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REDOX POTENTIAL AND ELECTROCATALYSIS OF O₂ REDUCTION ON TRANSITION METAL CHELATES

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ABSTRACT

The redox potentials of iron phthalocyanine (FePc), cobalt phthalocyanine (CoPc) and cobalt tetraazaannulene (CoTAA), irreversibly adsorbed on pyrolytic graphite, were investigated as a function of the pH by cyclic voltammetry. The reduction of oxygen was studied under the same conditions with the rotating disc electrode technique. At high pH, where the reduction to H₂O₂ on the cobalt-containing chelates is more reversible, the value of the redox potential is less important. At low pH, where this reduction is irreversible, there is a clear correlation between the redox potential of the central metal ion and the O₂ reduction behaviour. In acid media, a 470 mV more positive redox potential of CoTAA compared to that of CoPc, resulted in a half-wave potential, $E_{1/2}$, for the O₂ reduction being 400 mV more positive than the $E_{1/2}$ of CoPc.

INTRODUCTION

Since the introduction of cobalt phthalocyanine (CoPc) as an electrocatalyst for cathodic O₂ reduction by Jasinski [1] in 1965, transition metal chelates have been studied for this purpose [2]. In Fig. 1, the molecular structures of the most extensively investigated chelates are given. For a qualitative explanation of their activity, different concepts were developed. Application of the MO theory [2] to these systems has shown that the highest interaction of O₂ with the central metal ion is obtained with Fe(II) and Co(II). The higher this interaction, the more the O–O bond is weakened, and the more easily the molecule is reduced. Another approach has been given by Ulstrup [3]. If the electronic levels of the electrode and reactant lie too far apart, the transition of electrons is improbable. The catalyst should then act as a mediator, supplying intermediate levels, thus increasing the probability of electron transport. A third concept is that of redox catalysis, developed by Beck [4]. In this concept the redox potential of the central metal ion is crucial. During the

Fig. 1. Molecular structures of metal phthalocyanine (MePc), R-substituted porphyrin (MeTRP) and tetraazaannulene (MeTAA).

adsorption of O_2 , the metal ion is oxidized, thereby reducing the O_2 molecule. The simplest representation is as follows:

In order to account for supplementary experimental evidence, a somewhat modified model was developed [4] in which the central metal ion could also be partly oxidized.

From this scheme it is clear that the potential where O_2 is reduced should be closely related to the Me^{II}/Me^{III} redox potential of the central metal ion. Nevertheless, only in relatively few cases have these redox potentials actually been measured in the same electrolyte in which the O_2 reduction is studied. In most cases, if measured at all, these redox potentials were determined in water-free media, since this results in sharp peaks. The effect of the pH on the redox potential in such water-free media is rather difficult to translate to that of the pH in water as a solvent. Moreover, it is questionable whether or not it is feasible to identify values for the redox potential found in solution with that adsorbed on the electrode substrate. Recently, Ni and Anson [5] have shown a 340 mV difference between a dissolved and an adsorbed cobalt porphyrin. A meaningful correlation between O_2 reduction and the redox potential, however, is possible only if both processes are studied in the same electrolyte. A good example of such an approach is the work of Zagal-Moya [6], who investigated both the redox potentials and O_2 reduction of the water-soluble cobalt and iron tetrasulphonated phthalocyanines (TSPc), adsorbed on pyrolytic graphite, as a function of pH. From previous work in our laboratory [7,8], it has become clear that irreversibly adsorbed monolayers of FePc, CoPc and CoTAA can be prepared by dipping a pyrolytic graphite (Cp) disc into pyridine solutions of the corresponding chelates. Another result was that the half-wave potential, $E_{1/2}$, for the O_2 reduction at CoTAA in 0.5 M H_2SO_4 was 400 mV more positive than the $E_{1/2}$ of CoPc [9]. These phenomena gave rise to a more detailed study of pH effects on the adsorbed macrocycles. The objective of this research was

Fig. 2. Pourbaix diagram for O_2 reduction.

