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Investigation of O_2 reduction in alkaline media on macrocyclic chelates impregnated on different supports: influence of the heat treatment on stability and activity

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Several macrocyclic chelates impregnated on different carbon supports were investigated using a three-phase electrode. Pyrolysed CoTMPP on treated Vulcan yields comparable results to dispersed Pt. XPS investigations reveal, for the most stable compounds, either a special bond with carbon (CoTMPP) or in some cases nitride formation (MoNPc). With the most active compounds, the MeN_4 unit is preserved after heat treatment. The affinity of carbon or nitrogen with the metal compared to the O_2 affinity is essential.

1. Introduction

Macrocyclic compounds of Co and Fe, more specifically porphyrins, naphthalocyanines and phthalocyanines have been extensively scrutinized for their electrocatalytic properties towards O_2 reduction in alkaline media [1–6]. One of the most promising ways of improving the activity and the stability of the carbon supported transition metal chelates is by pyrolysis: heat treatment in an inert gas atmospheres [6] for several hours at 800° C. Several authors have attempted to explain the fundamental reasons for this increased activity and stability [7–15]. The differences in the basic explanation of this effect between the various research groups are significant. Wiesener [8] reported, using X-ray techniques, that the porphyrin molecule is destroyed after pyrolysis and a new catalyst is formed consisting of nitrogen and carbon. Thus, the central metal ion is no longer the active site, the activity results from a new catalyst formed by a carbon and nitrogen modified electrode. This finding is in conflict with that of Yeager's group: in their opinion a cobalt species, observed by Mössbauer spectroscopy, is responsible for the improved activity [9, 10].

A third explanation was provided by Van Veen [11] based on redox catalyst concepts. Their results prove that the chelate reacts with a carbon support, but the MeN_4 units remain intact ($T \leqslant 800°C$) according to EXAFS measurements. The formation of β metallic cobalt could occur and this has been confirmed [12].

More recently Van Veen [13], making a survey of all the hypotheses put forward by various groups, showed that the enhancement of the activity is not due to the formation of a highly active carbon [8], but of a chemical bond between the central metal ion and nitrogen; this is in accordance with the findings of Yeager [10]. However, from the point of view of industrial applications the long term stability of these catalysts needs improvement. The most active samples were obtained by subjecting this variety of chelate to heat treatment in an inert atmosphere at 800° C (Ar in the present case) [6].

The aim of this paper is to shed light on the relationships existing between the structure, stability and activity of the above compounds under industrial conditions.

2. Experimental

2.1. *Catalyst synthesis and characterization*

The catalysts investigated were as follows:

2.1.1. Untreated catalysts. CoTMPP, CoTPP, CoPc, FePc, FeNPc and MoNPc.

2.1.2. Treated samples. The following catalysts were explored: CoTMPP, CoTPP, Fe and MoNPc, AgTMPP and FeTMPP.

The pyrolysis treatment consisted in heating the catalysts deposited on carbon powder at 800° C for 2 h in an inert gas atmosphere (Ar).

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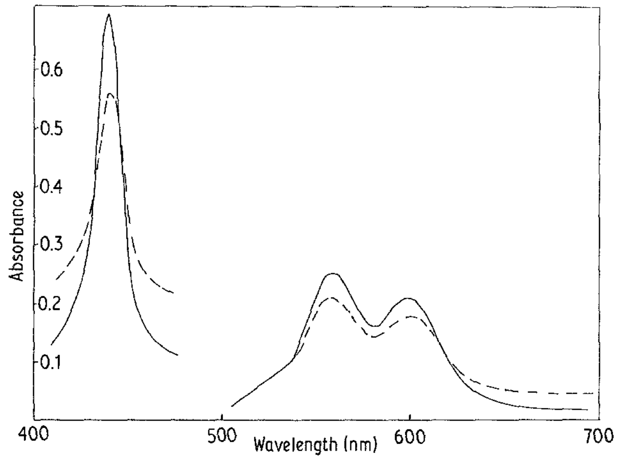

Fig. 1. CoTMPP optical absorption: (a) under N_2 (- - -); (b) under O_2 (——).

Two types of carbon black were employed: Vulcan XC72, BET surface $256\,m^2\,g^{-1}$; Degussa XE2, BET surface $1000\,m^2\,g^{-1}$; and an active charcoal, Norit BRX, BET surface $1800\,m^2\,g^{-1}$. Before pyrolysis these carbon blacks were treated for 5 h at 90° C in concentrated 7.5 M HNO_3 to introduce active surface groups [14].

CoPc and FePc were purchased from Eastman Kodak and used as received.

Following the route described in [16, 17] the porphyrins were synthesized by reaction of pyrrole and benzaldehyde (TPP) or paramethoxybenzaldehyde (TMPP) in refluxing propionic acid. All chemicals were purchased from Aldrich without further purification. CoTMPP samples were further examined by optical spectroscopy using a Cary 17 spectrometer. The powder was dissolved at a concentration of 10^{-5} M in pyridine using 10 mm quartz cuvettes for the Soret band and 10^{-3} M for the visible region.

Absorption spectra under N_2 and O_2 are depicted in Fig. 1a and b. No significant displacement of the peak position is observed despite a rise in intensity under O_2. The characteristic features of these spectra are in good agreement with those reported in benzene in references [10] and [18]. The modification of the peak intensity under O_2 suggests a chemical interaction with CoTMPP. The synthesis efficiency was relatively weak (20% maximum). The crude product obtained (TPP or TMPP) subsequently underwent several purification and recrystallization steps in acetone and chloroform before complexing the selected metal. The metal nucleus was fixed on the chelate by reaction of porphyrin and metallic acetate in refluxing glacial acetic acid.

