

J. Electroanal. Chem., 289 (1990) 189–201
Elsevier Sequoia S.A., Lausanne

Oxygen reduction in acid media on supported iron naphthalocyanine

Effect of isomer configuration and pyrolysis

A. Biloul, F. Coowar, O. Contamin, G. Scarbeck and M. Savy

Laboratoire d'Electrochimie Interfaciale du CNRS, 1 Place A. Briand, F-92195 Meudon Cédex (France)

D. van den Ham

Twente University of Technology, 7500 AE Enschede (The Netherlands)

J. Riga and J.J. Verbist

Facultés Notre Dame de la Paix, 61, rue de Bruxelles, B-5000 Namur (Belgium)

(Received 12 January 1990; in revised form 26 March 1990)

ABSTRACT

O₂ reduction in H₂SO₄ medium has been investigated on FeNPc impregnations on Norit BrX by the rotating disk electrode technique. Important differences in activity and stability were found between the 1,2- and 2,3-FeNPc isomers (pyrolysed or not). XPS analyses show, for the most inactive sample, strong demetallation and nitrogen losses. This phenomenon can be attributed to the differences in flexibility between the FeNPc isomers, which influences their stabilization on the substrate.

INTRODUCTION

Since 1973 [1] the search for active and stable electrocatalysts for O₂ reduction in acidic electrolytes has been a growing area of concern. Satisfactory current densities and voltages were reported by Meier et al. [2] for iron polyphthalocyanine impregnations on Norit BrX. However, in these experiments, more especially in acid media, the stability was decreased considerably as a result of demetallation and oxidation of the chelate by H₂O₂ formed as an intermediate [3].

At present, a possible alternative for platinum still remains the objective of several groups. Attempts were made [4–6] to improve the stability of N₄ chelates through heat treatment under an inert gas atmosphere of either Ar or N₂. The

question pending concerns the rôle of the central ion associated with the ligand after the pyrolysis treatment [6].

For non-pyrolysed samples, we put forward the rôle of the Norit BrX support [7] in the activity and stability of iron naphthalocyanine electrodes (FeNPc). In alkaline media, differences in activity and stability between MoNPc isomers were also reported [8]. Mo samples, however, are well known to be inactive in acid media.

According to some authors [3] the improved stability after the heat treatment results from a reaction of the active part of the chelate with the substrate, thus protecting the chelate from oxidation by H_2O_2 formed as an intermediate.

However, there is still some controversy between different groups [9–11] who have claimed that the central ion is no longer the active site and others like Yeager and co-workers [12] who emphasize the necessity for traces of the central metal ion. In the case of MoNPc and other N_4 macrocycles [13], the effect of pyrolysis in alkaline media is to promote a bond with the carbon substrate and eventually nitride formation; in all active samples the MeN_4 unit is conserved. This finding is in accord with the results of Van Veen's group [14].

In the case of FeNPc, where either a mixture of four isomers or only a single one can be present depending upon the preparation (see below), no attempt has yet been made to show the effect of isomer configuration or its activity and stability during O_2 electroreduction in acidic electrolytes.

The aim of this paper is to investigate the differences in activity and stability as a function of the isomer impregnation (non-pyrolysed and pyrolysed samples) supported on an active charcoal, Norit BrX, well known for its stability.

In addition, functional groups present on this substrate were identified by FTIR techniques [15]. Their possible rôle in the binding between the chelate and the support and in the electroactivity was also elucidated.

EXPERIMENTAL

Material synthesis and characterizations

2,3-Dicyanonaphthalene (2,3-DCN) was prepared according to the method given in the literature [16]. FeNPc was then synthesized by heating 2,3-DCN with Fe acetylacetonate (FeAcAc) for 5–6 h in the presence of ammonium molybdate as catalyst at $\approx 270^\circ C$ in a sealed tube [17]. In this synthesis mode, the mole ratio was 4 : 1 4 moles 2,3-DCN per mole of FeAcAc. The elemental analysis is given in Table 1.

TABLE 1
Elemental analysis of 2,3-FeNPc

	w/w %			
	C	H	N	Fe
Found	73.88	3.15	14.55	6.29
Expected	75.0	3.10	14.6	7.3

TABLE 2

Elemental analysis of 1,2-FeNPc

	w/w %			
	C	H	N	Fe
Found	77.0	3.10	14.92	4.17
Expected	75.0	3.10	14.60	7.3

The synthesis of 1,2-FeNPc isomers was done according to ref. 7. The elemental analysis is given in Table 2.

From these tables it can be inferred that the ligand structure is satisfactory in both samples, but in the 1,2-FeNPc isomers about 30% of the NPc is demetallated.

The samples were characterized further using UV-visible spectroscopy after dissolution in pyridine. From spectra reported in ref. 18, compared to FeNPc formed from 1,2-DCN, a shift to longer wavelengths of 80 nm for the maximum of the Q band absorption peak can be observed with 2,3-FeNPc. This finding is in good agreement with literature reports [19].

