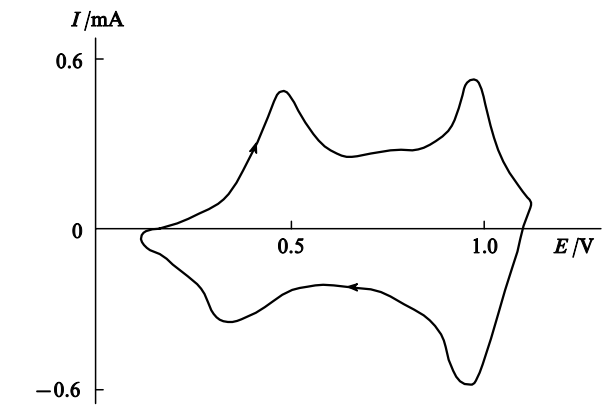


Figure 3. A cyclic voltammogram of a glassy carbon electrode modified by a polyaniline film.

‡ Hereinafter, the potential values E are shown with respect to the reversible hydrogen electrode in the same solution, unless otherwise specified.

redox reactions, which determine the redox activity of electron-conducting polymers. The intrinsic redox acitivity of a polyaniline film (Fig. 3) is manifesting itself in the vicinity of two pairs of anodic–cathodic peaks in the cyclic voltammogram (at ~ 0.45 and ~ 0.95 V). In the potential range between these peaks, the film exhibited a high electron conductivity (up to 10^5 S cm^{-1}).

The films can be synthesised using different modes, *viz*., potentiostatic, galvanostatic, potentiodynamic and pulsed modes. These modes were used in the synthesis of electron-conducting films of polyaniline[43, 50, 70–78] and polypyrrole.[11, 70, 79–82] An analysis of the experimental results obtained allowed the following conclusions to be drawn.

The number of aniline molecules incorporated into the polymeric film was roughly proportional to the charge passed through the system during the synthesis.

The mass of the polymeric film on the electrode, as a rule, was proportional to the charge consumed in its doping. However, the slopes of the corresponding linear dependences vary depending on the synthetic mode.

The results of measurements of these dependences for polyaniline have shown that, for a galvanostatic synthesis, the degree of doping decreases with a decrease in the current density. Under potentiostatic conditions, the maximum degree of doping was reached at the potential of 0.9 V. In the potential cycling mode, the dependence of the degree of doping on the potential scan rate also demonstrated a maximum.[50]

The following explanation to the regularities observed was proposed.[50] At low current densities, the film growth involves a small number of nuclei, which can result in a polymeric structure with a low redox activity. Probably this is the reason for the decrease in the redox activity observed for the films synthesised at the potentials below 0.9 V. As the potential increased above 0.9 V, the redox activity of films decreased probably due to the degradation processes § in the polymeric films.[51, 83–85] The decrease in the redox activity of polyaniline at high potential scan rates was probably due to either the finite rate of recombination of radical cations or the adsorption of the monomer on the polymer.[47] Syntheses under galvanostatic (the current density $>$ 0.1 mA cm^{-2}) and potentiostatic (the potential $>$ 1.0 V) conditions were accompanied by noticeable exfoliation of polymeric films formed.

Of different deposition modes used, the cyclic potential scanning allowed polyaniline of the maximum redox activity to be obtained.[50, 51] Films synthesised under such conditions also exhibited better adhesion to the electrode. The foregoing mainly concerns the films with thicknesses of $\sim 300–400$ nm.

c. The effect of solution composition ¶

Physicochemical properties of polypyrrole[43, 46, 80, 81, 86, 87] and polyaniline[88–114] films were shown to depend on the solution composition. This can be illustrated by several examples.

The polymerisation rate of aniline depends on the nature of an acid (supporting electrolyte) in the order $HCl < HClO_4 < HBF_4 < HF < H_3PO_4 < H_2SO_4$.[47]

The effect of organic additives, benzene and its derivatives serving as examples,[99–101] is defined by the character of their interactions with the polymer during the film growth, *viz*., on the possibilities of formation of chemical bonds with elements of the polymer chain and of co-polymerisation. Thus in the presence of phenol, the synthesis of polyaniline decelerated and, for a certain phenol/aniline concentration ratio (1 : 2) in solution, the synthesis stopped. The presence of phenol in the deposition solution enhanced by 15% the susceptibility of polyaniline to doping and prevented its degradation. The presence of phthalic acid in solution increased the porosity of the polymeric film, which was accompanied, on the one hand, by the increase in its susceptibility to doping and, on the other hand, a decrease in its stability towards degradation. The additions of salicylic acid had the opposite effect.

According to the results of other studies,[50, 51] no polymeric chains were formed in a two-dimensional adsorption layer at the polymerisation potential. For a polymer to form, its monomer should be present in solution in a certain concentration. For example, for polyaniline, this concentration was $\geqslant 10^{-4}$ mol litre^{-1} (see Refs 75, 76). Probably, the monomer can be adsorbed on the polymer and get incorporated into it under certain conditions.

d. Stability of film characteristics

Keen attention was drawn to the problem of stability of electrochemical parameters of modified electrodes.[70, 72, 73, 84, 85, 94, 95, 99–101, 115]

For acidic media, cyclic voltammograms measured on films synthesised on supports by the electrochemical polymerisation method were shown to be stable only in a certain potential range. The extension of the potential cycling range into anodic and cathodic directions entailed a decrease in the area under the peak of polymer doping in the voltammogram and caused irreversible changes in certain characteristics of the polymer, *e.g*., its conductivity. The limits of the potential range where a film exhibited stable electrochemical properties depended of many factors, *e.g*., on the electrolyte composition.

These changes in the film characteristics were caused by the degradation of polymers. According to the features of the changes occurring in the polymeric film, two main types of degradation could be singled out.[96, 97] For one of them, the specific doping ability of the polymer tended to decrease, whereas its mass remained constant; for the other, both the specific doping ability and the polymer mass decreased. Such processes of severe degradation resulting in disintegration of the film were also observed in the course of the polymer synthesis. For high potentials of the synthesis, the growth of the film bulk was accompanied by its exfoliation.

The radioactive tracer technique proved to be effective for studying polymer degradation.[94, 96, 115] Using this method, it became possible to confirm the existence of the degradation types mentioned above and show that different electrochemical synthetic modes produced polyaniline films with different stabilities towards oxidative degradation.

The differential radioactive tracer method has shown that the processes of oxidative degradation of polyaniline films with thicknesses $<$ 500 nm involve the whole mass of the polymer on the electrode. At the potentials of 0.7–0.75 V in 0.5 M H_2SO_4, the third degradation type named 'mild degradation' was observed.[97] It was shown that under these conditions, the polymer mass and its susceptibility to doping (the area under doping peaks) remained constant, chemical bonds of certain polymer molecules with the surface were broken with retention of the electrochemical bonding due to the interaction between polymeric chains.

e. Composite polymeric films

Composite materials containing nonconducting and ion-conducting polymers along with electron-conducting ones were proposed to improve unsatisfactory mechanical characteristics of conducting polymeric films (polyaniline, polypyrrole). Many studies are aimed at the development of such composite materials.[43, 105, 112, 116–129] These were synthesised in one or two steps. In one-step method, the electrode is immersed into a solution containing a matrix polymer and the monomer of a conducting polymer, and the electrosynthesis is carried out in this solution. Alternatively, a layer of an inert 'matrix' polymer which usually represents a nonconducting (ion-conducting) polymer with good mechanical properties, *e.g*., Nafion, is formed in the first step. In

§ Irreversible redox processes which occur during potential cycling.

