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The Surface-modified Carbon Materials for Electrocatalysis

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The principal trends and prospects in studies on the creation of carbon materials with a specified electrocatalytic activity and stability are examined and methods for the surface modification of disperse and compact carbon materials are surveyed. It is shown that charge transport in the electrocatalysis by surface-modified electrodes proceeds via both a mediator mechanism and via direct electron transfer. The electrocatalytic properties of electrodes modified by simple organic complexes, polymers, and biopolymers are discussed and the mechanisms of the acceleration of the electrochemical oxidation of organic substances, the evolution of hydrogen, and the electrochemical reduction of oxygen are analysed.
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I. INTRODUCTION

One of the main tasks in electrochemical science and technology is the creation of new types of electrode materials. For this purpose, vigorous studies have been carried out during the last decade on surface-modified electrodes whose electrochemical and electrocatalytic properties can be altered specifically by varying the surface composition. The "construction" of the surface composition of electrodes is achieved virtually at the molecular level and is therefore extremely promising.

The possibilities in the employment of surface-modified electrodes are wide. They can be used in electrocatalysis, photoelectrocatalysis, and electroanalysis.[1,2] The attachment to the surface of specific electrochemically active compounds makes it possible to create selective electrode materials. The attachment to semiconductors of compounds with a known molecular structure ensures the formation of a surface having the necessary energy level and photosensitive in the specified part of the spectrum.[3] Modification of the surface, especially by polymers, can ensure an increase in the corrosion stability of electrodes and photoelectrodes.[4]

The study of electrodes modified by organometallic complexes makes it possible to obtain information about the influence of molecular conformation on their catalytic and oxidation-reduction properties.

Surface-modified electrodes constitute a convenient system for the elucidation of the mechanism of electron transfer. Studies on electrodes coated by polymers can significantly supplement the available information about the physical chemistry of polymers and biopolymers. Electrodes modified by enzymes are of special interest. The study of enzymes in electrochemical systems opens up a way to the creation of synthetic complexes with a high electrocatalytic activity and selectivity.

Metals, oxides with semiconducting properties, and carbon materials of various types can be used as a basis for the creation of modified electrodes. In the present review attention will be concentrated on electrodes based on carbon materials. According to the authors, this type of surface-modified materials is of greatest interest for practical use.

II. WAYS OF CREATING SURFACE-MODIFIED CARBON MATERIALS

Various methods based on the unique properties of carbon substances are used at the present time to prepare modified carbon materials. Depending on the method of preparation, carbon materials can have compact or disperse forms with the necessary texture of the inner surface. The possibility of the existence of surface carbon atoms in different valence states is responsible for the great variety of the surface oxygen-containing groups. The above properties of carbon materials make it possible to use for the modification of their surfaces of virtually all the known methods for the heterogenisation of catalytically active compounds. They can be divided into three main groups: (1) adsorption methods based on the retention of the modifying agents by physical adsorption forces; (2) chemical attachment with fixation of the catalyst via different groups, including groups specially obtained on the carbon material; (3) deposition of a polymer film with incorporation in the latter of metal ions or an organometallic complex.

1. Crystal-Chemical Properties of Carbon Materials

The physicochemical properties of carbon materials have been fairly completely reviewed in a monograph[5] from the standpoint of their employment in electrochemical systems. We shall deal only with those features of carbon materials which must be taken into account for the successful modification of their surfaces.

(a) *Relation between the electronic structure and the physicochemical properties of carbon materials.* A characteristic feature of carbon materials is the variation of their physicochemical properties as a function of structure for a constant composition. In its turn, the possibility of the formation of a large number of structures is determined by the ability of the carbon atom to exist in different valence states and to form bonds of different types. Depending on the mixing of the *s* and *p* orbitals, the quadrivalent carbon

atom can exist in three different hybrid states, a particular structure being characteristic of each. Thus a three-dimensional polymer with tetrahedral bonds between the carbon atoms (sp^3-hybridisation) corresponds to the diamond structure. Graphite, which is a parquet type polymer with sp^2-hybridised carbon atoms, is most often used in electrochemistry. *sp*-Hybridisation is characteristic of a linear polymer carbon chain. The peripheral carbon atoms in graphite can also exist in the *sp*-hybrid state. A carbon material with the graphite structure exhibits a marked anisotropy of its physicochemical properties. Thus the electrical conductivities of single crystals in two directions at right angles can differ by three orders of magnitude.

A series of carbon materials having a crystal structure are known: they include graphite and its synthetic analogue (pyrographite), which are characterised by a pronounced anisotropy of their electrical conductivity and other properties. In electrochemistry, crystalline carbon materials are used as a rule to create model electrodes with a small specific surface.

Among the transitional forms of carbon, vitreous carbon, carbon black, and activated carbon are most often used in electrochemical research. Vitreous carbon is characterised by the highest corrosion stability. In terms of their structure, carbon blacks occupy an intermediate position between crystalline graphite and amorphous carbon. Activated charcoals are obtained in the carbonisation and subsequent activation of a wide variety of carbon-containing materials. The texture of the activated charcoal depends on the method of its activation and is characterised by a large set of pores.

The carbon materials used in electrochemical systems must possess a high electrical conductivity, which increases on heat treatment and graphitisation of the transitional forms as a result of the expansion of the graphite-like regions.[6]

(b) *Surface groups in carbon materials.* The bulk-phase and surface properties of carbon materials have been compared.[7] The composition of the surface can be changed during heat treatment in atmospheres of different gases: nitrogen, oxygen, the halogens, ammonia, etc. As a result of such treatment, functional groups capable in many instances of increasing the catalytic activity of the initial material without additional modification are formed on the surface.

Fig.1 presents the most important surface-modifying oxygen-containing groups. They are formed on the surfaces of carbon materials both during synthesis and as a result of the adsorption of oxygen. Among acid oxides, quinonoid, carboxy- and phenolic groups have been detected on carbon blacks and charcoals.[8] Basic oxides are formed under much milder conditions compared with acid oxides. The oxygen is weakly bound to the surface and the identification of basic oxides is difficult.[5] One should also note the possibility of the existence on the surfaces of carbon materials of free radicals, which arise on dissociation of a carbon–carbon bond. An unpaired electron is then liberated and passes to the cyclic carbon system.[9] The adsorption of oxygen entails either a reversible or irreversible decrease of the number of free radicals.

The hydrophobic-hydrophilic properties of carbon materials are closely related to the chemistry of their surfaces. Since the carbon material is apolar, the degree of its oxidation does not affect the adsorption of non-polar compounds. On the other hand, the wettability by water is greater the greater the number on the surface of oxygen-containing groups, which are the primary centres for the adsorption of water.[10] Detailed studies[11,12] established a relation between the nature of the surface oxides and the hydrophilic-hydrophobic properties: surfaces containing basic oxides are more hydrophobic; for low degrees of activation, only macropores and partly mesopores are hydrophobic.

The possibility of the variation within wide limits of the porous structure of carbon materials should also be noted. This is especially important for modification by macromolecules such as enzymes and polymers, because the micropores and some of the mesopores are inaccessible for their adsorption.

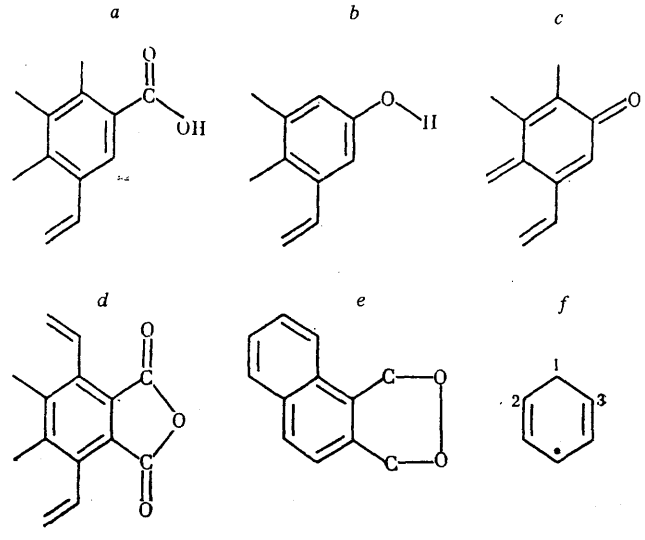


Figure 1. The surface groups of carbon materials: *a*) carboxy-group; *b*) phenolic group; *c*) carbonyl group of the quinone type; *d*) acid carboxy-group; *e*) cyclic peroxy-group; *f*) free σ-radical.

Thus the extensive use of carbon materials for the creation of surface-modified electrodes can be accounted for by the combination of a series of properties such as the presence on their surfaces of a wide variety of groups and free radicals, their high electrical conductivity, and the wide limits within which their porous structures and hydrophobic-hydrophilic properties vary.

2. Attachment by Adsorption

The method of adsorption modification of the surface is best known and simplest. Its principal disadvantage is the gradual desorption of the substance from the surface. The specificity of the adsorption interaction is determined by the type of carbon material and the chemical nature of the substance adsorbed.

Organic materials functioning as ligands for the formation of complexes[13] or metal complexes[14] are immobilised on carbon materials by the adsorption method. The degree of adsorption of organic compounds of this type increases with increase of the number of aromatic rings in the structure. The stronger and irreversible adsorption of N_4-complexes takes place both on polycrystalline pyrographite and on single crystals.[15] According to Zagal et al.[15], the N_4-complexes

of iron are adsorbed on the electrode surface in a planar fashion, while tetrasulphonated phthalocyanine complexes of cobalt and iron are disposed on the surface edgewise.

