

A CONTRIBUTION TO THE CHARACTERIZATION OF HEAT-TREATED ELECTROCATALYTICALLY ACTIVE TETRAMETHOXY-PHENYLPORPHYRINATO-COBALT-II

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Summary

The physico-chemical properties of activated material for electrodes for the electrochemical reduction of oxygen are discussed. These electrodes contained either tetramethoxyphenylporphyrinato-cobalt-II or cobalt acetate, and had been treated in a stream of inert gas at temperatures between 80 and 1200 °C. In this context, the current density-potential behaviour, electrochemical stability, electronic conductivity, and catalytic activity for the decomposition of hydrogen peroxide are presented. The most stable material of good performance is obtained by pyrolysis in an argon stream for 5 h. X-ray spectra confirm that carbon and β -cobalt are formed in the pyrolysis of the substrate-free compounds but, on the other hand, no β -cobalt can be detected in the pyrolysis of the material deposited on a substrate. Primarily, the carbon generated by the pyrolysis of the chelate should be considered responsible for the electrocatalytic activity of the oxygen or air electrodes prepared therefrom.

Zusammenfassung

Es werden physiko-chemische Eigenschaften von Aktivmaterial für Elektroden zur elektrochemischen Sauerstoffreduktion diskutiert, die entweder Tetramethoxyphenylporphyrinato-Cobalt-II oder Cobaltacetat enthalten und bei verschiedenen Temperaturen zwischen 80 und 1200 °C im Inertgasstrom behandelt worden waren. Dabei werden das Stromdichte-Potential-Verhalten, die elektrochemische Stabilität, die Elektronenleitfähigkeit und die Katalaseaktivität für die Wasserstoffperoxidzersetzung vorgestellt. Das stabilste Material mit diskutabler Belastbarkeit wird durch Pyrolyse im Argonstrom nach 5 h erhalten. Röntgenspektren belegen, dass bei der Pyrolyse der tragerfreien Verbindungen Kohlenstoff und β -Cobalt gebildet werden, aber β -Cobalt bei der Pyrolyse des tragerhaltigen Materials

nicht nachweisbar ist. In erster Linie sollte der aus der Pyrolyse des Chelates gebildete Kohlenstoff für die elektrokatalytische Aktivität der daraus hergestellten Sauerstoff- bzw. Luftertroden verantwortlich sein

Introduction

The catalytic acceleration of the electrochemical reduction of oxygen is of vital importance for the use of oxygen or air electrodes in fuel cells and metal-air cells respectively. Without the utilization of special electrocatalysts it is impossible, in acid electrolytes, to attain current density values that meet the technical demands. For this reason, various classes of compounds have been checked for their applicability. Apart from the platinum metals, the spinels [1] and especially the N_4 -chelates have been thoroughly tested [2 - 12].

The use of acid electrolytes, indeed, avoids the carbonation that occurs with alkaline cells, a factor which reduces the life-times, but results in a decrease in the performance of the electrodes when using the same catalyst, *e g*, platinum. Thus, the use of certain systems such as nickel and silver catalysts are self inhibiting. As for the platinum metals, their limited availabilities and, for the chelates and spinels, their short durabilities in an acid environment prevent commercial use.

Our investigations were aimed at the use of the metal tetraarylporphyrins as electrocatalysts in gas diffusion electrodes for oxygen reduction. A representative of this highly catalytically active class is tetramethoxyphenylporphyrinato-cobalt-II (TMeOPPCo) [13].

The synthesis of this compound has been described by Adler *et al* [14] and Menotti *et al* [15]. A simple purification method is to heat it under vacuum at 200 - 300 °C [10]. At still higher temperatures, the chelate is decomposed. The decomposition products are also electrocatalytically active.

As early as 1971 Sandstede *et al* (according to ref. 7) and, somewhat later, Jahnke *et al*. [16] described various chelate systems that can be converted into highly active, stable catalysts by a thermal treatment. In this way, pyrolysis products are obtained that are active not only for oxygen reduction but also, with slightly modified conditions of preparation, for fuel oxidation. Bagotsky *et al* [17] gave an optimum temperature range of between 800 and 900 °C for the pyrolysis of a porphyrine-containing material in an inert atmosphere.