¶ This review considers the systems using water as the solvent. Hence, the term 'solution composition' means the monomer concentration and concentrations and compositions of the supporting electrolyte and different additives.

the second step, the electrode covered with the matrix polymer layer is immersed into a monomer solution, and the conducting polymer is synthesised. In the course of electropolymerisation, particles of the matrix polymer become incorporated into the conducting polymer. For the details of the syntheses of composite materials see Ref. 43.

It should be borne in mind that, in many cases, the formation of a composite implies the appearance of new qualities rather than simple 'summation' of the properties of its components. An illustration to the issues mentioned above is provided by the results obtained using radioactive-tracer and electrochemical methods for the formation of polyaniline–Nafion composite films on platinum and glassy carbon.[128, 129] Particularly, for Nafion-covered electrodes, it was shown that aniline is first accumulated in the porous matrix polymer and only later transformed into polyaniline (the template synthesis[130, 131]). The degradation of such a film proceeds more slowly; hence, a substantially smaller amount of polyaniline fragments is removed from the electrode. This can be associated with the complex and branched structure of the polyaniline formed in the porous Nafion matrix.

III. Electrochemical reactions on polymer-modified electrodes

1. Films of nonconducting polymers

Ion-exchange polymeric films with incorporated redox systems are promising for electrochemistry of organic substances. Their use often made it possible not only to decrease the electrolysis overvoltage but also to enhance the selectivity of the main electrode reaction.[132, 133]

Thus manganese dioxide is known to selectively oxidise allyl alcohol to the corresponding aldehyde leaving the double bond intact. It was shown that the introduction of the Mn^{2+}/MnO_2 pair into the Nafion film provides the efficient electrolysis of cinnamyl alcohol to β-phenylacrolein.[134] The current efficiency in aldehyde increased from ~ 70% to ~ 82% with the changeover from the Pt–Nafion system to the Mn, Pt–Nafion one.

Figure 4 shows voltammograms of a glassy carbon electrode in an aqueous cysteine solution in the absence and in the presence of the Nafion–$Os(bipy)_3^{2+/3+}$ (bipy is bipyridyl) film on the surface. As can be seen, the diffusion current of cysteine electrooxidation reached its limiting value in the second case.[135]

Dimethylferrocene immobilised together with glucose oxidase in an ion-exchange film on a graphite support was used as the charge-carrier from the reduced enzyme (obtained as a result of glucose oxidation) to the conducting support.[136] In this system too, the limiting diffusion currents of glucose oxidation were reached, which allowed an amperometric sensor for glucose to be developed.

The oxidation of Fe^{2+} cations to Fe^{3+} carried out on a cross-linked poly(4-vinylpyridine) (PVP) and PVP-poly(α-lysine) films containing the $IrCl_6^{3-}/IrCl_6^{2-}$ pair[137, 138] can be cited as the example of the mediator catalysis for inorganic reactions. These studies have also theoretically discussed the possibility of estimating the contributions by the mass transfer, the kinetics of interactions of particles and the charge transport in the films into the general mechanism of the electrode process involving a mediator.

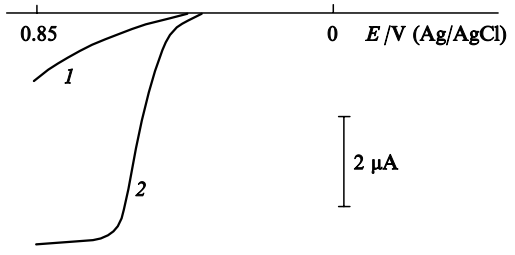


Figure 4. Voltammograms of cysteine oxidation on a rotating disk electrode of glassy carbon (*1*) in the absence and (*2*) in the presence on the surface of a Nafion film with the $Os(bipy)^{2+/3+}$ redox system;[135] $\upsilon = 1$ mV s^{-1}; cysteine concentration is 1.28 mol $litre^{-1}$, pH 4.

2. Electron-conducting polymeric coatings

To date, a considerable number of electrochemical reactions which occur on electrodes with electron-conducting films were studied. However, the occurence or the absence of the catalytic (electrocatalytic) effect for a particular process was debated more often than in the case of ion-exchange polymers. Apparently, this is largely caused by different conditions of film preparation and different compositions of supporting electrolytes used, because, as was shown above (see Section II.3), these factors strongly affect the physicochemical and electrochemical properties of electron-conducting coatings. The ambiguous interpretation of these results was due to the lack of a theory of electrocatalytic effects by such coatings, which would encompass the whole diversity of the occurring processes.[6, 10]

A typical electrocatalytic reaction studied on electrodes modified by conducting polymers is the oxygen electroreduction. Studies of this process on a gold electrode covered with a polypyrrole film have established the promoting effect by the polymer.[139, 140] Using the method of the rotating ring–disc electrode, the authors of these studies have shown that this effect is due to an increase in the selectivity to the oxygen electroreduction to give water.

It was also concluded[139, 140] that polypyrrole films are permeable to oxygen and the reaction mainly proceeds at the metal/polymer interface. In another study,[141] no promoting effect was observed for polypyrrole doped with perchlorate anions.

The promoting effect of polyaniline films on the oxygen electroreduction on glassy carbon electrodes in dilute acidic solutions was observed.[142, 143] It was noted that in the course of this process the electrochemical characteristics of polyaniline remained stable for a long time, *i.e.*, the polymer did not degrade.

Studies of oxygen reduction on polyaniline and Nafion films have revealed the promoting effects of polymers on the electrochemical reaction.[124]

The problems of organic reactions on electrodes modified by polymeric films were discussed.[144–152] Particularly, the electrooxidation of formic acid on polymer-modified platinum and gold electrodes was described in most detail.[144–147, 152] The promoting effect of a platinum-supported polyaniline film on this process in the potential range below 0.5 V was found.[146] Presumably, the polymer prevented accumulation of the products of strong adsorption of formic acid on the electrode, which thus increases the number of active sites for the oxidation reaction.

