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Electrocatalysis on Metalloporphyrins

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Results of theoretical and applied research on electrocatalytic reactions—the cathodic reduction of oxygen, hydrogen peroxide, and carbon dioxide and the anodic oxidation of organic and inorganic substances—on metalloporphyrins are analysed with a list of 132 references.

CONTENTS

I.	Introduction	718
II.	Electrophysical and catalytic properties of metalloporphyrins	718
III.	Kinetics and mechanism of the electroreduction of oxygen on metalloporphyrins	720
IV.	Use of organic complexes of metals to produce gas-diffusion electrodes	725
V.	Electrochemical reactions of hydrogen peroxide and other electrocatalytic reactions	726

I. INTRODUCTION

Organic complexes of metals constitute a novel and extremely promising class of electrocatalysts. Among them compounds containing as ligands various porphyrin derivatives (metal phthalocyanines, tetra-arylporphyrins) attract especial attention. The possibility of using these compounds as electrode materials is due to three main factors—great activity in various heterogeneous redox reactions, semiconductor properties, and high chemical and thermal stability—and would provide a method for replacing catalysts based on precious metals. Enlargement of the scale of application of new technical electrochemical processes, e.g. in sources of current, the photoelectrochemical transformation of solar energy, etc., will largely depend on solving this problem.

Investigation of the mechanism and the kinetics of chemical and electrochemical reactions on organic metal complexes is also of considerable theoretical interest, as it helps to reveal the role of collective and local effects in electrocatalysis and to establish the relation between chemical structure and catalytic activity. These results may be useful also for understanding several aspects of enzymic catalysis. Molecular complexes containing a porphyrin group serve as active centres in protein macromolecules—enzymes and electron-carriers in respiratory chains in living organisms—and play a decisive part in photosynthesis.

The most important task of current research on electrocatalysis is to establish rules for the selection of catalytically active systems. The importance of this problem is increasing especially as a consequence of the almost unlimited number of possible organic compounds.

The present Review, covering the literature to January 1977, examines in the greatest detail published information on the mechanism and the kinetics of the electroreduction of molecular oxygen. Other electrocatalytic and photocatalytic reactions, whose investigation is only beginning, are considered in less detail.

II. ELECTROPHYSICAL AND CATALYTIC PROPERTIES OF METALLOPORPHYRINS

Among organic metal complexes possessing semiconductor properties compounds of the porphyrin series occupy an important place in electrocatalytic investigations. Results on their chemical, electrophysical, and catalytic characteristics have been summarised in several monographs[1-4] and reviews[5-8]. In the present Review, therefore, we shall very briefly consider only those properties that are necessary for an interpretation of the electrocatalytic phenomena.

The two hydrogen atoms attached to nitrogen in the porphyrin molecule can be replaced by a metal to form coordination complexes. The three main groups of porphyrin derivatives are—(i) reduced porphyrins, (ii) porphyrins with substituents at positions 5, 10, 15, and 20, e.g. tetraphenylporphyrin (TPhP), and (iii) porphyrins with benzene rings attached at outer bonds, e.g. tetrabenzoporphyrin (TBP).

Among tetra-azaporphyrin derivatives phthalocyanines (Phth) are especially well known. X-Ray structural investigations have established[1,9] that phthalocyanines of bivalent metals (copper, nickel, iron, cobalt) belong to the monoclinic system, symmetry group D_4h; such high symmetry is a consequence of conjugation effects. Several polymeric metal phthalocyanines are known[1]. Polyphthalocyanines ($Phth_i$) are compounds of high molecular weight having a strip, network, or three-dimensional structure and containing tetra-azaporphyrin macrorings C_8N_8 alternating in a definite sequence. The joining of monomer units into a polymer can occur either through benzene rings (without disruption of conjugation) or through bridging groups (methylene, oxygen, nitrogen, etc.), which are either isolators or weak transmitters of conjugation. The unbroken chain of conjugation in polyphthalocyanines is short (4–6 units).

Monomeric phthalocyanines can exist in more than one modification differing in crystal structure and electrical properties[1]. The monoclinic unit cell comprises two molecules, and the distance between parallel molecules (e.g. in a crystal of copper phthalocyanine) is 3.38 Å; the area occupied by one molecule is 123 Å^2. The α-form has a tetragonal structure and is formed by precipitation from concentrated sulphuric acid or sublimation at high vapour pressures; the β-form can be obtained by heating the α-form above 300 °C. The transition occurs more rapidly and at a lower temperature in a vacuum than in air[1]. In the β-form the phthalocyanine molecules are more densely packed, which leads to stronger interplanar interactions than in the α-modification. For example, the interplanar spacings are 11.8 and 9.8 Å, while the size of the crystals increases from 100–200 Å to 1 μm for the α- and β-modifications of copper phthalocyanine respectively[1].

Porphyrin and its derivatives are characterised by a developed system of conjugated double bonds covering the whole molecule. The changes occurring in metal porphyrins during chemical reactions are associated with electronic transitions in the conjugated system of the ligand and in the electron system of the central metal ion. Therefore an understanding of the nature of catalytic and electrocatalytic processes on organic metal complexes requires a detailed study of their electronic structure.

Quantum-chemical calculations on porphyrin complexes of transition metals have shown[9-14] that the orbitals of the metal, other than those of copper and zinc, interact weakly with the π-system of porphyrin. Zinc and nickel porphyrins are diamagnetic, and those of copper and cobalt are paramagnetic; with iron and manganese several variants of the spin state are possible, because the energies of their obitals are so close to that of the $a_{2u}(\pi)$ molecular orbital. Similar results were obtained[12] for the phthalocyanines of bivalent nickel, cobalt, and iron; a somewhat different electronic configuration was found for manganese phthalocyanine.

The appearance of excited states in the visible and the ultraviolet was attributed[11] to the orbital transitions

$$a_{2u}(\pi)\rightarrow e_g^*(\pi) \qquad a_{1u}\rightarrow e_g^*(\pi).$$

The strong degeneracy and mixing of these energy levels leads to a low-energy state *Q* in the visible and a high-energy state in the region of the Soret band. The *Q*-bands approximate to a one-electron transition in the sequence

porphyrin > tetra-azoporphyrin > tetrabenzoporphyrin > > phthalocyanine.

The results of quantum-chemical calculations correlate satisfactorily with the electronic absorption spectra of porphyrin and its derivatives, although the participation of a large number of orbitals of the ligand system and perhaps *d*-orbitals of the metal must be taken into account in order to intepret the fine structure of these spectra[11,14].

The electronic absorption spectra of polyphthalocyanines on the whole are similar to the spectra of the monomers[15], but the less intense bands become flattened on polymerisation. The invariability of the long-wavelength band, representing the energy levels of the ground and lowest excited states of phthalocyanine, indicates that polymerisation does not affect the character of the π-electron interaction of the benzene and tetra-azaporphyrin rings of phthalocyanine.

A more detailed analysis of the electronic structure of metal derivatives of porphyrin, in particular of the spin state of the central metal ion, is made by comparing theoretical calculations[9,11,12] with experimental results obtained by electron spin resonance[4,5,16-18], Mössbauer spectroscopy[19,20], and measurements of magnetic susceptibility[21,22]. The e.s.r. data show that the unpaired electron in copper and cobalt phthalocyanines is located in $d_{x^2-y^2}$ [16] and d_{z^2} [17] orbitals respectively, which is consistent with the above results of quantum-chemical calculations.

An especially large number of studies have been made on the electronic state of iron ions in porphyrin complexes. However, this question has not yet been clarified. Thus some workers[19] have found the electronic configuration

$$(d_{xy})^2(d_{yz}d_{xz})^3(d_{z^2})^1,$$

but others[21] have found

$$(d_{xy,\ xz})^4(d_{xy})^1(d_{z^2})^1.$$

Calculations[11] indicate that the energy of the orbitals usually increases in the sequence

$$d_{xy}<d_\pi<d_{z^2}<d_{x^2-y^2}.$$

However, experimental and calculated positions for the band corresponding to electron transfer from metal to ligand have suggested[13,14] the alternative sequence

$$d_{z^2}<a_{xy}<d_\pi<d_{x^2-y^2}.$$

In view of the peculiarities of the electronic structure of manganese and iron porphyrins the distribution of d-electrons in these central ions is probably strongly dependent on the mode of preparation and the specific experimental conditions[20,23].

The porphyrin ring is amphoteric: in acid medium the lone pairs of the nitrogen atoms enable it to add one or two protons to form singly or doubly charged cations, and in alkaline medium singly and doubly charged anions can be formed[2]. Protons add to the central nitrogen atoms even at pH 2–3, and the excess charges are uniformly distributed throughout the whole π-electron system of the molecule[24]. In phthalocyanine the first proton is added at considerably lower pH values ($pK \cong 1.8$), probably at a bridging nitrogen atom[25]. The number and positions of protons added to phthalocyanines are still matters of controversy.

Important features of metalloporphyrins, of great value for the interpretation of their catalyic and electrocatalytic properties, are their ability to add additional ligands (extra coordination) and to exist in ionic forms. Possible participation of the latter in catalysis and electrocatalysis makes it necessary to establish the redox potentials of the ring and of the central ions in non-aqueous and aqueous solutions and to identify the path of electronic transfers (ring, metal). The two problems are solved respectively by polarography and by combined study of electron spin resonance[17,18,26,27], electronic[17,18,27-29], and infrared[27,30] spectra. The general approach to these questions and a comprehensive bibliography will be found in Refs. 27 and 31.

In contrast to metalloporphyrins, which form singly and doubly charged anions, the molecules of most metal phthalocyanines are capable of adding up to four electrons[12]. Porphyrin complexes in which the metal ion cannot be oxidised (zinc, magnesium, cadmium, copper) undergo oxidation in two one-electron stages[26] with formation of singly and doubly charged cations. In cobalt and iron complexes an electron is probably first detached from the metal, after which the porphyrin ring is oxidised[17,18]. Localisation of the charge depends substantially on the nature of the central metal ion: in singly charged anions of metal-free phthalocyanine and tetraphenylporphyrin the excess charge is localised on the ligand; in both of the cobalt complexes the electron is localised on the central atom[5,28,31]; and in the anions [FePhth]$^-$ and [FePhth]$^{2-}$ the negative charge is shared between the iron atom and the ligand[5,28].