In this paper, results are presented that permit the selection of an optimum temperature range, with respect to performance and electrochemical stability of the electrodes in 4.5N sulphuric acid, for the preparation of activated material containing TMeOPPCo, by pyrolysis in an argon stream. Moreover, further information is obtained on the variation of the catalyst structure, due to the heat treatment, considering in particular X-ray spectra

Experimental

(a) *Materials used*

The activated material was prepared by precipitating TMeOPPCo (which had been heated previously under vacuum at 300 °C) from 1,4-dioxane solution on active charcoal P 33 in a 1.9 ratio. By evaporation of a cobalt acetate solution together with active charcoal, a material was obtained that contained about the same quantity of cobalt. Furthermore, pure TMeOPPCo and $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ were also used as reference substances

(b) *Method of treatment*

All the substances were used immediately after purification, or subjected to a heat treatment in an argon stream in quartz tubes. In this paper, the temperatures listed are those that were measured before the completion of the pyrolysis

(c) *Catalytic activity*

The velocity of hydrogen peroxide decomposition served as the measure of the catalytic activity. Very finely-powdered and screened materials (see (a) and (b)) were rapidly stirred into a solution of 40 mmol/l of hydrogen peroxide and 4.5N sulphuric acid and the oxygen evolution was then measured. The calculations were based on the half-life period of the reaction.

(d) *Conductivity measurements*

For determining the conductivity of the pyrolysed porphyrine materials a simplified procedure according to Euler [18] was employed. The conductivity was measured with increasing pressure on a tablet of the powdered material as a function of density. The logarithm of the specific resistance was plotted against the density and then extrapolated to the value of 2.20 g/cm^3 , which corresponds approximately to the density of graphite

(e) *Preparation of electrodes*

Two-layer diffusion electrodes were made according to an optimized technique described by Iliev *et al.* [19]. They had an active layer consisting of 2.5 parts of activated material (according to (b)) and one part of wet-proofed acetylene black XC 35-1, mixed mechanically. The gas layer consisted entirely of wet-proofed acetylene black which had been pressed into a stainless steel grid (X8 Cr-Ni-Ti 18.10). The pressure was 0.22 MP.

(f) *Current density-potential and potential-time measurements*

These measurements were made galvanostatically in 4.5N sulphuric acid in a half-cell arrangement *versus* a mercury/mercury sulphate reference electrode in the same solution ($U_{\text{H}} = 635 \text{ mV}$, all potentials cited are against the reference hydrogen electrode). Lead sheet metal was used as the counter electrode. For the measurements with atmospheric oxygen and oxygen

under a slight overpressure as the depolarizing agent, an arrangement described by Iliev *et al* [20] was chosen

(g) X-ray studies

For this purpose, an X-ray diffractometer, TUR M 62. was used combined with a goniometer, HZG-3.

The radiation was Co K α (Fe-filter) high-voltage 30 kV, anode current 16 mA. The angular velocity of the goniometer was 1°/min. The divergence aperture and the entrance aperture were of 1 mm and 0.8 mm width, respectively. A Geiger-Mueller counter was used as detector.

(h) Determination of surface

The surface area was determined according to a simplified BET-method by Haul and Duembgen [24]

Results and discussion

In the pyrolysis of the pure compound the mass loss was determined from which, together with an elemental analysis (made by use of a CHN-O elemental analyzer 1102-Carlo Erba), Fig. 1 could be constructed. It can be seen from this that the carbon content of the specimen changes insignificantly. On the other hand, the hydrogen content decreases considerably, beginning at a pyrolysis temperature of 400 °C, while the nitrogen portion slowly falls above 600 °C. The oxygen is completely emitted with the decomposition of the porphyrine between 400 and 500 °C, starting as water or other low molecular weight compounds. Beyond 1000 °C the pyrolysis proceeds to such an extent that only carbon and cobalt are left as residuals. The most noticeable changes in the elemental composition are to be found between 450 and 750 °C.

