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ELECTROCATALYSIS OF CATHODIC OXYGEN REDUCTION BY METAL PHTHALOCYANINES *

PART I. INTRODUCTION, COBALT PHTHALOCYANINE AS ELECTROCATALYST: EXPERIMENTAL PART

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ABSTRACT

Macrocyclic organic N_4 -complexes of certain metals, especially Fe and Co, are promising electrocatalysts for cathodic oxygen reduction, and consequently, they have been extensively investigated. However, no clear picture of the pertinent electrocatalytic mechanism has evolved as yet. Therefore, relatively thick layers of iron and cobalt phthalocyanine were selected as model systems to find, firstly, accurate kinetic descriptions of cathodic oxygen reduction on these electrocatalysts and, secondly, a general mechanism appropriate to the kinetic findings. Here, the kinetics of the oxygen reduction on cobalt phthalocyanine will be presented. It is found that, at low cathodic overpotential, hydrogen peroxide is the stable reaction product. Only at more negative potentials is it partially reduced further to water. No direct reduction of O_2 to H_2O occurs over the entire potential range investigated. Electrolysis of oxygen labelled with ^{18}O shows that no O–O bond rupture occurs in the formation of hydrogen peroxide. The kinetic results are put in the context of the surface properties of the cobalt phthalocyanine film as determined by cyclic and ac voltammetry.

INTRODUCTION

The electrocatalysis of cathodic oxygen reduction by macrocyclic organic N_4 -complexes, such as porphyrins and phthalocyanines, has excited much interest in the past 15 years. The main reason for this is the promising features of these compounds as practical electrocatalysts, but also their similarity to compounds used in biological systems to transport and reduce oxygen is interesting. However, although many investigations have been reported upon their performance as oxygen reduction

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electrocatalysts [1], no unambiguous consensus of opinion seems to have been formed as yet as to their practical applicability [2].

The main problem appears to be that the activity and stability of macrocyclic N_4 -complexes as oxygen reduction electrocatalysts are usually inversely proportional. Attempts have been made to resolve the resulting dilemma, for example by stabilizing the central metal atom with basic surface groups of the substrate upon which the electrocatalyst is dispersed [2,3]. Such an approach is based upon the assumption that the metal atom is the electrocatalytically active site. We do not question this assumption, but in our view it should be elaborated upon. Therefore, it is necessary to have a rather detailed description of the electrocatalytic mechanism on a molecular scale. To obtain this, however, it is essential to have an accurate kinetic description of oxygen reduction electrocatalysis—and in our view this is still lacking.

Therefore, in a series of papers of which this is the first part, we aim to present the detailed kinetic description, with a tentative mechanistic description on a molecular level for a phthalocyanine system.

We have confined our investigations to only one type of macrocycle, viz. phthalocyanine (Pc) to avoid complications due to slight differences in the electrocatalysts, which are kinetically significant but will not alter the fundamental mechanism; it is well known that the macrocyclic structure itself exerts only a secondary influence, as compared to the effects of changing the central metal atom [1]. Furthermore, we found that iron and cobalt phthalocyanine showed strikingly different features as oxygen reduction electrocatalysts, so we decided to investigate FePc and CoPc.

The lack of accurate kinetic descriptions of oxygen electroreduction is, in our view, mainly caused by the fact that poorly defined and unstable electrocatalytic surfaces were usually investigated [1]. Therefore, we have chosen to investigate relatively thick layers (10–1000 nm) of the electrocatalyst. Thus, we were able to circumvent the effects of electrocatalyst instability, since a fresh layer of the electrocatalyst was always available and the electrode surface may be considered invariant whatever its porosity may be. Furthermore, the use of these thick, vacuum-deposited layers enabled us to apply sophisticated measuring techniques for unravelling the electrode kinetics, such as the rotating ring disc electrode (RRDE), by which the effects of diffusion of reactants and products to and from the surface can be separated from kinetic effects.

Cobalt phthalocyanine as oxygen reduction electrocatalyst

Although cobalt phthalocyanine (CoPc) has been covered in many of the publications cited [1], not many of these gave a full kinetic description. Most papers concern dispersions of the catalyst on active carbon, so that only values for Tafel slopes and reaction orders are reported. The Tafel slopes given diverge widely, due to differing electrode preparation and measuring conditions. In particular, the substrate upon which the electrocatalyst was deposited will have had a definite influence in many

reported cases—either because it was porous or because it is not inert in oxygen reduction. Usually, Tafel slopes of the order of 40–50 mV are found [4,5], while in some cases an increase is found at high overpotential [6,7]. In some papers ring–disc electrode measurements using a pasted [2,8,9], or solution-deposited electrocatalytic disc electrode [4,6] were presented, but these results were strongly influenced by the method of electrode preparation. This is not the case with the work of Yeager and Zagal [7,10–12], who used water-soluble tetrasulphonated phthalocyanine, reversibly adsorbed on to the basal plane of pyrolytic graphite, which is virtually inert in oxygen reduction—however, this preparation method has the drawback that the electrocatalytic surface is not very stable. Unfortunately, in most cases the RRDE results are analysed incompletely—mostly they are only used to establish whether or not any hydrogen peroxide is produced. If any further analysis is carried out, this is usually done only at some—it seems randomly selected—values of the electrode potential. Therefore, the study of thick CoPc films presented here, aiming at a complete kinetic description, is, to the best of our knowledge, the first of its kind.