The coordination of additional ligands by planar-coordinated metal porphyrins, termed "extra coordination", is their important property. In relation to heterogeneous catalysis and electrocatalysis it consists merely in the reversible adsorption interaction of reactants and components of the medium with the active centre of the catalyst. For specific aspects of catalysis and electrocatalysis it is of the greatest interest to examine the axial bonding of several simple electrochemically active molecules—oxygen, carbon monoxide, nitric oxide, sulphur dioxide, water—and also component ions of the electrolyte.

Nitric oxide is coordinated to iron, cobalt, and manganese porphyrins in the presence of axially bound ligands containing nitrogen[32-37]. The complex of cobalt porphyrin with nitric oxide can be regarded formally as Co^{III}–NO^- with charge transfer from the $3d_{xz}$ or $3d_{yz}$ orbitals of cobalt to anti-bonding $2p\pi^*$ molecular orbitals of the nitrosyl ligand. π-Interaction of these metalloporphyrins with nitric oxide weakens from manganese to iron and then to cobalt. The same porphyrins form mono- and di-adducts with carbon monoxide[38-41]. Adsorption of the latter gas is more stable than that of oxygen: if they are present together, oxygen is coordinated first, and is then displaced by carbon monoxide. The coordinating power for carbon monoxide falls in the sequence[38]

protoporphyrin > tetraphenylporphyrin > tetrabenzoporphyrin > phthalocyanine.

Electron spin resonance indicates the fully reversible formation of an almost axially symmetric complex by sulphur dioxide with cobalt tetraphenylporphyrin in toluene solution[42].

Optical and e.s.r. measurements have shown that cobalt phthalocyanines, tetraphenylporphyrins, and tetra-*p*-methoxyphenylporphyrins in anhydrous medium (e.g. toluene) at low temperatures (−80 °C) form equimolecular oxygen adducts reversibly[43–47]. In the presence of a strong donor (e.g. imidazole) a mononuclear adduct is formed even at room temperature. The e.s.r. spectra indicate that the oxygen complex of cobalt tetraphenylporphyrin has the electronic configuration $Co^{III}...O_2^-$: i.e. considerable delocalisation of the unpaired electron and partial charge transfer to the oxygen atom take place.

Two models—parallel and unsymmetrical or bent (the Griffiths and Pauling models respectively)—have been used in a quantum-chemical calculation[11] of the coordination of an oxygen molecule with iron porphyrins. With parallel orientation the π_x-orbital of oxygen will overlap the d_{z^2}-orbital of the metal, and the anti-bonding π_x^*-orbital of oxygen the $d_{xz}d_{yz}$-orbitals of the metal. The calculation showed that such coordination should be accompanied by transfer of negative charge (−0.53) from iron to oxygen, which should result in formation of the O_2^- ion in a vibrationally excited state. According to the Pauling version, on formation of a bond between oxygen and iron porphyrin the bent orientation is stabilised by formation of a σ-bond with the d_{z^2}-orbital. Maximum σ-bonding is achieved with an M–O–O angle of 120°. An approximation to this structure is found in oxyhaemoglobin.

A considerable quantity of experimental information has now accumulated on the heterogeneous catalysis of several reactions on metalloporphyrins, detailed accounts of which will be found in reviews[6–8,48]. The range of reactions activated by these complexes is extraordinarily wide; most of the studies have been made on the oxidation of organic compounds—mild oxidation of hydrocarbons (cumene[6,7,49–51], propene[48], mesitylene[52]), oxidative dehydrogenation (of alcohols[8,32,53–55] and cyclohexadiene[56–59])—and on decarboxylation[6,8], processes probably involving a stage of activated adsorption of molecular oxygen on the catalyst with formation of O_2^- or O^- ions. They are therefore of interest for predicting electrocatalytic activity in the cathodic reduction of molecular oxygen, as well as in other electrode reactions involving the adsorption of oxygen as an intermediate stage.

The main effects on the rate and the selectivity of redox reactions are attributed to the nature of the central metal ion[6,8,49,51,55–59], the chemical structure of the organic complex (effect of substituents in the ligand[56–59], polymerisation[6,7,48]), and the crystal structure[6,8,60]. The catalytic activities of phthalocyanines and tetraphenylporphyrins of transition metals—iron, cobalt, manganese, copper, nickel—in the oxidative dehydrogenation of cyclohexadiene have been compared[56–59] with the first oxidation potentials of the catalyst[17]. The catalytic activity of a phthalocyanine complex is greater the lower the first oxidation potential:

manganese > iron > cobalt > nickel, copper.

However, such comparison may well be ambiguous, since the localisation of charge accompanying the oxidation takes place in different regions of the complex—in the electronic system of the central ion in the iron, cobalt, and manganese complexes, or in the ligand in the copper and nickel complexes.

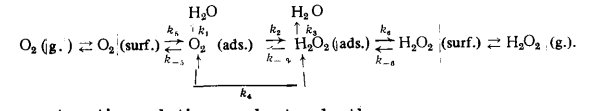
Such correlation is not observed at all for the catalytic properties of tetraphenylporphyrin complexes: the cobalt complex is more active than the iron complex, although their first oxidation potentials are respectively 0.52 and −0.32 V. This is probably connected with the complicated interrelated effects of organic ligand and metal on redox processes, and may indicate that not only the central atom but also the ligand is catalytically active. The latter has recently been convincingly shown[8] for the oxidation of isopropyl alcohol and the decomposition of oxalic acid. It must also be borne in mind that chemisorption bonds may differ in different redox processes, e.g. not only a π-bond with transition-metal ions of a chelate complex but also a bond using unpaired electrons. In the latter case the catalytic activity may correlate with the concentration of paramagnetic centres, as was found[61] for the ortho–para conversion of hydrogen on copper phthalocyanines.

The decomposition of hydrogen peroxide is very often used as model in investigations of the catalytic properties of organic semiconductors. This reaction is especially interesting for electrocatalysis, since in many cases hydrogen peroxide is formed as intermediate in the electroreduction of oxygen. Studies of the decomposition of hydrogen peroxide on phthalocyanines of various metals (iron, cobalt, nickel, copper, manganese, platinum, palladium, ruthenium, osmium, rhodium, and iridium)[6,7,48,62–64] have shown that monomeric ruthenium, osmium, and iron phthalocyanines[62] and polymeric copper phthalocyanine[7,48] are most active. They show also that neither the presence of unpaired *d*-electrons in the central atom nor oxidisability of the latter is a condition of catalase activity by metallophthalocyanines, which is probably due to the ability of certain such compounds to form intermediate complexes with hydrogen peroxide. The activity of a powdered metal (cobalt, copper, nickel) coated with a thin (10^{-5}–10^{-6} cm) continuous film of a phthalocyanine of the same metal far exceeds those of the individual components towards the decomposition of hydrogen peroxide[63]. This can be explained, in terms of the electronic theory of catalysis[65], by injection of electrons from the metal into the phthalocyanine film (when the thickness of the latter does not exceed the depth of shielding) with a consequent displacement of the Fermi level on the phthalocyanine surface.

This example is evidence of the contribution by collective electronic properties to the catalytic activity of organic metal complexes. However, most of the experimental results that have accumulated indicate a definite role for local electron transfers determined by the chemical properties of the catalytic complex organometallic molecule and its electronic structure. In organic semiconductors the interaction between separate molecules is considerably weaker than that between component parts of the same molecule, and every molecule in the crystal lattice is able to retain its individuality. This must probably be taken into account in the first place when catalytic and electrocatalytic research results are examined.

III. KINETICS AND MECHANISM OF THE ELECTROREDUCTION OF OXYGEN ON METALLOPORPHYRINS

The electroreduction of molecular oxygen, studied in the greatest detail with organic metal complexes, takes place on air or oxygen cathodes in chemical sources of current. Reduction of oxygen can follow different paths depending on the nature of the electrocatalyst[66]:



On the most active platinum electrode the process goes mainly via dissociative adsorption of oxygen directly to water (with rate constant k_1).[67,68] Hydrogen peroxide can be formed only in a parallel reaction (k_2). On a carbon electrode molecularly adsorbed oxygen undergoes reduction[69]. Hydrogen peroxide is formed in a two-electron reaction, and

its further transformation occurs at considerably more negative potentials, since $k_3 \ll k_2$. On several electrode materials hydrogen peroxide can be catalytically decomposed (k_4),[67,70] and oxidised by a reverse reaction (k_{-2}). The adsorption and desorption of oxygen (k_5 and k_{-5}) or of hydrogen peroxide (k_6 and k_{-6}) can also be slow stages[71,72]. Electrocatalysis can in principle consist in the acceleration of any stage of this process.

In view of the many-electron character of the electroreduction of molecular oxygen a study of this process should include two main stages—(i) elucidation of the mechanism or path of the process, i.e. establishment of the relation between the partial reactions in the overall process, and (ii) kinetic analysis of the most important partial reactions with the aim of elucidating the nature of the slow stage.

1. Model Systems

Organic metal complexes have low conductance, and are therefore deposited as a thin film on an electrically conducting carrier for the study of their electrocatalytic reactions. Several model systems have been designed for investigations under purely kinetic or strictly defined hydrodynamic conditions.

1. Thin films (10^2–10^4 Å) of organic metal complexes on a smooth, electrically conducting support, which are applied from solution[73–75] or by vacuum sputtering[20,76,77]. Gold or pyrographite is most often used as the support.

2. Extremely thin layers of catalysts comprising a highly dispersed (usually carbon) carrier coated with the organic metal complexes[78–88]. This system is more active than the first and is often used in investigations using a disc electrode with a ring. This method makes it possible to fix on the annular electrode an intermediate product (in the present case hydrogen peroxide) in the reaction occurring on the disc, and is most informative with respect to separation of the process into partial reactions and determination of kinetic parameters for each of the latter[89].