The applicability of the oxygen electrode is substantially determined by the electrocatalytic activity and the stability of the catalysts in connection with the substrate. The stability can be raised, on the one hand, by the use of "more corrosion-resistant" substances, and, on the other hand, by catalytic activity of the catalyst that keeps the concentration of the corrosive intermediate low during the operation of the electrode. The hydrogen peroxide formed in the oxygen reduction is aggressive to the substrate and the catalyst, thus lowering the lifetime of the electrode. Figure 2 shows the reciprocals of the half-life periods for the decomposition of hydrogen peroxide by the pure catalyst and the activated material when using a starting material containing 10% TMeOPPCo for the pyrolysis in the argon stream. A maximum catalytic activity is to be seen for both cases which, however, is shifted to lower pyrolysis temperatures and is appreciably higher for the activated material. The difference in the maximum heights may be assigned to the differing surface areas. A low electrical conductivity of the electrodes and, particularly, of the catalyst has a detrimental effect on

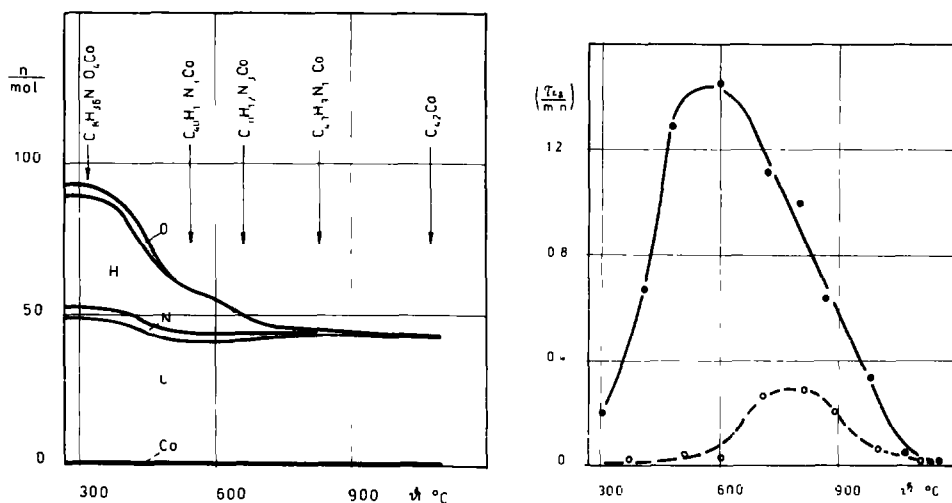


Fig 1 The composition n of TMeOPPCo as a function of the pyrolysis temperature ϑ (5 h in Ar, the specimens were obtained, in each case, by the application of fresh TMeOPPCo which had been previously treated at 300 °C under vacuum. The composition n is the elemental content in moles referred to one mol of the initial substance)

Fig 2 Reciprocal half-life periods for the hydrogen peroxide decomposition as a function of the pyrolysis temperature ϑ , measured at 25 °C (1 g/l catalyst, powdered and screened taking all fractions below 0.15 mm dia., active material, ●— with 10% TMeOPPCo, S_{BET} ca 700 m²/g, pure TMeOPPCo, ○—, S_{BET} see Fig 14, 0.04 mol/l H₂O₂, 2.25 mol/l H₂SO₄)

the performance of the electrodes. The resistance of the electrode can be minimized by additives that improve the electrical conductivity (e.g., graphite, use of carriers of high conductivity such as acetylene black) and optimum manufacturing conditions (method of blending the active material with wet-proofing agents, pressure, pressing temperature) to such an extent that the determination of the conductivity after addition of the activated material by mixing results in values from which no tendency is apparent, even though the catalyst materials have conductivity figures that extend over a range of 10 decades (Fig. 3). It can be deduced from this fact that the conductivity of the activated material is determined by the carrier and the wet-proofed acetylene black added by mixing. Unfortunately, the intrinsic conductivity of the catalyst in thin layers cannot be determined when there is a fine distribution on the substrate surface, which corresponds to the actual situation in electrodes. Of course, it has to be assumed that these layers have a conductivity behaviour which differs from that of catalyst powder without any substrate.