The ability of graphite electrodes to adsorb strongly aromatic molecules has been used[16] to attach the complex $[Ru(NH_3)_5L]^{2+}$, where L is a large aromatic ligand, for example 4-aminomethylpyridine or *N*-(4-picolinyl)benzamide. The complex $[Ru(bipy)_2]_2L^{2+}2(PF_6^-)$, where L is the dianion of 1,5-dihydroxyanthraquinone, has been adsorbed on vitreous carbon.[17] The adsorption of simpler phenanthroline and bipyridyl complexes and also the Salen and corrin complexes of cobalt has been investigated.[18] The strength of their adsorption is low. Macroheterocyclic complexes of cobalt have been adsorbed on carbon materials from their solutions in butanol by evaporating the organic solvent.[19] The complexes are retained on the electrode surface over a wide range of potentials.

The adsorption method for the modification of the surfaces of carbon materials by proteins and enzymes is most widely used in electrochemical measurements. The first studies on the immobilisation of hydrogenase, cytochrome *c*, and laccase on carbon materials already showed that they are strongly adsorbed and that the amount of adsorbed protein is greater the higher the degree of oxidation of the carbon material.[20–22] Peroxidase has been immobilised on carbon black;[23] glucose oxidase and cytochrome b_2 have been adsorbed on vitreous carbon.[24,25] Cytochrome *c* was adsorbed on carbon fibres after the preliminary anodic-cathodic treatment of the surface in the potential range +2.5 to −2.5 V.† This made it possible to observe oxidation-reduction reactions of cytochrome *c*.[26]

In all cases proteins were strongly held on the surface and retained a high catalytic activity. The activity of the enzyme depends on the type of carrier and its specific surface. For example, in the case of laccase immobilised on pyrographite,[2,27] the stationary potential established in an oxygen atmosphere does not exceed 0.9 V; on the other hand, the equilibrium oxygen potential is observed when laccase is adsorbed on carbon black.

An attempt has been made[28,29] to investigate the influence of the nature of carbon sorbents on their capacity with respect to the protein and on the catalytic activity of laccase. The activity of immobilised laccase is influenced by the degree of coverage of the surface by the enzyme, which depends in its turn on the degree of oxidation of the surface of the carbon black or on the porous structure when charcoals are used. The dependence of the activity of the immobilised laccase on the degree of surface coverage in both phenol oxidase and electrochemical reactions passes through a maximum. The greatest capacity with respect to the protein has been noted for charcoals with a large surface area of the mesopores, such as BM-4 and T-39. On the basis of adsorption measurements and porometric data, it has been suggested that macropores and partly mesopores are accessible to the adsorption of protein macromolecules.

However, one should note that, despite the high capacity with respect to the protein, activated charcoals proved to be less convenient electrode materials for the immobilisation of laccase, because in its presence a high anodic potential, inducing the electrochemical corrosion of the charcoal, is established. Carbon blacks exhibit a higher corrosion stability and are more promising for reactions at high anodic potentials with participation of enzymes such as laccase, tyrosinase, and peroxidase.

†Here and henceforth, unless otherwise stipulated, the potentials are quoted relative to the hydrogen electrode in the same solution.

The favourable and strong adsorption of proteins on carbon materials is determined by the crystal-chemical structure of their surfaces. One of the factors responsible for strong adsorption may be the formation of bonds between the surface groups of the carbon material and the aminoacid residues on the surface of the protein globule. Our studies have shown that the adsorption of many aminoacids and peptides is strong.# Thus glycine and valine cannot be desorbed from the surfaces of carbon materials in the range of their electrochemical stability potentials. Hydrophilic–hydrophobic interactions probably contribute appreciably to the adsorption interaction of the protein with the carbon surface. Their influence on the retention of the nativity of the immobilised proteins has been noted.[30]

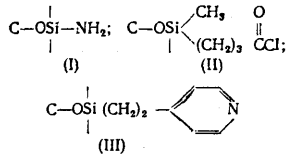
The relation between the isoelectric point of the protein, which determines the surface charge of the protein globule, and the structure of the electrical double layer at the carbon material–electrolyte interface is also noteworthy.

Thus, by virtue of the exceptional properties of carbon materials, strong attachment of the modifying substances, with retention of their high catalytic activity, may be achieved even by adsorption immobilisation.

3. Chemical Modification

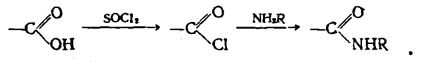
The chemical methods for the modification of the surfaces of carbon materials are based on various organic synthetic reactions.

The most general method for the chemical attachment of modifying agents to the surface involves its preliminary silanisation.[31] Organosilanes, such as the alkylamines (I), the chloroacids (II), and the pyridine derivatives (III) can be used to modify the carbon surface:



The active centres obtained as a result of silanisation are used for the subsequent "grafting" of various electrocatalytically active groups of complexes.[32,33] The ion exchange method,[34] which consists in the formation, for example, of an insoluble compound by reaction between the surface atoms and a ligand, can also be applied to carbon materials.

A very general procedure used for the modification of carbon materials involves reaction with thionyl chloride[34] or acetyl chloride[35] with the intermediate formation of chloride–oxygen compounds:

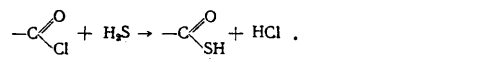


In order to increase the concentration of the oxygen-containing groups, the carbon material is subjected to preliminary oxidation in air or is treated with an oxygen plasma. The active groups are introduced by the action of amines or alcohols. This method has been used to prepare various modified materials with pyridine and porphyrin ligands.[36–38] The immobilised ligand may then be metallated with formation of electrocatalytically active complexes.

#L.R.Aleksandrova, V.N.Andreev, V.A.Bogdanovskaya, and A.Yu.Safronov, Elektrokhimiya, 1987 (in the press).

Amines have been attached[39] to the oxygen-containing groups on carbon materials. This leads to the possibility, in principle, of the subsequent grafting of any functional group.

The intermediate chloride–oxygen compounds on the surfaces of carbon materials can be used for the introduction of various heteroatoms,[40] for example:



Another way of creating surface-modified carbon materials involves the use of a surface free from oxides, which can be obtained by the mechanical cleaning of vitreous carbon in an atmosphere of nitrogen or by its treatment with argon plasma.[41] In the presence of vinylpyridine or vinylferrocene, such a surface is modified.

The possibility of attaching the butyl cation or CO_2 to graphite by cathodic treatment in dimethylformamide has been demonstrated.[42]

4. Deposited Films

A special and particularly rapidly developing field concerned with the creation of new electrode materials involves modification by polymers. Here one uses the adsorption, chemical, electrochemical, and radiation attachment methods. The thickness of the polymer films can vary from several to hundreds of nanometers. Depending on the type of reacting or coordinating groups in the polymer film, there is a possibility of its additional modification by metal ions or complexes.

The formation of the polyvinylpyridine complex of copper on various carbon materials by depositing a polymer film from its solution in methanol has been studied in detail.[43] The degree of dispersion of the carbon material influences the activity of the complex, which can be accounted for by the deposition of the polymer in different conformations. The deposition of the polymer film has also been used for the preparation of a surface modified by polystyrene with various functional groups.[44]

The preparation of polyacrylonitrile films on platinum, vitreous carbon, and stainless steel and of polyvinylpyridine films on platinum in a glow discharge at 250 °C has been described.[45–47]

The γ-radiation-induced cross-linking of alkylphenol films is used on metallic electrodes;[48] such cross-linking is also employed for other polymers, which are adsorbed in the monomeric state and are then polymerised.

The methods involving the electrochemical deposition of polymer films, which have many advantages compared with the traditional procedures because they make it possible to eliminate a number of intermedate stages such as the formation of the polymer, its dissolution, etc., have been developing vigorously. In the electrochemical deposition of films, it is possible to regulate the thickness and chemical composition of the resulting coating. On the other hand, electrochemical polymerisation permits the cross-linking of a film already deposited on the electrode.[49]

Polyacrylamide films have been obtained under the conditions of cathodic initiation.[50] Polymer deposits can be obtained electrochemically from solutions containing unsaturated carboxylic acids, certain aldehydes, and alcohols.[51] As a rule, polymer films are deposited electrochemically on metallic electrodes. The uses of polymer electrodes for various purposes, including electrocatalysis and photoprocesses, have been described in a review.[51]

III. ELECTROCHEMICAL PROPERTIES OF THE MODIFIED SURFACES

The study of the properties of surface layers on modified electrodes includes the study of the nature of the bonds between the modifying agents and the surface, the orientation of the modifiers, the degree of surface coverage, the thickness of the layer, the redox reactions of the groups attached to the surface, and the interactions of the species on the surface.

Among the non-electrochemical methods for the investigation of the surface groups of modified electrodes, spectroscopy with optically transparent electrodes,[52] mirror reflection spectroscopy,[53] and also IR and X-ray photoelectron spectroscopy[54,55] should be mentioned. The first two methods are used for the investigation of redox reactions of the attached groups and the last two provide proof that particular stages of the addition reactions have been effected.

The difficulty of measuring the spectra of the modified surfaces *in situ* arises from the necessity to obtain the spectral characteristics of molecules whose number does not exceed that corresponding to a monolayer. Anomalous extinction coefficients have been observed in a series of studies[57–59] on the adsorption of complexes with a conjugated system of π electrons. They all involve the intensification effect due to the roughness of the surface. In the measurement of Raman spectra, this phenomenon has been frequently observed and its possible causes have been considered.[56] In electronic spectroscopy the phenomenon of the anomalous increase of the extinction coefficients was observed for the first time in the adsorption of chlorophyll on an amalgamated gold electrode.[57] Later an analogous phenomenon was noted in the adsorption of tetrasulphonated complexes of cobalt and iron on platinum and pyrographite[58] and of the bipyridyl complexes of ruthenium on SnO_2.[59]

This apparently indicates an extremely strong chemisorption linkage between the modifying group and the electrode surface.