In the one and only case where it has been possible to separate the reaction products based on 1,2-DCN (the Mg case), it has been shown that substantial differences in chemical and physical properties exist. In ref. 20, the authors proposed that the swastika molecule, which exhibits the least strain, is the better soluble and most abundant form, but no proof was given. On the basis of our present experiments we doubt their view. The isomeric ratio appears to depend on the synthetic conditions. The optical properties also differ strongly. From our spectroscopic measurements on MgNPc synthesised from 1,2-DCN and separable in at least two fractions, the isomer presenting two planes of symmetry at 90° , both perpendicular to the plane of the molecule, seems to predominate (form (III) given by ref. 20).

For impregnations on Norit BrX, in the two cases the following procedure was followed. 2,4-Pentanedione and 1,2- or 2,3-DCN were heated at 300°C in a closed glass vessel for 24 h in a molar ratio of 1:4 in the presence of carbon, yielding a product that loses only half of its iron upon treatment by the standard washing procedure, as was found by atomic absorption spectroscopy. The more finely divided 2,4-pentanedione complex clearly competes with the destruction reaction of the 1,2- and 2,3-DCN. A small quantity of the product was eluted with pyridine. In both cases the resulting filtrate showed the colour characteristic of 1,2- or 2,3-FeNPc in pyridine solution. The amount of iron in both samples, found by atomic absorption spectroscopy, was between 0.68 and 0.73 w/w %.

Pyrolysis treatment

The pyrolysis treatment consisted in heating the catalysts deposited on Norit BrX at 500°C in an inert gas atmosphere (Ar) for 2 h. In the case of the iron compounds, higher heating temperatures gave rise to iron oxides [13], as shown by XPS.

XPS experiments

The XPS analyses were performed on an HP5950.A spectrometer using monochromatized (Al K_{α} 1.2) radiation ($h\nu = 1486.6$ eV). For more details, see ref. 7. The experiments were conducted on samples which had been immersed previously for 10 days in 0.25 M aerated sulphuric acid solutions.

Electrochemical experiments

Since a four-electron pathway has been demonstrated to occur on these types of electrodes [7], the electrode activities and stabilities were examined using rotating disc electrodes (RDE) and voltammetric equipment identical to those reported in the latter work. The electrode preparation was also similar, with a gold lacquer brushed in the hollowed cavity of the disc. A dynamic hydrogen electrode was used as reference. The electrode area A was 0.125 cm². All the experiments were performed at room temperature ($T = 22^{\circ}$ C) in 0.25 M H₂SO₄ media.

RESULTS AND DISCUSSION

Figure 1a shows i - E curves for 1,2-FeNpC on Norit BrX at different rotation frequencies for a constant scanning voltage velocity, $v_b = 1.5$ mV/s. Curves 1-6 were obtained under O₂ and curve (7), under N₂.

The salient feature is the emergence of a limiting current. After subtraction of the current under N₂, one obtains the true O₂ reduction current, as displayed on Fig. 1b. The limiting current, i_L , can be analyzed in terms of a Levich plot, I_L versus $f^{1/2}$, which yields a slope of $118 \mu\text{A rps}^{-1/2}$ with a correlation coefficient of 0.999. As this slope approaches the theoretical value of $125 \mu\text{A rps}^{-1/2}$ [21] corresponding to the four-electron pathway, a direct reduction of O₂ to water can be assumed as reported in ref. 7. The fact that the intercept does not pass through the origin can be interpreted in terms of internal sites with a porous character supplying an additional current [8] to the one resulting from the pure oxygen diffusion current.

A plot of E versus $\log i/(i_L - i)$ can be also obtained with the same correlation coefficient as above, with a slope of 122 mV/decade. Thus the rate determining step (r.d.s.) appears to be a one-electron transfer following O₂ diffusion in the electrolyte [7].

Voltammograms at different scan rates (9, 4 and 1.5 mV/s) on stationary electrodes are depicted in Figs. 2a and b under N₂ and O₂, respectively. Whereas no peak is detectable under N₂ within the potential range 600-1000 mV/RHE, an oxygen adduct is present at about 760 mV, as was also reported in ref. 7. From these voltammograms, the existence of a redox process cannot be assumed. In order to shed light on the redox process, further capacitance measurements were undertaken. No redox process was visible on the impregnations, but a considerably high value of capacitance was measured (275 mF). The main difference with ref. 7 is that in the present case the 1,2-FeNpC preparation was exposed to air for several months. This influences principally the Levich slope, which increases from 40 to $118 \mu\text{A rps}^{-1/2}$. This result can be explained in terms of a partially blocked electrode system [22] in