By combining radioactive-tracer and electrochemical methods, the promoting effect of polyaniline films on the steady-state oxidation of formic acid on platinum and gold electrodes was also confirmed.[144, 145] It was shown experimentally that the amount of products of strongly adsorbed formic acid on a polyaniline-film modified electrode was higher as compared with unmodified electrodes (Fig. 5). This result qualitatively agrees with the conclusions made earlier.[146] However, it was found[144, 145] that an eightfold increase in the polymer-film thickness did not change the amount of strong-adsorption products accumulated on the electrode, which contradicts the conclusions drawn in Ref. 146. At the same time, the authors of these studies[144–146] have agreed on the location of the oxidation process, *viz.*, that the reaction occurs on platinum areas unoccupied by the polymeric film. This conclusion was confirmed experimentally.[144, 145] It was shown that if the polyaniline-free platinum areas are filled with CO adsorption products, then virtually no HCOOH oxidation occurs.

The promoting effect was explained[144, 145] by assuming that polymers catalyse the oxidation of weakly bound adsorption products of formic acid just as it was shown in earlier studies

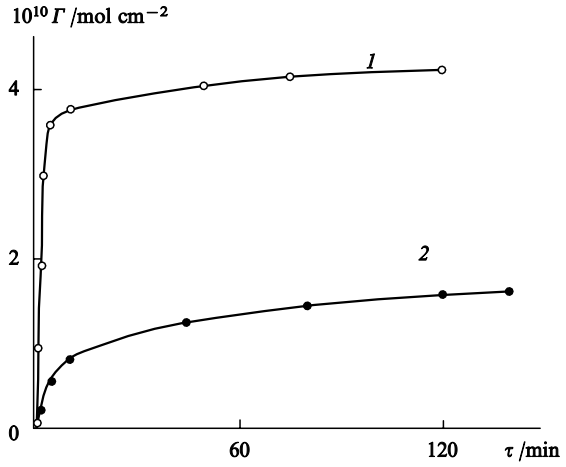


Figure 5. Kinetics of HCOOH adsorption at a potential of 0.2 V from a 10^{-2} M HCOOH + 0.5 M H_2SO_4 solution on (*1*) platinum electrode and (*2*) platinum electrode modified by a polyaniline film. Measurements were carried out by a radioactive tracer method.[144]

(*e.g.*, see Ref. 153) dealing with oxidation of organic substances on platinum modified by thallium adatoms.

The electrooxidation of methanol on polyaniline-modified platinum was also shown to be accompanied by a substantial decrease in the amount of products of strongly adsorbed methanol on the electrode; however, in this case, the polymer inhibited the electrooxidation.[154] Thus, as would be expected, the nature of the polymer effect (promotion, inhibition) on the oxidation process depends on the nature of the organic substance to be oxidised.

Polyaniline films were shown [149] to catalyse the electrooxidation of hydroquinone in a wide potential range. This effect was also confirmed later.[155–162] Figure 6 shows polarisation curves of electrooxidation of hydroquinone and reduction of benzoquinone on a film-free gold electrode and that covered with a polyaniline film. The half-wave potentials of these processes were shown to shift in the cathodic direction for the hydroquinone oxidation and in the anodic direction for the benzoquinone reduction. It was found [161] that the exchange current of hydroquinone oxidation increased by two orders of magnitude on freshly prepared polyaniline films (supported on platinum). Most scientists associated the

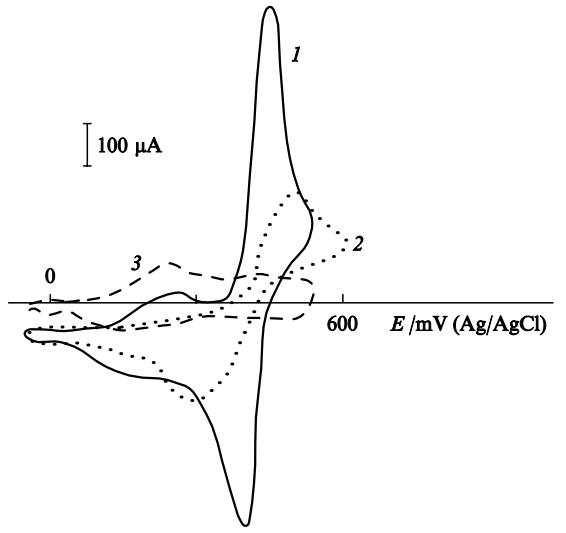


Figure 6. Cyclic voltammogram of (*2*) Au and (*1, 3*) Au–polyaniline system in (*3*) 0.5 M H_2SO_4 and (*1, 2*) *p*-benzoquinone solution (10^{-2} mol litre^{-1}) in 0.5 M H_2SO_4.[159]
Potential scan rate is 50 mV s^{-1}.

catalytic effect with the adsorption interaction between the polyaniline film and these compounds.[159–161] Some convincing evidence (based on experimental results) for the specific adsorption of hydroquinone on the emeraldine form of polyaniline has been obtained.[162] This case allows us to speak of 'classical' electrocatalysis directly by the conducting polymer. The effect of the polyaniline film morphology on the rate of hydroquinone oxidation was assumed [162] to be associated with the changes in the film surface areas involved in the adsorption and oxidation of the substrate. Alkyl derivatives of polyaniline behaved like polyaniline in the benzoquinone–hydroquinone reaction.[163–166] The differences in the kinetics of the hydroquinone–benzoquinone reaction on polyaniline and poly(*ortho*-phenylenediamine) films were explained [159] by the different distribution of equilibrium potentials at the polyaniline/solution interfaces.

The processes discussed above occurred in the potential range where the film was the electron conductor. In earlier studies (*e.g.*, see Ref. 167), it was assumed that in the 'nonconduction' potential range, electrode reactions should be entirely inhibited. However, this assumption turned out to be incorrect. Thus the reactions of hydrogen oxidation and oxygen reduction were shown to proceed (even if at much slower rates) in the potential region of 'nonconducting' films as well.[168] These processes were found to be strongly affected by the support nature. On nonconducting polyaniline films, the processes of reduction of oxygen [169] and naphthoquinonesulfonate [163] were observed to occur. To explain the occurrence of these processes, their rate-dtermining steps were assumed to be located at the metal/solution (due to porous structures of the films) and/or metal/polymer (for the mediator catalysis) interfaces [168] and the oxidant was supposed to inject positive charges into the polymeric matrix.[6,163] Moreover, it should be borne in mind that sufficiently thin films ($\leqslant$ 500 nm) across which the potential drop is small were used most often,[170] and that the relaxation from the conducting state to the nonconducting one is sufficiently slow.[171]

As is seen from the above examples, to date there is no agreement on the reasons for the appearance of catalytic effects in the systems containing electron-conducting films.[6,172] Some authors favoured the mediator mechanism, the other (without any strong evidence) assumed the potential change in such systems to be associated only with the potential drop across the polymer/electrolyte interface. An analysis of thermodynamic equilibria in the metal–polymer–electrolyte system at different interfaces has shown [172] that in the general case the potential drops across all the interfaces involved should be taken into account. For a more accurate elucidation of the role the polymer plays, additional information is required, particularly, on the exact location of the reaction and its rate-determining step. However, it is very difficult to obtain this information for electrodes with polymeric coatings.