2.1.3. Deposits of metal complexes on carbon (porphyrins). The metal complexes of TPP and TMPP were deposited on carbon substrates by dissolution in dioxane and precipitation after hot water addition. The same route was followed for Co and Fe phthalocyanines (Pc), but in this case the complexes were dissolved in concentrated sulphuric acid.

Table 1.

	Carbon	*Hydrogen*	*Nitrogen*	*Iron*
Found	77.0	3.10	14.92	4.17
Expected	75.0	3.10	14.60	7.3

2.1.4. FeNPc. For impregnations on Norit BrX the following procedure was followed. Heating at 300° C in a closed glass vessel for 24 h 2,4-pentanedione and 1,2-dicyanonaphthalene (DCN) in a molar ratio of 1 : 4 in the presence of carbon yields a product that loses only half of its iron upon treatment by the standard washing procedure [4] as was found by atomic absorption.

The more finely divided 2,4-pentanedione complex clearly competes with the destruction reaction of the 1,2-DCN. A small quantity of the product was eluted with pyridine. The resulting filtrate showed the colour characteristic of FeNPc in pyridine solution. The elemental analysis (wt %) of FeNPc pure powder is given in Table 1. As the other element compositions are close to the expected value the iron deficiency shows the presence H_2NPc which was found to be inactive for O_2 reduction.

2.1.5. MoNPc. For MoNPc on Norit BrX all impregnated samples were made by heating an intimate mixture of 1,2-DCN and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (AMTH) and carbon black in a closed evacuated glass capsule under the same conditions as above. The products were extracted with ethanol, boiled in 1 N HCl and then in 1 N NaOH and washed with distilled water until neutral. In this case the best results for the characteristic spectrum in pyridine were obtained when DCN and AMTH were used in a 2 : 1 ratio w/w which corresponds to 13.9 mol DCN mol^{-1} Mo compound. In a typical example, 30 g Norit BrX, 8 g 1,2-DCN and 4 g AMTH yielded a product with 3.9 wt % Mo as determined by atomic absorption. The elemental analysis (wt %) of MoNPc pure powder (prepared without support) is given in Table 2. The deficiency in carbon and nitrogen is relatively small. This may be due to a slight excess of AMTH, which is still present despite further purification.

2.2. *Electrode preparation*

The impregnated supported catalyst was mixed with a binding agent PTFE in a 2 : 1 ratio (w/w). The resulting paste was rolled and introduced into a nickel foam by pressing. This nickel foam acts simultaneously as a current collector and as a holder matrix for the catalyst. A hydrophobic microporous layer of PTFE was

Table 2.

	Carbon	*Hydrogen*	*Nitrogen*	*Molybdenum*
Found	65.73	2.96	12.45	11.84
Expected	72.2	2.97	13.86	11.80

achieved by spraying a Teflon suspension on one of the faces of the electrode. The electrode was then subjected to a sintering treatment at 300° C for 2 h under nitrogen. The electrodes under tests had an apparent surface area of 10 cm^2 and a thickness of 0.8 mm.

2.3. *Substrate treatment*

Substrates, such as Vulcan XC72 and Degussa XE2 treated by nitric acid 7.5 M at 90° C during 5 h, give rise to carboxylic, hydroxylic or phenolic groups on their surface [14, 15]. These surface groups, which were further characterized by FTIR [19], contribute to the fixation of catalytic compounds, thus enhancing the dispersion of the catalyst. The ratio of the catalyst over the carbon support is around 10 wt %.

2.4. *Electrochemical measurements*

The three phase electrodes were tested under 6 N KOH at ambient temperature (23° C). The electrode was fed by a constant air flow at its rearface with an overpressure of 30 Pa. After 10 h polarization *i–E* curves were plotted and the electrode was further polarized at a constant current density of 150 mA cm^{-2}. The electrode potential change was registered using a Hg/HgO reference electrode.

2.5. *Characterization: XPS experiments*

The XPS analyses were performed using a HP5950 spectrometer with monochromatized AlKα 1,2 radiation ($h\nu$ = 1486.6 eV).

The X-ray monochromator exploits Rowland's theorem. The monochromatic Al X-ray emission spectrum is obtained by reflection on three crystals. Only the AlKα 1,2 satisfies the Bragg diffraction law and is focussed on the sample. The other radiation in the X-ray spectrum is not reflected.

The energy dispersion of the incident X-ray photons on the sample is about 1 eV which is the width of the X-ray line. By using the energy dispersion compensation the resolution obtained on this spectrometer is equal 0.8 eV measured on Au 4f $\frac{7}{2}$ level.

Atomic ratios were calculated using the sensitivity core level factors tabulated by Elliott *et al.* [20]. The estimated error on the XPS atomic ratios was approximately 10%. The following samples were analysed by XPS: CoTMPP deposited on treated Vulcan before and after pyrolysis; FeNPc deposited on Norit after pyrolysis; MoNPc deposited on Norit after pyrolysis; CoTMPP deposited on Norit before and after pyrolysis; CoTMPP deposited on treated Degussa XE2 before and after pyrolysis; FeNPc deposited on Norit; MoNPc, deposited on Norit.