EXPERIMENTAL

Electrode preparation

Ring–disc electrodes with gold or pyrolytic graphite disc and platinum ring, or gold disc electrodes were used throughout. Electrode pretreatment consisted of polishing with alumina in water suspensions with average particle size down to 0.05 μm , followed by ultrasonic removal of alumina particles and rinsing with distilled water. The use of diamond paste in mineral oil for polishing was found to lead to erroneous results, probably because the mineral oil creeps into the crevices on the perimeter of disc and ring electrodes and later interferences with the processes occurring on these electrodes (oxygen reduction and hydrogen peroxide oxidation respectively). Cobalt phthalocyanine (purchased from Eastman Kodak and used without further purification) was deposited on the disc electrode in a Leybold Hereaus vacuum deposition apparatus at pressures between 2 and 7 mPa, where the phthalocyanine was heated to approximately 450°C in a tungsten container for 10–100 s.

During the deposition procedure the ring electrode and the gap were covered by a quartz mask. The film simultaneously deposited on the quartz mask was used to determine the film thickness spectrophotometrically (at a wavelength of 620 nm) and with a Tolansky multiple-beam interferometer. A linear relation between spectrophotometric extinction and interferometric thickness was found, which was thenceforth used to calibrate the spectrophotometrically measured thickness. Attempts were made to determine whether or not pores or cracks were present in the films. With light microscopy (magnifications up to 1500 $\times$) a smooth film was found. Owing to the high conductivity of the films, scanning electron microscopy could not be applied to detect the presence of holes. The stability of the electrodes was tested

galvanostatically. It was found that the electrode potential at constant oxygen reduction current density did not vary appreciably (< 5 mV) over periods of 60 h.

Rotating ring disc electrode (RRDE) experiments

The rotating ring disc assembly has been previously described [13]. The collection efficiency ($N = 0.27 \pm 0.03$) and shielding factor ($S = 0.61 \pm 0.01$) were calculated from the radii of disc and ring electrodes and verified by measurements of anodic and cathodic limiting disc and ring currents in an equimolar solution of $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ (about 5 mM) in 1 M KOH. The ring electrode, which served to detect hydrogen peroxide, was carefully platinized, obeying all the rules of platinizing [14]. Preliminary experiments showed that even at extremely low potential sweep rates (< 0.1 mV s $^{-1}$) the current in positive and negative sweeps differed considerably. Therefore, true stationary measurements are necessary. We used a completely automated set-up, where the potentiostat (Tacussel, Bipad), RRDE motor drive, thermostat and other peripherals were controlled by a Hewlett-Packard 9825A desk-top calculator, equipped with a 16-bit parallel and an IEEE-488 interface. The complete set-up has been described elsewhere [15]. To ensure maximum activity of the platinum ring electrode, it was, between measurements, pulsed between upper (1.5 V vs. RHE) and lower (0.3 V vs. RHE) potentials, using a Wenking DPC 72 double-pulse generator. The experiments were performed in a conventional thermostatted three-compartment electrochemical cell, with a reversible Pt hydrogen electrode (RHE) as reference electrode. A 1 M KOH solution was used as supporting electrolyte, where the KOH was of p.a. quality, while the solutions were prepared with water which was pre-purified in a millipore[®] water purification apparatus and then twice distilled, first from a potassium permanganate solution. To remove the last traces of organic contamination, the electrolyte was pre-electrolysed between two platinum electrodes. The gases used (oxygen and argon) were purified by leading them over an active carbon column.

The reduction of oxygen is treated using the general scheme given in Fig. 1 [16]. Two pathways can be distinguished, viz. the direct path (reaction 1) and the consecutive path (reactions 2 and 3). Furthermore, adsorbed hydrogen peroxide can be decomposed chemically (reaction 4) or desorbed (reaction 5). The superscript (s)

Fig. 1. Reactions involved in cathodic oxygen reduction.

refers to the bulk of the solution, (σ) to the diffusion layer and (o) to adsorbed species.

The results of RRDE measurements were analysed according to the method given by Wroblowa et al. [16] for experiments in oxygenated solution and by that given by the present authors [17] for experiments in solutions of hydrogen peroxide.

Therefore, in *oxygenated solution*, the ring electrode was kept at a potential where hydrogen peroxide is oxidized quantitatively (1100–1200 mV vs. RHE); disc and ring currents were measured as functions of disc potential ($0 \text{ mV} \leq E_D \leq 1000 \text{ mV}$) and RRDE rotation frequency ($1 \text{ s}^{-1} \leq \omega \leq 100 \text{ s}^{-1}$). With the general reaction scheme (Fig. 1), where k_1 , k_2^f , k_2^b and k_3 are electrochemical rate constants, k_4 is the rate constant of chemical decomposition of H_2O_2 and k_5^a and k_5^d are the rate constants for adsorption and desorption of H_2O_2 respectively, it can be shown that disc (I_D) and ring (I_R) currents at constant disc potential E_D are related to ω as

$$-N \frac{I_D}{I_R} = \left[\left(1 + \frac{2k_1}{k_2^f} \right) + \frac{1}{k_5^d} \left\{ \left(1 + \frac{2k_1}{k_2^f} \right) (k_2^b + k_3 + k_4) + (k_3 - k_2^b) \right\} \right] + \left[\left(1 + \frac{2k_1}{k_2^f} \right) (k_2^b + k_3 + k_4) + (k_3 - k_2^b) \right] \frac{K_{\text{ads}}}{\gamma_2 \sqrt{\omega}} \quad (1)$$

