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X-ray photoelectron spectra and electrochemical properties of imidazol-linked iron phthalocyanine carbon electrode systems

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Electrodes for the electrochemical reduction of oxygen have been studied both galvanostatically and by XPS and IR spectroscopy. The electrodes contain a polymeric phthalocyanine catalyst fixed to an activated carbon carrier by a covalent link of imidazol. Various preparation methods have been tried to make conditions for the coupling of imidazol to the carbon surface as mild as possible. It is concluded from the XPS measurements that about one imidazol molecule is present for every second C_6 unit on the carbon surface. The treatment described results in highly reversible electrode systems. The lifetime of the electrode is limited to several hundred hours, the sudden decrease thereafter is probably related to a solvolysis of the carbon–nitrogen bond linking the imidazol to the surface.

1. Introduction

In a previous paper [1] we showed that the electrocatalytic properties of iron phthalocyanine (FePc) preparations could be enhanced by a covalent link to the support. That link was made by joining the NH end of an imidazol molecule to the carbon structure and letting the iron coordinate the other nitrogen atom of the ring. The idea behind this procedure was to prevent the iron atom from leaking out from the phthalocyanine ring in an acidic medium and to effect a more efficient route of electron transfer.

Indeed, the need for a strong link between the iron atoms and the carbon support has recently been made evident. A Mössbauer investigation [2] has shown that the electronic structure of the iron atoms is not very strongly perturbed by the attachment of the phthalocyanine assembly to the carbon support. This situation is contrary to that for monomeric phthalocyanine [2] where a spin change from S = 1 to S = 0 takes place on precipitation on an activated carbon surface. This change indicates a coordination to the fifth position of the iron atoms by some group on the carbon surface. It is now our aim to devise a similar way of bonding for the polymeric preparations. They are likely to have a molecular weight corresponding to at least 20 sub-units [3]. They may therefore (because of steric reasons) have some difficulty in constraining all the Fe atoms to suitable sites on the carbon surface.

2. Method

The method of preparing the covalently bound imidazol–carbon complex was essentially the same as used previously [1]. $SOCl_2$ was reacted with groups resulting from partial oxidation of the carbon surface. The resulting carbon–chlorine groups were reacted with the N–H group of imidazol.

In order to increase the number of reactive sites, the carbon was subjected to attack from some suitable oxidizing agents. As has been pointed out by, e.g., Boehm [4] various types of oxidized sites can be formed (see Fig. 1). The preparative route for these different sites is presented in short in Fig. 1.

The degree to which imidazol was fixed and thus covered the surface can be determined at least qualitatively by the powerful method of X-ray photoelectron spectroscopy. The

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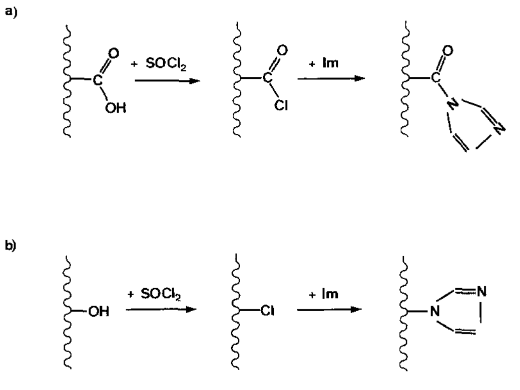

Fig. 1. Possible routes of anchoring imidazol to the carbon surface.

activated carbon was first examined; then it was examined after the oxidation treatment and thereafter when the imidazol reaction was completed. In principle it will be possible to estimate the ratio of nitrogen to carbon from the relative intensities of the N_{1s} and the C_{1s} peaks of the spectrum.

3. Experimental procedure

Preparation of the imidazol-carbon complexes:

A. 20 g of activated carbon was refluxed with 100 cm^3 of a freshly prepared solution of NaOCl (25% in water) for about 20 h. Activated carbon Norite SX-3 was used in all the preparations. The mixture was allowed to cool to room temperature. Thereafter it was filtered on a Büchner funnel, at first without suction, then with careful use of vacuum suction. In this way possible difficulties, similar to those reported previously [1] and related to a decrease in the hydrophobicity of the carbon, could be avoided.

The product was then washed several times with water and then with acetone. It was first dried at room temperature and then at 120° C for two days. (This substance is called A1 in the text.) Most of A1 (17 g) was refluxed for 16 h in 50 cm^3 of thionyl chloride, then cooled and filtered. The product was washed a few times with water-free CH_2Cl_2 and dried. (A2)

The dry substance was refluxed for 7 h with 10 g imidazol (reagent grade) in 80 cm^3 dry chloroform. It was filtered, washed with acetone then acetic acid (five times) and repeatedly with water and finally with acetone (ten times) to remove traces of adsorbed imidazol. The dried substance (A3) was then investigated with XPS and IR spectroscopy.