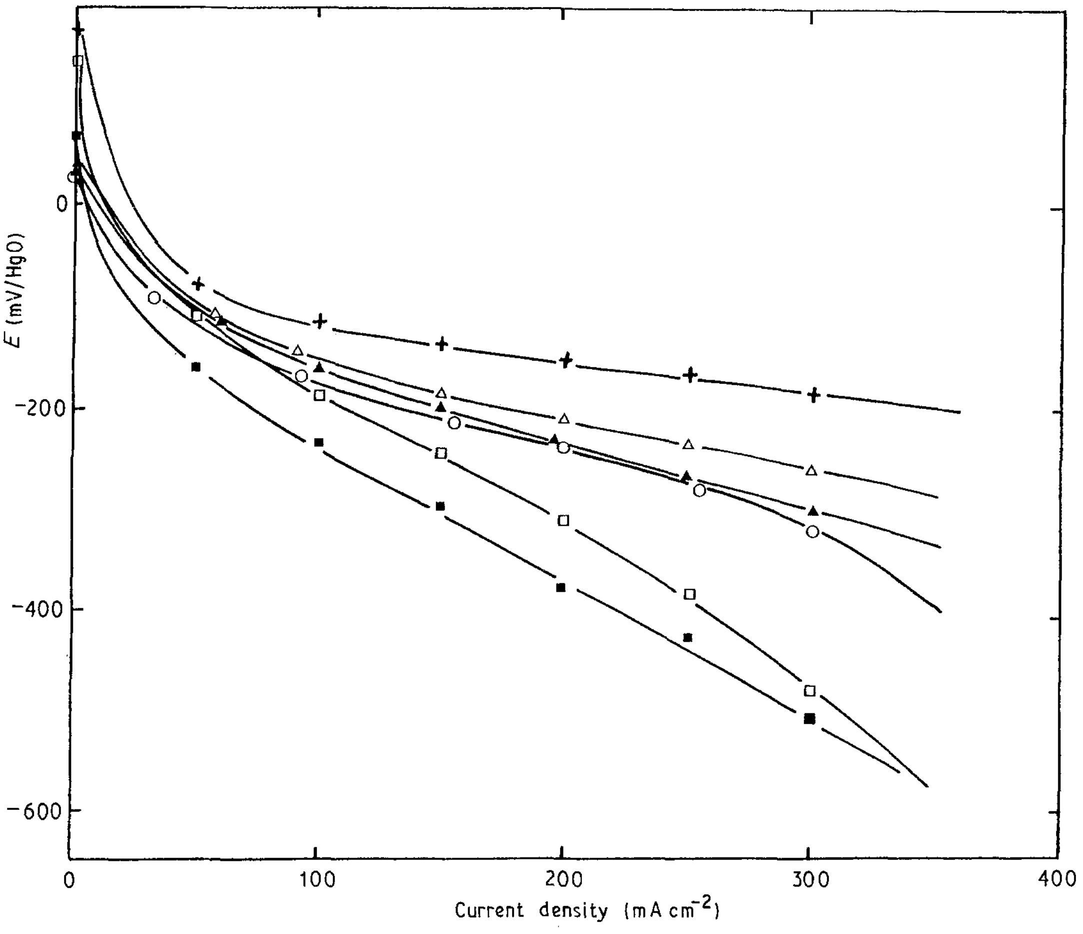

Fig. 2. *i–E* curves on the following macrocyclic compounds impregnated on Norit BrX: (+) Pt (dispersed on Vulcan); (△) FePc; (▲) CoPc; (□) FeNPc; (■) MoNPc; (○) CoTMPP.

Table 3.

Sample	*Potentials* (*mV w.r.t. Hg/HgO reference*)
Pt dispersed on Vulcan	−130
FePc deposited on Norit	−180
CoTMPP	−205
CoPc	
FeNPc	−250
MoNPc	−375

3. Results and discussion

3.1. *Electrochemical results*

Figure 2 shows the *i–E* curves obtained on the non-pyrolised catalysts. To compare their performance, a curve for Pt dispersed on Vulcan XC72 is indicated as a reference. The more positive rest potentials were given by Pt and FeNPc. In contrast, CoTMPP, CoPc, MoNPc and FePc gave roughly the same values. Among the various types of catalyst studied, an activity classification can be established concerning the potentials of these electrodes at a fixed galvanostatic load of 150 mA cm^{-2}. Results are summarized in Table 3. Thus, for Fe, the phthalocyanine ligand is more active than that of naphthalocyanine; for the same ligand (Pc and NPc), the trend in activity is Fe > Co and Fe > Mo.

Figure 3 depicts the *i–E* curves obtained on the pyrolysed catalysts. Compared with Fig. 2 one can observe an improvement for CoTMPP which becomes comparable to Pt dispersed on Vulcan XC72. This treatment seems to be detrimental for FeNPc. Whereas no significant difference in activity can be obtained for MoNPc, a slight decrease occurs for FeNPc after pyrolysis. From Fig. 3 we notice that there is no pronounced difference in activity between CoTMPP, CoTPP, AgTMPP and FeTMPP; in contrast a lower activity is obtained for MoNPc and FeNPc. The trend in activity may be summarised as: CoTMPP > CoTPP > FeTMPP > AgTMPP.

Thus, for a given ligand, the order of activity is Co > Fe > Ag. Similar results were reported by Van Veen *et al.* [21] on TPP in alkaline media.

To study catalyst stability in 6 N KOH we measured the potential variation for several hundred hours of operation under a steady galvanostatic load of 150 mA cm^{-2}. Figures 4 and 5 represent the potential variation with time of these catalysts before and after pyrolysis, respectively. Pt samples remained almost unchanged. It must be pointed out that this treatment is beneficial for the CoTMPP catalysts which show an activity comparable to Pt. In the non-pyrolysed state, greater stability is obtained for FePc and CoPc. However, a life time about 25% shorter than that observed on FePc or CoPc is obtained for CoTMPP, FeNPc and MoNPc catalysts. Thus, it can be concluded that the phthalocyanine ligand is more stable than that of