1. Oxidation-Reduction Reactions of the Modifying Complexes

Potentiodynamic and differential pulsed measurements make it possible to investigate the redox reactions of active groups on the surface-modified electrodes and to compare them with the oxidation-reduction properties of the complexes in solution. The possibility of redox reaction of covalently bound groups depends on their orientation on the carbon surface.[60,61] Of the two isomeric 1- and 2-aminoanthraquinones, only the former underwent pronounced redox reactions. It can be oriented parallel to the surface, which ensures the maximum degree of electronic interaction and facilitates electron transfer. Methylaminopropylviologen, attached to the surface via cyanuric chloride, is electrochemically active and stable for a long time.[54] The redox potentials of various ferrocene derivatives attached to graphite differ little from the corresponding values for derivatives in solution in acetonitrile.[40]

Much attention has been devoted to the study of electrodes modified by ruthenium complexes attached to polymers or directly to the carbon surface. In many instances,[13,16] the redox potentials of the adsorbed or chemically attached ruthenium complexes are close to the normal potential of the complex in solution. On formation of metal complexes with polymer films, redox transitions have been observed,[60] whose number depended on whether the metal was coordinated to one or two pyridine rings.

The potentiodynamic curves obtained in the presence of adsorbed phenanthroline complexes of copper[18] show maxima which may be attributed to the Cu^{2+}/Cu^{+} transition on the electrode surface, since the redox potential of the Cu^{2+}/Cu^{+} pair in the corresponding ligand environment is close to the potentials of the redox reactions in solution. As the electrode surface is covered by the complex, a steady increase of the amount of electricity corresponding to the given redox process is observed. The change in the orientation of the complex on the surface is manifested in its adsorption from solutions at different concentrations. A greater order of the adsorption layer, expressed by the fact that the entire complex is reduced and oxidised at similar potentials, is observed in adsorption from dilute solutions. The results of potentiodynamic measurements have shown that redox processes with participation of cobalt and copper complexes proceed under nearly reversible conditions. For complexes of the phenanthroline series, limiting surface coverage approaches the monolayer coverage.

Under the conditions of weak adsorption of the modifying agents,[61] the redox potentials of copper, cobalt, and iron complexes on the pyrographite surface also agree with the corresponding values in solution according to the results of potentiodynamic measurements.

Analysis of all the available data on the oxidation-reduction potentials of various groups attached to carbon carriers leads to the conclusion that their properties in the immobilised state and in solution are similar. This indicates a very high rate of electron transfer from the electrode to the modifying complex.

2. The Influence of the Polymer Coating on the Electrochemical Behaviour of the Carbon Material

The oxidation-reduction reactions of polymer layers on various electrode materials have been described.[62–64] The main results can be summarised as follows. At scanning rates <1 V s^{-1}, the cyclic curves are close to those observed for typical surface reactions. The curves are symmetrical and the current at the maximum is proportional to the rate of application of the potential. These data indicate the absence of transport-dependent limitations. However, at high rates of application of the potential,[65] particularly in the case of relatively thick films,[41,66] a discrepancy between the potentials of the anodic and cathodic maxima is observed. Similar phenomena have been noted on reducing the temperature and on increasing the size of the electrolyte ions.[64]

As a rule, in the case of symmetrical maxima, their parameters differ from those corresponding to equilibrium electronic transitions. Thus the width of the maximum at the level of half the height of the current peak was 0.09 V, which corresponds to a reversible one-electron transition, only in a few cases.[60] Usually this value ranged from 0.15 to 0.54 V. The broadening of the maxima is attributed to repulsive interactions[64] or to a distribution of the given species with respect to the potentials of the redox reaction caused by the existence of electrochemically non-equivalent sites in the polymer film.[3] The asymmetric character of the potentiodynamic $I-E$ curves for polymer coatings can be caused by the slow rearrangement (conformational changes) occurring in the oxidation or reduction of the polymer complex.[66–68] The swelling of the polymers is also possible. Thus significant differences in the behaviour of polymerised vinylferrocene in acetonitrile and water have been noted.[68]

The electrochemical behaviour of polyvinylpyridine (PVP), polycaproamide, and copper polyvinylpyridinate on carbon materials has been studied in detail.[69,70] Fig. 2 presents the potentiodynamic curves obtained on a pyrographite electrode with a deposited PVP film. The $I-E$ curves have an analogous form in the presence of a polycaproamide film. It has been noted that the cationic composition of the electrolyte has a significant influence on its polarisation capacity. The relative increase of the polarisation capacity then rises in the sequence Na < K < Ba in the presence of a PVP film and falls in the sequence K > Cs > Ba in the presence of polycaproamide.

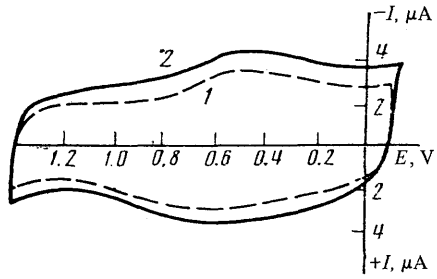
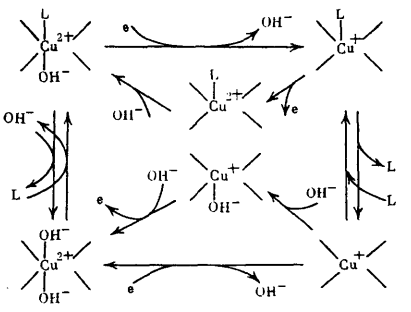


Figure 2. Potentiodynamic $I-E$ curves obtained at a pyrographite electrode (curve *1*) and a pyrographite electrode with a deposited PVP film (curve *2*) for $\nu = 0.05$ V s^{-1} at pH 7.0.[69,70]

When copper ions from an alcoholic solution are introduced into a PVP film, a stable complex is formed, namely Cu-poly-4-vinylpyridine (Cu-P-4VP), which is indicated by the possibility of measuring quasi-stationary potentiodynamic curves in the potential range 1.2–0.0 V.§ The potentiodynamic curves reveal the occurrence of the Cu^{2+}/Cu^{+} redox transition. The successive changes in these curves during the cyclic process suggested the possible conformational rearrangement of the complex in the course of the redox reactions and as a function of time. The stability of the polymer coating is fairly high and is independent of the degree of oxidation of the copper ion. In contrast to this, cobalt complexes decompose on transition of the metal to the bivalent state. The stability of the polymeric copper complex can apparently be explained by the formation of cross-linked structures,[71] as for the ruthenium complexes.[60]

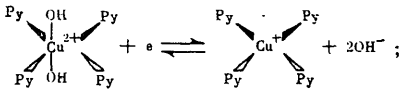
Analysis of the potentiondynamic curves at different rates of application of the potential and with a variable scanning amplitude suggests the presence of at least two types of coordination of copper as a function of the distance between the copper ion and the electrode surface.[43] One of these corresponds to the redox processes at the electrode–polymeric complex interface (type I copper) and the other to the processes occurring in the bulk of the polymer film (type II copper). The redox reactions of type I copper can be described by the following scheme on the basis of the data obtained:

§S.B.Orlov, M.R.Tarasevich, V.A.Bogdanovskaya, and V.S.Pshezhetskii, Elektrokhimiya, 1986, **22**, 768.



The surface groups of pyrographite or H_2O can serve as the ligand L. A significant feature of this scheme is the importance of the protonation–deprotonation reaction.

The maximum current for the redox reactions of type II copper is not a linear function of the rate of application of the potential. The following reaction most probably corresponds to this process:



Py = pyridine.

It is of interest to note that anodic polarisation at $E = 1.2$ V reduces the height of the anodic and cathodic maxima. The mechanism of this phenomenon can be formulated on the basis of the idea that there are different electrostatic repulsions between neighbouring copper ions in the oxidised and reduced forms, which leads to the contraction and expansion of the ion-containing polymer film in the course of redox reactions and the rate-limiting stage is the relaxation of the polymer chain.

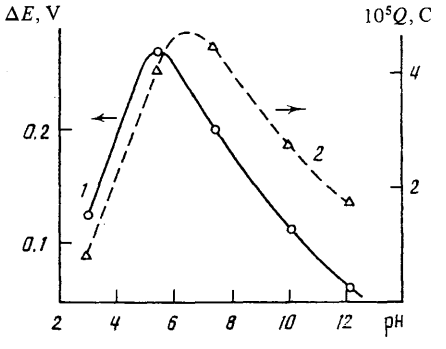


Figure 3. The pH dependence of the shift of the polarisation curve for the electrochemical reduction of oxygen relative to the background curve at $I = 0.03$ mA (curve *1*) and of the overall amount of electricity Q under the I–E curve obtained on pyrographite modified with Cu-P-4VP in the range of potentials 1.2–0.0 V (curve *2*).[43]

Whereas in the absence of copper ions in the polymer coating, the character of the I–E curves is influenced by the electrolyte cations, in the case of the copper-containing PVP the form of the potentiodynamic curves depends on the anionic composition of the electrolyte. Thus the replacement of the PO_4^{3-} ions by Cl^- yields more symmetrical potentiodynamic curves. In conformity with the ideas developed by Shigehara et al.[72], the observed phenomenon can be explained by the facilitation of charge transfer for the polymer layer as a result of migration whose rate is determined by the size of the diffusing counterion (in the given case Cl^-, OH^-, or PO_4^{3-}).

The dependence of the total amount of electricity under the I–E curve on the pH, reflecting the stability of the polymer complex, is illustrated in Fig. 3 (curve *2*). Comparison of this relation with literature data[73,74] shows that tetrapyridinate complexes formed at pH 5–6 are electrochemically active, while the dipyridinate complexes (pH 3–4) are electrochemically inactive. The decrease of the amount of electricity in alkaline solutions (pH > 7) is associated with the formation of copper hydroxide.

