Transition metal complexes of porphyrins and phthalocyanines as electrocatalysts for dioxygen reduction

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Introduction

The increasing technological importance of fuel cells and air batteries has intensified research on effective catalysts for electrochemical reduction of dioxygen. In 1964 Jasinski[1,7] reported oxygen reduction electrocatalysis with cobalt phthalocyanine, adsorbed on carbon and nickel electrodes. Subsequently many other macrocyclic organic N_4-complexes like porphyrins and phthalocyanines (monomers and polymers) with different transition metals were evaluated for their electrocatalytic activity. These complexes were considered promising as cathode electrocatalysts for fuel cells because they were relatively inexpensive as compared to noble metals. They also exhibit considerable activity in various heterogeneous redox reactions, are thermally stable and possess semiconductor properties. Several monographs, reviews and papers describe their physical and electrical properties, but the available literature on the electrocatalytic activities for oxygen reduction has not been adequately covered. Literature from 1963 to 1976 on metallophthalocyanines and metalloporphyrins was reviewed by Tarasevich *et al.*[2]. Appleby *et al.*[3] covered published material up to 1977 on the electrocatalytic properties of transition metal phthalocyanine. The number of papers in the next decade (1976–87) has increased significantly, meriting further attention.

Parameters influencing activity

Electrocatalytic activity is determined by several factors[4], such as the redox potential of the metal ligand couple (the nature of the central metal atom, ligand structure and substituents on the ligand macrocycle), the monomeric or polymeric state of the catalyst, pH of the electrolyte, type of support, method of synthesis *etc*. Oxygen reduction potential and magnitude of catalytic current is dependent on the pH of electrolyte and on the concentration ratio of complex to oxygen. The order of activity for different ligands seems to be: (In alkaline solution) Phthalocyanine > tetraphenyl porphyrin > dibenzotetraazaannulene, (In acid solution) Dibenzotetraazaannulene > tetraphenylporphyrin > phthalocyanine. With Cu as central atom, the order of activity for complexes is as follows[11]: CuPc polymer > CuPc > Cu porphyrazine. Polymerization seems to enhance activity by changing the mechanism of electron transfer and the rate determining step depending on the electrode polarization. For cobalt complexes the electrocatalytic activity for oxygen reduction decreases in the order[12]: $CoPc(NH_2)_4 > CoPc > CoPcCl_4$.

Thus, catalytic activity of metal phthalocyanines correlate with the increase in electron donor capacity of the reduced form of complex. The metal atom rather than any other part of the macrocyclic ring, is the active electrocatalytic site, while the chelate or oxide structures

serve predominantly to keep the metal in the stable form at the support surface[6,13]. The substituents in the second sphere of the organic molecule have less effect and metal-free phthalocyanine does not show any catalytic activity[14,15]. A linear dependence of electrochemical activity on electronic conductivity and activation energy has also been reported. For example, a system with iron polyphthalocyanine of higher electronic conductivity shows a lower potential drop than polymeric iron phthalocyanine of lower conductivity implying a high electronic delocalization within the ligand[16,68].

Oxygen electroreduction can proceed by two pathways: the direct 4-e^- reduction of dioxygen to give water or the two electron reduction to give hydrogen peroxide that may further get reduced to water. On many electrode surfaces, H_2O_2 formation predominates, preventing the system from delivering all its energy, thus reducing efficiency. Hence it is important to find an effective and inexpensive catalyst that promotes the direct reduction of oxygen to water[18].

Since dioxygen reduction involves adsorption of oxygen on the catalyst as well as electron donation from
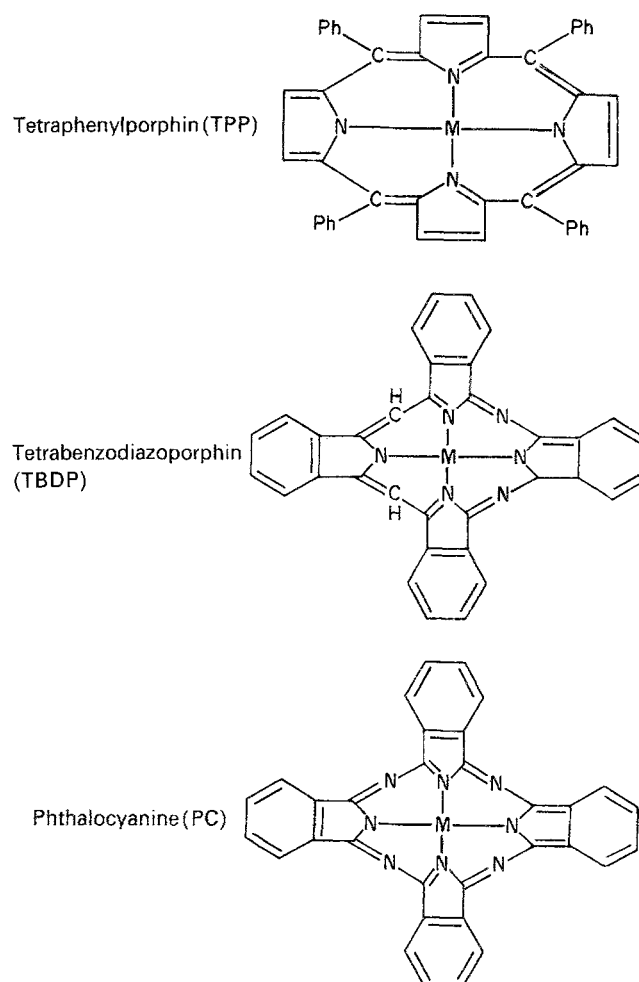

Figure 1. Structure of metal phthalocyanine and metal porphin complexes.

the catalyst to oxygen, both factors could play a major role. For example, in acid solution the activity order of metal phthalocyanines is: Fe > Co > Ni > Cu[17]. Alt *et al.* explained this gradation in activity for oxygen reduction by a model based on oxygen adsorption using MO theory[39]. According to this model, oxygen radical creation involves formation of a π-σ bond between molecular oxygen and the central metal ion. This partial electron transfer is favoured by empty d_{z^2} orbitals and back bonding from filled d_{xz} and d_{yz} metal orbitals to empty or partially filled π* orbitals of dioxygen. The π-σ orbital mechanism is difficult to reconcile with the formation of peroxide as an intermediate with most transition metal catalysts. The most probable structure for dioxygen adsorption is the Pauling model, in which the sp² orbitals of dioxygen interact with d_{z^2} orbitals of the transition metal to form an end-on bond. The square pyramidal complexes of iron(II) and copper(II) which are active in dioxygen reduction in acid solutions, appear to involve species of this type.