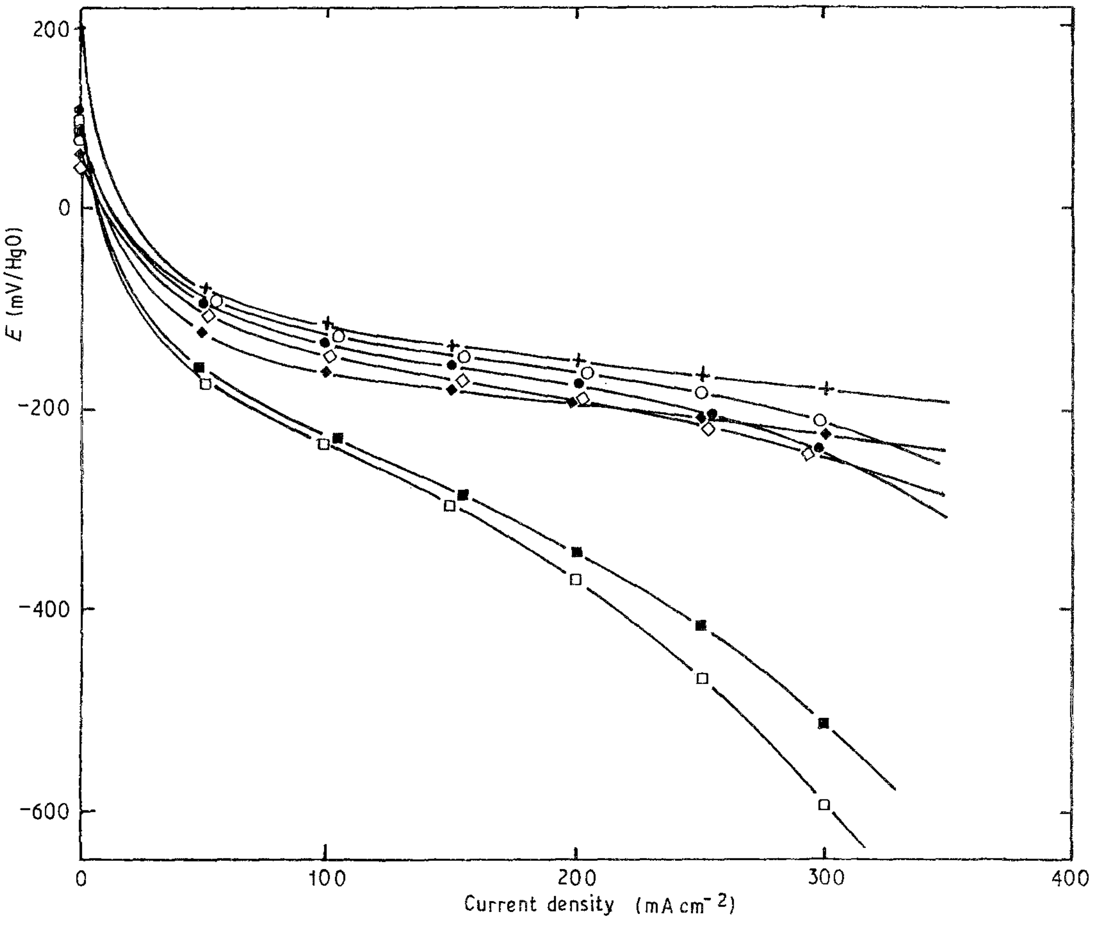

Fig. 3. *i–E* curves on the following samples (macrocyclic compounds on Norit BrX after pyrolysis); (+) Pt (dispersed on Vulcan); (○) CoTMPP; (◇) FeTMPP; (◆) AgTMPP; (●) CoTPP; (□) FeNPc; (■) MoNPc.

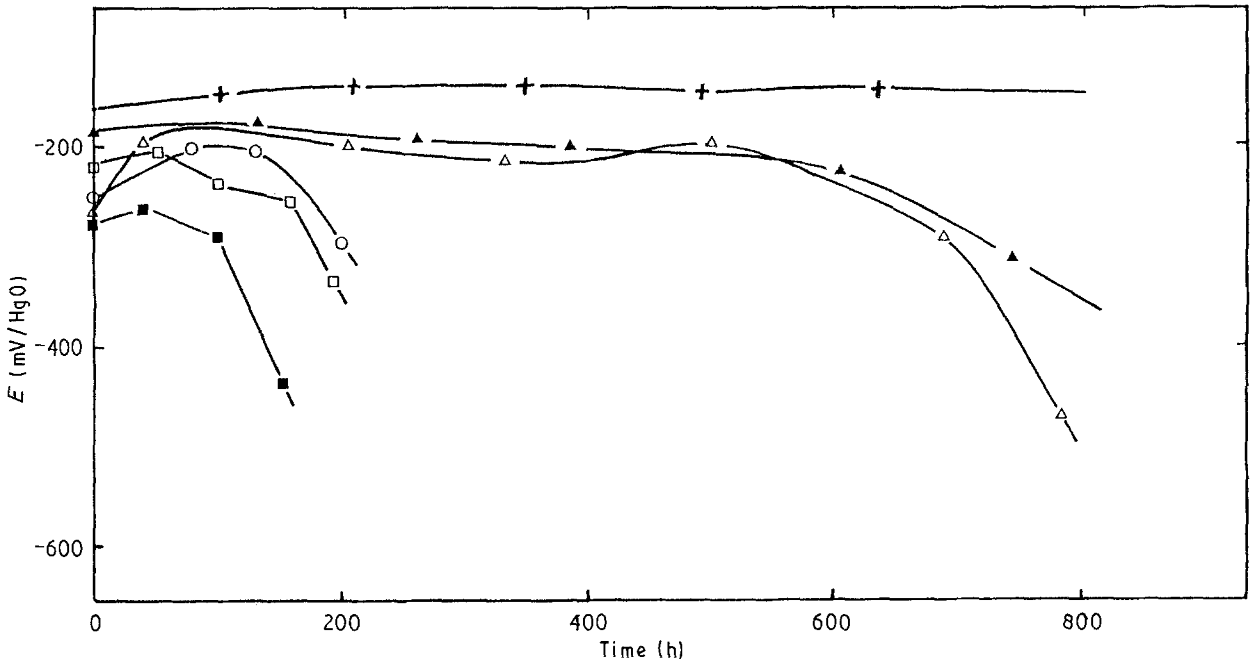

Fig. 4. E against time curves at $i = 150\,\mathrm{mA\,cm^{-2}}$ on the non-pyrolysed samples on Norit BrX: (○) CoTMPP; (+) Pt (dispersed on Vulcan); (△) FePc; (▲) CoPc; (□) FeNPc; (■) MoNPc.