and

$$N \frac{I_{D,1} + I_D}{I_R} = \left[1 + \frac{2\gamma_1}{\gamma_2} \frac{k_2^b + k_3 + k_4}{k_2^f} K_{\text{ads}} \right] + \frac{2}{k_2^f} \left(1 + \frac{k_2^b + k_3 + k_4}{k_5^d} \right) \gamma_1 \sqrt{\omega} \quad (2)$$

where $\gamma = 0.62 D^{2/3} \nu^{-1/6}$ ($1 = \text{O}_2$, $2 = \text{H}_2\text{O}_2$), $K_{\text{ads}} = k_5^a/k_5^d$ and $I_{D,1} = 4AF\gamma_1\sqrt{\omega}c_1^s$ is the absolute value of the limiting current for reduction of O_2 to H_2O on the disc electrode (with area A). The above equations may be written

$$-NI_D/I_R = A_1 + B_1/\sqrt{\omega} \quad (3)$$

and

$$N(I_{D,1} + I_D)/I_R = A_2 + B_2\sqrt{\omega} \quad (4)$$

respectively, which shows how the disc and ring currents at constant disc potential should be plotted.

Similarly, in *solutions of hydrogen peroxide*, the anodic ($I_{R,1}^a$) and cathodic ($I_{R,1}^c$) limiting ring currents were measured as a function of RRDE rotation frequency at zero disc current. They are given by

$$-\frac{I_{R,1}^a}{2NAFc_2^s} = \frac{k_4}{1+K} - \frac{\beta^{2/3}}{N} \gamma_2 \sqrt{\omega} \quad (5)$$

$$\frac{I_{R,1}^c}{2NAFc_2^s} = \frac{k_4}{1+K} + \left(\frac{K}{1+K} + \frac{\beta^{2/3}}{N} \right) \gamma_2 \sqrt{\omega} \quad (6)$$

where

$$K = \frac{2\gamma_1}{\gamma_2} \frac{k_{2,r}^b - k_{3,r}}{2k_{1,r} + k_{2,r}^f} \quad (7)$$

is a pseudo-constant, given by the values of the rate constants at the disc's rest potential (indicated by the subscript r). Therefore, from plots of $I_{R,1}^a$ and $I_{R,1}^c$, according to the above equations, the chemical rate constant k_4 can be found.

Impedance measurements

The ac impedance of Pc electrodes in argon-saturated 1 M KOH, in the potential range where the dc current is negligible, was measured potentiostatically with a lock-in amplifier (P.A.R. 5205) in the frequency range 20–5000 s⁻¹. Since phthalocyanine films behave as semiconductors [18], the impedance data were analysed using the equivalent circuit given in Fig. 2, with the assumption that $R_F \gg 1/\omega C_H$. Here, C_H is the Helmholtz capacitance, R_{bulk} and R_{elt} are the bulk semiconductor and electrolyte resistances, R_F the faradaic resistance and R_{sc} and C_{sc} are the surface resistance and capacitance of the phthalocyanine film respectively. Both R_{sc} and C_{sc} may be frequency dependent. Furthermore, C_{sc} may be the sum of the (parallel) capacitances due to space charge and the surface states respectively. The sum resistance $R_{\text{bulk}} + R_{\text{elt}}$ was determined independently from the current response to a small (1–10 mV) potential step. Then, R_{sc} and C_{sc} were calculated from the real and imaginary parts of the impedance, using an estimated, potential-independent, value for C_H . Although C_H may vary with potential, it is usually much larger than C_{sc} , so that such a variation will not invalidate the latter assumption.

¹⁸O-experiments

To be able to discriminate between oxygen reduction mechanisms where no O–O bond rupture is involved and those where OH radicals are intermediates in the formation of hydrogen peroxide, experiments with the stable oxygen isotope ¹⁸O were performed. In these experiments oxygen gas containing 50% ¹⁸O (purchased

Fig. 2. Equivalent circuit for a semiconductor electrode in concentrated electrolyte solution.

from the Gesellschaft für Kernforschung, Karlsruhe, F.R.G.) was diluted with $^{16-16}\text{O}_2$. This mixture was electrolysed at a phthalocyanine film electrode, supported by a large (36 cm^2) graphite disc, for at least 24 h, until the H_2O_2 concentration was 0.5 mol m^{-3} . Then the electrolyte solution was degassed and the hydrogen peroxide was decomposed with a platinum sol. The evolving oxygen gas, which is known to have the same isotopic composition as the H_2O_2 it originates from [19–21], was sampled and analysed in a mass spectrometer.

To test the validity of the method, some experiments were performed with an uncovered graphite electrode, which is known to reduce O_2 to H_2O_2 without O–O bond rupture [22]. This was indeed confirmed by our measurements.

RESULTS AND DISCUSSION

RRDE experiments

Oxygenated solution

A typical example of the voltammetric curves obtained in oxygenated solution is shown in Fig. 3. Since the collection efficiency of the RRDE is 0.27 it is seen that in the potential range between 800 and 300 mV, $I_R \approx NI_D$, so oxygen is, in this potential range, exclusively reduced to hydrogen peroxide, which is the stable reaction product. At potentials $< 300\text{ mV}$, the disc current increases while the ring current decreases, which indicates that either the direct reduction of oxygen to water begins to occur or hydrogen peroxide is reduced further to water.

