

metastable peaks corresponding to the fragmentations $202 \rightarrow 174$, $187 \rightarrow 159$, $143 \rightarrow 131$, $115 \rightarrow 103$, and $131 \rightarrow 103$ due to successive losses of CO and C. The fragment at $m/e = 115$ seems to be typical for phenylthiophenes^{7,13} and phenylfurans. Methyl 2-furylbenzoate was hydrolysed, giving 2-furylbenzoic acid in 87 % yield, m.p. ca. 90°, decomp. (Found: C 69.4; H 4.4. Calc. for $C_{11}H_8O_3$: C 70.2; H 4.3.) The mass spectrum of 2-furylbenzoic acid showed molecular ion at $m/e = 188$ (100) and fragments at $m/e = 160$ (52), 159 (46), 131 (64), 115 (60), 103 (33), 77 (41), metastable peaks corresponding to the fragmentations $188 \rightarrow 160$, $159 \rightarrow 131$ due to losses of CO.

Most of the arylfurans decompose slowly at room temperature.

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1. Nilsson, M. and Ullenius, C. *Acta Chem. Scand.* **22** (1968) 1998.
2. Nazarova, Z. N., Babaev, Yu. A. and Natal'ina, T. N. *Zh. Obshch. Khim.* **33** (1963) 1431.
3. Fanta, P. *Chem. Rev.* **64** (1964) 613.
4. Nilsson, M. and Ullenius, C. *Acta Chem. Scand.* **24** (1970) 2379.
5. Costa, G., Camus, A., Marsich, N. and Gatti, L. *J. Organometal. Chem.* **8** (1967) 339.
6. Nilsson, M. and Wennerström, O. *Acta Chem. Scand.* **24** (1970) 482.
7. Gjos, N. and Gronowitz, S. *Acta Chem. Scand.* **25** (1971) 2596.
8. Nilsson, M. and Ullenius, C. *Acta Chem. Scand.* **25** (1971) 2428.
9. Stephens, R. D. and Castro, C. E. *J. Org. Chem.* **28** (1963) 3313.
10. Nilsson, M., Ullenius, C. and Wennerström, O. *Tetrahedron Letters* **1971** 2713.
11. Sease, J. W. and Zechmeister, L. *J. Am. Chem. Soc.* **69** (1947) 270.
12. Wynberg, H., Sinnige, H. J. M. and Creemers, H. M. J. C. *J. Org. Chem.* **36** (1971) 1011.
13. Bowie, J. H., Cooks, R. G., Lawesson, S.-O. and Nolde, C. *J. Chem. Soc.* **B 1967** 616.

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ESCA and Mössbauer Investigations of Some Porous Teflon-Active Carbon-Phthalocyanine Electrodes

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In a study¹ on the electrocatalytic effect of iron-phthalocyanine polymers in porous active carbon-teflon electrodes in acid medium for use in, e.g., metal-air batteries it was observed that the catalytic effect decreased with time.

As it is of great importance to understand the mechanism behind this decrease we have made some spectroscopic investigations including Mössbauer and ESCA² measurements. Four different samples were compared, composed and treated as follows. A: NORIT FNX + 10 % Pe-Fe(II) 280°(A) (3 parts) and Teflon (1 part). B: As in A, but kept in 2.25 M H₂SO₄ for a week.

C: As A but kept in 2.25 M H₂SO₄ in the presence of oxygen for one week.

D: As A but treated as C and also used as cathode with a 20 mA/cm² current density.

Table 1. Mössbauer data (in mm/s) for samples A - D.

	I ^a		II ^a		I/II ^b
	IS(SS)	ΔE_Q	IS(SS)	ΔE_Q	
A	1.25	3.01	0.21	0.62	0.27
B	1.24	2.98	0.18	0.60	0.28
C	1.24	2.91	0.14	0.64	0.33
D	1.24	2.99	0.16	0.60	0.30

IS(SS) = Isomer shift relative to stainless steel. ΔE_Q = Quadrupole splitting.

^aThe Mössbauer spectra show two well-resolved doublets, I and II. I can be attributed to a high spin form, and II is most probably due to a low spin form.

^bI/II = Ratio between the surfaces of the bands of I and II, respectively.

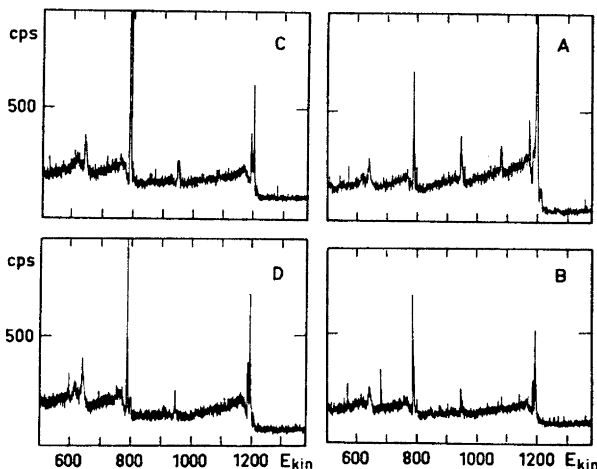


Fig. 1. Survey of the samples A–D. The instrument correction is 9.6 eV so that the binding energies can be calculated from $E_b = 1477.0 - E_{kin}$.

