

Electrocatalysis of cathodic oxygen reduction by metal phthalocyanines. Part IV. Iron phthalocyanine as electrocatalyst: mechanism

Citation for published version (APA):

Brink, van den, F. T. B. J., Visscher, W., & Barendrecht, E. (1984). Electrocatalysis of cathodic oxygen reduction by metal phthalocyanines. Part IV. Iron phthalocyanine as electrocatalyst: mechanism. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, 175(1-2), 279-289. [https://doi.org/10.1016/S0022-0728\(84\)80362-9](https://doi.org/10.1016/S0022-0728(84)80362-9)

DOI:

[10.1016/S0022-0728\(84\)80362-9](https://doi.org/10.1016/S0022-0728(84)80362-9)

Document status and date:

Published: 01/01/1984

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.

ELECTROCATALYSIS OF CATHODIC OXYGEN REDUCTION BY METAL PHTHALOCYANINES

PART IV. IRON PHTHALOCYANINE AS ELECTROCATALYST: MECHANISM

F. VAN DEN BRINK *, W. VISSCHER and E. BARENDRECHT

Laboratory of Electrochemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven (The Netherlands)

(Received 23rd November 1983; in revised form 30th March 1984)

ABSTRACT

The kinetics of oxygen reduction on thick iron phthalocyanine films as reported in Part III of this series are explained in terms of a redox mechanism. In this mechanism, oxygen is adsorbed on a reduced Fe site, which transfers an electron to give a $\text{Fe}^{\text{III}}\text{-O}_2^-$ complex. This complex gives, in a series of fast steps, the reduction products OH^- and HO_2^- . Such a process is very sensitive to the value of the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ redox potential in the N_4 -complex. Arguments are given that the kinetic results lead to a value of $E^\circ = 0.67$ V vs. RHE.

At high overpotential, an adsorption/desorption process occurs which "opens up" the film and makes an extra number of active sites available for oxygen reduction. This process is discussed in terms of the spin state of the Fe atom in the N_4 -complex as a function of the external electric field.

INTRODUCTION AND SUMMARY OF KINETICS

In Part III [1] we presented the results pertaining to the kinetics of the electrocatalysis of oxygen reduction by iron phthalocyanine (FePc). Using kinetic techniques (RRDE), we found the dependence of the pertinent rate constants on electrode potential. The kinetic description was expanded with the results of surface-sensitive techniques, viz. ac-impedance measurements and ellipsometry. In this paper we will try to give a mechanistic description and show that the results for FePc can be explained by a mechanism which is very similar to that which we proposed for the electrocatalysis of oxygen reduction by cobalt phthalocyanine [2]. It was shown [1] that, on FePc film electrodes, in 1 M KOH, oxygen is almost exclusively reduced to OH^- , i.e. $k_1 \gg k_2^f$ (see Fig. 1). Over the whole potential range investigated, a first-order dependence of the reaction rate in the oxygen concentration is found.

* Present address: DSM Central Laboratory, Department of Catalysis, P.O. Box 18, 6160 MD Geleen, The Netherlands.

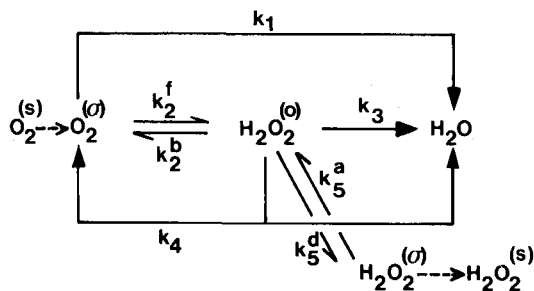


Fig. 1. Reactions involved in cathodic oxygen reduction on FePc. Superscripts refer to in bulk (s), in reaction plane (σ) and at electrode surface (o).

The kinetic results for FePc films which have already been polarized cathodically are summarized in Fig. 2. At high potential a Tafel slope of -120 mV is found for all the rate constants (k_1 , k_2^f , k_3), then at low potential $\log k$ becomes more or less independent of potential. Between 0.3 and 0.5 V a transition occurs, where the k 's start to increase again, with Tafel slopes of -120 mV or more negative, and finally level off again.

