The cathodic reduction of oxygen

Citation for published version (APA):
Brink, van den, F. T. B. J., Barendrecht, E., & Visscher, W. (1980). The cathodic reduction of oxygen: a review with emphasis on macrocyclic organic metal complexes as electrocatalysts. *Recueil des Travaux Chimiques des Pays-Bas*, *99*(9), 253-262. https://doi.org/10.1002/recl.19800990902

DOI:
10.1002/recl.19800990902

Document status and date:
Published: 01/01/1980

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Download date: 25. Aug. 2022

Recueil, Journal of the Royal Netherlands Chemical Society, 99/9, september 1980

Recueil Review

of progress in current research

The cathodic reduction of oxygen
A review with emphasis on macrocyclic organic metal complexes as electrocatalysts

F. van den Brink, E. Barendrecht and W. Visscher

Laboratory for Electrochemistry, University of Technology, 5600 MB Eindhoven, The Netherlands

(Received June 19th, 1980)

1. Introduction

Molecular oxygen* is, apart from nitrogen, the most abundant constituent of the earth's atmosphere (20.74 vol. %). Since it is capable of accepting electrons, and therefore an oxidator, it is an essential species in many oxidation reactions- e.g. biological systems use almost exclusively oxygen for their combustion processes. The situation in electrochemical systems is by no neans different. Although there are applications of the oxygen electrode in the domain of synthetic electrochemistry as well, the outranking areas of the application of the oxygen electrode are in energy storage and conversion, as in water electrolyzers and in fuel cells and metal oxygen batteries (local electricity production, power station peak shaving, automotive power).

Fuel cells are systems consisting of two electrodes, connected by some ionic conductor (electrolyte)[2]. At one of the electrodes a reductor (e.g. H_2, N_2H_4, CH_3OH) is oxidized, while at the other an oxidator (O_2) is reduced. An H_2/O_2-fuel cell is schematically shown in Fig. 1. As the electrolyte potassium hydroxide or phosphoric acid is used in the low temperature type, while a mixture of molten carbonates is commonly used in the high temperature type. The electrodes for the low temperature type are usually porous and made of a mixture of active carbon on which some catalyst is dispersed, and a hydrophobic material, such as polyethylene or teflon.

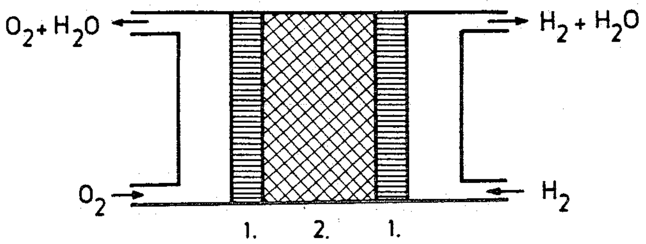
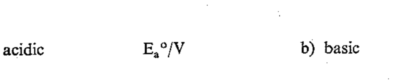


Fig. 1. Schematic of H_2/O_2 fuel cell; 1 = porous electrodes, 2 = electrolyte.

In these systems chemical energy is directly converted to electrical energy, an isothermal process which avoids the Carnot cycle and can therefore be very efficient. The theoretical efficiency of a fuel cell, i.e. of a reversible galvanic cell, is mainly determined by the entropy change in the cell reaction (the maximum obtainable electrical work being $-nFE = \Delta G$) so that depending on the sign of ΔS more or less energy can be obtained by the electrochemical route than available from the heat content ($-\Delta H$) of the fuel[3]. Therefore, the thermodynamic efficiency of a fuel cell is defined as

$$\eta = \frac{\Delta G}{\Delta H} = 1 - T\frac{\Delta S}{\Delta H}$$

For the hydrogen/oxygen fuel cell at 298 K, $\eta = 83\%$ can be calculated from thermodynamica data. This high theoretical efficiency is, however, not attained in practice, because of the rather high irreversibility of the reactions involved. Especially the oxygen electrode is a troublemaker in this respect, and a lot of effort has been spent to solve the problems involved in the reduction of oxygen. This will be the theme of this review.



	a) acidic	$E_a°/V$	b) basic	$E_b°/V$
(1)	$O_2 + 4\,H^+ + 4e^- \rightarrow 2\,H_2O$	1.229	$O_2 + 2\,H_2O + 4e^- \rightarrow 4\,OH^-$	0.401
(2)	$O_2 + 2\,H^+ + 2e^- \rightarrow H_2O_2$	0.695	$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$	−0.0649
(3)	$H_2O_2 + 2\,H^+ + 2e^- \rightarrow 2\,H_2O$	1.763	$HO_2^- + H_2O + 2e^- \rightarrow 3\,OH^-$	0.867
(4)	$H_2O_2 \rightarrow H_2O + \frac{1}{2}\,O_2$		$HO_2^- \rightarrow OH^- + \frac{1}{2}\,O_2$	

Fig. 2. Reduction of oxygen in protic media. Data on standard potentials vs. NHE taken from ref. 5 (NHE = Normal Hydrogen Electrode).

---

* Nomenclature used in connection with oxygen[1]:
- (a) dioxygen: all forms of O_2 with an O–O covalent bond.
- (b) molecular oxygen: free or isolated O_2 (refers usually to the ground state).
- (c) dioxygen-metal complex: includes one or more covalent bonds between dioxygen and a metal species.
- (d) superoxide: O_2^- ion. Superoxo: covalently bound dioxygen resembling O_2^-.
- (e) peroxide: O_2^{2-} ion. Peroxo: covalently bound dioxygen resembling O_2^{2-}.
- (f) oxide: O^{2-} ion. Oxo: covalently bound oxygen resembling O^{2-}.

[1] *L. Vaska*, Acc. Chem. Res. **9**, 175 (1976).

[2] *J. O'M. Bockris* and *S. Srinivasan*, "Fuel Cells; Their Electrochemistry", McGraw Hill Book Company, **1969**.

[3] *W. Vielstich*, "Fuel Cells", Wiley-Interscience, London/New York/Sydney/Toronto, **1970**.

In electrochemical (cathodic) reduction, oxygen reacts in protic media to give either hydrogen peroxide, H_2O_2, or water, H_2O. The pertinent reactions, with their electrochemical equivalent of free enthalpy change, the standard potential, are given in Fig. 2 (standard potential and standard free enthalpy change are related as $\Delta G^\circ = -nFE^\circ$). The anodic evolution of oxygen, the reverse of reaction 1 in Fig. 2 (which is one of the halfreactions in water electrolysis) is just as troublesome as the oxygen reduction.

An outline of the misbehaviour of the oxygen electrode is given in Fig. 3, where the difference between measured and theoretical potential (overpotential) of an oxygen electrode is sketched as a function of the current density at the electrode. The solid line (O) represents the reversible potential of the O_2/H_2O couple, i.e. the value of E when $i = 0$. In the reduction of O_2 not only H_2O but also H_2O_2 can be a reaction product; this gives rise to the occurrence of a mixed potential that may be considerably lower than the reversible potential for the reduction of oxygen to water.

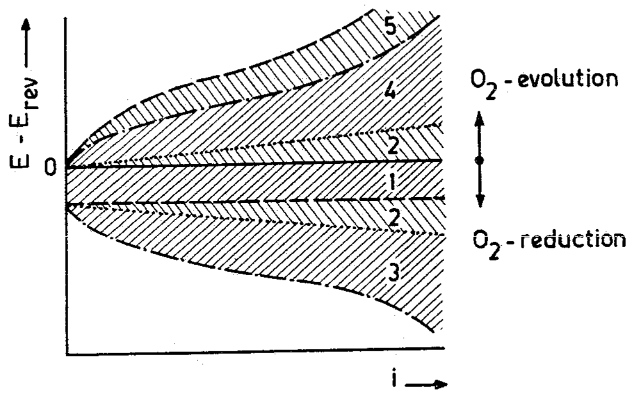


Fig. 3. Schematic of the potential-current relationship for the oxygen electrode.
0 = reversible potential; 1 = $O_2 \rightarrow H_2O_2$ (Berl); 2 = ohmic drop in electrolyte and electrode/electrolyte interphase; 3 = overpotential for reduction; 4 = overpotential for oxidation; 5 = ohmic drop caused by gas bubble evolution.

The potential drop caused by this side reaction (also known as the Berl reaction) is designated by the area 1. Area 2. is the result of the ohmic potential drop over the electrode-electrolyte interphase and in the electrolyte itself, and can be minimized by the proper choice of electrode geometry and electrolyte composition and temperature. The kinetic overpotentials for oxygen reduction and evolution are represented by the areas 3. and 4., respectively. Their origin is the low value of the rate constants for the pertinent reactions, i.e. their high enthalpy of activation. The magnitude of the activation enthalpy is strongly influenced by the substrate on which the heterogeneous reaction takes place, i.e. by the electrode material. The selection of the most suitable electrode material/electrolyte/solvent combination is in the realm of electrocatalysis. It should be noted that area 5. in Fig. 3 applies only to gas bubble formation during oxygen evolution.

