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REVIEW

Metal Phthalocyanines as Electrocatalysts for Redox Reactions

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1 INTRODUCTION

Owing to their dual donor π-acceptor function, metal phthalocyanines have been found to exhibit electrocatalytic activity for various technologically important redox reactions, such as the electroreduction of oxygen, carbon dioxide (CO_2), thionyl chloride (SO_2Cl_2) and the chlorate ion, and the electro-oxidation of hydrazine and glucose.[1–15] In the literature,[1–3] electrocatalytic properties of various metal phthalocyanines towards oxygen reduction have been reviewed by several authors. However, little is known about the electrocatalytic activity of metal phthalocyanines towards other redox reactions. We therefore have attempted to review the electrocatalytic properties of various metal phthalocyanines for redox reactions other than oxygen reduction. Most of these reactions are important for use in organic synthesis, removal of waste from water, and detection of low concentrations of compounds. This Review indicates probable directions for uses of these complexes as electrocatalysts for technologically important redox processes.

2 METAL PHTHALOCYANINES AS ELECTROCATALYSTS

Metal phthalocyanines (MPcs), which typically have the structure shown in Fig. 1, have been documented as catalysing various electrochemical reactions. The electrocatalytic activities of metal phthalocyanines towards certain technologically important reactions are summarized below.

2.1 Electroreduction of CO_2 and related compounds

Currently there is substantial interest in the electrocatalytic reduction of CO_2 for fuel generation, synthesis of organic chemicals and solar energy conversion.[16–20] A direct electrochemical reduction of CO_2 at carbon and some metal electrodes, including palladium, lead, mercury, indium and tin metals, proceeds at large overpotentials (above −2 V vs SCE) yielding formic acid in aqueous solution, along with oxalates and carbon monoxide (CO) in aprotic solvents.[21,22] Use of metal phthalocyanines results in reduction of CO_2 at a lesser negative potential with a

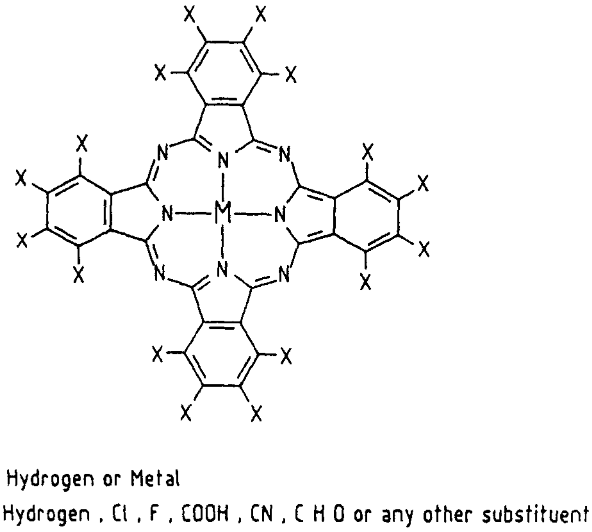

Figure 1 Monomeric phthalocyanine (MPc) systems.

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concomitant increase in the current densities, which are about ten times higher in relation to massive metal electrodes.[23–32] The magnitude of current increases with increasing concentrations of CO_2 and the catalyst, but the rate of increase becomes insignificant after the concentration ratio of CO_2 to catalyst attains a specific value.

Current efficiencies and distribution of the electrolysis products depend on the applied potential and pH of the electrolyte, the substrate type and the nature of the central metal coordinated to the phthalocyanine.[17, 33] As shown in Table 1, CoPc, NiPc, FePc and PdPc give CO as the main electrolysis product;[23, 34, 35] SnPc, PbPc, InPc, ZnPc and AlPc give formic acid as the main product;[35] ZnPc gives a sufficient amount of CO also; CuPc, GaPc and TiPc give methane (CH_4) as the main product. Except for the last three MPcs, the other MPcs give negligible amounts of CH_4. VPc, MnPc, MgPc, PtPc and H_2Pc show poor activity and give hydrogen (H_2) as the main product. ZnPc and AlPc have the lowest activity. Most of the MPcs give some amounts of other reduction products such as formates, glycolates and oxalates.

When quaternary ammonium salts such as NEt_4ClO_4, NEt_4Cl and NBu_4ClO_4 are used as supporting electrolytes, oxalate and glycolate are produced at carbon electrodes impregnated with either Co(II)Pc or NiPc; the presence of formic acid has not been detected in the catholyte. MnPc and PdPc are inactive, while CuPc and FePc exhibit only slight activity.[36]

Kapusta and Hackerman[37] have reported the formation of formate ion in a nearly neutral solution, and of formic acid and methanol in acidic solution on carbon cathodes containing NiPc/CoPc. Formation of formic acid in acidic solutions can be explained by supposing that during long-term operations, dehydration of the $CoPc(CO_2^-)H^+$ species initially formed may produce CO and H_2O.[38] In neutral and mildly acidic electrolytes (pH 5–7) the phthalocyanines become inactive on imposing cathodic potentials, probably due to irreversible reduction of the catalyst.[37]

In acidic media, CO and H_2 are the major products produced during the electroreduction of CO_2 at Co(II)Pc-impregnated gas-diffusion electrodes immersed in aqueous electrolytes, with trace amounts of oxalate and formate.[39–41] The relative amounts of CO and H_2 depend on the cathode potentials, with considerably higher amounts of hydrogen produced as the cathode potential is increased from − 1.5 V to − 2.2 V.[41] In acidic media, formic acid is produced at low rates on electrodes impregnated with MnPc, CuPc or ZnPc. It is reported that during the electroreduction of CO_2 at Co(II)Pc, the metal ion is the active centre which is reduced to cobalt(I), whereas for all other complexes the phthalocyanine ring is reduced to its radical anion.[29, 37, 39, 40]

The overall effectiveness of metal phthalocyanines for catalysing CO_2 electroreduction decreases in the following order:

Table 1 Electrocatalysis of CO_2 reduction at 23 °C on MPcs in $KHCO_3$ at a pH of approx. 7.6

MPc	Main product	Current efficiency (%)	Potential range (vs SCE)
CoPc, NiPc	CO	100	− 1 to − 1.75
NiPc	$CO+H_2+CH_4$	70	− 1.75 to − 2.15
SnPc, PbPc, InPc	$HCOOH+H_2$	—	—
SnPc	HCOOH	70	− 1.6
InPc	H_2	25 for HCOOH	− 2.0
		10 for CO	− 2.0
PbPc	HCOOH	65	− 1.6
	H_2	30	− 1.6
	CO	5	− 1.6
CuPc, GaPc, TiPc	CH_4	30	− 1.6
FePc, PdPc	H_2+CO	50	− 1.2
		80	− 1.5
ZnPc	H_2+CO	15 for CO	− 1.9
AlPc	$H_2+HCOOH$	15 for HCOOH	− 1.8
H_2Pc, MgPc, VPc, MnPc, PtPc	H_2	100	—

$$\begin{gathered}\mathrm{Co}^{2+} > \mathrm{Ni}\text{-}\\ {}^{2+} \geqslant \mathrm{Fe}^{2+} \simeq \mathrm{Mg}^{2+} \simeq \mathrm{Mn}^{2+} \simeq \mathrm{Zn}^{2+} \simeq\\ \mathrm{Cu}^{2+} > \mathrm{Cr}^{3+}, \mathrm{Sn}^{2+}\end{gathered}$$

and is quite different from that observed for the oxygen reduction reaction.[17, 36, 37] CoPc, the most active phthalocyanine for CO_2 reduction, exhibits an overpotential approx. 200 mV lower than the best metal cathodes at load currents up to 10 mA cm^{-2}. Taube[42] suggested that active CoPc and NiPc have occupied d_z^2-orbitals with an excess of ligand π-electrons, whereas MnPc and FePc do not have an occupied d_z^2-orbital or an excess of π-electrons, thereby suggesting that the occupied d_z^2-orbital of the metal atom of the phthalocyanine plays a central role in the electrocatalysis of CO_2 reduction; the ligand π-electrons may enhance the activity of the axial d_z^2-orbitals.

CoPc dissolved in homogeneous solution exhibits poor stability and lower activity than CoPc adsorbed on carbon electrodes.[39, 43, 44] The electrochemical behaviour of CoPc is critically dependent on the solvent used in the solution from which it is deposited onto the electrode.[38]

The phthalocyanines deposited on platinum and gold do not show any catalytic activity towards CO_2 reduction, suggesting that the bonding between the substrate and the catalyst also determines the electrode activity.[37] The chemical state of the CoPc thin films prepared by different vacuum deposition techniques on glassy carbon plays an important role in the electrocatalysis. In comparison with conventional vacuum deposition techniques, the metal phthalocyanine thin films prepared on a glassy carbon employing the intermittent plasma-assisted vacuum deposition technique have been found to enhance the activity and stability of phthalocyanine for CO_2 reduction in aqueous solutions.[17]

The catalytic activity of the tetrasulphonated metal phthalocyanines (MTSP) homogeneously dissolved in Clark–Lubs buffer solution, towards CO_2 electroreduction, has also been investigated. Among these, CoTSP and NiTSP are active electrocatalysts, while CuTSP and FeTSp are not. Interestingly, MTSPs exhibit more activity compared with MPcs.[32]

Nagakazu *et al.*[35] have reported that when CO is supplied to a fuel-cell gas-diffusion cathode containing NiPc, CoPc or SnPc, gaseous H_2 is formed in all cases except for NiPc, where traces of CH_4 are produced. Co(II)Pc and Co(II) - 4,4′,4″,4‴ - tetracarboxyphthalocyanine [Co(II)TcPc] gave metastable reduction products **R-1** and **R-2**, respectively, at around −0.7 V vs SCE. Reduction of CO, formaldehyde and formic acid by **R-1** or **R-2** have been conducted with vibrating carbon-fibre electrodes (cfe) modified with Co(II)Pc or Co(II)TcPc. The products during the reduction of CO are mainly formaldehyde and a small amount of methanol. Reduction products of formaldehyde could not be identified because of their low concentration. Reduction of formic acid by **R-1** and **R-2** seems to be difficult under these conditions. In the reduction of CO, **R-2**/cfe is approx. 17 times more efficient than **R-1**/cfe, which in turn is about 10 times more efficient than the former for reducing formaldehyde.[45] Reduction of CO on Co(II) TcPc/cfe has been attempted at lesser negative potentials (−0.5, −0.3 and −0.1 V vs SCE). No formaldehyde could be identified, suggesting that reduction occurs only on a reduced form of Co(II)TcPc/cfe. **R-1** and **R-2** reduce dimethyl sulphoxide (DMSO) to dimethyl sulphide. CoTSP also reduces DMSO to dimethyl sulphide.

2.2 Electroreduction of nitrogen to ammonia

N_2 can be reduced to NH_3 at ambient pressures and temperatures using a gas-diffusion electrode modified by FePc.[46] Current efficiency and stability of the electrocatalytic effect depend on the nature of the central metal ion in the MPc. KOH and $KHCO_3$ are better electrolytes in terms of current efficiency and stability of the gas-diffusion electrodes than the corresponding sodium analogues.[47] The best condition for electrolysis was −0.4 V/RHE under potentiostatic control.[33, 48] SnPc is the best electrocatalyst.[49] For H_2Pc and TiPc initial current efficiency was reported to be 0.6% and 0.24%, respectively. H_2Pc was more stable than TiPc. Current efficiency decreases in the following order:

$$\mathrm{FePc} > \mathrm{PdPc} > \mathrm{CoPc} > \mathrm{PtPc} > \mathrm{NiPc}$$

and

$$\begin{gathered}\mathrm{SnPc} > \mathrm{FePc} > \mathrm{PdPc} > \mathrm{InPc} > \mathrm{PbPc} > \mathrm{CuPc} > \mathrm{ZnPc}\\ > \mathrm{GaPc}\end{gathered}$$

Among the latter, CuPc has maximum stability.