The transition mentioned above is also reflected by the two potential regions of different activation energy, as found from the Arrhenius plot of current density as a

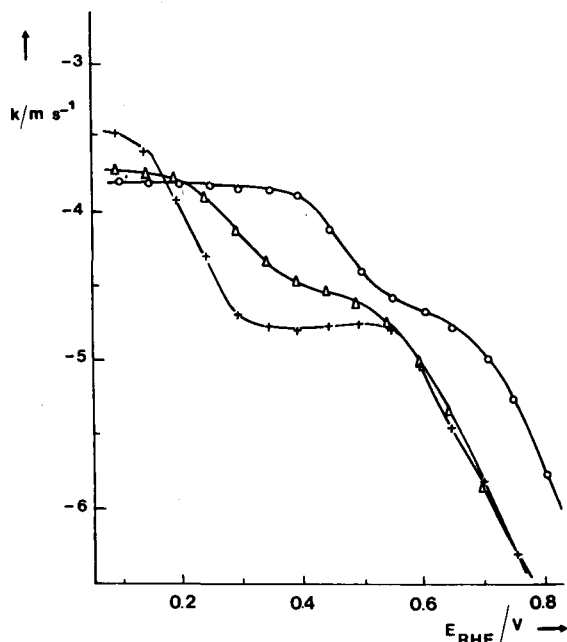


Fig. 2. Oxygen reduction rate constants as functions of the potential for FePc films at 298 K: (O) $0.1 \times k_1$; (+) k_2^f ; (Δ) k_3 .

function of temperature; for $0.6 \text{ V} < E < 0.7 \text{ V}$, $\Delta H_{\text{act}}^{\circ} \approx 38 \text{ kJ mol}^{-1}$ (0.39 eV) is found and for $E \leq 0.4 \text{ V}$, $\Delta H_{\text{act}}^{\circ} \approx 52 \text{ kJ mol}^{-1}$ (0.54 eV). Furthermore, this transition is manifest in ellipsometric results where the optical changes at 0.4–0.5 V were attributed, using an effective medium model, to a change from a hydrophobic to a hydrophilic character; moreover, ac-impedance measurements reveal surface states at 0.82, 0.67 and at ca. 0.4 V vs. RHE.

In particular, ac-impedance measurements can be interpreted if the FePc films are regarded as classical p-type semiconductors, in which the transport of holes is very much faster than that of electrons. In the potential range where oxygen reduction occurs, the main contribution to conduction is by the slow electrons, which leads to a considerable influence of ohmic resistance on the kinetics.

However, cathodic polarization of the film in 1 M KOH leads to a decrease of the ohmic resistance, which, from the ellipsometric data, could be explained by absorption of the electrolyte solution in the film, giving a decrease of the film grain boundary resistance. This process can also be seen from the impedance and conductivity data, which show a surface process as mentioned above. As for the slow surface processes at 0.82 and 0.67 V vs. RHE, the number of surface states at 0.82 V is estimated to be $1.5 \times 10^{-6} \text{ mol m}^{-2}$, implying that some 10% of the surface Pc molecules are involved.

So, for a mechanistic description, we have the following kinetic features to explain:

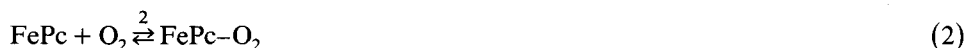
- (1) the surface states at 0.82, 0.67 and ca. 0.4 V vs. RHE as found with impedance measurements;
- (2) the mechanistic transition between 0.3 and 0.5 V vs. RHE; and
- (3) the similar Tafel behaviour of the rate constants of the direct ($\text{O}_2 \rightarrow \text{H}_2\text{O}$) and the consecutive ($\text{O}_2 \rightarrow \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O}$) reaction pathways.