Fig. 3. Stationary disc (—) and ring (---) currents of oxygen reduction at a 410 nm CoPc film on pyrolytic graphite at 290 K. The ring potential was 1150 mV. Rotation frequencies: (1) 14.2; (2) 37.0; (3) 70.1; (4) 109 s^{-1} .

Fig. 4. $1/I_D$ vs. $1/\sqrt{\omega}$ from the data in Fig. 3 at disc potentials of: (1) 800; (2) 750; (3) 650; (4) 300; (5) 200; (6) 100 mV.

The disc current data were analysed by plotting them as $1/I_D$ vs. $1/\sqrt{\omega}$. A typical example is shown in Fig. 4. The lines are in all cases almost perfectly straight, with correlation coefficients $r^2 \geq 0.99$, indicating first-order dependence of the overall reaction rate on oxygen concentration. From the intercepts, the kinetic

Fig. 5. $\log |i_k|$ vs. E for oxygen reduction on CoPc at: (O) 298; (+) 308; ($\square$) 318; (Δ) 328; ($\times$) 338 K (i_k in A m^{-2}).

current density can be obtained, i.e. the overall reaction rate corrected for diffusion, while the slopes give the number of electrons transferred in the overall reaction. Although some 20% scattering was found in different experiments, no unambiguous dependence of the kinetic current on the catalyst film thickness was found; this is contrary to the findings of Savy et al. for iron phthalocyanine [23], but the film thickness used in their work is typically one order of magnitude smaller than those we used, so we had the catalyst essentially as a bulk material, where the thickness should have no effect on electrocatalytic properties. Since there is no dependence on film thickness of any of the properties measured, in the following we will present the average of the results from 21 different CoPc films (in the thickness range of 100–700 nm) on a pyrolytic graphite substrate.

The logarithm of the kinetic current density at different temperatures is shown in Fig. 5. The slope of the curves in the vicinity of 800 mV corresponds to a Tafel slope $b \approx 40$ mV. Below 600 mV $\log |i_k|$ becomes a temperature-dependent constant, while below 300 mV the kinetic current density begins to increase again, reflecting the occurrence of the reduction to water. The number of electrons in the overall reaction, found from the slopes of the $1/I_D$ vs. $1/\sqrt{\omega}$ plots, is shown in Fig. 6. It does not vary with temperature, and in the potential range from 800 to 300 mV it has an approximately constant value of 2. Below 300 mV it begins to increase, reaching 3 at 0 mV.

Examples of plots of $-NI_D/I_R$ vs. $1/\sqrt{\omega}$ and $N(I_{D,1}^{H_2O} + I_D)/I_R$ vs. $\sqrt{\omega}$ [16] are given in Figs. 7 and 8. Reasonably straight lines are found for both plots in all cases examined, with correlation coefficients $r^2 > 0.8$ for those in Fig. 7 and $r^2 > 0.9$ for those in Fig. 8.

The intercept in Fig. 7 is unity over the entire potential range investigated. This indicates, first, that although at $E < 300$ mV reduction of hydrogen peroxide to water occurs, no direct reduction of oxygen to water occurs, and, secondly, that the desorption of hydrogen peroxide from the electrocatalytic site is fast [16]. For

Fig. 6. Number of electrons involved in the overall reduction of oxygen on CoPc vs. potential in the temperature range 298–338 K.

Fig. 7. Kinetic analysis of RRDE data for oxygen reduction at 298 K. Disc potential: (1) ≥ 300 mV; (2) 250 mV; (3) 200 mV; (4) 150 mV; (5) 100 mV.

Fig. 8. Kinetic analysis of RRDE data for oxygen reduction at 298 K. Disc potential: (1) 800 mV; (2) 750 mV; (3) 650 mV; (4) ≤ 450 mV.

potentials > 300 mV the slope in Fig. 7 is zero, indicating that no reduction of hydrogen peroxide to water occurs. Below 300 mV the slope in Fig. 7 begins to increase, which means that the rate constant k_3 for the reduction of hydrogen peroxide increases. From the slope in Fig. 8 the rate constant for the reduction of oxygen to hydrogen peroxide, k_2^f , can be calculated. Since the slope is constant at potentials < 450 mV, k_2^f is constant in this potential range.

Now the intercept of Fig. 7 (A_1) equals unity. From eqns. (1) and (3) it follows that

$$A_1 = \left(1 + \frac{2k_1}{k_2^f}\right) + \frac{1}{k_5^d} \left\{ \left(1 + \frac{2k_1}{k_2^f}\right) (k_2^b + k_3 + k_4) + (k_3 - k_2^b) \right\} \quad (8)$$

hence, we conclude that $k_1 = 0$ and $k_5^d \gg 2k_3 + k_4$. Therefore, with eqns. (2) and (4), the slope in Fig. 8 is

$$B_2 = 2\gamma_1/k_2^f \quad (9)$$

which gives k_2^f .