3. Suspension electrodes[82–86], enabling diffusion restraints to be eliminated and electrocatalytic activities of organic metal complexes deposited on a dispersed carrier to be compared under kinetic conditions. A disadvantage is the complicated character of the transfer of charge from particles of the suspension to the current leads[90], a stage which under certain conditions may become rate-determining.

4. Porous gas-diffusion electrodes promoted by organic complexes[58,88,91]. Comparisons of catalytic activity by this method are qualitative, since the characteristics of such electrodes depend significantly on several macrokinetic parameters[92].

Kinetic analysis of electrochemical reactions on organic metal complexes must take into account structural features of the electrical double layer on semiconducting materials, specifically the possible distribution of electrode potential between the Helmholtz layer in the electrolyte and the space charge in the semiconductor[93]. The potential distribution depends on the concentration and mobility of free charge carriers, the concentration of surface states, etc. If the thickness of the semiconductor film is less than the depth of shielding (for organic metal complexes it is 10^{-6}–10^{-5} cm), additional effects are possible as a consequence of injection of charge carriers from the conductor (support) into the semiconductor (catalyst)[65]. This requires investigation of the structure of the complex–electrolyte interface for the above specific systems.

Measurements of differential capacitance on cobalt, iron, and metal-free phthalocyanine films sputtered on to pyrographite have shown that the presence of the film lowers the electrode capacitance to some 10% of that of the support, to ~0.5–0.7 μF cm^{-2} (Fig. 1c).[78,93] The capacitance depends significantly on the a.c. frequency, which probably indicates that the measured capacitance is determined not by the charge of the depleted layer in the semiconductor but by rapid surface states. This suggests that migration of charge in a film is a rapid process.

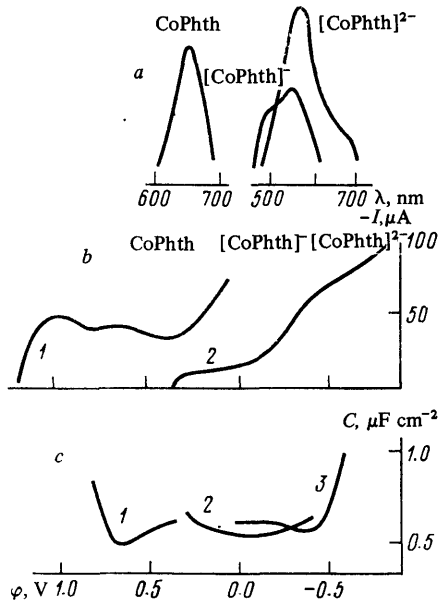


Figure 1. Investigation of cobalt phthalocyanine films at various pH.[78,93]
(*a*) Specular reflectance spectra.
(*b*) Potentiodynamic I–ϕ curves determined on film at pH: 1) 0.3; 2) 14.
(*c*) Dependence of differential capacitance of CoPhth on potential at pH: 1) 0.3; 2) 6.8; 3) 14.

The electronic structure of the neutral state of organic complexes is considered when the nature of catalytic and electrocatalytic activities is discussed. Under the conditions of electrochemical reactions, however, the charge on the complexes may vary (with formation of ionic modifications) as the pH and the electrode potential change. Interesting conclusions follow from a study of the surface state of cobalt phthalocyanine based on comparison of electrochemical and spectral measurements in aqueous solutions at pH 0.3 and 14 (Figs. 1*a* and 1*b*): independently of the pH the potentiodynamic current–potential (I–ϕ) curves of the complex contain several plateaux or maxima, from which to a first approximation three can be isolated in the potential ϕ_r ranges 1.2–0.75, 0.75–0.4, and 0.4–0 V†.

† Here ϕ_r is the potential relative to a hydrogen electrode in the same solution and ϕ the potential relative to a normal hydrogen electrode.

In order to identify electrochemical changes undergone by cobalt phthalocyanine in aqueous solution spectral studies have been made[93] by specular reflectance directly under conditions of electrochemical polarisation. A film of this complex, like all neutral metal phthalocyanines, has an absorption band in the range 600–670 nm. On cathodic polarisation ($\phi < -0.4$ V) the band due to the neutral molecule becomes weaker, and a double band appears at 400–500 nm (Fig. 1*a*). This indicates formation of a singly charged anion of cobalt phthalocyanine with the charge localised on the central cobalt ion. At large negative potentials ($\phi < -0.8$ V) in alkaline aqueous solution a broad band appears representing a doubly charged anion with the second electron localised on the ligand. The reflectance spectrum of iron phthalocyanines undergoes reversible changes under the influence of an electrolyte[94]. A qualitative correlation has been established[20] between the position of the main absorption peak and the spin state of the iron atom in phthalocyanines prepared by different methods. Thus over the potential range of electroreduction of the oxygen molecule the phthalocyanine molecule may be present in various electronic states depending on the pH and the nature of the central ion.

At present information on the structure of the interface between organic metal complex and electrolyte is extremely limited and is related only to a few specific systems used in studying the electroreduction of oxygen. From these results it can be suggested that the potential drop is mainly located in the electrolyte and that charge transfer in the semiconducting film is rapid[20].

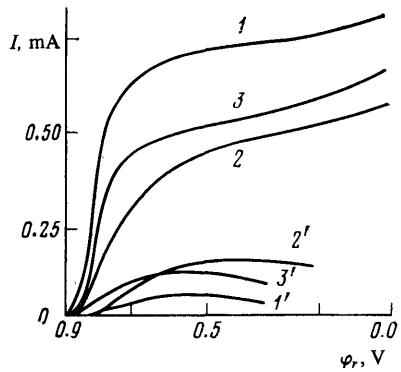


Figure 2. Polarisation curves for the reduction in 0.1 *N* KOH of oxygen on: 1) $CoPhth_i$; 2) CoTPhP; 3) CoTMPhP; 1′–3′) corresponding curves for the oxidation of hydrogen peroxide on a platinised platinum ring ($m = 680$ rev/min).

2. Mechanism of the Electroreduction of Oxygen

Published work reveals the effect of the structure of organic metal complex catalysts, their crystal structure, and the composition of the solution on the mechanism and the rate of the electroreduction of molecular oxygen. The most important factor is the chemical structure of the catalyst molecule—the type of ligand and substituents and the degree of polymerisation on the one hand, and the nature of the central ion on the other.

Macrocyclic complexes containing a system of conjugated π-electrons—phthalocyanines[73–88,95], tetraphenylporphyrins [58,80,81,83–85], dibenzotetra-aza-annulenes (DBTAA)[86,87]—exhibit greater or less activity in the electroreduction of oxygen both in acid and in alkaline solutions. (The number of π-electrons in the inner conjugated system of these complexes is roughly the same at ~18.) Polarisation curves for the reduction of oxygen at a rotating disc electrode coated with a thin layer of polymeric cobalt phthalocyanine, of cobalt tetraphenylporphyrin, or of cobalt tetrakismethoxyphenylporphyrin (CoTMPhP) in alkaline solution have a single wave (Fig. 2),[80,81] in contrast to those of pyrographite[69] or carbon black[96]. Fig. 2 includes for the above compounds the variation of the limiting currents for the oxidation of hydrogen peroxide on the ring. Numerical calculations applied to the results by the method of Ref. 89 have shown that the mechanism of the reduction of molecular oxygen on these organic metal complexes is different: on cobalt tetraphenylporphyrin reaction takes place only with intermediate formation of hydrogen peroxide ($k_1 = 0$);[80,81] on polymeric cobalt phthalocyanine and on cobalt tetrakismethoxyphenylporphyrin parallel direct reduction to water takes place, its contribution to the total process being respectively 50% and 30%.[80,81]

In acid solution only the reaction involving intermediate formation of hydrogen peroxide occurs on all the complexes investigated. The constant k_2 decreases in the sequence[80,81]

$$CoTMPhP > CoTPhP > CoPhth_i > CoPhth.$$

Phthalocyanines are less active in acid solutions than are tetraphenylporphyrin complexes[58,80,81,83–85]. The introduction of electron-donors into the phenyl groups increases the activity of cobalt tetraphenylporphyrin in the sequence[85]

$$-OCH_3 > \langle\bigcirc\rangle > H\ .$$

However, the method of preparation of the chelate is probably quite important. For example, the catalytic activity of cobalt tetraphenylporphyrin was unaffected[58] by the introduction of *p*-methoxy- and *p*-nitro-substituents. Electron-acceptors, e.g. the fluoride ion, do not influence the electrocatalytic activity of cobalt phthalocyanine[58], but lower that of iron phthalocyanine[58,82]. Cobalt dibenzotetra-aza-annulene is more active than the tetraphenylporphyrin chelate in acid solutions[86,87], and neither donor nor acceptor substitutents affect the rate of electroreduction of oxygen on this complex.

Thus, in relation to the electroreduction of molecular oxygen, the organic ligands investigated form the sequences

Phth > TPhP > DBTAA in alkaline solutions
DBTAA > TPhP > Phth in acid solutions.

The nature of the central metal ion has a still more substantial influence on the rate and the mechanism of the ionisation of molecular oxygen on the organic complexes[75–88,95]. In relation to the rate of electroreduction of molecular oxygen (independently of pH) the activity of the metal phthalocyanines varies in the seqence

$$Fe\ (II),\ Fe\ (III) > Co\ (II),\ Mn\ (II) > Ni\ (II) \geqslant Cu\ (II) > 2H\ .$$

With tetraphenylporphyrins at all pH [58,80,81,83–85] and with dibenzotetra-aza-annulenes in acid and alkaline solutions[86,87] the bivalent cobalt complexes are more active than the bi- and ter-valent iron complexes:

$$Co\ (II) > Fe\ (II,\ III) > Ni\ (II),\ Cu\ (II)\ \text{(on TPhP)}\ ,$$
$$Co\ (II) > Mn\ (II) > Fe\ (II,\ III) > Ni\ (II),\ Cu\ (II)\ \text{(on DBTAA)}\ .$$

Systematic investigations using a disc electrode with a ring[75,78–81] have established which reactions in the complicated reduction of molecular oxygen are catalysed by organic metal complexes and how their relative rates vary with the chemical structure of the catalyst. In acid solutions the reaction yielding hydrogen peroxide is accelerated in the presence of metal complexes of phthalocyanine, tetraphenylporphyrin, and tetrakismethoxyphenylporphyrin. In alkaline solutions this is accompanied, in the presence of monomeric and polymeric iron and manganese phthalocyanines, polymeric cobalt phthalocyanine, and cobalt tetrakismethoxyphenylporphyrin, by the direct reaction involving rupture of the O–O bond. Reduction of oxygen to water without intermediate formation of hydrogen peroxide[79] diverges significantly from conclusions reached by other workers[73,74,76,77,82–87], who accept that in all cases reaction occurs only via this intermediate stage.