MECHANISM FOR OXYGEN REDUCTION ON FePc

The Tafel behaviour of the rate constants for oxygen and hydrogen peroxide reduction on FePc with the -120 mV slope at low overpotential, followed by their levelling-off at higher overpotential is indicative of activation of oxygen by a one-electron transfer on the active sites, the number of which is rate-limiting. Furthermore, the parallelism between the kinetics and the surface processes observed indicates that the redox state of the surface is another important factor: at the potential where the Tafel slopes start to increase, a surface state is detected by capacitance measurements. Therefore, the situation is to some extent similar to that with CoPc [2]. There, our data could be explained by the assumption of a redox catalysis mechanism as originally proposed by Beck [3,4]. Such a mechanism is also in accordance with other data, such as the correlation between the redox potential of the central metal atom in the N_4 -complex and its electrocatalytic activity [5].

So, for the oxygen reduction on FePc, we assume that the redox character originates from the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple in the macrocyclic ligand; the oxygen molecule is expected to adsorb onto a Fe^{2+} site and oxidize it to the Fe^{3+} state. The

choice of this particular redox couple will be discussed later. The reaction sequence is then:



For such a scheme, the rate equation can be derived in a similar way to that given in Part II [2]:

$$\frac{i}{nF} = \frac{k_2[\text{O}_2]s}{1 + \exp f\eta_1 + (k_2[\text{O}_2]/k_1^\circ) e^{\alpha_1 f\eta_1}} \quad (4)$$

where the k 's represent the rate constants of the elementary reactions, s is the number of active sites, and $f = F/RT$. The Tafel slope predicted by this rate equation is

$$b/V = -0.059 \frac{1 + \exp f\eta_1 + (k_2[\text{O}_2]/k_1^\circ) \exp \alpha_1 f\eta_1}{\exp f\eta_1 + \alpha_1 (k_2[\text{O}_2]/k_1^\circ) \exp \alpha_1 f\eta_1} \quad (5)$$

For small values of $|\eta_1|$ and not too small values of the characteristic parameter $k_2[\text{O}_2]/k_1^\circ$ (i.e. ≥ 10), -120 mV is found (for $\alpha_1 = 0.5$), while for $\eta_1 \ll 0$ the slope approaches $-\infty$ for all values of $k_2[\text{O}_2]/k_1^\circ$. The reaction order in O_2 is

$$p = d \log i / d \log [\text{O}_2]$$

With eqn. (4) this gives

$$p = 1 - \frac{(k_2/k_1^\circ)[\text{O}_2] \exp \alpha_1 f\eta_1}{1 + \exp f\eta_1 + (k_2/k_1^\circ)[\text{O}_2] \exp \alpha_1 f\eta_1} \quad (6)$$

Figure 3 gives a calculated plot for p as a function of η_1 for a series of values of $k_2[\text{O}_2]/k_1^\circ$. It is seen that if the ratio $k_2[\text{O}_2]/k_1^\circ$ is large, a rather wide potential region around $\eta_1 \approx 0$ is predicted where the order in the oxygen concentration is considerably less than 1, but for $k_2[\text{O}_2]/k_1^\circ \leq 10$, the order in O_2 will be 1, independent of η_1 .

So, our experimental result that the order in oxygen is 1, while the Tafel slope is -120 mV for small $|\eta|$ and $-\infty$ for $\eta \ll 0$ means that $k_2[\text{O}_2]/k_1^\circ \approx 10$, i.e. that, except for $\eta_1 \geq 0.2$ V, the adsorption of oxygen on a reduced site is the rate-determining step. The transition from $b = -120$ mV to $b \rightarrow \infty$ in the high potential region k_1 occurs at ca. 0.7 V. Also, a surface process was found at $E \approx 0.67$ V. Therefore, the standard potential of reaction (1) can be identified as $E_1^\circ \approx 0.67$ V.