naphthalocyanine. In the pyrolysed state, a significant improvement in stability is obtained for AgTMPP and CoTMPP, which become comparable in performance to the platinum samples. The loss of activity is more pronounced for CoTPP and FeNPc. Compared to the non-pyrolysed samples the most salient feature concerns the increase in stability for CoTMPP and MoNPc and to a lesser extent, for FeNPc. From a practical point of view the heat treatment effect in an inert gas atmosphere is beneficial to the CoTMPP catalyst, where the lifetime and the activity are considerably increased. Since CoTMPP is one of the best catalysts its activity was measured during the first 500 h of functioning on three different supports: treated Vulcan XC72, treated Degussa XE2 and Norit BrX at a current load of $200\,\mathrm{mA\,cm^{-2}}$. The results are presented in Fig. 6. Because a small variation in E corresponds to a big variation in i, the performance of treated Vulcan is significant.

3.2. *XPS results*

To investigate the possible relationship between the structure and the electrochemical activity and long term stability of the impregnation defined above, XPS measurements were undertaken on the most active

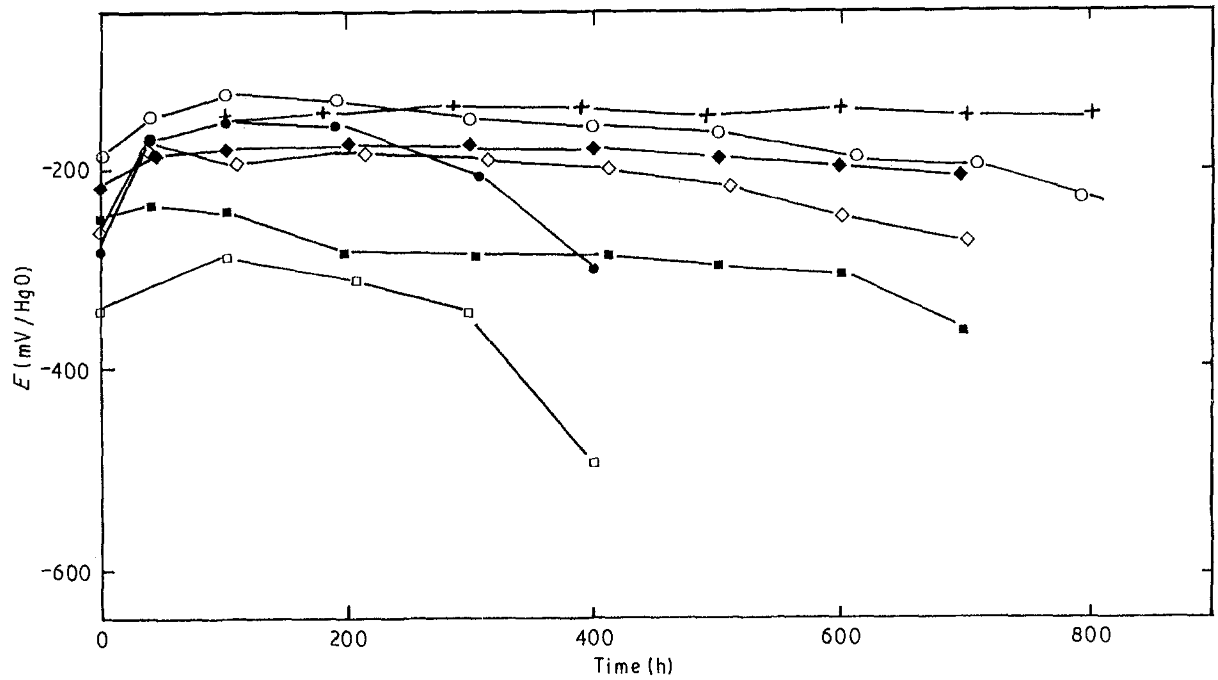

Fig. 5. E against time curves at $i = 150\,\mathrm{mA\,cm^{-2}}$ on the following pyrolysed samples on Norit BrX: (+) Pt (dispersed on Vulcan); (○) CoTMPP; (◇) FeTMPP; (◆) AgTMPP; (●) CoTPP; (□) FeNPc; (■) MoNPc.

