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Metallophthalocyanines as catalysts in electrochemical reactions

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A. INTRODUCTION

Metallophthalocyanines and other macrocyclic transition metal complexes of similar structure are well known as catalysts for both homogeneous and heterogeneous chemical reactions [1–5]. In most cases, these reactions involve the transfer of electrons. In the case of oxidations, the reaction is promoted by molecular oxygen

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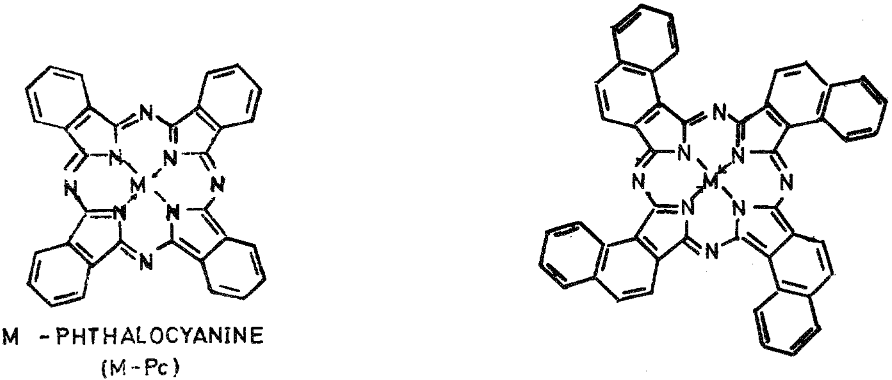
and mediated by phthalocyanine, which interacts with the molecule to be oxidized. If the metallophthalocyanine is attached by some suitable means to an electronic conductive surface such as an electrode, one might expect to observe catalytic activity for an electrochemical reaction, modifying in this fashion the electrode surface.

The first reaction studied using these complexes was the reduction of molecular oxygen. Jasinsky, in the mid-1960s [5,6] reported catalytic activity for Co-phthalocyanine for O_2 reduction. This finding led to extensive research in many places in the world on metal chelates as possible electrocatalysts for the reduction of O_2, a reaction of technological importance in the development of fuel cells. The topic has been reviewed by several authors [7–10]. The aim of many electrochemical investigations on metallophthalocyanines has been to obtain active materials that could replace platinum and other expensive substances as catalysts for the oxygen cathode in fuel cells.

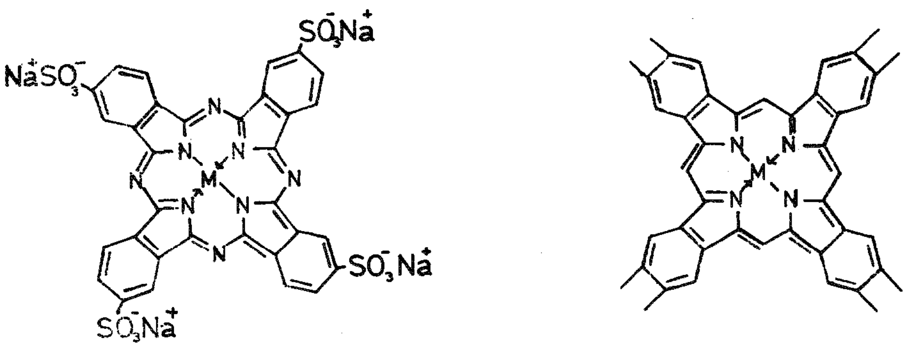
Metallophthalocyanines constitute a promising class of catalysts and they present some advantages over metal and metal oxides, not only because of the cost but also because they provide very interesting models for theoretical and experimental studies since their catalytic action can be described in terms of more definite parameters such as chemical structure, chemical and physical properties, their reactive centres can be identified, and their activity can be correlated to their activity in some chemical reactions that do not involve electrode surfaces. Figure 1 illustrates the structures of some metallophthalocyanines that have been studied for the electrocatalytic properties of O_2 reduction and other reactions. M-phthalocyanines (M-Pcs) are insoluble in water and they have been incorporated on electrodes by vacuum sublimation, vapour deposition or by precipitation or adsorption from a solution in an organic solvent or concentrated acid [7–10]. Water-soluble M-tetrasulphonated phthalocyanines (M-TSPcs) are irreversibly adsorbed on graphite surfaces from aqueous solutions [10]. Naphthalocyanines are incorporated on electrode surfaces by methods similar to those for M-Pcs. Polyphthalocyanines result from polymerization of M-Pcs by heat treatment in the presence of carbon powders and the electrode is then made with the resulting mixture [7].

Most of the work reported in the literature has been directed towards the oxygen reduction reaction and there are still relatively few papers published on the catalytic activity of these metal chelates for other electrochemical reactions. However, it has been demonstrated that some phthalocyanines and related macrocyclic complexes can promote the electro-oxidation of formic acid [7,11], CO [7,11–14], SO_2 [15–17], oxalic acid [18], hydrogen [19,20], hydrazine [7,11,21–26], mercaptoethanol [27], cysteine [22,28–30] hydroxylamine [25,31], glycine, alanine, and tyrosine [32], the evolution of oxygen [33], the reduction of H_2O_2 [34] and the electroreduction of CO_2 [35–38], cystine [28,39], alkylchlorides [40,41], molecular nitrogen [42], N_2O [43], NO [44], nitrate ions [45], thionyl chloride [46–60] and sulphuryl chloride [49]. It could be considered that the investigations on the electro-



M -PHTHALOCYANINE
(M-Pc)

M – NAPHTHALOCYANINE
(M-NPc)



M-TETRASULPHOPHTHALOCYANINE
(M-TSPc)

POLYMERIC PHTHALOCYANINE
$(M\ Pc)_n$

Fig. 1. Structures of some metallophthalocyanines.

catalytic activity of metallophthalocyanines for reactions other than the reduction of dioxygen are far from complete and there is a great variety of reactions to be studied using catalysts of this type.

Metallophthalocyanines are also promising for promoting photocatalytic reactions. They can act as spectral sensitizers deposited on semiconductor electrodes [61–78] so their applicability not only involves fuel cells but also solar energy conversion devices. The colour change of phthalocyanines following the oxidation state of the macrocyclic ligand has been recognized for some time and has opened up new investigations for its applications in electrochromic displays [79–81]. Related to this ability, the rare earth diphthalocyanines are noticeable by an electrochromic reversibility which allows their use as electro-optic transducers in plate screens [82–84]. Phthalocyanines are also promising as electrode materials not only as catalysts but as reactive species in lithium cells [85–87]. Combined with a lithium anode in an electrochemical cell, low-molecular unsubstituted phthalocyanines have shown discharge capacities ranging from 17 [86] to 26 equivalent electrons per phthalocyanine molecule [87].

B. OXYGEN REDUCTION ON METALLOPHTHALOCYANINES

(i) Theoretical aspects

The electrochemical reaction involving metal phthalocyanines as catalysts that has received by far the most attention in the literature is the electro-reduction of oxygen. This reaction takes place in the cathode in most known fuel cells and provides the maximum energy when the oxygen molecule is completely reduced to water via four electrons with a standard potential of 1.229 V vs. NHE. This reaction, which appears to be simple, is, in fact, rather complex. It proceeds via high-energy intermediates which slow down the overall reaction. On most electrode materials, it stops after the transfer of two electrons to give hydrogen peroxide with a standard potential of 0.695 V vs. NHE. If the reaction proceeds via two electrons, it provides nearly half of the energy given by the four e$^-$ reduction. Finding non-noble metal catalysts that promote the overall 4-e reduction of the oxygen molecule is one of the main tasks of the current research in the area. The tendency of the O_2 molecule to be reduced to H_2O_2 on most electrode materials is probably a consequence of the high stability of the O—O bond, which has a dissociation energy of 118 kcal mol^{-1}. In contrast, the dissociation energy of the O—O bond in H_2O_2 is only 35 kcal mol^{-1} . The O_2 molecule can be described according to the molecular orbital diagram shown in Fig. 2 [88–89]. According to Hund's rule, in the ground-state O_2 posseses two unpaired electrons located in a doubly degenerated π^* antibonding orbital. This corresponds to a triplet state. The O—O bond formed by a π bond between the 2p atomic orbitals consisting of a $\sigma(3\sigma_g)^2$ bond with two electrons and

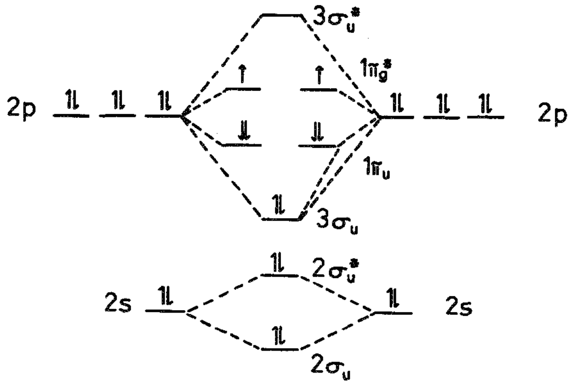


Fig. 2. Molecular orbital diagram of the oxygen molecule in the ground state. (Adapted from refs. 88 and 89.)

two $\pi(1\pi_u)^2(\pi_g)^1$ with three electrons each. These interactions give rise to a pair of bonding electrons and one anti-bonding on the same plane. The bond order is two. When O_2 undergoes reduction, the electrons added occupy anti-bonding orbitals, decreasing the bond order for O—O. This increases the O—O distance and the vibrational frequency decreases. The excess of bonding over non-bonding electrons in the diagram of Fig. 2 is four. This explains the high stability of the O_2 molecule and its relatively low reactivity, in spite of its high oxidizing power. Furthermore, the spin conservation principle restricts the reactions in which O_2 can participate. Dioxygen in its ground triplet state will lead to a triplet molecule when interacting with a singlet molecule. The life of the intermediate formed must be much greater than the time of a vibration in order to give a singlet state product. This is why oxygen acts as a one-electron oxidant instead of a two- or four-electron oxidant. The spin restriction can be overcome upon coordination of the O_2 molecule to a metal centre which, for our purposes could be surrounded by a macrocyclic ligand such as the phthalocyanine. The plausible 1:1 and 2:1 metal–dioxygen complex structures are illustrated in Fig. 3. Geometries **1** and **2** have been shown to give similar bonding patterns: each exhibits one σ and one π interaction. The Griffiths model [90] (**1**), involves a side-on interaction of O_2 with the metal. The bonding (see Fig. 4) can be viewed as arising from two contributions: a σ type of bond formed by the overlap between a mainly π orbital of oxygen and dz^2 (and s) on the metal and a π backbond interaction between the metal $d\pi$ orbitals and the partially occupied π^* antibonding orbital on O_2. In the Pauling model [91] (**2**), an end-on interaction of O_2 with the metal forming an angle close to 120° is proposed. This has been verified by crystallographic studies of O_2 adducts of metal complexes [92]. In this model, a σ-rich orbital of dioxygen donates electron density to an acceptor orbital dz^2 on the metal, forming a σ-type bond. A π interaction is also produced between the metal $d\pi$ (dxz, dyz) orbitals and π^* on dioxygen, with charge transfer from the metal to the O_2 molecule. The principal difference between geometries **1** and **2** are then steric factors and the nature of the σ bond formed. Both geometries can be viewed as exhibiting the strong σ donation of an electron pair from dioxygen but with different donor orbitals being

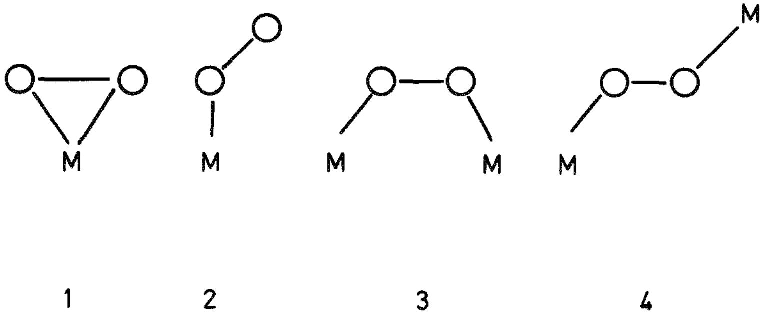


Fig. 3. Possible configuration of dioxygen interaction with a metal in a complex.

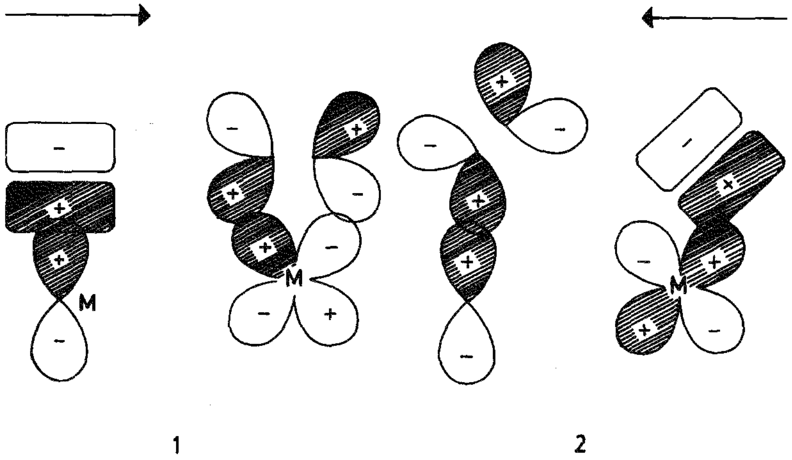


Fig. 4. Molecular orbitals involved in different interactions of O_2 with a metal centre.

considered: the geometry preferred must then largely be determined by the relative donating abilities of the filled π (geometry **1**) and σ (geometry **2**) dioxygen orbitals. Following Tatsumi and Hoffman [93], the bonding in the 2:1 complexes can be seen as arising from the interaction between the d-block orbitals on the metal with π^*, π and combinations of lone pair orbitals on O_2. The factors that govern the particular geometry, either bridge (**3**) or trans (**4**), can be traced by following the effect of lower symmetries on singlet and triplet dioxygen orbitals [94]. For macrocyclic ligands, such as porphyrins and phthalocyanines, steric effects can also be of great importance.

The bridge interaction was proposed by Yeager [95–97] and it is likely to occur on noble metals such as Pt where O_2 is reduced to water with little or no peroxide formed. A trans configuration is likely to occur with some cobalt phthalocyanines which form adducts with O_2 in solution [98–102]. Trans geometry is known to occur on a large series of dimeric cobalt dioxygen complexes [103]. Face-to-face porphyrins such as the ones reported by Collman et al. [104,105] and Chang and co-workers [106] are most likely to form these bridge configurations with O_2 and it will be discussed later that this type of interaction promotes the rupture of the O—O bond. A Griffith type of interaction could also lead to the rupture of the O—O bond. Some organometallic complexes described by Vaska [92] are known to form adducts with O_2 with a side-on interaction, as corroborated by X-ray studies. However, these compounds do not exhibit any catalytic activity for O_2 reduction, probably because the interaction leads to a stable adduct.

The interaction of the metal with the O_2 molecule is influenced by the electron density on the metal, which is obviously affected by the nature of the ligands, which determine the ligand field strength. From our previous discussion, the metal complex–O_2 bonding factors that influence the character of the d orbitals on the metal will have obvious consequences not only on the particular structure chosen but also on the ability of the metal complex to bind oxygen. Indeed, it is well known that the presence of π donors as a fifth ligand on phthalocyanines [107–112] increases their catalytic activity towards O_2 reduction. Another important factor is the particular symmetry of the ligand field which can alter the relative position and energy of the metal d levels and thus affects the overlap of these orbitals with the right orbitals of O_2.

Most of the experimental structures of the transition metal deoxy systems show only small deviations from the fourfold symmetry [112,113]. According to the work published in the literature, the complexes of Fe and Co show the highest electrocatalytic activity [114–147]. With phthalocyanines generally, the iron derivatives [7–10,129,130,135–137,144,145] are more active than cobalt complexes, whereas with porphyrins, the opposite is true in most cases [138]. Manganese chelates also show high activity, in some cases comparable with that of iron [137], but according to some authors [122,123,131,140], the activity diminishes with time.

It is clear at this point that a complete understanding of the nature of catalytic and electrocatalytic processes on metal macrocycles requires a detailed study of their electronic structure. There have been a considerable number of quantum-mechanical calculations on both porphyrins and phthalocyanine metal deoxy and oxy systems, but despite these efforts there are many unresolved questions.

Bonding in these tetradentate ligand systems can be viewed as arising from a σ coordination of nitrogen lone pairs with the metal and a π interaction of metal p-π and d-π with nitrogen p-π orbitals [148]. The smaller ring size, and consequently the smaller indole nitrogen–metal distances, gives rise to a larger ligand field in phthalocyanines compared with porphyrins. As a consequence, the $d_{x^2-y^2}$ metal orbital is strongly destabilized in the former due to the antibonding mixing between the mostly d orbitals with the appropriate symmetry ring MOs. The characterization of the ground electronic structure of the deoxy systems (and obviously the oxysystems) is still in doubt in some cases. Especially controversial are the Mn and Fe systems. Relevant to this problem appear to be the works of Coppens and co-workers [149–151] on relating transition metal orbital populations with X-ray diffraction data (and the spin-unrestricted X-α calculations on Fe porphyrin systems by Sontum et al. [152]. Finally, the mixing between d-π orbitals on the metal and p orbitals on indole nitrogens could provide a mechanism for back-bonding charge transfer from the metal to the ring, diminishing the electronic density at the metal and then its activity toward dioxygen. Experimental evidence in support of or against a significant metal π ring π back bonding has been discussed for the iron–porphyrin complexes [153,154,190–193]. Theoretical results on that problem consider Fe and Mn systems [154] but the information is not definitive. Clearly, more work is needed in order to identify the electronic structures that are responsible for the different behaviour of this macrocyclic compound.

(ii) Redox properties of phthalocyanines and electrocatalytic activity for O_2 reduction

The redox properties of metal phthalocyanines have been studied by many authors [155–189]. First-row transition metal phthalocyanines differ from those of the main-group M-Pcs due to the fact that metal "d" orbitals may be positioned between HOMO and LUMO of the phthalocyanine (Pc^{-2}) ligand [190–193]. This has been well established by several papers published by Lever et al. [155–163,173,181,182]. According to these studies, oxidation and reduction processes occurring on the metal in the phthalocyanine are expected only for Mn, Fe and Co derivatives. M(II)/M(I) and M(III)/M(II) reversible couples are observed for Co and Fe phthalocyanines and their tetrasulphonated parents. According to Lever et al. [158,173] only the Mn(III)/M(II) is observed for Mn phthalocyanines and not the Mn(II)/M(I) couple. For Cr, Ni, Cu and Zn phthalocyanines, redox processes take place on the phthalocyanine ring. In some circumstances, the Cr(III)/Cr(II) couple can be observed [183(b)].