A correlation has been found[97] between the electrocatalytic activity of metal phthalocyanines and their magnetic properties determined by the spin state of the central ion. In the view of other workers[91], however, no direct relation exists between magnetic moment and electrocatalytic activity. It should be noted that the latter workers[91] use results obtained on porous gas-diffusion electrodes, which diminishes the reliability of the conclusions because of possible distortion by macrokinetic effects.

The nature of the carrier has a considerable effect on the electrocatalytic activity of metal chelates. The greatest activity is achieved by the use of various forms of carbon, with the maximum effect when alkaline groups are present on the carbon surface[82]. The mechanism of these phenomena is still obscure. The electrocatalytic activity of the α-modification of iron(II) phthalocyanine is greater than that of the β-form[76,94]. The electronic spectra of transmitted and reflected light show a ~15 000-cm^{-1} shift of the band to longer wavelengths on passing from the β- to the α-modification, which is attributed[76,94], in agreement with Ref.13, to a greater concentration of high-spin iron(III) phthalocyanine in the latter form. This is due to adsorption of oxygen in the bulk of the α-form and transition of the greater part of the iron(II) complex into a high-spin form. Cathodic polarisation of a specimen of the α-modification leads to an irreversible loss of activity. The enhanced electrochemical activity is attributed to a complex $Fe^{III}Phth-O_2^-$, on which occurs secondary adsorption of the oxygen molecule involved in the electrochemical reaction[76,94].

Detailed investigations of the effect of the method of preparation of monomeric and polymeric iron phthalocyanines on their electrocatalytic activity and the spin state of the central ion have established[20] that a polymer formed on a carrier and containing iron(III) of intermediate spin is the most active; the least active is the iron(II) monomer in the triplet state. However, the state of iron phthalocyanine at the interface with the electrolyte and the mechanism of adsorption of molecular oxygen remain obscure.

The above discussion shows that the main factor in electrocatalysis of the oxygen reaction is local interaction between an oxygen molecule and a catalyst molecule: collective interaction effects may be of secondary importance, at least in the above specific model systems. This conclusion is supported[88] by the lack of correlation between the electrocatalytic activity of phthalocyanines of several metals and their electrical conductivity.

Thus the reaction path of the cathodic reduction of oxygen on organic complexes of metals is now in general clear. On all the metal porphyrins investigated at all pH molecular oxygen is reduced by a consecutive mechanism involving intermediate formation of hydrogen peroxide. On several organic complexes in alkaline solutions (pH 10–14) this is accompanied by simultaneous reduction of oxygen directly to water without intermediate formation of hydrogen peroxide, i.e. involving rupture of the oxygen–oxygen bond either in an oxygen molecule or more probably in the molecular ion O_2^-. In the case of iron phthalocyanine direct formation of water is the main reaction.

3. Kinetics of the Reduction of Oxygen

Investigation of the kinetics of the reduction of oxygen over a wide pH range is necessary in order to ascertain the nature of the slow stage, which has been undertaken for metal-free phthalocyanine, monomeric and polymeric cobalt phthalocyanines, and cobalt tetraphenylporphyrin (Fig.3).[80,81] Table 1 gives typical variations in the kinetic parameters $\partial\phi/\partial \lg i$ and $\partial\phi/\partial pH$ for the catalysts under different experimental conditions. Throughout the pH range 0–14 the rate of reduction of molecular oxygen to hydrogen peroxide is higher in the presence of the organic complexes than with carbon black as carrier. With the exception of cobalt tetraphenylporphyrin in acid medium the kinetic parameters of the reduction on the various catalysts are closely similar to those on carbon black. Such coincidence indicates a similar mechanism for the slow stage. Investigations on carbon black[96] and other carbonaceous materials[69,98] have shown that the cathodic reduction of oxygen is governed by the slowness of transfer of the first electron to an adsorbed oxygen molecule (or from an O_2^- ion in the reverse anodic oxidation of hydrogen peroxide):

$$(ML) + O_2 \rightarrow (ML)O_2,$$
$$(ML)O_2 + e \rightarrow (ML)O_2^- \text{ (slow stage)},$$
$$(ML)O_2^- + H_2O \rightarrow (ML)HO_2 + OH^-,$$
$$(ML)HO_2 + e \rightarrow (ML)HO_2^-,$$
$$[(ML)HO_2^- + H_2O \rightarrow (ML) + H_2O_2 + OH^-].$$

The remaining stages, leading to formation of hydrogen peroxide or HO_2^- in acid or alkaline solution respectively, are rapid. In acid and neutral solutions the reaction is irreversible, with $(\partial\phi/\partial pH)_{i=\text{const}} = 0$, $\partial\phi/\partial \lg i = 120$ mV, and the transmission or Brønsted coefficient $\alpha = 0.5$. With rise in pH the rate of the reverse reaction increases, and the O_2–$H_2O_2(HO_2^-)$ system approaches reversibility, with a consequent negative shift in potential and decrease in $\partial\phi/\partial \lg i$. It can quite justifiably be assumed that the reduction of oxygen has a similar mechanism on the organic complexes (except for cobalt tetraphenylporphyrin in acid solutions)[80,81].

The behaviour of cobalt tetraphenylporphyrin departs completely from the above scheme, a very interesting phenomenon that merits special attention. A formal explanation can be based on the hypothetical slow stage

$$(ML)O_2 + H^+ + e \rightarrow (ML)HO_2$$

with $\partial\phi/\partial \lg i = \partial\phi/\partial pH = 120$ mV when $\alpha = 0.5$. The change in the mechanism of the reduction of oxygen on cobalt tetraphenylporphyrin and tetrakismethoxyphenylporphyrin in acid solutions may exist because their protonation may differ in character from that of the phthalocyanines.

The kinetics of the reduction of oxygen at various pH has been investigated also on monomeric and polymeric cobalt and iron phthalocyanines[20,94]. Detailed comparison of these results with those of other workers[75,79–81] shows a certain parallelism: in both cases the reaction is of first order with respect to molecular oxygen, the derivative $\partial\phi/\partial \lg i$ decreases with increase in pH to reach ~40 mV at pH > 13, in alkaline solutions the potential becomes more negative with increase in pH, and the slopes of the polarisation curves on promoted

and unpromoted carbonaceous materials coincide. However, it is concluded[20], in contrast to the other workers[75,79–81], that in alkaline solutions chemical cleavage of the O–O bond

$$HO_2^-\,(\text{ads.}) + H_2O \rightarrow 2OH + OH^-$$

is the slow stage. This mechanism is clearly of limited value, since it does not explain all the experimental results, especially in non-alkaline media.

Table 1. Kinetic parameters of the reduction of oxygen to hydrogen peroxide on carbon black in the presence of organic complexes*.[80,81]

pH	$\partial\varphi/\partial$ pH, mV	$\partial\varphi/\partial \lg i$, mV
	carbon black	
2—10	0	—90—120
10—14	—60—30	—40—50
	cobalt phthalocyanine	
2—10	0	—100—120
10—14	—60—30	—40—50
	cobalt tetraphenylporphyrin	
0—4	—110	—100—120
4—10	0—10	—100—120
10—14	—60	—40—60

*Closely similar values of the kinetic parameters were observed on films of the phthalocyanines 500–1000 Å thick sputtered on a pyrographite electrode.

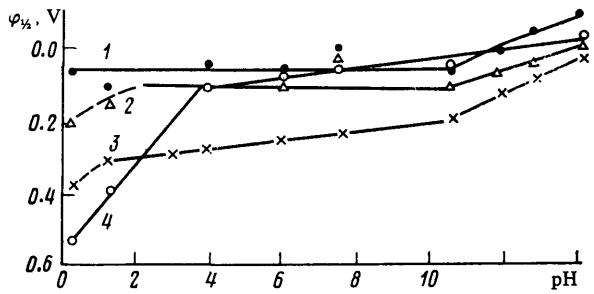


Figure 3. Dependence of half-wave potential on pH for the reduction of oxygen[80,81] on: 1) carbon black; 2) metal-free and cobalt phthalocyanine monomers; 3) cobalt phthalocyanine polymer; 4) cobalt tetraphenylporphyrin.

Several attempts have been made to explain the electrocatalytic action of metal porphyrins on the cathodic reduction of oxygen. The simplest approach is to establish a correlation between electrocatalytic activity and oxidisability[58], the latter measured by the first oxidation potential of the complex. Indeed, if the slow stage is electron transfer from the central ion, these reactions are similar. Good correlation between electrocatalytic activity and oxidation potential actually exists for monomeric iron, cobalt, and copper phthalocyanines, but the situation is considerably impaired with other ligands.

In the mechanism of "redox catalysis"[86,87] the activity of the complexes is related to the tendency of the central metal ion to pass into a higher valency state, i.e. to the third ionisation potential. The metal chelate is oxidised chemically by oxygen or an intermediate product to the cation, which then undergoes the electrochemical stage of cathodic reduction to the original compound. Such an approach does not actually consider the reduction of oxygen. Furthermore, it ignores the mutual influence of ligand and metal ion, which is evident e.g. in the difference in the activity series for phthalocyanines and tetraphenylporphyrins.

