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THE CATHODIC REDUCTION OF OXYGEN AT COBALT PHTHALOCYANINE

INFLUENCE OF ELECTRODE PREPARATION ON ELECTROCATALYSIS

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ABSTRACT

Oxygen reduction has been investigated in acid and alkaline solutions on electrodes with the same catalyst (cobalt phthalocyanine or cobalt tetrasulfonato-phthalocyanine), but prepared by different methods. It is concluded that the number of active sites can differ widely from the expected number of active sites as derived from the total amount of catalyst present on the electrode surface. In acid solution, where the reduction is irreversible, the half-wave potential shifts with respect to the number of active sites, according to a theoretical description. For the determination of the "intrinsic catalytic activity" (turnover number), electrodes with an irreversibly absorbed (sub)monolayer are recommended.

INTRODUCTION

In recent years a considerable number of papers have been published on oxygen reduction. In many of these investigations a metal chelate is used as a catalyst. These catalysts are attached to the electrode with the aid of different methods, such as irreversible adsorption [1]; vacuum deposition [2]; incorporation into a conducting polymer, as polypyrrole [3]; impregnation of porous carbon [4]; and evaporation of the solvent [5].

All these preparation techniques result in electrodes of different activity, even if the same catalyst and the same amount of catalyst are used. One of the most striking examples is the difference in activity between an electrode prepared by vacuum deposition of cobalt phthalocyanine (CoPc) and by incorporation of water-soluble cobalt tetrasulfonato-phthalocyanine (CoTSPc) in polypyrrole [3]. Especially in acid media, the catalyst incorporated in polypyrrole is much more active than the vacuum-deposited one, while in both cases a thick layer containing the catalyst is present. To explain the difference in activity, we have to take into account the conductivity of the catalyst layer and the possibility of the diffusion of oxygen through this layer. Both the conductivity of, and the oxygen diffusion velocity in the catalyst/polypyrrole layer is so high that all attached catalyst molecules can take part in the electrocatalysis, which is not the case for the vacuum-deposited film. as

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will be shown later in this paper. A comprehensive theoretical description of this phenomenon is given in a paper by Savéant and co-workers [6].

The purpose of the present paper is to demonstrate how preparation conditions affect the activity. This will be illustrated for the reduction of oxygen on the transition-metal chelate cobalt phthalocyanine (CoPc) or, in some cases, the water-soluble modification cobalt tetrasulfonato-phthalocyanine (CoTSPc).

The following preparation methods were investigated: (a) irreversible adsorption; (b) vacuum deposition; (c) incorporation in polypyrrole; (d) impregnation of porous carbon; (e) evaporation of the solvent. For a precise description see the Experimental section.

THEORETICAL ASPECTS

CoPc (or CoTSPc) gives under all circumstances a first reduction wave of oxygen to hydrogen peroxide. The kinetics of the reaction are in general much faster in alkaline solutions than in acid solutions. The main reason is that the probable intermediate $O_2^-$, or an $O_2^-$-like species, is relatively more stable in alkaline solutions than in acid solutions, as was stressed by Yeager [7]. With this in mind, we expect the effect of the preparation method on the activity to be more dramatic in acid than in alkaline solutions; therefore, for comparison, measurements were carried out in both electrolytes.

Clearly, the number of active sites is an important parameter determining the $i$–$E$ relationship, characterized by the half-wave potential $E_{1/2}$, as determined with the rotating disc electrode technique. It can be shown that this half-wave potential shifts when the number of active sites at an electrode is increased. Suppose, we have an irreversible electrochemical reaction with a rate-determining electron transfer as the first step. For the current density measured with a rotating disc electrode, the following relation has been derived for a first-order reaction (see Albery [8]):

$$i/i_L = \left(1 + k_D/k\right)^{-1}$$  \hspace{1cm} (1)

where $i$ is the current density (mA/cm$^2$), $i_L$ is the transport-limited current density (mA/cm$^2$), $k_D$ is the heterogeneous rate constant describing mass transport (cm/s) and $k$ is the observed heterogeneous rate constant of the electron transfer (cm/s).