Beck *et al.* have proposed a concept in which the dioxygen reduction is a redox process; molecule oxidizes the central metal ion and in so doing is itself reduced[62]. The charge transfer step, however, involves an end-on interaction between a dioxygen molecule and the central metal ion, just as in the Pauling model.

The four electron reduction of oxygen involves rupture of the O—O bond but no O—O bond breaking occurs in the formation of H_2O_2. An increase in the number of conjugated electrons (as in polymeric phthalocyanine or the introduction of electron-donating substituents, such as methoxy, in the porphyrin or phthalocyanine ring) leads to a parallel reaction: direct reduction of oxygen to water, because both the adsorption of oxygen and cleavage of the O—O bond is facilitated by an increase in the electron density on the central metal[19]. Rupture of the oxygen molecule is also facilitated by simultaneous interaction of oxygen with two active sites on the electrode surface, as probably occurs on platinum[20,21].

Electrocatalyst for oxygen reduction

This section is arranged according to the ligand structure of the complexes discussed.

Phthalocyanine (Pc) complexes

Table 1 contains the available data on this class of compound in the electrocatalytic reduction of dioxygen.

Table 1. Mechanism of oxygen reduction by metal phthalocyanine.

Complex	Mechanism	Solution pH	Ref.
FePc	4e⁻ reduction	no restriction	(6, 63)
MnPc	4e⁻ reduction	alkaline	(36)
CoPc	direct 4e⁻ reduction is absent. 2e⁻ reduction above 300 mv vs RHE, H_2O_2 formed is reduced below 300 Mv vs RHE	alkaline	(23)
PtPc	2e⁻ reduction predominates, H_2O_2 formed is reduced below 350 Mv vs RHE.		(28)

Kazarinov *et al.*[6] reported that regardless of pH the activity of metal phthalocyanines varies in the order: iron(II, III) > cobalt(II), manganese(II) ≫ nickel(II) > copper(II) > hydrogen. Kuczynski reported the same sequence in 6M NaOH at 20°C[65], and Shukla *et al.*[8] also found a similar trend in the order of electrocatalytic activity with the exception of MnPc *i.e.* FePc > CoPc ~ —Co—TPP > NiPc ≫ MnPc where TPP is tetraphenyl porphyrin.

The catalyst efficiency can be enhanced if H_2O_2 formed is decomposed by the catalyst/substrate. The order of decreasing activity towards H_2O_2 decomposition is: FePc > NiPc > CuPc > CoPc and FePc/SK > NiPc/SK > CuPc/SK > SK > CoPc/SK (SK is active carbon obtained from Saran)[65]. Copper hydroxychlorophthalocyanine is active in H_2O_2 decomposition[26]. Further variations are possible depending on electrode preparation. For example, iron phthalocyanine applied to carbon electrodes by three methods: by mixing (electrode 1), impregnation (electrode 2) and direct synthesis (electrode 3) has different activity for destruction of H_2O_2, the order being: electrode 3 > electrode 2 > electrode 1. Electrodes 2 and 3 showed higher potential during cathodic polarization than electrode 1[27].

Tetrasulphophthalocyanine (TSP) complexes

Oxygen reduction pathways for some metal TSP complexes are shown in Table 2; CoTSP and FeTSP have high catalytic activity.

With a methanolic electrolyte containing no dioxygen, FeTSP does not influence the hydrogen-peroxide reduction wave up to 10⁻⁵ M. This wave diminishes with time but the peroxide decomposition is slow. CoTSP is adsorbed on graphite in flat and side-on modes. In the flat mode, dioxygen can be adsorbed and reduced to hydrogen peroxide. A face to face type macrocyclic dimer could probably form in the side-on-adsorbed state, where H_2O_2 is adsorbed and reduced to water. Formation of the dimer is supported by UV/visible spectrophotometry[33].

With a mixture of Fe- and Co-TSP adsorbed on graphite, the percentage of H_2O_2 formed in dioxygen reduction decreases linearly as the fraction of Fe-TSP on the electrode surface increases[18], indicating that the catalysts act independently on the surface. H_2O_2 generated on Co-sites does not seem to decompose on Fe-sites, although both sites are separated on the electrode surface only by distances of the order of the diameter of the phthalocyanine molecule, which is small compared with the thickness of the Nernst diffusion layer. Further the dioxygen reduction on Fe-TSP seems to be first order in Fe coverage, which rules out the possibility of μ-peroxo complex formation with a dioxygen molecule bridging two parallel phthalocyanines.

Table 2. Mechanism of oxygen reduction by metal tetrasulphophthalocyanine.

Complex	Mechanism	Solution pH	Ref.
FeTSP	4e⁻ reduction	(1–14)	29–32
CoTSP	2e⁻ reduction	(1–14)	22, 29–32
NiTSP and CuTSP	2e⁻ reduction	alkaline	34

Table 3. Reduction pathway for tetracarboxyphthalocyanine metal complexes (MTcPc).

Complex	Mechanism	Ref.
FeTcPc	Successive reduction of O_2 to H_2O_2 to H_2O	35
CoTcPc	2e⁻ reduction. H_2O_2 formed can further reduce to water at same or more negative potential.	35

Table 4. Electroreduction by polymeric metal phthalocyanine.