Finally, we know that ca. 90% of the products are H_2O and ca. 10% H_2O_2 . Thus,

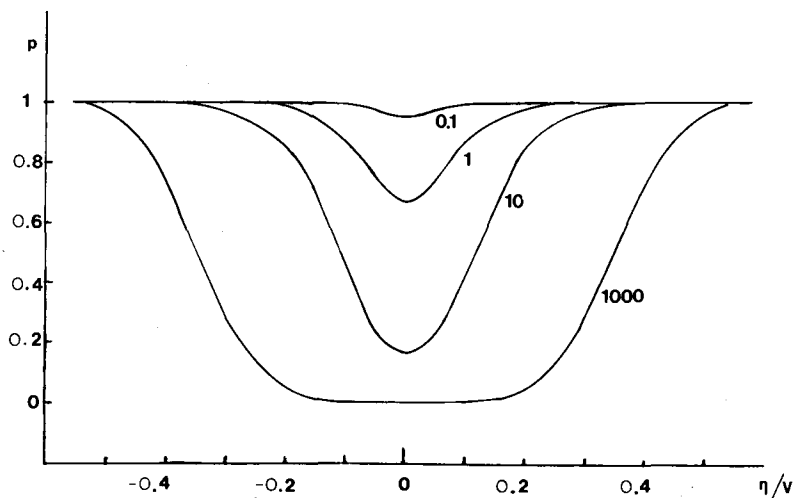


Fig. 3. Reaction order (p) in oxygen concentration for kinetic equation (4) as a function of the overpotential for reaction (1). Parameter: $(k_2[\text{O}_2]/k_1^\circ)$.

if x is the fraction of the complex FePc-O_2 which is reduced to H_2O , we find

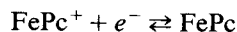
$$k_1 = \frac{xk_2s}{1 + \exp f\eta_1 + (k_2[\text{O}_2]/k_1^\circ) \exp \alpha_1 f\eta_1} \quad (7a)$$

$$k_2^f = \frac{(1-x)k_2s}{1 + \exp f\eta_1 + (k_2[\text{O}_2]/k_1^\circ) \exp \alpha_1 f\eta_1} \quad (7b)$$

Knowing that $E_1^\circ \approx 0.67$ V and that the corresponding surface process has a characteristic frequency of the order of 10^3 s $^{-1}$ [1], we find that k_2 must be in the range 100–1000 m 3 mol $^{-1}$ s $^{-1}$. From the (almost) potential-independent parts of k_2^f and k_1 , at $E \approx 0.6$ V, we find from Fig. 2 that $xk_2s \approx 2.5 \times 10^{-4}$ m s $^{-1}$ and $(1-x)k_2s \approx 1.6 \times 10^{-5}$ m s $^{-1}$, so $x \approx 0.94$ and $k_2s \approx 2.7 \times 10^{-4}$ m s $^{-1}$.

With $100 \leq k_2, k_3 \leq 1000$ m 3 mol $^{-1}$ s $^{-1}$, we find that $s \approx 10^{-7}$ – 10^{-6} mol m $^{-2}$. This result is in keeping with the finding [1] that the number of surface states responsible for the process at 0.67 V is of the order $N_{ss}(0.67 \text{ V}) \leq 2 \times 10^{-7}$ mol m $^{-2}$.

For the rate constant of the reduction of hydrogen peroxide, k_3 , a potential dependence almost identical to that of k_2^f is found (cf. Fig. 2). It therefore seems reasonable to postulate a similar mechanism for the HO_2^- reduction:



and so the overall rate constant k_3 is given by

$$k_3 = \frac{k_3 s}{1 + \exp f \eta_1 + (k_3 [HO_2^-] / k_1^o) \exp \alpha_1 f \eta_1} \quad (10)$$

The value of k_3 is, like that of k_2 , of the order of 10^2 – 10^3 $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$, as judged from the potential dependence, and again $s \approx 10^{-7} \text{mol m}^{-2}$ is found.