At the half-wave potential ($i = \frac{1}{2}i_L$), $k_D = k$. Rate constant $k$ corresponds to a surface with a certain number of active sites. If this number of active sites on the surface increases by a factor $p$, then the rate constant $k$ also increases by this factor because $k$ is based on the geometric surface area. Increasing the number of active sites neither affects the size of this geometric area nor the diffusion to this surface. Therefore, for the original and the new surface (1 and 2, respectively), we have, in the case of a cathodic reaction, the following relations:

Surface 1: $k_D = k_0 \exp(-\alpha F \eta_1/RT)$  \hspace{1cm} (2)

Surface 2: $k_D = pk_0 \exp(-\alpha F \eta_2/RT)$  \hspace{1cm} (3)
where \( k_0 \) is the value of \( k \) at \( E = E_{eq} \), \( E_{eq} \) is the equilibrium electrode potential, \( \eta_1 \) and \( \eta_2 \) \( (= (E_{1/2})_1 - E_{eq}, (E_{1/2})_2 - E_{eq}) \) are the overpotentials for surfaces 1 and 2, respectively, and \( (E_{1/2})_1 \) and \( (E_{1/2})_2 \) are the half-wave potentials of surfaces 1 and 2, respectively.

The difference between the two half-wave potentials is:

\[
(E_{1/2})_2 - (E_{1/2})_1 = \Delta E_{1/2} = \left( \frac{RT}{\alpha F} \right) \ln p \tag{4}
\]

For \( \alpha = \frac{1}{2} \), the decrease of the half-wave overpotential is 118 mV for a ten-fold increase of the number of active sites. Generally, the shift of the half-wave potential for a ten-fold increase of the number of active sites is equal to the Tafel slope.

EXPERIMENTAL

Chemicals

Cobalt phthalocyanine (CoPc) was obtained from Eastman Kodak. The sodium salt of cobalt tetrasulfonato-phthalocyanine (CoTSPc) was synthesized according to the method described by Weber and Busch [9]. All other chemicals were commercially available and used without further purification, except the pyrrole, which was distilled before use.

Preparation of the electrode systems

As will be explained below, five different electrode systems (a–e) were prepared. For electrode systems b and d, a gold disc with a surface area of 0.50 cm\(^2\) was used and for systems a, c and e, a pyrolytic graphite (C\(_p\)) disc with a surface area of 0.52 cm\(^2\). Before the preparation of the electrode systems the electrodes were polished with 0.3 \( \mu \)m alumina, rinsed with doubly distilled water and cleaned in an ultrasonic water bath for 1 min.

(a) Irreversible adsorption

A pyrolytic graphite electrode (C\(_p\)) was dipped into a solution of CoPc or CoTSPc, resulting in the irreversible adsorption of the complex on the electrode [1]. A (sub)monolayer of catalyst was obtained. Characterization by cyclic voltammetry is possible with these electrodes so the exact number of active sites can be determined. It is also possible to produce electrodes with different surface coverages by dipping the C\(_p\) electrode in solutions of CoPc in pyridine (or CoTSPc in water) with concentrations ranging from \( 10^{-3} \) to \( 10^{-5} \) mol/l. The time of exposure (dipping time) appeared to be unimportant.

(b) Vacuum deposition

This technique has already been previously employed in our laboratory [2]. In this way, it is possible to produce an electrode which is covered with a large amount of catalyst. The thickness of the layer was determined spectroscopically, as described in ref. 2.
(c) Incorporation in polypyrrole

The sodium salt of CoTSPc is soluble in water. The electrooxidation of pyrrole gives a polymer with positive charges, which must be compensated by negatively charged ions [10]. When the polymerization is carried out in the presence of the CoTSPc$^{4-}$ anion, this ion is incorporated in the film. For the preparation of this type of electrode system, a $10^{-3} \ M$ CoTSPc solution in water, containing 1 vol. % pyrrole, was used. The electrooxidation was carried out galvanostatically with a current of 0.2 mA. By varying the time, layers of different thickness were produced.

(d) Impregnation of porous carbon

The impregnation of the carbon support (Norit BRX) was realized by dissolving 10 mg of CoPc in 20 ml THF, adding 40 mg of the carbon, then refluxing and stirring for 30 min. The carbon particles were attached to the Au disc of the electrode via incorporation in a polypyrrole film, according to a previously described procedure [11]. The carbon support has a high conductivity and a high specific surface area, so many catalyst molecules can be adsorbed on the surface.

(e) Evaporation of the solvent

A drop (several microliters) of a CoPc solution in pyridine was placed on a C$_p$ electrode; thereafter, the solvent was allowed to evaporate, yielding electrodes with relatively thick layers of catalyst. By changing the concentration of the solution from $10^{-3}$ to $10^{-5}$ mol/l, the thickness of the layer could be regulated.