The effect of the central ion on the rate of the electroreduction of oxygen has been explained[20,77,78,84,85,94] on the basis of the quantum-chemical calculations of the electronic structure of metalloporphyrins and their oxygen complexes briefly considered in Section II. Stable complexes of oxygen with metal (e.g. iron) porphyrins are formed[11] by adsorption of the oxygen in a lateral position. The d_{z^2} orbital of the cobalt ion is most favourable for bonding an oxygen molecule, since its symmetry ensures the necessary overlap of orbitals[85]. It is assumed that the adsorption of an oxygen molecule on a metal phthalocyanine (tetraphenylporphyrin) is accompanied by formation of a σ–π double bond between the $d_{xz}d_{yz}$ and d_{z^2} orbitals of the central ion and the π^* molecular orbital of the oxygen molecule. Partial electron transfer from the central metal ion to the antibonding π^* orbitals of the oxygen atom weakens the O–O bond in the molecule. This tends to accelerate the cathodic reduction of oxygen.

Since formation of a donor–acceptor bond requires interaction of filled oxygen orbitals with vacant d_{z^2} metal orbitals, iron(II, III), cobalt(II), and manganese(II) complexes should exhibit the greatest activity, whereas only weak or completely absent catalytic activity can be expected for nickel(II) and copper(II) complexes#. Augmenting the number of delocalised π electrons (polymerising phthalocyanines or introducing donor groups into tetraphenylporphyrin) increases the electron density on the central ion, which facilitates electron transfer to the oxygen molecule and accelerates its reduction. On the other hand, increasing the degree of localisation of the electron on the adsorbed oxygen molecule weakens the O–O bond until it ruptures with direct formation of water. To explain the change in the activity sequence of ligands on passing from acid to alkaline solutions account must be taken of the possible occurrence of reaction on charged forms of the organic complexes (anions, cations), which may be present on the electrode surface within certain pH and potential ranges, as shown at the beginning of this Section.

Discussion of the nature of the electrocatalytic effects on the basis of approximate quantum-chemical calculations is, of course, only qualitative and leaves aside many experimental factors, e.g. the effects of the support or carrier[58,74,82], the crystalline modification[76,94], and the mode of preparation of the organic metal complex[58,78,80]. Their explanation requires a more profound (both theoretical and experimental) study of the adsorption interaction of such complexes with the reactants and investigation of the structure of the catalyst–electrolyte interface and the electronic structure of the adsorbed state.

The validity of this deduction depends on the adequacy of the quantum-chemical calculations in relation to the experimental results. Several discrepancies between them have been mentioned in Section II.

IV. USE OF ORGANIC COMPLEXES OF METALS TO PRODUCE GAS-DIFFUSION ELECTRODES

The great activity of several organic complexes of metals in the electroreduction of molecular oxygen has enabled them to be used to activate oxygen (air) electrodes in electrochemical sources of current[82,88,91,99–114], transducers[115], and other electrochemical devices. The production of active and stable gas-diffusion electrodes requires the solution of several macrokinetic problems in the optimum distribution of catalyst, electrolyte, and gas in a porous electrically conducting matrix with the aim of maximum development of the surface available for the electrochemical reaction[92]. Only results bearing directly on the use of organic metal complexes will be considered here.

Because of the low electrical conductivity of organic metal complexes they are used in combination with a highly dispersed carrier (a carbonaceous material or nickel powder). The catalyst is introduced into the carrier either by mechanical mixing[99,100] or by impregnating the carrier with a solution of the organic complex in concentrated sulphuric acid or other appropriate solvent (pyridine, dimethylformamide, etc.)[101–114]. The latter method is the most usual, since it will give a uniform distribution of the catalyst on the carrier surface. Another method is to form the organic metal complex directly on the carrier surface[91,108,116]. The chief design feature of the electrodes employed in work with these complexes is their water-repellancy, with a stable interface between gas and electrolyte achieved by introducing into the active mass a water-repellant agent (polyethylene or fluoroplastic), which is also a binder. The active mass is applied to a wire-gauze or porous metal base serving as current lead. Other details of the design and technique of preparation of the electrodes will be found in the literature[99–114].

Table 2. Electrochemical activity of oxygen electrodes comprising carbon black promoted with 20% of monomeric metal phthalocyanines in 12 *N* potassium hydroxide at 90 °C.[102]

Catalyst	–	H_2Phth	NiPhth	CuPhth	MoO_2Phth	CoPhth	FePhth	MnPhth	PtPhth	PdPhth
i, mA cm^{-2}, at φ_r = 0.80 V	40	60	8	60	70	130	120	140	110	140

Many monomeric phthalocyanines display extremely high electrochemical activity in porous gas-diffusion electrodes in an alkaline electrolyte. The rates of the electroreduction of oxygen on iron, cobalt, manganese, platinum, and palladium phthalocyanines are several times higher than that on pure carbon black. It is interesting that the introduction of metal-free phthalocyanine into carbon black increases the reaction velocity by ~50%. In the case of cobalt, molybdenyl, and copper phthalocyanines the change from monomer to polymer increases the current density by 100–200% (Fig.4).[102] A similar effect has been observed[108] with polymeric iron phthalocyanine. The influence of method of preparation on the activity of gas-diffusion electrodes has been investigated[102] for polymeric cobalt phthalocyanine.

The activity and the stability of gas-diffusion electrodes depend significantly also on their macrokinetic parameters, which are determined by the porous structure of the water-repellent active layer and the distribution of electrolyte and gas in the latter. These aspects have been investigated in the greatest detail[117,118] on water-repellent electrodes based on carbon black promoted with polymeric cobalt phthalocyanine. Mercury porosimetry indicates that contents of the polymer up to 10 mass % have no effect on the electrode structure; 20 mass % increases the total porosity; and up to 40 mass % some of the narrow pores become blocked. Application of this method to a frozen electrolyte has shown[119] that introduction of the polymer with the same fluoroplastic content leads to a considerable growth of liquid porosity.

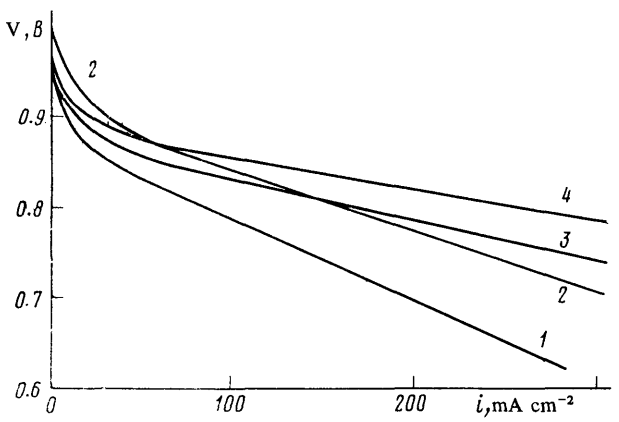


Figure 4. Polarisation curves for the reduction of oxygen, in 12 *N* KOH at 90 °C, on porous carbon electrodes promoted with polyphthalocyanines[102]: 1) $MnPhth_i$; 2) $CuPhth_i$; 3) MoO_2Phth_i; 4) $CoPhth_i$.

The correlation between current density at a gas-diffusion electrode and liquid porosity indicates a direct relation between the structure and the electrochemical activity of an electrode. Optimisation of the structure of the active layer [102,118] has enabled current to be generated under conditions close to optimum, i.e. inner kinetic[92]. The apparent activation energy for porous electrodes promoted with iron and polymeric cobalt phthalocyanines at $\phi_r = 0.83$ V is 4–5 kcal mole^{-1}, which confirms the predominantly kinetic character of the process. Carbon electrodes promoted with a cobalt phthalocyanine polymer have the highest electrochemical parameters in an alkaline electrolyte (0.3 A cm^{-2} at ϕ_r = 0.80 V).

An urgent problem in connection with electrochemical current sources is to develop an oxygen (air) cathode for acid media that does not contain scarce metals, which would avoid the complications associated with the carbonisation of alkaline electrolytes involved in the use of organic fuels or contaminated hydrogen with atmospheric oxygen as oxidant. However, no inorganic catalysts not containing precious metals and sufficiently stable in acid media have yet been reported. Certain organic metal complexes are very promising in this respect.

Table 3 compares the electrochemical characteristics of carbon–oxygen electrodes promoted with organic metal complexes (for acid media)[82,85,103–107,109,111–114,120,121]. The potential of such an electrode promoted with polymeric iron phthalocyanine is 0.85 V at a current density of 10 mA cm^{-2}, but the electrodes are unstable[82]. Some stabilisation of their

functioning could be achieved by varying the mode of preparation of the iron polyphthalocyanine[88,106,107]. The instability in acid solution of the electrochemical characteristics of carbon–oxygen electrodes containing phthalocyanines is probably due to partial dissociation of tetrabenzotetra-aza-porphyrin complexes in acid solutions. Hydrogen peroxide, formed in acid solutions as intermediate in the reduction of oxygen, may also have an adverse effect[80,81]. It oxidises metal phthalocyanines with cleavage of the macroring[1]. This probably limits the direct use of metal-containing porphyrin complexes in acid electrolytes.

Table 3. Electrochemical characteristics of carbon electrodes promoted with organic metal complexes in 3–6 *N* H_2SO_4 at 25–30 °C (τ = duration of functioning).

Active layer	φ_r, V, at i, mA cm^{-2}				τ, h	Ref.
	10	20	40	50		
Carbon black + $CoPhth_f$ + polyethylene	0.70	0.60	0.50	0.43	—	82
Carbon black + $FePhth_f$ + polyethylene	0.85	0.78	0.72	0.70	—	82
Norit BRX + 50% $FePhth_f$ + fluoroplastic	—	0.80	0.75	—	400	88, 106
Carbon + $FePhth_f$ + fluoroplastic	0.78	0.71	0.60	0.56	1000	107
Norit BRX + $CoPhth_f$ + fluoroplastic	0.72	0.69	0.64	—	150	103, 104
Norit FNX + CoTMPhP + fluoroplastic	0.75	0.70	0.65	0.63	300	85
Carbon AG-3 + macromolecular cpd. based on CoTMPhP	0.82	0.79	0.76	0.75	10000	120, 121

Heat-treatment of organic semiconductors at temperatures up to 1200 °C yields pyropolymers characterised by a narrow forbidden gap and significantly higher conductivity. The polymers are probably formed from highly unsaturated aromatic molecules[122] and possess great chemical stability. This group of polymeric compounds is extremely promising for electrolcatalysis.