Part of the A3 preparation was used to prepare the electrode mass exactly as described in the previous paper [1], i.e., by dissolving FePc in DMSO and precipitating with water of pH = 4. It must be noted that the same FePc preparation was used in all the electrodes investigated in the present paper. It was, however, a different sample from that used previously [1].

B. 20 g of activated carbon was refluxed in 100 cm^3 conc. HNO_3 for 20 h. The mixture was cooled and filtered as in the preparation of A1. The mass was washed repeatedly with water, 1 mol dm^{-3} NaOH and water again repeatedly until the filtrate which was red-brown at the beginning became almost colourless. After draining the water, the filter cake was washed repeatedly with acetone. The acetone filtrate was also dark red and gave, upon evaporation, a red-brown residue that was soluble in water and acetone.

After drying at room temperature, the filter cake was dried at 120° C for two days. (Sample B1.) 17 g of B1 was treated with $SOCl_2$ and thereafter with imidazol in the same way as for preparation A above. The final product (B3) was washed and purified analogously and dried.

C. In this preparation the oxidizing agents were replaced by a 25% solution of NaCl for comparison. 20 g of activated carbon was refluxed in 100 cm^3 25% solution of NaCl, then washed and dried as in preparation A. The preparation thus obtained is called C1.

17 g of C1 was treated with $SOCl_2$ and subsequently with imidazol as in preparation A. Likewise the washing and drying procedures were identical. The product, C3, was examined by XPS and IR. Part of C3 was transformed to the electrode mass (C4) as before.

Another series of preparations were made (D–F) with a much shorter time of reflux and also using less concentrated reagents.

D. 28 g of activated carbon was refluxed for

5–7 min with 100 cm^3 of a freshly prepared solution of 10% NaOCl in water. The mixture was cooled to room temperature, filtered, washed and dried as in the previous preparations. At this stage a sample of approximately 8 g was taken for reference (D1). The remaining D1 (about 20 g) was refluxed in 70 cm^3 $SOCl_2$ for 2–3 h, then cooled and dried. It was washed a few times with dry CH_2Cl_2 and dried (D2).

D2 was refluxed for 2 h with 10 g imidazol (reagent grade) in 80 cm^3 dry $CHCl_3$. The reaction mixture was filtered after cooling, washed and dried in the same manner as above. The final product (D3) is the imidazol-anchored carbon and was treated to give the electrode mass (D4).

E. 28 g of activated carbon was oxidized in 100 cm^3 boiling 10% HNO_3 for 5–7 min. The solid substance was then filtered, washed and dried as above to give E1. The main part of E1 was then treated with $SOCl_2$ and subsequently reacted with imidazol as in A to obtain the final imidazol-anchored carbon (E3).

F. 28 g of activated carbon in 100 cm^3 acetic acid (10% aqueous solution) and 10% potassium persulphate were refluxed as in D and a reference sample (F1) was kept. The remainder was treated with $SOCl_2$ and imidazol as in D to obtain preparation F3. Thereafter the electrode mass F4 was prepared.

The electrodes were prepared in the same way and examined in a half cell arrangement as in our previous investigations [1, 5]. 2.3 mol dm^{-3} H_2SO_4 was used as the electrolyte and the potential of the electrode was measured against a Hg/Hg_2SO_4 electrode via a Luggin capillary.

X-ray photoelectron spectra were registered on an AEI ES200 instrument. The material to be examined was pressed on to a lead metal foil. Reported binding energy values are referred to E_b (C_{1s}) = 285.0 eV. The infrared spectra were registered on a Perkin Elmer PE 580 instrument with a Perkin Elmer Data Station. The latter made it possible to present the difference between two spectra of rather low transmittance.

In all cases mentioned here the activated carbon was Norite SX-3.

4. Results

To make the presentation easier we have collected in Table 1 the various electrodes used in this investigation and the code used to denominate them. In Figs. 2–3 we present some typical data for the polarization of the different electrodes (at 10 mA cm^{-2}) as a function of time. The reproducibility of the potential readings at a given time for different electrodes prepared from the same mass was better than 5 mV. At first one can notice that the FePc polymer used in this work has a higher catalytic activity than the one used in the preliminary investigation [1]. This is shown by the higher potentials given by the electrode prepared in the conventional way without any imidazol treatment (G″ = □).