The slope of Fig. 7 is given by

$$B_1 = \left[\left(1 + \frac{2k_1}{k_2^f}\right) (k_2^b + k_3 + k_4) + (k_3 - k_2^b) \right] \frac{k_5^a}{k_5^d} \frac{1}{\gamma_2} \quad (10)$$

which, for $k_1 = 0$, reduces to

$$B_1 = (2k_3 + k_4)(k_5^a/k_5^d)(1/\gamma_2) \quad (11)$$

and, since $k_4 \approx 0$ (see below), this gives k_3 , provided that k_5^a/k_5^d is known.

The intercept of Fig. 8 is, under these circumstances, given by

$$A_2 = 1 + (2\gamma_1/\gamma_2)(k_3/k_2^f)(k_5^a/k_5^d) \quad (12)$$

since, in the potential range where B_1 differs from zero, it may safely be assumed that $k_2^b \approx 0$.

Therefore, when $B_1 > 0$, we should find a value for A_2 larger than unity. However, in this case, where k_1 , k_2^b and k_4 are zero, we can write A_2 as

$$A_2 - 1 = B_1 B_2 / 2 \quad (13)$$

Now, the maximum value of B_1 is measured at 0 mV and is approximately 4.5. Below 450 mV, which is where $B_1 > 0$, B_2 has the constant value of ca. 0.055, so that $A_2 - 1 \approx 0.12$ maximum, and this small amount is well within the experimental accuracy which is estimated at $\pm 20\%$ for the intercepts. On the other hand, the estimated error for the slopes is much smaller, since no extrapolation is involved in their evaluation.

The values for k_2^f , found from B_2 , are given in Fig. 9. It is seen that with these values for $E > 300$ mV, $2Fk_2^f [\text{O}_2]$ coincides with $|i_k|$ (see Fig. 5), while it remains constant for $E \leq 300$ mV, where i_k increases.

In Fig. 10, $\log(B_1\gamma_2/2)$ is plotted vs. potential. This quantity equals the rate

Fig. 9. Rate constant for the reduction of oxygen to hydrogen peroxide on cobalt phthalocyanine at 298 K as a function of potential.

Fig. 10. Rate constant for the reduction of hydrogen peroxide to water on cobalt phthalocyanine at 298 K as a function of potential. ($\times$ — $\times$) $k_3 K_{\text{ads}}$; ($\circ$ --- $\circ$) k_3 (see text).

constant for reduction of H_2O_2 , k_3 , multiplied by the equilibrium constant for adsorption K_{ads} . Since we know that, in the potential region involved, $k_1 = 0$ and k_2^f is constant (viz. $3.09 \times 10^{-4} \text{ m s}^{-1}$), we can calculate k_3 from the number of electrons n , found for the overall reaction, shown in Fig. 6, and k_2^f . In general, if $k_2^b = 0$, n is given by

$$n = 2 \left[(2k_1 + k_2^f) + k_2^f k_3 / (k_2^f + k_3) \right] / (k_1 + k_2^f) \quad (14)$$

which, with $k_1 = 0$, reduces to

$$n = 2 + 2k_3 / (k_2^f + k_3) \quad (15)$$

so that k_3 can be calculated as

$$k_3 = - \frac{n-2}{n-4} k_2^f \quad (16)$$

The result of this calculation is also given in Fig. 10. It can safely be assumed that K_{ads} does not vary with potential so we conclude that $\text{p}K_{\text{ads}} = 0.92$, or $k_5^a = 0.12k_5^d$. Furthermore, k_3 varies with potential, the slope corresponding to a Tafel slope of ca. -180 mV . The deviation at higher potentials, near 300 mV , is probably the result of the inaccuracy in the measurement of $n - 2$ where $n \approx 2$.

The temperature dependences of k_2^f and i_k are shown as Arrhenius plots in Fig. 11. The values of k_2^f given there are the limiting values at potentials $< 450 \text{ mV}$, while for i_k the value at 300 mV was taken. From the slopes of the Arrhenius plots the activation energies are calculated: $\Delta H_{\text{act}}^\circ(k_2^f) = 22.4 \text{ kJ mol}^{-1}$, corresponding to 0.23 eV , and $\Delta H_{\text{act}}^\circ(i_k) = 35.0 \text{ kJ mol}^{-1}$, corresponding to 0.31 eV . Since, at 300 mV , $k_3/k_2^f \approx 0.03 \ll 1$, the rate-determining step in i_k is the reduction of hydrogen peroxide, and $\Delta H_{\text{act}}^\circ(i_k) \approx \Delta H_{\text{act}}^\circ(k_3)$.

Fig. 11. Temperature dependence of k_2^f (+) and i_k (O) for oxygen reduction on CoPc.

H_2O_2 solution

Most of the electrodes used in the experiments described above were also used for experiments in solutions containing H_2O_2 , along the line of reasoning outlined by the present authors [17]. In all cases, the rest potential of the electrodes $E_{D,r}$ (i.e. the potential of the disc electrode under the conditions of the experiment where $I_D = 0$ and ω is varied) was constant (0.72 ± 0.02 V), so plots of the anodic limiting ring current $I_{R,1}^a$ vs. $\sqrt{\omega}$ [17] were used to determine the hydrogen peroxide concentration.

Fig. 12. Plot of limiting ring currents vs. $\sqrt{\omega}$ on a CoPc/Pt RRDE in a 3.6 mM solution of H_2O_2 in 1 M KOH at 298 K and zero disc current.