Considerable progress has been achieved in modifying electron-conducting polymers by different redox groups and catalytic centres such as porphyrins, phthalocyanines, transition-metal complexes, biological molecules, *etc.*[6,169,173–182] In most of such systems, the mechanism of mediator catalysis was realised. Thus it was found [152] that electroreduction of oxygen on glassy carbon can be accelerated by covering it with a polyaniline film containing anions of heteropolyacids $(SiW_{12}O_{40})^{4-}$ and $(PW_{12}O_{40})^{3-}$. The possibility of using polythiophene and polypyrrole films modified by heteropolyacid anions for catalysing this process was also considered.[183–187] On a polyaniline + cobalt tetra-2,3-pyridineporphyrin (CoTPP) composite film, the oxygen reduction potential shifted to more positive values as compared with its reduction potential on the electrosorbed CoTPP.[169] It is of note that even an increase in the currents was observed in the transition of polyaniline into the reduced state.

It was shown [186,187] that modification of a glassy-carbon electrode surface by an [Os(bipy)(PVP)Cl]Cl coating [PVP is poly(vinylpyridine)] allowed the limiting diffusion currents of nitrite electroreduction to be reached. This makes this system promising for the development of a sensor for nitrite anions.

IV. Electrodes coated with polymeric films with incorporated metal-catalyst particles

From the foregoing it follows that modifying polymeric films play the role of charge carriers in electrocatalysis, and their catalytic activities manifest themselves in the processes free from destruction of substrate molecules. Platinum-group metals are the best electrocatalysts (catalysts) for the processes which involve cleavage of interatomic bonds (*e.g.*, oxidation of hydrogen, organic substances, *etc.*). It is possible to prepare highly dispersed deposits of these metals by incorporating them into polymeric matrices.

A specific feature of the systems thus obtained is that the polymeric matrix determines the conditions for the metal phase development. The properties of the matrix (film) itself can be changed by choosing a particular polymer and varying the conditions of the surface film formation.

Keen attention was drawn to the processes of deposition of platinum-group metals in ion-exchange polymeric matrices,[188–201] because the latter are stable in different media and can be used as the solid polymeric electrolytes in electrochemical reactors. It was proposed in many studies to prepare deposits of platinum-group metals using electron-conducting polymers where the formation conditions and the behaviour of metal particles can differ substantially from those in ion-exchange films.[54, 154, 202–222] This can result in a three-dimensional structure representing a conducting matrix with sufficiently uniformly distributed catalyst microparticles. The porous structure of such a matrix can make the metal-catalyst accessible for reactants and provide the exit of the products to solution.

For these systems, the practically important effect of the increase in the electrocatalytic activity calculated either per the geometrical surface of the electrode or per a mass unit of the noble metal could be achieved mainly due to an increase in the surface area of the deposit. However, of prime scientific interest is to increase the activity per the surface unit of the metal catalyst as compared with the compact metal. This can be associated with the structural peculiarities of microdeposits (*e.g.*, the size effect [1]), the interaction of metal particles with the polymeric matrix and the changes in the reactant activities in the porous space of the matrix.

In theoretical studies, great attention was drawn to the electronic structure of microdeposits. Due to the high work function values for metals of the platinum group [223] as compared with other materials, it could be expected that the electrons would be partially transferred from the matrix to the microdeposit and, as a consequence, the mean electron density in the deposit would increase. However, such an effect was detectable only where the sizes of microdeposit particles were commensurable with the thickness of the electrical double layer. According to the estimates,[224, 225] even in the absence of their interaction with the matrix, the Fermi energy in small particles (the size $d \leqslant 3$ nm) should substantially differ from that in the compact metal.

1. Dispersion of particles of platinum-group metals in polymeric matrices

Different chemical procedures were developed for introducing metal particles into polymeric matrices.[194, 226–231] For example, deposits of Pt, Pt + Ru, and Pt + Sn were obtained by reducing the corresponding salt solutions by reactants diffused from the other side of a membrane.[226, 227] Membranes were often impregnated with solutions of platinum-group metal salts and then immersed into the reducing solution.[228, 229]

However, those methods which use the electrodeposition of metals are most convenient (especially, for films) for incorporating metal particles into polymeric matrices.[188–193, 195–222] By varying the potential, current and deposition time, one can control the accumulation rate and the amount of the metal deposited. Such methods can be divided into two groups, *viz.*, with single- and two-step deposition. In the former case, the film is first formed (by a chemical or electrochemical method), and then the metal is electrodeposited in it (often on it). In the latter method, the film is formed electrochemically from a solution containing both a monomer capable of electropolymerisation and a salt of a metal-catalyst. By varying the electrodeposition conditions (supporting electrolyte concentration, components concentrations, modes of current and potential variations, *etc.*) it is possible to prepare films with diverse morphologies and various contents and depth-distributions of metal particles.

Two-step deposition was used for both ion-exchange and electron-conducting films. In the films devoid of intrinsic electron conduction [*e.g.*, Nafion and poly(vinylpyridine)], the formation of metal particles begins from the support, and their further growth occurs along the pores 'from one particle to another' with retention of contacts between the particles (Fig. 7). Gradually, the electrodeposition process reaches the film surface (this stage is not shown in the figure), which can occur before the whole porous space is filled, as a result of the difference in the rates of formation and growth of films in different pores. Later, the metal layers are deposited on the film surface, and this process is only indirectly controlled by the film. Evidently, the specific behaviour of metal particles incorporated into the polymeric matrix should be judged based on the analysis of the behaviour of systems in which the metal deposit, at least, its greatest part, has not yet 'escaped' to the film surface. According to the literature data, as might be expected, the mechanism of deposit growth and the sizes of metal particles formed strongly depend on the modes of the support polarisation.

During the formation of metal particles in electron-conducting polymers, the metal-catalyst can be deposited directly onto the polymer. Though it was suggested [220] that during the deposition of metals on an electron-conducting polymer in the potential range where the polymer is dedoped and assumed [9, 13] to become 'nonconducting', the mechanism of metal deposition in the films remains virtually the same as for ion-exchange polymers (see Fig. 7 *a*). However, it was found [211, 222] that the deposition of a metal directly on the polymer can also occur in the potential range of its 'nonconducting' state. Using the AFM method for the

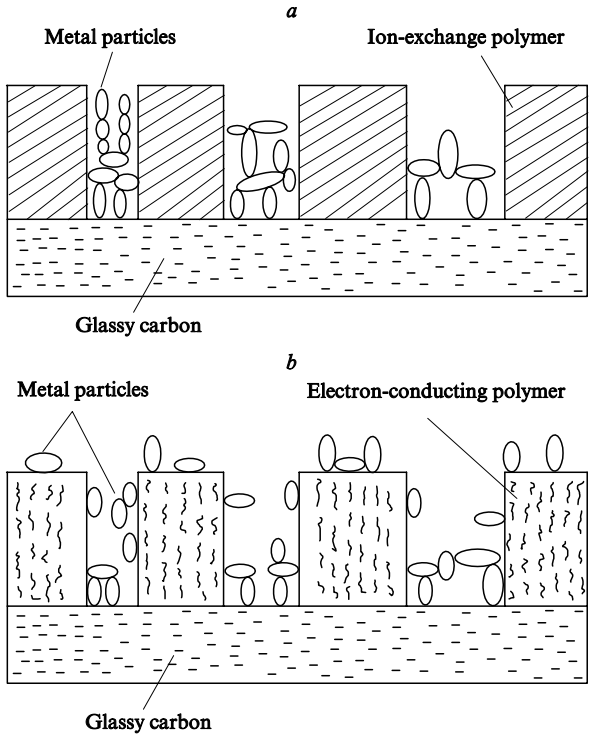


Figure 7. A scheme of accumulation of metal particles in a polymeric matrix formed on a glassy carbon support for (*a*) ion-exchange and (*b*) electron-conducting polymers.