Randin [194] and Beck [195] have explained the catalytic activity for O_2 reduction of phthalocyanines of different metals on the basis of a redox–catalysis type of process where the redox potential of the central metal ions plays a crucial role. According to these authors, during the adsorption of O_2 the metal ion in the phthalocyanine is oxidized, thereby reducing the O_2 molecule according to the scheme:

$$\mathrm{M(II)} + \mathrm{O_2} \rightarrow [\mathrm{M(III)}^+ \mathrm{O_2^-}] \qquad (1)$$

$$[\mathrm{M(III)}^+ \mathrm{O_2^-}] \rightarrow \text{products} + \mathrm{M(III)}^+ \qquad (2)$$

$$\mathrm{M(III)}^+ + e^- \rightleftharpoons \mathrm{M(II)} \qquad (3)$$

In order to account for supplementary experimental evidence, a somewhat modified model is proposed by Beck [195] in which the central metal ion could also be partially oxidized. According to reaction (1), the potential at which O_2 is reduced should be closely related to the M(III)/M(II) redox potential of the central metal ion. However, only in relatively few cases have these redox potentials actually been measured in the same electrolyte in which the O_2 reduction was studied. In most cases, as reported by Randin [194], these redox potentials were measured in non-aqueous solvents. The effect of pH on the redox potential in such water-free media is rather difficult to translate to that of the pH of water as a solvent. Moreover, the solution electrochemistry of phthalocyanines might differ from that when the complex is adsorbed or immobilized on an electrode surface. For example, Ni and Anson [196] have shown a 340 mV difference between a dissolved and an adsorbed cobalt porphyrin. Furthermore, correlations should be valid on the basis of this model only for those phthalocyanines that show redox processes occurring on the metal. Linear correlations, which are illustrated in Fig. 5, found by Randin [194] included Ni and Cu phthalocyanines and are debatable on the ground of the redox catalysis concept.

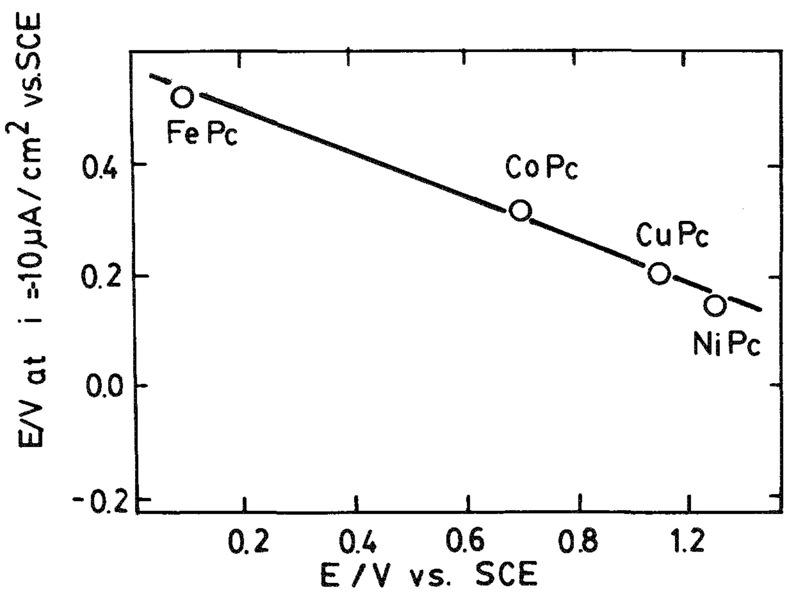


Fig. 5. Electrocatalytic activity for O_2 reduction shown by Fe, Co, Ni and Cu-Pc plotted vs. the first oxidation potential of the phthalocyanine. (Adapted from Randin [194].)

Van Veen et al. [12,131,138] using phthalocyanines and porphyrins of different metals, instead of finding linear correlations found curves that exhibit a maximum activity for metal chelates having intermediate M(III)/M(II) redox potentials. These volcano-shaped curves are illustrated in Figs. 6 and 7. Similar correlations between O_2 reduction and the redox potential are found if both processes are investigated in the same electrolyte. An example of such a work has been published by Yeager and co-workers [133–135], Zagal et al. [136,137], van der Putten et al. [197], and Savy and co-workers [198,199].

Figure 8 includes redox voltammetric data taken from ref. 136 and obtained in aqueous solution for phthalocyanines and tetrasulphophthalocyanines of Cr, Mn, Co and Fe adsorbed on a graphite electrode. The reversible voltammetry peaks labelled 1 correspond to the M(III)/M(II) process and peaks 2 to M(II)/M(I) even though, in the case of Mn phthalocyanines, it could correspond to an electron transfer process involving the ligand [158]. Figure 9 shows a curve that correlates the M(III)/M(II) redox potential of the metal chelates with their catalytic activity for O_2 reduction, expressed as potential at constant current. A volcano-shaped curve is observed. Figures 6, 7 and 9 illustrate very clearly that the M(III)/M(II) redox couple must be in the appropriate potential window in order to achieve catalytic effects. Volcano-shaped curves are common in chemical catalysis and electrocatalysis where activity is generally plotted against the heat of adsorption of a precursor or intermediate [200,201]. In the present case, the redox potential of the metal is probably correlated with the heat of adsorption of O_2 on the metal centre in the phthalocya-

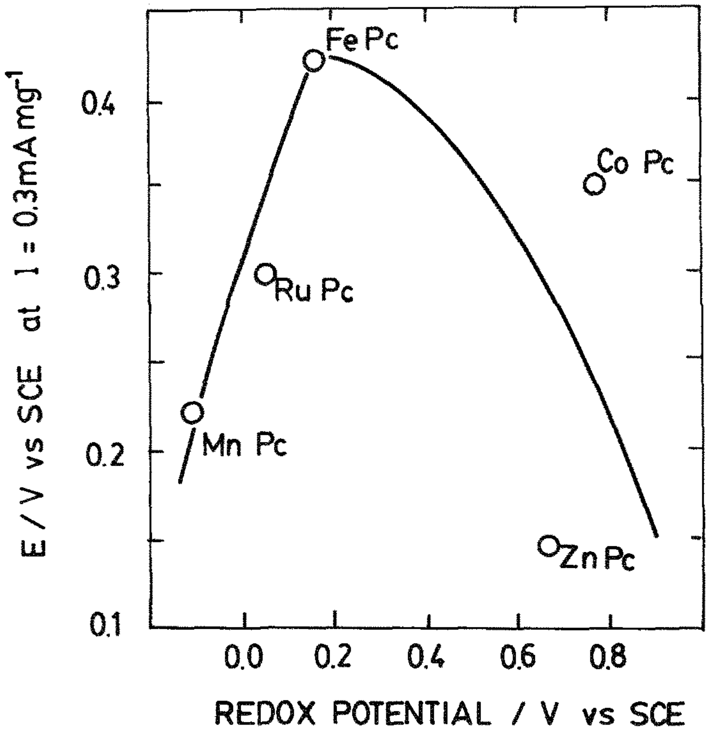


Fig. 6. Electrochemical activity for O_2 reduction of M-Pc plotted vs. the first oxidation potential of the metallophthalocyanine. (Adapted from van Veen and Visser [131].) Phthalocyanines deposited on Norit BRX carbon black electrodes.

nine. Recently, Savy and co-workers [198,199] have suggested that the M(II)/M(I) and not the M(III)/M(II) reversible couple is the one that plays the key role in determining the catalytic activity of M-Pc. Even if one plots the M(II)/M(I) redox potential against catalytic activity, the shape and maximum of the curves in Figs. 6, 7 and 9 should be about the same. Savy and co-workers worked with naphthalocyanines [198,199] but the ligand in this case should not affect the correlations found here.

The overall four-electron reduction of molecular oxygen in acid aqueous solution is:

$$O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O \qquad E_0 = 1.229 \text{ V} \tag{4}$$

In alkaline solution, O_2 reacts with water to give OH^- ions with $E_0 = 0.401$ V. Under exceptional conditions, the thermodynamic reversible potential for the four-electron reduction of oxygen has been achieved under open-circuit conditions but it is not generally the situation. The oxygen reduction process is not a reversible one in aqueous solutions and on most electrode surfaces proceeds via the transfer of two

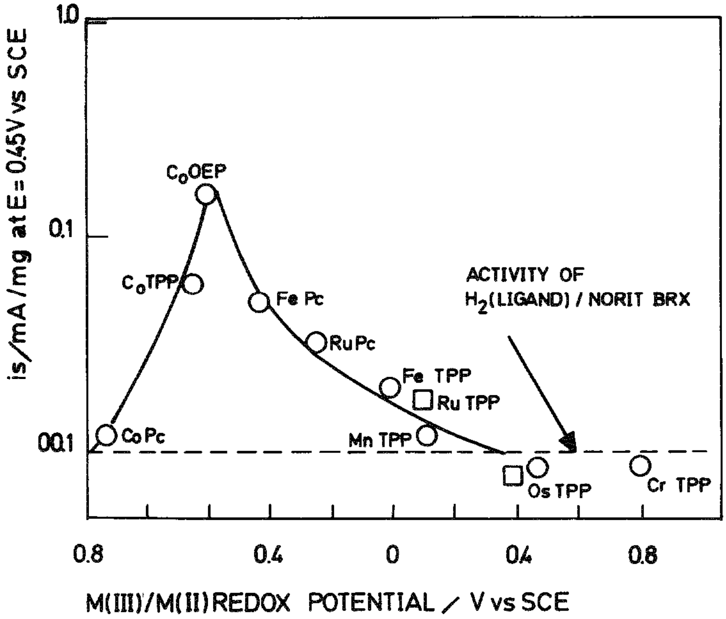


Fig. 7. Electrocatalytic activity of several metallophthalocyanines and metalloporphyrins for the reduction of O_2 plotted vs. the M(III)/M(II) redox potential. (Adapted from van Veen et al. [138].) TPP = tetraphenylporphyrin; OEP = octaethylporphyrin. Complexes deposited on Norit BRX carbon black electrodes.

electrons to give peroxide as the main or only product of the reaction, i.e.:

$$O_2 + 2H^+ + 2e \rightleftharpoons H_2O_2 \qquad E_0 = 0.695\ \text{V} \qquad (5)$$

The main interest in the electrocatalysis of O_2 reduction is finding electrode surfaces that promote the four-electron process since more energy is released in that reaction if, for example, O_2 is employed in the cathode in a fuel cell. The four-electron reduction of oxygen directly to water has been achieved using dicobalt cofacial porphyrin dimers adsorbed on graphite [104–106,202] and these studies have demonstrated the importance of the formation of a configuration involving the interaction of the oxygen molecule with two metal centres simultaneously. Unfortunately, these sorts of porphyrin dimer tend to lose their activity with time. Since the phthalocyanine nucleus is likely to be more stable [159], they look more attractive as possible catalysts for O_2 reduction. Binuclear phthalocyanines have been synthezised by Lever and co-workers [203,204]. The presence of two metal centres separated by a proper distance to promote the splitting of the O—O bond and then the four-electron reduction of oxygen seems not to be a necessary requisite since reduction directly to water has been observed on iron [128–130,135,136,144,145,205–208] and manganese phthalocyanines [137,205]. In the case of iron phthalocyanines, some authors have attributed this to the catalytic activity of Fe-Pc in chemically decomposing the peroxide generated electrochemically on the electrode surface and giving an apparent

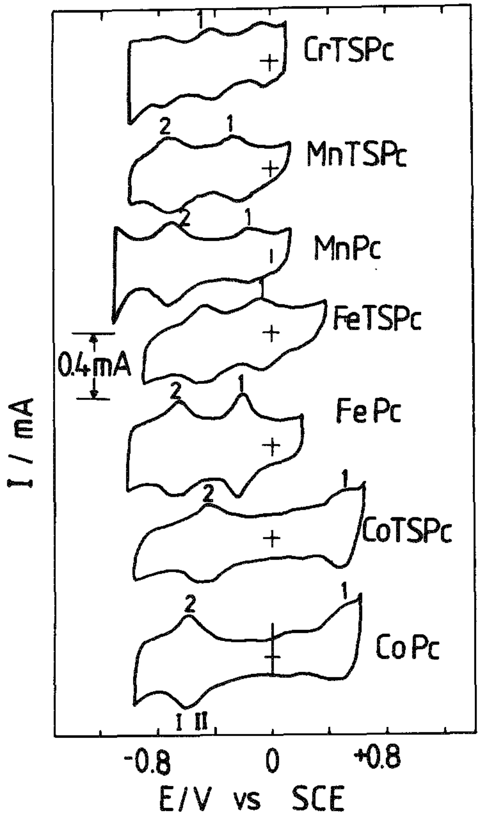


Fig. 8. Cyclic voltammograms of phthalocyanines and tetrasulphophthalocyanines adsorbed on pyrolytic graphite electrodes. Data taken in 0.1 M aqueous NaOH. (Adapted from Zagal et al. [137,205].)

four-electron reduction for O_2. In fact, it has been found that the catalytic activity for O_2 reduction of several phthalocyanines and porphyrins is directly correlated with their activity for peroxide decomposition. This can be seen in Fig. 10, taken from ref. 131.

Cobalt phthalocyanines behave differently from their Fe parents as they only promote the two-electron reduction [132–134,142,143,209–213] and could serve to solve this question. Investigations carried out with mixtures of Co and Fe phthalocyanines in different proportions [208] have indicated that these two catalysts, when co-adsorbed on the graphite substrate, behave independently, i.e. the peroxide generated on the Co centres is not decomposed on the Fe centres, which shows that Fe phthalocyanine is a true four-electron reduction catalyst for O_2, at least at low overpotentials, close to the Fe(III)/Fe(II) couple. The results are summarized in Fig. 11, which shows that the H_2O_2 yield varies linearly with the fraction of Co-TSPc co-adsorbed in a Fe-TSPc/Co-TSPc mixture. It is difficult to explain the splitting of the O—O bond if dioxygen interacts with only one Fe site at the time. It

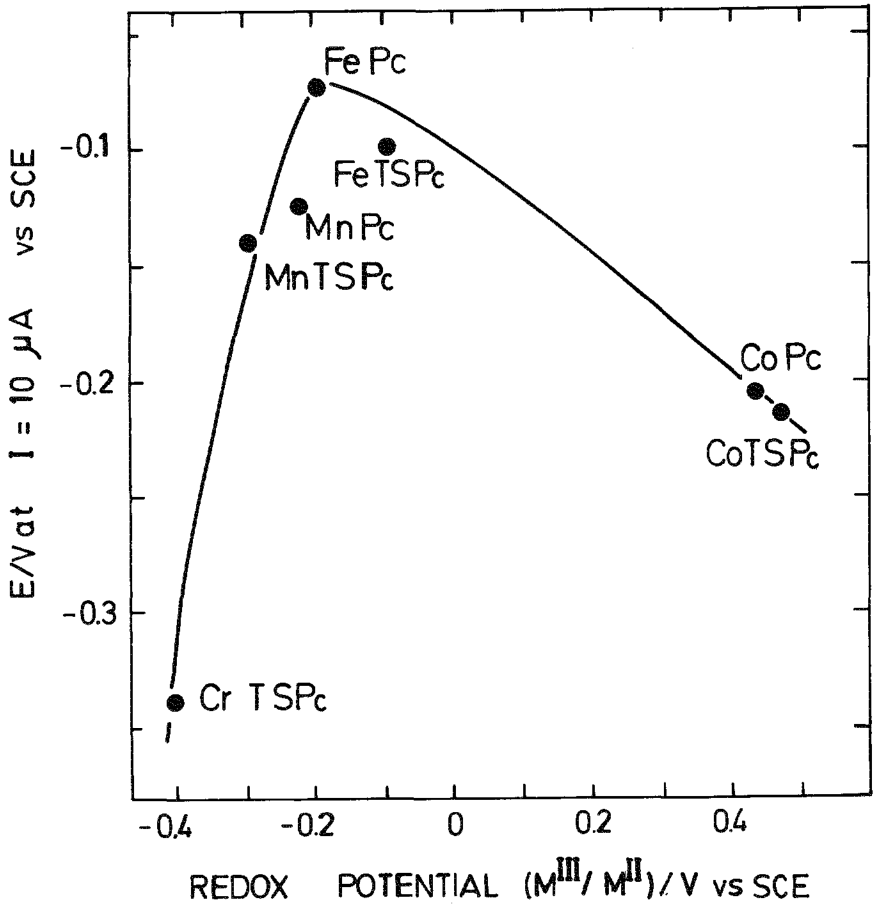


Fig. 9. Electrocatalytic activity of metallophthalocyanines for O_2 reduction vs. redox potential of the metal. (Adapted from refs. 137 and 205.)

is feasible that dimers are formed on the surface of the electrode as suggested by Yeager [95,96]. Another possibility is that dioxygen interacts side-on with the iron centre in the phthalocyanine (see Fig. 2). Semi-empirical all-valence electron calculations conducted by Sabelli and Melendres [110] have suggested that the side-on configuration is preferred to the end-on bonding in iron phthalocyanine, with the reverse being true for the oxygen–iron–porphyrin complex. Mn-Pc also promotes the four-electron reduction of O_2 at low overpotentials with no detectable amounts of H_2O_2 [205]. With both Fe and Mn phthalocyanines, the process takes place at potentials very close to the M(III)/M(II) reversible couple, whereas on Co and Cr phthalocyanines [137,205,214], the reduction of O_2 takes place at a potential far from that corresponding to the M(III)/M(II) reversible couple and the reduction of O_2 proceeds through the peroxide route. Phthalocyanines of metals that do not

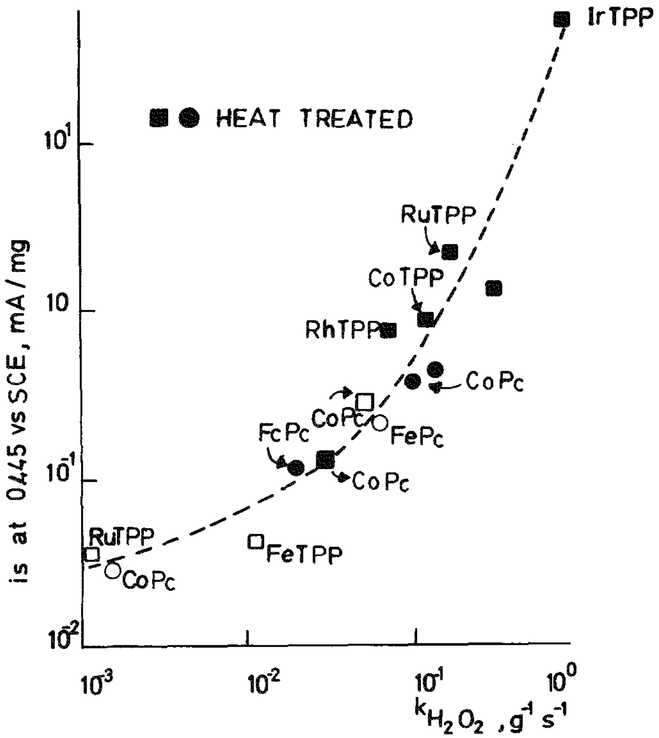


Fig. 10. Electrocatalytic activity of several phthalocyanines and tetraphenylporphyrins for O_2 reduction plotted vs. catalytic activity for H_2O_2 decomposition. (Adapted from ref. 138.)

exhibit redox processes, such as Ni, Cu and Zn, show very low activity and O_2 is reduced via two electrons to give peroxide [10,137,205,214].