One also notices that the electrodes made from carbons C (not oxidized but treated with NaCl) and D–F (oxidized for only a short period) all give potentials very close to that of the reference one, G″, (see Table 1). The carbon that had been strongly oxidized with NaOCl gave a much less positive value and the one oxidized with concentrated nitric acid had a very low catalytic activity with a potential around − 500 mV and is not included in the figure. This latter observation was

Table 1. Composition of the electrode masses used in the present investigation. G′ = Norite SX-3.

Electrode	*Code*	*Composition*
A4	◐	80% (25% FePc + 75% A3) + 20% PTFE
B4	◓	80% (25% FePc + 75% B3) + 20% PTFE
C4	○	80% (25% FePc + 75% C3) + 20% PTFE
D4	◇	80% (25% FePc + 75% D3) + 20% PTFE
E4	⬖	80% (25% FePc + 75% E3) + 20% PTFE
F4	⬘	80% (25% FePc + 75% F3) + 20% PTFE
G″	□	80% (25% FePc + 75% G′) + 20% PTFE

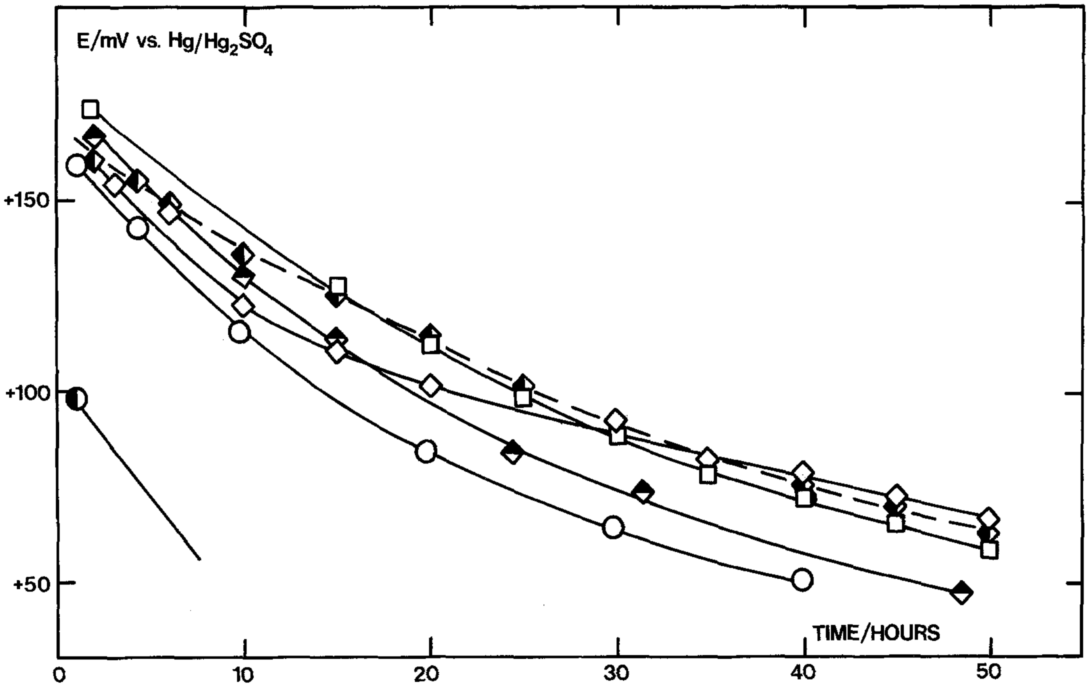

Fig. 2. The polarization of electrodes at 10 mA cm^{-2} as function of time during the first 50 h. Notation as in Table 1.