The complex character of the kinetic parameters obtained for the electrochemical behaviour of polymer electrodes indicates the necessity to resort to other physicochemical methods for the development of detailed ideas about the mechanism of the redox reactions. One can only note that the redox potentials of a whole series of polymer complexes in solution and in the immobilised state[75,76] change little in the irreversible interaction with the electrode, which indicates the absence of strong ion pairs[77] and shows that the environment of the copper ion on the electrode is close to its environment in aqueous solution.[78,79]

3. The Capacity of Protein Macromolecules for Oxidation-Reduction Reactions in the Immobilised State

The necessity to investigate the electrochemical behaviour of protein macromolecules arises from the prospect of the use of proteins and enzymes in electrocatalysis. The first studies on redox reactions of proteins and enzymes were carried out on mercury electrodes.[2,80,81] However, the interaction of a protein with mercury leads to the partial or complete uncoiling of the protein globule and either the denatured protein or the protein adsorbed on the second layer undergoes the oxidation-reduction reactions.[2] Furthermore, in their interaction with mercury, sulphur-containing proteins form compounds of the type $(HgS)_2$ and the potentiodynamic curves reflect their redox reactions.[81] It has been established that the potential of the oxidation-reduction reactions of these compounds is identical with the redox potential of the transition $HgS \rightleftharpoons Hg^{2+} + S^{2-}$ observed for a sulphur-containing aminoacid—cysteine.

In this respect, carbon materials are superior to mercury. In the first place, it has been shown[2,14,27] that proteins and enzymes retain their catalytic activity after adsorption on the carbon carrier and are therefore not denatured. Some decrease of activity may be explained by the restriction of mobility on formation of bonds between the surface groups of the protein globule and the corresponding groups of the sorbent.

The redox reactions of cytochrome *c* on carbon fibres have been described[26,82] and it has been shown that cytochrome *c* is oxidised and reduced almost reversibly. Our investigations¶ on a pyrographite electrode subjected to preliminary anodic-cathodic activation in the potential range 2.0 to −2.0 V showed that cytochrome *c* is oxidised and reduced at potentials close to the oxidation-reduction potential of the

¶V.A.Bogdanovskaya, A.M.Kuznetsov, M.R.Tarasevich, E.D.German, and E.F.Gavrilova, Elektrokhimiya, 1987 (in the press).

protein. The rate of reduction of the protein in the temperature range 5–20 °C is independent of temperature. Calculation carried out on the assumption that one electron is consumed on the reduction of the active centre of cytochrome *c* showed that the surface coverage of pyrographite by the protein does not exceed a monolayer.

It has been noted[83] that, in electrochemical systems with electrodes made of carbon materials, the redox reactions of the active centre may be accompanied by the oxidation of certain aminoacids, for example, tyrosine. However, this hypothesis is unlikely, because the oxidation of aminoacids at a potential of +0.66 V relative to the silver, silver chloride electrode is hardly feasible; it is contradicted by data on the electrochemical oxidation of aminoacids.[84–86]

The electrochemical reactions of enzymes on carbon materials have been investigated[81,87,88] and it has been shown[81] that peroxidase does not undergo redox reactions in the experimental potential range. On the other hand, when peroxidase is denatured, the haem liberated gives rise to almost reversible maxima. It has been stated that laccase is reduced on carbon black at a potential of 0.75 V.[87] The possibility of the oxidation-reduction of glucose oxidase has been noted,[88] but systematic studies of the oxidation-reduction properties of enzymes have not so far been carried out. One of the causes of this may be the high redox potentials of enzymes, which require the use of special electrode materials stable at these potentials. Mercury electrodes dissolve at fairly low potentials and carbon materials are corroded at potentials more positive than 1.0 V.

IV. CHARGE AND MATERIAL TRANSFER IN THE SURFACE LAYER

An adequate description of the mechanism of charge and material transfer in the surface layer at the interface between the conducting support and the bulk of the electrolyte is the main fundamental task in the problem of modified electrodes. Only on the basis of data for the mechanism and kinetics of transport stages can one estimate the possible limits of the acceleration of electrochemical reactions and optimise the electrocatalytic effect.

The main trends in the study of transport processes are the calculation of the rate of transfer of charged species, the search for phenomenological models for the representation of experimental data, and direct experimental investigation of the electron (charge) transfer stage.

In the case of monolayer coverage, the transport stages as such are absent and the mechanism of the electron transfer between the metal and the substrate is determined by the character of the electronic interaction of the metal, the catalytically active group, and the substrate. For a distributed catalytically active layer, the redox reaction of the substrate can occur throughout its bulk and electron transport is achieved via jump or mediator mechanisms, with the simultaneous diffusion of counterions. Depending on the morphology of the active film, account must be taken also of the diffusion of the substrate in the pores or through the film (Fig. 4).

As shown above, the redox potentials of compounds immobilised on electrodes differ little from the corresponding values in solution, which indicates rapid electron transfer in those cases where a direct electronic interaction of the active group and the support is established as a result of the overlap of the corresponding electron orbitals. In a series of studies,[3,67,89] the potentiodynamic *I–E* curves for surface-modified electrodes were examined quantitatively taking into account the interaction of neutral and charged surface groups, the heterogeneous properties of the surface, and the effect associated with the rearrangement of the surface layer as a function of time. The dependences of the potential of the maximum and of the current at the maximum on the rate of scanning of the potential are described by fairly complex equations. By means of numerical computer calculations, it is possible to "adjust" the shape of the calculated *I–E* curve to agree fairly well with the experimental curve. However, in view of the large number of initial assumptions, this can hardly serve as proof of their validity.

The general relations governing electron jumps via the tunnel mechanism† have been examined in a number of studies.[90–93] The influence of the degree of interaction of the adsorbate with the surface on the tunnel electron transfer in the electrode/adsorbate/redox pair system has been analysed. For a very strong interaction, a volcano-like dependence of the exchange current on the electron work function of the metal has been predicted.[92] The height of the potential barrier on the residence time of the electron in the intermediate state determines whether electron transfer is of the two-channel type or the multichannel type.

Tunnel electron transfer takes place in the redox reaction of immobilised ferrocene[94] at a distance of 8 Å from the surface of the electrode. The temperature variation of the rate of reaction obeys the Arrhenius equation. The change in the rate of reaction by two orders of magnitude on passing

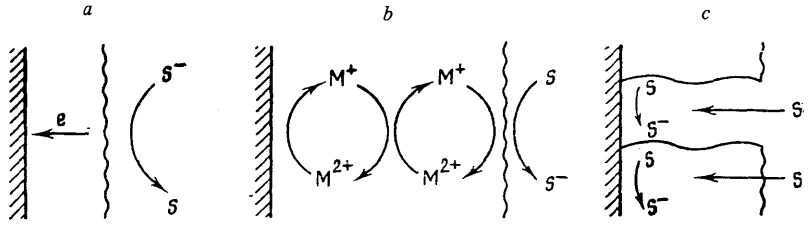


Figure 4. Methods of carrying out the redox reactions of the substrate S on surface-modified electrodes: *a*) injection of charge into the film; *b*) mediator transport (M = mediator); *c*) diffusion through the film or in the pores.[5]

†Since the number of studies devoted to tunnel transport is small, we shall employ the available data regardless of the type of conducting support.

from sulpholan to acetonitrile is associated with the change of the activation energy from 44 to 34 kJ mol^{-1}. Using the elastic tunnelling model, the authors[94] begin with the fact that the overall activation energy for the electronic transition in the given system is made up of the energies of the reorganisation of the solvent and of the change in the bond lengths. However, this assumption is arbitrary, since the first process is adiabatic and the other is not.

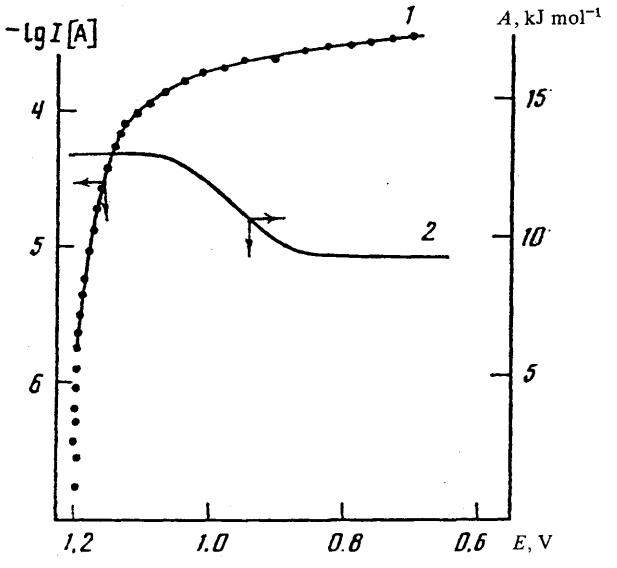


Figure 5. Dependence of the rate of electrochemical reduction of oxygen (curve *1*) and the activation energy for this reaction (curve *2*) on the potential of a carbon black electrode with immobilised laccase.[97]

Tunnel electron transfer has been examined as the transport stage for carbon electrodes modified by enzymes.[95-97] The dependence of the rate of the cathodic reduction of oxygen on a carbon black containing laccase on the thickness of the lipid layer between the protein globule and the support has been investigated.[95] For a thickness of the lipid layer in excess of 20 Å, the rate of reaction falls sharply, which is caused, according to the authors, by the decrease of the effective tunnel electron transfer. The estimates of the possible distance over which tunnel electron transfer takes place[95,97] were based on the hypothesis of rapid electron transfer between the electrode and the active centre and that the rate of the process is limited by the rate of the enzyme reaction.

Detailed studies of the kinetic characteristics and of the temperature variation of the rate of reaction[97] deepened the existing ideas about the mechanism of the bioelectrocatalytic oxygen reduction reaction. In the region of relatively low polarisations, the rate of the electrochemical reduction of oxygen is limited by the rate of the electron transfer stage and is described by the Tafel relation between the current and the potential (Fig.5). In the region of the limiting current, the process is controlled by the stage characteristic of enzyme catalysis.