2.3 Electroreduction of nitrogen oxides

The electrochemical reduction of nitrate in strongly alkaline solutions using nickel, lead, zinc or iron cathodes gives NH_3 with intermediate formation of nitrite ion. Uncoated iron cathodes show significant weight losses, while modifying the iron cathode with phthalocyanine film stabilizes it. Coating a porous nickel electrode with phthalocyanine renders it less active towards nitrate reduction, but the iron electrode appears to be activated.[50, 51] Electrolysis between zinc or lead cathodes and a nickel anode is an efficient means of removing nitrate from alkaline solution. CoPc is reported to electroreduce nitric oxide (NO) to NH_3 at -0.6 V vs SCE.[52] In acidic solution (pH=3) CoTSP also catalyses electroreduction of NO.[53]

2.4 Electroreduction of cystine

Phthalocyanines (Pcs) and tetrasulphonated phthalocyanines (TSPs) of manganese, iron, cobalt, nickel and copper catalyse electroreduction of cystine (RSSR) to cysteine (RSH). Among various MPcs, FePc is the most active material for cystine reduction.[54] The activity of metal-tetrasulphonated phthalocyanines varies as follows:

$$\mathrm{Mn > Fe > Co > Cu > Ni > graphite}$$

For both substituted and unsubstituted metal phthalocyanines, the electrocatalytic activity is dependent on the nature of the central metal ion.[55] As shown in Fig. 2, the activity varies almost linearly with the number of *d*-electrons in the metal.[56]

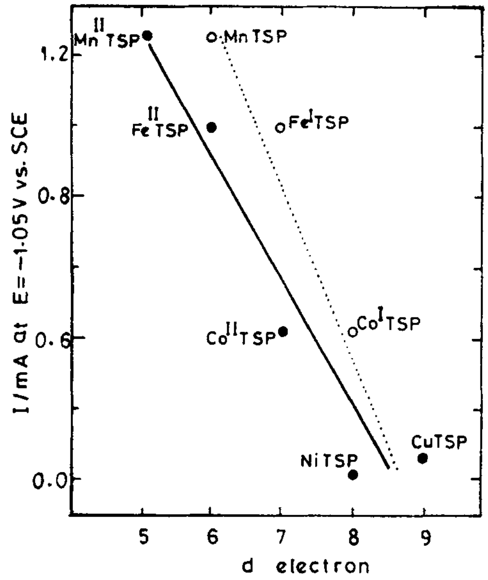

Figure 2 Plot of the activity of different phthalocyanines for the electroreduction of cystine (Ref. 56).

2.5 Electroreduction of thionyl chloride and sulphonyl chloride

The lithium–thionyl chloride battery is well developed for high power-density application.[57, 58] The cell reaction is given by Eqn [1].

$$2SOCl_2+4Li \rightarrow S+SO_2+4LiCl \qquad [1]$$

Doddapaneni[59–61] proposed that in the absence of MPc, the first step is the one-electron reduction of $SOCl_2$ to the SOCl radical. This dimerizes and then decomposes to several intermediate species, some of which are hazardous. The SOCl radical adsorbed on the MPc can undergo a further one-electron reduction leading to safe battery operation.[62–64] A two-electron catalytic cycle is indicated for the reduction of thionyl chloride in a $Li/SOCl_2/(CoTnPc,C)$ battery (where Tn=tetraneopentoxy).

The transition-metal N_4-chelates such as CoPc, FePc, NiPc and CuPc and polymeric CoPc (pCoPc) and pFePc have been employed by either dissolving them in the electrolyte or adsorbing them on the cathode in lithium–$SOCl_2$ batteries to increase the battery lifetime and discharge rates.[59, 60, 65–78] FePc shows the highest activity. The presence of MPc increases cell power output and output voltage as well as extractable energy content at moderate current densities. In comparison with the electrodes of acetylene black containing 20% Cu, the observed improvement in performance with FePc lies in the increase of the discharge duration.[79] Open-circuit potential and quasi-exchange currrent density increase upon the addition of MPc, without a significant change in the transfer coefficients.[65, 80–83] The presence of FePc increases the open-circuit potential by 100 mV and the cell operating voltage by *ca* 200 mV in comparison with the cell without FePc.[80] Thus, FePc effects more than just a change in the free energy of the reaction. The most likely cause of the difference in the cell operating voltage is the reduction in Cl^- concentration at the electrode surface as opposed to that in a cell without FePc. The slope of the voltage–time curve is less than that for the reference cell and the cell lifetime is increased through a modification of the LiCl precipitation process, depending on the discharge temperature and current load.[61,66,81] The effect of FePc on cell lifetime diminishes as the discharge current increases and becomes insignificant at current densities above 100 mA cm^{-2}.[84] Other metal phthalocyanines yield qualitatively the same results. Use of phthalocyanine improves low-temperature performance characteristics. In comparison with FePc, pFePc gives longer cell lifetimes at high temperature.[85] Phthalocyanines improve rates of reaction and the specific cathode capacity.[59] They decrease the overpotential[59] and increase the efficiency of the Li/$SOCl_2$ cell.[75] Octathiahydrophthalocyanine derivatives, $[M(Pc)X]_n$ (where M=Ga, Ge, Si and X=O, S) and $[Fe(Pc)F]_n$ catalyse electroreduction of $SOCl_2$.[86] The activity of MoPc is equal to that of FePc in $SOCl_2$ reduction.[87,88] Tetracarboxylated CoPc prevents anode passivation and premature battery failure.[89]