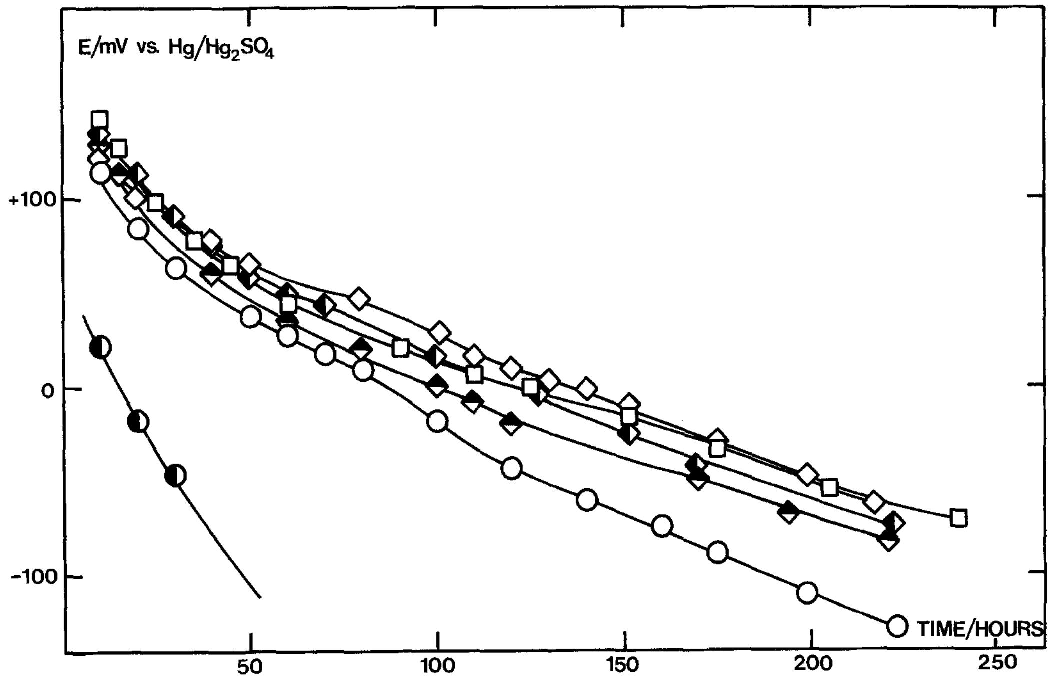

Fig. 3. The polarization of electrodes at 10 mA cm^{-2} up to 250 h. Notation as in Table 1.

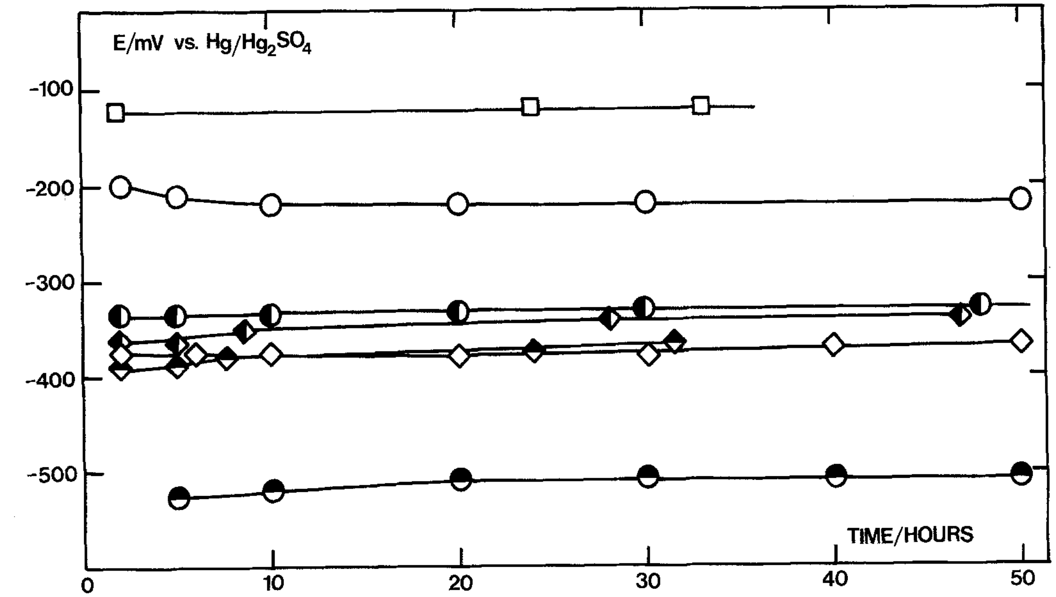

Fig. 4. The polarization of electrodes made from activated carbon and Teflon only. ◐ = 80% A3 + 20% PTFE; ◒ = 80% B3 + 20% PTFE; ○ = 80% C3 + 20% PTFE; ◇= 80% D3 + 20% PTFE; ⬖= 80% E3 + 20% PTFE; ⬘= 80% F3 + 20% PTFE; □ = 80% G′ + 20% PTFE.