In the region of low polarisations, the activation energy A is low and the acceleration of the reaction is to a large extent caused by the change in the pre-exponential factor ν in the equation

$$i=\nu\exp(-A/kT)\ .$$

Application of modern quantum theory[98] permitted the conclusion that a collectivised state of the adsorbent–adsorbate system arises in the immobilised laccase–carbon electrode system. The electron density is not localised on the active centre of the enzyme, because its interaction with the solvent is weak. The oxygen electrochemical reduction current is

$$i\cong\int d\varepsilon\rho_a(\varepsilon)f(\varepsilon)W(\varepsilon)\sim\rho_a(\varepsilon^*)f(\varepsilon^*)W(\varepsilon^*)\ ,$$

where $f(\varepsilon)$ is the Fermi function of the distribution of the energy of the electrons, $W(\varepsilon)$ the probability of electron transfer from the level ε on the active centre to the substrate molecule, $\rho_a(\varepsilon)$ the density of electronic states associated with the active centre, and ε^* the energy for which the contribution to the total current is a maximum. Since the active centre of the enzyme is at a distance of ~10 Å from the electrode their potentials are different. The dependence of the pre-exponential factor on the potential is then determined by the influence of the latter on the energy of the electronic level of the active centre of laccase.

In the study of charge transfer# in multilayer (including polymer) electrodes containing active centres, three possible mechanisms are taken into account: electron jumps, exchange of electrons between the active centres, and the diffusion of counterions. It is usually assumed that the electron transfer process through the polymer is analogous to diffusion:[99]

$$D_{exp}=D_0+\pi k\delta^2c/4\ , \qquad (1)$$

where D_0 characterises the actual contribution of diffusion, k is the rate constant for electron exchange between the redox centres in the polymer layer, c the concentration of the species reduced at the electrode, and δ the distance over which the electron is transferred.

In order to elucidate the mechanism of electron transfer, one investigates the influence on the latter of temperature, the type of solvent, the nature of the electrolyte, the degree of cross-linking of the polymer, and the concentration of charges. The determination of the apparent diffusion coefficient D_{exp} for a polymer of the nafion type on a pyrographite electrode[101] showed that the charge transfer mechanism depends on the type of cation incorporated. Fig.6 illustrates schematically the dependence of D_{exp} on the concentration of active groups for polymers of two types differing in the strength of attachment of the active centres. An example of the system of type (*a*) is provided by a copolymer containing ruthenium and osmium ions;[102] the system (*b*) obtains for a polymer containing the $Ru(bipy)_3^{3+/2+}$ ions.[101] Section *2* is described in both cases by Eqn.(1) presented above. In region *3*, the rate of transfer is determined by the mobility of the polymer lattice or polymer chains. In region *1* (*a*), ions are separated by a distance greater than the characteristic diffusion distance and the rate of transfer diminishes. Region *1* (*b*) corresponds to simple diffusion of ions. Comparison of the diffusion coefficient and of the rate of quenching of the luminescence of $Ru(bipy)_3^{2+}$ [103] leads to the conclusion that the slow stage is the movement of counterions. The diffusion mechanism is

#The electronic properties of the polymers themselves, including those which have been doped electrochemically, have been examined in a review[100] and a monograph.[101]

most important for thick films and when there is a significant difference between the potentials of the substrate and the attached mediator.

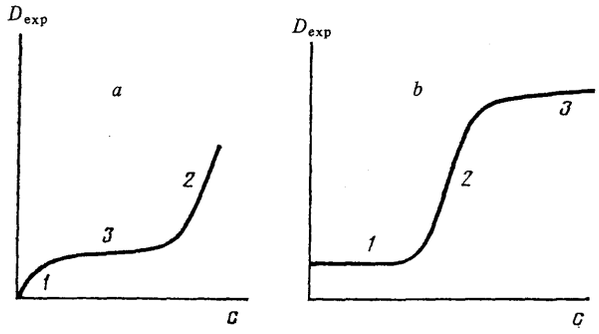


Figure 6. Schematic illustration of the dependence of D_{exp} on the concentration of active groups for polymers with chemically attached (*a*) and electrostatically bound (*b*) ions; for the characteristics of sections *1–3*, see text.[101]

A series of experimental facts outside the framework of the ideas formulated above have been described in the literature. Thus it has been observed[104] that, when copper ions are incorporated in polyphenol oxidase films at Cu^{2+} concentrations above the critical value, there is an avalanche-like increase of the rate of electron transfer. A phenomenon, previously unknown, involving an increase in the polarisation capacity in the pyrographite–polymer–electrolyte system has been described.[69,70] The magnitude of the effect depends on the nature of the cation and decreases with decrease of the radius of the hydrated cation. It has been suggested that this is associated with the shielding by the cationic charge of the free electrons of the support, entering the polymer layer, and not with the doping of the polymer by electrolyte cations.

The ideas about the mechanism of charge transport are used to solve two main problems: the analysis and quantitative description of the redox reactions in the surface layer and the estimation of electrocatalytic effects which can be attained using electrodes of the type considered. In the interpretation of the form of the *I–E* curves, one begins with the idea of slow heterogeneous electron transfer and data on the kinetics of the reorganisation of the film and the interaction within the film.[67,105]

An attempt has been made to estimate the efficiency of electrocatalysis on the surfaces of modified electrodes compared with homogeneous catalysis. It has been shown[89] that, for the same activation energy, homogeneous catalysis is more effective than electrocatalysis under conditions where the concentration of the active centres corresponds to monolayer coverage. Bearing in mind the influence of binary and ternary collisions and also the electrostatic work of the double layer and the reflection layer, large effects cannot be expected in the case of an outer-sphere mechanism of electrocatalysis. This is confirmed by calculations for a surface-modified disc electrode.[89]

In estimating the electrocatalysis effect for electrodes with a distributed active layer, one must take into account the rate of transfer of both electrons and of the substrate to the active centre. Various instances of electrocatalysis on polymer electrodes with redox centres have been investigated theoretically and experimentally.[106,107] If the electron transfer stage is rapid (on the electrochemical scale), then polymer or multilayer coatings are useful when the transport stage is relatively slow and the films are readily permeable. However, this conclusion is hardly valid if the polymer exhibits electronic conductivity[108] or when a conducting filler, for example, carbon particles, has been introduced into the film.

The stationary diffusion equations for a disc electrode coated by an electrochemically active polymer film have been examined.[89,109] In this case the thickness of the diffusion layer δ is replaced by the quantity $\delta' = l + (D_f/D_s)_\delta$, where D_f and D_s are the diffusion coefficients in the film and in the free solution. If the rate of diffusion in solution is much smaller than in the film ($D_s/\delta \ll D_f/\delta$), then the usual voltage–current curves are obtained. For the opposite relation, the system becomes more reversible than on the "clean" electrode. However, this is manifested by the approach of the half-wave potential to the reversible value and not by the increase of the overall current.

V. NON-ELECTROCATALYTIC REACTIONS ON MODIFIED ELECTRODES

In simple oxidation-reduction reactions unaccompanied by a redistribution of the bonds or strong coordination of the molecules, the modifying groups serve as mediators in electron transfer processes. The rates of reaction of this type are independent of the nature of the electrode material after the application of corrections for changes in the structure of the double layer, but data for their kinetics yield much information necessary for the understanding of the mechanisms of electrocatalytic reactions.

Three types of non-catalytic reactions on surface-modified electrodes are possible. If the substance is oxidised more readily than the mediator modifying the surface and the film of the modifying agent is poorly permeable to the reacting substance, the process proceeds on the outer boundary at the redox potential of the mediator. If the redox potentials of the mediator and the reactant are equal, the reaction proceeds in the same way as on an unmodified surface. The third case, where the mediator is oxidised more readily than the substrate and its transfer becomes dominant, is of greater interest. This mechanism has in fact been observed.[110] The complex $K_4Mo(CN)_8$, introduced into a PVP film on pyrographite, can act both as an oxidant and as a reductant. The processes occurring in the system are illustrated schematically in Fig. 7. The redox potential of the $Mo(CN)_8^{4-}/Mo(CN)_8^{3-}$ transition for the complex incorporated in the film is +0.52 V, while for the Fe^{2+}/Fe^{3+} system it is +0.49 V. The closeness of these redox potentials makes it possible to accelerate both the oxidation of Fe^{2+} and the reduction of Fe^{3+}. The above hypotheses are confirmed by the curves (Fig. 7) obtained for electrodes of three types: unmodified, modified with PVP, and modified with PVP containing the complex $K_4Mo(CN)_8$.

The second cause of the interest in non-catalytic reactions on modified electrodes is the possibility of investigating the redox reactions of proteins on such electrodes. Studies of the electrochemical reactions of their active centres are of special interest. In such systems, the modifying agents play the role of mediators and at the same time serve as enzyme substrates, which makes it possible to achieve the redox transformations of the active centres. As a rule the redox reactions of proteins are investigated on modified

metallic electrodes. Thus the immobilisation of methyl- or benzyl-viologen on gold makes it possible to carry out the oxidation-reduction reactions of myoglobin,[111] while the immobilisation of polyvinylviologen permits the reduction of cytochrome *c*.[112] Cytochrome *c* can be oxidised and reduced electrochemically on gold and platinum electrodes with adsorbed 4,4′-bipyridyl.[113]

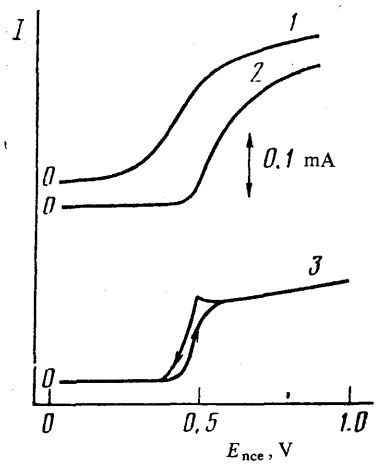


Figure 7. Polarisation curves for the oxidation of Fe^{2+} (at a concentration of 4 mM) at pH 1.5 and $\nu = 0.0075$ V s^{-1} at a rotating pyrographite electrode (curve *1*) and a pyrographite electrode modified with PVP (curve *2*) and the PVP–$Mo(CN)_8^{4-}$ complex (curve *3*).[110]

On a carbon surface, the redox reactions of proteins have been observed both after the modification of the electrode and after the preliminary electrochemical treatment of the surface. Cytochrome *c* is reduced on pyrographite modified by polymeric methylviologen[114] and peroxidase, glucose oxidase, and xanthine oxidase, as well as certain other enzymes are reduced on vitreous carbon.[115,116] The electrochemical reactions of laccase occur in the presence of a whole series of modifying agents and the positions of the potential maxima depend on their nature. On modification of 2,9-dimethylphenanthroline, the maximum is at 0.64 V, while on modification with 4,4′-bipyridyl it is at +0.74 V (n.h.e.).[115,117]

The anodic-cathodic treatment of the surface can result in the appearance of a large number of oxygen-containing groups which function as modifying agents. The redox reactions of cytochrome c have been observed on electrochemically treated carbon materials.[26] It is most likely that oxygen-containing groups, including quinone-hydroquinone groups, effect the oxidation-reduction reactions of the active centres of the proteins via the mediator mechanism.