Summarizing, we have found that, for low overpotential, i.e. for $E \geq 0.5$ V vs. RHE, cathodic reduction of oxygen and of hydrogen peroxide on FePc films occurs by way of a heterogeneous redox catalysis mechanism. In this mechanism, which occurs on sites with a concentration of ca. 10^{-7} – $10^{-6} \text{mol m}^{-2}$, i.e. involving less than 10% of the surface FePc molecules, the FePc molecule is reduced in a relatively fast reaction ($k_1^o \sim 10^3 \text{s}^{-1}$) with a standard potential $E_1^o \approx 0.67$ V. On the reduced electrocatalyst, the reactant (O_2 , HO_2^-) is adsorbed, which leads to de-stabilization. The adsorption is the rate-determining step, with rate constants k_2 , k_3 of the order of $\sim 10^2$ – $10^3 \text{m}^3 \text{mol}^{-1} \text{s}^{-1}$. Of the adsorbed oxygen, 94% is reduced to H_2O and 6% to HO_2^- in a fast reaction, i.e. with a rate constant $\gg 10^3 \text{s}^{-1}$.

Between 0.3 and 0.4 V vs. RHE, a mechanistic transition occurs. The rate constants k_1 , k_2^f and k_3 start to increase again, with Tafel slopes of -120 mV or more negative, but from $E \approx 0.3$ V vs. RHE they become, again, independent of potential. From the surface-sensitive techniques employed [1], it was found that this transition may be due to a decrease of the grain boundary resistance of the film. In other words, due to some, as yet unexplained, phenomenon, the film “opens up” and the number of catalytic sites available increases. The activation enthalpy for this phenomenon is 0.54 eV. When the overpotential is negative enough to overcome this extra barrier, i.e. at a potential around 0.4 V vs. RHE, a mechanism similar to that described in eqns. (1)–(3) and (8) and (9) becomes active. The number of extra active sites can be estimated as follows. The surface process at 0.4 V is obviously connected with these sites. Since this process was found to have a characteristic frequency of the order of 1000s^{-1} , the rate constant for their reduction will be of the same order of magnitude. From capacitance data, the number of surface states around $E \approx 0.4$ V was estimated to be $1.5 \times 10^{-6} \text{mol m}^{-2}$, i.e. the number of sites becoming active at low potential is slightly larger than that already active at high potential. The limiting values at low potential ($E \approx 0.2$ V) of the rate constants k_1 , k_2^f and k_3 are six- to ten-fold higher than those at $E \approx 0.5$ – 0.6 V, so, assuming expressions for them similar to eqns. (6), (7) and (10), the rates of adsorption of oxygen or HO_2^- , respectively, are slightly larger (i.e. less than ten-fold) on the low potential sites than on the high potential sites.

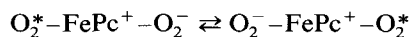
The nature of the surface state located at $E = 0.82$ V vs. RHE remains to be explained. In the case of oxygen reduction on CoPc films, we found a surface state at the same potential [2] and explained its origin as reduction of adsorbed oxygen, i.e. as the standard potential of reaction (3). However, in the case of FePc, this state was found in deoxygenated as well as in oxygenated solution. Furthermore, from the kinetics we have concluded that reaction (3) is relatively fast, while ac-impedance

measurements showed that the surface state has a characteristic frequency not exceeding 10^3 s^{-1} , i.e. the rate is comparable to that of reactions (1) and (2).

On the other hand, it is well known that oxygen can be adsorbed *in* Pc films [6,7], and that its presence has a profound influence on, among other things, the film's electrocatalytic behaviour, as witnessed, for example by our own kinetic results [1]. The influence of adsorbed oxygen on the conductivity behaviour of FePc-films has been explained by a mechanism, where charge is conducted along chains such as [8,9]



where excited oxygen can be ionized:



Possibly, the surface state at 0.82 V is connected with charge injection in this type of chains. However, the precise nature of the process remains rather obscure.

Summarizing: the oxygen reduction on FePc films occurs on two types of sites, one of which becomes active at low overpotential ($E \geq 0.8 \text{ V}$ vs. RHE). The other type does not take part in the reduction at potentials above ca. 0.4 V vs. RHE. At this potential it becomes available for oxygen reduction due to some process which "opens up" the film. Apart from the potential where it occurs, oxygen reduction on both types of sites follows quite similar mechanisms. Slow reduction of the site is followed by equally slow adsorption of oxygen (or hydrogen peroxide). The adsorption de-stabilizes the adsorbed species (O_2 or HO_2^-) to such an extent that its reduction occurs in a (series of) fast step(s).