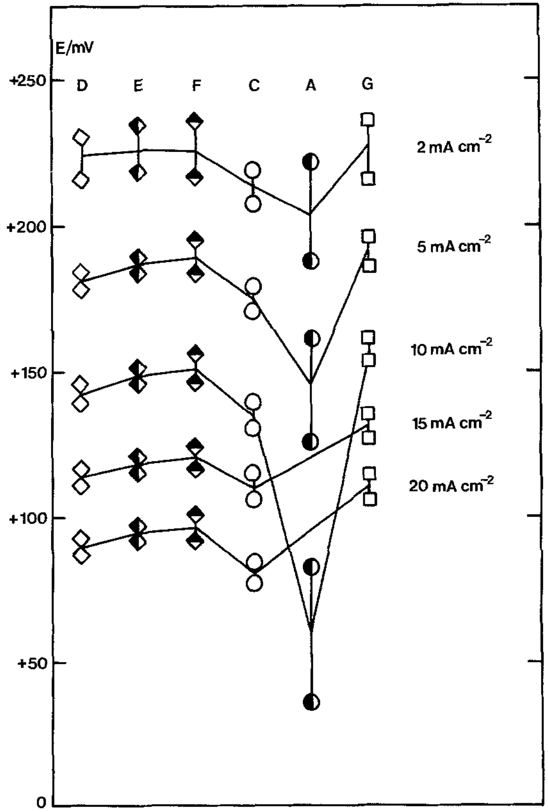

Fig. 5. Potentials at different loads. Upper points represent values at increasing current, lower points are values read at the decrease of current. Notations as in Table 1.

expected as the chemical treatment led to nitration of the carbon and a substantial destruction of the surface of the activated carbon. Figure 4 shows a similar set of data for electrodes made from the imidazol-linked carbons but with no FePc. The performance is in all cases worse than for a ‘pure’ carbon (G′). This indicates probably that those groups on the surface of the activated carbon that are catalytically active in themselves are participating in forming the carbon–imidazol bridge or they are blocked by the imidazol groups.

When the iron phthalocyanine is added to the carbon–imidazol complex, however, it seems that a ‘skin’ of catalytically active material is compensating this decrease. The electrode potential is thereby reactivated. Contrary to what was hoped for at the time of our previous publication, however, the increase of the catalytic activity is not as large as that of a conventional FePc electrode.

One can notice, on the other hand, a pronounced effect on the hysteresis of the polarization curve (Fig. 5). By this term we mean the difference in potential at the same current density when the current load is being increased or decreased again. The more reversible the electrode system is, the smaller is this difference. One observes from Fig. 5 that preparations D4, E4 and possibly C4 are better in this respect than the reference system (G″).

Another feature of importance is obvious in Figs. 2 and 3. After a while (about 20 h) the 'best' electrodes – in the sense just discussed, i.e., D4 and E4 – are at higher potentials than the standard electrode (G″). This means that the imidazol bridge protects the iron phthalocyanine system from some of the decomposition reactions that change the potential when the electrode is loaded. This situation prevails for about 100–150 h. Then the potential drops rather suddenly to a similar or lower value than that of the reference sample. It must be emphasized that the same effect was observed before [1] and with about the same time of decline. We suggest that this decline is caused by an acid hydrolysis of the carbon–nitrogen bond. The detailed kinetics of this reaction will depend on several factors, such as the number of anchored imidazol molecules, the type of anchoring sites (i.e., the type of oxidation agent used) and the pH of the solution. Could this solvolysis be overcome, one should expect a substantial improvement of the long-term electrocatalytic efficiency of iron phthalocyanines.

Infrared spectra were recorded for each of the preparations A1 and A3, B1 and B3, C1 and C3. The difference between spectrum (3) and spectrum (1) was computed by the data system of the instrument. Only for the unoxidized samples (C) could we obtain an acceptable spectrum. The spectra of the other preparations had a very low signal to noise ratio. Probably the existence of other types of bonds dominating for the oxidized species (e.g. $-CO-N<$, see below) contributed so strongly that the separate bands all fused together. The (C) spectrum is recorded in Fig. 6 together with a spectrum of solid imidazol. The patterns are similar enough to allow one to recognize the main features of imidazol in the difference spectrum. They are however also dissimilar enough to allow one to realize that the imidazol has undergone a chemical change, it is not merely physisorbed. One can also notice that the major bands seem to appear two and two. This indicates the existence of two different species (e.g., 'a' and 'b' of Fig. 1).