O_2 reduction on iron phthalocyanines give Tafel slopes of ca. -35 mV per decade ($-2RT/3F$) which change to -120 mV per decade ($-2RT/F$) at higher overpotentials. The order in protons is one only in the low Tafel region and the order becomes zero at higher overpotentials [10,12,13,132,135–137,144,145]. It is interesting to note that a pure four-electron reduction process is only observed in the low Tafel slope region ($-2RT/3F$), which is the potential region where the redox type of catalysis takes place. When the Tafel slope increases to $-2RT/F$, some peroxide is formed. The same kinetic parameters are observed for O_2 reduction on Mn-TSPc and Mn-Pc [205]. The mechanism proposed by several authors [10,12,13,132,135–137,144,145] for the $-2RT/3F$ slope potential region is:

$$\mathrm{M(III)OH} + e^- \rightleftharpoons \mathrm{M(II)} + \mathrm{OH} \qquad \text{fast} \qquad (6)$$

$$\mathrm{M(II)} + O_2 \rightleftharpoons \mathrm{M(III)}^+ - O_2^- \qquad \text{fast} \qquad (7)$$

$$\mathrm{M(III)}^+ - O_2^- + e^- \rightarrow \text{intermediates leading to O—O rupture} \qquad \text{slow} \qquad (8)$$

where M = Fe and Mn.

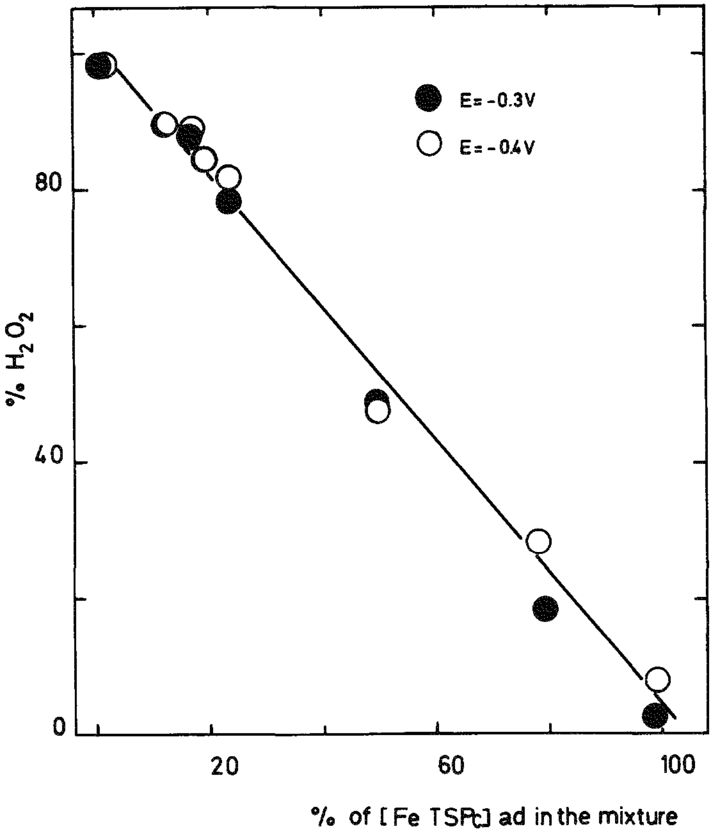


Fig. 11. H_2O_2 yield as a function of electrode composition on graphite with mixtures of Co-TSPc and Fe-TSPc co-adsorbed on the electrode surface. (Taken from ref. 208 and reproduced by permission of Elsevier.)

For Fe-Pc, Fe-TSPc, Mn-Pc and Mn-TSPc, the number of active sites M(II) is potential-dependent (under Nernstian control) as the reduction of oxygen starts at potentials close to the M(III)/M(II) couple. Tafel slopes of −40 mV at very low currents have been also observed by van den Brink et al. [143] on Co-Pc in alkaline media so the mechanism described above could operate on Co-Pc under those conditions. For those catalysts where the reaction takes place at potentials much more negative than the M(III)/M(II) couple, peroxide is the main product of the reaction, the number of active M(II) sites becomes potential independent, and only a −120 mV per decade ($2RT/F$) Tafel slope is observed [10,12,13,133,135–137,142,143]. The transfer of a first one-electron step becomes rate-controlling:

$$\mathrm{M(II)} + \mathrm{O_2} + e^- \rightarrow [\mathrm{M(II)} - \mathrm{O_2^-}] \quad \text{r.d.s.} \tag{9}$$

One considerable difficulty encountered in studying the transition metal phthalocyanines as catalysts for O_2 reduction has been long-term stability. In the case of the best catalyst, Fe-Pc, the oxidation of Fe(II)-Pc to Fe(III)-Pc increases the rate of oxidative attack on Fe-Pc by the hydrogen peroxide produced at more negative potentials [215–217]. Paliteiro et al. [218–221] have studied Pt-Pc, which is much more stable than Fe-Pc, and have found similar catalytic activity with reduction of O_2 via 4-e to give water. Even though the kinetic parameters (Tafel slopes of -35 mV at low overpotentials that change to -130 mV at more negative potentials) are similar to those observed for Fe-TSPc and Fe-Pc [135,205,206], the catalytic activity of Pt-Pc cannot be understood within the framework of a classical redox film [222] since the absence of any redox peaks for Pt-Pc films in voltammograms recorded in the absence of oxygen (as those obtained on other M-Pcs, see Fig. 9) suggests that a highly specific interaction between oxygen molecules and the Pt-Pc film can occur. The structure of α-Pt-Pc differs from that of the first-row phthalocyanines in that the Pt–Pt distance is shorter (ca. 0.38 nm or 0.39 nm in the γ form) than the first-row derivatives (ca. 0.46 nm) [222]. It may therefore be that this structure difference is enough to bring the Pt–Pt distance into the critical range for cooperative oxygen reduction, giving, for the initial stages of the mechanism:

$$\text{Pt-Pc} + O_2 \rightleftharpoons \text{Pt-Pc{—}O{—}O{—}Pt-Pc} \tag{10}$$

which is essentially similar to what occurs on binuclear face-to-face cobalt porphyrins [104–106]. The peroxy bridge cannot react by a disproportionation step in the rigid film and the O—O bond is presumably split by the subsequent electron transfer step [218]. Rotating disk and rotating ring-disk experiments [219] have shown that the reduction of oxygen occurs by two parallel mechanisms, with the four-electron reduction process being dominant. Small amounts of H_2O_2 are detected but the low activity of the Pt-Pc film towards reduction of H_2O_2 confirms that this is not an intermediate in the reduction of O_2 to water.

(iii) Electrocatalytic activity in terms of molecular orbital considerations

The catalytic activity of a metal chelate involving the formation of intermediates that interact with an active centre should be correlated with the ability of these complexes to bind extraplanar ligands. As discussed above, the ability of the metal to form these charge transfer intermediates could be correlated to the redox potential of the metal. The electronic structure of the metal in the phthalocyanine, which is obviously related to the redox potential, could serve to explain the activity of phthalocyanines of different metals. As discussed before, oxygen reduction is favoured by allowing the O_2 to accept charge from a filled or half-filled metal d orbital via back-bonding to the π^* orbital and/or to donate charge from the filled π MO to an empty or half-filled orbital of the metal. This catalytic bond would then be favoured by filled or half-filled dxz, dyz and dz^2 orbitals. Formation of this "most favourable" bond between O_2 or other reactant molecule at the axial position will further require, according to perturbation theory [223], that the energies of the predominantly d orbitals be the same or of similar energy as those of the intermediate species. Thus the catalytic activity should be related to the relative energies between the d orbitals of the metal in the phthalocyanine and the axial ligand, as explained by Hoffmann et al. [223,224] using symmetry and perturbation theory arguments. Molecular orbital calculations by Taube [225] using a simple LCAO-MO model indicate that the energy of the d orbitals in the metal phthalocyanine decreases almost linearly on going from Mn to Ni. The calculated energies are shown in Fig. 12. This is expected since the electronegativity increases along the transition metal series from Mn to Cu. According to Hoffmann, the energy of the π^* HOMO of the O_2 molecule may lie between the two extremes of the d orbital energies for the transition metal series (see Fig. 13). One would then expect a volcano-shaped curve if activity is

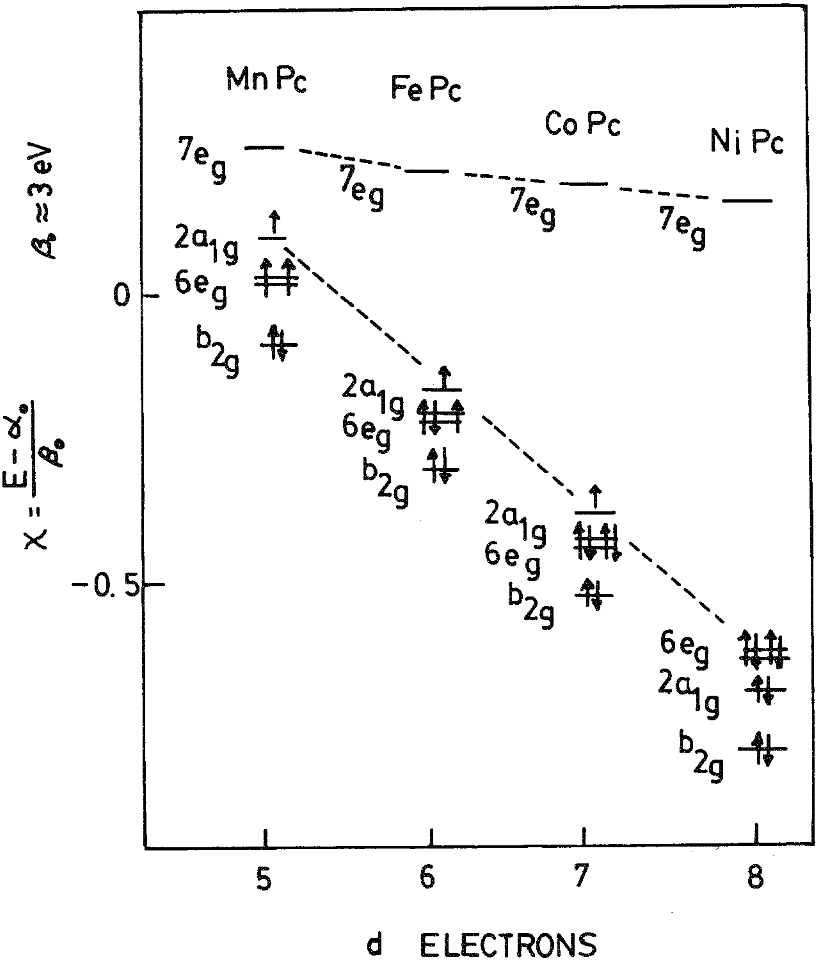


Fig. 12. Approximate position of the energy levels of homonuclear diatomics (left) and the first transition series (right). The metal levels will vary with the ligand and the charge on the metal according to ref. 224.

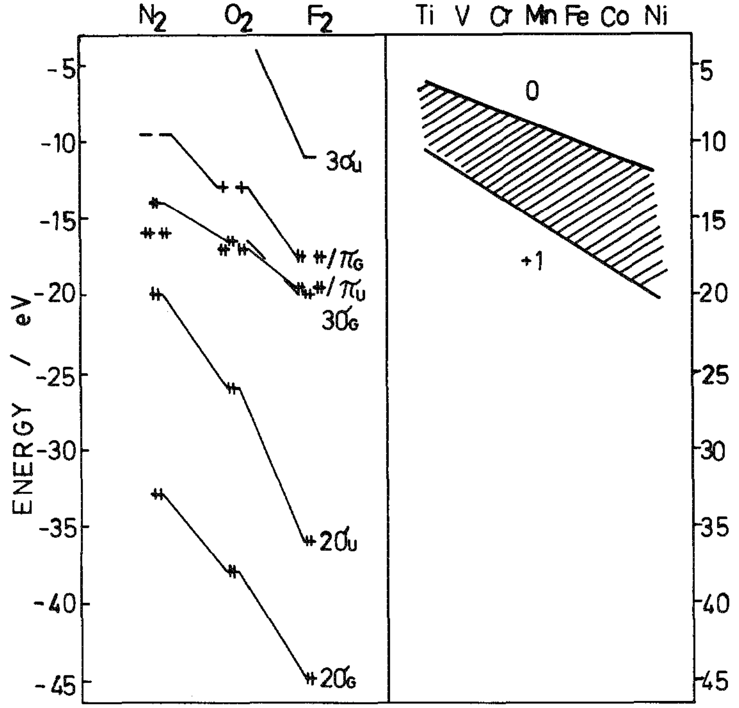


Fig. 13. Calculated orbital energies of metallophthalocyanines according to Taube [225].

plotted for this series going from Cr to Cu. Metals having the d orbitals very different in energy from that of O_2 will show lower activity than those lying at energies similar to the HOMO of O_2. Figure 14 shows a plot that illustrates that the assumptions made above are correct. It also shows that the energy of the d orbitals of Fe in Fe-TSPc may match with the energy of the corresponding π^* orbitals of dioxygen.

Ulstrup [226] has provided an alternative explanation for the catalytic activity of transition metal phthalocyanines in terms of a mediating role of the catalyst for the reaction which essentially supports the considerations discussed above. If the electronic levels of a bare electrode (without phthalocyanines) and the reactant molecule lie too far apart, the transition of electrons is improbable. The phthalocyanine catalyst should then act as a mediator, supplying intermediate electronic levels, thus increasing the probability of electron transfer.

C. ELECTRO-OXIDATION OF NITROGEN-CONTAINING COMPOUNDS CATALYZED BY METALLOPHTHALOCYANINES

(i) Electro-oxidation of hydrazine

Similar concepts to those discussed above for oxygen reduction can be applied to other electrochemical reactions. In principle, any molecule or species that requires

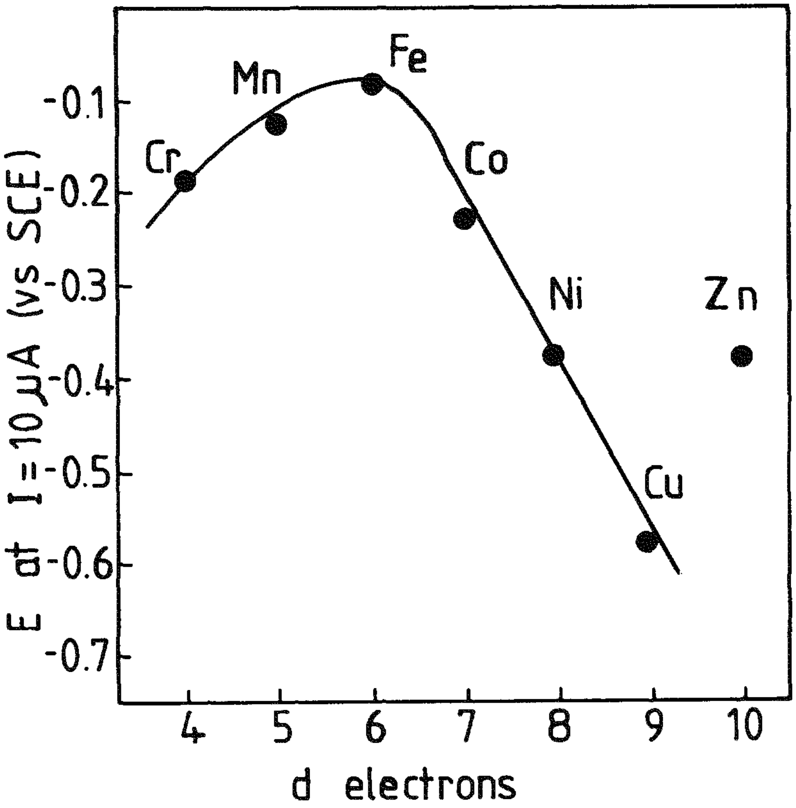


Fig. 14. Electrocatalytic activity of different M(II)-TSPs for O_2 reduction in 0.1 M aqueous NaOH as a function of the number of d electrons. (Adapted from refs. 137 and 205.)

the interaction with a metal centre or active site in order to undergo an electron transfer process could react catalytically in the presence of a metal phthalocyanine. Hydrazine is a highly reactive molecule that can be oxidized via four electrons to give molecular nitrogen ($E_0 = 1.16$ V vs. SHE). It has been used in the anode of fuel cells [227]. Hydrazine is known to interact with transition metal phthalocyanines [228] and this has been confirmed by several spectroscopic studies including IR [229] and EPR [230]. Oxidation of hydrazine by air is also catalyzed by metal phthalocyanines and tetrasulphophthalocyanines [230–232]. Several studies have shown that the electro-oxidation of hydrazine to molecular nitrogen is catalyzed by the phthalocyanines and tetrasulphophthalocyanines of several transition metals [21–26,137,233].

The redox catalysis concept can also be applied to the oxidation of hydrazine and the mechanisms proposed [21–26] take into account the M(II)/M(I) reversible couple of the metal in the phthalocyanine, i.e.

$$\mathrm{Co(I)L^-} \rightleftharpoons \mathrm{Co(II)L} + e^- \qquad (11)$$

$$\mathrm{Co(II)L + N_2H_4 \rightleftharpoons [LCo(I)^-(N_2H_4)^+]} \tag{12}$$

$$\mathrm{[LCo(I)^-(N_2H_4)^+] + OH^- \rightarrow products} \tag{13}$$

where L = Pc, TSPc.

$$\mathrm{M(II)L + N_2H_4 \rightarrow [L{-}M(I)^-(N_2H_4)^+]} \tag{14}$$

$$\mathrm{[L{-}M(I)^-(N_2H_4)^+] + OH^- \rightarrow L{-}M(II){-}N_2H_3 + H_2O + e^-} \tag{15}$$

$$\mathrm{[L{-}M(II){-}N_2H_3] + OH^- \rightarrow M(II)L + N_2H_2\cdot + H_2O} \tag{16}$$

where L = Pc, TSPc and M = Fe, Mn and Cr.