Summarizing, we can state that the search for a practically feasible oxygen cathode concentrates on the selection of an electrode material which should satisfy two requirements:
(i) high intrinsic reaction rate for O_2-reduction;
(ii) high specificity, in that the reaction product is H_2O rather than H_2O_2.

From Fig. 3 it will be obvious that there is, at practical current densities, a large difference (up to 1V) between the potential at which oxygen is reduced and that at which oxygen evolution takes place. As a result, catalysts which are feasible for oxygen reduction will, more often than not, be destroyed by oxidation when they are applied to oxygen evolution electrodes (platinum being the obvious exception). This is the reason why, from an electrocatalytical point of view, reduction and evolution are treated as entirely different processes, each requiring their own type of catalysts, although chemically they are each others reverse. So, the reversible oxygen electrode, for instance for rechargeable batteries, though realized at platinum under high purity conditions, is still a long way off and will not be discussed here.
Knowledge of the nature of oxygen reduction, and of the influence of the interaction between the oxygen molecule and the substrate on the reaction, is by no means of importance only to those interested in electrochemical reduction of oxygen. As mentioned earlier, biochemical systems reduce oxygen, using complicated enzymes as substrate. Possibly, electrochemical oxygen reduction can be used as a model system for the description of the factors involved in the interaction between oxygen and those enzymes. Also, there are many inorganic reactions where heterogeneous oxygen reduction plays a role. Part of these reactions are of the corrosion type, i.e. catalyst particles have anodic and cathodic sites; when oxygen is reduced on the cathodic sites, we have essentially the electrochemical half reaction of cathodic oxygen reduction, so that knowledge obtained from the study of the electrochemical reaction can be applied to these catalytic reactions to gain a deeper insight into their mechanism.

2. O_2-species and models for their reactions

Although oxygen is the most reduntant oxidizing agent on earth, it is by no means a very good oxidator. The oxygen molecule is rather stable, which is fortunate from the viewpoint of the possibility of life on earth, but on the other hand is a drawback in those instances where a fast reduction is required.

In the ground state the sixteen electrons of the O_2 molecule are distributed over its molecular orbitals according to $(\sigma_g1s)^2$ $(\sigma_u{}^*1s)^2$ $(\sigma_g2s)^2$ $(\sigma_u{}^*2s)^2$ $(\sigma_g2p_x)^2$ $(\pi_u2p_{y,z})^4$ $(\pi_g{}^*2p_{y,z})^2$, which is a ${}^3\Sigma_g^-$-state with bond order 2. In this state the O—O distance is 0.121 nm[4] and the bond strength corresponds to ΔH_f° (298 K) = -498.7 kJ mole^{-1}.
This may be compared to -334 kJ mole^{-1} for the C—C bond, -431 kJ mole^{-1} for H—H and -160 kJ mole^{-1} for C—H.
The rather high bond strength indicates that one of the bottlenecks in oxygen reduction will be breaking of the O—O bond. The other possible first step in the reaction is the transfer of the first electron, i.e. $O_2 + e^- \rightarrow O_2{}^-$. Due to the fact that this reaction is energetically unfavourable ($\Delta G^\circ = 31.8$ kJ mole^{-1}, $E^\circ = -0.33$ V[5]), this step is slow as well. However, when it takes place, the O—O bond strength in the superoxide ion $O_2{}^-$ is lowered to approximately -350 kJ mole^{-1} [6].

The task of the electrocatalytic system is therefore to promote these two reactions. When the electrocatalyst acts first to form the superoxide ion, $O_2{}^-$, the ultimate reaction product may be either H_2O_2 or H_2O; when the breaking of the O—O bond is catalyzed first, the product is H_2O only.

---

[4] Gmelins Handbuch der Anorganische Chemie, 3, Sauerstoff, 8. Auflage, **1958**.
[5] *J. P. Hoare*, GMR 2948 Research Publication, **1979**.
[6] *M. R. Tarasevich*, Elektrokhimiya **9**, 599 (1973).

The latter case is known as the direct process: reaction (1) of Fig. 2. When H_2O_2 is an intermediate, the process is called consecutive or the peroxide pathway: reaction (2), followed by either reaction (3) or reaction (4) in Fig. 2.

In either case, the reaction is a 4-electron transfer, because in the sequence (2)–(4) oxygen is recycled. The direct process (1) may involve a peroxo complex, but differs from the peroxide path in that the reduction does not lead to peroxide in the solution phase as a stable intermediate.

Since both processes lead in the end to an overall 4-electron transfer, efforts to find electrocatalysts which promote the direct path preferentially may seem futile, but are not. The reason for this is, as already pointed out, that the potential is lowered in the peroxide path. Moreover, almost all electrocatalysts used in practice are dispersed on some active carbon or graphite, and solution phase peroxide attacks the carbon surfaces very strongly, thus affecting the long term performance and stability of the electrode.

The MO-description of the oxygen molecule suggests the following possible interactions between O_2 and the substrate.

(i) a *dative* interaction, caused by overlaps of the occupied bonding $\pi_u 2p$-orbital of O_2 and empty orbitals of the substrate. This interaction will loosen the O–O bond and change the electron density distribution in O_2.

(ii) a *retrodative* interaction consisting of overlaps of occupied orbitals of the substrate and the partially occupied antibonding $\pi_g{}^*2p$-orbital of O_2. This will mainly reduce the bond order of O_2.

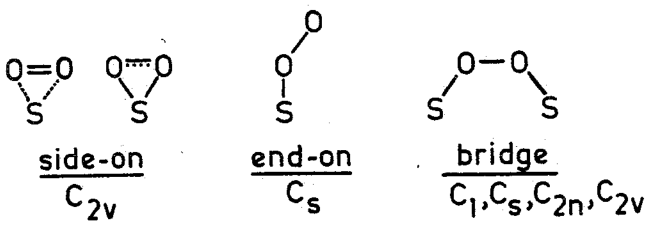


Fig. 4. Interactions of oxygen with a substrate, with their symmetry groups[13].

The interactions can be visualized on the basis of three models (Fig. 4). In the *side-on* model[7], both the dative and the retrodative interactions occur (Fig. 5) and weaken the O–O bond. This way of binding oxygen to the substrate occurs in *Vaska* complexes[8-17,19] which are good catalysts for selective oxidation of cyclic olefins[18] but have no activity for the electroreduction of oxygen.

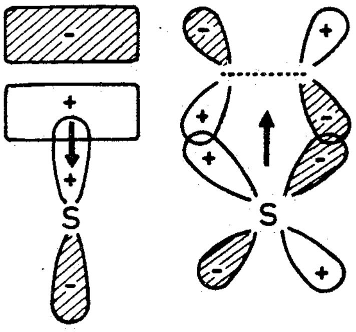


Fig. 5. Orbital overlap in side-on interaction.

Table I Thermodynamic data on reactions of oxygen species in aqueous medium at 298 K.

Reaction	pH	E° [a]	ΔH° [b]	ΔG° [b]	S° [c]
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	0	1.229	0	0	205.18
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	14	0.401			
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	7	0.815			
$O(g) + 2H^+ + 2e^- \rightarrow H_2O$	0	2.430	249.35	231.91	161.06
$O(g) + H_2O + 2e^- \rightarrow 2OH^-$	14	1.602			
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0	0.695			
$O_2 + H_2O + 2e^- \rightarrow OH^- + HO_2^-$	14	−0.0649			
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	0	1.763	−191.30	−134.19	232.80
$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$	14	0.867	−160.45	−67.4	23.9
$O_2 + e^- \rightarrow O_2^-$		−0.33			
$HO_2 + H^+ + e^- \rightarrow H_2O_2$	0	1.50		10.3	
$O_2^- + H_2O + e^- \rightarrow HO_2^- + OH^-$	14	0.20		31.9	
$HO_2 + 3H^+ + 3e^- \rightarrow 2H_2O$	0	1.674			
$O_2^- + 2H_2O + 3e^- \rightarrow 4OH^-$	14	0.645			
$O_2 + H^+ + e^- \rightarrow HO_2$	0	−0.106			
$OH + e^- \rightarrow OH^-$	14	1.985	39.0	34.3	192.14
$OH + H^+ + e^- \rightarrow H_2O$	0	2.813			
$H_2O_2 + H^+ + e^- \rightarrow OH + H_2O$	0	0.714			
$HO_2^- + H_2O + e^- \rightarrow OH + 2OH^-$	14	−0.251			
$O + e^- \rightarrow O^-$		1.33			
$O^- + H_2O + e^- \rightarrow 2OH^-$	7	1.87			

[a] Standard potential in V vs. NHE; [b] (free) enthalpy of formation (kJ mole^{-1}) for reacting oxygen species; [c] entropy (J K^{-1} mole^{-1}) of reacting oxygen species. (From ref. 5.)

