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Oxygen reduction in an acid medium: electrocatalysis by CoNPc(1,2) impregnated on a carbon black support; effect of loading and heat treatment

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Abstract

O₂ reduction in an acid medium has been investigated on a transition metal macrocycle, CoNPc(1,2), impregnated on a carbon black support with a high dibutylphthalate adsorption value, using a rotating disk electrode and voltammetry techniques described previously, combined with X-ray photoelectron spectroscopy measurements. Optimal activity was found for a bilayer coverage ($n = 2$) at 17%–18% w/w loading. Heat treatment seems to be beneficial for $n \leq 3$: it increases the overall number N of exchanged electrons and improves the electrode wetting. For the most active samples, mixed Co(II)/Co(III) valencies were displayed.

INTRODUCTION

In the last decade or more, extensive study has been devoted to O₂ electrocatalysis in aqueous media by different N₄–transition metal (Co and Fe) macrocycles such as porphyrins [1–4], phthalocyanines [5–8], tetraazaannulene [9,10] and naphthalocyanines [11–13].

In acid media, Co and Fe macrocycles generally give rise to a two-electron reduction pathway. However, dicobalt porphyrin dimers were reported to be potent catalysts for a four-electron pathway in acid media [1,2].

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Heat treatments were generally applied and considered to be a prerequisite for high stability and electrocatalytic activity of these catalysts [9,14–16].

Different explanations have been put forward for the enhancement in activity and stability. Tanaka et al. [17] claimed that thermal treatment of these large-area carbon-supported macrocycles generates nitrogen-containing surface groups which serve as coordination centres for metal ions such as cobalt or iron. However, the Me–N₄ moiety is no longer responsible for the activity at temperatures above 800°C.

In contrast, on the basis of extended X-ray absorption fine structure (EXAFS) data, Van Veen et al. [18] came to the conclusion that the Me–N₄ moiety favours both activity and stability, but the working temperature should not exceed 550°C. Another theory was proposed by Wiesener [10], who insisted that the role of the metal atom was merely to catalyse the formation of an active catalyst.

Recently, mixed valence behaviour has been observed for flexible clam-shell phthalocyanines with zinc [19] and inflexible binuclear cobalt phthalocyanines [20]. In the latter case the redox couples were assigned to both Co(II)/Co(I) and Co(III)/Co(II), thereby increasing their stability via delocalization of the charges. Other authors [21] found increased activity and stability with bilayers of Co and Mn porphyrins, O₂ reduction being governed by the Co(III)/Co(II) couple in acid media.

The effect of heat treatment has been studied on both Fe and Co naphthalocyanines impregnated on a high dibutylphthalate (DBP) adsorption characteristic (300–400 ml per 100 g) carbon black support [13,22]. In the case of the Fe compound, by interpretation of X-ray photoelectron spectroscopy (XPS) data, it was shown that optimal activity was obtained for 10% w/w loading, corresponding to a monolayer coverage. In contrast to the data obtained on porphyrins [23], samples with 20% loading were less active.

Substitution of Fe by Co leads to an enhancement in activity and stability [24]. In addition, from XPS data no evidence was found concerning the demetallization process for Co samples.

The aim of the present paper is to investigate the effect of the loading of CoNPc(1,2) impregnated on a well-known carbon black, Printex XE2, and to correlate the activities of the samples with the catalyst distribution on the support as determined from XPS measurements.

EXPERIMENTAL

Preparation and characterization

The preparation and characterization of various samples of CoNPc(1,2)/Printex XE2 have already been described in detail elsewhere [11–13]. The preparation involves heating dicyanonaphthalene(1,2) (DCN) in the ratio of 4 mol DCN per 1 mol Co acetylacetonate (Co(AcAc)₂). The synthesis was achieved *in situ* in the

TABLE 1

Atomic ratios for unsupported CoNPc(1,2) powder

C:N	C:Co	N:Co	C:O	N:O
4.90	80	16	28	5.8

presence of the reactants and the support. UV-visible spectra and fast atomic bombardment spectroscopy (FABS) characterizations were conducted on both unsupported and supported powders.

From the analyses on supported CoNPc(1,2) powder the theoretical mass spectra were obtained and the UV-visible spectra were found to be identical for unsupported and supported samples after dissolution in pyridine.