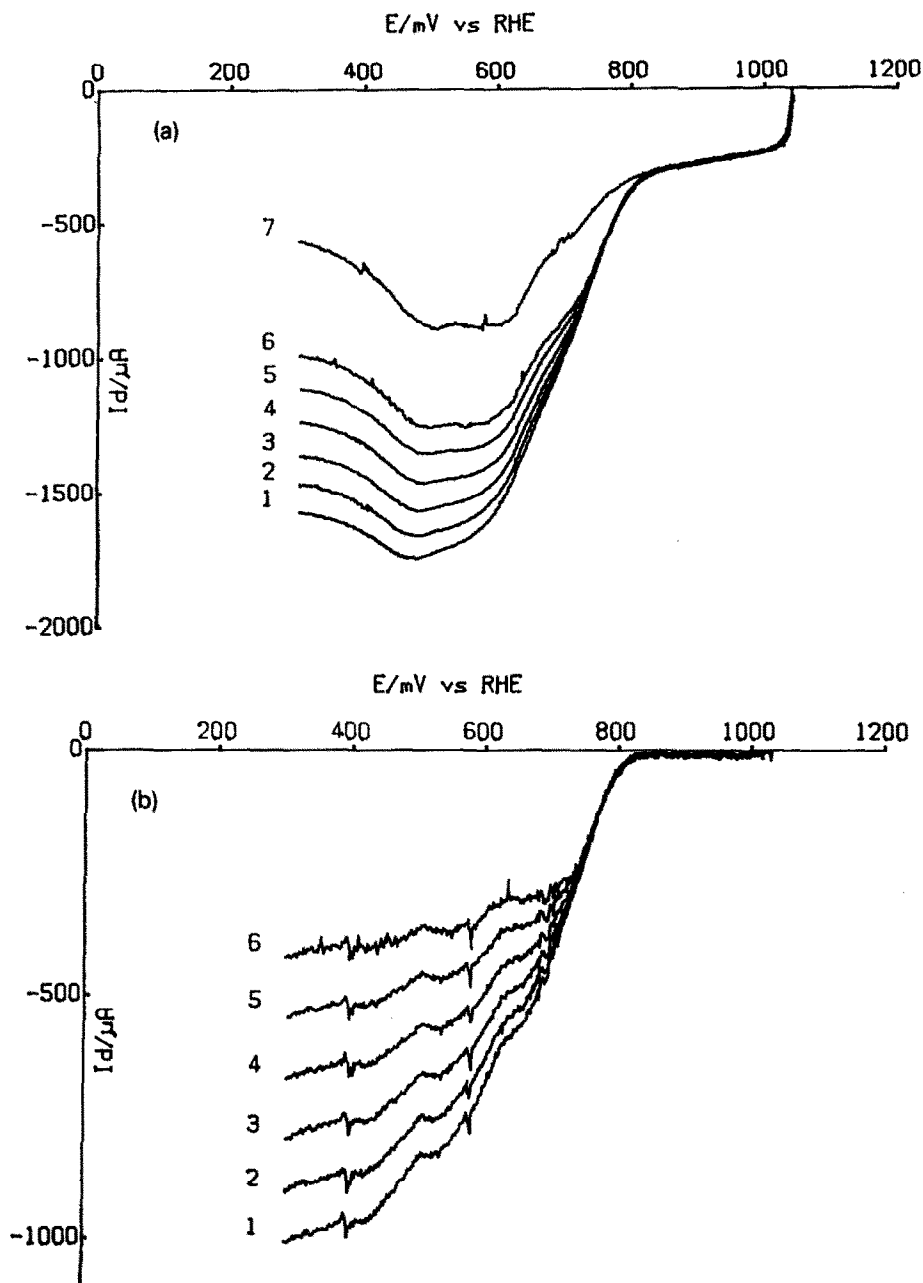


Fig. 1. (a) $i-E$ curves on impregnated non-pyrollysed 1,2-FeNPc samples at a constant scanning velocity $v_b = 1.5$ mV/s for different rotation frequencies f : (1) 64, (2) 49, (3) 36, (4) 25, (5) 16, (6) 9 rps; (7) curve under nitrogen. (b) Same as (a) after subtraction of the curve under nitrogen. Same labels.