palladium deposition in sufficiently thick polymeric matrices where the metal volume was an order of magnitude lower than that of the porous space (estimated from the results of Ref. 232), palladium particles were observed on the film surface at the deposition potential of 0.14 V, *i.e.*, in the range where polyaniline is nonconducting. The appearance of metal particles was explained by the 'residual' conductivity which is retained after the polymer is dedoped [233] and ensures sufficiently small potential drops across thin ($\sim$ 500 nm) polymeric films. The results of layer-by-layer Auger-spectroscopic studies [211] of a polyaniline film † with palladium particles have shown that deposition of palladium preferentially occurs in the external regions of the film. Figure 7 *b* shows the model for deposition of metal particles into an electron-conducting film. In this case, the contact between metal particles is not necessary: the most pronounced manifestation of the catalytic activity can be expected at the potentials of high conductivity of the polymer (especially, for thick films).

A single-step method of preparation of composite M – electron-conducting polymer films was used less frequently. Potential cycling in the range from sufficiently high positive values at which the monomer is preferentially polymerised, to the potentials close to that of the reversible hydrogen electrode, at which the metal is preferentially deposited, made it possible to provide a largely uniform distribution of metal-catalyst particles throughout the film.[211, 222] Moreover, the formation of substantial amounts of metal on the film was ruled out. However, the single-step synthesis by periodic application of sufficiently high potential values to the electrode led to noticeable degradation of the polymer even during the formation of the electrocatalytic system,[220] and the degradation became more pronounced in the presence of particles of platinum-group metals.[222]

The use of polymeric matrices (especially those of ion-exchange polymers) made it possible to obtain ultradispersed deposits of platinum-group metals (with the grain diameter of 3 – 5 nm) with larger specific surface areas. As a rule, the most dispersed deposits were formed at small metal-to-polymer mass ratios, *i.e.*, where the deposit fraction remained within the polymeric matrix is substantial.[195, 200] For large amounts of deposited metals and/or small film thicknesses, the specific surfaces substantially decreased and, as would be expected, often approached those of individual metal deposits.[200, 201, 203, 219, 233 – 235]

At attempt was made to deposit platinum in preformed polyaniline films from aqueous H_2PtCl_6 solutions.[154] The form in which platinum is accumulated in the film was concluded to be strongly dependent on the lower limit of the potential cycling interval, *viz.*, in the 0.1 – 0.7 V range, it was accumulated as two- and four-charged ions, whereas in the 0 – 0.7 V interval, platinum metal particles prevailed.

A comparison of the data shown in Table 1 allows one to assess the possibilities of increasing the catalyst surface area by using polymeric matrices. The table shows the maximum values of specific surface areas for several metals of the platinum group electrodeposited into Nafion and poly(vinylpyridine) (the results [196 – 199, 220] were averaged) and similar values for electrodeposits of these metals on platinum. The greatest effect was observed for palladium. It is important that the polymeric matrix also favoured the stabilisation of particles. This made it possible, for example, to observe the size effect, *viz.*, a sharp decrease in the amount of absorbed hydrogen, for palladium particles of sizes < 7 nm [poly(vinylpyridine) matrix].[198]

The attempts to achieve such a great development of the metal-catalyst surface area for electron-conducting polymeric films have failed.[219, 120, 222] This indirectly confirmed that the metal deposit can grow on the film surface even for small metal-to-polymer mass ratios.

† The film was deposited by the two-step method, and palladium was deposited in the potential range of 'nonconducting' polyaniline.

Table 1. Maximum specific real surface areas ($m^2\ g^{-1}$) for deposits obtained for metal – polymer – glassy carbon systems (S_1) and metal electrodeposits on platinum (S_2).[196 – 199, 220]

Metal	Polymer	S_1	S_2
Pt	poly(vinylpyridine)	100	18 – 25
	Nafion	80	
Pd	poly(vinylpyridine)	100	10 – 15
	Nafion	90	
Rh	poly(vinylpyridine)	60	30 – 40

However, for palladium microdeposits in polyaniline, the specific surface areas of 35 – 45 $m^2\ g^{-1}$ were reached (see Refs 220, 222).

2. Determination of the real surface area of metal-catalyst particles in polymeric matrices

The determination of the real surface area of metal-catalyst particles incorporated into polymeric matrices presented a serious problem for comparing correctly the specific electrocatalytic activities of deposits. Unfortunately, many studies of the electrocatalytic activity of metal-catalyst – polymeric matrix systems did not pay due attention to this problem and did not separate the contributions to the electrocatalytic activity into those caused by the surface development and by the changes in the intrinsic specific activity of the incorporated particles.[54, 154, 212 – 218]

Determination of specific surface areas of metal deposits in polymeric films S ($m^2\ g^{-1}$) also presented independent interest for estimating the degree of dispersion of the metal-catalyst. The use of a certain model allows the average sizes of metal particles to be calculated roughly from the S values. The modern physical methods such as the scanning tunnelling microscopy and atomic force spectroscopy made it possible not only to assess more accurately the average size of particles but also to determine their size distribution.[236] However, the use of these methods for characterising the particles located inside the polymeric matrix is associated with considerable experimental difficulties.

The method for estimating the real surface areas from the hydrogen adsorption, which is commonly accepted for platinum group metals,[237, 238] often gave insufficiently correct results and in many cases could not be used at all. Thus the 'hydrogen regions' of metal particles in polymeric matrices can be deformed due to the small sizes of these particles, their adsorption interaction with the polymeric matrix and the changes in the pseudo-capacity of the support.[197, 239, 240] In systems with electron-conducting polymeric matrices such as polyaniline and polypyrrole, additional difficulties arose due to the severe overlapping of the potential ranges of hydrogen adsorption – desorption and those of the intrinsic redox activity of the polymer.[154, 219, 220] The method for determination of the surface area by hydrogen adsorption cannot be used in principle for palladium particles, because the hydrogen absorption in the Pd(H) α-phase substantially exceeds the hydrogen adsorption.[241, 242] Many of the difficulties noted above could be avoided if the real surface area was estimated by the underpotential deposition (upd) of copper.[196, 220, 241 – 243] In the Pt – poly(vinylpyridine) system (a glassy carbon support), a 10% deviation between the specific surface areas of platinum determined from hydrogen adsorption and upd of copper appeared only for $S > 80$ $m^2\ g^{-1}$. The use of copper adatoms for determination of the real surface area of palladium particles deposited into poly(vinylpyridine) and Nafion films proved to be effective.[198, 199] At present, this is the most correct electrochemical method for determination of real surface areas of palladium particles incorporated into polymeric matrices. Calculations of real surface areas of palladium electrodes by the oxygen adsorption [241, 243] proved to be useless, because the polarisation of electrodes to high anodic potentials often caused irreversible changes in the M – polymer – support systems.[83, 85, 98, 115, 196]