Complex	Mechanism	Medium	Ref.
Polymeric MnPc	4e- reduction	alkaline	36
Polymeric CoPc	4e⁻ reduction contribute 50% in overall reduction	alkaline	36.5
Polymeric NiPc	mainly 2e⁻ reduction	–	5

Carboxyphthalocyanine complexes

References to this class of compounds are given in Table 3. $Fe^{III}TcPc$ is catalytically active in the reduction of H_2O_2 to water, but activity of $Fe^{III}TcPc$ is lower than that of $Fe^{III}OcPc$, where OcPc is octacarboxyphthalocyanine[24]. In H_2O_2 decomposition, the electrocatalysis may require the presence of free radicals or unpaired electrons on the catalyst surface[25].

Polymeric phthalocyanine

Relevant data is given in Table 4. The activity of iron polyphthalocyanine catalyst is very close to that of platinum catalysts, particularly in alkaline media. Mixed iron-tin diphthalocyanine shows the same activity as iron polyphthalocyanine up to 50% substitution of iron by tin in iron polyphthalocyanine. However, mixed iron-copper diphthalocyanine shows lower activity indicating that copper ion appears to act as an inert diluent in mixed polymers but tin sites are as active as iron sites[38].

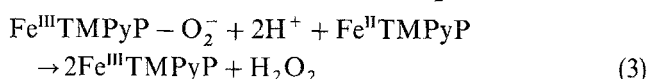In both acid and alkaline solutions, Fe-hydroxypolyphthalocyanine has a higher activity than Co-hydroxypolyphthalocyanine[37].

Porphyrin based complexes

Stepwise reduction processes ($O_2 \rightarrow H_2O_2 \rightarrow H_2O$) have been reported for monomeric iron porphyrins (Table 5),

but only a direct 4e⁻ reduction has been observed for FeTMAP. Iron tetrapyridylporphyrin (FeTPyP) has low activity.

Reduction of oxygen at a glassy carbon (GC) electrode modified with Fe-tetraphenylporphyrin derivatives (FeTPPs) having zero, one or four amino groups showed that to attain 4e⁻ reduction, the number of porphyrin layers required are 8,5 and 2 respectively, indicating that the rate constants are larger for FeTPPs with more amino groups. This result highlights the influence of functional groups on the oxygen reduction mechanism[40].

The reduced form of Fe tetrakis(N-methyl-4-pyridyl) porphyrin, ($Fe^{II}TMPyP$), electrogenerated at a highly polished glassy carbon electrode, is capable of reducing molecular oxygen to H_2O via a multistep mechanism as shown below[45]:

$$Fe^{III}TMPyP + e^- \rightarrow Fe^{II}TMPyP \tag{1}$$

$$Fe^{II}TMPyP + O_2 \rightarrow Fe^{III}TMPyP - O_2^- \tag{2}$$

$$Fe^{III}TMPyP - O_2^- + 2H^+ + Fe^{II}TMPyP$$
$$\rightarrow 2Fe^{III}TMPyP + H_2O_2 \tag{3}$$

Here the porphyrin-oxygen intermediate is further reduced by $Fe^{II}TMPyP$ or by an electrode electron, to H_2O_2. A reaction pathway allowing a two-electron reduction of H_2O_2 to H_2O may involve an intermediate complex similar to that of oxygen with the iron porphyrin. Similarly a porphyrin-H_2O_2 intermediate could be reduced by another iron(II) porphyrin or by the electrode.

Kolpin and Swofford[47] have shown that heme adsorbed on a mercury electrode reduces oxygen to water via the same mechanism as that associated with oxygen reduction by $Fe^{II}TMPyP$. They suggested that Fe^{II}heme-O_2 and Fe^{II}heme-H_2O_2 were formed in the rate limiting step of the overall reduction process.

Details for cobalt porphyrin derivatives are shown in Table 6.

In alkaline solution, the activity order is: CoPc polymer > CoTMPP > CoTPP, CoPc. In acid solution only successive stepwise reduction of oxygen occurs, activity increases in the series CoPc polymer → CoTPP → CoTMPP[36].

Jiang *et al.*[9,10] described catalytic activity order for TPP: FeTPP > CoTPP > MnTPP, but Kazarinov *et al.* reported that, for TPP, at all pHs the cobalt complexes are more active than those with $Fe^{II, III}$ *i.e.* $Co^{II} > Fe^{II, III} > Ni^{II}, Cu^{II}$.

Vanadyl porphyrin obtained from heavy, high sulphur crude petroleum oil reduces oxygen in alkaline media, but not in acidic solution[49].

Table 5. Electroreduction by porphyrin based complexes.

Complex	Mechanism	pH	Ref.
Mesotetrakis(P-Carboxyphenyl porphinato iron[III] (FeTcPP); Fe[III]protoporphyrin IX (FePPIX) and Fe[III] mesotetraphenyl porphine(FeTPP)	Successive reduction	–	41–43
Iron tetra-(4-N-methylpyridyl) porphyrin pentachloride	2e⁻ reduction	wide	46,24
Iron[III] tetra(N, N, N-trimethyl-anilinium) porphyrin(FeTMAP)	4e⁻ reduction		44

Table 6. Reduction pathway for Co porphyrin complexes.

Complex	Mechanism	Ref.
CoTPP, CoTPyP and Co tetrakis (N-methyl-4-pyridyl) Porphyrin (CoTMPyP)	Mainly 2e⁻ reduction	43,36,6,45 48,84
Co tetra(P–methoxyphenyl) porphyrin (CoTMPP)	4e⁻ process contributes 30%	36,6

Ir(OEP)H(H₂OEP = 2, 3, 7, 8, 12, 13, 17, 18 octaethyl-porphyrin) adsorbed on graphite, catalyses four-electron oxygen reduction. The electrocatalytic activity of Ir(OEP)H is equal or superior to that of the best dicobalt co-facial porphyrins and is unprecedented for a monomeric macrocycle[50].