---

[7] *J. S. Griffiths*, Proc. R. Soc. (A) **235**, 73 (1956).

[8] *N. W. Terry, E. L. Amma* and *L. Vaska*, J. Am. Chem. Soc. **94**, 653 (1972).

[9] *L. Vaska, L. C. Chen* and *W. V. Miller*, J. Am. Chem. Soc. **93**, 6671 (1971).

[10] *J. A. McGinnety, N. C. Payne* and *J. A. Ibers*, J. Am. Chem. Soc. **91**, 6301 (1969).

[11] *S. I. La Plaka* and *J. A. Ibers*, J. Am. Chem. Soc. **87**, 2581 (1965).

[12] *J. A. McGinnety, R. Doedens* and *J. A. Ibers*, Science **155**, 709 (1967).

[13] *M. S. Weininger, I. F. Taylor* and *E. L. Amma*, Chem. Commun. **1971**, 1172.

[14] *T. Kashtwagi, M. Yasuoka, N. Kasui, M. Kakudo, S. Takahashi*, and *N. Hagihara*, Chem. Commun. **1969**, 763.

[15] *P. T. Cheng, C. D. Cook, S. C. Nyburg* and *K. Y. Wan*, Can. J. Chem. **49**, 3772 (1971).

[16] *L. Vaska*, Science **140**, 809 (1963).

[17] *J. McGinnety, R. Doedens* and *J. Ibers*, J. Am. Chem. Soc. **88**, 3511 (1966).

[18] *J. Collman, M. Kubola* and *J. Hosking*, J. Am. Chem. Soc. **89**, 4809 (1967).

[19] *A. V. Savitskii* and *V. I. Nelyubin*, Russ. Chem. Rev. **44**, 110 (1975).

The *end-on* binding[19-30], likely to occur on transition metal electrocatalysts, was first described by *Pauling*. The bonding scheme can be visualized as in Fig. 6. This shows that electrocatalysis will be most effective with transition metals having occupied d_{xz} and d_{yz} orbitals and an empty d_{z^2} orbital. This interaction is frequently supposed to give a superoxo (O_2^-) ligand by partial charge transfer from the metal to the oxygen molecule, although there is some evidence that the oxygen molecule may stay neutral as a whole, the interaction only giving a decrease in O–O bond order[31].

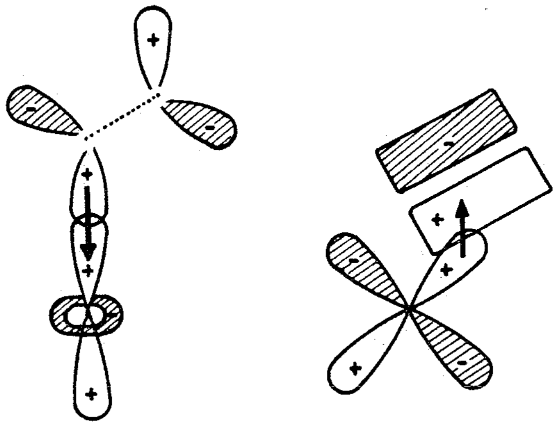


Fig. 6. Orbital overlap in end-on interaction.

The *bridge* model[32] involves similar electronic interactions, where the O_2-molecule interacts with two metal centers at the same time. It is supposed to prevail in interactions of oxygen with clean oxide free metal surfaces, where the metal atoms are properly spaced. It may also occur on bimetal complexes with a macrocyclic ring provided the spacing of the metal atoms is proper[33,34].

A compilation of thermodynamic data on oxygen species in aqueous solution has been given in ref. 5. A selection of these data for those species most likely to occur as intermediates in oxygen electroreduction is given in Table I, along with values for the standard potentials of the reactions involved.

3. Methods for studying the mechanism of oxygen reduction

The methods used for the investigation of the oxygen electrode are mainly electrochemical in nature, although some other physicochemical methods are used as well. However, it is a moot question whether results obtained with ex situ methods, such as ESCA, LEED or Auger spectrocopie (AS), are applicable to the description of what happens at the oxygen electrode. Clearly, the interaction of an oxygen molecule and an electrocatalytic site will be strongly ininfluenced by the dielectric medium, especially when the electrocatalytic site is part of a charged phase, i.e. the electrocatalytic surface. Therefore the behaviour of an oxygen molecule near an electrocatalytic site in vacuo as in ESCA, LEED or AS, will be very different from that in (aqueous) solution, where it is surrounded by charged particles and dipoles, facing the highly charged electrode surface (the surface charge density is of the order of $0.1\ C\ m^{-2}$, hence the electrical field strength is of the order of $10^9\ V\ m^{-1}$). Spectrochemical methods are therefore only applied to advantage if they can be used in situ. Examples are ellipsometry, reflectometry, photoacoustic spectroscopy, electron spin resonance and resonance Raman spectroscopy. Only ellipsometry and reflectometry have been applied so far. Of the electrochemical methods, the first to be described are steady state methods. Here the electrocatalyst is dispersed on active, highly porous carbon and the properties of the resulting active mass are studied in either a slurry electrode cell or in a gas diffusion electrode. In a slurry cell[35-37], small carbon particles are suspended in the electrolyte by vigorous stirring while their potential is controlled by collision with a large inert feeder electrode. Although this method gives some qualitative information, this information must be treated with a due measure of mistrust, since the matter of potential control of the catalyst particles is wrapped in uncertainties[37].

Gas diffusion electrodes[38] are much more apt to give sound information. Here, the catalyst mass is mixed with some hydrophobic component, e.g. teflon or polyethylene. This mixture is sprayed, painted or pressed onto a porous electrical conductor, such as sintered nickel foil, or onto a metallic gauze. Since this type of electrode is highly hydrophobic it is possible to use it as a gas diffusion electrode, where the gas phase is on one side of the electrode and the electrolyte on the other; in the pores of the electrode a three-phase-boundary exists, where the oxygen gas diffuses into the electrolyte to react at the electrocatalytic sites of the pore walls. With this method it is possible to determine whether a given electrocatalyst is feasible for oxygen reduction and whether it is stable in the electrolyte. With this configuration current-potential relationships can be found in a meaningful way, giving indicative insight into the mechanism of the electroreduction of oxygen. The long term performance of the electrocatalyst can be studied by measuring the overpotential of a gas diffusion electrode as a function of time at constant current density. For more quantitative insight into the processes pertaining to the oxygen reduction, more sophisticated methods must be used. Unfortunately, these methods are not applicable to electrodes where the electrocatalyst is dispersed on small carbon particles, as in the slurry or gasdiffusion electrode, so that other methods of electrode preparation must be used.

The most frequently used device is the *rotating disc electrode* (RDE)[39,40]. In a laminar flow regime convective diffusion to and from a rotating disc can be described exactly. So, it is

---

[20] *L. Pauling* and *C. D. Coryell*, Proc. Natl. Acad. Sci. USA **22**, 210 (1936).

[21] *L. Pauling*, Nature **203**, 182 (1964).

[22] *J. J. Weiss*, Nature **202**, 83 (1964).

[23] *J. Dunitz* and *L. Orgel*, J. Chem. Soc. **1953**, 2594.

[24] *B. Hoffman*, *D. Diemente* and *F. Basolo*, J. Am. Chem. Soc. **92**, 61 (1970).

[25] *D. M. Mingos*, Nature **230**, 154 (1971).

[26] *G. Henrici–Olivé* and *S. Olivé*, Angew. Chem. Int. Ed. **13**, 29 (1974).

[27] *E. I. Ochiai*, J. Inorg. Nucl. Chem. **35**, 3375 (1974).

[28] *J. P. Collman* et al., J. Am. Chem. Soc. **97**, 1427 (1975).

[29] *F. Basolo*, *B. M. Hoffman* and *J. A. Ibers*, Acc. Chem. Res. **8**, 384 (1975).

[30] *G. McLendon* and *A. E. Martell*, Coord. Chem. Rev. **19**, 1 (1976).

[31] *B. H. Huynh*, *D. A. Case* and *M. Karplus*, J. Am. Chem. Soc. **99**, 6103 (1977).

[32] *E. Yeager*, in "Electrocatalysis on Non-Metallic Surfaces", NBS Spec. Publ. **455**, 203 (1976).