The current density-potential measurements were made on two-layer electrodes with current collectors. Figure 4 shows the results obtained with this method. The air electrode exhibits, at about 50 mA cm⁻², a point of inflection since the transport obstructions become considerable at lower current densities compared with pure oxygen. The curve for the oxygen

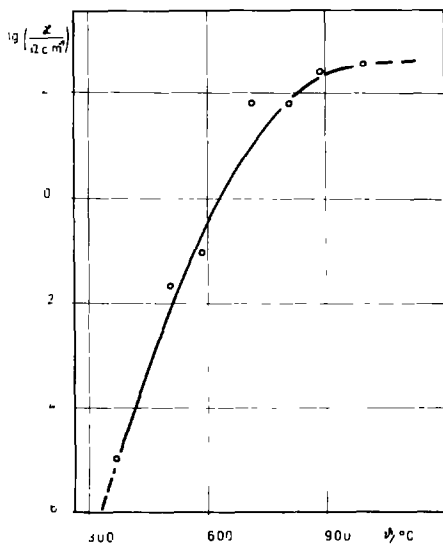


Fig 3 The specific conductivity of tabloids made from pyrolysed (5 h in an argon stream at temperatures θ) and powdered TMeOPPCo

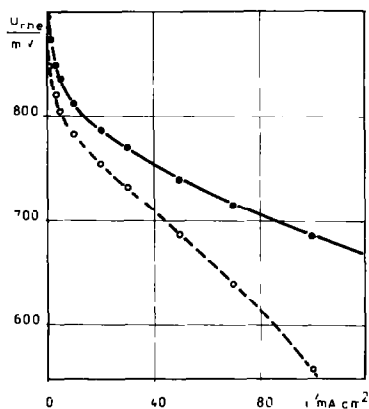


Fig 4 Current density-potential curves of two-layer electrodes in air \circ —, and oxygen \bullet —, 4 N sulphuric acid, room temperature. Composition of the electrodes 100 mg/cm^2 gas layer made of XC 35-1, 50 mg/cm^2 active layer, consisting of 32.1 mg/cm^2 active carbon P 33 + 3.6 mg/cm^2 TMeOPPCo (treated in argon 5 h at 600°C) and mixed with 14.3 mg/cm^2 XC 35-1, stainless steel grid, pressed at 0.22 MPa

electrode does not show a point of inflection until the current is essentially higher. Figure 5 has been drawn on the basis of typical values of the $i-U$ curves. This Figure illustrates the performance of oxygen electrodes at various constant potentials as a function of the pyrolysis temperature of the activated material employed. Broad maxima are obtained between 400 and 850°C . The catalyst with highest activity is obtained by pyrolysis at about 550°C . A performance increase of five or six times the initial value is attained in the potential range of interest, between 650 and 750 mV , as compared with the untreated material. 700 mV can be obtained at a current density of 0.5 A , and 550 mV at 1 A , with an air electrode of 10 cm^2 geometrical area. Unfortunately, the life-time of activated material treated below 700°C is too short. While the stability of the material prepared at 480°C is sufficient at 5 mA/cm^2 and room temperature (Fig. 6, upper curve) to exhibit, even after 1000 h , the lowest polarization, at higher current densities there is a rapid destruction of the activated material so that after 500 h the performance of the electrodes becomes inferior to those made from material which has been treated at a pyrolysis temperature above 900°C . Sufficiently low degradation rates that are, after the initial decline (after 100 to 200 h), below 0.02 mV/h at 30 mA/cm^2 and 50°C or 0.003 mV/h at 5 mA/cm^2 and room temperature, respectively, are only attained above 750°C . An air electrode, the active material of which has been treated

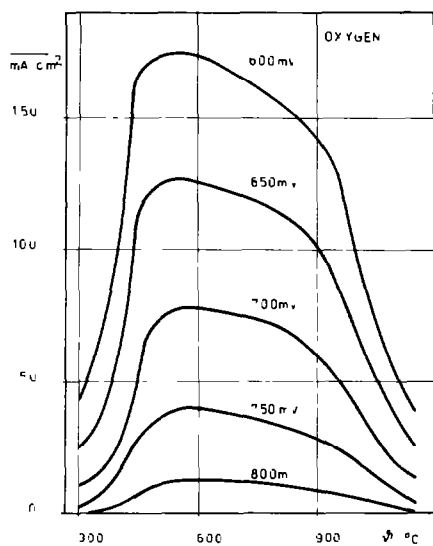


Fig 5 Current densities i , of two layer electrodes at different potentials (*versus r h e*), room temperature and 4.5N sulphuric acid. Composition of the electrodes as in Fig 4 but treated for 5 h at different temperatures in an argon stream