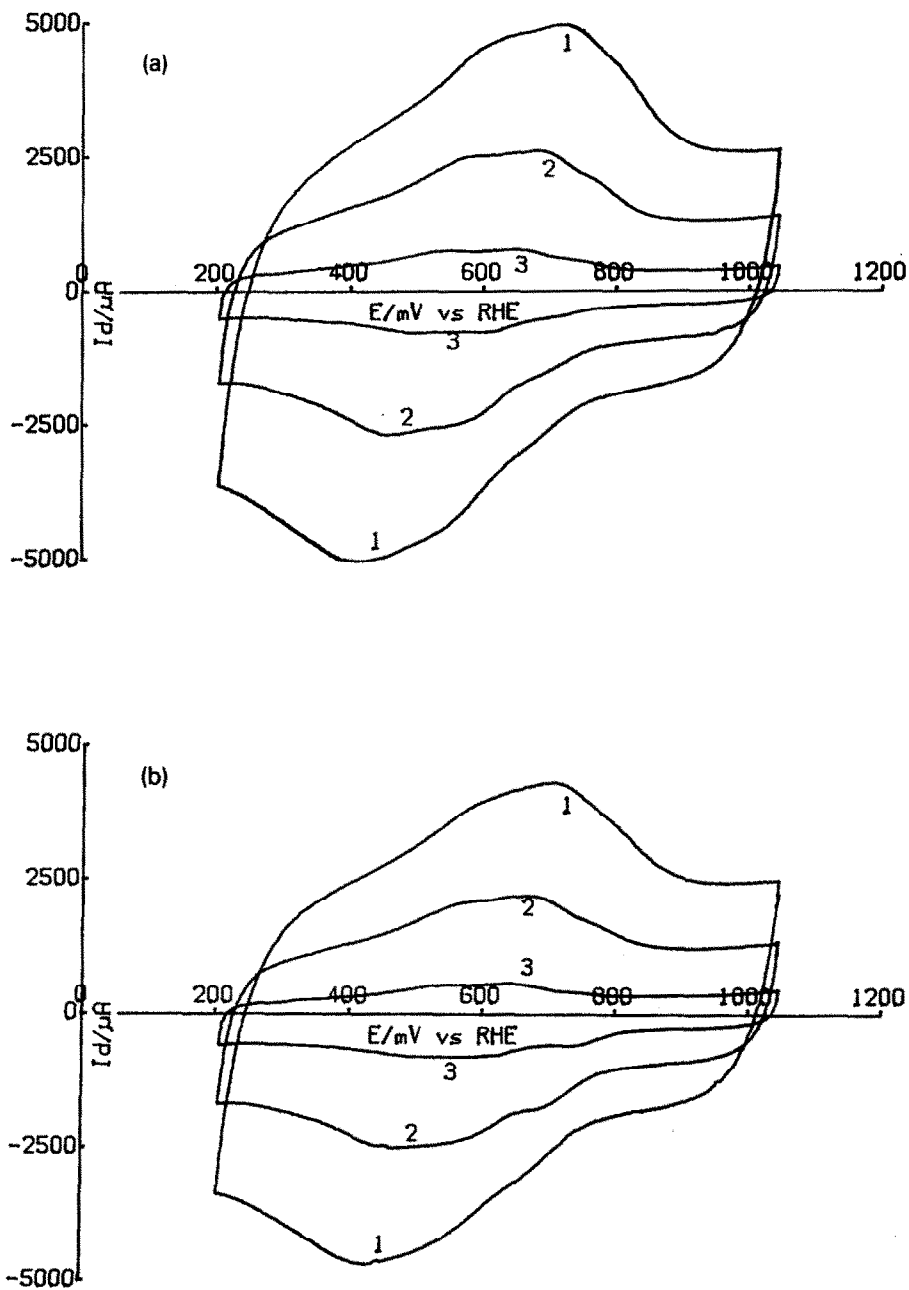


Fig. 2. (a) Voltammograms on stationary electrodes at different scanning velocities under N_2 on impregnated 1,2-FeNpc/Norit BrX. (1) 9, (2) 4, (3) 1.5 mV/s. (b) Same as (a) under O_2 . Same labels.

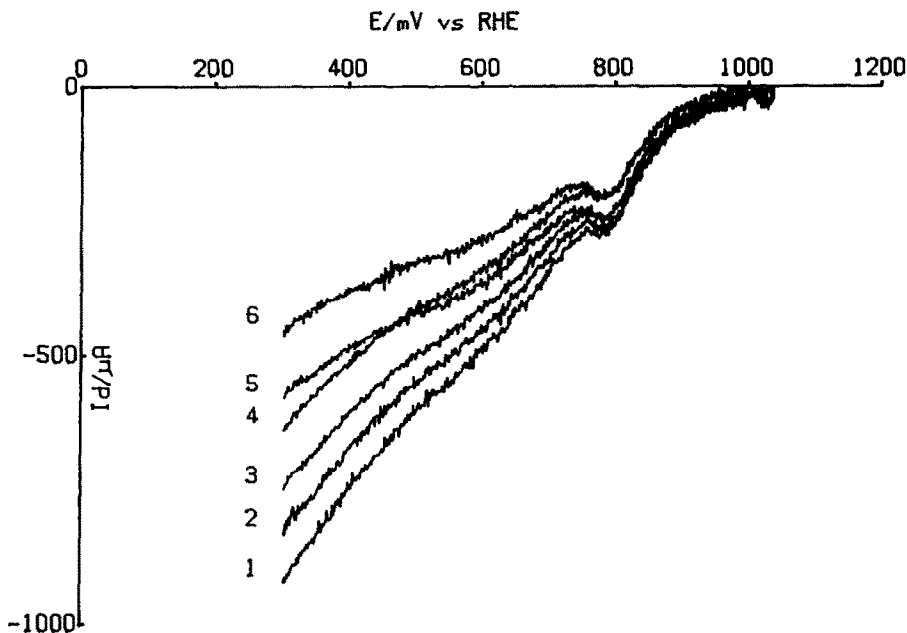


Fig. 3. $i-E$ curves on impregnated 2,3-FeNpc. Same as Fig. 1b after subtraction of the curve under N_2 .