Table 4. Effect of heat-treatment temperature t on durability τ of oxygen–carbon electrodes containing 5 mass % CoTMPhP in 4.5 *N* H_2SO_4 at 10 mA cm^{-2}.

t, °C	400	600	700	800	900	1000
τ, h	150	350	500	10000	10000	10000

Polyacrylonitrile pyrolysed at 600–1000 °C has been used[123] to activate an oxygen electrode in an acid electrolyte. At current densities of 50–80 mA cm^{-2} the potential of such an electrode was 0.7 V, but in durability tests it fell appreciably.

A method has been proposed[121] for preparing a catalyst based on carbon promoted with organic cobalt complexes (tetraphenylporphyrin, tetrakismethoxyphenylporphyrin, phthalocyanine) to ensure prolonged (>10 000 h) stable functioning of oxygen (air) electrodes in an acid electrolyte (4.5 *N* sulphuric acid). A mixture of carbon and the organic complex (e.g. cobalt tetrakismethoxyphenylporphyrin) is subjected to heat-treatment in an inert gas (helium) at 800° to 900 °C, which does not affect the initial activity of the catalysts, but has a substantial effect on the stability of their operation [Table 4].[120] X-Ray structural examination and elementary analyses have shown that the heat-treatment of cobalt chelates yields new macromolecular compounds whose chemical stability in sulphuric acid exceeds considerably that of the original compounds.

These investigations have shown that the principal parameters of the porous active layer—the total porosity and also the ratio of liquid and gas pores—are not affected by heat-treatment. Results obtained by means of a disc electrode with a ring indicate that microkinetic factors have a decisive role in stabilising the electrochemical characteristics of electrodes having heat-treated catalysts. The rate of conversion of hydrogen peroxide in the presence of thermally stabilised catalysts is increased some tenfold in comparison with the initial organic complexes, which lowers its concentration in the pores of the active layer and stabilises the working of oxygen electrodes in an acid electrolyte.

V. ELECTROCHEMICAL REACTIONS OF HYDROGEN PEROXIDE AND OTHER ELECTROCATALYTIC REACTIONS

Other electrocatalytic reactions on organic metal complexes have been studied in less detail than the electroreduction of molecular oxygen.

1. Reactions of Hydrogen Peroxide

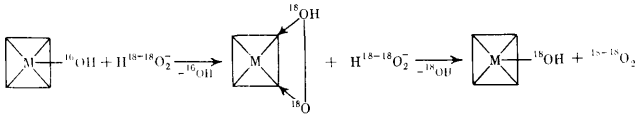
It is of interest from various points of view to investigate the electrode behaviour of hydrogen peroxide. As shown above, in several cases this compound is formed as intermediate in the reduction of oxygen, and its subsequent transformation determines the efficiency of operation of the oxygen (air) cathode. On the other hand, the decomposition of hydrogen peroxide is used as a model in investigations of heterogeneous catalysis on organic complexes. The possibility that it may undergo electrochemical reactions on complexes possessing semiconductor properties is usually ignored§.

Qualitative studies have been made of the cathodic reduction of hydrogen peroxide on phthalocyanines of several metals[73,88,106]. Comparisons have been made[88,106] between the catalytic activity and the conductivity of polymeric cobalt and iron phthalocyanines. The lack of correlation between these parameters led to the catalase activity of phthalocyanines being attributed to acceptor sites, assumed to be defects, dislocations, etc.

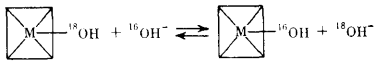
A combination of polarisation measurements, gasometry, and isotopic analysis of the oxygen evolved by the decomposition of hydrogen peroxide labelled with oxygen-18 has permitted[124] separate examination of the chemical and the electrochemical reactions of hydrogen peroxide on monomeric iron and cobalt phthalocyanines. Typical polarisation and gasometric curves are shown in Fig. 5 for cobalt phthalocyanine. Cathodic polarisation of the electrode entails reduction of the peroxide, and anodic polarisation its oxidation with evolution of molecular oxygen (curves *1* and *2*). Decomposition occurs also by a chemical mechanism, as is indicated by the maximum in the potential dependence of gas evolution, in the region of which the decomposition is bimolecular. At more anodic and more cathodic potentials the

§ The work of Roginskii and his colleagues[7] forms an exception.

order of the reaction decreases to unity. The oxygen evolved on decomposition of the labelled peroxide indicates that the peroxy-bond remains unbroken. These results suggest that the mechanism of the breakdown of hydrogen peroxide (e.g. in alkaline solutions) at a steady potential is



which is followed by rapid isotope exchange



so that the evolved oxygen has the same isotopic composition as the original hydrogen peroxide. The phthalocyanine molecule can function only after the chain is complete. Intermediate compounds—complexes of phthalocyanine with one or two adsorbed molecules (ions) of hydrogen peroxide—are essentially the Chance–Ogura complexes formed in the decomposition of hydrogen peroxide by catalase.

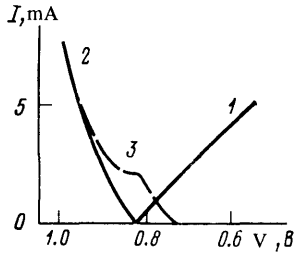


Figure 5. Curves obtained on a pyrographite electrode coated with CoPhth in 1 *N* KOH + 0.005 *N* H_2O_2:[80] 1, 2) polarisation; 3) gasometric.

On the application of electrochemical polarisation the central metal ion becomes able either to donate or to accept electrons, which permits the occurrence of a stationary electrochemical reaction with a consequent change in the order of the reaction to unity. A mechanism for the anodic oxidation and the cathodic reduction of hydrogen peroxide on cobalt and iron phthalocyanines has been suggested[124] on the basis of kinetic results. The pH dependence of the kinetics of the cathodic process enables two regions to be distinguished: $\partial\phi_C/\partial pH \cong 0$ or 120 mV according as the pH is below or above 12. This indicates that the cathodic reaction is controlled by the slowness of the stage

$$H_2O_2 + e \rightarrow OH + OH^- .$$

With respect both to chemical (catalase) and to electrochemical activity the phthalocyanines investigated form the sequence

polymeric cobalt > monomeric iron > monomeric cobalt phthalocyanines.

2. Photocatalytic Reactions

As noted in Section II, phthalocyanines are photoconductors. When thin layers are illuminated in the wavelength range 0.5–0.8 μm, free charge carriers are formed: an internal photoeffect arises. The concentration of free carriers may increase more than hundredfold[1,65] in metal-free phthalocyanine. Recently the effect of illumination on the electroreduction of oxygen has been studied on metalfree, copper, cobalt, and iron phthalocyanines either sputtered on to a support (pyrographite, gold, platinum, etc.)[125,126,128] or deposited from solution on the surface of a mercury drop[127]. Both photoactivity and dark activity are greatly influenced by the nature of the central ion[125,127], the material of the support[125–128], and the solution pH.[125]

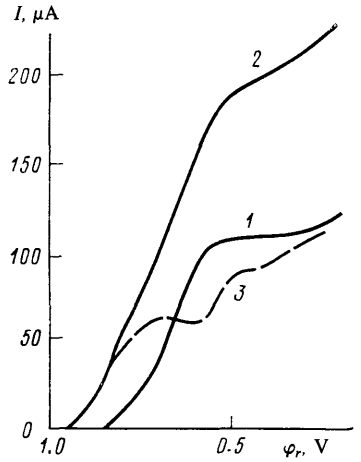


Figure 6. Polarisation curves for the reduction of oxygen on an H_2Phth film (100 Å) in 0.1 *N* KOH: 1) without illumination; 2) illumination with white light; 3) photocurrent[80].

Light has the greatest effect on the rate of the electroreduction of oxygen on metal-free phthalocyanine, the photoelectrochemical activity diminishing in the sequence of phthalocyanines

metal-free > copper > cobalt, iron.

Thus the sequence of electrocatalytic activity of phthalocyanines in the reduction of oxygen with the electrode illuminated has been opposite to that observed under dark conditions. It has been suggested[125,126,128] that light increases the concentration of O_2^- ions without changing the mechanism of the electroreduction of oxygen. According to other workers[127] it increases the rate of cathodic reduction of hydrogen peroxide. Fig.6 shows polarisation curves obtained in 0.1 *N* aqueous potassium hydroxide for the reduction of oxygen on a thin film of metal-free phthalocyanine sputtered on pyrographite. The photocurrent (curve 3) exceeds or equals the dark current, which probably indicates a change in reaction mechanism on illumination of the phthalocyanine—occurrence of the direct reaction to water.

3. Other Reactions

According to the patent literature organic complexes of metals are beginning to be used for activation of the electrooxidation of carbon monoxide[129], hydrogen[110,130], hydrazine [129,130], and several organic compounds (methanol[130], and

formic[129,131] and oxalic[129] acids) and of the electroreduction of carbon dioxide[132] (Table 5). As in the electroreduction of oxygen, phthalocyanines, tetraphenylporphyrins, and dibenzotetra-aza-annulenes of several metals are used. The oxidation of organic and inorganic compounds is catalysed by metal-free, copper, palladium, chromium, and vanadyl phthalocyanines and by nickel, zinc, and platinum tetraphenylporphyrins, i.e. by compounds that are relatively inactive towards the electroreduction of oxygen. Monomeric cobalt, nickel, manganese, palladium, copper, and iron phthalocyanines have been investigated for the electroreduction of carbon dioxide[132]. A high rate of electroreduction to oxalic and gluconic acids was observed only in the presence of cobalt and nickel phthalocyanines. The mechanism of these reactions was not investigated, but this work is evidently promising and will be developed both theoretically and by extending the ranges of electrochemical reactions and catalytically active organic compounds.

Table 5. Electrochemical activities of organic complexes towards oxidation.