Cathodes for Li/$SOCl_2$ batteries were fabricated by sintering Shawinigan acetylene black doped with CoPc, NiPc or CuPc, at 600–800 °C. The discharge capacity and voltage of cathodes containing the electrocatalysts increased and was found to depend on sintering temperature.[90] The catalyst species is formed during sintering of a carbon black/MPc mixture at approx. 600 °C. Sintering at 800 °C causes decomposition of the MPc macrocycle and the metal binds to carbon, forming a catalyst that promotes voltage but with only minor enhancement of cell capacity.[91] Heat treatment of pCoPc for 2 h at 550 °C increases the operating voltage of the cell.[73] Moderate catalytic activity was observed for cathodes containing VOPc and MnPc while non-transition metal phthalocyanines, such as SnPc, $SiPcCl_2$, LiPc, ZnPc and MgPc, were found to be inactive.[90] Catalytic activity for $SOCl_2$ reduction depends on the types of central metal ion and macrocycle ring and on the presence of substituents on the macrocyclic ring. Substitution of electron-withdrawing groups such as —SO_3H and —COOH on the aromatic ring decreases the activity of metal macrocyclic complexes, but increases the stability in the $SOCl_2$ environment. Electrocatalytic activity of some phthalocyanines towards the reduction of thionyl chloride is:[92–95]

$$\beta\text{-}H_2Pc > \beta\text{-CuPc} > \text{pCuPc} > \text{octacyanoCuPc}$$

The electron-donating ability of the central *d*-metal ion and the ligand stability of the complex play an important role in the electrocatalysis of $SOCl_2$ reduction. For optimum activity, *d*-levels of the central ion must be filled but sufficiently spaced from the highest occupied molecular orbital (HOMO) level to prevent oxidation of the ligand which would cause breaking of the Pc ring.

High-rate and high-capacity Li/SO_2Cl_2 cells are achieved when cathodes are coated with CoPc. CoPc catalyses the electrochemical reduction of SO_2Cl_2, probably via the formation of $SOCl_2$.[96] Use of FePc, CoPc and pCoPc gives batteries with higher voltage.[97] Li/tetrachloroethane (Li/TCE) has a similar discharge life to Li/$SOCl_2$ batteries. Metal phthalocyanines are reported to improve efficiency of Li/TCE cells.[98]

2.6 Electrocatalytic reduction of chlorate ion

Electrodes of carbon coated/impregnated with transition metal complexes of phthalocyanines markedly accelerate the cathodic reduction of chlorate ion (Eqn [2])

$$ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O \qquad [2]$$

and permit relatively high current densities. The overvoltage of cathodic reduction of ClO_3^- is considerably decreased when transition-metal N_4-complexes are used as electrocatalysts.[99] The reaction is employed for the electrochemical determination of ClO_3^- and in electrochemical neutralization of ClO_3^--containing waste solutions.

2.7 Electrochemical reduction of sulfur dioxide

In high power-density Li/SO_x batteries, use of FePc as an electrocatalyst for cathodic reduction of SO_2 increases the discharge voltage.[100] The battery employs a solution of $LiClO_4$ in propylene carbonate as electrolyte. FePc is found to be the best electrocatalyst. CoPc deposited on carbon black was pyrolysed (*ca* 900 °C) in an inert atmosphere and used as the cathode of an Li/SO_2 battery. The increase in the discharge characteristics of CoPc after heat treatment is related, apparently, to the change in the nature of the bonding of the complex with the surface of the carbon carrier, and more precisely to the weakening of the N-bond (of the Pc) with the carbon of the substrate.[101]

2.8 Electro-oxidation of SO_2

The process of SO_2 electro-oxidation on a pyrographite electrode proceeds with a considerable overvoltage. With increasing acidity of the solution, the reaction rate decreases, particularly at H_2SO_4 concentrations between 0.5 and 5 M. Metallophthalocyanines catalyse the anodic oxidation of SO_2. CoPc is reported to exhibit four- to five-fold higher reaction rates than on pyrographite alone.[102–106] The activities of MPcs towards electro-oxidation of SO_2 vary as

$$\text{FePc,MnPc} > \text{CoPc} > \text{VOPc} > \text{MoOPc-} \gg \text{CuPc,CrPc,Ti(OH)}_2\text{Pc,H}_2\text{Pc,Cypr (pyrographite)}$$

An increase in the film thickness of MPcs from 500 to 10 000 Å is accompanied by a concomitant decrease in activity and can be attributed to the increase in ohmic resistance.

Polymeric MPcs are found to be more active than the monomers. The polymer in which the monomer units are joined through benzene rings is significantly more active than the complex joined through SO_2 bridges, which evidently disrupt the conjugation in the molecule.[107, 108]

Iron, manganese and cobalt-substituted phthalocyanines are also the most active electrocatalysts for cathodic reduction of molecular O_2. Thus, in electrocatalytic reactions, these metal phthalocyanines may take part as electron donors and also as electron acceptors. The influence of the chemical structure of the complex on the rate of electro-oxidation of SO_2 is similar to that observed in the case of the electroreduction of O_2 on metal–N_4-complexes. SO_2 has a high electron affinity and is a better acceptor than O_2. However, SO_2 acts as an electron donor in the presence of MPc. Such a dual donor–acceptor function of MPc is due to the buffer nature of the conjugated π-electrons.[109]

The degree of purity of the phthalocyanines has an appreciable influence on the rate of the electrocatalytic process. Additional purification of FePc and CoPc by repeated sublimation increases the activity. The lower activity of the original phthalocyanines in comparison with the purified materials may be due to the presence of impurities as well as free radicals formed of bonds in the course of their synthesis under severe conditions.[108]