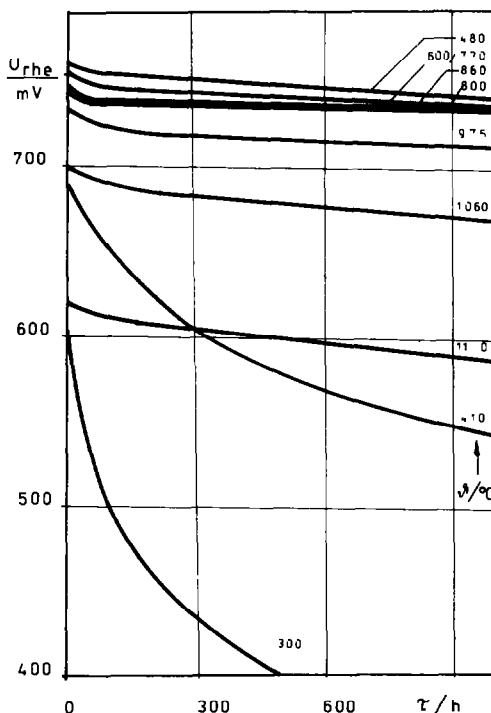


Fig 6 Galvanostatic potential-time curves of two layer electrodes with current collector (5 mA/cm^2 , room temperature 4.5N sulphuric acid, air). Composition of the electrodes, see Fig 4, but treated at different temperatures in an argon stream

at 800°C , should be capable of attaining an operating life-time of about 10 000 h before the potential falls below 700 mV working at 5 mA/cm^2 . But such an extrapolation does not take into consideration the fact that during the life test, the pores of the active zones become increasingly filled with electrolyte, which results in increasing obstruction to the transport and distribution of the molecular oxygen within the active layer. Therefore, it is to be expected that this process will lead to an additional deterioration of the electrode characteristic curve.

On the basis of the X-ray diffraction patterns, further information on the structural variations of the catalyst and the active material, as compared with the pure substrate and cobalt acetate as reference substances, should be obtained.

Figure 7 shows the X-ray spectra of pure untreated and pyrolyzed TMeOPPCo. The compound is undecomposed up to 370°C . A degradation of the TMeOPPCo occurs between 400 and 500°C and, disregarding a rise at 15° , the spectrum is structureless. After a further rise in the pyrolysis

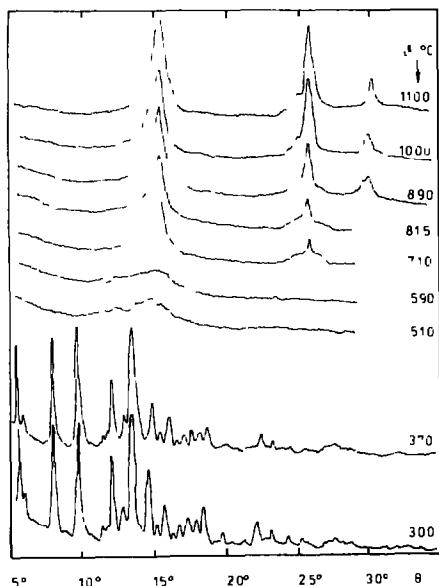


Fig 7 X-ray spectra of pure TMeOPPCo, treated 5 h in an argon stream at the temperatures listed

temperature a broad band occurs at 15.5° which has sharp contours at 800°C . Beginning at 700°C a slight rise is also to be seen on which a line at 26° is superposed. In this range there is a series of very strong reflections due to various carbon phases so that this rise can be explained in this way. The line at 26° can be assigned to the formation of cobalt and this has been supported by measurements made at higher angular ranges. Thus, the porphyrin residue contains, beginning at 500°C , carbon, and at 700°C β -cobalt in quantities that can be demonstrated by X-ray photographs.

The distinct activity rise between 400 and 550°C (Figs. 2 and 5) can be associated with the structural change which is confirmed by elemental analysis (Fig. 1).

Cobalt acetate with and without a carrier was used as the comparison material. It is generally known that this substance has no electrocatalytic activity after pyrolysis. Pure cobalt acetate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, see Fig. 8) yields, on pyrolysis, cobalt of the α - as well as β -modifications.