According to these mechanisms, the metal must be oxidized before accepting charge from the N_2H_4 molecule. Figure 15 shows a plot of activity versus redox potential for the M(II)/M(I) couple and a volcano-shaped curve similar to that obtained for

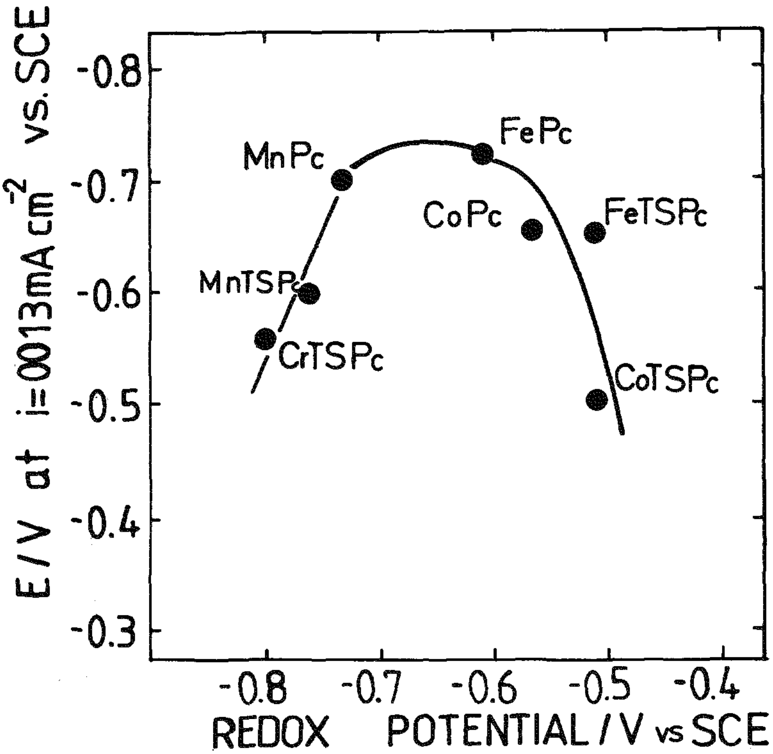


Fig. 15. Electrocatalytic activity of different metallophthalocyanines for the oxidation of hydrazine in 0.1 M NaOH as a function of the M(II)/M(I) redox potential. (Reproduced by permission of Elsevier (ref. 26).) Note that according to Lever and Wilshire [156], for Mn the redox process could involve the ligand.

the reduction of O_2, suggesting that the redox potential of the metal phthalocyanine plays an important role in determining the activity of the complex.

Molecular orbital considerations similar to those discussed before for O_2 reduction should be valid for hydrazine electro-oxidation, but different orbitals for the axial ligand are involved. The hydrazine non-bonding orbitals responsible for the oxidation of this molecule results from the π–σ^* and π^*–σ orbital mixing due to the pyramidalization at each N centre as shown in Fig. 16, in which only one of the hybridizations is depicted. This hybridization changes the original π^* character of the HOMO to a non-bonding orbital similar to the 3_{a1} lone-pair of ammonia [234]. The resulting MOs are ideally polarized for a σ interaction with a metal orbital such as the dz^2 shown in Fig. 16. It is interesting to note that, in contrast to the O_2 activation, in this case electron donation is in one direction, from N_2H_4 to the metal.

Figure 17 shows a volcano curve in which the activity is plotted vs. the number of d electrons in the metallophthalocyanine. Again, as observed for O_2 reduction, the iron complexes show the highest activity. This strongly suggests that the best match of energies between the metal d orbitals and the hydrazine HOMO occurs for iron phthalocyanines. This seems to indicate that the energies of the O_2 and N_2H_4 HOMOs are not far from each other. In fact, if one plots overpotential for O_2 reduction vs. overpotential for N_2H_4 oxidation for each metallophthalocyanine, a linear correlation is obtained as shown in Fig. 18.

(ii) Electro-oxidation of hydroxylamine

Hydroxylamine is known to interact with phthalocyanines. EPR spectroscopic studies conducted at low temperature have indicated that hydroxylamine forms stable adducts with Co and Fe-TSPs [230]. It has also been shown that hydroxylamine is catalytically oxidized by oxygen in the presence of M-TSPs in aqueous solutions

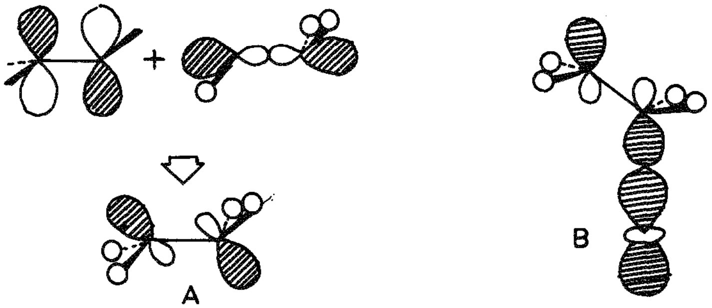


Fig. 16. (A) Orbital mixing of the π^* and σ orbitals during a planar (D_{2h}) to anti distortion (C_{2h}) of hydrazine. The most stable structure is obtained upon rotation around the N–N bond yielding the gauche symmetry (C_{2h}) symmetry. The latter is not depicted in the figure for simplicity. (B) Interaction between the lone-pair of hydrazine with an empty or half-filled dz^2 orbital of the metal.

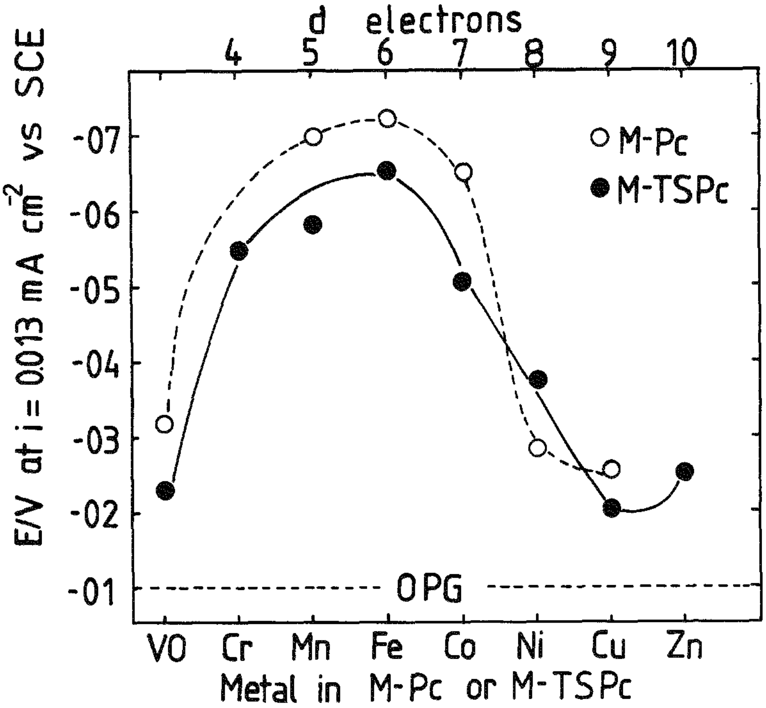


Fig. 17. Electrocatalytic activity of different metallophthalocyanines for the oxidation of hydrazine in 0.1 M NaOH as a function of the number of d electrons [26]. (Reproduced by permission of Elsevier.)

[230,232,235]. From these results, one would expect that phthalocyanines, when adsorbed on a graphite electrode surface, would catalyze the electrochemical oxidation of NH_2OH. This is indeed the case. Fe-TSPcs has been found to possess some catalytic activity for the reaction [31] but the catalytic effects are not as pronounced as those observed for other reactions such as O_2 reduction and hydrazine oxidation. This has been attributed to the formation of a "stable adduct" formed between Fe-TSPc and NH_2OH which would block the Fe active sites, preventing new molecules of hydroxylamine to interact and react. To have pronounced catalytic effects, the adducts or intermediates have to be labile and decompose quickly to maintain the catalytic cycle functioning. Electrochemical evidence was found for the formation of such adducts as the cyclic voltammogram of adsorbed Fe-TSPc is modified in the presence of small amounts of hydroxylamine. This is illustrated in Fig. 19. It can be seen that both Fe(II)/Fe(I) and Fe(III)/Fe(II) reversible couples disappear in the presence of hydroxylamine and there appears between them a new couple which can be assigned to the electrochemical response of the Fe-TSPc–NH_2OH adduct [31]. These results indicate that the energies of the orbitals involved in hydroxylamine are different from, for example, hydrazine. Studies using different M-TSPcs have shown that Ni-TSPc shows the highest activity [25], in contrast to what has been found

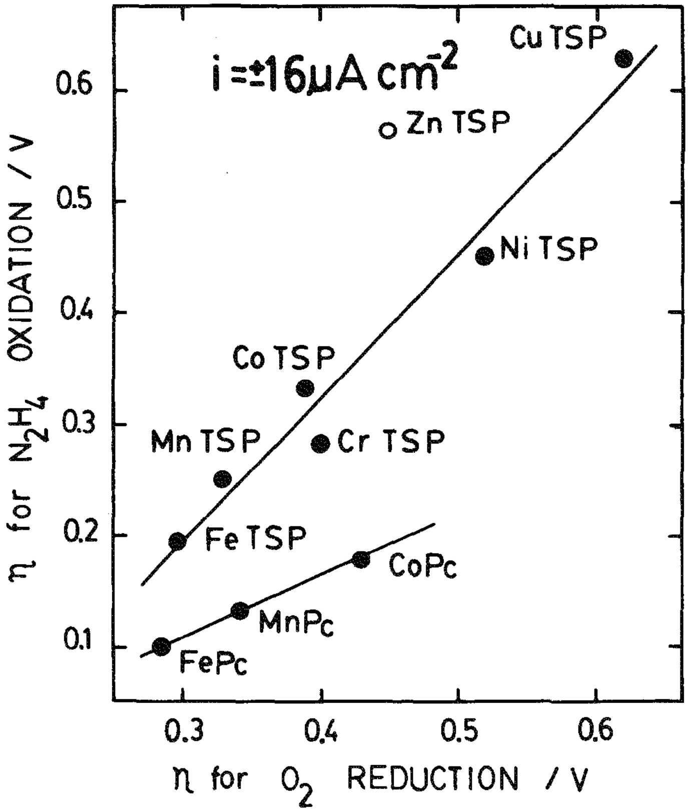


Fig. 18. Comparison of the electrocatalytic activity of metallophthalocyanines for O_2 reduction with their activity for hydrazine oxidation. Overpotential (η) for hydrazine oxidation at $i = 10\ \mu A$ is plotted vs. overpotential for oxygen reduction at $i = -16\ \mu A$. (Adapted from ref. 137.)

for O_2 reduction and N_2H_4 electro-oxidation where Co and Fe derivatives show the highest activity. These results are summarized in the form of a volcano plot in Fig. 20. The catalytic effects are small as the reaction rates for the most active M-TSPc is only seven times greater than the least active ones. This could be explained in terms of the formation of stable adducts as discussed above. Evidence for the formation of these adducts has also been found electrochemically for Co-TSPc [236,237].

From the kinetic parameters determined electrochemically, the following mechanism has been proposed [25,31,236,237].

$$\mathrm{M{-}L + NH_2OH \rightarrow L{-}M{-}NH_2OH} \qquad (17)$$

$$\mathrm{L{-}M{-}NH_2OH + OH^- \rightarrow [L{-}M{-}NHOH]^- + H_2O} \quad \text{(r.d.s.)} \qquad (18)$$

$$\mathrm{L = Pc,TSPc}$$

which agrees with a −1 order in protons.

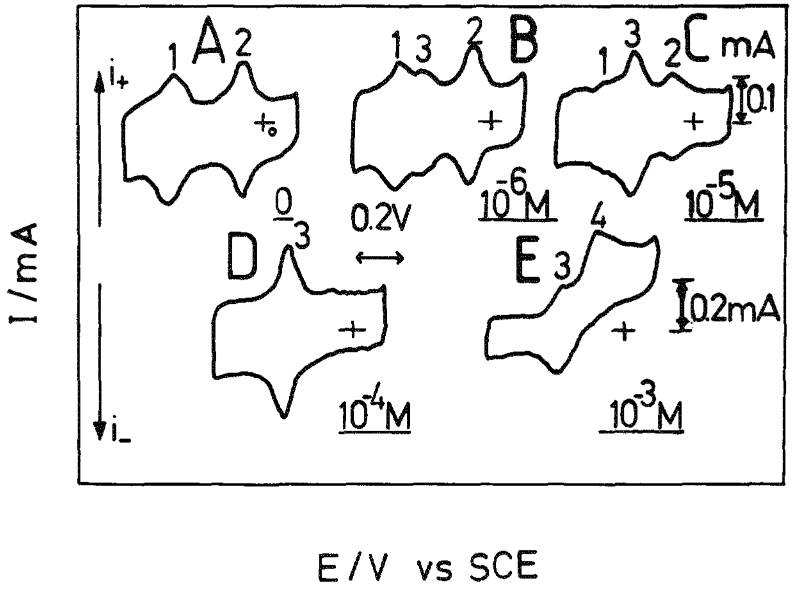


Fig. 19. Cyclic voltammograms of Fe-TSPc adsorbed on graphite in deaereated 0.5 M NaOH with A, no hydroxylamine; B,C,D and E with increasing amounts of hydroxylamine, concentrations indicated in the figure. (Taken from ref. 31 and reproduced by permission of Elsevier.)

D. ELECTROCATALYTIC PROPERTIES OF METALLOPHTHALOCYANINES IN ELECTROCHEMICAL REACTIONS INVOLVING SULPHUR COMPOUNDS

(i) Electrochemical oxidation of mercaptoethanol

The oxidation of thiols (R–SH) to disulphides (R–SS–R) is an important reaction and it is involved in oil-sweetening processes and in biological systems. Transition metal macrocyclics, such as some phthalocyanines and porphyrins [238–240], are known to promote the auto-oxidation of thiols by oxygen. In particular, cobalt tetrasulphophthalocyanine has been found to be a catalyst for the oxidation of 2-mercaptoethanol [241–248] and other thiols [242,243]. Water-soluble Co-tetrasulphophthalocyanine (Co-TSPc) readily adsorbs very strongly on certain polymeric resins and has been used to prepare catalytic surfaces for the oxidation of mercaptans. These results suggest that metal phthalocyanines adsorbed on graphite are potential catalysts for the electrochemical oxidation of mercaptans.

$$\text{R–SH} + \text{OH}^- \rightleftharpoons \text{R–S}^- + \text{H}_2\text{O} \tag{19}$$

$$\text{R–S}^- \rightarrow \text{R–S}\cdot + e^- \quad \text{(r.d.s.)} \tag{20}$$

$$\text{R–S}\cdot + \text{R–S}\cdot \rightarrow \text{R–S–S–R} \tag{21}$$

The slopes range from 0.1 to 0.12 V per decade (ca. $2RT/F$), suggesting a

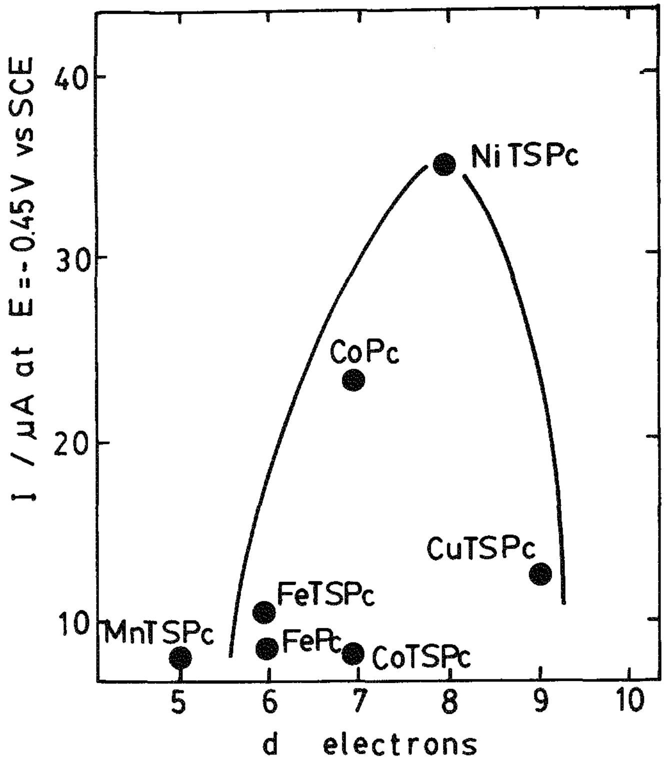


Fig. 20. Activity as current at constant potential for the electro-oxidation of hydroxylamine in 0.1 M NaOH as a function of the number of d electrons of different M(II) metallophthalocyanines. (Adapted from ref. 25.)

common electron-transfer mechanism for all of them. The activity of several metallophthalocyanines is compared vs. the central metal in Fig. 21. A volcano-shaped curve is obtained. The highest activity corresponds to Co-TSPc. As pointed out above when discussing O_2 reduction, the energy of the highest occupied molecular orbital in metal(II) phthalocyanines decreases almost linearly with the number of d electrons in the metal complex [225] (see Fig. 12). Considering these factors, the data in Fig. 21 then suggest that a better match of orbital energies takes place between Co and sulphur [223]. The energy of the MO for Cr at one extreme is probably too high, and the opposite is true for Cu. Furthermore, the interaction between the metal and the sulphur involves transfer of electron density from a sulphur orbital to dz^2 and dxz orbitals of the metal. These are filled for Ni, Cu and Zn and this type of interaction is strongly inhibited for these metals. This could provide another explanation for the lower activity of these M-TSPcs.

The orbitals for the sulphur in an alkane thiol are shown in Fig. 22. Three p orbitals and an s orbital are fully occupied in the neutral thiol. The pz orbital can interact with an empty orbital in the transition metal in the phthalocyanine. In the

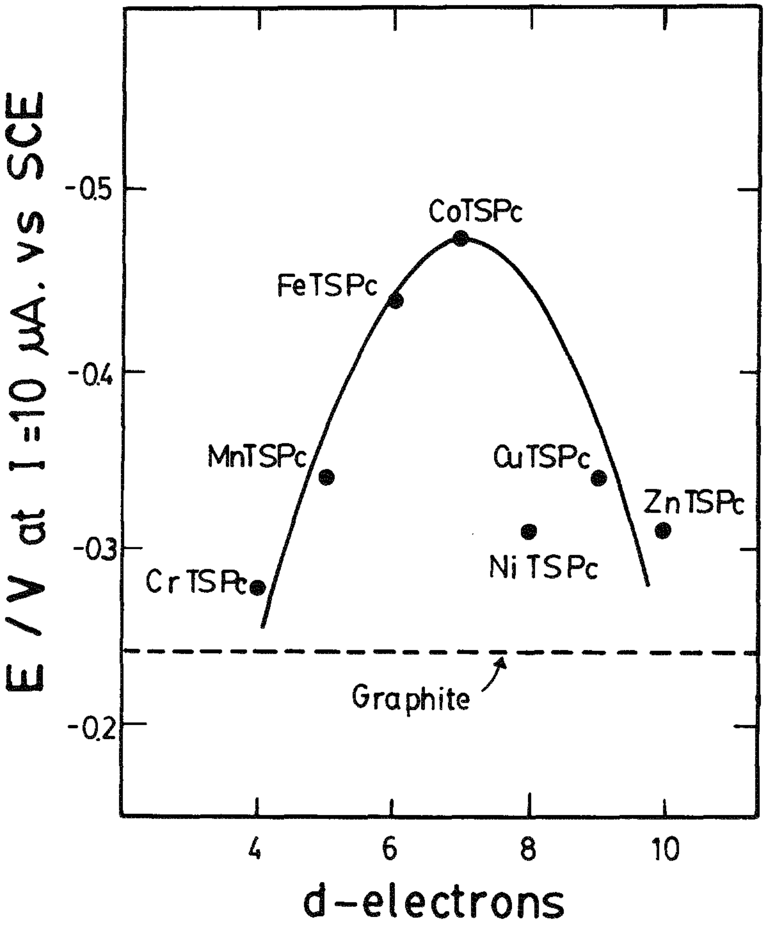


Fig. 21. Electrocatalytic activity of several M(II)-TSPcs for the electro-oxidation of 2-mercaptoethanol as a function of the number of d electrons in the metal. (Taken from ref. 27 by permission of Pergamon Press.)

case of disulphide, the most stable configuration is that in which the non-bonding orbitals are at 90° to each other, thus minimizing electron repulsion. In the case of a disulphide, it is unlikely, for steric reasons, that both sulphur atoms simultaneously interact with a metal centre in the phthalocyanine. It is most likely that the interaction takes place via one sulphur atom at a time, inhibiting the electron transfer. This could explain why this reaction is irreversible (reduction of the disulphide) for 2-mercaptoethanol. As radicals are formed during the reaction, it is possible that the magnetic properties might have a role in the catalysis as suggested by Randin [194] for O_2 reduction on phthalocyanines. This could explain the relatively low activity of diamagnetic Ni-TSPc compared with paramagnetic Cu-TSPc, inverting the trend in catalytic activity illustrated in Fig. 21. It can be concluded that cobalt and iron

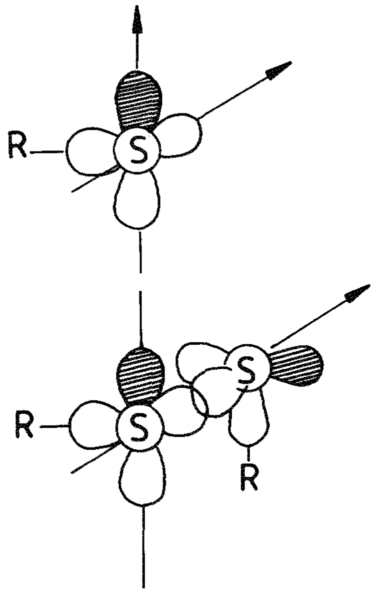


Fig. 22. Molecular orbitals in sulphides and disulphides.

phthalocyanines show remarkable catalytic activity for the oxidation of 2-mercaptoethanol, which suggests that they are potential catalysts for the electro-oxidation of other thiols as well. Phthalocyanines of other metals show much less activity, which demonstrates once more that the electronic structure and energy levels in the metal play a key role in determining the catalytic activity.