Electroreduction of oxygen by dicobalt binuclear porphyrin complexes

Certain binary metal complexes such as the dicobalt face-to-face porphyrins, in which two cobalt centres are positioned so that a dioxygen bridge can be formed, catalyse the overall 4-e⁻ reduction of dioxygen in acid solution[70]. For maximum efficiency, the reduction should proceed as closely as possible to the thermodynamic potentials for the O_2/H_2O couple $(E = +1.23 V)$[54].

Dicobalt cofacial porphyrin Co₂(FTF4), in which a pair of four atom bridges link the porphyrin ring, (Figure 2) is the most impressive catalyst [55,56]. The electrochemically produced dicobalt(II,II) species is active and, as the pH increases, reduction shifts from a four electron process to a two electron process. Tests show that Co₂(FTF4) is not a catalyst for the reduction or the disproportionation of H_2O_2[56]. Monomeric Co porphyrin, *1*, also reduces dioxygen to H_2O_2 under the same conditions, a result which suggests that at high pH, Co₂(FTF4) catalyses the reduction of dioxygen by a pathway that does not involve the participation of more than one of the cobalt centres. However the adsorbed catalyst is not permanently altered by exposure to 1 M NaOH, because transferring the electrode to an acidic solution saturated with dioxygen catalyses the same 4-electron reduction of dioxygen as is obtained in the acidic solution with a freshly coated electrode. Co₂(FTF4) catalyses the 4e⁻ reduction at *ca.* 0.68 V *versus* NHE at pH < 3.5, with a turnover rate of *ca.* 400 dioxygen molecule S⁻¹ per catalyst site. This result may be compared with platinum, the most effective metal catalyst, which operates at 0.63 V *versus* NHE in acid, with a turnover rate of 0.3–5 dioxygen molecule S⁻¹ per platinum site[54].

Monochlorinated Co₂(FTF4) is a better catalyst than the nonfunctionalized parent molecule Co₂(FTF4) for the direct four-electron reduction of dioxygen. Electronegative substituents, *eg.* chlorine, shift the reduction potential of the cobalt(III) centres towards more positive values, thus enhancing the efficiency of these electrocatalysts[57].

The interaction of both catalyst metal centres with dioxygen influences the course of reaction. CoMn-, CoAl-, CoPd-, and CoH₂-(FTF4) are catalytically no more effective than the monomeric Co porphyrin[55,56], although the second metal can influence the potential, where the Co centre is reduced. The corresponding monomeric porphyrin complexes of the second metal show no activity in dioxygen reduction. However, CoAg(FTF4), dioxygen reduction proceeds by two parallel pathways, one leading to H_2O_2 and the other to H_2O. Electrodes coated with a monomeric Ag
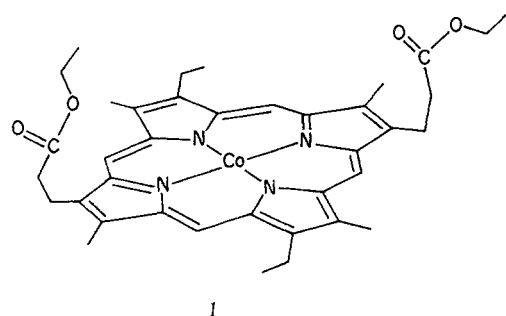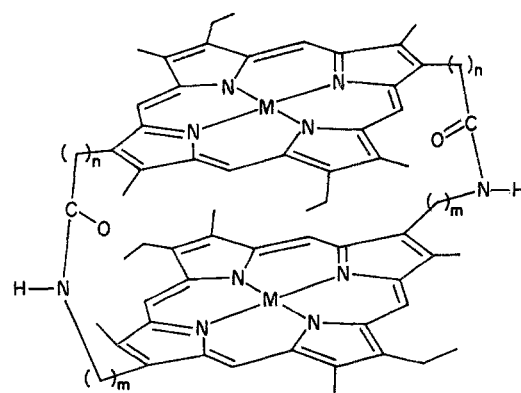

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Figure 2. Molecular structures and abbreviations for the metallo-binuclear porphyrins, structure *1* is monomeric cobalt porphyrin (Ref. 55).

M	M'	n	m	Abbreviation
Co	Co	2	2	Co₂(FTF6)
Co	Co	1	2	Co₂(FTF5)
Co	Co	1	1	Co₂(FTF4)
Co	Co	0	2	Co₂(FTF4*)
Co	Co	0	1	Co₂(FTF3)
Co	2H	1	1	CoH₂(FTF4)
Co	Fe	1	1	CoFe(FTF4)
Co	Mn	1	1	CoMn(FTF4)
Co	Ag	1	1	CoAg(FTF4)
Co	Al	1	1	CoAl(FTF4)
Ag	Ag	1	1	Ag₂(FTF4)

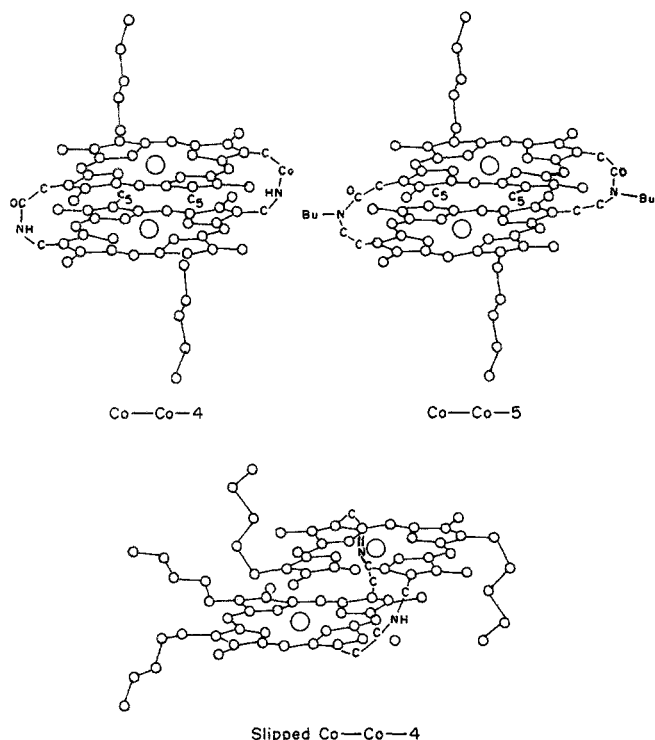Co—Co—4   Co—Co—5

Slipped Co—Co—4

Figure 3. Perspective drawings of the dicobalt diporphyrine Co-Co-4, Co-Co-5 and "slipped" Co-Co-4 (Ref. 59).