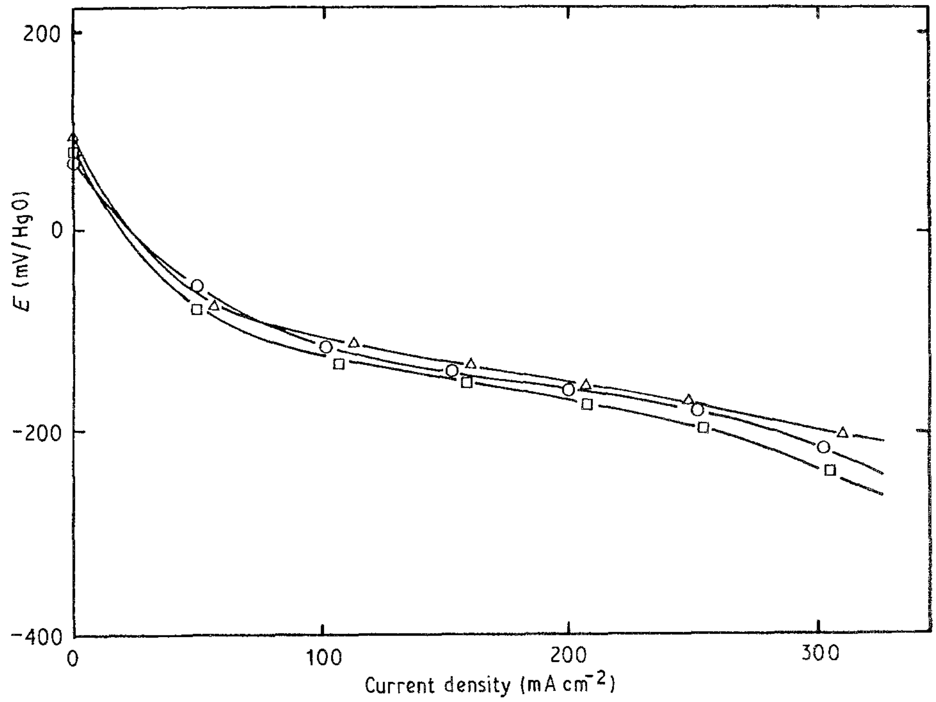

Fig. 6. *E–i* curves of pyrolysed CoTMPP impregnation: treated Degussa XE2 (□); treated Vulcan (△); Norit BRX (○).

samples; pyrolysed CoTMPP impregnations on treated Degussa XE2, treated Vulcan and Norit BrX, and FeNPc and MoNPc impregnations on Norit BrX in the pyrolysed and non-pyrolysed state.

By examination of the core level spectra it is possible to analyse the elements present on the surface up to a depth of 3 to 4 nm and to gain information on their valence state.

3.2.1. CoTMPP impregnations. The samples investigated are labelled as follows: 1. non-pyrolysed CoTMPP deposited on Degussa XE2; 1′. pyrolysed CoTMPP deposited on Degussa XE2; 2. non-pyrolysed CoTMPP deposited on Vulcan XC72; 2′, pyrolysed CoTMPP deposited on Vulcan XC72; 3. non-pyrolysed CoTMPP deposited on Norit BrX; 3′. pyrolysed CoTMPP deposited on Norit BrX; With samples 1, 1′ and 2, 2′, Co_{2p} shows a peak at 780.3 eV with a satellite structure at 788 eV characteristic of Co(II). In accordance with the chemical structure of CoTMPP for the N_{1s} level, a single peak is visible at 398.2 eV on the non-pyrolysed samples 1 and 2, Fig. 7, curve 1. The O_{1s} spectrum at 532.0 eV is characteristic of a weakly bonded oxygen on samples 1, 1′ and 2, 2′ (Fig. 8), curve 1. With samples 1′ Fig. 7, curve 2, the most salient feature is the emergence of two N_{1s} peaks localized at 400 and 398 eV. Although in the porphyrin structure the nitrogens lie in the same chemical environment, they cannot usually give rise to two different peaks. The peaks at about 398 and 400 eV are also encountered with the phthalocyanine and naphthalocyanine structure [5]. Therefore, we suggest that they are characteristic of a MeN_4 unit.

In the case of the Co spectra of samples 1, 1′ and 2, 2′, a mixture of Co(III) and Co(II) is observed, where Co(II) is predominant. From these data it can be concluded that the oxidation of Co(II) by oxygen is relatively low. Samples 2 and 2′ are similar to samples 1, 1′ for their $Co_{2p}N_{1s}$ and O_{1s} spectra. The Co_{2p} level gives a maximum at 780.1 eV, whereas the N_{1s} and O_{1s} levels do not present significant differences from those of samples 1, 1′. With samples 1′ and 2′ the major difference with samples 1 and 2 lies in the intensity of the Co_{2p} spectrum with the Co/C ratio being larger

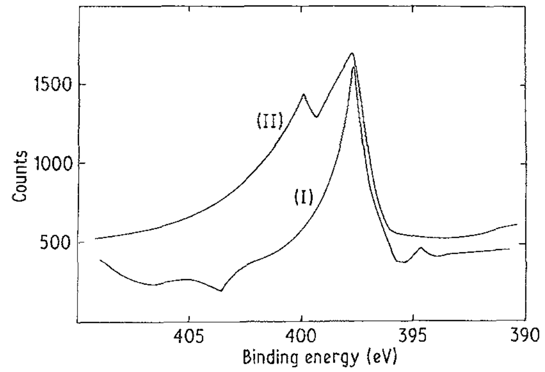

Fig. 7. Typical N_{1s} levels for CoTMPP (counts versus bindings energies) samples 1 and 2 (I), samples 1′, 2′ and 3′ (II).

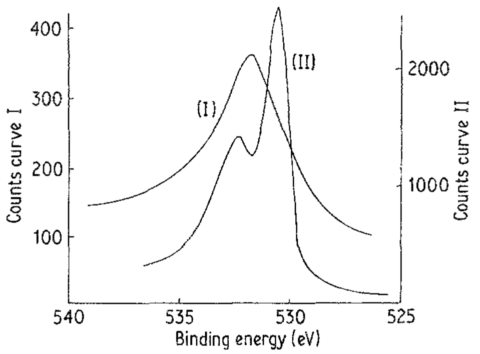

Fig. 8. Typical O_{1s} levels for CoTMPP (counts versus binding energies) samples 1, 1′ and 2, 2′ (I), samples 3′ (II).

Table 4.

Sample	*2*	*2′*
C/O	42	55
C/N	130	50/55
C/Co	80	40
O/N	2.85	1.10

Table 5.