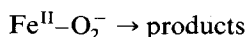
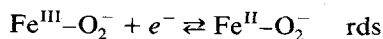
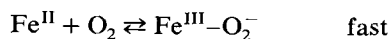
DISCUSSION

An interesting point remains: the nature of the process occurring at ca. 0.4 V vs. RHE, where the second high overpotential type of electrocatalytic sites are activated. To discuss it we must, however, first discuss the value of the redox potential of the surface $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple, which we postulated to be ca. 0.67 V. The reasoning for this is similar to that given for the redox potential of the $\text{CoPc}^+/\text{CoPc}$ couple [2], which was found to be ca. 0.80 V vs. RHE. The $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox potential is expected to be somewhat lower because the redox potential of "free" $\text{Fe}^{3+}/\text{Fe}^{2+}$ is lower than that of "free" $\text{Co}^{3+}/\text{Co}^{2+}$ in aqueous solution. Also, $\text{Fe}^{\text{II}}\text{Pc}$ is expected to form a complex with oxygen, contrary to $\text{Fe}^{\text{III}}\text{Pc}$ [10].

Iron can be in redox state I in Pc and porphyrins, but the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{I}}$ transition lies at least 1 V more negative than the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ transition [11], so the process at $\sim 0.4 \text{ V}$, generating the second high overpotential type of sites, cannot be ascribed to a reduction of Fe^{II} . Furthermore, in Part III [1] we described a probable phthalocyanine ring reduction at low potentials ($E \leq 0.1 \text{ V}$). Ring reductions have been reported in this potential range [3,11], so it is improbable that the process at $E = 0.4 \text{ V}$ is a ring reduction as well. Surface states for thin-film metal-free and zinc phthalocyanine, centred at ca. 0.4 V have been reported [12], but no explanation as to the nature of the surface states was offered.

Our results on the ellipsometric behaviour of FePc films indicate that some adsorption/desorption process may provide the explanation, in particular that of OH^- or H_2O . Quantum mechanical calculations [13] indicate that spin state transitions can occur in the d^5 system of $\text{Fe}^{\text{III}}\text{Pc}$ in the D_{4h} , C_{4v} or C_{2v} symmetries. Such transitions can be brought about by changes in the crystal field parameters. These parameters are mainly determined by the properties of the ligands surrounding iron and by the electric field strength over the interphase, so that a change in potential may well bring about a spin state transition. A similar situation may exist for $\text{Fe}^{\text{II}}\text{Pc}$, where, in the D_{4h} , C_{4v} or C_{2v} symmetries low spin ($S = 0$) and high spin ($S = 2$) states are possible. Also, intermediate spin states seem to be possible in phthalocyanines, depending on the crystal field parameters [7,14,15]. So, the spin state may be profoundly influenced by potential for surface iron phthalocyanine molecules, and it is reasonable to assume that the spin state of the active site will determine its adsorption behaviour. Therefore, we suggest the following explanation for the observed phenomena. At $E = 0.67$ V, $\text{Fe}^{\text{III}}\text{Pc}$ is reduced to $\text{Fe}^{\text{II}}\text{Pc}$; due to the effect of underlying phthalocyanine layers and oxygen and/or water molecules incorporated in the surface layer, the resultant $\text{Fe}^{\text{II}}\text{Pc}$ is distributed over two spin states; one of these leads to adsorption of OH^- or H_2O , while the other leaves the active Fe^{II} site free. On the free sites, oxygen reduction occurs at all potentials in the range investigated, while the blocked sites only become available for oxygen reduction below $E \approx 0.4$ V, where desorption of the adsorbed species occurs. Another possibility is that oxygen adsorbs on sites in all possible spin states, but that reduction of adsorbed O_2 occurs only on sites in certain states. In any case, we submit that the electrode potential influences the crystal field parameters and thus the spin state of the electrocatalytic sites. The spin state, in turn, determines the adsorption behaviour of the site and the electronic distribution of the adsorbed species. This may also explain the different activation enthalpies in the low and high overpotential regions—different spin states lead to different activation processes. It must be admitted that this explanation is somewhat tentative, but it is, at least, plausible, since it explains the observed dependence of the kinetics on electrode potential and it is in keeping with the phenomenological description of the state of the electrode surface.