to measure the redox potentials of the different chelates as a function of the solution pH and to establish the correlation between these values and the observed $E_{1/2}$ s for O_2 reduction in the same electrolytes.

pH AND THERMODYNAMICS OF O_2 REDUCTION

The study of O_2 reduction is complicated by the fact that different products can be formed: O_2 can be reduced either directly to water or to H_2O_2 , which can be the stable end product or may be subsequently reduced to H_2O . The first step in the reduction mechanism is most likely the formation of the superoxide [10,11]: $O_2 + e^- \rightarrow O_2^-$. The equilibrium potential of this couple is -0.33 V (vs. SHE) and is independent of the solution pH. The equilibrium potentials of both the O_2/H_2O couple and the O_2/H_2O_2 couple decrease by 60 mV for each increase in pH (Fig. 2). The driving force for superoxide formation increases rapidly with increasing pH. In fact, at Hg, the reduction of O_2 to H_2O_2 at high pH is a reversible reaction [12]. Therefore, if the reduction of O_2 on transition metal chelates is investigated as a function of the pH, two simultaneously occurring effects have to be accounted for:

- (a) the stability of superoxide changes as a function of pH; and
- (b) the redox potential of the central metal ion can change and thus influence the kinetics of the reaction.

EXPERIMENTAL

In order to eliminate mass transport problems, the rotating disc electrode technique was used [13]. The chelates were applied onto a polished ($0.3 \mu m$ Al_2O_3 , Buehler) Cp disc ($A = 0.5 cm^2$) via irreversible adsorption for 1 min from $10^{-3} M$ pyridine solutions. Three chelates were studied: CoPc and FePc (Eastman Kodak)

and CoTAA, kindly provided by Professor K. Wiesener (Technische Universität, Dresden, G.D.R.). The electrodes were studied in the following buffer solutions: pH 0: HClO_4 ; pH 2: KCl/HCl ; pH 4: $\text{KH phthalate}/\text{HCl}$; pH 6: $\text{KH}_2\text{PO}_4/\text{NaOH}$; pH 8: $\text{HCl}/\text{H}_3\text{BO}_3/\text{NaOH}$; pH 10, 12: $\text{NaOH}/\text{glycine}/\text{NaCl}$; pH 14: NaOH . All electrochemical experiments were performed in a standard three-compartment electrochemical cell. A Pt foil was used as the counter-electrode; a reversible hydrogen electrode (RHE) was the reference. All the measured potentials are given with respect to RHE. Redox potentials were determined by scanning the disc potential in O_2 -free solution (N_2) from 1.0 to 0.0 V and back again with 100 mV s^{-1} . In some cases (pH 0–4), the upper scan limit was 1.2 V, since there is a CoPc redox peak present in that region.

The O_2 reduction was measured by scanning the disc potential with 50 mV s^{-1} in O_2 -saturated solutions from 1.0 to 0.0 V and vice versa, at a rotation frequency of 16

Fig. 3. Determination of the redox potentials of FePc (a), CoTAA (b) and CoPc (c), irreversibly adsorbed on Cp. The dashed curves represent the Cp background. Electrolyte: O_2 -free 1 M NaOH; scan rate = 100 mV s^{-1} .

s^{-1} . With lower scan rates, the same results were obtained. Since the conductivity of the solutions of pH 2–6 was insufficient, during O_2 reduction experiments $1 \text{ mol KNO}_3 \text{ l}^{-1}$ electrolyte was added. This addition had no effect on the measured redox potentials.

RESULTS

An example of the cyclic voltammograms of the different adsorbed chelates in 1 M NaOH is given in Fig. 3. Compared to the Cp background (dashed curves), the adsorbed molecules give rise to one or more redox peaks. Sometimes also the non-faradaic current region deviated somewhat from the bare Cp background after modification with the catalyst, but this was only a minor effect. In the case of a reversible electron transfer to adsorbed species, the redox potential is equal to the peak potential and the peak area is proportional to the catalyst loading. Although a difference in the number of active sites affects the location of the O_2 reduction wave

Fig. 4. The same as Fig. 3, but now at pH 2.