(ii) Electro-oxidation of cysteine and electroreduction of cystine

Cysteine, a sulphur-containing aminoacid R–SH, and its oxidized version cystine (R–SS–R) play a very important role in living systems and their electrochemical properties have been studied by many authors.

The catalytic properties of phthalocyanines and tetrasulphophthalocyanines in the chemical oxidation of cysteine by oxygen have been reported [230,231,249]. The oxidation product is cystine. EPR studies with Co-TSPc solutions have shown that cysteine interacts with Co-TSPc [230]. This interaction is likely to occur via the sulphur atom in the cysteine and a dz^2 orbital in the metal chelate. Electrochemical studies conducted with M-TSPcs adsorbed on graphite electrodes have shown that the phthalocyanines exhibit remarkable activity for the electro-oxidation of cysteine under different conditions [22,28,29]. Practically no reaction takes place on the graphite electrode when phthalocyanines are absent from its surface. The oxidation reaction can then be entirely attributed to catalysis by the metal macrocyclics. Cyclic voltammetry experiments have demonstrated that cystine formed after the oxidation of cysteine can be reduced back to cystine at more negative potentials [29]. The activity of different M-TSPcs for the oxidation of cysteine and reduction of cystine is illustrated in Figs. 23 and 24. In both cases, volcano-shaped curves are obtained.

As observed for other reactions, the nature of the metal plays an important role in determining the catalytic activity. The kinetic parameters found [29] suggest a mechanistic scheme similar to that proposed for the oxidation of mercaptoethanol (see reactions (19)–(21)).

(iii) Electrochemical oxidation of glutathione

Glutathione is the most important non-protein thiol in living systems. This thiol is known to function directly or indirectly in many important phenomena, including the synthesis of proteins and ADN, transport, enzyme activity, metabolism, and protection of cells. The multifunctional properties of glutathione are reflected by the growing interest in this molecule on the part of investigators of such diverse subjects as enzyme mechanisms, biosynthesis of macromolecules, intermediary metabolism, drug metabolism, radiation, cancer research, oxygen toxicity, transport phenomena, endocrinology, environmental toxins and aging [250]. The electrochemistry

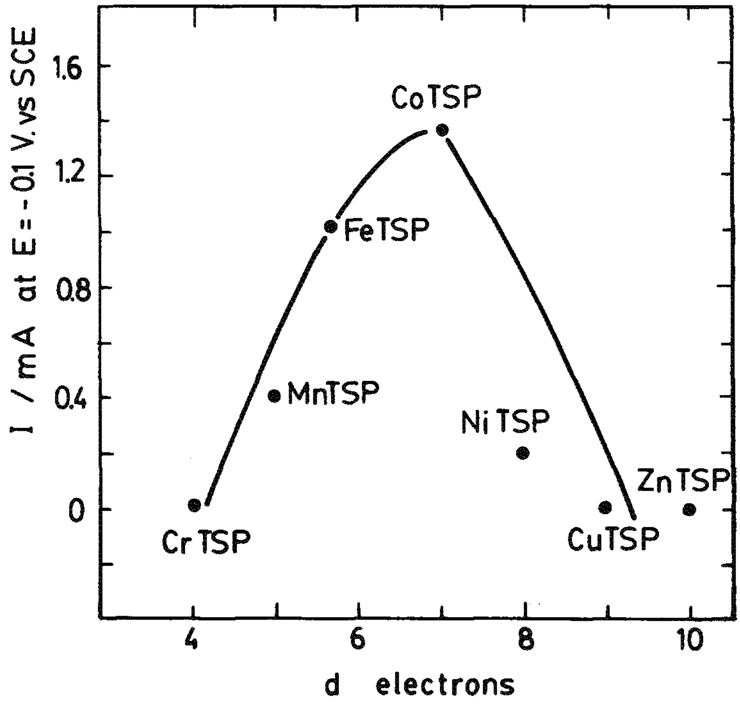


Fig. 23. Electrocatalytic activity of several M(II)-TSPcs for the electro-oxidation of cysteine (R—SH) as a function of the number of d electrons in the metal. (Taken from ref. 29 by permission of Pergamon Press.)

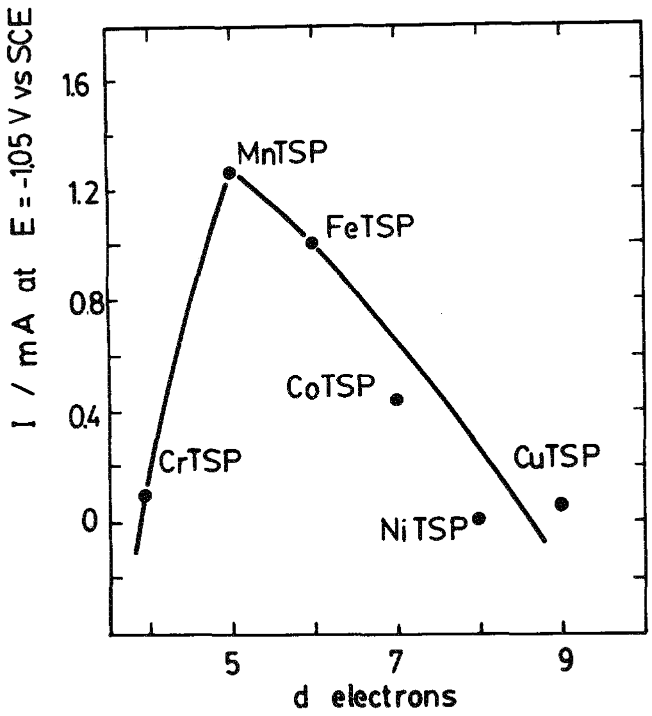


Fig. 24. Electrocatalytic activity of several M(II)-TSPcs for the electroreduction of cystine (R—SS—R) as a function of the number of d electrons in the metal. (Taken from ref. 29 by permission of Pergamon Press.)

of glutathione (G-SH) is known from polarographic studies [251–254]. It undergoes a one-electron oxidation process to give the oxidized version G—SS—G. On mercury, however, its behaviour is complicated by the formation of mercurous compounds and more than one oxidation wave has been observed [251–253]. Evidence for the catalytic activity of vitamin B_{12} (which is a macrocyclic cobalt complex) for the oxidation of thiols has been known for some time [255]. It has been shown recently [30] that carbon paste electrodes with added Co-Pc can serve as sensors in the amperometric detection of sulphidryl-containing aminoacids. Glutathione is also known to inhibit the O_2 reduction reaction [256] on Fe-Pc–graphite electrodes. It was suggested that the inhibiting effect is due to the adsorption of glutathione on the active sites (Fe centres) on Fe-Pc. The electrochemical activity of Co-Pc, Co-TSPc and vitamin B_{12}, adsorbed on graphite have been investigated [257] and their catalytic activity varies as Vit B_{12} > Co-Pc > Co-TSPc, which correlates with the trend in redox potential for the Co(II)/Co(I) couple. All three cobalt macrocyclic catalysts show a similar behaviour with identical kinetic parameters for the oxidation of glutathione, i.e. an order of one in G-SH, −1 in protons for pH values lower than 9, and Tafel slopes of $2RT/F$. All give smaller Tafel slopes (RT/F) in alkali. The results obtained with the three cobalt macrocyclic catalysts are consistent with the following mechanism:

$$\text{G–SH} + \text{OH}^- \rightleftharpoons \text{G–S}^- + \text{H}_2\text{O} \tag{22}$$

$$\text{G–S}^- \rightarrow \text{G–S}\cdot + \text{e}^- \tag{23}$$

$$\text{G–S}\cdot + \text{G–S}\cdot \rightarrow \text{G–SS–G} \tag{24}$$

with reaction (23) being the rate-determining step. This agrees with a Tafel slope of $2RT/F$, an order of 1 for G-SH and of -1 in protons. The mechanism depicted by eqns. (18)–(20) is essentially similar to that observed for the electro-oxidation of other thiols such as 2-mercaptoethanol and cysteine and illustrated by eqns. (22)–(24) above. The pH at which the order in protons changes from 1 to a lower value is 8.3–9.0. The pK for reaction (22) must be in that pH range. The Tafel slope of RT/F obtained for alkaline pH values is observed at potentials close to the Co(II)/Co(I) reversible transition. The reaction is probably controlled by the surface coverage by Co(II). The following mechanism is consistent with an RT/F slope:

$$\text{Co(I)}^- \rightleftharpoons \text{Co(II)} + \text{e}^- \tag{25}$$

$$\text{Co(II)} + \text{G–S}^- \rightarrow [\text{Co(I)–G–S}]^- \quad \text{r.d.s.} \tag{26}$$

$$[\text{Co(I)–G–S}]^- \rightarrow \text{Co(I)}^- + \text{G–S}\cdot \tag{27}$$

where step (26) is rate-controlling. The Co(II) catalyst is rapidly regenerated on the surface by reaction (25) from Co(I) formed in reaction (27). Evidence for the formation of a stable adduct between vitamin B_{12} and G–SH for pH values lower than 4 has been reported and is similar to that found for Fe-TSPc and hydroxylamine [31]. The trend in catalytic activity [257], cobalamine > Co-Pc > Co-TSPc, correlates well with their redox potential for the Co(II)/Co(I) couple which shifts to more positive values from vitamin B_{12} to Co-TSPc. The catalytic activity is then related to the facility to oxidize the cobalt centre from Co(I) to Co(II). Recent studies have shown that Fe-TSPc also catalyzed the oxidation of glutathione [258] with similar kinetic parameters and then similar reaction mechanisms.

(iv) Electrochemical reduction of thionyl chloride and sulphuryl chloride

The increasing importance of the Li/$SOCl_2$ battery, the highest energy density system known to date [259], has given rise to numerous recent investigations of the stoichiometry and mechanism of $SOCl_2$ reduction [259–268] and a number of reaction paths have been proposed [261–268]. The most generally accepted cell reaction involves the formation of sulphur, sulphur dioxide, and lithium chloride:

$$2\text{SOCl}_2 + 4\text{Li} \rightarrow \text{S} + \text{SO}_2 + 4\text{LiCl} \tag{28}$$

It has been shown in recent years that the addition of metal complex catalysts such as the phthalocyanines (M-Pcs) [46–54,269] and related macrocyclic metal chelates [55] to the electrode enhance the rate of reduction of thionyl chloride in Li/$SOCl_2$ cells. In spite of all the work published, there is no agreement about the reaction paths and the nature of intermediate species. Modified mechanisms are proposed to occur on carbon cathodes doped with transition metal complexes [47–50]. Doddapaneni [50] studied the activity of Fe-Pc, Co-Pc and metal-free Pc deposited on a pressure-annealed pyrolytic graphite electrode and found Co-Pc to be the most active material. In a cyclic voltammogram, the $SOCl_2$ reduction peak with Co-Pc is shifted by 0.1 V to more positive potentials compared with that observed on the bare graphite, a rather small, but none the less substantial, catalytic effect in improving the battery performance. Madou et al. [51,52] conducted similar studies using a glassy carbon electrode and saturated Fe-Pc $SOCl_2$ solutions. In a cyclic voltammogram, they observed a shift in the reduction peak of thionyl chloride from +2.6 V for glassy carbon to +2.9 V vs. Li when Fe-Pc saturates the electrolyte. The shift in potential of 0.1 V by the presence of Co-Pc, as reported by Doddapaneni [50], indicates a small catalytic effect of the phthalocyanine. However, the presence of the complex prevents the passivation of the electrode by LiCl formed in reaction (28) as the curves are reproduced after many scans [50,59]. The main reduction peak is affected only slightly for the smaller concentrations. However, a pre-peak appears at potentials less negative than the main peak when the concentration of Co-Pc increases [59] and its height varies linearly with Co-Pc concentration. This suggests that, for this particular case, the reduction of $SOCl_2$ is first order in Co-Pc. Doddapaneni found that the chemical order in $SOCl_2$ is also one. A plausible explanation for this behaviour is that an adduct is formed between Co-Pc and $SOC1_2$ that is reduced at a potential less negative than the bulk reduction of $SOCl_2$. The possible formation of an adduct has been reported by Bernstein and Lever [60]. Remarkable changes in the visible spectrum of M-Pc in the presence of thionyl chloride are observed [59,60]. The homogeneous catalytic effect due to the phthalocyanine in the solution phase, which acts like a depolarizer, is very large and this is probably combined with a catalytic effect of Co-Pc adsorbed on graphite surface. Madou et al. [51,52] have reported similar results with Fe-Pc but they did not study the effect of Fe-Pc concentration. They worked with a Fe-Pc/$SOCl_2$ saturated solution and observed the reduction peak at 2.9 V vs. Li, much less positive than the one observed by Doddapaneni [50] and Zagal et al. [59]. A possible explanation for this discrepancy is that Madou et al. used glassy carbon as the working electrode instead of OPG. Co-Pc probably does not adsorb on this material as well as on OPG and the combined catalytic effect from the possible adduct formed in the solution phase is lost. Details of the reaction paths for $SOCl_2$ electroreduction are not known so the catalytic effect of Co-Pc could also be attributed to an interaction of Co-Pc with some reaction intermediates or products and may not be limited to the charge transfer reaction, and may directly or indirectly affect other elementary processes as well. A more detailed investigation of the interaction of metallophthalocyanines with $SOCl_2$ has been published by Bernstein and Lever [60]. Working with Co tetraneopentoxyphthalocyanine (CoTnPc), they have found this complex to react with thionyl chloride in a $Li/SOCl_2$ cell. Under open circuit conditions, the thionyl chloride oxidizes CoTnPc to $Cl_2Co(III)TnPc(-1)$. Under closed circuit conditions, Co(II)TnPc can be reduced down to $[Co(I)TnPc(-2)]^-$. These species can then react according to the scheme:

$$[Co(I)TnPc(-2)]^- + SOCl_2 \rightarrow [Cl_2Co(III)TnPcPc(-2)]^- + SO \tag{29}$$

$$Co(II)TnPc(-2) + SOCl_2 \rightarrow [Cl_2Co(III)TnPcPc(-1)] + SO \tag{30}$$

"SO" represents the initial reduction product of $SOCl_2$ and it most likely reacts further. Reaction (29) is fast and reaction (30) slow. The oxidation process in eqn. (29) involves the two-electron oxidation of $[Co(I)TnPc(-2)]^-$ and not two sequential one-electron oxidations via Co(II)TnPc(−2) since the latter is not observed as a one-electron oxidation intermediate. Similarly, no intermediate oxidation product is observed when reaction (30) is followed by electron spectroscopy [60]. A two-electron catalytic cycle is then confirmed for the thionyl chloride reduction in a $Li/SOCl_2$(CoTnPc,C) battery. This might provide a two-electron reduction process that could be safer in such batteries, which are known to explode. Similar reaction schemes could take place when Co-Pc and other M-Pcs are employed as catalysts.

(v) Other reactions involving sulphur compounds

Fe-Pc and Co-Pc have been reported [15–17] to have electrocatalytic activity in the electro-oxidation of SO_2 in acid medium. However, no mechanistic studies were provided. It is likely, however, that the activity of these metal chelates can be attributed to interactions of the SO_2 molecule via the sulphur atom with the metal centre, in an analogous fashion to other sulphur compounds discussed above. Sulphide ions can also be catalytically oxidized in the presence of Co-Pc and Fe-Pc adsorbed on graphite [58] but this ion displaces the phthalocyanine molecules from the electrode surface and the activity is lost.

In fuel cells and other energy conversion devices, sulphur compounds act generally as poisons in both cathodic and anodic reactions. In this respect, metal phthalocyanines are promising dopants for electrodes that are rapidly deactivated by, for example, fuels that are contaminated with sulphur. Advantage could be taken in the construction of an electrode from the recent advancement in the field of heat-treated porous electrodes containing phthalocyanines and other macrocyclic complexes, which are more stable over long periods of operation but which have been designed for O_2 reduction [8,10,12].

E. OTHER REACTIONS OF INTEREST

(i) Electroreduction of carbon dioxide

The electrocatalytic activity for CO_2 reduction of Co-Pc and Ni-Pc has been investigated [35,270] using these phthalocyanines adsorbed on amalgamated platinum electrodes, and they show a single reduction step preceded by the formation of a CO_2 complex. The activity was found to decrease after very negative potentials were achieved. Kapusta and Hackerman [38] conducted similar experiments but using a carbon electrode. In acid solutions ($pH = 3.7$), they found that, with both Co-Pc and Ni-Pc, carbon dioxide is reduced to formic acid. The overpotential for CO_2 reduction on Co-Pc is approximately 300 mV lower than the best metal catalysts known to date, at currents up to 10 mA cm^{-2}. At $pH > 5$, formate ions are formed. Methanol is also produced at lower pH values. The loss of activity at very negative potentials has been attributed to an irreversible reduction of the phthalocyanine [37]. The mechanism of carbon dioxide reduction on cobalt phthalocyanine is thought to involve cobalt hydride intermediates [35–37] but more evidence about the existence of such species has been provided by Christensen et al. [37] using SNIFTIRS techniques as changes in the spectrum are observed in the presence of CO_2. From their studies [37], they have concluded that the process occurs via two reduction steps, the first involving the macrocyclic ring in the phthalocyanine giving $[Co(II)Pc(-3)]^-$. A second reduction gives $[H\text{-}Co(I)Pc(-3)]^-$ which, in the presence of CO_2 reacts to give an insertion product [36,271–273]. Long-term studies have demonstrated that the insertion product reacts via dehydration [273]. Christensen et al. [37] have suggested that the electrochemical behaviour of Co-Pc for carbon dioxide reduction is critically dependent upon the solvent in the solution from which it was deposited on the electrode. It is rather surprising that reduction of the Pc ring takes place before reduction of the Co(II) centres since this contradicts what has been found by many other authors [153–161,163,179–181,230).