[33] *J. H. Zagal–Moya*, Ph.D. Thesis, Case Western Reserve Univ. **1978**.

[34] *J. P. Collman* et al., J. Electroanal. Chem. **101**, 117 (1979).

[35] *J. A. Podwjasin* and *A. J. Shlygin*, Russ. J. Phys. Chem. **31**, 1305 (1957).

[36] *J. Held* and *H. Gerischer*, Ber. Bunsenges. phys. Chem. **67**, 921 (1963).

[37] *J. F. van der Plas* and *E. Barendrecht*, Electrochim. Acta **1980** (accepted for publication).

[38] *W. M. Vogel* and *J. L. Lundquist*, J. Electrochem. Soc. **117**, 1512 (1970).

[39] *V. G. Levich*, *"Physicochemical Hydrodynamics"*, Prentice Hall, Inc., Englewood Cliffs, N.J., **1962**.

[40] *V. Yu. Pleskov* and *Yu. V. Filinovskii*, "The Rotating Disc Electrode", Consultants Bureau, New York/London, **1976**.

possible to separate the influence of mass transfer of reactants and products in the measured reaction rate (current density) from the kinetic behaviour of the electrocatalytic surface. If the electrocatalyst is a metal or some other solid, machinable material, the disc electrode is manufactured from this material. If it can not be machined, it is pressed, sprayed, painted or vacuum deposited onto a disc, which is made of some suitable substrate material such as carbon, gold or platinum. The method of preparation should, however, be chosen to give a well defined surface of known area. For characterizing the surface, *cyclovoltammetry* is a useful technique – it enables one to discriminate between surface processes, involving only the surface layer and the solvent, and heterogeneous processes, involving reactants from the bulk of the solution as well. In the study of cathodic oxygen reduction, the RDE serves a number of purposes. From measurements of the limiting current (i.e. the current at a potential where the surface reactant concentration becomes zero) as a function of the RDE's rotation frequency, the number of electrons involved in the overall reaction can be obtained; also the reaction orders of the various reactants and intermediates can be found. Furthermore, the current density i as a function of potential E, after correction for mass transfer, can be plotted as E vs. log i_k, where i_k is the kinetic current density; the slope of this plot is a powerful diagnostic criterion in the determination of the reaction mechanism.

A still more refined insight into the electrode reaction is obtained when a *rotating ring-disc electrode* (RRDE)[40,41] is used. When oxygen is reduced at the disc electrode, the products may be either H_2O or H_2O_2; the latter can be detected at the ring electrode (usually platinum). A number of methods have been proposed to analyse RRDE data, which show that it is possible with the RRDE to distinguish between the various reaction paths in Fig. 2[42-48].

A very sophisticated technique for the study of electrode processes is *impedance spectrometry,* i.e. the measurement of the impedance of the electrode-electrolyte interphase as a function of excitation frequency. The impedance is determined by superposition of a small amplitude ac-potential on the electrodes dc-potential and measuring the response, i.e. the amplitude and phase of the resulting *ac-current.*

The amplitude gives an indication of the occurrence of reactions (dispersion), while the phase is determined by the reaction rates. To our knowledge, this method has only been used in the study of oxygen reduction at a mercury electrode[49-50], but we think that it may also prove very useful for solid electrodes, e.g. for semiconductor electrodes, where processes in the bulk of the electrode material play a role in the reaction mechanism.

4. Electrocatalysts for oxygen reduction

As described in section 2, the interaction of dioxygen with the electrode material in the cathodic reduction of oxygen plays a paramount role in determining the reaction mechanism, while an other important determining factor is the electrolyte/solvent system. For instance, oxygen reduction on gold in alkaline and acid medium gives H_2O_2; the reaction product on platinum in acid medium is solely H_2O, while in alkaline medium also some H_2O_2 is formed. To describe this synergistic effect of electrochemical and catalytical factors the term electrocatalysis is used – a term coined by *Kobosev* et al.[51] and much later, in 1963, defined more correctly, by *Grubb*[52]. So, whenever the term electrocatalyst is used, a combination of an electrode material and an electrolyte/solvent system is meant.

The high value of the standard potential of the oxygen/water couple strongly restricts the number of available electrocatalysts, because they must be stable in the working potential range of the oxygen cathode, i.e. between 1.0 V and 0.5 V vs. NHE. So, most non-noble metals cannot be used, unless they are passivated by the formation of an oxide layer.

Of the metals, Pt, Au and Ag have been studied extensively. Since oxygen reduction on platinum is rather well understood and, moreover, illustrative for many of the principles involved, it will be treated in some detail here.

Platinum is by far the best electrocatalyst known for oxygen reduction as regards activity, selectivity and stability[6,38,53-82]. Still, the exchange current density (i.e. the

---

[41] *W. J. Albery* and *M. L. Hitchman,* "Ring Disc Electrodes", Clarendon Press, Oxford, **1971**.

[42] *V. S. Bagotskii* et al., Sov. J. Electrochem. **4** 1129 (1968); *ibid.* **5**, 1158 (1969).

[43] *A. Damjanovic, M. A. Genshaw* and *J. O'M. Bockris,* J. Chem. Phys. **45**, 4057 (1966).

[44] *J. D. E. McIntyre,* J. Phys. Chem. **73**, 441 (1969).

[45] *M. R. Tarasevich,* Sov. J. Electrochem. **4**, 182 (1967); *ibid.* **6**, 1468 (1970).

[46] *H. S. Wroblowa, Yen-Chi-Pan* and *G. Razumney,* J. Electroanal. Chem. **69**, 195 (1976).

[47] *M. R. Tarasevich* and *K. A. Radyushkina,* Sov. J. Electrochem. **6**, 370 (1970).

[48] *F. van den Brink, E. Barendrecht* and *W. Visscher,* J. Electrochem. Soc. **1980** (accepted for publication).

[49] *M. M. J. Pieterse, M. Sluyters–Rehbach* and *J. H. Sluyters,* J. Electroanal. Chem. **107**, 247 (1980).

[50] *A. A. Moussa, E. A. Radwan* and *H. A. Galy,* Electrochim. Acta **16**, 1369 (1971).

[51] *N. I. Kobosev* and *V. V. Monblanova,* J. Phys. Chem. USSR **7**, 645 (1936).

[52] *W. T. Grubb,* Nature **198**, 883 (1963).

[53] 3^me^ Journées Internationales d'Etude des Piles à Combustibles, Bruxelles, Comptes Rendus, Presses Academiques Européennes, Bruxelles, **1969**.

[54] *J. O'M. Bockris* and *S. Srinivasan,* "Fuel Cells; Their Electrochemistry", McGraw Hill Book Company, **1969**.

[55] *C. H. Fabjan* and *M. Azizian,* Ber. Bunsenges. phys. Chem. **80**, 560 (1976).

[56] *V. I. Luk'yanycheva* et al., Elektrokhimiya **7**, 1287 (1971).

[57] *D. C. Johnson* and *S. Bruckenstein,* Anal. Chem. **43**, 1313 (1971).

[58] *A. J. Bard,* "Encyclopedia of Electrochemistry of the Elements", vol. II, M. Dekker, Inc., New York, **1974**.

[59] *M. D. Gol'dshtein* et al., Elektrokhimiya **10**, 1533 (1974).

[60] *A. Damjanovic* and *V. Brusic,* Electrochim. Acta **12**, 615 (1967).

[61] *A. Damjanovic* and *M. A. Genshaw,* Electrochim. Acta **15**, 1281 (1970).

[62] *A. Damjanovic, D. B. Sepa* and *M. V. Vojnovic,* Electrochim. Acta **24**, 887 (1979).

[63] *M. Paucirova, D. M. Drazic* and *A. Damjanovic,* Electrochim. Acta **18**, 945 (1973).

[64] *J. P. Hoare,* J. Electrochem. Soc. **112**, 602 (1965); *ibid.* **113**, 1163 (1966).

[65] *J. P. Hoare,* J. Electroanal. Chem. **30**, 15 (1971).

[66] *J. P. Hoare,* Electrochim. Acta **20**, 267 (1975).

[67] *L. N. Nekrasov* and *E. J. Krusheva,* Elektrokhimiya **3**, 677 (1967).

[68] *J. Marie,* thèse, Univ. de Paris VI, Paris, **1974**.

[69] *A. Damjanovic, A. Dey* and *J. O'M. Bockris,* Electrochim. Acta **11**, 791 (1966).

[70] *M. R. Tarasevich* et al., Elektrokhimiya **6**, 372, 376 (1970).

[71] *A. Damjanovic, M. A. Genshaw* and *J. O'M. Bockris,* J. Electrochem. Soc. **114**, 1107 (1967).

[72] *M. Appel,* thèse, Cons. Nat. des Arts et Métiers, Paris, **1974**.