Cpd.	Catalyst	Rate of oxidation	Ref.
HCOOH	CoDBTAA	11.0 mA mg^{-1} (φ_r = 0.5 V), 2 *N* H_2SO_4	129
	CoDBTAA, heat-treated	6.8 mA mg^{-1} (φ_r = 0.35 V), 2 *N* H_2SO_4	131
N_2H_4	CoDBTAA	7.5 mA mg^{-1} (φ_r = 0.5 V), 2 *N* H_2SO_4	129
	Co bis-1-hydroxy-anthraquinone	10 mA cm^{-2} ($\Delta\varphi$ = 0.1 V), KOH	130
H_2	PdPhth	500 mA cm^{-2} (φ_r = 0.5 V), 2 M H_2SO_4	130

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Intensive reserach on electrocatalysis by organic complexes of metals has been undertaken during the past five years, but appreciable progress has already been made during this short period, both in understanding the nature of electrocatalytic activity and in elucidating the possible practical application of organic catalysts for the activation of electrochemical reactions. Local interaction of the electrochemical reactants with the catalyst molecule is shown to play the chief part. In the electroreduction of oxygen the direction and the rate are determined by the nature of the central metal ion in the organic complex and hence by the character of the adsorption interaction of an oxygen molecule with it. Detailed kinetic investigations have suggested phenomenological schemes for electrode reactions. Several metalloporphyrins are promising electrocatalysts for alkaline electrolytes. New possibilities, especially in acid media, are opened up by the use of thermally stabilised macromolecular compounds.

The task of future research is to extend the range of electrocatalytically active systems and electrocatalytic reactions. A more profound theoretical study is required of the adsorption interaction of reactants and catalyst, which governs the main effects of electrocatalysis. This needs the development of combined physical and electrochemical methods for determining the structure of the interface between organic catalyst and electrolyte.

REFERENCES

1. F.H.Moser and A.L.Thomas, "Phthalocyanine Compounds", Reinhold, New York, 1963.
2. J.E.Falk, "Porphyrins and Metalloporphyrins", Elsevier, New York, 1964.
3. F.Gutmann and L.E.Lyons, "Organic Semiconductors" (Wiley, New York, 1967) (Translated into Russian), Nauka, Moscow, 1970.
4. L.P.Kayushin, Z.P.Gribova, and O.A.Azizova, "Elektronnyi Paramagnitnyi Rezonans Fotoprotsessov Biologicheskikh Soedinenii" (Electron Spin Resonance of Photoprocesses of Biological Compounds), Nauka, Moscow, 1973.
5. A.N.Sidorov and V.G.Maslov, Uspekhi Khim., **44**, 577 (1975) [Russ.Chem.Rev., No.4 (1975)].
6. W.Hanke, Z.Chem., **9**, 1 (1969).
7. S.Z.Roginskii, "Elektronnye Yavleniya v Geterogennom Katalize" (Electronic Phenomena in Heterogeneous Cata-Catalysis), Nauka, Moscow, 1975.
8. S.A.Borisenkova and A.P.Rudenko, Vestnik Moskov. Univ., **17**, 3 (1976).
9. Y.Niwa, H.Kobayashi, and T.Tsuchiya, J.Chem.Phys., **60**, 799 (1974).
10. A.M.Schaffer and M.Gourterman, Theor.Chim.Acta, **25**, 63 (1972).
11. M.Zerner, M.Gouterman, and H.Kobayashi, Theor. Chim.Acta, **6**, 363 (1966).
12. R.Taube, Z.Chem., **6**, 6 (1966).
13. S.C.Mathur and J.Singh, Internat.J.Quant.Chem., **6**, 57 (1972).
14. M.J.Stillman and A.J.Thomson, J.Chem.Soc., Faraday Trans.II, **70**, 805 (1974).
15. B.D.Berezin and L.P.Shormanova, Vysokomol.Soed., **10A**, 384 (1968).
16. D.J.E.Ingram, "Biological and Biochemical Applications of Electron Spin Resonance" (Hilger, London, 1969) (Translated into Russian), Mir, Moscow, 1972.
17. A.Wolberg and J.Manassen, J.Amer.Chem.Soc., **92**, 2982 (1970).
18. F.A.Walker, J.Amer.Chem.Soc., **92**, 4235 (1970).
19. B.W.Dale, R.J.P.Williams, P.R.Edwards, and C.E.Johnson, J.Chem.Phys., **49**, 3445 (1968).
20. A.J.Appleby, J.Fleisch, and M.Savy, J.Catalysis, **44**, 281 (1976).
21. C.G.Barraclough, R.L.Martin, S.Mitra, and R.S.Sherwood, J.Chem.Phys., **53**, 1638 (1970).
22. C.G.Barraclough, R.L.Martin, S.Mitra, and R.S.Sherwood, J.Chem.Phys., **53**, 1643 (1970).
23. D.C.Grenoble and H.D.Drickamer, J.Chem.Phys., **55**, 1624 (1971).
24. V.M.Mamaev, G.V.Ponomarev, S.Z.Zenin, and R.P.Evstigneeva, Teor.Eksper.Khim., **6**, 40 (1970).
25. B.D.Berezin, Izv.Vys.Ucheb.Zaved., Khim.i Khim. Tekhnol., **14**, 336 (1971).
26. J.Fajer, D.C.Borg, A.Forman, D.Dolphin, and R.H.Felton, J.Amer.Chem.Soc., **92**, 3451 (1970).
27. J.-H.Fuhrhop, K.M.Kadish, and D.G.Davis, J.Amer. Chem.Soc., **95**, 5140 (1973).
28. D.W.Clack and J.R.Yandle, Inorg.Chem., 11, 1738 (1972).
29. A.P.Bobrovskii and A.N.Sidorov, Zhur.Strukt.Khim., **17**, 63 (1976).
30. M.J.Stillman and A.J.Thomson, J.Chem.Soc., Faraday Trans.II, **70**, 790 (1974).
31. L.D.Rollman and R.T.Iwamoto, J.Amer.Chem.Soc., **90**, 1455 (1968).
32. C.Ercolani and C.Neri, Chem.Comm., 1715 (1967).