It was found [219] that due to many similar charges being consumed in the removal of hydrogen adatoms from incorporated platinum particles and in the polyaniline film oxidation, the real surface areas estimated in parallel experiments from the hydrogen adsorption differed twofold even for the platinum-to-polymer mass ratio of ~ 70. According to experimental results,[220] well reproducible real surface areas estimated from upd of copper could be obtained for platinum and palladium particles incorporated into polyaniline when the metal-to-polymer mass ratio was ~ 0.2.

The formation of monolayer coverages by adatoms (Cu, Ag, *etc.*) with the subsequent removal of their ions from the solution bulk, allowed the surface areas of metal-catalysts to be determined by suppressing the hydrogen adsorption.

To determine the surface area of platinum particles in a polyaniline matrix, it was proposed [177] to use the CO adsorption. However, depending on the structures formed by adsorbed CO (bridge or linear), the real surface areas estimated can differ twofold. Moreover, carbon monoxide can be sorbed by the polyaniline film itself.[221]

The possibilities of using physical methods for the estimation of the sizes of particles incorporated into polymeric matrices could be remarkably increased, if the film could be separated from the support. Thus composite films of polypyrrole with palladium particles were deposited on plates of In–Ti oxides and then separated from them and analysed using a transmission electron microscope.[244] The average size of palladium particles was found to be ~ 5 nm.

3. Electrode processes on polymeric films with incorporated particles of metal-catalysts

The results on the electrode processes on polymeric films with incorporated metal-catalyst particles are discrepant and unequal with respect to their quality and scientific importance.[245–265] This often means not only the quantitative discrepancies, but also concerns qualitative deviations in experimentally observed effects. This was caused by a number of factors, the main of which are as follows:

(1) the difference in the procedures used for synthesising the metal-catalyst – polymeric matrix systems;

(2) the wide scatter in the metal-to-polymer mass ratios; this can cause substantial differences in the behaviour of electrodes with essentially similar metal-catalysts and polymers (see Section IV.1);

(3) different conditions of measuring polarisation curves;‡

(4) uncertainty associated with the steady-state criteria;

(5) the low 'sample-to-sample' reproducibility of the electrochemical reaction rates (like electrooxidation of organic substances) even for individual electrodes of platinum-group metals;§

(6) in most studies, the specific currents were expressed per the geometrical surface area of the electrode, which dramatically reduced the fundamental importance of the results (see Section IV.2).

The difficulties mentioned above were caused by the complicated nature of both the electrode systems themselves and the electrocatalytic processes on them, as well as by different factors which could promote or inhibit the electrode reactions. Hence, the attempts to explain the results obtained for the modified electrodes under consideration have yet involved only phenomenological interpretations. In connection with the aforesaid, when choosing the data for the discussion, we focused attention on the results of those studies in which the measurements were carried out under steady-state conditions on electrodes with small metal-to-polymer mass ratios and which provided the estimates of the metal-phase surface area. The literature data on the methanol and formic acid electrooxidation and oxygen electroreduction in acidic solutions well illustrate the variety of experimental results on the electrocatalysis by particles of platinum-group metals deposited in/on polymeric coatings (Table 2).

Most of the studies in which the promotion of the methanol electrooxidation was detected, measured non-steady-state currents calculated per unit of the geometrical surface area (with several exceptions [196, 200, 201, 213, 219, 222, 247]), *i.e.*, considered the gross effect. (Sometimes, the oxidation rate increased only two- to three-fold, *e.g.*, in Refs 219 and 247.)

When the effect of Nafion and poly(vinylpyridine) matrices on the behaviour of platinum particles was studied for extremely small amounts of the metal deposited (no more than 21 μg cm^{-2}), it was found [196, 200] that the specific rates of CH_3OH electrooxidation (under steady-state conditions) decreased as compared with the oxidation rate on platinised platinum (Pt/Pt). A similar effect of the Nafion matrix for the platinum mass < 60 μg cm^{-2} was mentioned.[201] In the Pt – poly(vinylpyridine) – glassy carbon system, with an increase in the metal-phase dispersion, the rate of CH_3OH electrooxidation decreased.[196, 200]

At the same time, for platinum deposits incorporated into Nafion films with the platinum mass < 60 μg cm^{-2}, higher steady-state specific currents of CH_3OH electrooxidation as compared with the currents on Pt/Pt were found.[200] The increase was explained by the changes in the binding energy of the products of CH_3OH adsorption with the surface due to the changes in the deposit structure. Inasmuch as small-mass deposits are much more dispersed as compared with large-mass ones, one can speak of the qualitative agreement between different estimates [196, 200, 201] of the effect of the degree of platinum dispersion on the methanol electrooxidation rate.

For the electrooxidation of formic acid on platinum particles incorporated into poly(vinylpyridine) and Nafion, it was found that the specific rates increased with an increase in the degree of metal-phase dispersion.[196, 200] Moreover, the activity of highly dispersed platinum deposits ($\geqslant 30$ m^2 g^{-1}) was higher as compared with electrodeposits of platinum on platinum. A similar effect was greater for the Pt – Nafion – glassy carbon system (Fig. 8).[199]

The results discussed above show that the changes in the activity of metal particles incorporated into polymeric matrices largely depended on the nature of the substrate. Thus the effects of the degree of dispersion were found to be opposite for the

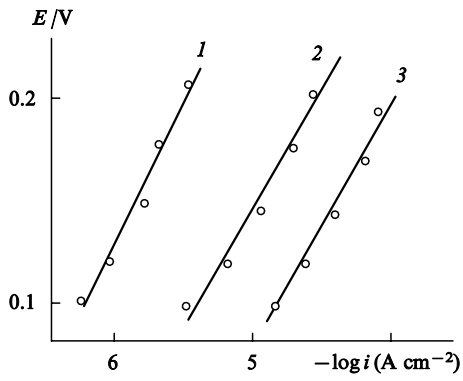


Figure 8. Stationary polarisation curves for electrooxidation of formic acid in the Pd/Pt (*1*), Pd – Nafion – glassy carbon (*2*) and Pd – polyaniline – glassy carbon (*3*) systems in a 0.5 M HCOOH + 0.5 M H_2SO_4 solution.[199, 222]

‡ Unfortunately, the authors of the overwhelming majority of studies used the potentiodynamic method for recording relatively fast polarisation curves. As a rule, this involved measuring non-steady-state currents, the interpretation of which was especially difficult due to the uncertainty in the surface coverages by original particles, their products, solution ions, *etc.*

§ Naturally, as one passes to more complicated M – polymeric matrix systems, the reproducibility of the results is reduced. Hence, the comparative estimates of the activity based only on the experimentally observed two- to three-fold change in the currents should be considered with caution.