Interesting results have been obtained using metallophthalocyanines dispersed in porous carbon-based gas-diffusion electrodes [274–279]. Furuya and Matsui [279] studies CO_2 electroreduction on these electrodes using phthalocyanines of several metals, namely Mn, Co, Ni, Fe, Pd, Sn, Pb, In, Zn, Al, Cu, Ga, Ti, V, Mg, Pt and H. As expected, they found that activity strongly depended on the nature of the metal. For transition metals of Group VII, the main product of the reaction is carbon monoxide. With Sn, Pb and In phthalocyanines, mainly formic acid is formed. Cu, Ga and Ti phthalocyanines promote the formation of methane. The reason for some Mn-Pc to give CO or CH_4 while others yield HCOOH has been interpreted in terms of the electron configuration in the metal [280]. The reduction of CO_2 to give CO is attributed to the strongly electron-donating HOMO of $M\text{-}Pc^-$ arising from the electron-accepting LUMO of neutral M-Pc, which spreads over the nitrogen atoms surrounding the metal centre. The final production of CO occurs when the created CO is promptly desorbed from the metal atom M having a bare d shell with the doubly occupied $2a_{1g}$ (dz^2) orbital. If, on the other hand, the CO molecule is bound to the metallic atom by a σ bonding, the reduction may proceed so methane is formed. For metals having outermost s or p electrons, the electron occupation of the spread LUMO by ionization does not occur and such a strong reduction as to produce CO may not be possible. The electron transfer from M-Pc to CO_2 will then result in the production of CO_2^- followed by HCOOH formation instead of CO. The anion CO_2^- bends with a OCO angle of 134°. C– then probably forms a σ bond with dz^2 or pz of M, making the so-called carbon dioxide complex, until further reduction to HCOOH [280].

Metal phthalocyanines are promising electrocatalysts for the electroreduction of CO_2 in aqueous solutions, but further work is needed towards the understanding of the mechanism of reaction and deactivation of the catalysts in order to increase its long-term stability.

(ii) Reduction of the nitrate ion

Chambers and co-workers [45] have reported that Fe-Pc incorporated on iron electrodes promotes the reduction of nitrate ions in alkaline media to give nitrogen gas and ammonia amongst the main products. The activity of the Fe/Fe-Pc is similar to that of non-coated electrodes but weight losses due to corrosion are greatly diminished. These studies were of an exploratory character and no details of the mechanisms were provided.

(iii) Reduction of NO

Axial coordination of NO on phthalocyanines of Mn, Fe, Co, Ni, Cu and Zn has been found by means of XPS and a gravimetric method [281]. No axial coordination was detected with Ni-Pc and Cu-Pc. Coordination of NO to Fe-Pc, Co-Pc and Mn-Pc is accompanied by chemical shifts of electron binding energies of the central metal atoms, indicating appreciable electron transfer between the central metal and NO. The electrochemistry of metal macrocycles–NO adducts has been studied in organic solvents [282]. Ogura and Yamasaki [283] have studied the electrocatalytic activity of Co-Pc films deposited by evaporation on glassy carbon and they succeeded in electroreducing NO to NH_3 at -0.6 V vs. SCE. More recently, Fierro and co-workers [44] have reported catalytic activity of Co-TSPc for NO reduction in acid (pH = 3). They found that some cooperative effects between the carbon substrate and the Co-TSPc play some role in the catalytic process but no details of a possible mechanism were provided.

(iv) Oxygen evolution

Oxygen evolution is a reaction of great technological importance as it is involved in the process of water electrolysis. Hydrogen, also produced by water electrolysis, can be produced as a form of transforming electrical energy in excess into chemical energy. Water electrolysis is mainly achieved by the utilization of a catalyst to decrease the voltages employed. Molybdenum and iron naphthalocyanines (MNPcs) have recently been found to catalyze the O_2 evolution reaction [33] with MoNPc being more active than FeNPc. On the basis of XPS studies [284], the main difference between MoNPc and FeNPc is that with Mo, O_2 d species are formed whereas with Fe the covalent oxygen form is observed. The radicals can act as bridges between the free oxygen molecules and the OH^- ions. One can then assume that the electronic transfer reactions take place amongst the valency oscillations Mo(IV)–Mo(VI), the metal–oxygen and OH-oxygen ligands. They can give rise to OH or O_2^- radical formation, which are precursors in the oxygen evolution reaction [33]. The activities of Mo naphthalocyanines were found to be higher than those reported for other catalysts in the literature and the electrodes were stable for over a week [33]. This makes this material promising in the development of catalysts for oxygen evolution.

(v) Electrochemical reactivity of phthalocyanines in lithium cells

Phthalocyanines are also promising as electrode materials not only as catalysts but as reactive species due to their lamellar structure in the solid state [85], similar to that of graphite. Metal-free phthalocyanine molecules are stacked parallel to each other along the *b* crystal axis in a base-centred monoclinic molecular crystal. This structure allows phthalocyanine to react reversibly with ions. Combined with a lithium anode in an electrochemical cell, low-molecular unsubstituted phthalocyanines have a discharge capacity of 17 electrons per molecule as reported by Yamaki and Yamaji [86] and even an exchange of 26 equivalent electrons has been reported [87].

Yamaki and co-workers [285] have reported that metallophthalocyanines catalyze the decomposition of propylene carbonate (PC) in a lithium/MPc cell. This occurs via the formation of a product MPcLi from MPc and Li which then reacts chemically with PC to produce propylene according to the reaction scheme:

$$\mathrm{MPcLi}_x + 2\mathrm{Li}^+ + 2\mathrm{e}^- \rightarrow \mathrm{MPcLi}_{x+2} \tag{31}$$

$$\mathrm{MPcLi}_{x+2} + \mathrm{C_3H_6CO_3} \rightarrow \mathrm{MPcLi}_x + \mathrm{C_3H_6} + 2\mathrm{Li}^+ + \mathrm{CO_3^{2-}} \tag{32}$$

According to this study, the amount of gas produced is strongly dependent on the nature of the transition metal in the phthalocyanine. The trend in activity was as follows: FePc > Co-Pc > Mn-Pc > NiPc > CrFPc > AgPc. H_2Pc, Li_2Pc, Na_2Pc, GaClPc and Cd-Pc did not show much activity. A similar trend is obtained when activity is measured in terms of the discharge capacity of the cell [285], measured in mA h^{-1}. The authors have compared the activity of several MPcs vs. the first oxidation potential in the phthalocyanine. As discussed for O_2 reduction, it might not be correct to plot the first oxidation potential of the MPc since this parameter might reflect oxidation changes on the metal for Mn, Fe and Co and redox processes on the ring for Cu and Ni. However, if one plots activity vs. the number of d electrons, which reflects the decreasing energy of the HOMO in the MPc as the number of d electrons increases, a volcano-shaped curve is obtained. Figure 25 depicts a plot constructed from data reported by Arakawa et al. [285] and shows that activity increases for metals with half-filled d energy levels and reaches a maximum for FePc. The correlation in Fig. 25 illustrates once more the importance of the electronic structure in the M-Pc in determining the electrocatalytic activity as similar relations have been found for the other electrochemical reactions discussed here.

F. OTHER ASPECTS OF THE ELECTROCATALYTIC ACTIVITY OF METALLOPHTHALOCYANINES

Most of the work discussed so far in connection with the electrocatalytic activity of metallophthalocyanines for O_2 reduction and other electrochemical reactions has considered phthalocyanines deposited or adsorbed at monolayer levels on graphite or carbon surfaces from a solution of the metal chelate. Studies using multilayer deposits and also polymerized and/or heat-treated phthalocyanines were

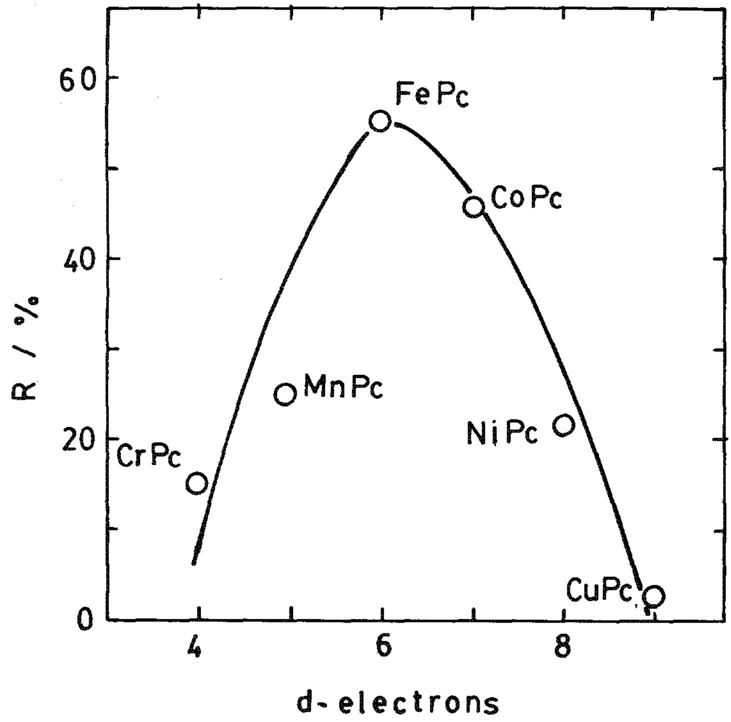


Fig. 25. Gas evolution ratio (*R*) plotted vs. the first oxidation potential of Mn-Pc. (Adapted from ref. 285.)

not considered in most of the discussions since most emphasis was placed on comparing the activity of phthalocyanines of different metals and establishing correlations between the redox properties, the electronic structure, molecular orbital interactions and electrocatalytic activity. However, the method of incorporation of the phthalocyanines on the electrode surface as well as the nature of the substrate itself can affect their effectiveness as catalysts. Various types of carbonaceous materials, such as activated carbons, carbon blacks, natural and artificial graphites, have been used as substrates or supports, and the surface properties of the carbon influence dramatically the degree of dispersion of supported M-Pcs and in turn their catalytic activity [286–291]. The surface area of supported M-Pcs is higher when the surface heterogeneity of the carbon increases [290]. A method commonly used in the dispersion of metallophthalocyanines on high surface carbon involves the suspension of the support particles in a solution containing the M-Pc. Strong Lewis bases such as pyridine have been used because of the high solubility of the M-Pcs in such solvents, which is in part due to the ability of the macrocycle for axially coordinating the pyridine and forming an adduct of the form $M{-}Pc{-}L_2$ [292]. Mössbauer spectroscopic studies using Fe-Pc [293] have shown that removing the liquid pyridine from such suspensions by heating to the boiling point of the solvent leads to the formation of $FePc(Py)_2$, possibly in the form of small crystallites dispersed in the carbon matrix [293,294]. It is necessary to eliminate the axially bound pyridine in order to obtain maximum activity since this molecule blocks the active site. Yeager and co-workers [293,294] have reported that heating the carbon specimens containing the $FePc(py)_2$ crystals at temperatures of ca. 300°C results in a loss of the MES doublet corresponding to the pyridine adduct and the simultaneous appearance of another doublet, with a much smaller quadrupole splitting than that of the adduct. This is attributed by several authors to the Fe-Pc bound to the carbon substrate through a bond which involves the iron centre and an oxygen atom of a carbon functional group [213,293–296]. However, Yeager and co-workers [294] have provided further MES evidence to suggest that such heat treatment might lead to the decomposition of Fe-Pc to yield FeOOH. This is surprising since the thermal stability of Fe-Pc, at least in bulk form, is well documented [297]. In any case, it remains unclear how the heat-treatment of phthalocyanines increases their electrocatalytic activity and stability. Heating up to a certain temperature produces polymerization of the M-Pcs. These polymers are better conductors when used as thick layers and the electrotransfer process becomes favoured [123,215,298–302] as the π system becomes more delocalized. In fact, naphthalocyanines are better catalysts than the phthalocyanines, probably because they have an enlarged delocalized π electron system [303]. Carbon electrodes have also been made by chemically bonding Fe tetrachlorophthalocyanine to a chemically modified carbon acetylene black [304]. The product was then heat treated which caused the phthalocyanine to polymerize. The electrode obtained exhibited greater activity and stability compared with a similar unmodified electrode [304]. Another approach to modify the carbon has been attempted by Larsson et al.

[305] by covalently binding imidazol to the carbon substrate and then letting Fe-Pc coordinate to the free nitrogen of the imidazol molecule. These electrodes also show higher activity and stability than M-Pc/C electrodes without chemical treatment.

The new field of conductive polymers [306] offers a great variety of possibilities for making novel electrodes with specific catalytic properties [307]. Fe-TSPc has been incorporated into a polypyrrole matrix, exhibiting catalytic activity for O_2 reduction in acid [213]. Similar results have been found using Fe-Pc [308]. Co-TSPc also shows catalytic activity for O_2 reduction in both acid and alkaline media when incorporated into polypyrrole [309]. Co-TSPc has also been incorporated into polyaniline films [310]. According to these authors, better results are achieved if the conductive polymer is electrogenerated in a solution containing the phthalocyanine. Other authors have attempted to incorporate the phthalocyanines onto the conductive polymer by vacuum deposition [311] but the same authors point out that the electrodes obtained are not stable. Hirabaru et al. [312] have covalently bound Co tetracarboxyphthalocyanine to poly(2-vinylpyridine CO-styrene) and used it in a reversible cell as catalyst for the reduction of oxygen during the discharge process. During the charging process, dioxygen produced by H_2O electrolysis is stored in the polymer matrix containing the phthalocyanine, and then electrochemically reduced during discharge.

Recently [313], anodic electrodeposition of a polymer and phthalocyanines on an indium tin oxide (ITO) transparent electrode has been investigated for the fabrication of a thin microcolour fibre applied to full colour liquid crystal displays. These processes are gaining worldwide acceptance for automotive coatings, appliances and in the development of flat colour TV screens [314].

G. CONCLUSIONS

From the work reviewed, metallophthalocyanines and their derivatives appear as promising electrocatalysts for a great variety of electrochemical reactions. The factors that control the activity of these chelates are not fully understood but parameters such as redox potentials of the metal and electronic structure appear to be crucial. They indirectly determine the ability of the central metal to interact with an extraplanar ligand that is, in this case, the reacting molecule. In more complex systems where the phthalocyanines have been heat treated and/or polymerized, it becomes difficult to determine those parameters even though such systems are more interesting from the technological point of view, since those electrodes containing phthalocyanines are not only more active but also more stable over long periods of time.

From the basic point of view, phthalocyanines provide very interesting models for studying the phenomenon of electrocatalysis since the chemistry and electrochemistry of the electrodes containing these molecules can be understood in terms of the physicochemical properties of the phthalocyanines, whose reactivity and structure can be understood separately. The active sites on a relatively inert electrode surface can be attributed almost entirely to the metallophthalocyanine, which makes studies on the reaction mechanisms more reliable. In many cases, the electrodes modified with phthalocyanines are very specific for a given reaction and the presence of impurities does not cause interference. This is not always true for metal electrodes.

The technological applications of these materials are vast and are well beyond the scope of this article but include, to mention just a few: electrocatalytic materials for energy conversion devices such as O_2 fuel cells, lithium batteries, organic conductive polymer batteries, electrochemical sensors, electrochromic devices, photogalvanic cells and organic electrosynthesis. Phthalocyanine-like molecules such as porphyrins, and other macrocyclic metal complexes show similar properties and many papers have been published in this field. They were not discussed in this paper and the interested reader is referred to some reviews that have appeared in the literature [7–10].

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REFERENCES

1 F.H. Moser and A.L. Thomas, The Phthalocyanines, Vols. 1 and 2, CRC Press, Boca Raton, FL, 1983.
2 M. Kropf and F. Steinbach (Eds.), Katalyse und Phthalocyaninen, Thieme, Stuttgart, 1973.
3 J. Manassen, Catal. Rev. Sci. Eng., 9 (1974) 223.
4 L.J. Boucher, in G.A. Melson (Ed.), Coordination Chemistry of Macrocyclic Compounds, Plenum Press, New York, 1979.
5 R. Jasinski, Nature, 201 (1964) 1212.
6 R Jasinski, J. Electrochem. Soc., 112 (1965) 526.
7 H. Jahnke, M. Schönborn and G. Zimmermann, Top. Curr. Chem., 61 (1976) 133.
8 F. van den Brink. E. Barendrecht and W. Visscher, Rec. J. R. Neth. Chem. Soc., 99 (1980) 253.
9 M.R. Tarasevich and K.A. Radyushkina, Russ. Chem. Rev, 49 (1980) 718.
10 M.R. Tarasevich, A. Sadkowski and E. Yeager, in B. Conway, J. Bockris, E. Yeager,

S. Khan and R. White (Eds.), Comprehensive Treatise of Electrochemistry, Vol. 7, 1983, Plenum Press, New York, pp. 301–398.
11 B.R.D. Patent 2,128,842, 1972; Chem. Abstr., 78 (1973) 79028.
12 J.A.R. van Veen, Ph.D. Thesis, Rijks Universiteit, Amsterdam, 1981.
13 J.T. van Baar, J.A.R. van Veen and N. de Wit, Electrochim. Acta, 27 (1982) 57.
14 J.F. van Baar, J.A.R. van Veen, J.M. van der Eijk, Th.J. Peters and N. de Wit, Electrochim. Acta, 27 (1982) 1315.
15 K.A. Radyushkina, M.R. Tarasevich and E.A. Akhundov. Elektrokhimiya, 15 (1979) 1884.
16 E.A. Akhundov, Mater. Konf. Molodykh Uch. Aspir., (1979) 46.
17 V.V. Zvezdina, L.V. Oparin, E.A. Vinogradova, V.P. Bochin, B.D. Berezin and D.A. Golubchikov, Vopr. At. Nanki i Tekhn. Atom-vodorov. Energ. i Teckhnol. (Moskba), 2/9 (1981) 10.
18 S. Meshitzuka and K. Tamaru, J. Chem. Soc. Faraday Trans., 73 (1977) 236.
19 U.S. Patent 3,585,079, 1971.
20 U.S. Patent 3,617,388, 1971.
21 J.H. Zagal, J. Electroanal. Chem., 109 (1980) 389.
22 J.H. Zagal, C. Fierro, E. Muñoz, R. Rozas and S. Ureta, in W.E. O'Grady, P.N. Ross and F.G. Will (Eds.), Electrocatalysis, The Electrochemical Society Symposium Series, 1982, p. 389.
23 J. Zagal and S. Ureta-Zañartu, J. Electrochem. Soc., 129 (1982) 2242.
24 J. Zagal, E. Munoz and S. Ureta-Zañartu, Electrochim. Acta, 27 (1982) 1373.
25 J. Zagal, P. Herrera, K. Brinck and S. Ureta-Zañartu, in J.D.E. McIntyre, M.J. Weaver and E. Yeager (Eds.), Physics and Chemistry of Electrocatalysis, The Electrochemical Symposium Series, 1984, p. 602.
26 J. Zagal, S. Lira and S. Ureta-Zañartu, J. Electroanal. Chem., 210 (1986) 95.
27 J. Zagal and C. Páez, Electrochim. Acta, 34 (1989) 243.
28 J. Zagal, C. Fierro and R. Rozas, J. Electroanal. Chem., 119 (1981) 403.
29 J. Zagal and P. Herrera, Electrochim. Acta, 30 (1985) 449.
30 M.K. Halbert and R.P. Baldwin, Anal. Chem., 57 (1985) 591.
31 J. Zagal, E. Villar and S. Ureta-Zañartu, J. Electroanal. Chem., 135 (1982) 343.
32 M. Estévez and J. Zagal, XV Jor. Chil. Chim., Valparaiso, Chile, (1984) 69.
33 M. Dieng, O. Contamin and M. Savy, Electrochim. Acta, 33 (1988) 121.
34 R. Jiang and S. Dong, Electrochim. Acta, 35 (1990) 1227.
35 S. Meshitsuka, M. Ichikawa and K. Tamaru, J. Chem. Soc. Chem. Commun., (1974) 158.
36 H. Tanabe and K. Ohno. Electrochim. Acta, 32 (1987) 1121.
37 P.A. Christensen, A. Hamnett and A.V.G. Muir, J. Electroanal. Chem., 241 (1988) 361.
38 S. Kapusta and N. Hackerman, J. Electrochem. Soc., 131 (1984) 1511.
39 Z. Wang and D. Pang, J. Electroanal. Chem., 283 (1990) 349.
40 D. Lexa, J.M. Saveant and J.P. Soiufflet, J. Electroanal. Chem., 100 (1979) 159.
41 C.M. Elliot and C.A. Marrese, J. Electroanal. Chem., 119 (1981) 395.
42 N. Furuya and L.H. Yoshiba, J. Electroanal. Chem., 263 (1989) 171.
43 J.P. Collman, N. Marrocco, C.M. Elliot and M.L. Her, J. Electroanal. Chem., 124 (1981) 113.
44 X.K. Xing, A.A. Tanaka, C. Fierro and D. Scherson, 170th Meeting of The Electrochemical Society, San Diego, 1986, Abstr. 727, pp. 1071–1072.
45 H.L. Li, J.Q. Chambers and D.T. Hobbs, J. Appl. Electrochem., 18 (1988) 454.
46 H.K. Venkatasetty, U.S. Patent 4,279,973, 1981.
47 N. Doddapaneni, Spring Meeting of The Electrochemical Society, Minneapolis, 1981, Abstr. 83.