The concentrations used were in the range 3–5 mol m⁻³. Since $E_{D,r}$ was found to be constant, the constant

$$K = \frac{2\gamma_{O_2}}{\gamma_{H_2O_2}} \frac{k_{2,r}^b - k_{3,r}}{2k_{1,r} + k_{2,r}^f}$$

is a real constant [17]. Therefore, the analysis is considerably simplified, and plots of $-I_{R,1}/2NFAc_{H_2O_2}^s$ vs. $\gamma_{H_2O_2} \sqrt{\omega}$ give all the information required. Such a plot is shown in Fig. 12. Obviously, the intercepts of the anodic and cathodic branches are zero within experimental accuracy, indicating that the rate constant of the chemical decomposition of H_2O_2 , k_4 , is close to zero. From the difference between the slopes of the anodic and cathodic branches, a value of $K \approx 0.15$ is derived. This indicates that, at the rest potential, the backward rate of the reaction O_2 to H_2O_2 , k_2^b , is < 0.05 times that of the forward reaction k_2^f .

We may conclude that the previously used assumption is justified—the rates of the oxidation of H_2O_2 to O_2 , k_2^b , and that of the chemical decomposition, k_4 , are negligible with respect to those of the reduction of oxygen to hydrogen peroxide, k_2^f , and of reduction of hydrogen peroxide to water, k_3 .

Surface properties of cobalt phthalocyanine films

A simple and often useful method of investigating surface properties of electrocatalysts is cyclic voltammetry. Cyclic voltammograms of cobalt phthalocyanine in oxygen-free and oxygen-containing 1 M KOH solution are shown in Fig. 13. The voltammogram in oxygen-free solution is rather featureless and does not show any detail. Probably, any surface process occurring is hidden under the rather large capacitance current. On the other hand, the voltammogram in oxygen-containing solution shows, along with the expected rise of the cathodic current due to oxygen

Fig. 13. Cyclic voltammograms of a CoPc film on pyrolytic graphite in 1 M KOH with (—) and without (---) oxygen. Scan rate 250 mV s⁻¹.

reduction, a very distinct peak at 800 mV. The fact that this peak occurs only in the presence of oxygen indicates that some oxygen-containing species is reduced at 800 mV. That the peak at 800 mV is not found in stationary measurements shows that the species involved is a surface species.

More information about the electrocatalytic surface can be obtained from the impedance of the electrode, measured in oxygen-free solution.

First, the current response of the CoPc on pyrolytic graphite electrode to a small (1–5 mV) potential step was measured in the potential range from 0 to 1000 mV RHE. Using the equivalent circuit of Fig. 2, it is seen that for $t = 0$, i.e. at the beginning of the potential step, the current is determined by the sum of the resistances of the CoPc film and the electrolyte. Therefore, the measurement of $i(t = 0)$ gave $R_{\text{bulk}} + R_{\text{elt}}$. Then, the same type of measurement was done with the ring electrode of the RRDE used. The resistance of the ring electrode, $R_{\text{elt}}(\text{ring})$, was independent of potential, so it is a true electrolyte resistance. Since the geometry of the measuring cell (e.g. the position of the auxiliary electrode) was practically the same for the disc and ring electrodes, the electrolyte resistance for the disc electrode was calculated from the ratio of the disc and ring electrode areas, A_D and A_R

$$R_{\text{elt}}(\text{disc}) = (A_R/A_D) R_{\text{elt}}(\text{ring}) \quad (17)$$

The value for the electrolyte resistance thus found was subtracted from the total resistance of the disc electrode, giving its true bulk value R_{bulk} . From R_{bulk} , the film's specific conductivity was calculated

$$\sigma = d/A_D R_{\text{bulk}} \quad (18)$$

where d is the film thickness. The measurement of specific conductivity was carried

Fig. 14. Specific conductivity vs. potential of CoPc films on pyrolytic graphite in deoxygenated 1 M KOH.

Fig. 15. Capacitance vs. potential of CoPc films in deoxygenated 1 M KOH. Excitation frequency: (1) 40; (2) 90; (3) 200; (4) 500; (5) 1000 s^{-1} .

out for a number of electrodes, with the thickness of the CoPc film ranging from 100 to 700 nm. All results can be represented as a single curve, shown in Fig. 14. It shows a very distinct peak at 480 mV.

Secondly, ac response of the electrode to a small ac potential perturbation was measured as a function of dc potential and frequency. From the magnitude and phase of the ac response the electrode's impedance was calculated by subtraction of the electrolyte resistance. The impedance was used to calculate the capacitance of the film, using the equivalent circuit given in Fig. 2. In this circuit, R_{bulk} is known from the potential step experiment described above. $R_F \rightarrow \infty$ since no faradaic reactions occur in the absence of oxygen, so the only unknowns are C_{sc} , R_{sc} and C_{H} . Now the assumption was made that C_{H} is large and depends little on potential and frequency. Then, a value for C_{H} was selected which made C_{sc} independent of frequency at high values of the potential, where the dispersion of the impedance is already relatively small. Usually, a value of ca. 2 F m^{-2} for C_{H} sufficed to bring this about. The resultant curves for C_{sc} did not differ significantly for different electrodes, and are shown in Fig. 15. To explain the shape of C_{sc} vs. E curves, C_{sc} is considered to be composed of two parallel capacitances $C_{\text{sc}} = C_{\text{space charge}} + C_{\text{ss}}$ [24]. The first component is due to the space charge existing near the semiconductor-electrolyte interface. The second component is the result of the presence of surface states. The distinction between the two components is made because their frequency dependence differs vastly.