2.9 Electro-oxidation of hydrazine

Hydrazine (N_2H_4) is a highly reactive molecule and has been used as fuel in fuel cells. N_2H_4 possesses two free electron pairs located on the nitrogen atoms having sp^3-hybridization. This accounts for both the basic and nucleophilic characters of molecule. Metal phthalocyanines and their tetrasulphonated analogues efficiently catalyse the electro-oxidation of hydrazine when the complexes are attached or adsorbed on the surface of graphite electrodes: the activity order with respect to the metal is:[54, 110–118]

$$\text{Fe} > \text{Co} > \text{Cu} \simeq \text{Ni} > \text{graphite}$$

Tafel slopes of 40 mV/decade for FeTSP and FePc, 60 mV/decade for CoPc and CoTSP, 90 mV/decade for VOPc, and *ca* 130 mV/decade for NiTSP, CuTSP, NiPc, VOTSP, ZnTSP, CuPc and the bare graphite were observed.[120] MnPc and MnTSP show two linear regions with slopes of 40 and 60 mV/decade. The catalytic process occurs at potentials close to the M(I)/M(II) redox couple in the phthalocyanine, illustrating the importance of the redox properties of the catalyst in determining its activity.[55, 119] The electrocatalytic activity of the phthalocyanines varies as:[110, 111, 121, 122]

$$\text{MnPc} > \text{MnTSP} > \text{CrTSP} > \text{NiTSP} > \text{VOPc} > \text{NiPc} \simeq \text{CuPc} \simeq \text{VOTSP} \simeq \text{ZnTSP} > \text{graphite}$$

MPcs substantially decrease the overpotential for the electro-oxidation of hydrazine in relation to the ordinary pyrolytic graphite (OPG) substrate by *ca* 0.7 V. N_2 is the main product of the reaction obtained via the four-electron path.

The N_2H_4 electro-oxidation process on CuTSP, CuPc, NiPc and graphite is independent of the N_2H_4 concentration. The order of the reaction for electro-oxidation of N_2H_4 is 0.5 for ZnTSP and 1 for CrTSP, MnPc, MnTSP, VOPc and VOTSP. Tafel slopes show that when a mixture of FeTSP and CoTSP are co-adsorbed on graphite electrodes, they act independently to catalyse electro-oxidation of hydrazine.[123]

Volcano-shaped curves in Figs 3 and 4 can be explained in terms of a variation in the ability of the MPc to bind N_2H_4, which relates to the electronic structure of the metal. Taube[124] suggests that the energy of the a_{1g} (dz^2) HOMO in different metal phthalocyanines decreases almost linearly from MnPc to NiPc. This is correlated with the ability of the metal to form adducts with electron donors such as N_2H_4. MnPc, FePc and CoPc show the highest activity because they

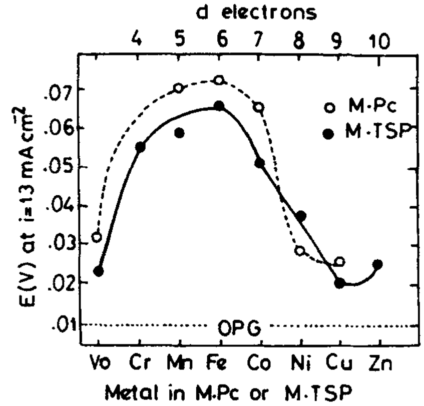

Figure 3 Electrocatalytic activity of phthalocyanines for the electro-oxidation of hydrazine in 0.5 M N_2OH+0.05 M $N_2H_4 \cdot H_2SO_4$.

have an empty or half-filled a_{1g} orbital, which has the proper symmetry for the interaction. The energy of the empty a_{1g} orbital for chromium is probably too high for a favourable interaction and the activity of CrTSP is slightly less as opposed to MnTSP. The electron drain from N_2H_4 upon interaction is not favoured with nickel and copper derivatives since the a_{1g} orbital for these two metals is completely filled. The marginal increase in activity observed for ZnTSP can be explained, as adduct formation with N_2H_4 is possible since zinc is able to change from a planar to a five-coordinated pyramidal configuration.

Chemically modified electrodes containing 3,3′,3″,3‴-tetranitrophthalocyanine coordination compounds of Fe(II), Co(II), Ni(II) and Cu(II) (MLCMEs) were prepared by using the irreversible adsorption method. FeLCME and CoLCME show very strong electrocatalytic activity towards oxidation of N_2H_4 and the stabilities of their electrocatalytic effects are very high. NiLCME has lower electrocatalytic effects for the oxidation of N_2H_4. CuLCME also has an electrocatalytic effect on the oxidation of N_2H_4, but the stability of the electrocatalytic effect is low. There is a linear relationship between the peak currents of the electrocatalytic oxidation of N_2H_4 and its concentration for FeLCME and CoLCME.[125] The detection and quantification of N_2H_4 is facilitated by the use of CoPc-containing chemically modified electrodes as sensors in the LCEC (electrochemical detection in liquid chromatography) determination of N_2H_4.[126]

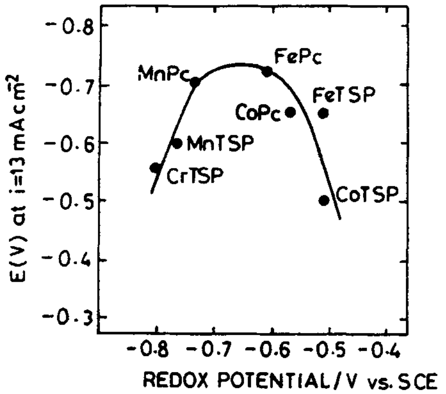

Figure 4 Effect of redox potential of the metal phthalocyanines on the catalytic activity for N_2H_4 electro-oxidation (Ref. 172).