which the distance between two active sites is greater than the diffusion layer thickness. The increase in the density of active sites compared to that in ref. 7 can be calculated using the equation:

$$(E_{1/2})_2 - (E_{1/2})_1 = (RT/\alpha F) \log p \quad (1)$$

$(E_{1/2})_2$ being the potential corresponding to $i = i_L/2$ in the present case (780 mV/RHE) and $(E_{1/2})_1$, the same for ref. 7 (700 mV/RHE). p is the relative increase of the active site density ($p = 1.9$). Thus, exposing the 1,2-FeNpc preparation on Norit BrX to air for several months turns out to be beneficial.

As the oxidation of the electrode increases with time, its surface (as shown by XPS [7]) becomes more negatively charged, enhancing the wetting process. Therefore, in acid media contact with the electrolyte is better.

Figure 3 depicts $i-E$ curves for 2,3-FeNpc at different rotation frequencies after subtraction of the residual current under nitrogen. The current can be analyzed as a Koutecky-Levich plot. For this sample, different conclusions to those above can be drawn concerning the electrochemical process, the difference lying in the smaller rate of O_2 adsorption prior to electron transfer.

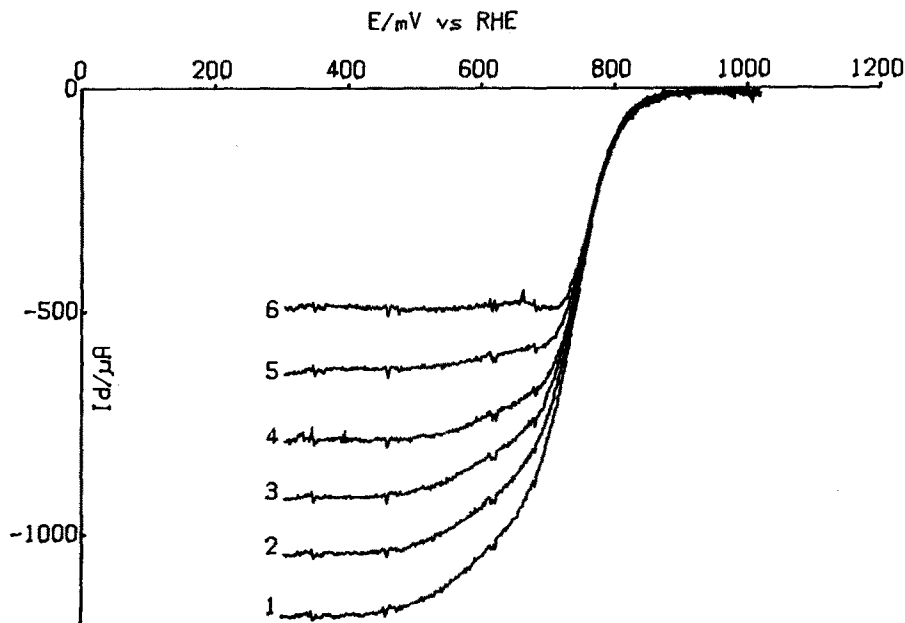


Fig. 4. $i-E$ curves on pyrolysed 1,2-FeNpc after subtraction of the curve under N_2 . Same labels as Fig. 1b.

Effect of pyrolysis

1,2-FeNpc impregnation

Figure 4 depicts the $i-E$ curves under O_2 at the same rotation frequencies as above, after subtraction of the current under N_2 . As in the preceding case, a limiting current is observed with a Levich slope of $137.7 \mu A \text{ rps}^{-1/2}$ and a correlation coefficient equal to 0.999. Concerning the intercept, the same conclusions as above can be drawn. The $E_{1/2}$ value is close to that observed in the non-pyrolysed case: 784 mV/RHE.

A Tafel slope can also be obtained, with a value of 108 mV per decade. Comparison between Figs. 4 and 1b shows an improvement of the activity, which becomes closer to that of Pt after pyrolysis. However, as far as the electrochemical mechanism is concerned, pyrolysis of 1,2-FeNpc on Norit BrX results in only a small change in the Tafel slope.

The resulting voltammograms obtained for these samples are similar to those of Figs. 2a and b and rule out the possibility of a redox mechanism.

2,3-FeNpc impregnation

In contrast with the 1,2-FeNpc impregnation, the effect of pyrolysis appears to have no influence on the electrochemical process of 2,3-FeNpc impregnations on Norit BrX. The Koutecky-Levich slopes and $i-E$ curves are roughly the same.