[73] *J. O'M. Bockris* and *J. McHardy,* J. Electrochem. Soc. **120**, 61 (1973).

[74] *K. F. Blurton* and *E. McMullin,* Energy Convers. **7**, 141 (1969).

[75] *W. M. Vogel* and *J. T. Lundquist,* Am. Chem. Soc., Div. Fuel Chem. Prep. **13**, 44 (1969).

[76] *F. Bayer* and *C. Fabjan,* in ref. 53, pp. 220–235.

[77] *M. Voinov, D. Buchler* and *H. Tannenberger,* Proc. Symp. Electrocatal., M. W. Breiter, ed., Electrochem. Soc.: Princeton, N.J. **1974**, 268.

[78] *W. M. Vogel, J. T. Lundquist* and *A. Bradford,* Electrochim. Acta **17**, 1735 (1972).

current density at the thermodynamic equilibrium potential) is only in the range of 10^{-7}–10^{-5} A m^{-2}, which reflects the high value of the enthalpy of activation (for comparison, the other half cell reaction in the hydrogen/oxygen fuel cell, $H^+ + e^- \rightarrow \frac{1}{2}H_2$ has on platinum $i_o \approx 10$ Am^{-2}).

On platinum (and other platinum-like metals) the presence of oxide layers plays a predominant role in the mechanism of oxygen reduction. These oxides range from Pt(OH) at low potentials to PtO_2 at about 1.5 V vs. NHE. It has been shown that in acid[53-67] as well as in alkaline[68-82] solution, the presence of surface oxides decreases the rate of all reactions in Fig. 2, except the chemical decomposition (4). However, the rate of the direct reaction of oxygen to water (1) is decreased more than that of the reaction to peroxide (2). As a consequence, at low overpotentials, where oxides are present, a certain amount of hydrogen peroxide is produced, while at higher overpotentials, where the Pt-surface is reduced, the main reaction product is H_2O[70,84]. The difference in reaction mechanism on oxidized and reduced platinum electrodes is reflected in a dependence of the Tafel slope on overpotential[6,53,56,58,61,64]. However, the oxygen coverage of Pt surfaces is not only a function of overpotential, but also of time. Ageing of the surface oxides has influence on the reaction mechanism[84] in the sense that ageing increases the reaction rate.

These results can be summarized as follows[66].

Oxygen reduction on oxide free platinum occurs mainly via the 4-electron direct path, probably rate limited by dissociative adsorption of the oxygen molecule, the dissociation being induced by adsorption in the bridge form. On oxide covered Pt, on the other hand, an end-on adsorption prevails; the presence of oxygen atoms in the platinum lattice changes the electron distribution at the surface (by influencing the Fermi level), facilitating an adiabatic electron transfer to the adsorbed oxygen molecule. So, on Pt oxides the superoxide ion O_2^- is formed, causing the reduction to follow, at least partially, the 2 electron peroxide path. Whether or not the hydrogen peroxide formed in this path will be reduced further to H_2O is mainly determined by the level of impurities in the solution[53] and by the nature of the electrolyte used[19,80].

The other group VIII metals, Pd[58,74,85-87], Rh[88-92], Ir[93], Ru[94-96] and Os[97] show similar mechanisms for oxygen reduction as Pt. Of the group Ib metals, Au has a low exchange current density, $i_o = 1.3 \times 10^{-7}$ A m^{-2}[98], i.e. considerably lower than Pt. Due to the fact that Au has a completely filled d-orbital, the reaction product, at moderate overpotential, is exclusively H_2O_2.

Furthermore, the gold surface is oxide free in the potential region for oxygen reduction, which fact is responsible for its low activity in H_2O_2 reduction and decomposition.

Silver has a much higher exchange current density, $i_o = 10^{-4}$–10^{-5} A m^{-2}[99], but its use as an oxygen reduction electrocatalyst is very much hampered by the presence of silver oxides on the surface, especially in acid medium.

Carbon is an excellent electrode material for the reduction of oxygen to hydrogen peroxide, – the Berl cathode (i.e. graphite or active carbon in alkaline medium)[100] is almost reversible. However, H_2O_2 is the end product and is not reduced or decomposed[68,101-112]. So, although carbon electrodes can be used for the production of H_2O_2, they are not fit as oxygen electrodes in fuel cells. On the other hand, as said before, active carbon or graphite is commonly used as substrate material for oxygen electrodes, on which a catalyst, such as Pt, is dispersed. In this way, the cost of the electrode is very much decreased, although some specific oxygen reduction catalyst, such as Pt, is still necessary. Furthermore, the amount of dispersed catalyst cannot be reduced arbitrarily, because with low catalyst loadings on carbon, the carbon itself will begin to reduce oxygen resulting in high concentrations of H_2O_2 in the pores of the carbon particles. This process is very destructive and leads to a fast deterioriation of the electrode's performance.

For this reason it will be advantageous to have either another substrate material that costs about the same as carbon, but has a higher corrosion resistance, or another catalyst that has electrocatalytic properties comparable to those of platinum, but costs less (if necessary, it can then be used in higher loadings on carbon).

An example of the first alternative are the so called bronzes, non-stoichiometric compounds with formula M_xTO_3 ($0 < x < 1$, M is an alkali or alkaline earth metal and T a transition metal). Bronzes, especially tungsten bronzes, were for some time considered as good O_2 reduction electrocatalysts in their own right[53,54,113], but it was soon claimed that their catalytic activity had to be contributed to traces of platinum[114,115]. Even this is, however, a matter of dispute[116], just like the applicability of the bronzes for oxygen reduction[117-119].

---

[79] *H. R. Kunz* and *G. A. Kruver*, Electrochim. Acta **23**, 219 (1978).

[80] *V. I. Luk'yanycheva* et al., Elektrokhimiya **12**, 952 (1976); *ibid.* **13**, 506 (1977).

[81] *M. R. Tarasevich* and *V. A. Bogdanovskaya*, Elektrokhimiya **7**, 1072 (1971).

[82] *N. A. Urisson*, *G. V. Shteinberg* and *V. S. Bagotskii*, Elektrokhimiya **12**, 1635 (1976).

[83] *J. G. Norman*, Inorg. Chem. **16**, 1328 (1977).

[84] *V. G. Bagotskii*, Elektrokhimiya **6**, 1074 (1970); *ibid.* **7**, 1287 (1971); *ibid.* **12**, 267 (1975).

[85] *A. J. Appleby*, J. Electrochem. Soc. **117**, 1373 (1970).

[86] *A. Damjanovic* and *V. Brusic*, Electrochim. Acta **12**, 1171 (1967).

[87] *M. R. Tarasevich* and *V. S. Vilinskaya*, Elektrokhimiya **8**, 1489 (1972); *ibid.* **9**, 98 (1973); *ibid.* **9**, 1187 (1973).

[88] *S. Chernyshov* et al., Elektrokhimiya **5**, 435 (1969).

[89] *J. P. Hoare*, Electrochim. Acta **13**, 417 (1968).

[90] *A. J. Appleby*, J. Electroanal. Chem. **27**, 335 (1970).

[91] *D. S. Gnanamuthu* and *J. V. Petrocelli*, J. Electrochem. Soc. **114**, 1036 (1967).

[92] *K. A. Radyushkina* and *M. R. Tarasevich*, Elektrokhimiya **6**, 1352 (1970); *ibid.* **7**, 248 (1971).

[93] *A. J. Appleby*, J. Electroanal. Chem. **27**, 325 (1970).

[94] *L. D. Burke* and *T. D. O'Meara*, J. Chem. Soc. Faraday Tans. I, **68**, 839 (1972).

[95] *A. J. Appleby*, J. Electroanal. Chem. **27**, 335 (1970).

[96] *L. N. Nekrasov* and *E. I. Krusheva*, Elektrokhimiya **3**, 166 (1967).

[97] *A. J. Appleby*, J. Electrochem. Soc. **117**, 1157 (1970).

[98] *J. P. Hoare*, J. Electrochem. Soc. **110**, 245 (1963).

[99] *D. Sepa*, *M. Vajnovic* and *A. Damjanovic*, Electrochim. Acta **15**, 1355 (1970).

[100] *W. G. Berl*, Trans. Electrochem. Soc. **83**, 253 (1943).

[101] *E. Yeager* and *A. Kozawa*, ASTIA Rept. AD429248, **1964**.

[102] *M. O. Davies* et al., J. Electrochem. Soc. **106**, 56 (1959).

[103] *J. P. Hunt* and *H. Taube*, J. Am. Chem. Soc. **74**, 5999 (1952).

[104] *M. R. Tarasevich* et al., Elektrokhimiya **6**, 1130 (1970).