In addition, in the present paper XPS analysis has been performed using the same equipment as described in refs. 12 and 13. The atomic ratios for the unsupported CoNPc(1,2) powder are given in Table 1.

The N1s and Co2p spectra are shown in Figs. 1(a) and 1(b) respectively. No shoulder can be detected on the N1s spectrum, while the Co2p spectrum is characteristic of valency II.

For the supported samples the loadings were assayed as usual by atomic absorption.

Electrochemical equipment

This is identical to that described in refs. 11–13. The electrolyte consists of a solution of sulphuric acid (0.25 M H_2SO_4). The surface area of the electrode is 0.125 cm^2 . Potentials are quoted with respect to the reversible hydrogen electrode (RHE).

Electrode preparation

The electrode preparation on the disk is also identical to that reported in refs. 11–13. It involves fixing the carbon black impregnations in the disk cavity with a Teflon binding agent. The electrical contact is secured by a gold lacquer.

The present work is concerned with samples 1–5 corresponding to the loadings given in Table 2. These various impregnations, after 10 days in an oxygenated sulphuric acid medium (0.25 M), were subjected to further XPS analyses in order to shed light on the possible correlation between the electrocatalytic activity and

TABLE 2

Samples and loadings

Sample	1	2	3	4	5
Loading/%	11.4	17	27	41	60

Fig. 1. (a) N1s and (b) Co2p spectra for unsupported CoNPc(1,2) powder.

the distribution of the catalyst on the support. The samples were examined before and after heat treatment.

Different thermal treatment conditions were tested only on sample 3. It appears that the optimal condition for these materials is 500°C for 2 h under N₂ (see Fig. 2). For all thermal treatments the temperature programme consisted of a rise of 20°C min⁻¹ and a cooling period which took about 3 h.

Fig. 2. Optimization of thermal treatment conditions (I - E curves at 64 rev s^{-1} , scanning velocity $v_b = 1.5 \text{ mV s}^{-1}$): 1, 500°C after 2 h heating; 2, 400°C after 2 h heating; 3, 500°C after 4 h heating; 4, 600°C after 2 h heating.

RESULTS AND DISCUSSION

I vs. E curves for different loadings at a rotation frequency of 64 rev s^{-1} (limiting value for which the Levich plots are obeyed) before and after heat treatment are shown in Figs. 3(a) and 3(b) respectively. All these curves are corrected for the residual current under nitrogen.

In the low polarization domain above 700 mV(RHE) in both Figs. 3(a) and 3(b) optimal activity is obtained for the sample with 17% loading.

For both the untreated and heat-treated samples a Tafel plot of E vs. $\log I$ can be ascribed for applied potentials higher than 730 mV(RHE) . The slopes for the various samples are given in Table 3.

TABLE 3

Tafel slopes obtained for different loadings (a) before and (b) after heat treatment (potential domain above 730 mV(RHE))

Sample	(a)		(b)	
	Slope/ mV per decade	Correlation coefficient	Slope/ mV per decade	Correlation coefficient
1	89.7	0.99	53	0.99
2	82	0.99	55	0.99
3	88	0.98	53	0.98
4	101	0.97	—	—
5	72	0.98	—	—

For the untreated samples (1–3) the Tafel slopes are close to 80 mV per decade, which from ref. 3 would suggest a rate-determining step controlled by the catalyst concentration on the support. However, since different activities are clearly visible, with an optimum for sample 2, it turns out that the catalyst distribution on the support cannot be uniform over the whole set of samples.

At higher polarizations no limiting currents can be noted and the differences in activity are smeared out.

Since $1/I$ vs. $f^{-1/2}$ plots (where f is the rotation frequency) can be obtained (with the exception of sample 3), it can be assumed from ref. 25 that a rate-determining chemical reaction between O_2 and the catalyst occurs which is almost independent of the loading value.

Figure 3(b) displays the enhancement in activity resulting from the heat treatment. The Tafel slopes are identical and drop below 60 mV per decade in accordance with a two-electron transfer rate-determining step [1]. As mentioned above, the optimal activity still holds for sample 2. Since the three most active samples present the same Tafel slopes but different activities, it can be concluded that the active site density is higher in the case of sample 2. For sample 2 the overall number of exchanged electrons is close to $N=4$, since the current approaches the theoretical Levich current of about 1000 μA as calculated from ref. 26.