TABLE 3

Stability tests for $A = 0.125 \text{ cm}^2$, $f = 64 \text{ rps}$

Potentials mV/RHE	$I/\mu\text{A}$				
	Samples		Pyrolysed ^a		2,3-FeNPc ^a
	Pt/Vulcan	1,2-FeNPc ^a	2,3-FeNPc	1,2-FeNPc	
<i>(a) Initial currents</i>					
600	1430	1230	790	1180	730
700	950	430	360	785	200
800	350	50	250	120	50
<i>(b) Final currents after 10 days under load</i>					
600	1030	790	430	850	450
700	970	290	70	530	45
800	320	25	–	72	–

^a Samples supported on Norit BrX.*Stability tests (10 days under load)*

In order to test the performance of these electrodes, long term stability tests were carried out at different potentials: 600, 700 and 800 mV/RHE. The initial and final currents are gathered in Tables 3a and b, respectively, for a rotation rate of 64 rps. 10% weight Pt on Vulcan Carbon black samples are also given as reference.

The existence of initial currents exceeding the theoretical value by about 1000 μA can be interpreted on the basis of internal sites which vanish for long time polarisation. In the case of Pt supported Vulcan, the initial and final currents do not differ to a great extent. With the exception of pyrolysed 1,2-FeNPc, the variation between initial and final current is relatively large.

From Table 3 it is apparent that 1,2-FeNPc approaches the performance of Pt on Vulcan. The difference between 1,2-FeNPc and 2,3-FeNPc must be emphasized and can be interpreted on the basis of XPS experiments.

XPS experiments

In order to get some insight into this isomeric effect, XPS investigations were undertaken on samples after a 10 days stay in aerated 0.25 M H_2SO_4 solutions. In Table 4 are gathered the atomic ratios C/N, C/O, O/N and N/Fe, deduced from XPS measurements, for pyrolysed samples. Results for non-pyrolysed samples 1,2-FeNPc on Norit BrX have been presented in ref. 7. The amount of iron detected there was of the order of that found in pure Norit BrX. In contrast, with non-pyrolysed 2,3-FeNPc samples, no iron was detectable for the same conditions and duration of XPS exposure (3 days).

From Table 4 it is obvious that the most active and stable compounds correspond to those containing iron. The C/O and O/N ratios are similar for pyrolysed 1,2-

TABLE 4

Atomic ratios from XPS

	Pyrolysed 1,2-NPcFe	2,3-NPcFe	
		Pyrolysed	Non-pyrolysed
C/N	55	70	100
C/O	13	14	
O/N	4.2	4.7	
N/Fe	40 to 50	> 100	> 100
O _{1s}	55%, 532 eV	55%, 532.4 eV	
	45%, 531 eV	45%, 530.9 eV	
N _{1s}	55%, 400.4 eV	65%, 400.5 eV	
	45%, 398.7 eV	35%, 398.7 eV	

and 2,3-FeNPc impregnations and therefore play a negligible rôle in the stability. As the C/N ratio is lower in 1,2-FeNPc than in 2,3-FeNPc on pyrolysed impregnations, this result, together with the presence of Fe in the most active samples, suggests a stronger binding between FeNPc and Norit BrX with the mixture of (1,2) isomers than with the (2,3) ones. It should be recalled [7] that with non-pyrolysed 1,2-FeNPc impregnations on Norit BrX, despite considerable demetallation, the activity and stability were maintained.

XPS experiments in which the depth of penetration of the X-ray beam was about 3–4 nm, showed that the amount of iron in these isomers is of the same order as in pure Norit BrX. As H₂NPc is well-known to be inactive towards O₂ reduction, one could suggest that the NPc ligand must lie in the vicinity of the iron sites so as to form FeNPc via the nitrogen atoms. According to ref. 7, in which the fractal character of Norit BrX has been reported, the (1,2) active catalysts should possess some degree of flexibility so as to be in intimate contact with the substrate through the iron sites.

In contrast to 1,2-FeNPc, the amount of iron in the case of the 2,3-FeNPc isomer is below the detection threshold. The amount of 2,3-FeNPc is well below 20% of the overall deposited iron or the amount of iron detected at the Norit BrX surface.

The steric hindrance resulting from the chemical structure in the case of 2,3-FeNPc must shield the iron surface sites of the Norit BrX in the range of X-ray penetration. This phenomenon can be correlated to the lack of flexibility of the (2,3) isomer (insoluble in many solvents, in contrast to the (1,2) isomers). Binding between the nitrogen atoms and the iron sites is thus hampered. This situation sheds light on the action of the pyrolysis treatment. According to Table 4, the amount of iron in 1,2-FeNPc isomer impregnation is highest in the case of pyrolysed samples. Fe remains up to about 20 mole % NPc, whereas on non-pyrolysed samples, as mentioned above, only the iron of the Norit BrX substrate was visible.