porphyrin or the disilver analogue, Ag₂(FTF4), showed no catalytic activity. Adsorption of a mixture of monomeric Co- and Ag-porphyrin produced an electrode with a response similar to that obtained from the Co monomer alone. The CoAg(FTF4) complex resembles Co₂(FTF5) in its ability to catalyse the dioxygen reduction[55]. CoAg(FTF4) is the only heterobimetallic derivative in which the two centres are reduced at about the same potential in the porphyrin dimer.

With Co₂(FTF6) reduction proceeds with the formation of a substantial quantity of H₂O₂[55,56]. Coated

Co₂(FTF3) catalyses the reduction of dioxygen to H₂O₂ but not to H₂O. Due to less structural symmetry, the Co₂(FTF4*) complex catalyses the two-electron reduction instead of four electron reduction, achieved by Co₂(FTF4).

A combination of steric and electronic constraints imposed simultaneously on the μ-peroxo group and the cobalt centres by the cofacial porphyrin ligand with four-atoms in its amide bridges seems to be of crucial importance to its unique catalytic action.

Dicobalt diporphyrins, Co-Co-4, and slipped Co-Co-4 each possess a pair of four-atom linkages, but the rings are noticeably displaced from a vertically stacked configuration in the slipped Co-Co-4 and Co-Co-5 (a pair of five atom linkages), Figure 3[59]. The most favourable oxygen reduction kinetics are obtained for Co-Co-4 and yield predominantly H₂O. For slipped Co-Co-4 and Co-Co-5 complexes the four electron pathway contributes to a lesser extent. Oxygen is bound in a *cis* configuration in Co-Co-4, and *trans* in the other two dimers. The exceptional catalytic activity of Co-Co-4, and, by inference of Co₂(FTF4), may involve a *cis*-μ-peroxo intermediate. Such a configuration would render the peroxo intermediate more accessible to solvent molecules, thereby facilitating the multiple proton transfer and concomitant cleavage of the dioxygen bond necessary to complete the four-electron pathway.

On both the dicobalt and monocobalt derivatives of anthracene-bridged dimeric porphyrin (Anthracene is bonded *meso* on both porphyrin rings as shown in Figure 4), direct four-e⁻ reduction occurs. Both derivatives also catalyse the reduction of H₂O₂, but at lower rates.

The cavities of molecules *(1)-(3)* (Figure 4) may be more accessible to dioxygen molecules, and the distance between the two cobalt centres might encompass a wider range of values than is true for more rigid doubly bridged cofacial porphyrins. The anthracene link connecting the two rings is likely to withstand acidic environments for
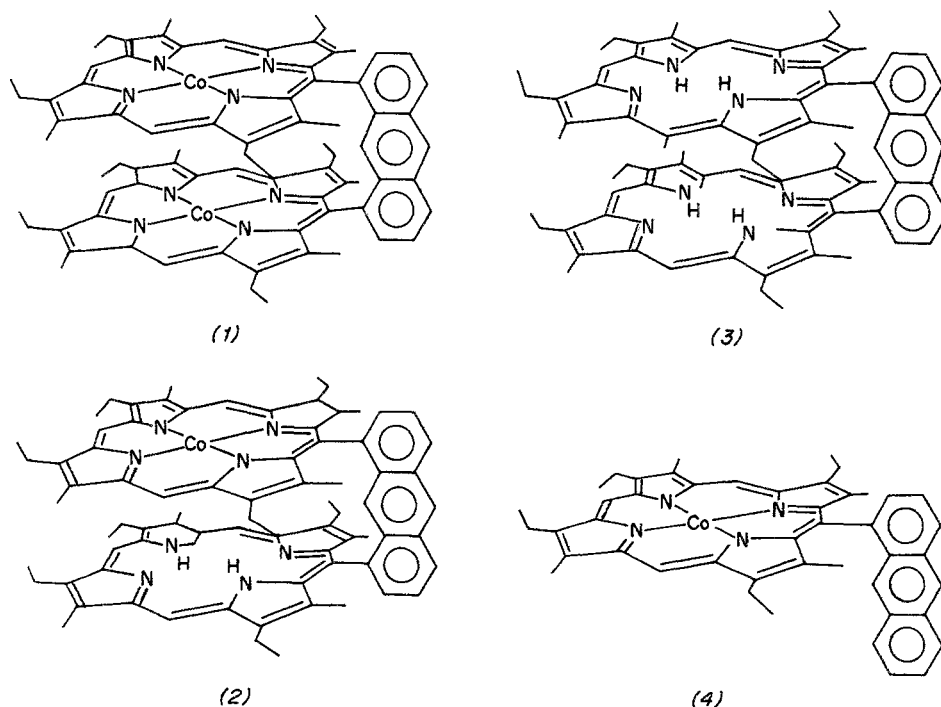

(1)   *(3)*

(2)   *(4)*

Figure 4. Structure of the anthracene bridged dimeric cobalt porphyrin and other related porphyrins[60].

longer than the amide linked dimers[60]. These molecules and their diphenylene-bridged analogues[61] represent the first effective macrocyclic metal complex electrocatalyst not depending upon the four atom separation demonstrated to be essential in the diamide-bridged catalysts described by Collman *et al.*[50].