Electrochemical measurements

The electrochemical experiments were carried out in a standard three-compartment electrochemical cell filled with 100 ml of electrolyte. As electrolyte, both acid (0.5 $M$ or 0.05 $M$ H$_2$SO$_4$) and alkaline (1 $M$ or 0.1 $M$ KOH) solutions were used. The polypyrrole electrodes were tested only in 0.1 $M$ KOH and not in 1 $M$ KOH because of the lack of stability of polypyrrole in alkaline solutions [12]. For characterization of the electrode, cyclic voltammetry was conducted in oxygen-free solutions. The oxygen reduction was measured in oxygen-saturated solutions, with the rotating disc electrode technique. The electrochemical measurements were carried out using a Tacussel bipotentiostat (Bipad). As reference electrode, a reversible hydrogen electrode (RHE) was used. All potentials in this paper are given vs. the RHE.

The reduction curves of electrode systems in which polypyrrole was used are corrected for the high capacitive current of the polypyrrole itself.

RESULTS AND DISCUSSION

Acid media

Figure 1 gives the result for the oxygen reduction on the electrode systems (a–e). In Table 1 the amounts of attached catalyst for the different electrode systems are
given. It is obvious that each electrode system catalyses the reduction of oxygen, to a
different extent, however, indicating that the number of active sites is not automatic-
ically the same as the total number of catalyst molecules present. An electrode
prepared via irreversible adsorption is even more active than a thick vacuum-de-
posited film.

To illustrate the shift in half-wave potential due to a change in active sites, as
derived in eqn. (4), the oxygen reduction was investigated as a function of the
CoTSPc/polypyrrole layer thickness (type c). Since the polymer layer is very thin
compared to the thickness of the diffusion layer, $k_D$ will remain unchanged for all
layer thicknesses. In Fig. 2 the oxygen reduction on CoTSPc adsorbed on C$_p$ (1), and
on various CoTSPc/polypyrrole layers (2-6) in 0.05 M H$_2$SO$_4$ is shown. In this
figure, the thickness of the layer is expressed as the charge passed during the
electropolymerization of pyrrole. In order to determine the amount of catalyst in a
film, a cyclic voltammogram in an oxygen-free solution was measured for a 30 mC
thick layer (see Fig. 3). In this figure the cyclic voltammogram of CoTSPc adsorbed
on C$_p$ is also given (a). The characterization of the electrodes is somewhat hampered
by the instability of CoTSPc in acid solutions. Moreover, at potentials above 1 V (vs.

\[
\text{TABLE 1}
\]

\begin{tabular}{|l|l|l|}
\hline
Electrode type & Description & Amount of catalyst/mol cm$^{-2}$ \\
\hline
a & Irreversible adsorption (10$^{-3}$ M CoPc) & 2.6$\times$10$^{-10}$ \\
b & Vacuum deposition (180 nm) & 6.3$\times$10$^{-8}$ \\
c & Incorporation in polypyrrole (30 mC) & 1.67$\times$10$^{-8}$ \\
d & Impregnation of porous carbon (20%) & 1.8$\times$10$^{-7}$ \\
e & Evaporation of the solvent & 4.0$\times$10$^{-8}$ \\
\hline
\end{tabular}
Fig. 2. Oxygen reduction as a function of the CoTSPc/polypyrrole layer thickness. Electrolyte: 0.05 M H$_2$SO$_4$, oxygen-saturated; scan rate = 50 mV/s; rotation frequency = 64 s$^{-1}$. For comparison, the oxygen reduction on an irreversibly adsorbed layer of CoTSPc on C$_p$ is also included.

RHE), the polypyrrole degrades rapidly. Despite these difficulties, for an electrode obtained from irreversible adsorption, a surface coverage of $1.4 \times 10^{-10}$ mol/cm$^2$ can be determined from the area under the reduction peak at 1.1 V. The 30 mC CoTSPc/polypyrrole layer (b) gives a coverage of $7.8 \times 10^{-9}$ mol/cm$^2$. If it is assumed that for the oxidation of pyrrole to neutral polypyrrole two electrons per molecule are involved, and that in the oxidized form of polypyrrole, every four pyrrole units carry one positive charge [10], a coverage of $1.67 \times 10^{-8}$ mol/cm$^2$ can be calculated for a 30 mC CoTSPc/polypyrrole layer. This theoretical value will be used in this paper.