2.10 Electro-oxidation of glucose

The glucose electro-oxidation reaction can be used in devising sensors to determine blood-sugar concentration and in fuel cells to power artificial hearts. In neutral solution, phthalocyanines of cobalt, manganese and iron oxidize glucose with marked current densities, which decrease in the order: Co>Mn>Fe. However, their values at these electrodes are very poorly reproducible and depend strongly on the electrode pretreatment conditions.[127, 128] Glassy carbon electrodes modified with pCuPc are also reported to exhibit activity towards glucose electro-oxidation.[129]

2.11 Electro-oxidation of hydroxylamine

Phthalocyanines of manganese, iron, cobalt, nickel and copper catalyse electro-oxidation of hydroxylamine (NH_2OH). A volcano-shaped curve is obtained when the activity is plotted versus the number of *d*-electrons in the metal. NiPc and NiTSP show the highest activity for electro-oxidation of NH_2OH.[54] Electrocatalytic activity depends on the redox potential and the electronic structure of the transition metal in the macrocycle.[55]

Chemically modified electrodes containing a polymeric coating of CoPc (CoPc-CMEs) catalyse the electro-oxidation of NH_2OH and its *N*-mono-, *N*,*N*-di-, and *O*-substituted derivatives. All of these compounds were oxidized at unmodified glassy carbon electrodes only at potentials greater than 1 V vs Ag/AgCl, but gave substantial anodic currents between 0.25 and 0.55 V at the CoPc surface. The number of electrons transferred for the oxidation was found to vary between 1.2 and 1.6, depending on the particular hydroxylamine compound and the specific conditions of the electrolysis, and the reaction products included oximes, azoxy compounds and dimeric species. These observations were consistent with an electrocatalytic mechanism involving oxidation of the hydroxylamine by electrogenerated Co(III)Pc and subsequent reaction of the initially formed oxidation products by several pathways. When a CoPc-CME was used as the sensor in amperometric detection following liquid chromatography, the detection limit obtained at 0.55 V ranged from 0.4 pmol for hydroxylamine and up to 40 pmol for *N*,*O*-dimethylhydroxylamine. By maintaining the applied potential at 0.2 V, the detection could be made selective only for hydroxylamine and *N*-monosubstituted hydroxylamine compounds.[130]

FeTSP adsorbed on ordinary pyrolytic graphite electrodes catalyses the electro-oxidation of hydroxylamine to N_2O. The Tafel slope of the reaction for a graphite substrate is 120 mV, whereas for FeTSP adsorbed on graphite it is 85 mV. For values of log $[NH_2OH]$ greater than -1.4 the currents become more-or-less independent of $[NH_2OH]$, with a slight decrease in activity for higher concentrations of NH_2OH.[131] This indicates that the active sites on the electrode surface become gradually covered with NH_2OH molecules and/or intermediates. The activity of FeTSP for this reaction is not as pronounced as those observed with oxygen reduction.[132] and hydrazine electro-oxidation.[111] This is probably due to the formation of stable adsorbed species on the iron sites, which inhibit the reaction.

2.12 Electro-oxidation of organic acids

Oxalic acid, ascorbic acid and *α*-keto acids can be determined in blood, plasma or urine by reversed-phase HPLC with electrochemical detection (LCEC) using a CoPc-modified electrode.[133–135] This method is sensitive, simple and accurate. CoPc electrocatalyses oxidation of oxalic acid, several *α*-keto acids (pyruvic, phenylpyruvic, *α*-ketobutyric, *α*-ketoglutaric and *α*-ketoisocaproic) and ascorbic acid. CoPc does not catalyse electro-oxidation of analogous carboxyl compounds not possessing keto substitution in the *α*-position, e.g. malonic, maleic and succinic acids. Oxalic acid and *α*-keto acids undergo oxidation at unmodified carbon electrodes at potentials more positive than 1.2 V vs Ag/AgCl but show substantially anodic peaks between 0.75 and 0.9 V vs Ag/AgCl at the CoPc-containing surface. Peak currents are proportional to the acid concentration. At higher potentials peak currents decrease due to potential-dependent electrode deactivation. The detection limit for oxalic acid at 0.75 V is 0.3 pmol injected and less than 1 nmol for the *α*-keto acids. CoPc tetrasulphonate also catalyses electro-oxidation of oxalic acid.[134]

The CoPc-modified electrode reduces the overpotential necessary for the oxidation of ascorbic acid by approximately 150 mV to 0.21 V vs SCE; the process is dependent on the pH of the supporting electrolyte, but independent of ionic strength over the range studied. The optimum supporting electrolyte was 0.05 M phosphate buffer ($pH \approx 5$). Amperometry in stirred solution was performed at an applied potential of 0.25 V. The limit of detection was 0.65 ng ml^{-1}.[136] Calibration graphs were linear up to 2 mM concentration of ascorbic acid.[137]

The oxidation of ascorbic acid is irreversible at MLCMEs i.e. chemically modified electrodes containing 3,3′,3″,3‴-tetranitrophthalocyanine coordination compounds of iron(II), cobalt(II), nickel(II) and copper(II)] as well as at the unmodified electrode. No reduction of ascorbic acid was noticed in the voltage range studied. Under the same experimental conditions, compared with the unmodified glassy carbon electrode, the oxidation peak voltage of ascorbic acid at the MLCMEs shifts by ~150 mV in the negative direction while the oxidation peak current of the ascorbic acid increases significantly. There was a good linear relationship between the peak current of the electrocatalytic oxidation of ascorbic acid and its concentration when the electrodes were MLCMEs, but this relationship was not found for the unmodified glassy carbon electrodes. Since the oxidation peak voltage of ascorbic acid at the MLCMEs was near the oxidation peak voltage of M(II)→M(III), it is proposed that M(II)/M(III) redox sites at the MLCMEs transport electrons from the adsorbed ascorbic acid molecules to the glassy carbon electrodes, bringing about electrocatalytic oxidation of ascorbic acid.[138]

2.13 Electro-oxidation of sulphydryl compounds

Phthalocyanines and tetrasulphophthalocyanines of several transition metals catalyse electro-oxidation of sulphur-containing compounds such as cysteine, glutathione, lipoic acid, disulphiram, L-cysteine monohydrochloride, L-cysteine, 3-mercaptopropionic acid, homocysteine, 2-mercaptoethanol, sulphide, *N*-acetylcysteine, dithiothreitol, antitumour drug 6-mercaptopurine, and the antihypertensive agent captopril, and penicillamine.[55, 137, 139–141, 142] Transition-metal N_4-complexes substantially reduce overpotential for electro-oxidation of these compounds.[114, 142, 143]

Redox potential and the electronic structure of the central metal ion also play an important role in the electrocatalysis.[54] For the electro-oxidation of cysteine the catalytic activity of MPc and MTSP varies in the order:[56]

$$\mathrm{Co>Fe>Mn>Ni>Cu}$$

Volcano-shaped graphs are obtained when the activity is plotted versus the number of *d*-electrons in the metal, as shown in Fig. 5.