Certain porphyrin based natural pigment derivatives such as hemes of bovine liver catalase, heminchloride and the enzyme laccase supported on a graphite electrode catalyse the reduction of oxygen[51,52,53].

Effect of electrode preparation on electrocatalysis

The complexes described above exhibit low electrical conductivity and for practical utilization in fuel cells, they must be deposited on a high electrical conductivity support[64]. The influence of the surface compound, its basic character, the method of catalyst deposition, the support specific surface area and the distribution of support pores, affect the electrochemical activity of the support-catalyst system. The higher the concentration of basic surface compounds the smaller the potential drop with time and the higher the electrocatalytic activity[66].

Oxygen reduction electrocatalysts have been attached to electrodes by different methods, such as irreversible adsorption[71], vacuum deposition[23], incorporation into a conducting polymer such as polypyrrole[72], impregnation of porous carbon[64], and solvent evaporation[83]. In acid solution, CoPc or FePc films prepared by evaporation of a solution on an electrode surface, as well as by irreversible adsorption (immersion of electrode in such a solution), showed significantly higher activity for oxygen reduction than those prepared by vapour deposition[73,74]. The activity of the former films does not depend on the solvent used since the same cathodic current has been observed when organic liquid or concentrated H_2SO_4 is used as solvent. Films prepared by vapour deposition are known to crystallize in the β-polymorphic form, whereas those precipitated from solution are in the α-form[75]. The latter has high electrical conductivity and hence is more active. For CoPc, in 1 M KOH, the three electrode systems cited above show about the same activity. Vacuum deposited films show relatively higher activity in alkaline than in acid solution.

The catalyst obtained by deposition of polyiron-phthalocyanine, (pFePc), is more active than that obtained by direct synthesis on carbon[19,66]. Iron polyphthalocyanine was prepared directly on a carbon support in order to create carbon-based electrodes, by three synthetic methods: melt, liquid-phase and gas-phase. The activity order of poly-FePc for oxygen reduction in KOH solution is melt > liquid-phase > gas-phase synthesis[76] and it is suggested that the highest activity of the poly-FePc made by melt method is due to the presence of a few monomer units within the polymer, without a central iron atom.

The catalytic effects of Fe phthalocyanine (FePc) and CoPc in two types (A and B) of practical air electrodes were examined. For type A electrodes, PTFE powder was heat-treated at 400° C. For type B electrodes, PTFE dispersions were used with treatment at 250° C. Both FePc and CoPc (modified electrode) showed high H_2O_2 decomposition rates which resulted in low oxygen electrode polarization at high current density. The type B electrode performed better than the type A possibly due to the presence of more pores in the former[77].

The electrochemical activity of Fe polyphthalocyanines (pFePc) prepared from an iron salt and pyromellitic dianhydride (PMDA), or tetracyanobenzene (TCB) and dicyanobenzene, or TCB, or dicyanonaphthalene, or octamethoxy phthalocyanine were examined for oxygen reduction reaction in 4 N H_2SO_4. The pFePc derived from PMDA has the highest activity[68].

The increase in the $FeCl_2$: pyromellitic dianhydride ratio for preparation of pFePc (iron-polyphthalocyanine) leads to an increase in electrochemical activity which is probably the result of different amounts of free polyphthalocyanine to iron polyphthalocyanine ratios in the catalyst[69].

The characteristics of air electrodes of acetylene black with applied CoPc polymer(pCoPc) are better than active carbon electrodes with applied pCoPc. Identical results were obtained with pFePc[19,67].

Changes in the ratio of catalyst to wet-proofed carbon black in the electrode active layer also lead to substantial changes in electrode characteristics. At optimum layer thickness, maximum current density is obtained. For polymeric CoPc/C and polymeric FePc/C electrodes the optimum active layer thickness is $30 \, mg/cm^2$.

The electrode coated with the CoPc-containing polystyrene exhibited higher catalytic activity than the glassy carbon electrode, during long continuous operation, and had a longer life than the electrode on which CoPc was directly attached by adsorption or by chemical modification[78].

Polypyrrole can be doped with anionic group-containing metallomacrocycles such as $CoTPPS_4$ [meso-tetrakis(4-sulphonatophenyl) porphyrinato cobalt] and FeTSP (tetrasulphonated iron phthalocyanine) by the anodic oxidation of pyrrole in solution with only $CoTPPS_4$ or FeTSP[79,80]. The advantages of this include ease of preparation, high conductivity and high porosity of the polypyrrole film, leading to rapid transport of both charge and solution substrate within the electrode structure[80,81]. For the GC/PP/FeTSP electrodes (GC = glassy carbon; PP = polypyrrole), significant catalytic activity for oxygen reduction occurs at less negative potentials compared to bare GC or GC/PP electrodes. As pH increases, reduction moves from the $2e^-$ to the $4e^-$ mechanism. Direct reduction of H_2O_2 is possible, but $H_{12}O_2$ destabilizes PP and results in loss of catalytic activity.

The PP background often hinders the collection of precise peak and limiting current data required for quantitative kinetic analysis. Incorporation of FeTSP into PP usually has no significant effect either on the mechanism or catalytic behaviour. However, the highly conductive and porous support enhances catalyst effectiveness by providing more surface area and a large percentage of active centres than are present in adsorbed films or catalysts in non-conducting polymers. At low pH, PP reduction begins at slightly negative potentials during the dioxygen reduction. The stability of PP/FeTSP catalysts increases at higher pH.