48 N. Doddapaneni, Proceedings of the 30th Power Sources Symposium, Atlantic City, NJ, 1982, The Electrochemical Society, Princeton, NJ, p. 169.
49 N. Doddapaneni, Fall Meeting of the The Electrochemical Society, Detroit, 1982, Abstr. 360.
50 N. Doddapaneni, in J.D. McIntyre, M.J. Weaver and E.B. Yeager (Eds.), The Chemistry and Physics of Electrocatalysis, The Electrochemical Society Softbound Proceeding Series, Vol. 84–12, 1984, p. 630.
51 M. Madou, K. Kinoshita, M.C.M. McKubre and S. Szpak, in J.D. McIntyre, M.J. Weaver and E.B. Yeager (Eds.), The Chemistry and Physics of Electroanalysis, The Electrochemical Society Softbound Proceeding Series, Vol. 84–12, 1984, p. 618.
52 M.J. Madou, J.J. Smith and S. Szpak, J. Electrochem. Soc., 134 (1987) 2794.
53 N. Doddapaneni, U.S. Patent 4,405,693, 1983.
54 W.P. Kilroy, M. Alingir, E.B. Willstaed and K.M. Abrahams, in K.M. Abrahams and M. Salomon (Eds.), Primary and Secondary Lithium Batteries, The Electrochemical Society, Princeton, NJ, Vol. 91–3, 1991, p. 12.
55 N. Doddapaneni, U.S. Patent 4,439,503, 1984.
56 A.J. Hills and N.A. Hampson, J. Electrochem. Soc., 135 (1988) 1861.
57 R.J. Nowak, D.R. Rolison, J.J. Smith and S. Szpak, Electrochim. Acta, 33 (1988) 1313.
58 J.H. Zagal, C. Páez and S. Barbato, in S. Srinivasan, S. Wagner and H. Wrobloba (Eds.), Electrode Materials and Processes for Energy Conversion and Storage, The Electrochemical Society, Princeton, NJ, Vol. 87–12, 1987, p. 211.
59 J.H. Zagal, J. de la Fuente and G. Lagos, Bol. Soc. Chil. Quim., 34 (1989) 301.
60 P.A. Bernstein and A.B.P. Lever, Inorg. Chem., 29 (1990) 608.
61 M. Tachikawa and L.R. Faulkner, J. Am. Chem. Soc., 100 (1978) 4379.
62 N. Minami, T. Watanabe, A. Fujishima and K. Honda, Ber. Bunsenges. Phys. Chem., 83 (1976) 476.
63 F.F. Fan and A.J. Bard, J. Am. Chem. Soc., 101 (1979) 6139.
64 Y.S. Shuov, S.S. Chakhmakhchyan, V.I. Ityaev and G.G. Komissarov, Zh. Fiz. Khim., 53 (1979) 1834.
65 V.R. Shepard, Jr. and N.R. Armstrong, J. Phys. Chem., 83 (1979) 1268.
66 F. Fan and L.R. Faulkner, J. Am. Chem. Soc., 101 (1979) 4779.
67 W.M. Ayers, Faraday Discuss. Chem. Soc., 70 (1980) 247.
68 N. Minami, J. Chem. Phys., 72 (1980) 6317.
69 C.D. Jaeger, F.F. Fan and A.J. Bard, J. Am. Chem. Soc., 102 (1980) 2592.
70 A. Giraudeau, F.F. Fan and A.J. Bard, J. Am. Chem. Soc., 102 (1980) 5137.
71 Y. Nakato, M. Shioji and M. Tsuboura, J. Phys. Chem., 85 (1981) 1670.
72 T. Mezza, C.L. Linkous, V.R. Shepard, N.R. Armstrong, R. Nohr and M. Kenney, J. Electroanal. Chem., 124 (1981) 311.
73 N.R. Armstrong, T. Mezza, C.L. Linkous, B. Thacker, T. Klofta and R. Cielinski, in J.S. Miller (Ed.), Chemically Modified Surfaces in Catalysis and Electrocatalysis, ACS Symp. Ser. 192, American Chemical Society, Washington, DC, 1982, p. 205.
74 T. Klofta, C. Linkous and N.R. Armstrong, J. Electrochem. Soc., 185 (1985) 73.
75 P. Loempoel, A. Castro-Acuna, F.R.F. Dan and A.J. Bard, J. Phys. Chem., 86 (1982) 1396.
76 P. Loempoel, F.R. Fan ad A.J. Bard, J. Phys. Chem., 87 (1983) 2948.
77 N. Minami, T. Watanabe, A. Fujishima and K. Honda, Ber. Bunsenges. Phys. Chem., 83 (1979) 476.
78 C.A. Melendres and X. Feng, J. Electrochem. Soc., 130 (1983) 811.
79 P.N. Moskalev and I.S. Kirin, Russ. J. Phys. Chem. (Engl. Trans.), 46 (1972) 1019.
80 M.M. Nicholson and F.A. Pizzarelo, J. Electrochem. Soc., 127 (1980) 821.

81 H. Djellab and F. Dalard, J. Electroanal. Chem., 221 (1987) 105.
82 M.M. Nicholson and R.V. Galiardi, Final Rep. Contract N 62269–76–C0574, AD–A039596, May 1977; Chem. Abstr., 87 (1977) 144073v.
83 M.M. Nicholson and T.P. Weissmiller, Rep. C82–268/201, NTIS Order NAD–A120483, Rockwell, Anaheim, CA, 1982.
84 J.L. Kahl, L.R. Faulkner, K. Dwarkanath and H. Tachikawa, J. Am. Chem. Soc., 108 (1986) 5434.
85 J.H. Sharp and M. Lardon, J. Chem. Phys., 72 (1968) 3230.
86 J.I. Yamaki and A. Yamaji, J. Electrochem, Soc., 129 (1982) 5.
87 D. Worhle, M. Kirschmann and N.I. Jeager, J. Electrochem. Soc., 132 (1985) 1150.
88 H. Taube, J. Gen. Phys., 49 (1965) 29.
89 J.S. Valentine, Chem. Rev., 73 (1973) 235.
90 J.S. Griffith, Proc. R. Soc. London Ser. A, 235 (1956) 23.
91 L. Pauling, Nature, 203 (1964) 182.
92 L. Vaska, Acc. Chem. Res., 9 (1976) 175.
93 K. Tatsumi and R. Hoffman, J. Am. Chem. Soc., 103 (1981) 3328.
94 R.D. James, D.A. Summerville and F. Basolo, Chem. Rev., 79 (1979) 139.
95 E. Yeager, in Electrocatalysis on Non-metallic Surfaces, Natl. Bur. Stand. U.S. Spec. Publ., 455 (1976) 203.
96 E. Yeager, J. Electrochem. Soc., 128 (1981) 160 C.
97 E. Yeager, D. Scherson and B. Simic-Glavaski, in J.D.E. McIntyre, M. Weaver and E.B. Yeager (Eds.), Chemistry and Physics of Electrocatalysis, The Electrochem. Soc. Proc. Ser., Electrochemical Society, Princeton, NJ, 1984, p. 247.
98 T.D. Smith and J.R. Pilbrow, Coord. Chem. Rev., 39 (1981) 295 and references cited therein.
99 E.W. Abel, J.M. Pratt and R. Whelan, J. Chem. Soc. Chem. Commun., (1971) 449.
100 L.C. Gruen and R.J. Blagrove, Aust. J. Chem., 25 (1972) 2553.
101 T. Veprek-Siska, E. Schwertnerova and D.M. Wagnerova, Chimia, 26 (1972) 2553.
102 D.M. Wagnerova, E. Schwerterova and T. Veprek-Siska, Collect. Czech. Chem. Commun., 39 (1974) 1980.
103 K. Fenkart and C.H. Brubaker, Jr., J. Inorg. Nucl. Chem., 30 (1968) 3245.
104 J.P. Collman, M. Marrocco, P. Denisevich, C. Koval and F.C. Anson, J. Electroanal. Chem., 101 (1979) 717.
105 J.P. Collman, P. Denisevich, Y. Konai, M. Marrocco, C. Koval and F.C. Anson, J. Am. Chem. Soc., 102 (1980) 6027.
106 H.Y. Liu, M. Weaver, C. Yang and C.K. Chang, J. Electroanal. Chem., 145 (1983) 439.
107 L.K. Hanson, Proceedings of the International Symposium on Quantum Biology and Quantum Pharmacology, (1979) 311.
108 A. Didieu, M.M. Rohmer and A. Veillard, Adv. Quantum Chem., 16 (1982) 43 and references cited therein.
109 N.H. Sabelli, L.K. Lee and C.A. Melendres, in W.E. O'Grady, P.N. Ross, Jr. and F.G. Wills (Eds.), Electrocatalysis, Electrochem. Soc. Proc. Ser., The Electrochemical Society, Princeton, NJ, 1982, p. 131.
110 N.H. Sabelli and C.A. Melendres, J. Phys. Chem., 86 (1982) 4342.
111 E. Bayerand and P. Schretzmann, Struct. Bonding (Berlin), 2 (1967) 181.
112 J.L. Hoard, in K.M. Smith (Ed.), Porphyrins and Metalloporphyrins, Elsevier, Amsterdam, 1975, pp. 317–380.
113 A.B.P. Lever, Adv. Inorg. Chem. Radiochem., 7 (1965) 27.
114 M. Jahnke and M. Schönborn, 3ieme Journees Internationales d'Etude des Piles a Combustibles, Bruxelles, Comptes Rendus, Presses Academiques Europeennes, Bruxelles, 1969.

115 H. Alt, H. Binder and G. Sandstede, J. Electroanal. Chem., 31 (1971) 19.
116 H. Alt, H. Binder and G. Sandstede, J. Catal., 28 (1973) 8.
117 M. Savy, P. Andro, C. Bernard and G. Magner, Electrochim. Acta, 18 (1973) 191.
118 M. Savy, P. Andro and C. Bernard, Electrochim. Acta, 19 (1974) 403.
119 F. Beck, W. Zammert, J. Heiss, H. Miller and R. Polster, Z. Naturforsch. Teil A, 28 (1973) 1090.
120 F. Beck, Ber. Bunsenges. Phys. Chem., 71 (1973) 353.
121 K.A. Radyushkina, R.Kh. Burstein, B.D. Berezin, M.R. Tarasevich and S.D. Levina, Elektrokhimiya, 9 (1973) 410.
122 K.A. Radyushkina, M.R. Tarasevich and S.I. Andrusyova, Elektrokhimiya, 11 (1975) 1079.
123 M.R. Tarasevich, K.A. Radyushkina and S.I. Andruseva, Bioelectrochem. Bioenerg., 4 (1977) 18.
124 S.I. Andruseva, K.A. Radyshkina and M.R. Tarasevich, Sov. Electrochem., 13 (1977) 412.
125 A.J. Appleby, J. Fleisch and M. Savy, J. Catal., 44 (1976) 281.
126 M. Behret, W. Clauberg and S. Sandstede, Ber. Bunsenges. Phys. Chem., 81 (1977) 54.
127 Chr. Kretzchmar and K. Wiesener, Z. Phys. Chem. (Leipzig), 257 (1976) 39.
128 A. Kozawa, V.E. Zillinois and R.J. Brodd, J. Electrochem. Soc., 11 (1970) 1470.
129 A. Kozawa, V.E. Zillinois and R.J. Brodd, J. Electrochem. Soc., 11 (1970) 1474.
130 R.J. Brodd, V.Z. Leger, R.F. Scarr and A. Kozawa, Natl. Bur. Stand. U.S. Spec. Publ., 455 (1976) 253.
131 J.A.R. van Veen and C. Visser, Electrochim. Acta, 24 (1979) 921.
132 E. Yeager, J. Zagal, B. Nikolić and R.R. Adzić, in S. Bruckenstein, J.D.E. McIntyre, B. Miller and E. Yeager (Eds.), Proceedings of the Third Symposium on Electrode Processes, The Electrochemical Society, Princeton, NJ, 1979, p. 409.
133 R.K. Sen, J. Zagal and E. Yeager, Inorg. Chem., 16 (1977) 3379.
134 J. Zagal, R.K. Sen and E. Yeager, J. Electroanal. Chem., 83 (1977) 207.
135 J. Zagal, P. Bindra and E. Yeager, J. Electrochem. Soc., 127 (1980) 1506.
136 J. Zagal, in Electrocatálisis de la Reducción de Oxigeno, Electrocatálisis, Tópicos Especiales, Fundación para la Educación, la Ciencia y la Cultura, Buenos Aires, 1983, pp. 179–228.
137 J. Zagal, M. Páez and C. Fierro, in S. Srinivasan, S. Wagner and H. Wrobloba (Eds.), Electrode Materials and Processes for Energy Conversion and Storage, The Electrochemical Society, Princeton, NJ, Vol. 87–12, 1987, p. 198.
138 J.A.R. van Veen, J.F. van Baar, C.J. Kroese, J.G.F. Coolegem, N. de Wit and H.A. Colljn, Ber. Bunsenges. Phys. Chem., 85 (1981) 693.
139 H. Behret, M. Binder, G. Sanstede and G.G. Scherer, J. Electroanal. Chem., 117 (1981) 29.
140 H. Behret, W. Clauberg and G. Sandstede, Ber. Bunsenges. Phys. Chem., 83 (1979) 139.
141 F. van den Brink, E. Barendrecht and W. Visscher, J. Electrochem. Soc., 127 (1980) 2003.
142 F. van den Brink, W. Visscher and E. Barendrecht, J. Electroanal. Chem., 157 (1983) 283.
143 F. van den Brink, W. Visscher and E. Barendrecht, J. Electroanal. Chem., 157 (1983) 305.
144 F. van den Brink, W. Visscher and E. Barendrecht, J. Electroanal. Chem., 172 (1984) 301.
145 F. van den Brink, W. Visscher and E. Barendrecht, J. Electroanal. Chem., 175 (1984) 279.
146 A. van der Putten, A. Elzing, W. Visscher and E. Barendrecht, J. Electroanal. Chem., 221 (1987) 95.
147 J.A.R. van Veen, Electrochim. Acta, 27 (1982) 1403.
148 B.C. Tofied, Struct. Bonding (Berlin), 21 (1975) 1.
149 K. Tanaka, E. Elkaim, L. Li, Z.N. Jue and P. Coppens, J. Chem. Phys., 84 (1986) 6969.
150 P. Coppens, A. Haladat and E. Stevens, J. Am. Chem. Soc., 104 (1982) 3546.