It can also be pointed out that the change in the Tafel slopes resulting from the heat treatment should involve an enhancement in the catalyst dispersion on the support (see discussion of XPS data below).

With the exception of heat-treated sample 3 which yields a Levich plot, all the data can be compiled using a Koutecky–Levich plot [27] for potentials ranging from 300 to 450 mV(RHE). From the slope of the linear relationship one can obtain the overall number N of exchanged electrons. These data are listed in Table 4 for both the untreated and heat-treated samples. For sample 3 it is obvious that N was obtained in a different mode.

In connection with Table 4 it should be emphasized that the rate of H_2O_2 decomposition is enhanced after application of the heat treatment, especially for the most active samples (1–3). These findings are consistent with refs. 28 and 29.

TABLE 4

Overall number N of exchanged electrons for all samples investigated

Sample	N	
	Untreated	Heat treated
1	2.60	3.22
2	2.64	3.55
3	2.73	2.88
4	2.30	2.33
5	2.41	2.54

Voltammetry

Typical voltammetric curves under O_2 and N_2 for the 17% CoNPc(1,2)/Printex XE2 thermally treated samples are shown in Figs. 4(a) and 4(b) respectively.

Under N_2 one cannot observe any redox couple or faradaic reaction. However, a pseudocapacitance can be defined, since the current is nearly proportional to the scanning velocity v_b .

Fig. 3. $I-E$ curves for different loadings at 64 rev s^{-1} (corrected for residual current under N_2): (a) before heat treatment; (b) after heat treatment. Numbers on curves are sample numbers.

Fig. 4. Voltammetric curves obtained under (a) O_2 and (b) N_2 on stationary electrodes at different scanning velocities for thermally treated sample 2: 1, $v_b = 10.8 \text{ mV s}^{-1}$; 2, $v_b = 5.4 \text{ mV s}^{-1}$; 3, $v_b = 3.6 \text{ mV s}^{-1}$.

In contrast, under O_2 a prominent peak corresponding to an oxygen adduct is clearly visible, with a maximum shift to more negative potentials as v_b increases.

The coincidence of the prominent peak potential resulting from the oxygen adduct reduction observed by voltammetry with the potential values characteristic of the O_2 reduction presented in Fig. 3(b) stresses the role of the complex formation kinetics in the overall O_2 reduction process.

These findings are in strong agreement with those reported by Tanaka et al. [17] for CoTMPP/Vulcan XC 72 in 0.05 M H_2SO_4 and by Durand et al. [3] for a monomeric Co porphyrin adsorbed on pyrolytic graphite in 1 M CF_3COOH .

TABLE 5

Capacitance values obtained for untreated and heat-treated CoNPC(1,2)/Printex XE2 under N₂

Sample	Capacitance/mF	
	Untreated	Heat treated
1	72.4	83
2	84	140
3	91	109
4	40	37
5	30.6	42.3

For the other samples under N₂ as well as O₂, similar conclusions can be drawn (no peak under N₂ and a prominent one under O₂).

Table 5 lists the pseudocapacitance values obtained under N₂, determined from voltammetric curves for all the samples investigated.

In the case of the active samples (1 and 2), especially sample 2, a drastic increase in the capacitance value is observed after heat treatment.

The charge Q for the O₂ adduct peak can be defined at $v_b = 3.6 \text{ mV s}^{-1}$. For the most interesting heat-treated samples (1–4) the integral charge values are given in Table 6.

The above results can be compared with the findings of ref. 28. According to ref. 28, heat treatment will enhance the wetting of the catalyst surface, leading to an increase in the active site density. Thus the data in Tables 5 and 6 suggest a special effect of the loading on the active site formation.

XPS experiments

In previous papers [22,24] we evaluated from XPS data the average number n of catalyst layers present on the support. The determination of the C:N atomic ratios at different loadings using eqn. (11) in ref. 30 yields the average number n of catalyst layers. Figure 5 shows the result for a sample with 30% w/w loading.