Only the outermost layers of the Fe porphyrin participate in the catalysis when multilayers are deposited on the electrode surface. The catalytic efficiency of such catalysts would be improved if more of the metalloporphyrin were made accessible on the electrode surface. Thus, copolymerization of 1-vinyl-2-pyrrolidone with *meso*-(triphenyl)mono(*p*-methacrylamidophenyl)-porphine followed by incorporation of iron(III) into the
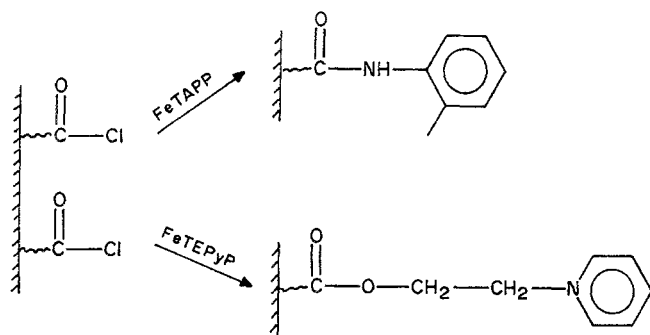
Figure 5. General scheme of chemically modified metalloporphyrin glassy electrodes through the amide formation or esterification of poly (methylacrylchloride) anchors.

porphine group of the copolymer produces an insoluble metallopolymer which when well wetted, swells in aqueous media, so that most of the iron porphyrin centres were accessible to dioxygen[85], 4-electron reduction results at sufficiently negative potentials. Loss of Fe-porphyrin catalytic activity in the copolymer when exposed to H_2O_2 did not differ significantly from that observed with coatings of monomeric Fe porphyrins.

FeTAPP[Fe^{III} tetra-(O-aminophenyl)porphyrin] and FeTEPyP[Fe^{III} tetra-(N-(2-hydroxyethyl)pyridyl)porphyrin] were attached to glassy carbon electrodes through amide formation or esterification of polymethylacryl chloride[86], Figure 5. The polymer-bound metal porphyrins are more stable due to the hydrophobic environment of polymer protected chemical bonds (such as esters and amides).

The current is enhanced and the overpotential is reduced by *ca.* 400 mv when dioxygen is reduced in the presence of FeTAPP-or FeTEPyP-modified electrode by 4-electron and 2-electron process respectively. The coverage of the bound FeTEPyP is much less than the FeTAPP on the carbon-polymer because the solubility of the FeTEPyP is limited in non-aqueous solvents, high solubility is necessary for carrying out the surface binding reactions. Direct 4-electron reduction for the FeTAPP modified electrode is possibly due to the high surface concentration of FeTAPP. For example, with FeTSP, metal porphyrin complexes and Hemin, as concentration of complex in electrolyte or at the electrode surface increases, the initial two-electron reduction process shifts to a four-electron reduction process[34, 29, 45]. Thus, a way to obtain higher coverage of the bound FeTEPyP has to be found to enhance its efficiency.

Stability

One problem encountered with FePc and CoPc concerns long-term instability. Deactivation of FePc films by repeated cycling is associated with oxidative attack on FePc by H_2O_2 produced as an intermediate[87–90]. PtPc is chemically more stable than FePc because it resists oxidation by strong oxidants, especially in alkaline media. Studies of the interactions of the phthalocyanines with carbon black substrates indicated that their catalytic properties are lost when free valencies of the central metal atom are saturated by phenolic surface groups of the carbon black[91]. The phthalocyanines are less stable in acid electrolytes. In acid electrolytes, at temperatures > 50° C the FePc stability is reduced due to disintegration[93].

FeTSP treated with 0.1 M H_2O_2 for *ca.* 30 min before addition to the electrolyte does not evoke the catalytic effect on the oxygen reduction wave. For metal tetraphenylporphyrin modified electrodes, the stability order is: CoTPP > FeTPP > MnTPP[10]. Adsorbed FeTMAP showed higher stability, especially in solutions at pH > 2, than adsorbed CoTPyP probably due to the lower H_2O_2 yield (5% with FeTMAP compared to > 90% with CoTPyP)[44]. Repetitive scanning of the electrode potential in the -0.2 V to -0.6 V range revealed a gradual decrease in catalytic activity.

Relaxation of the open circuit potential (OCV) of the electrode for more than one hour following a cyclic voltammetric sweep to the dioxygen reduction region showed that the OCV relaxes to its original value rather slowly[90, 92] and FePc is again active towards dioxygen reduction. However, the activity was less than that originally. Thus, although the deactivation appears to be primarily due to the adsorption of a peroxide intermediate, some activity is also permanently lost as a result of catalyst degradation, presumably through loss of metal centres or of complex from electrode surface. Recoating spent electrodes with catalyst restores activity although usually incompletely, full restoration requires mild polishing of the surface before recoating[56].

Effect of heat treatment

High temperature treatment of transition metal chelates on carbonaceous material in an inert atmosphere results in a significant increase in activity, stability and selectivity for electroreduction of dioxygen[94]. Heat-treated catalysts are very effective for peroxide elimination in alkaline solution.

Heat treatment in N_2 or Ar in the 700° C–800° C range enhances the activity and stability of CoPc/C[66]. The activity improvement upon an untreated CoPc catalyst is *ca.* 50 fold (twice that of FePc/C) at 700 mv. Although FePc/C is not activated, its stability increases. At 650° C the RuPc/C activity increases 20 fold at 800 mv reaching nearly the same level as heat treated CoPc/C; but RuPc/C stability does not improve. The activity and stability of ZnPc/C, MnPc/C and C itself is unaffected by heat treatment. Heating PtPc above 500° C generates Pt particles on the carbon surface, which are active in the electrochemical oxidation of hydrogen.