33. C.Ercolani, C.Neri, and G.Sartori, J.Chem.Soc.A, 2123 (1968).
34. P.K.Picuilo, G.Rupprecht, and W.Schedit, J.Amer. Chem.Soc., **96**, 5293 (1974).
35. B.B.Wayland and L.W.Olson, J.Amer.Chem.Soc., **96**, 6037 (1974).
36. W.R.Scheidt and M.E.Frisse, J.Amer.Chem.Soc., **97**, 17 (1975).
37. W.R.Scheidt and P.L.Picuilo, J.Amer.Chem.Soc., **98**, 1913 (1976).
38. C.J.Welchler, D.L.Anderson, and F.Basolo, J.Amer. Chem.Soc., **97**, 6707 (1975).
39. V.Stynes and B.R.James, J.Amer.Chem.Soc., **96**, 2733 (1975).
40. Shie-Ming Peng and J.A.Ibers, J.Amer.Chem.Soc., **98**, 8032 (1976).
41. I.Collamati, C.Elcolani, and G.Rossi, Inorg.Nuclear Chem.Letters, **12**, 799 (1976).
42. B.B.Wayland and D.Mohajer, Chem.Comm., 776 (1972).
43. Y.Iwamoto and T.Kwan, J.Catalysis, **18**, 354 (1970).
44. D.W.Wagnerowa, E.Schwertnerova, and J.Veprek-Siska, Coll.Czech.Chem.Comm., **39**, 1980 (1974).
45. D.V.Stynes, B.R.James, and J.A.Ibers, J.Amer. Chem.Soc., **95**, 1796 (1973).
46. F.A.Walker, J.Amer.Chem.Soc., **95**, 1154 (1973).
47. K.M.Kadish and M.M.Morrison, Third International Symposium Biochemistry, Jülich, 1975, p.100.
48. S.Z.Roginskii, Problemy Kinetiki i Kataliza, **15**, 12 (1973).
49. B.D.Berezin and L.N.Shlyapova, Izv.Vys.Ucheb Zaved., Khim.i Khim.Tekhnol., **14**, 1665 (1971).
50. T.I.Andrianova, A.I.Sherle, and A.A.Berlin, Izv. Akad.Nauk SSSR, Ser.Khim., No.3, 531 (1973).
51. F.Steinbach, Kinetika i Kataliz, **16**, 1094 (1975).
52. E.Kwaskowska-Chec, K.Fried, H.Przywarska-Boniecka, and J.J.Ziolkowski, React.Kinetics Catalysis Letters, 2, 425 (1975).
53. F.Steinbach and K.Hiltner, Z.phys.Chem.(Frankfurt), **83**, 128 (1973).
54. H.Kropf and O.J.Witt, Z.phys.Chem.(Frankfurt), **76**, 331 (1971).
55. N.N.Ionescu, R.H.Schuster, D.Trestianu, and A.Mikhailescu, Z.Chem., **15**, 496 (1975).
56. J.Manassen and A.Bar-Ilan, J.Catalysis, **17**, 86 (1970).
57. A.Bar-Ilan and J.Manassen, Intra-Sci.Chem.Reports, **6**, 65 (1972).
58. J.Manassen, J.Catalysis, **33**, 133 (1973).
59. A.Bar-Ilan and J.Manassen, J.Catalysis, **33**, 68 (1974) [sic].
60. A.D.Simonova, N.P.Keier, N.N.Kundo, E.K.Mamaeva, and G.V.Glazneva, Kinetika i Kataliz, **14**, 988 (1973).
61. J.K.Acres and D.D.Eley, Trans.Faraday Soc., **60**, 1157 (1964).
62. B.D.Berezin and A.N.Shlyapova, Izv.Vys.Ucheb. Zaved., Khim.i Khim.Tekhnol., **12**, 1641 (1968).
63. S.D.Levina, T.I.Andrianova, M.M.Sakharov, O.A.Golovina, K.P.Lobanova, and Z.A.Rotenberg, Zhur.Fiz.Khim., **40**, 1229 (1966) [Russ.J.Phys.Chem., No.6 (1966)].
64. P.Waldmeier and H.Sigel, Chimia, **24**, 196 (1970).
65. F.F.Vol'kenshtein, "Fizikokhimiya Poverkhnosti Poluprovodnikov" (Physical Chemistry of the Surface of Semiconductors), Nauka, Moscow, 1973.
66. M.R.Tarasevich, Elektrokhimiya, **9**, 599 (1973).
67. M.R.Tarasevich and K.A.Radyushkina, Elektrokhimiya, 6, 376, 372 (1970).
68. M.R.Tarasevich and V.S.Vilinskaya, Elektrokhimiya, 8, 1489 (1972).
69. M.R.Tarasevich, F.Z.Sabirov, and R.Kh.Burshtein, Elektrokhimiya, **7**, 404 (1971).
70. A.M.Khutornoi, G.I.Zakharkin, and M.R.Tarasevich, Zhur.Fiz.Khim., **7**, 404 (1971) [Russ.J.Phys.Chem., No.2 (1971)].
71. M.R.Tarasevich, K.A.Radyushkina, V.Yu.Filinovskii, and R.Kh.Burshtein, Elektrokhimiya, **6**, 1522 (1970).
72. H.S.Wroblowa, Yen-Chi Pan, and G.Razumney, J. Electroanalyt.Chem., **69**, 195 (1976).
73. A.Kozawa, V.E.Zilionis, and R.J.Brodd, J.Electrochem. Soc., **117**, 1470, 1474 (1970).
74. A.Kozawa, V.E.Zilionis, and R.J.Brodd, J.Electrochem. Soc., **118**, 1705 (1971).
75. M.R.Tarasevich and V.A.Bogdanovskaya, Bioelectrochem.Bioenerg., **2**, 69 (1975).
76. M.Savy, G.Magner, and G.Perslerbe, Compt.rend., **275**, 163 (1972).
77. M.Savy, C.Bernard, and G.Magner, Electrochim.Acta, **20**, 383 (1975).
78. V.E.Kazarinov, M.R.Tarasevich, K.A.Radyushkina, and V.N.Andreev, J.Electroanalyt.Chem., **100**, 225 (1979).
79. K.A.Radyushkina, M.R.Tarasevich, and S.I.Andruseva, Elektrokhimiya, **11**, 1079 (1975).
80. M.R.Tarasevich and K.A.Radyushkina, Izv.Vys.Ucheb. Zaved., Khim.i Khim.Tekhnol., **19**, 1639 (1976).
81. M.R.Tarasevich, K.A.Radyushkina, and S.I.Andruseva, Bioelectrochem.Bioenergy., **4**, 3 (1977).
82. H.Jahnke and M.Schönborn, Cömptes rendus des Troisièmes Journées internationales d'Etude des Piles à Combustible, 1969, Presses academiques Européennes, Bruxelles, p.60.
83. H.Alt, H.Binder, W.Lindner, and G.Sandstede, J. Electroanalyt.Chem., **31**, Appl.19 (1971).
84. H.Alt, H.Binder, A.Köhling, and G.Sandstede, Electrochim.Acta, **17**, 873 (1972).
85. H.Alt, H.Binder, and G.Sandstede, J.Catalysis, **28**, 8 (1973).
86. F.Beck, W.Dammert, J.Heiss, H.Hiller, and R.Polster, Z.Naturforsch., **28a**, 1009 (1973).
87. F.Beck, J.Appl.Electrochem., **7**, 239 (1977).
88. H.Meier, W.Albrecht, U.Tschirwitz, and E.Zimmerhackl, Ber.Bunsengesellschaft phys,Chem., **77**, 843 (1973).
89. V.S.Bagotskii, M.R.Tarasevich, and V.Yu.Filinovskii, Elektrokhimiya, **6**, 84 (1972).
90. G.Ya.Slaidin', V.S.Bagotskii, M.R.Tarsevich, L.Yu.Balode, Ya.B.Shimshelevich, G.V.Shteinberg, and Ya.E.Chakste, in "Materialy IV Vsesoyuznoi Konferentsii po Kataliticheskim Reaktsiyam v Zhidkoi Faze" (Proceedings of the Fourth All-Union Conference on Catalytic Reactions in the Liquid Phase), Alma-Ata, 1974, p.346.
91. R.Dabrowski, M.Matysiak, and Z.Witkiewicz, "Electrochemical Power Sources", Prague, 1975, p.178.
92. Yu.A.Chizmadzhev, V.S.Markin, M.R.Tarasevich, and Yu.G.Chirkov, "Makrokinetika Protsessov v Poristykh Sredakh" (Macrokinetics of Processes in Porous Media), Nauka, Moscow, 1971.
93. K.A.Radyushkina, M.R.Tarasevich, and S.I.Andruseva, Zhur.Fiz.Khim., **52**, 1311 (1978) [Russ.J.Phys. Chem., No.5 (1979)].
94. M.Savy, P.Andro, G.Bernard, and G.Magner, Electrochim.Acta, **18**, 191 (1973).
95. W.Beyer and F.Sturm, Angew.Chem., **84**, 154 (1972).
96. S.I.Andruseva, M.R.Tarasevich, and K.A.Radyushkina, Elektrokhimiya, **13**, 253 (1977).
97. J.P.Randin, Electrochim.Acta, **19**, 83 (1974).

98. R.J.Taylor and A.A.Humffray, J.Electroanalyt.Chem., **64**, 63 (1975).
99. R.Jasinski, J.Electrochem.Soc., **112**, 526 (1965).
100. H.Tanaka, A.O.Negishi, and J.Ono, Denki Kagaku, **39**, 596 (1971).
101. K.A.Radyushkina, R.Kh.Burshtein, B.D.Berezin, M.R.Tarasevich, and S.D.Levina, Elektrokhimiya, **9**, 410 (1973).
102. K.A.Radyushkina, O.A.Levina, M.R.Tarasevich, R.Kh.Burshtein, B.D.Berezin, O.A.Kofman, and L.P.Shormanova, Elektrokhimiya, **11**, 989 (1975).
103. M.Musilova, J.Mrha, and J.Jindra, J.Appl.Electrochem., **3**, 213 (1973).
104. L.J.Johansson, J.Mrha, and R.Larsson, Electrochim. Acta, **18**, 255 (1973).
105. J.A.S.Bett and J.T.Lemquist, Amer.Chem.Soc., Div. Fuel Chem.Progr., **13**, 44 (1969).
106. H.Meier, W.Albrecht, U.Tschirwitz, and E.Zimmerhackl, Ber.Bunsengesellschaft phys.Chem., **76**, 1104 (1972).
107. C.Kretzschmar and K.Wiesener, Z.phys.Chem.(Leipzig), **257**, 39 (1976).
108. A.J.Appleby and M.Savy, Electrochim.Acta, **21**, 567 (1976).
109. French P.1 582 905 (1969); Chem.Abs., **73**, 5165 (1970).
110. US P.3 585 079 (1971); Chem.Abs., **77**, 13 245 (1972).
111. BRD P.Application 2 046 354 (1972); Chem.Abs., **77**, 69 412 (1972).
112. BRD P.Application 2 049 008 (1973); Chem.Abs., **78**, 91 840 (1973).
113. French P.2 100 585 (1972); Chem.Abs., **78**, 51 860 (1973).
114. BRD P.Application 2 549 083 (1977); Chem.Abs., **87**, 104 469 (1977).
115. S.J.Yao, M.Michuda, F.Markley, and S.K.Wolfson, "Direct Conversion of Thermal into Electrical Energy and Fuel Cells", Inf.Byull., **4**, 141 (1974).
116. S.N.Pobedinskii, A.A.Trofimenko, M.I.Bazanov, A.N.Aleksandrova, K.N.Belongov, and M.I.Al'yanov, in "III Vsesoyuznyi Simpozium po Kinetike i Mekhanizmu Reaktsii s Uchastiem Kompleksnykh Soedinenii" (Third All-Union Symposium on the Kinetics and Mechanism of Reactions Involving Complex Compounds), Ivanovo, 1974, p.102.
117. A.V.Dribinskii, M.R.Tarasevich, R.Kh.Burshtein, N.N.Lezhnev, K.A.Radyushkina, O.A.Levina, and R.I.Zusman, Elektrokhimiya, **14**, 22 (1978).
118. A.V.Dribinskii, M.R.Tarasevich, R.Kh.Burshtein, K.A.Radyushkina, and O.A.Levina, Elektrokhimiya, **13**, 1631 (1977).
119. A.V.Dribinskii, M.R.Tarasevich, and R.Kh.Burshtein, Elektrokhimiya, **7**, 1144 (1971).
120. V.S.Bagotskii, M.R.Tarasevich, K.A.Radyushkina, O.A.Levina, and S.I.Andruseva, Dokl.Akad.Nauk SSSR, **233**, 889 (1977).
121. O.A.Levina and K.A.Radyushkina, USSR P.542 416 (1975); Byull.Izobr., No.27, 205 (1977).
122. A.A.Berlin, Uspekhi Khim., **44**, 502 (1975) [Russ. Chem.Rev., No.3 (1975)].
123. G.Richter and G.Luft, Ber.Bunsengesellschaft.phys. Chem., **76**, 1105 (1972).
124. G.I.Zakharkin and M.R.Tarasevich, Elektrokhimiya, **11**, 1019 (1975).
125. G.A.Alferov and V.I.Sevast'yanov, Elektrokhimiya, **11**, 827 (1975).
126. V.I.Sevast'yanov, G.A.Alferov, A.N.Asanov, and G.G.Komissarov, Biofizika, **20**, 1004 (1975).
127. Yu.S.Schumov and M.Heyrovsky, J.Electroanalyt. Chem., **65**, 469 (1975).
128. B.Schreiber and M.Savy, Compt.rend., **282**, 787 (1976).
129. BRD P.Application 2 128 842 (1972); Chem.Abs., **78**, 79 028 (1973).
130. US P.3 617 388 (1971).
131. H.Jahnke, M.Schönborn, and G.Zimmermann, Topics Cur.Chem., **61**, 133 (1976).
132. S.Meshitsuka, M.Ichikawa, and K.Tamaru, Chem. Comm., **5**, 158 (1974).

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