[105] *G. Bianchi*, Corros. Anti-Corros. **5**, 146 (1957).

[106] *E. Yeager* et al., Electrochim. Acta **9**, 1057 (1964).

[107] *I. Morcos* and *E. Yeager*, Electrochim. Acta **15**, 953 (1970).

[108] *J. B. Donnet* and *A. Sevenster*, Chimie et Industrie – Gênre chimique **105**, 23 (1972).

[109] *M. Appel* and *A. J. Appleby*, Electrochim. Acta **23**, 1243 (1978).

[110] *A. J. Appleby* and *J. Marie*, C.R. Acad. Sc. Paris Série C **285**, 29 (1977).

[111] *I. A. Legenchenko* et al., Russ. J. Phys. Chem. **51**, 56 (1977).

[112] *G. V. Shteinberg* et al., Elektrokhimiya **15**, 527 (1979).

[113] *D. Sepa*, *A. Damjanovic* and *J. O'M. Bockris*, Elektrochim. Acta **12**, 746 (1967).

[114] *R. D. Armstrong*, *A. F. Douglas* and *D. E. Williams*, Energy Conversion **11**, 7 (1971).

[115] *J. H. Fishman* et al., Electrochim. Acta **14**, 1314 (1969).

[116] *J. P. Randin*, J. Electrochem. Soc. **121**, 1029 (1974).

[117] *J. McHardy*, J. Electrochem. Soc. **122**, 742 (1975).

[118] *E. I. Krusheva* et al., Collect. Czech. Chem. Commun. **49**, 3298 (1975).

[119] *W. N. Cathey*, *L. J. Nicks* and *D. J. Bauer*, U.S. Bur. Mines, Rep. Invest. **1979**, RI 8341.

The second alternative mentioned, i.e. using cheaper electrocatalysts than Pt in higher loadings on carbon, presents itself if we look at the way nature itself handles oxygen. In biochemical systems, oxygen is transported and reduced with the help of enzymes with a porphine-like structure – transition metal ions, chelated in a square planar complex by a macrocyclic organic molecule containing four nitrogen atoms as ligands (Fig. 7). Examples are heme, which is a reversible oxygen binder, and the cytochromes, involved in the reduction of oxygen. For electrochemical applications, work has been done mainly on phthalocyanines, porphyrins and tetraazaannulene, which will be the subject of the next section.

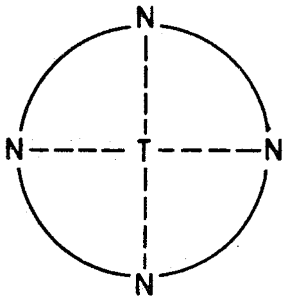


Fig. 7. Schematic of macrocyclic organic metal complexes (T = transition metal).

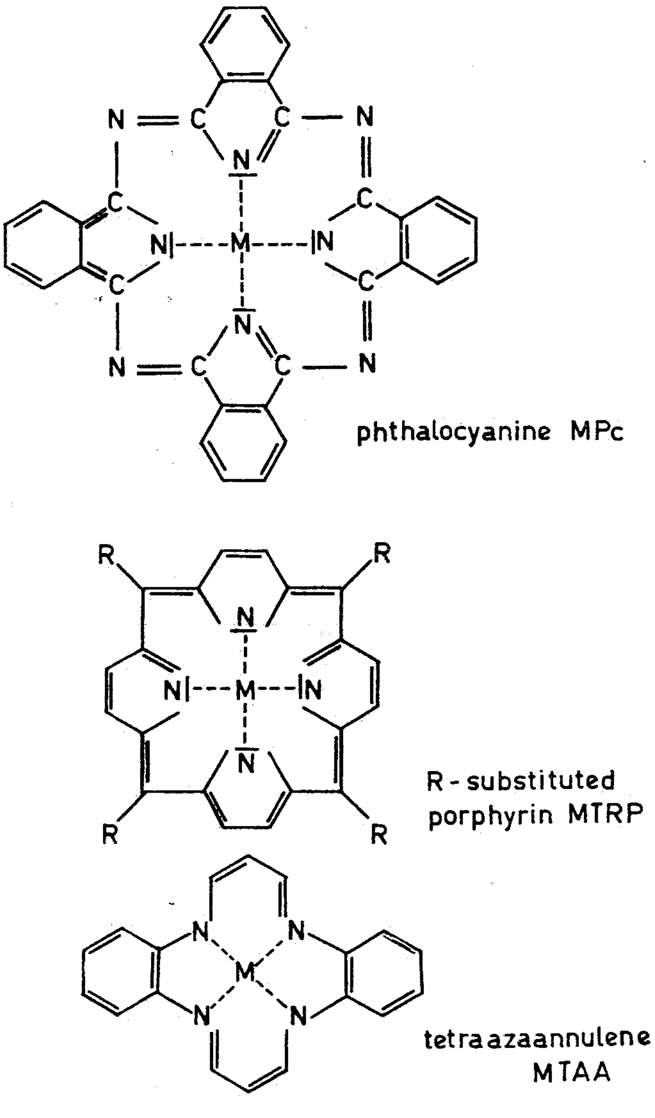


Fig. 8. Structural formulae of some macrocyclic organic metal complexes.

5. Macrocyclic organic complexes

Structural formulae of metal phthalocyanine (MPc), tetra-substituted metal porphyrin (MTRP) and dihydrodibenzo tetraazaannulene (MTAA) are given in Fig. 8. The similarity of their structure with that of heme, chlorophyll and cytochromes is striking, and for that reason these organic dyestuffs are expected to have some kind of reactivity towards oxygen. Cobalt phthalocyanine was first mentioned as an oxygen reduction electrocatalyst by Jasinski in 1965[120]. Since then, the number of publications on this type of electrocatalysts has roughly followed the ups and downs in general fuel cell research, with peaks in the years 1968 and 1978 and a valley around 1972 – the peaks reflecting the NASA space program during the sixties and the apparition of the energy crisis in the early seventies, respectively.

In the first period, the main research effort was directed towards a qualitative appraisal of the different factors influencing the electrocatalytic activity of macrocyclic organic metal complexes. The results of these investigations indicate that modifications of the general structure (given in Fig. 7) have a greater effect on the activity, the nearer they are to the center of the molecule. So, changing the central metal atom has a much greater effect than substitutions on the outer ring structure. The various factors, affecting the electrocatalytic properties, in the order of their importance, are given below.

(i) *the central metal atom.* All results clearly indicate that complexes of iron (as Fe(II) or Fe(III)) and cobalt (as Co(II)) have the highest electrocatalytical activity[120-131], although for some complexes Fe is best, for others Co. The manganese complex has a rather high initial activity[125,128-130], but its stability in alkaline and acid medium is poor. A large number of metals have been tested, such as Cu, Ni[121-131], Al, Cr, Sn, uranyl ion, Ga, Sb, Na, Zn, Ag[131] and Ru, Pd, Pt, Zn and vanadyl ion[130], but their activity is much less than that of the Fe- and Co-complexes.

(ii) *the nature of the ligands.* Chelates with four nitrogen ligands show a high activity and usually a reasonable stability. N_2O_2-, O_4-, N_2S_2- and S_4-chelates have been tested as well[121,122] but their activity as well as their stability are poor.

(iii) *the macrocycle structure.* The highest activity is shown by complexes of TAA, followed by phthalocyanine and tetraazaporphyrins on an equal footing[121,126-128]. Tetraphenylporphyrin is a poor electrocatalyst[121,128], unless the phenyl para position is substituted with an electrondonating

---

[120] *R. Jasinski,* J. Electrochem. Soc. **112**, 526 (1965).

[121] *H. Jahnke, M. Schönborn* and *G. Zimmermann,* Topics in Current Chemistry **61**, 133–181 (1976); Photosynthetic Oxygen Evolution, H. Metzner, ed., Academic Press, London, **1977**, p. 439.

[122] *H. Jahnke* and *M. Schönborn,* in ref. 53.

[123] *M. Savy* et al., Electrochim. Acta **18**, 191 (1973).

[124] *H. Alt* et al., J. Electroanal. Chem. **31**, 19 (1971).

[125] *F. Beck,* Ber. Bunsenges. phys. Chem. **77**, 353 (1973).

[126] *H. Alt, H. Binder* and *G. Sandstede,* J. Catal. **28**, 8 (1973).

[127] *S. I. Andruseva, K. A. Radyushkina* and *M. R. Tarasevich,* Sov. J. Electrochem. **13**, 412 (1977).

[128] *M. R. Tarasevich, K. A. Radyushkina* and *S. I. Andruseva,* Bioelectrochim. Bioenerg. **4**, 18 (1977).