The result of the Mössbauer investigation (Table 1) showed that no significant change in the bonding of the iron atoms had been caused by the treatment of samples B–D compared to what was found for sample A. The decrease in electrochemical activity cannot, therefore, be caused by a change in the phthalocyanine bonding of iron. This important result must be remembered in the continued discussion of the ESCA work. Really, from the work of Berezin,³ one should expect that the iron atoms should be set free in the rather strongly acidic medium used. It is possible that the structure of the phthalocyanine groups would tend to stabilize the iron-nitrogen bonding as well.

The ESCA-spectra were run on an AEI ES 100 spectrometer and the samples were applied on a copper thread mesh. The overall picture of the results is given in Fig. 1, presenting the four survey spectra in the range 500–1500 eV kinetic energy (ALK α radiation was used for the excitation). There is one major effect immediately observed: In sample A there is a very strong signal from carbon (active carbon) but a rather medium-sized one from fluorine (teflon). This situation is entirely reversed in the spectra of samples C and D where the fluorine signal is very strong and the carbon one is markedly diminished in magnitude. Furthermore, there appears a second carbon line at lower kinetic energy

(higher binding energy) corresponding to the carbon in the CF₂ units (*cf.* Fig. 1: 16 of Ref. 2). The spectrum of sample B presents a picture somewhere between these two extremes. It seems obvious, remembering that the ESCA-technique is a sensitive surface investigation method, that the most profound change in going through the series A–B–C–D is the partial oxidation of the active carbon surface. This oxidation is caused by the presence of free oxygen and hydrogen peroxide in the electrolytic solution and may probably be the cause of the decreasing electrochemical activity as the balance of the position of the three-phase-zone must depend on the surface teflon-graphite composition.⁴

The iron spectra (Fe 2p_{3/2}) of the four samples are given in Fig. 2. The result confirms the conclusion from the Mössbauer investigation that the iron atoms are not profoundly perturbed by the treatment B–C–D. The intensity is seen to be a little greater in the spectra of samples C and D but this may be caused by a slightly better adhesion to the copper grid of these two samples. Another explanation is that there is a slight increase in surface concentration of iron(II) phthalocyanines in samples C and D. The iron spectra (Fig. 2) do not show the very sharp lines often found,⁵ but a very broad band. The two bands of the 2p_{3/2} and 2p_{1/2} states, *e.g.* in spectrum D, can be seen only with dif-

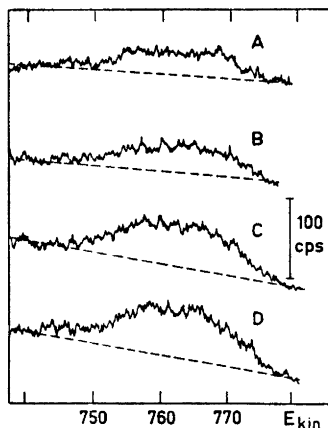


Fig. 2. Iron $2p_{3/2} - 2p_{1/2}$ spectra.

ficulty. This effect will be treated further in a future communication. It may be noted that a similar effect was found by Kramer and Klein⁶ investigating $KFeS_2$ and FeS .

The only observation, seemingly contradicting the above interpretation, is the strong decrease of the nitrogen signal in the A-B-C-D sequence (Fig. 3). If the iron signal is constant or even slightly increasing one should expect the same to be

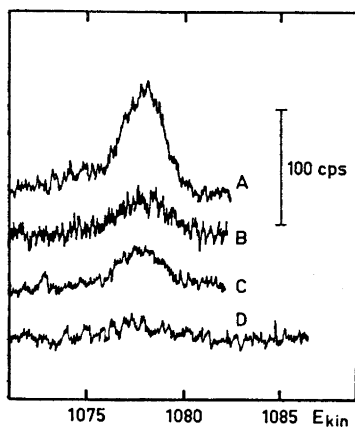


Fig. 3. Nitrogen $1s$ spectra.

the case with the nitrogen one. However, there seems to be a slight change in position of the nitrogen band maximum between A and D. We suggest, therefore, that the weak signal (showing a very broad band) found for sample D really corresponds to the phthalocyanine nitrogens, but that the band observed in sample A is caused by surface adsorbed nitrogen species (ammonia from the teflon-dispersion used in the preparation of the electrode) that are desorbed and possibly oxidized away in the acid medium. For the pure polymer $Pc-Fe(II)$ 280°A the nitrogen signal appears at 1077.5 eV, corresponding quite well to the position of the weak signal of sample D.

In conclusion, we feel that the use of ESCA as a semiquantitative tool for surface studies, exemplified in this work, will yield valuable information also on other electrochemical problems.

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1. Mrha, J. and Larsson, R. *Electrochim. Acta*. To be published.
2. Siegbahn, K. et al. *ESCA, Atomic, Molecular and Solid State Structure studied by means of Electron Spectroscopy*, Almqvist & Wiksell, Uppsala 1967.
3. Berezin, B. D. *Russ. J. Inorg. Chem.* **6** (1961) 1349.
4. Mrha, J. *Kem. Tidskr.* **83** (1971) 46 (Nos. 7-8).
5. Wertheim, G. K. and Rosencwaig, A. J. *Chem. Phys.* **54** (1971) 3235.
6. Kramer, L. N. and Klein, M. P. *Chem. Phys. Lett.* **8** (1971) 183.

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