Table 2. Results on the electrooxidation of methanol and formic acid and electroreduction of oxygen in the M – polymer – support systems.

M – polymer – support system [a]	Film thickness /μm	M content /μg cm^{-2}	Substrate	Polarisation curves	Catalytic effect [b]	Ref.
Pt – polyaniline – glassy carbon	3 – 4	2 – 51	CH_3OH	non-steady-state	+ (geometrical)	202
Pt – polypyrrole – platinum	–	–	O_2	steady-state	+ (geometrical)	129
Pt – polypyrrole – glassy carbon	–	–	O_2	non-steady-state		129
Pt – polypyrrole – gold	–	–	O_2	"	+ (geometrical)	129
Pt – Nafion/polyaniline – glassy carbon [c]	1.4 – 9.3	11 – 31	O_2	steady-state, non-steady-state	– (geometrical)	126
Pt – polyaniline – platinum	–	–	HCOOH	the same	+	213
Pt – Nafion – glassy carbon	0.5	4 – 55	CH_3OH	"	+ (geometrical)	265
Pt – polyaniline – glassy carbon	–	25 – 750	CH_3OH	steady-state	+ (real)	219
(Pt + Pb) – polyaniline – glassy carbon	–	–	CH_3OH	"	+ (real)	219
Pt – polyaniline – platinum	–	–	HCOOH	non-steady-state	+ (geometrical)	252
Pt – polypyrrole – platinum	⩽7	–	HCOOH	"	+ (geometrical)	252
Pt – polypyrrole – glassy carbon	–	45 – 131	CH_3OH	non-steady-state, steady-state	+ (geometrical)	255
Pt – polypyrrole – gold	–	57	CH_3OH	the same	+ (geometrical)	264
Pt – Nafion – glassy carbon	5	2 – 1000	CH_3OH	steady-state, non-steady-state	+ (real)	201
Pt – polyaniline – glassy carbon	0.3	–	CH_3OH	the same	+ (geometrical)	154
	0.3	–	HCOOH		+ (geometrical)	
Pt – polyaniline – gold	–	–	CH_3OH	"	+ (geometrical)	54
Pt – polypyrrole – SnO_2/glassy carbon [c]	0.08 – 0.16	13.1	O_2	"	+ (geometrical)	263
Pt – Nafion – glassy carbon	1.0	4 – 21	CH_3OH	steady-state	– (real)	200
	1.0	4 – 21	HCOOH	"	+ (real)	200
Pt – poly(vinylpyridine) – glassy carbon	1.0	5 – 20	CH_3OH	"	– (real)	200
			HCOOH		+ (real)	
Pt – polypyrrole – glassy carbon [d]	0.5 – 10	200 – 1000	CH_3OH	non-steady-state	+ (geometrical)	246
Pt – poly(vinylpyridine) – glassy carbon	1.0	5 – 120	CH_3OH	steady-state	– (real)	196
	1.0	5 – 120	HCOOH	"	+ (real)	196
Pd – Nafion – glassy carbon	4 – 6	1.6 – 6.5	HCOOH	"	+ (real)	199
Pt – polyaniline – glassy carbon [e]	0.25 – 0.3	62 – 76	CH_3OH	"	+ (real)	222
	0.25 – 0.3	62 – 76	CO		+ (real)	
	0.25 – 0.3	62 – 76	HCOOH		+ (real)	
Pd – polyaniline – glassy carbon [e]	0.25 – 0.3	5 – 30	HCOOH	"	+ (real)	222
Pd – polyaniline – glassy carbon	0.25 – 1.5	8 – 30	HCOOH	"	+ (real)	170
Pt – polypyrrole – (Pt, Ni)	1.0	100	CH_3OH	non-steady-state	+ (geometrical)	247

[a] Electrodeposition was used for incorporating metal into polymers unless otherwise specified. [b] Signs 'plus' and 'minus' designate the presence or absence (as assessed by the authors of the cited paper) of the catalytic effect; in the parenthesis, the surface area type (geometrical or real) used for calculating the currents is shown. [c] Chemical deposition was also used. [d] Three methods were used. [e] One-step method.

methanol and formic acid electrooxidation processes. A similar phenomenon was also mentioned for other catalytic systems, *viz*., not only for systems containing Pt particles, but also for those with Rh, Pd and Ir (see references in Ref. 240). This can be explained by assuming that particles involved in methanol electrooxidation occupy the greater number of surface sites than the sites required for the adsorption of HCOOH or CH_3OH.[240]

On the whole, the specific steady-state currents of methanol electrooxidation on platinum particles deposited in/on polyaniline films were found to be higher than the currents of its oxidation on Pt/Pt particles.[219, 222] However, a substantial catalytic effect was observed [219] only for the platinum mass > 60 μg cm^{-2}. Inasmuch as only very thin films were studied (35 – 50 nm), it can be assumed that the effect was caused by the peculiarities of the structures of platinum deposits formed on the surface of a polyaniline film (see Section IV.1).

The higher electrocatalytic activity of platinum particles in a polyaniline matrix as compared with Pt/Pt particles was also found [222] for the electrooxidation of formic acid and carbon monoxide. For CO, the effect was explained by the growth of its concentration in the polymeric film. The fact that CO is sorbed by the film was confirmed by a special study.[221] For platinum dispersed in polyaniline, the effect of promotion of formic acid electrooxidation was apparently of the same nature as for the aforementioned (see Section III.2) increase in its electrooxidation rate on platinum electrodes observed upon covering them with polyaniline films.

The greatest increase in the specific rates of formic acid electrooxidation was found for palladium particles incorporated into polyaniline (see Fig. 8). Moreover, the steady-state currents increased more than by an order of magnitude when both single-[222] and two-step[170] methods were used for synthesising Pd – polyaniline – glassy carbon systems. It is remarkable that the slope of polarisation curves remained virtually unchanged, although the process occurred in the potential range of polyaniline 'nonconduction'. This suggests, first, that the mechanism of HCOOH electrooxidation of palladium remains unchanged[248] and, second, that the electrode reaction rate can remain virtually unaffected by the ohmic potential drops in sufficiently thin films of electron-conducting polymers in the potential ranges of their 'nonconduction' (see also Section III.2).