Fig. 5. Redox potentials of FePc, CoTAA and CoPc as a function of the solution pH. Note that all the potentials are given with respect to the RHE, which is a pH-dependent reference electrode.

Fig. 6. O_2 reduction on CoTAA, irreversibly adsorbed on Cp, as a function of the solution pH. Rotation frequency = 16 s^{-1} . To compensate for the different O_2 solubilities in the various buffer solutions, the disc current I_D was divided by the diffusion-limited current for O_2 reduction to H_2O_2 in the corresponding electrolyte, $I_{DL}(H_2O_2)$.

Fig. 7. O_2 reduction on CoPc, irreversibly adsorbed on Cp, as a function of the solution pH.

Fig. 8. O_2 reduction on FePc, irreversibly adsorbed on Cp, as a function of the solution pH.

[7], this difference is only small ($1.6 \times 10^{-10} \text{ mol cm}^{-2}$ for FePc; $2.3 \times 10^{-10} \text{ mol cm}^{-2}$ for CoTAA and $2.6 \times 10^{-10} \text{ mol cm}^{-2}$ for CoPc) and will therefore have only a small effect. In acid media the peaks in the cyclovoltammograms were somewhat less resolved (Fig. 4). The peak potential for this peak broadening is unclear but was not investigated further. At pH 0, no accurate determination of the CoTAA redox potential was possible. The redox potentials as a function of the pH are summarized in Fig. 5.

The results of the O_2 reduction experiments are depicted in Figs. 6–8. Since the diffusion-limited currents depend on the electrolyte under consideration, mainly due to differences in O_2 solubility, the disc current is plotted as I_D divided by $I_{DL}(\text{H}_2\text{O}_2)$, the latter being the diffusion-limited current for O_2 reduction to H_2O_2 ($n = 2$). Since CoTAA reduces O_2 to H_2O_2 exclusively [9], the limiting current obtained at CoTAA in the corresponding electrolyte was taken as $I_{DL}(\text{H}_2\text{O}_2)$.

DISCUSSION

The assignment of the different redox peaks is not completely straightforward. Both CoPc and FePc behave similarly to the water-soluble CoTSPc and FeTSPc [7,14]; only the values of the different redox potentials are somewhat shifted. The high potential of CoPc at low pH is related to the $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$ redox couple. As already established by Zagal-Moya [6], this redox process is pH-independent; its peak, measured vs. RHE, therefore shifts ca. 60 mV in a positive direction for each increase in pH. The CoPc peak, observed at high pH (Fig. 3c), is probably related to the $\text{Co}^{\text{I}}/\text{Co}^{\text{II}}$ redox couple [14]. Below pH 7, this redox process becomes pH-dependent: the potential vs. the pH-dependent RHE reaches a constant value. The most positive peak of FePc (Fig. 3a) is related to the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ redox process [6]. This redox couple is pH-dependent for $6 < \text{pH} < 14$. The other FePc peak is probably related to the $\text{Fe}^{\text{I}}/\text{Fe}^{\text{II}}$ redox couple. This peak is pH-dependent from pH 0 to 8; at higher pH, this process becomes pH-independent. This redox process will not be

discussed any further since for the first wave of the O_2 reduction, the Fe^{II}/Fe^{III} peak is involved. The only available information about the redox behaviour of CoTAA was obtained with a slurry electrode [4] in 2.25 M H_2SO_4 . A redox process was observed at ca. 0.5 V (vs. RHE) which was attributed to either the two-electron oxidation of the ring system or to the Co^{II}/Co^{III} redox couple. In our opinion, however, the CoTAA redox process more likely represents the Co^I/Co^{II} redox couple; for a Co^{II}/Co^{III} system, the potential would be very low. Compared to CoPc, the Co^I/Co^{II} peak of CoTAA shows the same pH dependence; however, the values of the CoTAA redox potentials are several hundreds of millivolts higher.