Thus, the XPS data show that the effect of pyrolysis treatment is to promote the binding of the chelate to the substrate in the case of the (1,2) isomers, but not of the

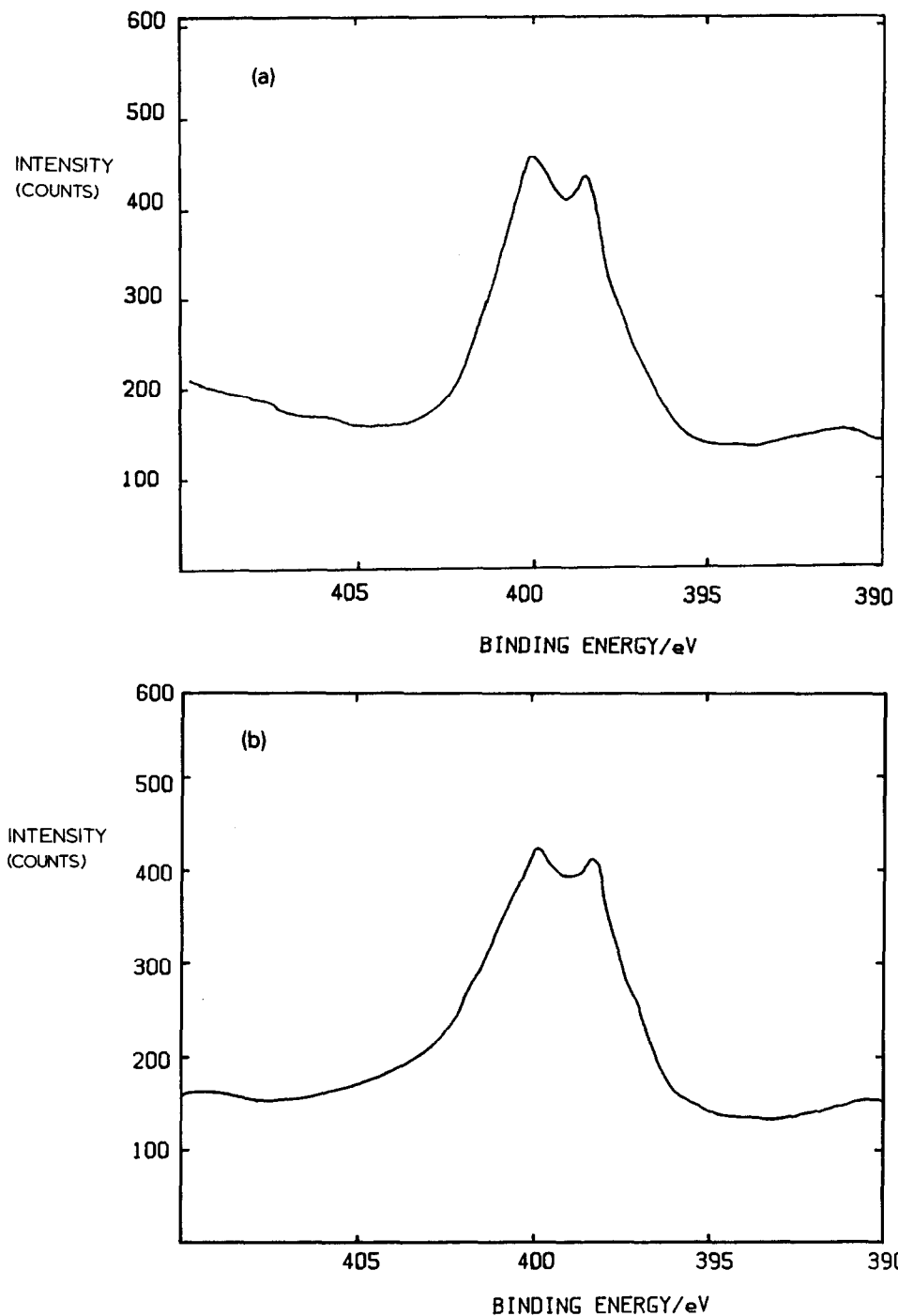


Fig. 5. (a) N_{1s} spectrum counts vs. binding energy for pyrolysed 1,2-NPcFe. (b) Same as (a) but for pyrolysed 2,3-NPcFe.

(2,3) ones. As the oxygen peaks are similar in both cases, the binding to the substrate probably does not involve the oxygen atoms.

In contrast, the differences in the N_{1s} peaks found in the two pyrolysed samples must be emphasized. According to Figs. 5a and b and Table 4, the relative intensities of the two N_{1s} peaks are different in both samples. A more important oxidation process occurs with the (2,3) isomer. Therefore, the structure stabilization visible for the (1,2) isomer mixture shows that a binding between iron, nitrogen and the carbon atoms of the substrate is likely to take place. This feature turns out to be substantiated by the atomic C/N ratio, which is smaller in the case of the (1,2) than the (2,3) isomer. Apparently a higher degree of nitrogen atom oxidation plays a detrimental rôle in the demetallation process taking place simultaneously with the nitrogen losses. In contrast to active samples, in inactive samples (2,3-FeNPc) the MeN_4 unit is destroyed completely.