Investigation of *para*-substituted CoTPP (methyl and methoxy) shows that Hammett's equation holds for the untreated and heat treated catalysts, *i.e.* there is a linear relationship between the normalized current density and the substituent effect. Heat treatment results in a decrease in resistivity. With heat treated CoTPP, variation of the electronic states of the central metal ion, resulting from an extension of the π-electron system by polymerization is also responsible for enhanced electrocatalytic activity[95,96]. Heat treatment of CoTPP, CoTMPP and Co-tetrabenzoporphine in an inert gas at 800°–900° C improves catalytic stability and activity[97,100,101]. Higher temperatures (1100–1200° C) have a deleterious effect on electrode performance[98]. Carbon supported CoTMPP and Fe(TMPP)$_2$O (heat treated at 800° C) show similar activity and better stability than Pt-C cathode[102]. In acid solution, pyrolysed FeTMPP was more active than pyrolysed CoTMPP. Iliev *et al.* prepared electrodes from catalyst made by three methods: (i) carbon and metal-free tetramethoxyphenyl porphyrin

(H$_2$TMPP) pyrolysis product, (ii) carbon and the pyrolysis products of Co-acetate and H$_2$TMPP added separately to the carbon (regardless of the order of the addition to the carbon and heating) and (iii) carbon and the pyrolysis products of CoTMPP. In all media (acidic, alkaline and neutral) the activity of these three electrodes is found practically same[99].

The pyrolysis products (in He at 800°C for 30 min) of vanadyl porphyrin obtained from heavy, high-sulphur crude petroleum oil are useful electrocatalysts in alkaline media but are not active in acidic solution[49,104].

Begotskii et al.[97] investigated the catalyst made from pyrolysed CoTMPP and found that the pyrolysis products are metallic cobalt (β modification) and a carbon-containing residue from the decomposition of the porphyrin ring. These results were confirmed by the x-ray spectra[106]. On the other hand, no β-Co was detected in the pyrolysis of the CoTMPP deposited on a substrate. Elemental analysis shows the heat treated compound consists mainly of cobalt and carbon[95]. The metal free complex upon similar thermal treatment in a mineral free carbon support did not show catalytic activity beyond that of the carbon support, thus confirming the importance of the transition metal for high catalytic activity in the complex[107,108,109]. The role of transition metals in pyrolysis of the porphyrin system is in promoting the formation of an active new structure, by partial decomposition and consolidation, resulting in the formation of a secondary structure with a higher degree of condensation.

According to Scherson et al.[110] microanalysis confirms that in (FeTMPP)$_2$O and CoTMPP some nitrogen is retained after heat treatment at 400–500°C. Vender et al.[111] also reported that the central metal ion-N$_4$ unit remains the active site after pyrolysis. Van Veen et al.[112] noted that heat treatment helps to bond the FeTMPP to the carbon surface and that the iron is still in an Fe—N$_4$ centre. Begotsskii et al.[97], Wesener and Fuhrmann[113] and Kaisheva et al.[100] reported that after heat treatment at 800–900°C the macrocyclic structure is completely destroyed, but these authors do not share the view that the transition metal is important to electrocatalysis. However, the carbon used for their studies contained substantial amounts of iron. Further studies are needed in order to enhance our understanding of the role of central metal ion on the activity of heat treated catalysts.

Photoelectrochemical reduction of oxygen

The dark and photostimulated reactions involving reduction of oxygen and the oxidation of H$_2$O$_2$ on Pt electrodes coated by porous film of metal free phthalocyanine, CuPc, MgPc and chlorinated AlPc complexes have been investigated quantitatively[103,105] by the rotating disc electrode and pulsed oscillographic method.

Visible light assisted electrochemical reduction of oxygen with no applied potential was performed on a Pt electrode coated with surface active cobalt(II) and manganese(II) tetrakis (N-stearylpyridinium porphyrin) tetraiodide monohydrate complexes[58]. The photocurrent was found to depend on the solution pH and dissolved oxygen concentration. CoTPP deposited on P-type GaP acts as catalyst for photoelectrochemical

reduction of oxygen[82] and the order of photoelectrochemical activity of some cobalt phthalocyanines is: CoPcCl$_4$ > CoPc > CoPc(NH$_2$)$_4$ Photoelectrochemical activity correlates with the electron-acceptor capacity of the phthalocyanine[12].

Conclusions

A comprehensive literature review thus leads to the following conclusions:

1. The central metal atom plays a dominant role in the oxygen reduction mechanism. For example, the monomeric cobalt complexes of phthalocyanine/porphyrin promote oxygen reduction by a two-electron pathway to give H$_2$O$_2$ whereas oxygen is reduced by a four-electron pathway with iron complexes.
2. H$_2$O$_2$ is further reduced to water on some of these complexes.
3. The nature of ligand is important and electron delocalization affects the mechanism. Electron donating substituents seem to enhance the activity. Steric factors can also influence the activity affecting both adsorption of the complex on the support surface and adsorption of dioxygen onto the electrocatalyst. Thus although Co-complexes usually lead to a two electron reduction, on certain dimeric cofacial cobalt porphyrins, 4e$^-$ reduction can be achieved. The ligand structure also contributes to enhanced electrical conductivity, especially when polymerized.
4. The performance of the catalyst ultimately depends on the electrochemical system as a whole. The physical nature of the catalyst, e.g., its crystal structure, porosity etc. have an influence in its ultimate performance and hence the mode of deposition of catalyst on the substrate influences the ultimate performance.
5. In practice, the catalyst has to be evaluated in the total electrochemical system. The environment, nature of substrate in terms of its electrical conductivity, porosity, wettability, etc. and the physical nature of interaction of the catalyst with substrate including the catalyst concentration, distribution and exposure to the environment, determine the overall performance. Electrode activity depends on the number of active sites which is not solely determined by the catalyst concentration. The pH of the environment affects both the reduction mechanism and catalyst stability. A higher acidic medium tends to remove the metal from complex.

The efficiency of oxygen reduction depends upon the adsorption rate and reduction rate of oxygen as well as the removal of end products from the catalyst surface. The problem of finding a cheaper, efficient and durable macrocyclic catalyst, preferably with non-noble metals still eludes solution. However, the volume of research reports published in the last decade are indicative of the optimism shared by various research groups in tackling this problem. As shown in this review, new directions, are being explored.

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