The vibrations of pure 1–H imidazol have been analysed – *inter alia* – by Osipov *et al.* [6]. From their results we can identify all the bands in the spectrum of Fig. 6. Some of the more important ones are assigned as follows: The 662 cm^{-1} band is a ring deformation mode, the 740 cm^{-1} and 760 cm^{-1} bands are out of plane C–H + N–H or C–H modes, the 1055 cm^{-1} band corresponds to a C–H deformation mode and the 1263 cm^{-1} band is a $\nu_{CN} + \nu_{CC}$ mode. 1- N-methylimidazol has also been analysed by Osipov *et al.* [7]. As this molecule can be regarded in many aspects as a model for compound (b) of Fig. 1 it is interesting to make the following comparisons:

A band at 665 cm^{-1} is described as corresponding to a $\nu_{N-CH_3} + \delta_{ring}$ mode. This band is, indeed, found in the upper curve of Fig. 6. Similarly, a band at 1076 cm^{-1} corresponds to $\delta_{CH} + \nu_{ring}$ according to Osipov *et al.* [7]. It is also detected in our spectrum at about 1075 cm^{-1}. The 1109 cm^{-1} band in methylimidazol (δ_{CH}) may correspond to the weak component at about 1115 cm^{-1} in our spectrum and may furthermore be related to the 1100 cm^{-1} ($\delta_{CH} + \delta_{NH}$) of free imidazol.

It is worth noting that Osipov and colleagues [7] assign 1230 cm^{-1} and 1286 cm^{-1} as $\nu_{CN} + \nu_{CC}$ vibrations containing δ_{CH} or δ_{CH_3} and ν_{N-CH_3}, respectively. These bands are found in our spectrum at about 1240 cm^{-1} and 1285 cm^{-1}. The 1325 cm^{-1} band in our spectrum corresponds to 1330 cm^{-1} of methylimidazol. These assignments make it clear that the patterns observed are real. Therefore it is now worth noting that a lot of other bands do not correspond to methylimidazol as mentioned by Osipov *et al.* [7], but may be related to the compound (a) of Fig. 1. For example, the set of 1260 cm^{-1} and 1305 cm^{-1} may be the counterparts of the 1240 cm^{-1} and 1285 cm^{-1}, mentioned above. The band at 1090 cm^{-1} may be of δ_{CH} parentage and be the counterpart of the 1075 cm^{-1} band. The band at 750 cm^{-1} is not reported for methylimidazol [7] but may very well be related to the out-of-plane CH bending at 740 and 760 cm^{-1} and getting intensity from the neighbourhood of the C=O group.

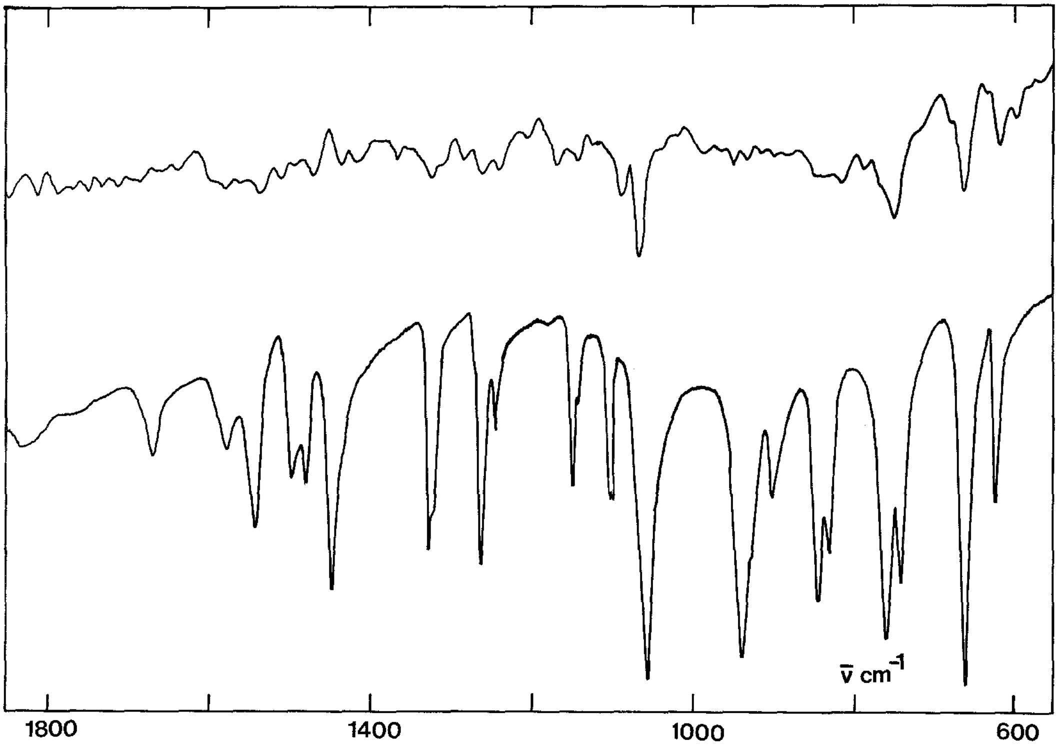

Fig. 6. Infrared spectrum of imidazol + carbon minus the spectrum of carbon (upper curve). Infrared spectrum of imidazol in KBr dispersion (lower curve).