CONCLUSION

The activity and stability of a mixture of 1,2- and 2,3-FeNPc isomers have been examined in impregnations on Norit BrX for O_2 reduction in H_2SO_4 medium on pyrolysed and non-pyrolysed samples. The effect of pyrolysis treatment turns out to be beneficial only in the case of the 1,2-FeNPc isomer mixture, yielding an activity and stability close to those of Pt supported on Vulcan.

The XPS data reveal a strong demetallation process taking place in the inactive samples. The absence of any traces of iron in 2,3FeNPc, pyrolysed or not, and the fractal character of the Norit BrX structure indicate a steric hindrance in the binding of the chelate to the support. In contrast, the greater flexibility of some 1,2-FeNPc isomers allows a binding to the substrate via the carbon, nitrogen and iron atoms, preserving the MeN_4 unit.

Therefore, the ability of the catalyst to fit the surface atoms of the substrate appears to be a prerequisite for long term stability. The flexibility of the 1,2-FeNPc isomers confers on them their activity.

ACKNOWLEDGEMENTS

The authors wish to acknowledge "l'Agence Française de la Maîtrise de l'Énergie" for its financial support under contract 9030042 and Mr. Charlie Teerlink for his syntheses and analyses of the FeNPc isomers.

REFERENCES

- 1 F. Beck, Ber. Bunsenges. Phys. Chem., 77 (1973) 353.
- 2 H.M. Meier, V. Tschirwitz, E. Zimmerhackl, W.A. Albrecht and G. Zettler, J. Phys. Chem., 818 (1977) 712.
- 3 A. van der Putten, B. Elzing, W. Visscher and E. Barendrecht, J. Electroanal. Chem., 205 (1986) 233.
- 4 E. Yeager, J. Mol. Catal. 38 (1986) 5.
- 5 S. Dong and R. Jiang, Ber. Bunsenges. Phys. Chem., 91 (1987) 479.

- 6 R. Franke, D. Ohms and K. Wiesener, *J. Electroanal. Chem.*, 260 (1989) 63.
- 7 F. Coowar, M. Savy, G. Scarbeck, D. van den Ham, J. Riga and J.J. Verbist, *J. Electroanal. Chem.*, 259 (1989) 241.
- 8 F. Coowar, O. Contamin, M. Savy, G. Scarbeck, D. van den Ham, J. Riga and J.J. Verbist, *J. Electroanal. Chem.*, 269 (1989) 143.
- 9 A. Fuhrmann, K. Kliesner, I. Iliev, S. Gamburtsev and A. Kaisheva, *J. Power Sources*, 6 (1981) 69.
- 10 G. Gruenig, K. Wiesner, S. Gamburtsev, I. Iliev and A. Kaisheva, *J. Electroanal. Chem.*, 159 (1983) 155.
- 11 G. Gruenig, K. Wiesener, A. Kaisheva, S. Gamburtsev and I. Iliev, *Elektrokhimiya*, 19 (1983) 1571.
- 12 D.A. Scherson, S.L. Gupta, C. Fierro, E.B. Yeager, M.E. Kordesch, J. Eldridge, R.W. Hoffman and J. Blue, *Electrochim. Acta*, 28 (1983) 1205.
- 13 M. Savy, F. Coowar, J. Riga and J.J. Verbist, G. Bronoel and S. Besse, *J. Appl. Electrochem.*, 20 (1990) 260.
- 14 J.A.R. van Veen, J.F. van Baar, K.J. Kroese, *J. Chem. Soc., Faraday Trans. 1*, 77 (1981) 2826.
- 15 C. Prado Burguete, A. Linares Solano, F. Rodriguez Reinoso and C. Salinas Martinez de Lecea, *J. Catal.*, 115 (1989) 98.
- 16 E.A. Lukyanets and S.A. Mikhalenko, *J. Gen. Chem. USSR*, 39 (1969) 2449.
- 17 S. Deger and M. Hanack, *Synth. Met.*, (1986) 319.
- 18 F. Coowar, M. Savy, G. Scarbeck, D. van den Ham, J. Riga and J.J. Verbist, *J. Electroanal. Chem.*, 282 (1990) 141.
- 29 E.A. Lukyanets and S.A. Mikhalenko, *Zh. Obsh. Khim.*, 39 (1969) 2129.
- 20 E.F. Bradbrook and R.P. Linstead, *J. Chem. Soc.*, (1935) 1744.
- 21 K.E. Gubbins and R.D. Walker, *J. Electrochem. Soc.*, 134 (1965) 469.
- 22 O. Contamin and E. Levart, *J. Electroanal. Chem.*, 136 (1982) 259.