VI. THE MECHANISMS OF ELECTROCATALYTIC REACTIONS

By virtue of the possibility of the specific creation of an active layer, surface-modified electrodes have been finding increasing application in a whole series of electrocatalytic reactions, because they exhibit an increased selectivity and a high catalytic activity.

1. The Activation of Organic Molecules

The oxidation reactions of organic molecules proceed as a rule at high anodic potentials on platinum group metal electrodes. The use of surface-modified electrodes permits in many cases the elimination of noble metals or it is even possible to achieve reactions which cannot occur on other electrodes.

Using modified pyrographite, sulphoxide has been synthesised[118] and anisole and toluene have been chlorinated.[119] The yield of the target products, namely carbinol and pinacol, on a graphite electrode modified with amine depended on the nature of the surface oxides.[119] In the presence of basic oxides, pinacol was synthesised preferentially, while on a surface coated with acid groups, carbinol was the main product. Presumably the strength of the bond between the modifying amine and the electrode surface plays an important role.

Data have been published[55] on the acceleration of the oxidation of ascorbic acid on pyrographite electrodes with chemically bound benzidine. It is noteworthy that preliminary treatment with plasma leads to an increase of the true surface area of the pyrographite electrode and the true acceleration effect is therefore not unduly great. Graphite electrodes modified with vinylferrocene are the most effective in this reaction.[120] The electrocatalytic current is limited by the rate of diffusion of ascorbic acid in the polymer film. The graphite electrode modified with quinone[54] accelerates the electrochemical oxidation of NADH to NAD^+. The oxidation of NADH is accelerated to an even greater extent in the presence of polymer films of dopamine (DP), phenazine methanesulphonate (PPMS), and phenazine ethanesulphonate (PPES).[121] [The latter two films are not mentioned in Ref.121 (Ed.of Translation)]. Data concerning the acceleration of the reaction in the presence of the above compounds are compared in the Table. It is noteworthy that the half-wave potentials ($E_{1/2}$) and current maxima (E^*) for the oxidation of NADH (see Table) are remote from the redox potential of the $NADH/NAD^+$ pair, which is −0.56 V (s.c.e.).

The half-wave potentials ($E_{1/2}$) and the potentials at the maximum (E^*) for the oxidation of NADH on electrodes modified by different compounds at pH 7.0.[121]

Type of modifying agent	Quinone	PD	PPMS	PPES
$E_{1/2}$, V	+0.16	+0.12	−0.16	−0.21
E^*, V	+0.26	+0.21	−0.05	−0.10

The high catalytic activity of pyrographite modified with tetrasulphonated water-soluble phthalocyanine complexes of iron and cobalt in the oxidation of certain organic molecules has been noted.[1,2] The phthalocyanine complex of cobalt accelerates the oxidation of cysteine to cystine. In both acid and alkaline solutions, the slope of the Tafel curve is close to $2 \times 2.3RT/F$. In the region pH < 8.5, we have $\partial \lg i / \partial \text{pH} \cong 1$, whereas at higher pH the corresponding function is close to zero. These kinetic parameters correspond to the following possible reaction mechanisms:

$$R{-}SH \rightleftharpoons RS^- + H^+,$$
$$RS^- \rightarrow RS^{\cdot} + e,$$
$$2RS^{\cdot} \rightarrow R{-}S{-}S{-}R.$$

The use of carbon electrodes modified by enzymes for the oxidation of various organic substrates has been examined fairly fully.[96] Enzymes of the oxidase class—cytochrome b_2, peroxidase, glucose oxidase, xanthine oxidase, and galactose oxidase—effect the reaction of their substrates in the immobilised state on the electrode. Two reactions take place consecutively on two-enzyme electrodes based on glucose oxidase and peroxidase:

$$\text{glucose} + O_2 \xrightarrow{\text{glucose oxidase}} \delta\text{-gluconolactone} + H_2O_2;$$

$$H_2O_2 + 2Fe(CN)_6^{4-} + 2H^+ \xrightarrow{\text{peroxidase}} 2Fe(CN)_6^{3-} + 2H_2O.$$

Xanthine oxidase or uricase may be used in two-enzyme electrodes. Analysis of the experimental data shows that the rate-limiting stage in the overall process is the first reaction,[123] i.e. the oxidation of glucose, hypoxanthine, or uric acid. The efficiency of such electrodes is extremely low and the creation of electrochemical sensors for the detection of various substrates is a more realistic application of such devices.

Immobilised enzymes belonging to the class of dehydrogenases can be used for the oxidation of organic substrates. As a rule, the regeneration of coenzymes, which can be achieved with the aid of enzymes, is essential for their functioning. NAD was regenerated in the presence of alcohol dehydrogenase and lactate dehydrogenase.[124] However, such a system is unduly complex and its employment is hardly promising.

Enzyme electrodes based on hydrolases immobilised on a graphite paste electrode or vitreous carbon have been examined.[96] The enzymes are retained in the vicinity of the electrode surface with the aid of membranes. The operation of such electrodes is based on the fact that the hydrolase, for example, cholinesterase, effects the reaction which is typical for such enzymes, involving the cleavage of a covalent bond in the substrate, while the product of the enzyme reaction participates in the electrochemical reaction. Catechol mono-orthophosphate, indoxyl acetate, and other substrates have been oxidised in this way.[96]

The mechanisms of the electrochemical oxidation reactions on electrodes whose surfaces have been modified by enzymes have been studied little. As a rule, the authors confine themselves to comparing the enzyme and electrocatalytic activities and to the calculation of the Michaelis constant. On the basis of these data, it is concluded that the nature of the rate-limiting stage is kinetic or diffusional.[96] Systems in which the electrochemical and enzyme reactions are coupled with the aid of mediators have been studied in greater detail. In essence, such systems do not belong to the class of surface-modified electrodes, because the enzyme immobilised on the electrode effects the enzyme reaction and the acceleration of the electrode reaction is due to the overall effect of all the processing occurring in the system.

Our studies on the oxidation of model compounds derived from lignin (hydroquinone, guaiacol, syringol, and veratrole) on a carbon black electrode modified with laccase demonstrated the possibility, in principle, of the oxidation of these compounds.§ According to the results of chromatographic analysis, the products of electrochemical oxidation on the unmodified and laccase-modified carbon black electrodes are different.

§V.A.Bogdanovskaya, M.R.Tarasevich, and V.G.Vorob'ev, in "Novosti Elektrokhimii Organicheskikh Soedinenii" (New Aspects of the Electrochemistry of Organic Compounds), Moscow–Lvov, 1986, p.65.

2. Acceleration of the Hydrogen Evolution Reaction

Carbon materials modified by titanium compounds, namely $C-OTiCl(OC_2H_5)_2$ or $C-OTiCl(OH)_2$, have been used to activate the hydrogen reaction.[39] The potentiodynamic curves obtained for such electrodes show an anodic maximum in the potential range between −0.3 and −0.4 V after cathodic polarisation to $E = -0.6$ V. After prolonged cycling, the shape of the curves does not change, which indicates fairly strong binding of the titanium compounds. With increase of the amount of attached compound, the rate of hydrogen evolution also increases. The reaction on the unmodified carbon material may be represented as follows:

$$2Ti^{IV} \xrightarrow{2e} 2Ti^{III} \xrightarrow{2H^+} 2Ti^{IV} + H_2.$$

The reverse reaction involving the anodic oxidation of molecular hydrogen is not accelerated in the given system, which agrees with the results of a study[125] where it was shown that carbon modified by titanium compounds does not catalyse the hydrogenation of aromatic compounds by molecular hydrogen.

Carbon materials with an immobilised hydrogenase have been used[2,126] to accelerate the electrochemical oxidation of hydrogen. Methylviologen (MV) was used as the mediator in this system. The redox potential of the MV^{2+}/MV^+ pair is +0.011 V, i.e. is extremely close to the equilibrium hydrogen potential. The overall result of the set of reactions is the oxidation of molecular hydrogen:

$$E + H_2 \rightleftharpoons EH_2,$$
$$EH_2 \rightleftharpoons EH^- + H^+,$$
$$EH^- + MV^{2+} \rightleftharpoons MV^{\ddagger} + E + H^+ + e,$$
$$MV^{\ddagger} \rightarrow MV^{2+} + e,$$
$$E = \text{enzyme}.$$

The activity of the immobilised hydrogenase and the rate of reaction are higher the greater the amount of enzyme adsorbed on the carbon black, which may be due to the fact that at low coverages there is a strong interaction of the enzyme with the carrier leading to partial denaturation of the protein. With increase of the surface coverage, the interaction of the enzyme with the support weakens, the molecules are oriented in the most favourable manner, and the activity of the enzyme approaches that of the native form.