ESCA (XPS) spectra were registered for the six imidazol–carbon systems A3–F3 (Fig. 7) and also for pure imidazol (Fig. 8). From the latter spectrum two things can be extracted:

(a) The two nitrogen atoms in solid imidazol are chemically different to such an extent that they give N_{1s} peaks separated by about 1.6 eV. This value is estimated from the halfwidth of the peak (3.3 eV) and from the Appendix D of Siegbahn *et al.* [8]. The halfwidth of a single N_{1s} peak was measured to be 1.8 eV. Clark and Lilley [9] give a separation between the two peaks of 1.6 ± 0.4 eV.

(b) As the intensity of the recorded signal is quite high, one can consider the C_{1s} peak to originate mainly from the imidazol carbons. This means that we neglect the presence of spurious carbon from pump oil and other contaminants. From the data we can now determine the relative sensitivity for N and C atoms at the experimental conditions used: Measuring the approximate area as full height times halfwidth for the N_{1s} and the C_{1s} peaks we arrive at $I(N)/I(C) = 1.08$, where $I(X)$ is the sensitivity for the element X. (This value is somewhat less than that given by Jørgensen and Berthou [10] namely, 1.5, but they used an instrument of quite other design). Using the value 1.08 for the relative sensitivity we can estimate an approximate ratio of N atoms/C atoms that will give spectra as those presented in Fig. 7 (only the N_{1s} peaks are shown there). The numbers given at the side of the spectral curves are the results of such calculations.

About 1 nitrogen atom for every 12–15 carbon atoms for the A–C preparations can be detected. This figure might be wrong up to about 50% because of errors in estimating the area of the rather unsymmetrical peaks. Even so it contains interesting information. It must mean that the carbon surface is covered to a considerable extent by imidazol molecules. Remembering that the free mean path of escape for an electron of the kinetic energy involved here in graphite is about 2.0 nm [11] the main part of the intensity must come from the uppermost three or four layers of the graphite structure. (The interplanar distance

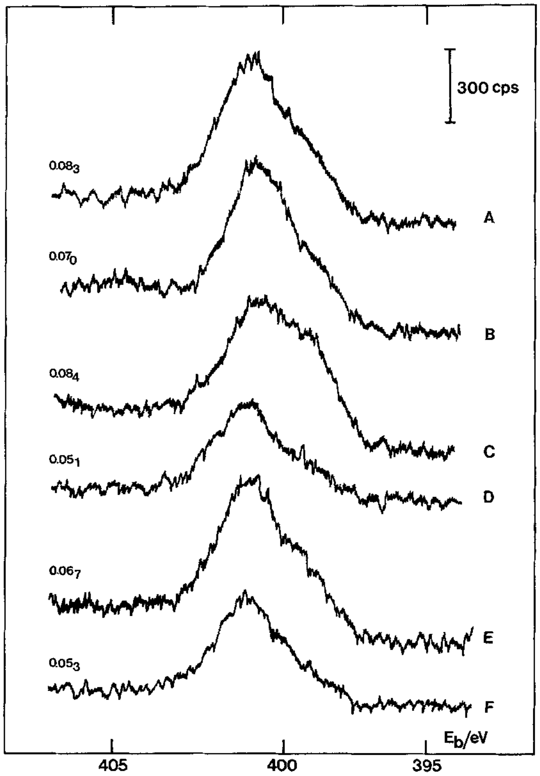

Fig. 7. XPS spectra in the N_{1s} range of the various imidazol–carbon preparations (before addition of FePc). The figures to the left express the estimated N/C atom ratio.

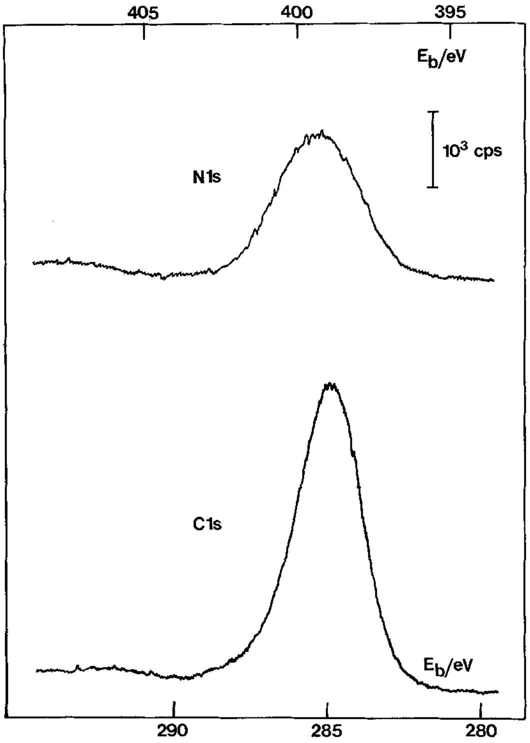

Fig. 8. N_{1s} and C_{1s} XPS spectra of imidazol sampled on a copper grid.