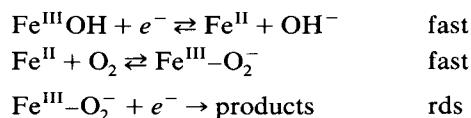
A few detailed mechanisms have been published hitherto, pertaining to oxygen reduction to H_2O on FePc [3,4,6,8,16]. Based upon an observed Tafel slope of -120 mV, it was proposed by Zagal and co-workers [16] that the rate-determining step of oxygen reduction to H_2O on FePc at high overpotentials is the reduction of the charge transfer complex $\text{Fe}^{\text{III}}-\text{O}_2^-$:



In the first place, this mechanism predicts a Tafel slope of -120 mV at potentials more negative than the standard potential of the second reaction only if its intrinsic

rate is orders of magnitude smaller than that of the chemisorption step. We have demonstrated that this is an improbable proposition. Further, the +3 oxidation state is not expected to be very stable, even when it is brought about by oxygen. So, the standard potential for the r.d.s. in the mechanism given above is certainly not expected to be very low, i.e. below the range of potentials where oxygen reduction is investigated. Therefore, the second reaction given here is expected to be rate-determining over, at most, part of the potential range, and beyond its standard potential the chemisorption step is certainly expected to become rate-determining, which predicts an infinite Tafel slope. However, Zagal and co-workers [16] found $b = -120$ mV at high overpotential for FePc. Such behaviour would, in our view, be better explained by assuming that the reduction of the central metal ion from its +3 state to its +2 state is rate-determining, where it is most able to form the charge transfer complex with oxygen. In that proposition, the thermodynamics of the problem, reflected in the value of the standard potential of the reduction of $\text{Fe}^{\text{III}}\text{-O}_2^-$ to $\text{Fe}^{\text{II}}\text{-O}_2^-$, are reasonably satisfactory, and the kinetics take their rightful place.

For low overpotential, a mechanism for oxygen reduction to H_2O or OH^- on FePc has been proposed by Zagal et al. [16], which is essentially the same as that proposed here:



For this mechanism a rate equation is derived in which the implicit assumption is made that only a small part of the available Fe^{II} sites is occupied by oxygen. Granting this condition, a Tafel slope of $-\log eRT/(1 + \alpha)F$ is predicted. To explain the observed $b = -35$ mV, a value $\alpha \approx 0.71$ must be adopted, for which no explanation is offered. Maybe such an explanation could be found in the orientation of the (in this case reversibly adsorbed) phthalocyanine molecule on the graphite surface used as substrate in this work [17]. On the other hand, the first step of the mechanism given above gives an explanation for the observed order of the reaction rate in hydroxyl ions of -1 [8,16].

FINAL REMARKS

The principal source of uncertainty in the determination of the mechanism of oxygen reduction on FePc, and, for that matter, on any macrocyclic N_4 -chelate transition metal complex, seems, in our opinion, to be the value of the redox potential of the $\text{M}^{\text{III}}\text{Pc}/\text{M}^{\text{II}}\text{Pc}$ couple.

We have assumed for thick FePc layers that this value is $E = 0.67$ V vs. RHE. This proposition is also supported by inductive reasoning from our results for the redox couple $\text{Co}^{\text{III}}\text{Pc}/\text{Co}^{\text{II}}\text{Pc}$. For irreversibly adsorbed FeTSP on the basal plane of pyrolytic graphite (where TSP stands for tetrasulphonated phthalocyanine, which is

soluble in aqueous solution), a somewhat higher value has been reported [14], which is undoubtedly due to differences in the actual environment of the central metal atom. An even higher value was inferred from in-situ Mössbauer spectroscopy measurements on FePc supported on high-surface-area carbon [18]. Although in this last case the formation of crystalline FePc was claimed, which would contradict our propositions, some interesting parallels can be drawn. Firstly, the FePc content is not so high as to exclude a strong interference of surface groups of the carbon with FePc molecules (a physical surface area of 2000 m² per 7.5 cm² of geometric surface area containing ca. 0.5 g of FePc is given, which corresponds to four to five FePc layers on the carbon). So, we see that the value of the Fe^{III}/Fe^{II} redox potential, which is crucial to the reaction pathway, is very sensitive to the environment of the iron atom, especially the fifth and sixth ligands.