M(II) species are the most active. Co(II) is stable over a wide potential range and shows the best catalytic activity for this reaction. Both FeTSP and CoTSP have unpaired electrons in the d_z^2-orbital of the constituent metal which has the right symmetry for interacting with the RSH molecule and hence the higher activity. This interaction may take place by the sulphur atom because MPcs show low activity for amino-acids without sulphur atoms. On CoTSP, the order of reaction in protons at pH values lower than 8.5 is − 1; this proton is supplied by the reaction of the − SH group in the cysteine. At higher pH values, the reaction becomes independent of pH. Cysteine undergoes a one-electron oxidation to give cystine. In acid, cystine was found to be the major product of the oxidation reaction, with traces of cysteinic acid (RSO_3H) produced. In alkaline media, there were other products apart from cystine; they were probably due to the chemical decomposition of cystine.[140, 144] At higher potentials, the major product of the reaction is cysteinic acid. On CoTSP, Tafel slopes range from 0.14 V in alkali to 0.12 V in acid, indicating that the electron transfer is rate-determining.[144]

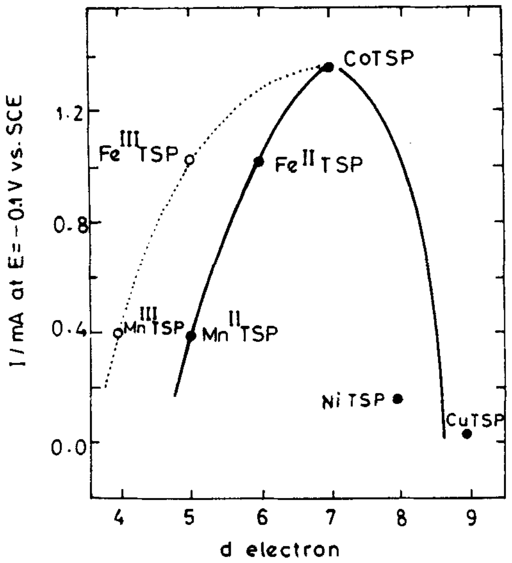

Figure 5 Volcano plot for electro-oxidation of cysteine on different phthalocyanines.

CoPc was found to be more active than CoTSP for anodic oxidation of glutathione. The trend in activity seems to be correlated to the Co(I)/Co(II) redox couple. One-electron oxidation of glutathione gives the disulphide (GSSG). The order of chemical reaction in glutathione and number of protons is 1 and − 1, respectively. The reaction order in protons becomes zero at pH>10. The Tafel slopes are *RT*/*F* at pH>10 and close to 2*RT*/*F* for more acidic values.[145]

The use of CoPc and CoTSP electrodes in high-performance liquid chromatography with electrochemical detection (LCEC) permits detection of these sulphydryl compounds in blood, urine and plasma samples. At 0.75–0.85 V vs Ag/AgCl on CoPc electrodes a detection limit above 4 pmol was obtained for cysteine, glutathione, *N*-acetylcysteine and homocysteine.[139, 140, 143] However, potential-dependent electrode deactivation at higher potentials severely limits the high-potential operation of the electrode as an LCEC detector.[139]

LCEC incorporating a novel carbon–epoxy-resin working electrode modified with CoPc has been employed for the determination of normal circulating levels of reduced glutathione (GSH) in human plasma. The process was dependent on the ionic strength and pH of the supporting electrolyte. The mobile phase consisted of 0.05 M phosphate buffer (pH≃3) containing 0.1% (m/m) ethylenediaminetetra-acetic acid (EDTA).[146] The oxidation of GSH in the presence of CoPc was found to occur at two potentials, namely 0.27 and 0.75 V. The first wave (E_p=0.27 V) was found to give optimum sensitivity for the measurement of GSH concentration in the range 2.5×10^{-6}–6.25×10^{-5} M, whereas the second ($E_p=0.75$ V) was preferential for GSH concentrations of 1.25×10^{-4}–2.5×10^{-3} M. The different calibration ranges suggest that peak 1 might be suitable for the determination of the low GSH levels present in human plasma; however, for the higher GSH concentrations present in blood, the measurement of peak 2 might be more suitable.[147]

2.14 Other applications of metal phthalocyanines

CoPc has been employed as an electrocatalyst for the oxidation of coenzyme-A and it is found that CoPc reduces the overpotential required for the oxidation of coenzyme-A.[137, 148]

CoPc catalyses the electro-oxidation of bile acids in 0.1 M NaOH. For various bile acids, namely deoxycholic, chenodeoxycholic, ursodeoxycholic, glycocholic, taurocholic and taurodeoxycholic acid, anodic peak potentials between 0.54 and 0.59 V were observed.[114]

Carbon paste electrodes (CPE) containing CoPc have been used for the amperometric detection of compounds that are virtually non-electroactive or oxidizable at extreme potentials, e.g. for thiopurines,[149] carbohydrates, alditols and acidic sugars[150, 151] and organic peroxides.[115] Polymeric phthalocyanines are also used as electrocatalysts in analytical devices for immunoassay.[152]

Electropolymerized films of MPcs catalyse the electrochemical oxidation of hydroquinone and catechol. MPc films catalyse the electrochemical reduction of $Mn_2(CO)_{10}$ in acetonitrile.[153]