in graphite is 3.41 Å [12].) If one also includes the three carbon atoms of the imidazol molecule in the C_{1s} signal, one can conclude that there is about one imidazol molecule per every second surface C_6 unit. Here we have assumed the structure of graphite to represent that of the surface of the activated carbon. The relation between the surface of activated carbon and graphite is discussed at some length by Boehm [4]. The main point here is to show whether there is a dilute or heavy concentration of imidazol on the surface. Our interpretation of the ESCA spectra favours the latter view.

The shapes of the N_{1s} peaks recorded in Fig. 7 are worth some comments. Considering curve C first, one can detect two peaks of almost equal intensity. The distance between the two peaks (positioned at about 399.1 eV and 400.8 eV) is about 2.0 eV. The one with the higher binding energy is, however, somewhat more intense and one can observe indications of another component at about 402.2 eV. We suggest that the curve is composed of two major sets of N_{1s} peaks as sketched in Fig. 9.

The first set of peaks at low binding energy probably corresponds to bonding of the imidazol as depicted in Fig. 1b. Such a species is most frequently found at the unoxidized carbon, whereas the type of bonding shown in Fig. 1a will correspond to the other set of peaks. It is reasonable that an electron-withdrawing group such as the C=O one will cause a more positive charge on the imidazol molecule and hence a higher binding energy on the nitrogen atoms. One also expects that the 'a-type' of bonding will increase in proportion when the carbon surface is subjected to an extended oxidation as in experiments A and B.

The same pattern is found for the samples oxidized for a short period of time (D–F). As expected, however, the N/C ratio is somewhat smaller, namely, about 1 N per every 15–20 carbon atoms.

The XPS spectra are complimentary to the

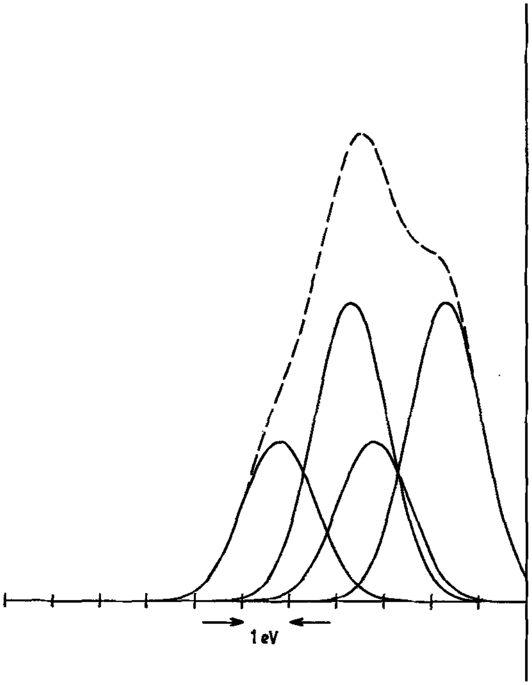

Fig. 9. Schematic presentation of a spectral contour (——) resulting from the overlapping of two spectra, each with two equally sized peaks. Peak separation for both systems is 2.0 eV. Separation between the two systems is 1.5 eV. Half-width of the peaks is 1.8 eV.

IR ones in characterizing the binding of the imidazol. We have already mentioned that the 1.6 eV separation between the peaks of pure imidazol agrees well with the data of Clark and Lilley [9]. The same authors point out that there is a shift from 1.3 eV to 2.3 eV for the peak separation of pyrazol and N-methyl pyrazol. They suggest [9] that this effect is caused by the presence of a hydrogen bond to the N-atom in the pure pyrazol and the absence of it in the methylated compound. A similar difference is met in the present work if our interpretations of the spectra are correct: 1.6 eV for the unbonded imidazol and around 2.0 eV in the imidazol – carbon complex.

5. Conclusions

We can now summarize our observations. It seems that XPS is a method well suited for the study of surface-treated carbon electrodes. The concentration of imidazol on the surface can be estimated and the type of bonding can be inferred. The most important step in the development of the present type of electrodes is to avoid the solvolysis of the carbon–nitrogen bond. We expect that a detailed mapping of the various species that are chemically fixed at the surface will help us towards this goal.

6. Acknowledgements

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