Kinetic studies have been made of the hydrogen reaction under the conditions of the direct electron transfer from the active centre of the enzyme to the electrode.[127] However, analysis of the electrochemical data refers to the range of potentials where the process is concentration dependent and the observed stoichiometric number yields no information about the mechanism of the kinetic stage.

The use of electrodes modified by polymers and complexes based on them for the activation of the hydrogen reaction has not as yet been described.

3. The Oxygen Reaction

The majority of studies of the use of surface-modified electrodes in electrocatalysis are associated with the reduction of molecular oxygen. At the present time several ways of making modified electrodes for this purpose have been developed: the binding of quinones and phenanthroline and bipyridyl complexes and N_4-complexes, the "assembly" on the electrode surface of polymer systems of various types, and finally the modification of the electrode surfaces by enzymes.

Fig.8 presents the group of quinones which have been used to accelerate the reduction of oxygen in neutral electrolytes.[39] When the quinones R^3 and R^4 with asymmetric substituents are adsorbed, steric hindrance obtains, and they exhibit only

a weak catalytic activity. On the other hand, the molecules of R^2 and R^5, which each contain two NH_2 groups, apparently assume a planar disposition on the surface and in their presence the highest stationary potential $E = 1.02–1.05$ V is established on the charcoal. At a current of 0.25 mA g^{-1}, the shift of the electrochemical reduction potential of oxygen in the positive direction is more than 0.3 V.

A large group of relatively simple copper, cobalt, manganese, and iron complexes of *NN'*-disalicylidene-ethylenediamine, adsorbed on a pyrographite electrode, have been investigated. αα'-Bipyridyl and *o*-phenanthroline are known as ligands with a polyfunctional activity which can participate in the resonance transfer of electrons via systems of conjugated bonds. Furthermore, they are effective catalysts of the oxidation of various substrates by molecular oxygen in homogeneous systems.[128,129] Fig. 9 illustrates the polarisation curves obtained at disc and ring electrodes for an approximately monolayer coverage of the disc electrode surface by the complex investigated. In the presence of cobalt complexes (curves *2*, *2'*, *3*, and *3'*) the half-wave potential shifts in the positive direction, but oxygen is reduced solely via the formation of hydrogen peroxide. When copper complexes are deposited (curves *4* and *4'*), the reaction proceeds both via the intermediate formation of hydrogen peroxide and with direct reduction to water, the ratio of the constants $K_1/K_2 = 0.23$ for $[Cu(5NO_2phen)]Cl_2$. The activity of the copper complexes depends on the degree of surface coverage by the latter and on the type of substituents. The activity is a maximum for a low coverage and falls when the coverage increases. This type of dependence can be explained if it is assumed, by analogy with homogeneous catalysis,[129] that the substrate (O_2) and the electrode surface are in the *cis*-conformation relative to the central ion of the adsorbed complex. The synchronous transfer of two electrons to the oxygen molecule is possible under these conditions. With increase of the degree of surface coverage, the possibility that such a conformation occurs diminishes, and the activity falls. Thus, in the case of phenanthroline complexes of copper, the role of the support (the carbon material) is manifested directly. The study of Vol'pin et al.[18] is the first in which it was possible to achieve the electrocatalysis of the oxygen reaction by organic copper complexes.

The tetrasulphonated phthalocyanine complexes of cobalt,[15,130] haemin and the chlorin e_6 complex of iron,[21] and the porphyrin complexes of iron and cobalt[131] exhibit a notable electrocatalytic activity in the cathodic reduction of oxygen.

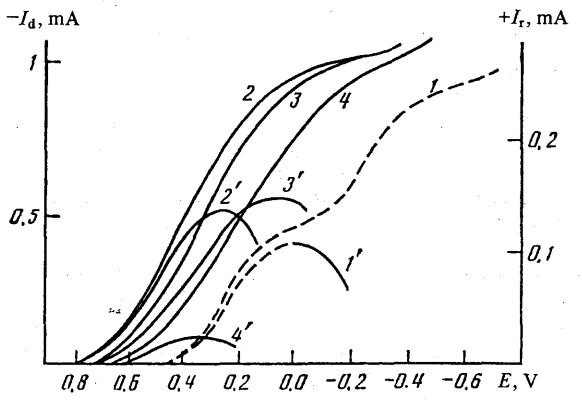


Figure 9. Polarisation curves for the electrochemical reduction of oxygen on a platinum disc electrode (curves *1–4*) and for the oxidation of hydrogen peroxide on a platinum ring electrode (curves *1'–4'*) in the absence (curve *1*) and presence of the complex adsorbed on the disc electrode: *2*) cobalt–salen; *3*) cobalt–decamethyloctadehydrocorrin; *4*) $[Cu(5NO_2phen)]Cl_2$.[18]

The mechanism of the reduction of oxygen by these substances differs little from that which obtains on carbon materials coated by a thick layer of the N_4-complexes.[130] The adsorbed phthalocyaninecobalt complex accelerates only the two-electron reaction and the phthalocyanineiron complex promotes the occurrence of the direct reduction to water.[130]

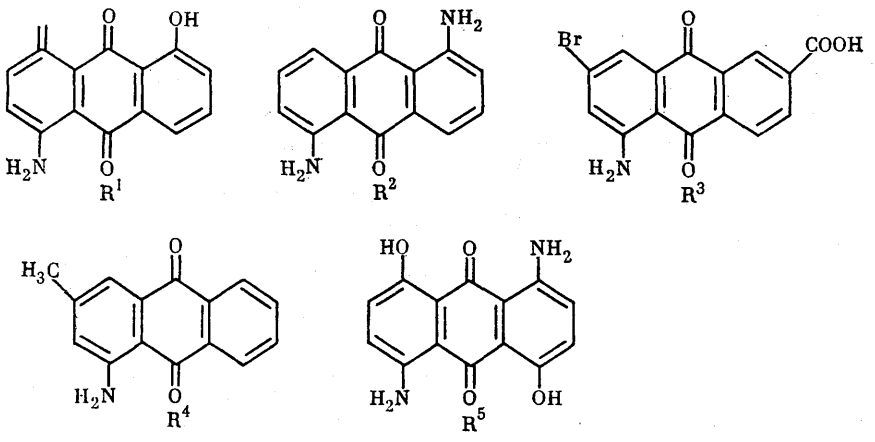


Figure 8. Different types of quinones used for the surface modification of carbon materials.[39]

In the region of high polarisation the slope of the $-\lg I-E$ plots is close to $2 \times 2.3\ RT/F$, which corresponds to slow addition of the first electron. For low polarisations, $\partial E/\partial \lg I$ ranges from $2.3\ RT/2F$ to $2.3\ RT/F$. According to the authors,[130,131] this is due to the approach to the O_2/HO_2^- equilibrium in alkaline electrolytes at low polarisations. According to Zagal et al.[130], such slow slopes can be accounted for also by the operation of different versions of the redox mechanism:

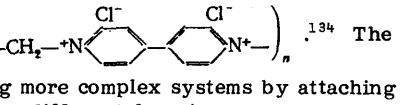
$$M^{III}OH + e \rightleftharpoons M^{II} + OH^-,$$
$$M^{II} + O_2 \rightleftharpoons M^{III}—O_2^-,$$
$$M^{III}—O_2^- + H_2O + e \rightarrow M^{III}—H_2O_2 + OH^-.$$

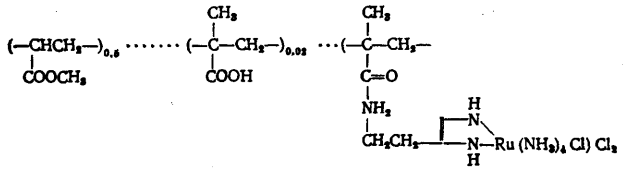
Unfortunately, lack of data for the surface coverage of the electrode by N_4-complexes hinders the quantitative comparison of the electrocatalytic properties of the complexes at a molecular level and the elucidation of the role of the carbon support.

Dinuclear complexes—covalently bound ("face to face") porphyrins—have been used recently[132] to modify the carbon surface. The activation of oxygen by these complexes can be represented schematically as follows:

$$LCo^{III}—Co^{III}L + 2e \rightarrow LCo^{II}—Co^{II}L,$$
$$LCo^{II}—Co^{II}L + O_2 \rightarrow LCo^{II}—O—O—Co^{II}L,$$
$$LCo^{II}—O—O—Co^{II}L + H^+ \rightarrow [LCo^{II}—OH—O—Co^{II}L]^+,$$
$$[LCo^{II}—OH—O—Co^{II}L]^+ + 2e + 3H^+ \rightarrow LCo^{III}—Co^{III}L + 2H_2O.$$

The 4-atom connecting chain between the ligands apparently corresponds to the optimum conditions for the coordination of the oxygen molecule between two cobalt atoms. When the monomer and the dinuclear cobalt dimer with the connecting fixed atom chain are adsorbed on pyrographite, the oxygen reduction reaction in an acid medium (0.5 M $HClO_4$ or CF_3. .COOH) is accelerated compared with pure pyrographite, but proceeds via the intermediate formation of hydrogen peroxide. The quantity $\partial E/\partial \lg I \cong 2.3 \times 2RT/F$ agrees with the concept of the slow transition of the first electron.