According to the literature data, electrodes modified by composite Pt – polyaniline coatings can also be used for the oxidation of propan-2-ol,[249] ethylene glycol,[178,250] and D-glucose[251] (the latter can also be oxidised on a Pr – polypyrrole coating[218]) at moderate anodic potentials. However, the authors of these studies have used the potentiodynamic method for measuring voltammograms and have not estimated the real surface area of the metal phase. Hence, even if certain 'electrocatalytic effects' were found in these studies, this is more likely to be attributed to the surface development of the metal-catalyst. A minor increase in the specific steady-state currents was found for ethanol electrooxidation on platinum particles incorporated into a polyaniline matrix by the chemical deposition procedure.[229]

Most authors associated the promoting effect of polymeric matrices on the electrooxidation of simple organic substances at moderate potentials (before the onset of oxygen adsorption) either with the deceleration of the appearance on the surface of metal-catalyst of strongly chemisorbed species, which are the 'poison' for the current-controlling reaction, or/and with an increase in the amount of weakly bound species.[245] The 'parallel mechanism' of electrooxidation of organic compounds, which was first proposed in Refs 253, 254 for the reaction of methanol electrooxidation have gained substantial recognition.

Inasmuch as, as a rule, the sizes of metal-catalyst particles in polymeric matrices exceed 5 nm, the 'pure' size effect can hardly be considered. It is most probable that the catalytic effect is caused by the changes in the structure and/or the composition of the surface. Moreover, the changes in the latter can be caused not only by the adsorption of polymeric molecules and their fragments but also by the adsorbed impurities which could get into the metal phase from the deposition solution.[197,222] The surface composition was shown to strongly affect the formation of adsorbed OH groups, which play an important role in electrooxidation of organic compounds.[245]

Only few interpretations of the results took into account that the activities of water and substrate molecules in the pores of the M – polymer – support system can differ from those in the solution bulk.[194,222] However, the difference in these characteristics is quite probable, because, according to experimental results, *e.g.*, for Nafion[194] and polyaniline,[232] the polymers have channels with the mean size of $\sim$ 1 nm, *i.e.*, approaching the thickness of the electrical double layer. Evidently, the effect of the triple metal/polymer/solution interface on the kinetics of electrocatalytic processes should also be taken into account.

A new in principle interpretation of the promotion of formic acid electrooxidation in the Pt – polyaniline – glassy carbon system was given for the case where the incorporation of platinum into the film was accomplished by the potential cycling in the 0.1 – 0.7 V range.[154] It was assumed[154] that under these conditions platinum is preferentially accumulated as complex ions (Pt^{2+} and Pt^{4+}) which catalyse the process. The effect was unsteady and decreased in time very quickly, because the complex ions were removed from the film being exchanged for solution ions. Methanol was not electrooxidised on such platinum complexes which confirms again the substantial differences between the electrooxidation mechanisms of methanol and formic acid.

The electrocatalytic acitivity of M – polymeric matrix systems in electrooxidation of organic compounds could be enhanced (as in the case of individual metal-catalysts[240,245]) by the deposition of adatoms of foreign metals (*e.g.*, see Refs 251, 256, 257).

The high currents of hydrogen evolution on composite electrodes Pt – polymer [poly(vinylpyridine), Nafion, polyaniline] – glassy carbon and Rh – poly(vinylpyridine) – glassy carbon could be obtained for very small amounts of metal-catalysts ($\sim$ 20 μg cm^{-2}).[200,222,234] For small overvoltages, the parameters of polarisation curves with the currents calculated per 1 cm^2 of the geometrical surface area turned out to be similar to those for compact metal electrodes for which the hydrogen evolution was controlled by diffusion.[258,259]

Some of these results[200,222] correlated well with the results of studies[189,202] which showed that the 'hydrogen reaction exchange currents' in the Pt – polyaniline and Pt – Nafion systems virtually coincide with those on smooth platinum. However, it is more likely that the currents measured in the latter studies[189,202] were also of the diffusion nature rather than of the kinetic nature.

It was found[200,222,234] that with an increase in the overvoltage, the hydrogen evolution current on Pt – polymer – glassy carbon electrodes became smaller than those observed on smooth platinum. This was explained by the earlier transition to the mixed-kinetics region. The potentials of the transition depended on the polymer structure; for the polymers under consideration they changed in the following order: polyaniline > poly(vinylpyridine) > Nafion. Indeed, this points to the decrease in the real exchange currents of the hydrogen reaction in composite electrodes due to the adsorption interaction between the metal-catalyst particles and the polymer and/or its destruction products.[200,222] The results obtained for the Pt – Nafion – glassy carbon system, namely, that the diffusion currents estimated per 1 cm^2 of the geometrical surface area exceeded the specific currents on smooth platinum, are of special interest.[200] This was explained by the more effective stirring of the near-electrode layer by hydrogen bubbles on the hydrophobised surface.

A number of studies[126,260–263] have mentioned a possibility in principle of oxygen electroreduction on platinum particles incorporated into polyaniline or polypyrrole, but did not provide any correct comparison with the activity of platinum in this reaction. A lower activity was reported[126] for platinum deposited on a mixed polyaniline – Nafion film as compared with compact platinum. This was explained by the peculiarities of the formation of metal-catalyst deposits on such a film. Other scientists assumed the oxygen electroreduction rate to be largely controlled by the oxygen diffusion in the polymeric matrix. On the whole, the sufficiently fast degradation of electron-conducting polymers in the presence of oxygen and the catalysis of this process by incorporated particles of platinum-group metals were shown[96,97,115,200,222] to have an adverse effect on the stability of properties of electrocatalytic systems involving these polymers and used in the oxygen electrode.

V. Conclusion

The results shown above suggest that the research carried out to date with polymer-modified electrodes is largely aimed at the elucidation of interrelations between the properties of support materials, polymeric coatings and incorporated metal-catalyst particles and/or certain functional groups. The fact that polymeric materials cannot provide the destructive chemisorption of substrate molecules gives the grounds to expect that the systems with polymeric matrices containing microparticles of catalytically active metals are more promising for a number of electrode reactions (particularly, those in fuel cells).

Inasmuch as the properties of polymeric matrices and microparticles are interrelated, the theoretical concepts describing the dependence of fine particles on the properties of phases in contact with them are of special importance. These studies are directly connected with the development of concepts on the structure of

different interfaces in the systems studied, including the three-phase interfaces, *viz*., support/polymer/solution and polymer/metal-catalyst/solution. Taking into account the polymer–solvent interaction and possible changes in the activities of solvent and substrate molecules in the polymeric matrix also appears to be very important.

The cited examples of polymer-containing electrode systems comprise only a small fraction of those available in the literature. However, at present, the development of theoretical concepts should be aimed at more comprehensive and deep experimental research to reveal more distinctly the catalytic effects for electrode reactions rather than at the increase in the number of systems studied. For this purpose, not only the complex use of modern experimental techniques (physical, physicochemical, analytical, *etc*.) but also the modernisation of experimental methods (see Section IV.3) are necessary.

This review only mentions certain examples of the use of polymer-covered electrodes in practice. Great interest to the new type of electrode systems was associated, first of all, with the great diversity of their practical applications, namely, the modernisation of present-day electrolysers and electrochemical generators and development of their new types, synthesis of effective anti-corrosion coatings, the development of biosensors, the extension of the possibilities of electrocatalysis, the development of electrochromic devices, applications in micro- and nanoelectronics, *etc*.

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