[129] *H. Behret, W. Clauberg* and *G. Sandstede,* Ber. Bunsenges. phys. Chem. **83**, 139 (1979).

[130] *J. A. R. van Veen* and *C. Visser,* Electrochim. Acta **24**, 921 (1979).

[131] *R. J. Brodd, V. Z. Leger, R. F. Scarr* and *A. Kozawa,* in: "Electrocatalysis on Non-Metallic Surfaces", NBS Spec. Publ. **455**, 253 (1976).

group, such as methoxy $-OCH_3$[126]. However, the influence of the ring structure and substituents on the electrocatalytic activity is much less than that of central metal atom and ligands.

(iv) *polymerization,* especially of phthalocyanines, increases the activity significantly – probably by increasing the electric conductivity[121,127,128,132-134].

(v) in the case of electrocatalyst dispersed on carbon, the *nature of the carbon surface groups* plays a significant role[121,130,135]. Substrates with basic surface groups give electrocatalysts with higher activity than those with neutral or acidic surface[130]. This, however, applies only when the loading of the catalyst on the substrate is of the order of one monolayer. Catalyst performance can be improved by thermal pretreatment of the carbon/catalyst mass in inert atmosphere[120,130,136]. This treatment enhances the electrocatalytic activity as well as the stability of the complex. Since the instability of the complexes is caused by demetallation and ring cleavage[137,138] the effect of thermal treatment can be understood as a rearrangement of the catalyst molecules over the carbon surface, stabilizing the complex by providing it with a basic surface group as an extra ligand for the metal atom.

The observations quoted above all point toward the central metal atom as the catalytically active site. Obviously, the metal atom has a strong interaction with oxygen, while all other factors mentioned only influence the electron density on the metal, i.e. determine the ligand field strength.

It is therefore logical to start an explanation of the electrocatalytic behaviour of macrocyclic organic metal complexes by a careful examination of the ligand field and its effect on the atomic orbitals of the metal atom[121,140].

In section 2 we have seen that, on transition metal electrocatalysts, and end-on interaction of oxygen with the metal is most likely, although the formation of a side-on complex has been considered as well[126]. The interaction can be described as the result of a bonding overlap of π_u and d_{z^2}: $\sigma(\pi_u \rightarrow d_{z^2})$ and a backbonding overlap of $\pi_g{}^*$ with the degenerate $d_{xz,yz}$-orbitals: $\pi(d_{xz,yz} \rightarrow \pi_g{}^*)$ (see Fig. 6).

Thus the interaction will be strongest with transition metal atoms having an unoccupied d_{z^2}-orbital and occupied $d_{xz,yz}$-orbitals. Now, the presence of a ligand field strongly influences the energy levels of the metals d-orbitals. The relative positions of these levels are sketched, in a rough approximation, in Fig. 9 for three symmetries of the ligand field[139]. From this it can be seen that in the tetragonal configuration Mn^{2+}, Fe^{2+} and Co^{2+} fulfill the condition of filled $d_{xz,yz}$ and empty or partially filled d_{z^2}-orbitals, while in the complexes of Ni^{2+} and Cu^{2+} the d_{z^2}-orbital will be fully occupied. The tetragonal symmetry requires a fifth ligand, which could be furnished by either basic surface groups of the substrate or by the meso nitrogen atoms in underlying molecules (for tetraazaporphyrins and phthalocyanines) or by oxygen or water molecules incorporated in the electrocatalyst lattice.

In this picture a qualitative explanation can be given of the large difference between the electrocatalytic activities of Mn^{2+}-, Fe^{2+}- and Co^{2+}-complexes on one hand and those with Ni^{2+} and Cu^{2+} as central metal ion on the other, because the latter have, in a tetragonal ligand field, an occupied d_{z^2} orbital. One can also envisage what happens when an oxygen molecule approaches the central metal ion. Because of the occupancy of the d-orbitals, the oxygen will be able to enter into a weak chemisorption with the tetragonal complex, involving the bonding and back-bonding interactions mentioned before.

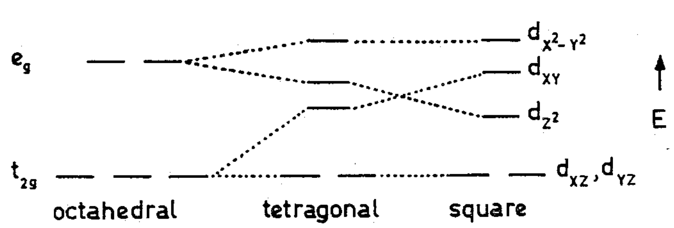


Fig. 9. Relative energy of transition metal d-orbitals in various ligand symmetries.

This means that, according to the Franck-Condon rule, the condition for adiabatic (inner-shell) electron transfer is fulfilled – the energies of electron donor and acceptor states being equal. And this is really all that electrocatalysis is about – matching the electronic energy levels of the electron donating and accepting species.

Once the chemisorption is accomplished, the electron transition probability, i.e. the electrocatalytic activity as measured by the current density at given electrode potential, will be determined by the average electron density at the electrocatalytically active site, the metal atom. This calls for a good electronic conductivity of the catalyst layer, electrondonating substituents on the ring structure, a large conjugated π-electron system in the molecule etc., all factors which have been shown to enhance the catalytic activity. This picture is, however, by no means complete. There are, in the first place, not only the ligand field interactions to consider[140]. For one thing, the oxygen molecule itself will, on its approach to the active site, act as a sixth ligand, thereby influencing the symmetry of the field; but solvent species as H_2O and OH^- will do the same. So, there will be a certain amount of elastic coupling of depolarizer-catalyst, depolarizer-solvent species and solvent species-catalyst interactions. Furthermore, we will have to take into account electrostatic interactions (the electrode is highly electrically charged), electron affinities and ionization energies of depolarizer and active site and magnetic coupling.

Nevertheless, it has been shown that it is possible to apply the qualitative data to a quantummechanical model describing the electrocatalysis of oxygen reduction by phthalocyanines[132,140-143]. This model, which is a second order

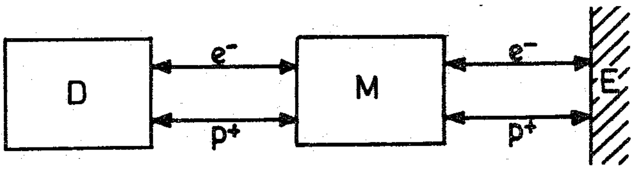


Fig. 10. Model describing electrocatalysis of oxygen reduction by a mediator.
E = electrode surface, M = mediator, D = depolarizer (viz. oxygen), e^- = electron, p^+ = hole.

---

[132] *A. J. Appleby, J. Fleisch* and *M. Savy,* J. Catalysis **44**, 281 (1976)

[133] *M. Musilova, J. Mrha* and *J. Jindra,* J. Appl. Electrochem. **3**, 213 (1973).

[134] *L. J. Johansson, J. Mrha* and *R. Larsson,* Electrochim. Acta **18**, 255 (1973).

[135] *A. J. Appleby* and *M. Savy,* Electrochim. Acta **21**, 567 (1976).

[136] *H. G. Jahnke, M. F. Schönborn* and *G. Zimmermann,* Proc. Symp. Electrocatalysis, M. F. Breiter, ed. (1974).

[137] *P. O'Carra,* in: Porphyrins and Metallophorphyrins, K. M. Smith, ed., Elsevier, Amsterdam (1975).

[138] *B. D. Berezin* and *G. V. Sennikova,* Kinet. Catal. **9**, 528 (1968).

[139] *R. B. Heslop* and *P. L. Robinson,* Inorganic Chemistry, Elsevier, Amsterdam (1967).

[140] *M. Savy, P. Andro, C. Bernard* and *G. Magner,* Electrochim. Acta **18**, 191 (1973).

[141] *M. Savy, P. Andro* and *C. Bernard,* Electrochim. Acta **19**, 403 (1974).

[142] *M. Savy, C. Bernard* and *G. Magner,* Electrochim. Acta **20**, 383 (1975).

[143] *J. Ulstrup,* J. Electroanal. Chem. **79**, 191 (1971).

modification of the (first order) Marcus-Levich theory of electron transfer, is shown in Fig. 10. The catalyst acts as a mediator between the electrode and depolarizer (viz. oxygen) in the transfer of electrons and/or holes.

On this basis, an expression is derived for the transition probability as a function of the number and energy of electronic levels contributing to the transition and from this an expression for the Tafel slope is inferred. Comparison with experimentally determined Tafel slopes indicates that cathodic reduction of oxygen on phthalocyanine electrodes occurs via a pull-push mechanism, where first an electron is transferred from catalyst to oxygen, after which the hole in the catalyst is filled by an electrontransfer from the electrode. For FePc the latter is the rate determining step, for CoPc the former.