Ratios	*Treated Degussa Xe2*	*Treated Vulcan*	*Norit BrX*
C/Co	1000	40	5
N_{1s}/C_{1s}	0.0108	0.019/0.017	0.016
O_{1s}/C_{1s}	0.016	0.020	0.50*

* In the Norit BrX case it is possible to identify carboxylic groups [19]. The C_{1s} spectra are different from those of the carbon blacks.

with samples 1′ and 2′. The characteristic of sample 2′ are similar to those of sample 1′. With these samples the N_{1s} peak offers two components at 398.3 and 400.5 eV. For samples 2 and 2′ the ratios C/O, C/N, C/Co and O/N are given in Table 4. The decrease in the C/N and C/Co ratios by about the same factor of two indicates a diminution by this factor of the surface amount of carbon atoms whereas the increase in the C/O ratio suggests a greater decrease in O_2 due, probably, to combustion effects as also shown by the decrease in the O/N ratio. As the N_{1s} peaks at 400.2 and 398.3 eV are almost equal, it turns out that about half of the nitrogen atoms are oxidized during pyrolysis. For samples 1, 1′ and 2′, note that Co remains invariant at the valency II.

With samples 3, 3′ the major difference with the previously examined samples lies in the existence of a highly developed O_{1s} spectrum corresponding to two components; a major one at 531.5 eV and another at 530.5 eV, whereas two components are also visible with the N_{1s} spectrum at 400.7 and 398.3 eV.

In the case of non-pyrolysed impregnations on Norit the four nitrogens are not equivalent and a partial oxidation is already visible.

On sample 3′ two kinds of oxygen at 530.3 and 532.3 eV in the 2:1 ratio, in favour of the strongly bonded oxygen, can be distinguished (Fig. 8, curve 2). The major difference lies in the Co_{2p} signal which has a very high intensity in the 3:1 ratio in favour of Co(III).

The C/Co N_{1s}/C_{1s} ratios for (respectively) treated Degussa XE2 and treated Vulcan and Norit BrX, are given in Table 5. From this table it appears that Norit BrX presents very high oxygen and cobalt contents compared to the other samples. The higher cobalt content can be attributed to the fractal character of Norit BrX compared to the carbon blacks [22].

3.2.2. Fe and MoNPc immpregnation. Samples 4 pyrolysed FeNPc deposited on Norit BrX; 4′ non-pyrolysed FeNPc; 5 pyrolysed MoNPc; 5′ non-pyrolysed MoNPc. On Norit BrX, before and after pyrolysis, for Fe and Mo impregnations, compositions are given in Table 6, deduced by XPS. In this table the nitrogen composition is arbitrarily fixed to eight nitrogen atoms in the NPc molecule. The existence of a considerable difference in the C/N ratio, which increases after pyrolysis in contrast with CoTMPP impregnations, is noteworthy. This may be due to an appreciable removal of nitrogen as reported in [23, 24]. The difference between MoNPc and FeNPc after pyrolysis, where loss of nitrogen is more pronounced in the case of FeNPc, is significant. With this latter compound the removal of nitrogen is accompanied by a strong increase of oxygen, the amount being three-fold stronger than in the MoNPc case.

In the case of FeNPc the pyrolysis effect is to promote iron oxide formation. This result is consistent with a decrease in the N/C ratio, more pronounced with FeNPc, involving a more complete destruction of the molecule after pyrolysis.

Special attention must be given to the N_{1s} peaks (Fig. 9a and b). In the case of pyrolysed MoNPc, the N_{1s} level appears to be rather complex (Fig. 9b). Three components are clearly detectable instead of two in the non-pyrolysed samples (Fig. 9a). These peaks are located at 401, 397.6 and 394 eV instead of 400.9 and 398.8 eV. The peaks at 397.6 and 394 eV can be assigned to a nitride formation, which would correspond to a diminution of the binding energy, as observed.

In contrast, on pyrolysed FeNPc, only two components are visible, located at 400.8 and 398.3 eV (Fig. 9c) giving rise to small variations in the binding energy compared to the non-pyrolysed FeNPc. In this latter case nitride formation is improbable.

Table 6. Fe and MoNPc elemental composition

Sample	*C*	*N*	*O*	*Mo/Fe*	*Fe/Mo*	*% Mo(IV)*	*% Mo(VI)*
Before pyrolysis							
MoNPc	198	8	7.7	0.9		20	80
FeNPc	112	8	11.2	1.07			
After pyrolysis							
MoNPc	465	8		0.9	2	55–60	40–45
FeNPc	1280	8	27.5	1.5		mixture Fe(II)/Fe(III) undiscernible	

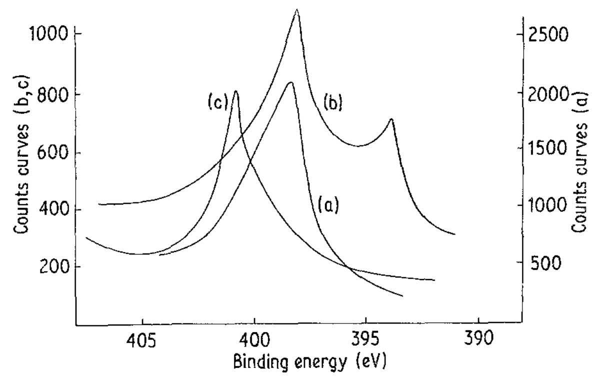

Fig. 9. Typical N_{1s} levels for Mo and FeNPc (counts versus binding energies) samples 5 (a), samples 5′ (b), samples 4 and 4′ (c).

3.3. *Interpretation*

From the XPS spectra the effect of pyrolysis is seen to be different in both the activation and stabilization between CoTMPP and MoNPc impregnations. Whereas with CoTMPP impregnations the pyrolysis effect results in an oxidation of about half of the nitrogen atoms, giving rise to N_{1s} spectra similar to those encountered with phthalocyanine and naphthalocyanine structures before pyrolysis, in the case of MoNPc the same treatment leads to the reduction of the nitrogens.

In the MoNPc case our data strongly suggests the formation of a chemical bond of the MeN type different from that existing in the MeN_4 which, however, still continues to survive as indicated by the 400.3 eV peak. If there were no influence of the central metal ion on the nitride formation one would obtain the same effect with Fe and MoNPc. In the case of FeNPc, in contrast, Fe oxide formation takes place.