At low frequencies, the capacitance is dominated by the presence of surface states, which is responsible for the bell shape of the curves 1–3. Charge transfer from and to these states is rather slow, as shown by the decrease of the maximum found in these curves with increasing frequency. At frequencies above ca. 1000 Hz, its contribution has completely disappeared. Then, the remaining capacitance has the general shape as seen in curve 5. This shape is typical for a p-type semiconductor. At high potentials, i.e. $E \geq 700$ mV, it is independent of frequency, since the surface region is enriched in majority carriers (holes), which have a high mobility (accumulation layer). On the other hand, at low potentials, viz. $E \leq 400$ mV, the surface region is depleted in holes, and the concentration of the slow minority carriers (electrons) may even exceed that the majority carriers, resulting in a strong dispersion of the capacitance (depletion and inversion layer).

The maximum of the surface state capacitance, $C_{ss}^{\max}$, occurring at $E = 480$ mV, is found by subtracting from the observed C_{sc} the value of the space charge capacitance. This value was estimated by taking the average of the C_{sc} values found at high ($E \geq 700$ mV) and low ($E < 200$ mV) potential, where the contribution of the surface states is negligible. The complete expression for the capacitance has been given by Myamlin and Pleskov [24]. They have shown that if diffusion of minority carriers (i.e. electrons) is fast, the expression for the capacity has the form

$$C = C_1^o + C_{ss} \quad (19)$$

where C_1^o is the capacitance of space charge and C_{ss} is the surface state capacity. From their eqns. (43.23) and (43.24), it follows that C_{ss} can be written as

$$C_{ss} = \frac{N_{ss} e^2}{kT} \frac{\Omega^2}{\Omega^2 + \omega^2} \frac{\bar{p}^s/p'}{(1 + \bar{p}^s/p')^2} \quad (20)$$

where Ω is the characteristic frequency of the surface states, N_{ss} the concentration of surface states, $\bar{p}^s$ the concentration of free carriers at the surface and p' the concentration of free carriers in bands when the Fermi level coincides with the surface level.

With the Fermi distribution function

$$\bar{p}_s/p' = \exp(E_F - E_{ss})/kT \quad (21)$$

it follows that

$$C_{ss} = \frac{N_{ss} e^2}{kT} \frac{\Omega^2}{\Omega^2 + \omega^2} \frac{\exp(E_F - E_{ss})/kT}{[1 + \exp(E_F - E_{ss})/kT]^2} \quad (22)$$

Hence

$$C_{ss}^{\max} = \frac{N_{ss} e^2}{4kT} \frac{\Omega^2}{\Omega^2 + \omega^2} \quad (23)$$

Thus, by plotting $1/C_{ss}$ vs. ω^2 , it is possible to find $C_{ss}^{\max}$ ($\omega = 0$) and Ω . Such a plot is given in Fig. 16. However, the graph does not show a straight line at low ω -values.

A possible explanation for this lack of linearity could be that at the time-scale employed here 50 ms (20 s^{-1}) diffusion cannot be neglected.

Nevertheless, from Figs. 15 and 16 and results from other ac impedance measurements at frequencies down to 20 s^{-1} , it can be seen that the capacitance at zero frequency is close to 4.5 F m^{-2} , giving for the number of surface states ca. $3 \times 10^{18} \text{ m}^{-2}$ or $5 \times 10^{-6} \text{ mol m}^{-2}$. This corresponds to an area per surface state of 0.33 nm^2 . Now the dimensions of phthalocyanines are ca. $1.2 \times 1.2 \times 0.4 \text{ nm}^3$ [25], so the area of one molecule is ca. 1.4 nm^2 . This means that probably each phthalocyanine molecule located in the interface acts as surface state, and that the roughness factor of the surface is ca. 4. This roughness factor would also account for the rather high value of the Helmholtz capacitance, $C_H = 2 \text{ F m}^{-2}$, estimated from the impedance measurements.

The slowness of diffusion of electrons is also the reason why it proved impossible to construct a Mott-Schottky plot (i.e. $1/C^2$ vs. E) from the curves shown in Fig. 15. For, at frequencies where C_{ss} may assumed to be zero (i.e. at $f \gg 1000 \text{ s}^{-1}$), the capacitance of the space charge region has become almost potential independent ($\sim 0.2 \text{ F m}^{-2}$) and the theory underlying the Mott-Schottky plot does not apply. However, the potential-independent capacitance is given, for a p-type semiconductor, by (ref. 24)

$$C_\infty = (p^s \epsilon_0 \epsilon_r e^2 / 2kT)^{1/2} \times \text{constant} \quad (24)$$

where, for heavily doped semiconductors, the constant is ≈ 1 . Assuming that the relative dielectric constant $\epsilon_r \approx 10$ – 20 , we find that $p^s \approx 10^{26} \text{ m}^{-3}$ (or $p^s \epsilon_r = 1.5 \times 10^{27}$).

Fig. 16. Maximum surface state capacitance on CoPc films vs. excitation frequency; C_{ss} was measured at 480 mV.