This description is in accordance with the experimentally found correlation between the first oxidation potential of the MPc and its electrocatalytical activity[144-146].

A similar mechanism has been proposed, based on purely electrochemical experiments and named redox catalysis[147,148].

Furthermore, the presence of Fe(III) in a FePc thin film, a prerequisite for the description to be valid, was demonstrated with Mössbauer spectroscopy[132]; however, the usefulness of this type of measurements is uncertain (see section 3).

However, even if an accurate description of the chemisorption of oxygen on organic metal complexes were available, this would be only a first step towards the elucidation of the reduction mechanism, because the chemisorption could lead to a direct reaction to water as well as to a hydrogen peroxide reaction path.

It has even been claimed that metal phthalocyanines only catalyze the chemical decomposition of H_2O_2 and do not play a significant role in the electrocatalysis itself[149]. This would also explain the close correlation between electrocatalytic activity and catalase activity, found experimentally[130]. On the other hand, it certainly does not explain the current-potential relation found. So, it is vital that knowledge of the exact reaction path is obtained (see Fig. 2): reaction (1) or reaction (2) and (3) or reaction (2) and (4). This means that experiments with the RRDE (see section 3) are necessary. Then, however, the question of electrode preparation arises.

There are a number of fundamentally different methods of electrode preparation. First it is possible to use water soluble complexes, that are adsorbed reversibly, such as tetrasulphonated phthalocyanine[33,150,151], tetra (N-methyl pyridyl) porphine[152,153] or heme[154,155] or water insoluble compounds, that are irreversibly adsorbed[34,156]. A serious drawback of these methods is that the state of the catalyst is largely unknown and may vary in time (in the case of irreversible adsorption).

An other possible method is chemical modification of electrodes (CME), where the catalyst is chemically bound to a substrate such as glassy carbon. It has been shown to be possible to prepare porphyrin electrodes in this way[157] but as yet little or nothing is known about their performance as oxygen electrodes. However, in this case a stable, well defined electrode surface would be available, so that the study of oxygen reduction on these surfaces could be undertaken with confidence.

The methods most frequently used are those of precipitation, either directly on the disk[129,158] or on active carbon, which is then pasted onto a disk[135,127,128,159,160].

Thus, the substrate is covered with a thin layer of the catalyst, whose crystallinity is undetermined, while the coverage varies over the surface[158]. So, the electrocatalytic surface can not be described exactly and results obtained with these electrodes are extremely difficult to interpret and can probably not be generalized.

For instance, general trends concerning the activity of the various electrocatalysts are the same throughout the available literature, while the proportion of H_2O to H_2O_2 in the reaction product varies from almost zero to practically infinity. This is undoubtedly due to the different, in most cases ill-defined, preparation procedures used by the various authors.

In this context it must be emphasized that, whenever there is a bulk phase of the organic metal complexes (as is virtually always the case, except when CME's are used), their semiconductor properties must be taken into account. As a consequence, not only the surface must be well defined, but the bulk phase as well. A preparation method that satisfies this condition is vacuum deposition of the catalyst onto the substrate[142] – this method has however to our knowledge not been applied to the RRDE, where it should prove most fruitful. For this reason in our laboratory thin vacuum deposited films of FePc and CoPc are now being investigated, using electrochemical techniques, like the RRDE, impedance spectrometry etc., and ellipsometry. Our results, which will be published in due course, indicate that indeed bulk properties of the films play a significant role in the mechanism of oxygen reduction. One of the processes involved is the diffusion and chemisorption of oxygen in the bulk of the catalyst[141,160]:

$$O_2 \text{ (surface)} \rightarrow O_2 \text{ (bulk)}$$

$$O_2 \text{ (bulk)} + \text{Fe}^{\text{III}}\text{Pc} - O_2^- \text{ (bulk)} \rightarrow$$
$$\rightarrow O_2^* \ldots \text{Fe}^{\text{III}}\text{Pc} - O_2^- \text{ (bulk)}$$

where O_2^* is an activated oxygen molecule.

By the transfer of electrons and holes through the film similar structures with activated oxygen appear in the semiconductor-electrolyte interphase, thereby creating surface states, i.e. sites that are activated and will play a pronounced role in any reaction, e.g. oxygen reduction, that occurs in the interphase.

The mechanism described here was inferred from the fact that, with Mössbauer spectroscopy, Fe^{III} was found in the bulk of the electrocatalyst and that the activity of the catalyst was higher for higher proportions of Fe^{III}.

---

[144] *J. P. Randin*, Electrochim. Acta **19**, 83 (1974).

[145] *H. Meier*, *W. Albrecht*, *U. Tschirwitz* and *E. Zimmerhackl*, Ber. Bunsenges. phys. Chem. **77**, 843 (1973).

[146] *J. Manassen* and *A. Bar-Ilan*, J. Catalysis **17**, 86 (1970).

[147] *F. Beck*, Ber. Bunsenges. phys. Chem. **77**, 353 (1973).

[148] *F. Beck*, J. Appl. Electrochem. **7**, 239 (1977).

[149] *A. Tseung*, Conf. Proc., Fuel Cell Catalysts Workshop, E.P.R.I. S.R.-13, 89 (1975).

[150] *J. Zagal*, *R. K. Sen* and *E. Yeager*, J. Electroanal. Chem. **83**, 207 (1977).

[151] *B. Z. Nikolic*, *R. R. Adric* and *E. B. Yeager*, J. Electroanal. Chem. **103**, 281 (1979).

[152] *T. Kuwana* et al., J. Electroanal. Chem. **88**, 299 (1978).

[153] *N. Kobayashi* et al., J. Electroanal. Chem. **101**, 269 (1979).

[154] *M. Brezina*, *W. Khalil*, *J. Koryta* and *M. Musilova*, J. Electroanal. Chem. **77**, 237 (1977).

[155] *C. F. Colpin* and *H. Swolford*, Anal. Chem. **50**, 920 (1978).

[156] *L. Müller* and *H. Moritz*, Z. phys. Chem. Leipzig **259**, 331 (1978).

[157] *J. C. Lennox* and *R. W. Murray*, J. Electroanal. Chem. **78**, 395 (1977).

[158] *H. Behret*, *W. Clauberg* and *G. Sandstede*, J. Electroanal. Chem. **74**, 393 (1976); Ber. Bunsenges. phys. Chem. **81**, 54 (1977); *ibid.* **83**, 139 (1979); Electrochim. Acta **23**, 1023 (1978).

[159] *V. S. Bagotskii*, *M. R. Tarasevich*, *K. A. Radyuskhina*, *O. A. Levina* and *S. I. Andrusyova*, J. Power Sources **2**, 223 (1977/78).

[160] *A. J. Appleby* and *M. Savy*, in: "Electrocatalysis on non-metallic Surfaces", N.B.S. Spec. Publ. **455**, 241 (1975).

The description is, however, by no means complete; our ellipsometric measurements indicate that the presence of OH^- and H_2O influence the electric and dielectric properties of the film dramatically – which has also been found in a study of the transmission spectra of dry and wetted films[160]. So, again, results of non-in-situ-measurements must be treated with care.

Finally, the possible use of macrocyclic organic metal complexes in solar cells must be mentioned[161]. In photochemical reactions, their semiconductor properties (especially the band gap and the presence of surface states) play a more obvious role and have therefore been taken into account from the beginning. However, if the catalysts have to be regarded as semiconductors in the oxidation of water, they surely ought to be treated the same way in the inverse reaction, the reduction of oxygen.

6. Concluding remarks

In the search for suitable catalysts for the cathodic reduction of oxygen, macrocyclic organic metal complexes play a significant role. When the prime interest lays in a description of the interaction between oxygen and one catalyst molecule (or a small number of them), the best approach would be to investigate chemically modified electrodes, where isolated catalyst molecules are bound to the substrate surface.
When on the other hand, thin layers of the catalyst are used, so that there is a bulk phase, the description should be adapted to include the semiconductor properties of the catalyst bulk phase. This fact has not been properly taken into account until now, probably because the methods used in electrode preparation led, in most cases, to ill-defined electrode surfaces.
As indicated in this paper, only vacuum deposited catalyst films give well defined surfaces and consequently should be used to obtain generally applicable results. These results can then be used to develop a description of the electrocatalytic behaviour of macrocyclic organic metal complexes in which the interaction of oxygen with the catalyst on a molecular level as well as the influence of the semiconductor properties of the bulk catalyst are incorporated.

Acknowledgement

This work has been carried out with financial support from the Netherlands Organisation of Pure Research (ZWO).

---

[161] *Fu-Ren Fan* and *L. R. Faulkner*, J. Am. Chem. Soc. **101**, 4779 (1979).