Secondly, it was reported by Scherson et al. [18] that a considerable change in the Mössbauer quadrupole splitting of the central iron atom occurs when the FePc-on-carbon sample is immersed in an aqueous alkaline solution, which is explained by the occurrence of an axial C–O–Fe–OH complex, where the other ligands in the octahedral complex are the four phthalocyanine nitrogens. This assumption is quite similar to that made here for the explanation of the process occurring in thick FePc films below ca. 0.5 V vs. RHE.

In conclusion, our kinetic and surface characterization data can be explained rather satisfactorily by assuming a redox catalysis mechanism. Such a mechanism may lead to a variety of kinetic equations, depending on, firstly, the potential where the electrocatalyst is reduced and, secondly, on the relative rates of the elementary reactions involved. These quantities, however, are found to be strongly influenced by the precise geometry of the electrocatalytic site.

ACKNOWLEDGEMENTS

The present investigations were carried out with the support of the Netherlands Foundation for Chemical Research (S.O.N.) and with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

REFERENCES

- 1 F. van den Brink, W. Visscher and E. Barendrecht, *J. Electroanal. Chem.*, 172 (1984) 301.
- 2 F. van den Brink, W. Visscher and E. Barendrecht, *J. Electroanal. chem.*, 157 (1983) 305.
- 3 F. Beck, *Ber. Bunsenges. Phys. Chem.*, 77 (1973) 353.
- 4 F. Beck, *J. Appl. Electrochem.*, 7 (1977) 239.
- 5 J.P. Randin, *Electrochim. Acta*, 19 (1974) 83.
- 6 M. Savy, P. Andro, C. Bernard and G. Magner, *Electrochim. Acta*, 18 (1973) 191; M. Savy, P. Andro and C. Bernard, *ibid.*, 19 (1974) 403; M. Savy, C. Bernard and G. Magner, *ibid.*, 20 (1975) 383.
- 7 G. Magner, M. Savy and G. Scarbeck, *J. Electrochem. Soc.*, 127 (1980) 1076; G. Magner, M. Savy, G. Scarbeck, J. Riga and J.J. Verbist, *ibid.*, 128 (1981) 1674.
- 8 A.J. Appleby and M. Savy, *N.B.S. Spec. Publ.*, 455 (1975) 241.
- 9 A.J. Appleby, M. Savy and J. Fleisch, *J. Catal.*, 44 (1976) 281.
- 10 B.R. James in D. Dolphin (Ed.), *The Porphyrins*, Vol. V, Academic Press New York, 1978, p. 207.

- 11 R.H. Felton in D. Dolphin (Ed.), *The Porphyrins*, Vol. V, Academic Press New York, 1978, p. 53.
- 12 Fu-Ren Fan and L.R. Faulkner, *J. Am. Chem. Soc.*, 101 (1979) 4779.
- 13 P. Caro, M. Faucher, M. Savy and H. Pankowska, *J. Chem. Phys.*, 68 (1978) 1045.
- 14 M. Savy, C. Bernard and G. Magner, *Electrochim. Acta*, 20 (1975) 383.
- 15 A.J. Appleby, M. Savy and P. Caro, *J. Electroanal. Chem.*, 111 (1980) 97.
- 16 J. Zagal, Ph.D. Thesis, Case Western Reserve University, 1978; J. Zagal, P. Bindra and E. Yeager, *J. Electrochem. Soc.*, 127 (1980) 1507.
- 17 R. Kötz and E. Yeager, *J. Electroanal. Chem.*, 113 (1980) 113.
- 18 D. Scherson, S.B. Yao, E.B. Yeager, J. Eldridge, M.E. Fordesch, R.W. Hoffman, *Appl. Surf. Sci.*, 10 (1982) 325.