Table 7 gives the C:N ratios and the n values deduced from Fig. 5 after loading correction for the various samples before and after heat treatment. These values were obtained after 10 days in oxygenated 0.25 M H₂SO₄ solution.

For high loading values the heat treatment seems to have no influence on the C:N value or therefore on n . It has to be pointed out that the mean escape depth for naphthalocyanine (rich in carbon) does not exceed about 5 layers [31]. Thus at high loading coverages n values higher than 5 cannot be assessed.

TABLE 6

Charge Q determined for heat-treated samples at $v_b = 3.6 \text{ mV s}^{-1}$

Sample	1	2	3	4
Q/mC	5.18	8.17	5.21	2.07

Fig. 5. Plot of n vs. C:N calculated from eqn. (11) in ref. 30 for 30% w/w loading.

At lower loadings, in the case of crystallite formation with the simultaneous presence of bare surfaces, only the surface crystallite layers are visible by XPS, thus undervaluing n . After heat treatment the effect of more complete dispersion will enhance the n value.

These results hold for samples 1 and 2 (lowest loadings). In the case of totally covered surfaces, with n values detectable by XPS, i.e. $n < 5$, the heat treatment

TABLE 7

C:N and n determined from Fig. 5 after correction for the loading value

Sample	1	2	3	4	5
Loading/% w/w	11	17	27	41	61
C:N (untreated)	88	74	40	28	28
C:N (heat treated)	87	79	47	32	29
n (untreated)	< 1	1.5	4	> 5	> 5
n (heat treated)	< 1	2	3	> 5	> 5

TABLE 8

O:N and N:Co ratios determined from XPS for all samples investigated

Sample	1	2	3	4	5	6 (unsupported)
O:N (untreated)	1.8	0.85	2	0.6	0.7	0.17
O:N (heat treated)	1.45	1.3	1.7	0.7	0.8	
N:Co (untreated)	31	16	14	16	17	16
N:Co (heat treated)	17	16	18	17	20	C:N = 5

TABLE 9

Co valencies for all samples investigated

Sample	1	2	3	4	5	6 (unsupported)
Untreated	Co(III)	50% Co(II)/Co(III)	40%–60% (Co(II)/Co(III))	Co(II)	Co(II)	Co(II)
Heat treated	Co(III)	50% Co(II)/Co(III)	50% Co(II)/Co(III)	Co(II)	Co(II)	Co(II)

will result in a decrease in the n value, which is the case for sample 3. Table 8 presents the O:N and N:Co atomic ratios for samples 1–5 after 10 days in acid solution. The atomic ratios determined on the unsupported CoNPc(1,2) powder and also its C:N ratio are given as reference values.

For the thermally active samples the N:Co ratio is close to that of the unsupported sample. These results display the absence of any demetallization and of course also the retention of the Co–N₄ moiety. These findings conflict with those reported by Tanaka et al. [17] for porphyrins dispersed on Vulcan XC 72. However, it must be emphasized that in ref. 17 the thermal treatment temperature was 800°C instead of 500°C as in the present case.

It can be noted from Table 8 that the lower O:N ratios are observed for the thicker samples. Therefore a contribution of the oxygen content in the carbon black support is likely.

The Co valency is given in Table 9 for all the samples investigated. From this table it can be inferred that the most active samples correspond to a Co(II)/Co(III) mixture in about equal proportions (see also Fig. 6 for sample 2).

Fig. 6. Co2p spectrum for sample 2.

TABLE 10

N1s maximum peak binding energies (BEs)

Sample	1	2	3	4	5	6 (unsupported)
BE/eV (untreated)	398.5	398.7	399.5	398.9	399	399
BE/eV (heat treated)	398.5	398.6	397.8	398.8	399	399

Since the most reduced forms of Co are observed for the highest loadings, a correlation is suggested between the Co valency and the oxygen content probably confined in the support.

Mixed valencies correspond to n values of 2 or 3. Since the distance between two NPc layers [32] is close to 3.5 Å and the required distance for O₂ to bridge between two Co sites is 4 Å [2,3], a bridging model is plausible [1,2]. Since the current obtained from the I - E curves for the most active bilayer sample ($n = 2$) approaches its theoretical value (with N determined from the Koutecky-Levich plots as approximately 4), the bridging model reported in the literature is more likely.