151 P. Coppens and L. Liang, J. Chem. Phys., 81 (1984) 1983.
152 S.F. Sontum, D.A. Case and M. Karpluz, J. Chem. Phys., 79 (1983) 1939.
153 A.M. Schaffer, M. Gouterman and E.R. Davidson, Theor. Chim. Acta, 30 (1973) 9.
154 M. Gouterman, in D. Dolphin (Ed.), The Porphyrins, Vol. 3, Academic Press, New York, 1978, pp. 1-165.
155 J.F. Myers, G.W. Rayner Canham and A.B.P. Lever, Inorg. Chem., 14 (1975) 461.
156 A.B.P. Lever and J.P. Wilshire, Can. J. Chem., 54 (1976) 2514.
157 A.B.P. Lever and J.P. Wilshire, Inorg. Chem., 17 (1978) 1145.
158 A.B.P. Lever, P.C. Minor and J.P. Wilshire, Inorg. Chem., 20 (1981) 2550.
159 A.B.P. Lever, Adv. Inorg. Chem. Radiochem., 7 (1965) 27.
160 A.B.P. Lever and P.C. Minor, Adv. Mol. Relaxation Processes, 18 (1980) 115.
161 A.B.P. Lever and P.C. Minor, Inorg. Chem., 20 (1980) 4015.
162 A.B.P. Lever, S. Liccocia, B.S. Ramaswamy, A. Kandil and D.V. Stynes, Inorg. Chim. Acta, 51 (1981) 169.
163 A.B.P. Lever, S. Liccocia, P. Minor, B.S. Ramaswamy, S.R. Pickens and K. Magnell, J. Am. Chem. Soc., 103 (1981) 6800.
164 J.T.S. Irvine, B.R. Eggings and J. Grimshaw, J. Electroanal. Chem., 271 (1989) 161.
165 L.D. Rollman and R.T. Iwamoto, J. Am. Chem. Soc., 90 (1968) 1455.
166 A.Wolberg and J. Manassen, J. Am. Chem. Soc., 92 (1970) 2982.
167 D. Lexa and M. Reix, J. Chem. Phys., 71 (1974) 510, 517.
168 D.W. Clack, N.S. Hush and I.S. Wooley, Inorg. Chim. Acta, 19 (1976) 129.
169 K.M. Kadish, L.A. Bottomley and J.S. Cheng, J. Am. Chem. Soc., 100 (1978) 2731.
170 V.R. Shepard, Jr. and N.R. Armstrong, J. Phys. Chem., 83 (1979) 1268.
171 V.I. Gavrilov, L.G. Tomilova, I.V. Shepelin and E.A. Lukyanets, Elektrokhimiya, 15 (1979) 1058.
172 R.O. Loutfy and Y.C. Cheng, J. Phys. Chem., 74 (1980) 2902.
173 A.B.P. Lever, S. Liccocia, K. Magnell, P.C. Minor and B.S. Ramaswamy, ACS Symp. Ser. 201, American Chemical Society, Washington, DC, 1982, p. 237.
174 C.Y. Li and D.H. Chin, Anal. Lett., 8 (1975) 291.
175 S. Zecević, B. Simić-Glavaski, E. Yeager, A.B.P. Lever and P.C. Minor, J. Electroanal. Chem., 196 (1985) 339.
176 B. Simić-Glavaski, S. Zecević and E. Yeager, J. Am. Chem. Soc., 107 (1985) 5625.
177 B. Simić-Glavaski, S. Zecević and E. Yeager, J. Electroanal. Chem., 150 (1983) 469.
178 B. Simić-Glavaski, S. Zecević and E. Yeager, J. Phys. Chem., 87 (1987) 4555.
179 B. Simić-Glavaski, A.A. Tanaka, M.E. Kenney and E. Yeager, J. Electroanal. Chem., 229 (1987) 285.
180 R. Adzić, B. Simić-Glavaski and E. Yeager, J. Electroanal. Chem., 194 (1985) 155.
181 P.C. Minor, M. Gouterman and A.B.P. Lever, Inorg. Chem., 24 (1985) 1894.
182 W.A. Nevin, W. Liu, M. Melnik and A.B.P. Lever, J. Electroanal. Chem., 213 (1986) 217.
183 (a) A.B.P. Lever, M.R. Hempsted, C.C. Leznoff, W. Liu, M. Melnik, W.A. Nevin and P. Seymour, Pure Appl. Chem., 58 (1986) 1467.
(b) A.B.P. Lever, in C.C. Leznoff and A.B.P. Lever (Eds.), The Phthalocyanines, Vol. 2, VCH, New York, 1992.
184 W.A. Nevin, M.R. Hempsted, W. Liu, C.C. Leznoff and A.B.P. Lever, Inorg. Chem., 26 (1986) 570.
185 D.K. Geiger, G. Ferraudi, K. Madden, J. Granifo and D.P. Rillema, J. Phys. Chem., 89 (1985) 3890.
186 R.H. Campbell, G.A. Heath, G.T. Hefter and R.C.S. McQueen, J. Chem. Soc. Chem. Commun., (1983) 1123.

187 H. Djellab and F. Dalard, J. Electroanal. Chem., 221 (1987) 105.
188 A. Elzing, A. van der Putten, W. Visscher and E. Barendrecht, J. Electroanal. Chem., 279 (1990) 137.
189 J.M. Green and L.R. Faulkner, J. Am. Chem. Soc., 105 (1983) 2950.
190 M. Gouterman, G.H. Wagniere and L.C. Snyder, Jr., J. Mol. Spectrosc., 11 (1963) 2.
191 C. Weiss, H. Kobayashi and M. Gouterman, J. Mol. Spectrosc., 16 (1965) 415.
192 A. McHugh, M. Gouterman and J. Weiss, Theor. Chim. Acta, 24 (1972) 346.
193 A. Henriksson and M. Sundbom, Theor. Chim. Acta, 27 (1972) 213.
194 J.P. Randin, Electrochim. Acta, 19 (1974) 83.
195 F. Beck, J. Appl. Electrochem., 7 (1977) 191.
196 C.L. Ni and F.C. Anson, Inorg. Chem., 24 (1985) 4754.
197 A. van der Putten, A. Elzing, W. Visscher and E. Barendrecht, J. Electroanal. Chem., 221 (1987) 95.
198 D. van den Ham, C. Hinnen, G. Magner and M. Savy, J. Phys. Chem., 91 (1987) 4743.
199 F. Coowar, O. Contamin, M. Savy and G. Scarbeck, J. Electroanal. Chem., 226 (1988) 119.
200 A.J. Appleby, Catal. Rev., 4 (1970) 221.
201 A.J. Appleby, in J.O.M. Bockris and B.E. Conway (Eds.), Modern Aspects of Electrochemistry, Vol. 9, Plenum Press, New York, 1974, Chap. 5.
202 R.R. Durand, Jr., C.S. Bencosme, J.P. Collman and F.C. Anson, J. Am. Chem. Soc., 105 (1983) 2710.
203 S.M. Marcuccio, P.I. Svirskaya, S. Greenberg, A.B.P. Lever, C.C. Leznoff and K.B. Tomer, Can. J. Chem., 63 (1985) 3057.
204 W.A. Nevin, M.R. Hempstead, W. Liu, C.C. Leznoff and A.B.P. Lever, Inorg. Chem., 26 (1987) 570.
205 J. Zagal, M. Páez, A.A. Tanaka, J.R. dos Santos and C. Linkous, J. Electroanal. Chem., in press.
206 J. Zagal, Ph.D. Thesis, Case Western Reserve University, 1978.
207 A. van der Putten, Ph.D. Thesis, Technische Universiteit Eindhoven, 1986.
208 J. Zagal, M. Páez, J. Sturm and S. Ureta-Zañartu, J. Electroanal. Chem., 181 (1984) 295.
209 P. Waldmeir and H. Siegel, Chimia, 24 (1970) 195.
210 P. Waldmeir and H. Siegel, Inorg. Chim. Acta, 5 (1971) 659.
211 A. van der Putten, A. Elzing, W. Visscher and E. Barendrecht, J. Electroanal. Chem., 214 (1986) 523.
212 A. Elzing, A. van der Putten, W. Visscher and E. Barendrecht, J. Electroanal. Chem., 233 (1987) 99.
213 A. Elzing, A. van der Putten, W. Visscher and E. Barendrecht, J. Electroanal. Chem., 233 (1987) 113.
214 J. Zagal, Contrib. Cient. Tec. Spec. Publ., XVIII (1988) 107.
215 H. Meier, U. Tschirwitz, E. Zimmerhackl, W. Albrecht and G. Zeitler, J. Phys. Chem., 81 (1977) 712.
216 J. Blomquist, U. Helgeson, L.C. Moberg, L.Y. Johansson and R. Larson, Electrochim. Acta, 27 (1982) 1445.
217 J. Riga, M. Savy, J.J. Verbist, J.E. Guerchais and J. Sala-Pala, J. Chem. Soc. Faraday Trans. 1, 78 (1982) 2773.
218 C. Paliteiro, A. Hamnett and J.B. Goodenough, J. Electroanal. Chem., 160 (1984) 359.
219 C. Paliteiro, A. Hamnett and J.B. Goodenough, J. Electroanal. Chem., 239 (1988) 273.
220 C. Paliteiro, A. Hamnett and J.B. Goodenough, J. Electroanal. Chem., 249 (1988) 167.
221 A.K. Shuka, C. Paliteiro, R. Manoharan, A. Hamnett and J.B. Goodenough, J. Appl. Electrochem., 19 (1989) 105.

222 R. Hillman and W.J. Albery, Annu. Rep. Chem. Soc. London Ser. A, (1982) 377.
223 R. Hoffman, Acc. Chem. Res., 4 (1971) 1.
224 R. Hoffman, M. Chen and D.L. Thorn, Inorg. Chem., 16 (1977) 503.
225 R. Taube, Pure Appl. Chem., 38 (1974) 347.
226 J. Ulstrup, J. Electroanal. Chem., 79 (1977) 526.
227 K. Tamura and T. Kahara, J. Electrochem. Soc., 123 (1976) 776.
228 F. Steinbach and M. Zobel, Z. Phys. Chem. N.F., 111 (1978) 113.
229 F. Steinbach and M. Zobel, J. Chem. Soc. Faraday Trans. 1, 82 (1979) 113.
230 F.J. Cookson, T.D. Smith, J.F. Boas, P.R. Hicks and J.R. Pilbrow, J. Chem. Soc. Dalton Trans., (1977) 109.
231 D.M. Wagnerova, E. Schwertnerova and J. Veprek-Šiska, Collect. Czech. Chem. Commun., 38 (1973) 756.
232 E. Schwertnerova, D.M. Wagnerova and J. Veprek-Šiska, Z. Chem., 14 (1974) 311.
233 K.M.K. Korfhage, K. Ravichandran and R.P. Baldwin, Anal. Chem., 56 (1984) 1517.
234 T.A. Albright, J.K. Burdett and M.H. Whango, Orbital Interaction in Chemistry, Wiley–Interscience, New York, 1985.
235 D.M. Wagnerova, E. Schwertnerova and J. Veprek-Šiska, Collect. Czech. Chem. Commun., 39 (1974) 3036.
236 J. Zagal, K. Brinck and S. Ureta-Zañartu, VIII Reunión Latinoamericana, Electroquím. Corr., Córdoba, Argentina, 1988, Abstr. 1.36, p. 160.
237 J. Zagal, S. Ureta-Zañartu and K. Brinck, to be published.
238 W.K.T. Gleim and P. Urban, U.S. Patent 2,966,453, 1960.
239 P. Urban, U.S. Patent 3,039,855, 1962.
240 N.N. Kundo and N.P. Keir, Russ. J. Chem., 42 707 (1968).
241 F. Steinbach and H.H. Schmidt, J. Catal., 52 (1978) 302.
242 W.M. Brouwer, P. Piet and A.L. German, J. Mol. Catal., 29 (1985) 335.
243 W.M. Brouwer, P. Piet and A.L. German, J. Mol. Catal., 29 (1985) 347.
244 J. Zwart, H.C. van der Weide, N. Broker, C. Rummens, G.C. Schuit and A.L. German, J. Mol. Catal., 3 (1977) 151.
245 A. Skorobogaty and T.D. Smith, J. Pol. Chem., 16 (1982) 131.
246 J.H. Schutten and J. Zwart, J. Mol. Catal., 5 (1979) 109.
247 J.H. Schutten, P. Piet and A.L. German, Makromol. Chem., 180 (1979) 2341.
248 W.M. Brouwer, P. Piet and A.L. German, J. Pol. Chem., 22 (1984) 297.
249 N.N. Kundo, N.P. Keir, G.V. Glazneva and E.K. Mamaeva, Kinet. Katal., 8 (1966) 1119.
250 A. Meister and M. Anderson, Annu. Rev. Biochem., 52 (1983) 711.
251 W. Stricks and I.M. Kolthoff, J. Am. Chem. Soc., 74 (1952) 4646.
252 G. Patriarche, Anal. Chim. Acta, 76 (1975) 299.
253 Y. Sakane and Y. Osajima, Nippon Kagaku Kaishi, 3 (1981) 353.
254 L.J. Nunez-Vergara and J.A. Squella, Bioelectrochem. Bioenerg., 16 (1986) 333.
255 J.L. Peel, J. Biochem., 88 (1963) 296.
256 O. Contamin, E. Levart and M. Savy, J. Electroanal. Chem., 115 (1980) 267.
257 C. Páez, A. Prelle, S. Ureta-Zañartu and J. Zagal, Bol. Soc. Chil. Quim., 35 (1990) 299.
258 C. Páez, S. Ureta-Zañartu and J. Zagal, XVIII Jornadas Chil. Quím., Santiago, Chile, 1989, Abstr. EQ7, p. 222, to be published.
259 W.L. Bowden and A.N. Day, J. Electrochem. Soc., 127 (1980) 1419.
260 G.E. Blomgren, V.Z. Leger, M.L. Kronenemberg, T. Kalnoki-Kis and R.J. Brodd, Proceedings of the 11th International Power Sources Symposium, Brighton, UK, 1978, p. 583.
261 C.R. Schalaijer, F. Goebel and N. Marinic, J. Electrochem. Soc., 126 (1979) 513.
262 A.N. Day, Thin Solid Films, 43 (1977) 131.

263 J.C. Bailey and J.P. Kohut, Proceedings of the 12th International Power Sources Symposium, Brighton, UK, 1980, p. 17.

264 A. Attia, C. Sarrazin, K.A. Gabriel and R.P. Burns, J. Electrochem. Soc., 131 (1984) 2523.

265 R. Williams, F. Tsay, S. Khim, M. Evans, Q. Kim, A. Rodriguez, B.J. Carter and H. Frank, in A.N. Dey (Ed.), Lithium Batteries, The Electrochemical Society, Princeton, NJ, 1984, p. 60.

266 F.W. Dampier and T. Cole, J. Electrochem. Soc., 133 (1986) 938.

267 F.W. Dampier and T. Cole, J. Electrochem. Soc., 134 (1987) 2383.

268 W.K. Istone and R.J. Brodd, J. Electrochem. Soc., 129 (1982) 1853.

269 N. Doddapeneni, U.S. Patent 4,613,551, 1986.

270 K. Hiratsuka, K. Takahashi, H. Sasaki and S. Toshima, Chem. Lett., (1977) 1137.

271 C.M. Lieber and N.S. Lewis, J. Am. Chem. Soc., 106 (1984) 5033.

272 R. Eisenberg and B. Fisher, J. Am. Chem. Soc., 102 (1980) 7361.

273 J.L. Grant, K. Goswami, L.O. Spreer, J.W. Otvos and J.M. Calvin, J. Chem. Soc. Dalton Trans., (1987) 2105.

274 M.N. Mahmood, D. Masheder and C.J. Harty, J. Appl. Electrochem., 17 (1987) 1159.

275 M.N. Mahmood, D. Masheder and C.J. Harty, J. Appl. Electrochem., 17 (1987) 1223.

276 N. Furuya, K. Matsui and S. Motoo, Denki Kagaku, 55 (1987) 787.

277 N. Furuya, K. Matsui and S. Motoo, Denki Kagaku, 56 (1988) 288.

278 N. Furuya, K. Matsui and S. Motoo, Denki Kagaku, 56 (1988) 980.

279 N. Furuya and K. Matsui, J. Electroanal. Chem., 271 (1989) 181.

280 N. Furuya and K. Matsui, Electrochim. Acta, 36 (1991) 1309.

281 K. Uchida, M. Soma, T. Onishi and K. Tamaru, J. Chem. Soc. Faraday Trans. 1, 75 (1979) 2839.

282 R. Guilard, G. Lagrange, A. Tabard, D. Lancon and K.M. Kadish, Inorg. Chem., 24 (1985) 3649.

283 K. Ogura and S. Yamasaki, J. Appl. Electrochem., 15 (1985) 279.

284 J. Riga, M. Savy, J.J. Verbist, J.E. Guerchais and J. Sala Pala, J. Chem. Soc. Faraday Trans. 1, 78 (1982) 2773.

285 M. Arakawa, J. Yamaki and T. Okada, J. Electrochem. Soc., 131 (1984) 2605.

286 P. Ehrburger, A. Mongilardi and J. Lahaye, J. Colloid Interface Sci., 91 (1983) 151.

287 A.J. Appleby and M. Savy, Electrochim. Acta, 21 (1976) 567.

288 A.J. Appleby and M. Savy, Electrochim. Acta, 22 (1977) 1315.

289 L. Kreja and A. Plewka, Electrochim. Acta, 27 (1982) 251.

290 P. Ehrburger, A. Mongilardi and J. Lahaye, Carbon 80, Deutsche Keramische Gesellschaft, 1980 p. 227.

291 A.A. Tanaka, C. Fierro, D. Scherson and E.B. Yeager, J. Phys. Chem., 91 (1987) 3799.

292 T. Kobayashi, F. Kurokawa, T. Ashida, N. Uyeda and E. Suito, Chem. Commun., (1971) 1631.

293 D.A. Scherson, C.A. Fierro, D. Tryk, S.L. Gupta, E. Yeager, J. Eldridge and R.W. Hoffman, J. Electroanal. Chem., 184 (1985) 419.

294 D.A. Scherson, S.B. Yao, E. Yeager, J. Eldridge, M.E. Kordesh and R.W. Hoffman, J. Phys. Chem., 87 (1983) 932.

295 D.A. Scherson, C. Fierro, E. Yeager, J. Eldridge, M.E. Kordesh and R.W. Hoffman, J. Electroanal. Chem., 169 (1984) 287.

296 C.A. Melendres, J. Phys. Chem., 84 (1980) 1936.

297 J.W. Buckler, in K.M. Smith (Ed.), Porphyrins and Metalloporphyrins, Elsevier, Amsterdam, 1976, Chap. 5.

298 L. Kreja and A. Plewka, Electrochim. Acta, 27 (1982) 251.

299 L. Kreja, Electrochim. Acta, 28 (1983) 1807.

300 R. van Veen, J.F. van Baar and J.K. Kroese, J. Chem. Soc. Faraday Trans. 1, 77 (1981) 2827.

301 C.A. Melendres and F.A. Cafasso, J. Electrochem. Soc., 128 (1981) 755.

302 B.N. Achar, G.M. Fohlen and A.J. Parker, J. Polym. Sci., 20 (1982) 2073.

303 C. Magner, M. Savy and G. Scarbeck, J. Electrochem. Soc., 127 (1980) 1076.

304 M. Yamana, R. Darby and R.E. White, Electrochim. Acta, 29 (1984) 329.

305 R. Larsson, L.Y. Johansson and L. Jonsson, J. Appl. Electrochem., 11 (1981) 489.

306 T.A. Skotheim (Ed.), Handbook of Conducting Polymers, Vol. 1, Dekker, New York, 1986.

307 H. Laborde, J.M. Leger, C. Lamy, F. Garnier and A. Yassar, J. Appl. Electrochem., 20 (1990) 524.

308 R.A. Bull, F.R. Fan and A.J. Bard, J. Electrochem. Soc., 131 (1984) 687.

309 W.E. O'Grady, T. Skotheim, M. Rosenthal and M.I. Florit, Spring Meeting of the Electrochemical Society, Cincinnati, OH, 1984, Abstr. 415.

310 R. Jang and S. Dong, J. Electroanal. Chem., 246 (1988) 101.

311 E. Barendrecht, A. Elzing, L.J.J. Janssen, A. van der Putten, W. Visscher and F. Volk, Makromol. Chem. Makromol. Symp., 8 (1987) 211.

312 O. Hirabaru, T. Nakase, K. Hanabusa, H. Shirai, K. Takemoto and N. Hojo, J. Chem. Soc. Chem. Commun., (1983) 481.

313 M. Suginoya, H. Kamamori and K. Iwasa, J. Electrochem. Soc., 137 (1990) 3761.

314 M. Suginoya, H. Kamamori and K. Iwasa, in L.T. Romankiw and T. Osaka (Eds.), Electrochemical Technology in Electronics, The Electrochemical Society Softbound Proceeding Series, 1988, p. 309.