A limiting current of 2.5 mA is reached below 0 V (vs. RHE) in curve 2, Fig. 2. (The plateau is not shown in the figure.) This value equals the theoretical diffusion limiting current for the reaction of oxygen to hydrogen peroxide. Curve 6, in the same figure, shows, although not very clearly, a first wave and the start of a second wave. In our view, the first wave corresponds to the reaction of oxygen to hydrogen peroxide; the second wave is attributed to the further reduction of hydrogen peroxide to water. With this in mind, the half-wave potentials for curves 2 and 6 can

Fig. 3. Cyclic voltammograms of CoTSPc adsorbed on C$_p$ (a) and of a 30 mC CoTSPc/polypyrrole layer (b) Electrolyte: 0.05 M H$_2$SO$_4$, oxygen-free, scan rate = 100 mV/s
be determined with reasonable accuracy if only the reaction of oxygen to hydrogen peroxide is considered. The results are 70 and 395 mV, respectively. With the use of these values for the coverage in the two cases, the shift in half-wave potential as a function of the number of active sites can be calculated. The result is 155 mV/decade of active sites.

For the Tafel slope of the first wave of curve 6 (Fig. 2) a value of $-155$ mV has been determined. Notwithstanding the difficulty of the determination, this is the same value as that reported by Zagal-Moya [7] for the oxygen reduction on CoTSPc adsorbed on $\text{C}_\text{p}$. The value of the Tafel slope corresponds very well with the observed shift in the half-wave potential. This agreement may be somewhat flattered because of two "each-other" compensating effects. First, the amount of catalyst in the film is probably taken as too high if we compare this with the results of the cyclic voltammetric measurements; secondly, it is probably not correct to neglect the oxygen reduction on the polypyrrole matrix completely.

Returning to the results for the five different electrode systems as presented in Fig. 1, we note that a vacuum-deposited layer (b) has a lower activity than an irreversibly adsorbed layer (a), notwithstanding its thickness. Since the film has a relatively low conductivity, the reaction must take place mainly at the interface between the substrate and the phthalocyanine film. Oxygen must diffuse through the inactive outer parts of the film to reach the active sites at the interface. The electrode obtained by evaporation of the solvent (e) has a comparable physical structure, but probably a somewhat higher porosity and/or conductivity, resulting in a slightly increased activity for this electrode system as compared with system b.

The two other electrode systems consist of a catalyst dispersed on a matrix with high porosity and high conductivity so that the whole layer, or at least a major part of it, is involved in the electrocatalysis. The direct incorporation in polypyrrole results in the most efficient utilization of the catalyst.

*Alkaline media*

Electrode systems a, b and e all show about the same activity in $1\ M\ \text{KOH}$, as can be concluded from Figs. 4 and 5. Owing to the greater stability of CoPc (or CoTSPc) in alkaline solutions than in acid solutions, a more precise characterization of the electrode is now possible. In Fig. 4a, the results are given for an irreversibly adsorbed layer prepared using solutions of different concentrations. The surface coverage increases from $6.4 \times 10^{-11} \ \text{mol/cm}^2$ (for a concentration of $10^{-5} \ M$ CoPc) to $2.6 \times 10^{-10} \ \text{mol/cm}^2$ (for a concentration of $10^{-3} \ M$ CoPc). Figure 4b demonstrates that the increased coverage is accompanied only by a slight increase in activity. The vacuum-deposited film (110 nm), also drawn in Fig. 4b, has the same activity as the a-type electrode prepared from a $10^{-3} \ M$ solution mentioned above.

An electrode with a vacuum-deposited film gives non-reproducible and featureless cyclic voltammograms in $\text{O}_2$-free solutions. From the measured activity, it can be concluded that the conductivity and porosity of the layer are such that about the same activity as that obtained for a monolayer is realized. On comparing Figs. 1 and
Fig 4. (a) Cyclic voltammogram of CoPc adsorbed on C. The concentrations of the dip solutions are given in the figure. Electrolyte: 1 M KOH, oxygen-free; scan rate = 100 mV/s. (b) Oxygen reduction on the electrodes of (a) compared with a vacuum-deposited layer of CoPc. Electrolyte: 1 M KOH, oxygen-saturated; scan rate = 50 mV/s; rotation frequency = 16 s⁻¹.

4b, it appears that the vacuum-deposited films show a relatively higher activity in alkaline than in acid solution. In our opinion, this difference is not caused by the electrolytes themselves, but is a result of the preparation method used. It is difficult to obtain films with identical physical properties. Different films have a somewhat different conductivity and/or porosity, depending on the exact preparation conditions; these conditions cannot be kept constant with the applied method. Nevertheless, in both electrolytes only one monolayer, or even less, is electrochemically active.