The use in electrocatalysis of carbon electrodes modified by polymers constitutes an exceptionally promising trend. Polyfunctional electrocatalysts ensuring the simultaneous transfer of more than one electron in the slow stage, the optimum hydrophobic–hydrophilic environment in the active centres, and the reversibility of the protonation reaction can be created on their basis. However, despite the fact that an enormous number of studies on the electrochemical properties of polymer electrodes have been carried out, at the present time there have been only isolated studies devoted to electrocatalysis on such electrodes. The properties of polymeric acrylonitrile films on vitreous carbon and platinum have been investigated in the oxygen reaction.[133] Some acceleration of the electrochemical reduction of oxygen has been observed on the pyrographite electrode in the presence of a polymer coating made up of polyxylylviologen with a molecular weight of 11000: .[134] The possibility of constructing more complex systems by attaching two active groups fulfilling different functions was reported in the same communication. The ruthenium(III) complex of the polymer is a highly active catalyst of the electrochemical reduction of hydrogen peroxide:



The complex is soluble in water but becomes insoluble at an electrolyte concentration in excess of 0.1 M. This makes it possible to obtain a stable polymer coating on the pyrographite surface. The complex $[Cu(o\text{-phen})_2(ClO_4)_2]$, which is a highly effective catalyst of the two-electron reaction, is added to the immobilised polymer. Thus the simultaneous attachment to the pyrographite electrode of two active groups permits the creation of an electrocatalyst of the reduction of oxygen to water.

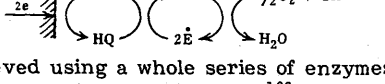
The PVP complex of copper shows a high catalytic activity in the cathodic reduction of oxygen.[43] However, its activity falls rapidly. Thus in the absence of current a potential of 1.15 V was recorded in the initial instance. The potential then shifts in the cathodic direction and is stabilised near 0.9 V. The stationary potential, established for charcoals modified by the complex, is higher than for pyrographite electrodes and reaches 1.2 V.

There is a correlation between the degree of saturation of the polymer by copper ions and the electrocatalytic activity, whose measure is the shift of the polarisation curve relative to the background curve. The extremum in the relation between the activity of the modified electrode and the pH (Fig. 3, curve *1*) can be explained by taking into account data on the stability of the polymer complex. It has been shown[73,74] that copper mono- and di-pyridinate complexes are formed at pH 3–4 and are converted into the tetrapyridinate complexes at pH 5–6. One may therefore conclude that copper tetrapyridinate complexes exhibit catalytic activity. The pH dependence of the total amount of electricity corresponding to the redox transitions for the modified electrode (Fig. 3, curve *2*) also passes through an extremum, which confirms the hypothesis that copper tetrapyridinate complexes are electrochemically active. The decrease of the amount of the active complex with alkaline pH can be explained by the decomposition of the catalytic complex with formation of copper hydroxide.

As the particle size of the highly disperse carbon materials increases, the catalytic activity of the complex also rises for low polarisations.[43] Having compared this result with data showing that the high-molecular-weight polymer (molecular weight 160000) is 2.5–4 times less active than the polymer having a lower molecular weight (50000), one may suppose that, depending on the ratio of the sizes of the polymer globule and the carrier particles, the character of the adsorption varies.[43] The difference between catalytic activities can be caused by the different macrokinetic characteristics of the highly disperse carbon catalysts and the polymers with different molecular weights deposited on them.

The most stable equilibrium oxygen potentials have been obtained using enzymes as modifying agents for the carbon surface.[2,22,23,27–29,135]

The mediator mechanism of the acceleration of the electrochemical reduction of oxygen, i.e.



has been achieved using a whole series of enzymes immobilised on carbon materials: peroxidase,[136] cytochrome *c* oxidase,[137] tyrosinase,[135] and laccase.[26]

In the case of the electron-transport protein cytochrome *c* [21] and also the enzymes tyrosinase [135] and laccase,[22,26] it has been possible to achieve a non-mediator mechanism of acceleration of this process in neutral solutions. The most reproducible data have been obtained with laccase. The adsorption of the enzyme on carbon black electrodes is almost irreversible. The parameters $\partial E/\partial pH$ and $\partial E/\partial \lg p_{O_2}$ for this electrode correspond to the coefficients of the Nernst

equation for the O_2/H_2O pair. The small deviation from the theoretical equilibrium potential is apparently caused by the local increase of the pH in the layer of the adsorbed protein relative to the pH in the bulk of the solution.

The mechanism of the electrocatalytic reduction of molecular oxygen by immobilised laccase has been studied in detail.[97] The observed variation of the rate of reaction with the pH, the oxygen pressure (Fig.10), the concentration of laccase inhibitors (Fig.11), and temperature suggested the following mechanism of the activation of molecular oxygen in the electrode/laccase/oxygen system:

$$E + O_2 \rightarrow EO_2 \qquad (\Delta E = 0.2 - 0.6\,V),$$
$$EO_2 + e \rightleftharpoons EO_2^- ,$$
$$EO_2^- + H^+ \rightarrow EO_2H \qquad (\Delta E = 1.15 - 1.10\,V),$$
$$EO_2H + 2e + H^+ \rightarrow EO^- + H_2O \qquad (\Delta E = 1.20 - 1.15\,V),$$
$$EO^- + e + H^+ \rightarrow EOH^-,$$
$$EOH^- + H^+ \rightarrow E + H_2O .$$

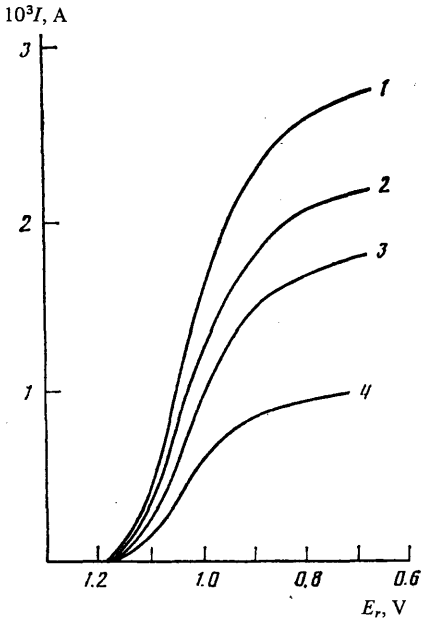


Figure 10. Polarisation curves for the electrochemical reduction of oxygen on an electrode with immobilised laccase at pH 4.5 and different oxygen partial pressures (atm): *1*) 1; *2*) 0.3; *3*) 0.25; *4*) 0.12.[97]

On the basis of the entire set of data, one may regard as entirely justified the claim that, in the region of low polarisations, the rate of electrochemical reduction of oxygen is limited by the rate of electron transfer stage, while in the region of the limiting current it is limited by the stage characteristic of enzyme catalysis. In the latter case, the dependences of the rate of the electrochemical reaction on the pH, the oxygen pressure, and the concentration of the inhibitors should be analogous to the experimentally observed dependences for the enzyme reaction[97] (Figs.10 and 11). In the region of low polarisations, the Tafel relation between the rate of reaction and the potential is observed, which shows that the electron transfer stage is slow.

The temperature variation is important for the elucidation of the mechanism of the cathodic reduction of oxygen on the enzyme electrode. In the first place, one should note that, over the entire potential range, the Arrhenius relation between the rate of reaction and temperature holds. The activation energy in the experimental potential range varies from 14.0 to 9.0 kJ mol^{-1} as the potential shifts in the cathodic direction (Fig.5).[97] Within the framework of the proposed mechanism of the electrocatalysis of the reduction of oxygen on the electrode with immobilised laccase, the rate-determining stage in the region of high polarisations is that characteristic of the enzyme reaction—this may be the binding (adsorption) of molecular oxygen to the active centre of laccase. The activation energy found in this range of potentials is virtually identical with the activation energy for the phenol oxidase reaction of the solubilised enzyme (10 kJ mol^{-1}). The activation energy for the solubilised enzyme was determined from the rate of oxidation of hydroquinone by atmospheric oxygen in the same temperature range as in the electrochemical reaction. Thus the conclusion that the slow stages in the enzyme reaction and in the biocatalytic reduction of oxygen are the same in the range of potentials more negative than 0.8 V has been confirmed.

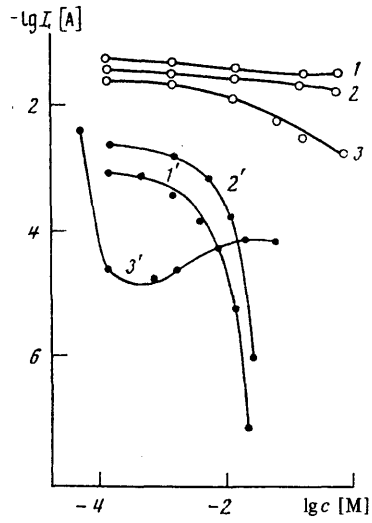


Figure 11. The influence of the concentration of inhibitors on the electrocatalytic activity of the electrode with immobilised laccase in the reduction of oxygen at pH 4.5; curves *1*–*3* were obtained for E = 0.8 V and curves *1'*–*3'* for E = 1.15 V in the presence of different ions: *1*) and *1'*) iodide; *2*) and *2'*) chloride; *3*) and *3'*) fluoride.[97]

In the region of low polarisations, the activation energy is likewise low. As shown above (Section IV), the rate-limiting stage is electron transfer from the active centre of the enzyme to the oxygen molecule.

Other examples of electrocatalysis on carbon electrodes modified by enzymes have also been described. In the presence of peroxidase adsorbed on pyrographite or carbon black,[23] a stationary potential ranging from 1.05 to 1.24 V is established in a hydrogen peroxide solution. Since the active centre of peroxidase (haemin) accelerates the reaction

of H_2O_2 to an insignificant extent, peroxidase functions as the electrocatalyst, retaining its integrity and catalytic activity on immobilisation.

Comparison of data for the application of chemically modified carbon electrodes in electrocatalysis shows that the most important results have been achieved for enzyme electrodes. In the immediate future, one can probably expect the creation of active surface-modified electrodes on the basis of synthetic polymer systems. However, the lack of methods for the creation of such electrodes with an adequate chemical and electrochemical stability and activity in the anodic oxygen evolution reaction and other anodic reactions of electrochemical synthesis at high anodic potentials constitutes a serious gap. This problem is one of the most urgent in electrochemistry.

Analysis of the available data shows that the creation of electrodes on the basis of polymer systems closest to macromolecular biological systems is likely to be most useful.

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