For the most active sample, CoTMPP, the MeN_4 unit is also preserved with new MeNC chemical bonds. The crucial point is to know whether the activity and stability can be attributed to this unit MeN_4, or MeN as suggested by Van Veen [11, 13] or if they are due to a special type of active carbon as outlined by Wiesener [8].

Our data are in conflict with those reported by Yeager [9], who suggests that the MeN_4 unit is destroyed during the pyrolysis treatment. But the results presented in this work for the MoNPc and CoTMPP cases rather suggest that formation of different bonds between C and N or Me and C [25]. The comparison of MoNPc and FeNPc reveals the decisive role played by the central ion for long-term stability and activity. In the CoTMPP case, as shown by the atomic ratios C/Co and C/N displayed by XPS, the heat treatment strengthens the interaction forces between the Co(II) and the carbon atoms on the surface so that these ions can attach to the surface of the electrode more firmly and thus improve stability. In the case of MoNPc a chemical bond, MoNC, is a prerequisite for long-term stability. From a practical point of view it turns out that metals which have a greater affinity for N_2 and C seem to be more effective than those which have an O_2 affinity (FeNPc case). Among the investigated catalysts the most active and stable compounds possess the highest N_{1s}/C_{1s} ratio with a relatively low amount of oxygen. If one compares our data with those of Yeager [9], it must be stressed that the main effect of the Vulcan treatment is to preserve the CoN_4 unit. In Yeager's case, despite the destruction of this unit, the catalyst still remains active.

4. Conclusion

Several macrocyclic compounds already investigated elsewhere as impregnations on carbon blacks, such as Vulcan or active charcoals and Norit BrX, have been investigated here.

The effect of pyrolysis on MoNPc proved to be beneficial for its electrocatalytic properties. XPS studies on impregnated CoTMPP (on treated Vulcan, treated Degussa XE2 and Norit BrX) and MoNPc/Norit BrX, FeNPc/Norit BrX reveal, for the most active samples, the establishment of a bond with carbon or nitride formation and, in all cases of activity, the conservation of the MeN_4 unit.

These carbide and nitride formations appear to be essential to prevent demetalisation, thus preserving long-term stability. Whereas the oxygen metal affinity seems to be detrimental, the metal–nitrogen or carbon affinity appears to be a favourable factor.

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References

[1] R. Jasinski, *J. Electrochem. Soc.* **112** (1965) 526.
[2] R. R. Durand, C. S. Bencosme and J. P. Collman, *J. Am. Chem. Soc.* **105** (1983) 2710.
[3] A. J. Appleby, J. Fleisch and M. Savy, *J. Catal.* **44** (1976) 281.
[4] C. Magner, M. Savy and G. Scarbeck, *J. Electrochem. Soc.* **127** (1980) 1076.
[5] G. Magner, M. Savy, G. Scarbeck, J. Riga and J. J. Verbist, *ibid.* **128** (1981) 1674.
[6] H. Jahnke, M. Schonborn and G. Zimmermann, *Topics in Current Chem.* **61** (1976) 133.
[7] A. Fuhrmann, K. Wiesener, I. Iliev, S. Gamburtsev and A. Kaisheva, *J. Power Sources* **6** (1981) 69.
[8] K. Wiesener, *Electrochim. Acta* **31** (1986) 1073.
[9] D. A. Scherson, S. L. Gupta, C. Fierro, E. B. Yeager, M. E. Kordesch, J. Eldridge, R. W. Hoffman and J. Blue, *ibid.* **28** (1983) 1205.
[10] D. A. Sherson, A. A. Tanaka, S. L. Gupta, D. Tryk, C. Fierro, R. Holze, E. B. Yeager and R. P. Lattimer, *ibid.* **31** (1986) 1247.
[11] J. A. R. Van Veen, J. F. Van Baar and K. J. Kroese, *J.C.S. Faraday Trans.* (1981) 1,77,2827.
[12] A. Van Der Putten, B. Elzing, W. Visscher and E. Barendrecht, *J. Electroanal. Chem.* **205** (1986) 233.
[13] J. A. R. Van Veen, H. A. Collijn, J. F. Van Baar, *Electrochim. Acta* **33** (1988) 801.
[14] N. Miura, K. Gomyo, N. Yamazoe, T. Seiyama, *Chem. Lett.* (1981) 1279.
[15] S. Besse, D. E. A. Electrochimie, Université Paris VI (1984).

[16] A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour and L. Korsakoff, *Org. Chem.* **32** (1967) 476.

[17] A. D. Adler, F. R. Longo, F. Kampas and J. Kim, *J. Inorg. Nucl. Chem.* **32** (1970) 2443.

[18] M. Neot Ner and A. D. Adler, *J. Am. Chem. Soc.* **97** (1975) 5107.

[19] C. Prado Burguete, A. Linares-Solano, F. Rodrigues Reinoso and C. Salinas Martinez de Lecea, *J. Catal.* **115** (1989) 98.

[20] I. Elliott, C. Doyle and J. D. Andrade, *J. Electron. Spectrosc. Relat. Phenom.* **28** (1983) 303.

[21] J. A. R. Van Veen, J. F. Van Baar, C. J. Kroese, J. G. F. Coolegem, N. de Wit and H. A. Colijn, *Ber. Bunsenges, Phys. Chem.* **85** (1981) 693.

[22] F. Coowar, M. Savy, G. Scarbeck, D. Van Den Ham and J. J. Verbist, *J. Electroanal. Chem.* **259** (1989) 241.

[23] E. Yeager, *Electrochim. Acta* **29** (1984) 1527.

[24] S. Dong and R. J. Jiang, *Ber. Bunsenges, Phys. Chem.* **91** (1987) 479.

[25] E. Hegenberger, N. L. Wu and J. Phillips, *J. Phys. Chem.* **91** (1987) 5067.