With electrode system e (deposition of CoPc by evaporation of the solvent), the characterization also results in a featureless cyclic voltammogram, as can be observed in Fig. 5a. The amount of catalyst has almost no effect on the activity, as is demonstrated in Fig. 5b.

The oxygen reduction on electrode system c (CoTSPc incorporated in polypyrrole) was examined in 0.1 M KOH solutions. The result is shown in Fig. 6. For

Fig 5. (a) Cyclic voltammogram of electrode system e (evaporation of the solvent). The amounts of deposited catalyst are given in the figure. Electrolyte: 1 M KOH, oxygen-free; scan rate = 100 mV/s (b) Oxygen reduction on the same electrodes as in (a). Electrolyte: 1 M KOH, oxygen-saturated; scan rate = 50 mV/s; rotation frequency = 16 s⁻¹.
comparison, the oxygen reduction curve measured on a layer prepared from irreversible adsorption of CoTSPc (coverage $1.4 \times 10^{-10}$ mol/cm$^2$) has been drawn in the same figure. As can be seen from these curves, there is almost no difference in activity despite the high catalyst loading in the case of the 30 mC CoTSPc/polypyrrole film ($1.67 \times 10^{-8}$ mol/cm$^2$). With the CoTSPc/polypyrrole layer, again a second wave appears. This wave can be ascribed, as is also done for acid electrolytes, to the further reduction of hydrogen peroxide to water. The appearance of the second wave is due to the large number of active catalyst molecules. For the vacuum-deposited layer, there is no second wave, again suggesting that only part of the vacuum-deposited layer is active. At high overpotential, the current decreased owing to the change of polypyrrole to a reduced, non-conducting form.

It is difficult to determine one unique Tafel slope for the first wave of the oxygen reduction on a 30 mC CoTSPc/polypyrrole layer in 0.1 M KOH: the results vary from $-60$ mV at low overpotentials to $-130$ mV at higher overpotentials. Tafel slopes of $-120$ mV have been reported by Zagal-Moya for an irreversibly adsorbed layer of CoTSPc [7]. Figure 6 shows that the shift of the half-wave potential as a function of the amount of catalyst is not equal to the observed Tafel slope. The reason for this is that an adsorbed monolayer already accomplishes a reversible (or quasi-reversible) reduction of oxygen to hydrogen peroxide in 0.1 M KOH. Any further increase in the number of active sites does not bring about an enhanced activity, as is characteristic of reversible reactions.

Electrode system d was not examined in alkaline solutions.

CONCLUSIONS

The investigations of five electrode systems demonstrate that the number of active sites is an important factor determining the activity of an electrode. This number is by no means the same as the total amount of catalyst present on the surface.

A layer prepared by irreversible adsorption on an inert electrode material is
recommneded to study electrocatalysis, becaue of the possibility of determining the
exact number of active sites and, moreover, the diffusion to the surface is well-de-
dined. The use of this electrode system enables the determination of the “intrinsic
catalytic activity” of a catalyst. By “intrinsic catalytic activity” we mean the
(catalytic) activity of a surface expressed as an exchange current density and
corrected for the number of active sites on this surface. The quantity obtained can be
called the turnover number.

The use of this turnover number instead of the exchange current density will not
give very different results for metal electrodes since they all have about the same
number of surface atoms per unit surface area. However, this is not the case with
large organic molecules as catalyst which contain only one active site per molecule.
For instance, when the catalytic activity of a surface, covered with CoTSPc, is
compared with the activity of platinum, the use of exchange current densities gives a
false picture. If the same geometric surface area is taken into account, an adsorbed
monolayer of CoTSPc contains $5 \times 10^{13}$ molecules/cm$^2$, assuming an area of 2 nm$^2$
per molecule with the molecules lying parallel to the surface. For platinum, however,
a number of $1.35 \times 10^{13}$ atoms/cm$^2$ can be calculated using a density of 21.45
g/cm$^3$. Thus, a platinum electrode has 27 times more active sites than an adsorbed
monolayer of CoTSPc. An (imaginary) CoTSPc electrode that would contain the
same number of active sites as platinum per unit surface area (and which, therefore,
allows a fair comparison) would show in acid electrolytes a half-wave potential that
is shifted 220 mV in the positive direction, compared with the electrode, described
by curve 2 in Fig. 2.

REFERENCES

University, 1978.