In favour of this active structure the following considerations should be noted.

(1) N determined from the Koutecky-Levich plots is 3.55.

(2) $n = 2$.

(3) The active site density is optimal for sample 2 (as determined from both the I - E curves and voltammetry).

Table 10 gives the N1s maximum peak binding energies (electronvolts) for all samples. The most salient feature is the negative charge seen with heat-treated sample 3.

Fig. 7. N1s spectrum for sample 2.

A typical N1s spectrum for sample 2 is shown in Fig. 7 (the spectra are identical for untreated and heat-treated samples). This curve is similar to that for the unsupported powder but with a maximum at 398.6 eV instead of 399 eV as in the supported case, characterizing a more negative charge on the nitrogen atoms.

- [I] Initial chemical step [Proton fixation]
 [II] First electron transfer
 [III] 2 electron transfer [rds]
 [IV] Electron transfer and μ -peroxo formation

Fig. 8. Proposed reaction mechanism for the four-electron reduction of oxygen catalysed by CoNPc(1,2).

Correlation with electrochemistry

On the most active heat-treated samples (1–3), as mentioned above, a Tafel slope of 53 mV per decade is obtained. From the XPS data the optimal activity is reached for a homogeneous dispersion with $n = 2$ and mixed Co(II)/Co(III) valencies in equal proportions. This configuration is somewhat different from that reported in ref. 1, in which the O_2 molecule is bonded to two Co sites of valency III. In our case it is obvious that the dissymmetry will enhance a fast electronic transfer between the Co(II) and Co(III) sites and the bridging O_2 molecule, giving rise in acid media to protonation. The configuration in which the HO_2 radical is bound between two Co(III) sites has been reported by Collman et al. [33] to favour its stabilization.

The rate-determining step (RDS) in the case of the transfer reaction [34] can be obtained from

$$\alpha N = \frac{N^*}{\nu} + \beta N' \quad (1)$$

where N is the overall number of electrons exchanged in the reaction ($N \approx 4$) as determined above, N^* is the number of electrons transferred before the RDS, α is the empirical transfer coefficient ($\alpha \approx 0.5$), ν is the stoichiometric number ($\nu = 1$ in the present case), β is the symmetry factor ($\beta \approx 0.5$) and N' is the number of electrons exchanged in the RDS. From eqn. (1) and electrochemical data, $N^* = 1$ and $N' = 2$.

These kinetic and structural data from XPS are consistent with the model presented in Fig. 8.

The enhancement in the rate of O_2 adsorption with increasing nitrogen charge should be emphasized. It is a maximum for sample 3, where it results in a Levich plot.

Increasing n above 3 leads to a drop in activity due to the simultaneous effects of

- (1) inhibition of the O_2 adsorption rate on the outer layer,
- (2) mass transfer to the active sites and
- (3) active site deterioration caused by a depletion of the Co(III) valency in the outer layers, which can be attributed to a lack of interaction with the support.

CONCLUSIONS

Examination of the loading effects on the activities and stability of CoNPc(1,2) impregnations on Degussa Printex XE2 leads to the following conclusions:

- (1) The O_2 adsorption rate displays a maximum for a homogeneous distribution of $n = 2$ catalyst layers.
- (2) The negative charge on the nitrogen atoms and the Co valencies vary as a function of both the heating temperature and the loading. Optimal activities are found for a bilayer coverage with a mixed valency consisting of equal proportions of Co(II) and Co(III).

(3) Under these conditions the effect of heat treatment is to increase the overall number N of exchanged electrons to 3.55. Electrode performances approach those of 10% w/w Pt on Vulcan.

(4) From the stability of the N:Co ratio after prolonged immersion in oxygenated acid solutions (the ratio equals the initial value for the unsupported powder), long-term stability can be envisaged.

(5) Inactive samples display n values of 4 or more and the presence of O_2 at the carbon black–CoNPc(1,2) interface turns out to be crucial in the catalyst crystallite formation.

(6) From a fundamental viewpoint the O_2 reduction fits a bridging model similar to that reported by Collman et al. [33]. However, the couple which tracks the O_2 reduction involves a mixed Co(II)/Co(III) valency in which Co(III) is stabilized by the O_2 groups confined to the support.

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