Experiments with ^{18}O

The rate of hydrogen peroxide production by a cobalt phthalocyanine-covered graphite electrode in 1 *M* KOH containing ^{18}O enriched oxygen, as measured by a Pt microelectrode, confirms our result that CoPc reduces oxygen exclusively to H_2O_2 .

Two independent experiments showed that in the formation of H_2O_2 no O–O bond rupture occurs. The proportion of the concentrations of $^{16-18}\text{O}_2$ and $^{18-18}\text{O}_2$ in the oxygen gas which was electrolysed was (1.92 ± 0.07) and (1.85 ± 0.06) respectively, as measured by mass spectrometry. The oxygen gas evolving from the H_2O_2 produced by the electrolysis at +0.5 V vs. RHE had the same isotopic composition—here, the proportion was (1.89 ± 0.02) and (1.82 ± 0.02) respectively. Since any mechanism involving O–O bond breaking leads to stochastic mixing, electrolysis of oxygen containing $^{16-16}\text{O}_2$, $^{16-18}\text{O}_2$ and $^{18-18}\text{O}_2$ in the proportion $x : y : z$, gives the corresponding H_2O_2 isotopes in the proportion $(x^2 + xy + 1/4y^2) : (2xz + xy + yz + 1/2y^2) : (z^2 + yz + 1/4y^2)$. In the two cases examined the amount of $^{16-16}\text{O}_2$ was so chosen that after electrolysis the proportion $^{16-18}\text{O}_2 : ^{18-18}\text{O}_2$ would have been 7.69 and 7.14 respectively. The difference between these and the observed values clearly shows that no O–O bond rupture is involved.

CONCLUSIONS

The kinetic description of cathodic oxygen reduction electrocatalysed by cobalt phthalocyanine, as presented above, can be summarized as follows:

(1) On cobalt phthalocyanine, oxygen is exclusively reduced to hydrogen peroxide at potentials > 300 mV; below 300 mV, hydrogen peroxide is reduced further to water.

(2) With respect to the kinetics of these reactions: (a) the rate constant for the reduction $\text{O}_2 \rightarrow \text{H}_2\text{O}_2$, k_2^f , has a Tafel slope $dE/d \log k_2^f$ of ca. –40 mV in the vicinity of $E = 800$ mV; below 800 mV the slope increases to infinity at 450 mV; (b) the order of the reduction $\text{O}_2 \rightarrow \text{H}_2\text{O}_2$ in oxygen is 1, i.e. the current is proportional to $[\text{O}_2] - i_2 = -2F k_2^f [\text{O}_2]$; (c) the rate constant for the reduction $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O}$ increases at potentials < 300 mV, with a Tafel slope of ca. –180 mV.

(3) In the reduction $\text{O}_2 \rightarrow \text{H}_2\text{O}_2$, the oxygen–oxygen bond is not broken.

(4) A surface process is detected at 480 mV both in oxygenated and deoxygenated solution; it has a characteristic frequency of ca. 500 s^{-1} .

(5) A second surface process at ca. 800 mV is found only in the presence of oxygen.

These results are, at least qualitatively, comparable to those reported in the available literature. In particular, the fact that hydrogen peroxide is the main product at low overpotential has been found before [4,6], while the values found for the Tafel slope also agree with previously published values [4–7]. Furthermore, the constant value of k_2^f at high cathodic overpotential found by us is in good agreement with the literature values.

However, only part of our results can be compared to previously published results. We feel that our results present more pertinent data compared to those found in the available literature. In the first place, we are certain that our experiments have been carried out at well-defined electrocatalytic surfaces—even if we have not investigated electrode texture in depth. Secondly, our results present a consistent and complete description of the kinetics of oxygen reduction on cobalt phthalocyanine electrodes—for the potential dependence of individual rate constants has been found and has been shown to run parallel to surface processes occurring on the electrodes. We feel that these features will prove their significance in the formulation of a mechanism—to which task the next part of this series will be devoted.

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LIST OF SYMBOLS

<i>A</i>	area, m^{-2} ; intercept
<i>B</i>	slope
<i>c</i>	concentration, mol dm^{-3} or mol m^{-3}
<i>C</i>	capacitance, F m^{-2}
<i>d</i>	thickness, m
<i>e</i>	electronic charge, C
<i>E</i>	potential, V
<i>F</i>	Faraday's constant, C mol^{-1}
<i>H</i>	enthalpy, J mol^{-1}
<i>i</i>	current density, A m^{-2}
<i>I</i>	current, A
<i>k</i>	heterogeneous rate constant, m s^{-1}
<i>K</i>	equilibrium constant; constant
<i>N</i>	collection efficiency
<i>p</i>	concentration of holes, m^{-3}
<i>R</i>	resistance, Ω
<i>s</i>	number of sites, m^{-2}
<i>T</i>	temperature, K
β	geometric factor of RRDE
γ	diffusion rate constant of RDE, $\text{m s}^{-1/2}$
ϵ	dielectric constant, F m^{-1}
ω	(rotation) frequency, s^{-1}

Abbreviations

RDE	rotating disc electrode
RRDE	rotating ring disc electrode
RHE	reversible hydrogen electrode
Pc	phthalocyanine

Subscripts

l	limiting
D	disc
R	ring
r	at rest potential
ss	surface state
sc	semiconductor; space charge

Superscripts

σ	in reaction (or outer Helmholtz) plane
$^{\circ}$	at electrode surface; in standard state
s	in bulk
a	anodic
c	cathodic

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