Chemically modified electrodes (CMEs) containing CoPc catalyse the electro-oxidation of nucleic acid species. The oxidation, which occurred between 0.4 and 0.5 V vs Ag/AgCl in 0.15 M NaOH, was observed only for ribose-containing compounds such as the ribonucleosides, but not for deoxyribonucleosides such as thymidines or for the purine and pyrimidine bases by themselves. When used for electrochemical detection of the ribonucleosides following liquid chromatography, limits of detection were at the nanomolar level with the linear response extending at least two orders of magnitude higher. The stability of the CME response was such that 20–30 injections over 1 h showed virtually no decrease in peak current with a relative standard deviation of only 2.5%.[154]

CoPc showed no electrocatalytic action towards hypophosphorous and tetrathionate anions.[155] Inorganic anions containing sulphur, such as SO_3^{2-}, $S_2O_3^{2-}$ and SCN^-, selenium in SeO_3^- and $SeCN^-$, nitrogen in NO_2^-, and arsenic in AsO_2^- readily oxidize at a carbon paste electrode (CPE) modified with CoPc (CoPc-CPE). On CPE, all of these anions (with the exception of $SeCN^-$) were found to be virtually non-electroactive. The CoPc-CPE was used as an amperometric flow sensor for the direct determination of SCN^- and $SeCN^-$. An alternating potential between an anodic detection potential and a cathodic reactivation potential provides a more stable detection response for both anions. Alternating potentials in the ranges 0.85 to −0.30 V and 0.60 to −0.30 V were used for SCN^- and $SeCN^-$, respectively. The linear response ranges and the detection limits were 2–50 μM and 0.8 μM (at pH 2), respectively, for SCN^-, and 0.2–20 μM and 0.1 μM (at pH 7), respectively, for $SeCN^-$. Thiocyanate can be readily determined in saliva samples following 100-fold dilution with the supporting electrolyte solution. CoPc-CPE electrocatalytic action on SCN^- is highly pH-dependent, reaching a maximum at pH≃4 and virtually disappearing at pH>9. Selenocyanate is unstable in acidic solutions, slowly releasing colloidal selenium even at pH≃5. At pH<4, the electrochemical oxidation of selenocyanate proceeds reversibly. With gradual increase in pH, the oxidation becomes irreversible. Excess of CN^- and sulphide ions interfere in the determination of selenocyanate. The CoPc-CPE electrocatalyses oxidation of Br^- and I^-. The electrochemical oxidation of I^- was completely reversible at the CoPc-CPE and irreversible at the CPE.

The use of phthalocyanine-coated electrodes provides fast, accurate, on-line monitoring of sulphide concentrations in aqueous effluent, e.g. from pulp and paper plants, and oil and gas refineries.[156, 157] The electrode is substantially unaffected by other species which may be present in the aqueous sample.

Chemically modified electrodes containing CoPc show a selectivity sequence in the order:

$$NO_2^- > SCN \simeq I^- > ClO_4^- > Bu^- > NO_3^-$$
$$> Cl^- > OAc$$

The electrodes show a linear response towards NO_2^- in the range 6×10^{-2}–5×10^{-6} M. The electrode has a satisfactory reproducibility and a rapid potential response.[158]

Co(II)Pc is a highly efficient catalyst for the electro-oxidation of NO to NO_3^-.[159] Metal phthalocyanines also catalyse the electro-oxidation of CO and formic acid.[160]

A fuel cell having oxygen electrode activated with FePc, pFePc or pCoPc can be used as an electrochemical sensor for hydrogen and hydrogen-containing reducing agents. The use of the phthalocyanine makes it possible for the sensor to operate in a mixture of oxygen and hydrogen or hydrogen-containing reducing agents without preliminary separation of the components. The current produced from the overall reaction is measured and related to hydrogen concentration. The sensitivity of the sensor to hydrogen is 10^{-4}–10^{-3} vol %. The apparatus was also used to determine propane, formaldehyde and hydrazine in air.[161, 162]

Metal phthalocyanines are also known to catalyse the decomposition of propylene carbonate in Li/MPc cell to propylene. The order of activity is found to be:

FePc>CoPc>MnPc>NiPc>CrFPc>AgPc

H_2Pc, Li_2Pc, Na_2Pc, GaClPc and CdPc show poor activity.[163]

3 CONCLUSIONS

As discussed in this Review, MPcs are active electrocatalysts for various oxidation and reduction reactions. This is possible because of the presence of two types of active sites in MPc, namely chelate-bound metal/metal-free sites,. and sites with a buffer character of the conjugated system of π-electrons.[109, 164]

In all the reactions described above, use of phthalocyanines has been found to reduce overpotentials, thus enhancing sensitivity and selectivity for the detection and determination of these compounds. Improved selectivity on phthalocyanine-containing electrodes has been achieved by incorporating phthalocyanines into cellulose acetate[116] or Nafion coating[165] whereas enhanced stability is obtained by entrapping the electrocatalyst and the graphite in epoxy-resins.[136, 166, 167]

Electrocatalytic activity depends on redox potential and the electronic structure of the transition metal in the macrocycle.[55, 119] For exhibiting high electrocatalytic activity phthalocyanines should have intrinsic redox activity in the potential regime of the reaction, and it should not bind the reactant strongly. Heat treatment of phthalocyanines in inert atmospheres improves their electrocatalytic activity.

As is clear from this Review, sulphur-containing compounds can also be reduced/oxidized by using phthalocyanines as electrocatalysts. This has an advantage over the use of transition metals such as platinum, which are poisoned by sulphur-containing compounds.

It may be rewarding to examine phthalocyanines as electrocatalysts for other redox reactions such as the electroreduction of sulphite, the electro-oxidation of hydrocarbons and the electro-oxidation of carbon monoxide, since these reactions are known to be catalysed by metal porphyrins.[168–170]

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