Before the relation between the redox potentials and the observed O_2 reduction is considered, some general features of Figs. 6–8 will be discussed. As stated before, with CoTAA only H_2O_2 is produced (Fig. 6). With CoPc (Fig. 7), H_2O_2 is initially formed which is to some extent further reduced to H_2O at pH 6–12. At pH 14, only H_2O_2 is formed. In the case of FePc (Fig. 8), the main product is H_2O at high pH. This difference in selectivity of FePc compared to the cobalt-containing chelates has been discussed elsewhere [8,15]. Even at pH 14, the reduction to water occurs at potentials which are far away from the theoretically obtainable 1.23 V. Contrary to the reduction of O_2 to H_2O_2 , the reduction to H_2O is still slow at this pH.

For the comparison of CoTAA with CoPc, for both complexes, both the redox potentials E_p and the half-wave potentials $E_{1/2}$ for O_2 reduction to H_2O_2 are presented in Fig. 9. The CoTAA redox potential decreases 60 mV per pH unit going from pH 14 to pH 10. The same applies to the $E_{1/2}$ for the O_2 reduction at CoTAA. Below pH 10, the redox potential remains constant. Figure 9 shows that the same is true for $E_{1/2}$. With CoPc, similar behaviour is obtained; only the values deviate.

Especially in acid media, the difference in redox potential between CoPc and

Fig. 9. pH dependence of the redox potentials E_p of CoPc and CoTAA, and $E_{1/2}$ of the O_2 reduction to H_2O_2 .

CoTAA is also reflected in the $E_{1/2}$ s. At pH 0, $E_{1/2}$ of CoTAA is 400 mV more positive than the $E_{1/2}$ of CoPc. At higher pH, this difference becomes smaller; at pH 14 it is 70 mV, despite a 300 mV difference in redox potential. Similar values for $E_{1/2}$ at pH 14 have been found on other peroxide-producing substrates such as Au and Hg [8,12]. This shows that at this pH, the reduction to H_2O_2 has become so reversible that the actual redox state of the catalyst is less important: the transfer of an electron onto an oxygen molecule is so easy that the electrode only has to act as a source of electrons. No strong interaction of oxygen with the electrode surface is necessary to accomplish this electron transfer. An interesting observation is that, despite the inferior results in acid as compared to alkaline solution, from the fuel cell point of view the O_2 reduction to H_2O_2 as such is catalysed more in acid than in alkaline media. At pH 14, $E_{1/2}$ for O_2 reduction is shifted ca. 300 mV in the positive direction, compared to the standard potential of superoxide formation; at pH 0, this shift is ca. 900 mV with CoTAA.

In the case of FePc, the Fe^{II}/Fe^{III} redox peak is constant from pH 6 to pH 14. In general, this is also true for the measured O_2 reduction, but at high pH there is some deviation. A measurement at pH 13 (not displayed) resulted in a wave that virtually coincided with the wave of pH 14. Whether this behaviour is due to a drastic increase in conductivity, going from pH 12 to pH 13, or that Fe chelates are more influenced by complexing anions of the buffer solutions is unclear.

CONCLUDING REMARKS

This work has shown that in the case of an irreversible O_2 reduction there is a clear correlation between the redox potential of the central metal ion and the observed O_2 reduction behaviour. With increasing reversibility of the reaction, the actual redox state of the catalyst becomes less important.

A comparison between CoPc and CoTAA in acid media shows that differences in the redox potential influence the activity severely. In our opinion, this influence has been underestimated so far, probably because most of the work published has been performed with gas-diffusion electrodes. The presence of a vast number of catalyst molecules and the nature of this electrode (wetting properties) overshadow the performance of the individual molecules. With gas-diffusion electrodes, only small differences in activity are found [2], contrary to the results of rotating disc experiments. This work demonstrates that changes in the macrocyclic ring structure have a profound effect on the catalytic activity (400 mV increase in $E_{1/2}$ on going from Pc to TAA), due to differences in ligand strength. In particular, the size and form of the conjugated π -system and the N_4 -cage (square in the case of CoPc, rectangular for CoTAA) deserve more attention.

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