Additionally, at first, cobalt oxides occur on thermal decomposition and these too become visible in the X-ray diffraction photogram. A small amount of carbon (0.4%) can also be detected by elemental analysis in cobalt acetate that has been treated at 550°C . On the other hand, there is no evidence of carbidic phases. After evaporating an aqueous solution of cobalt acetate along with active charcoal P 33 and subsequently pyrolysing in an argon stream, diffraction patterns of the type shown in Fig. 9 are obtained. The strongest line at 15.5° can be assigned to carbon. X-ray crystalline cobalt cannot be conclusively proven as either the α - or the β -modifications

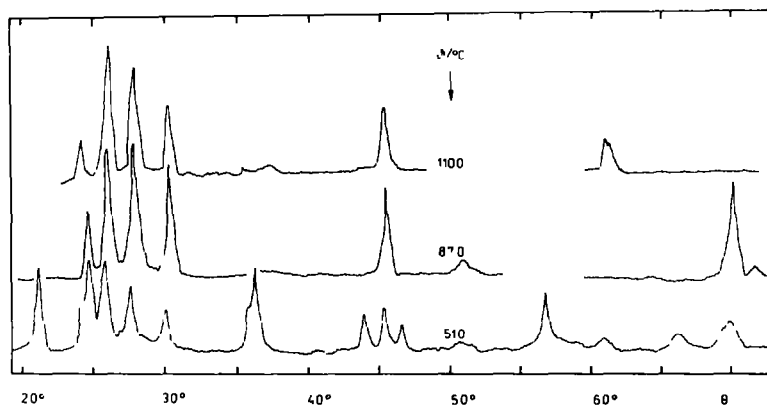


Fig 8 X-ray spectra of cobalt acetate, treated at the temperatures listed in an argon stream

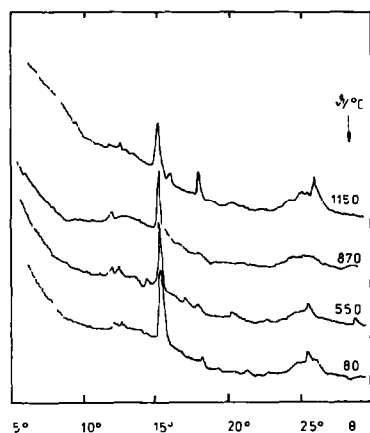


Fig 9 X-ray spectra of 3.5% $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and active charcoal P 33 evaporated from water and treated 5 h in an argon stream at the temperatures listed

The maximum occurring at 26° has the typical intensity distribution also found with pyrolysed active charcoal P 33 which certainly does not contain any cobalt (Fig. 12). The line at 18.2° , on the other hand, can come from Co_3O_4 or be identical with the line found for pure, active charcoal.

The X-ray patterns of the activated materials require a high equipment resolving power. Active charcoal P 33 exhibits a very high degree of texture (Fig. 10). Moreover, the carbon absorbs some of the diffracted radiation (see Figs. 7, 9 and 11). In the pyrolysis of the activated material, the spectrum changes in a similar manner to that of the pure compound. The carbon formation cannot be observed very distinctly. Visibly it starts at 600°C .

Above 1000°C a line similar to that for pure, active charcoal P 33 occurs at 26° (Fig. 12) and similar to cobalt acetate-containing material. Most interesting is the splitting of the rise at 25° into several individual

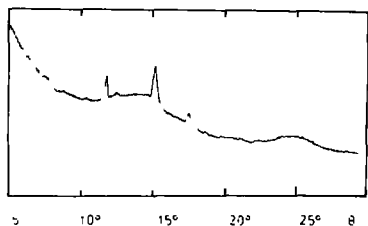


Fig 10 (left) X-ray spectrum of active charcoal P 33

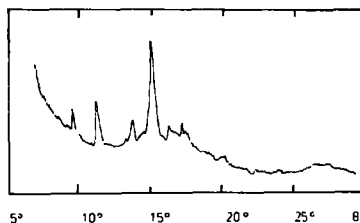


Fig 11 (right) X-ray spectrum of active charcoal P 33, mechanically mixed with 10% TMeOPPCo

peaks, which is to be seen only with material containing active charcoal. This phenomenon allows the conclusion to be drawn that several carbon phases are formed having different lattice parameters. Their percentages are changed at different temperatures. When comparing the spectra of the materials containing cobalt acetate (Fig 13) only slight differences are to be found. For the latter, phase formation already starts at a low temperature. Apart from this fact, the formation of new carbon can be shown in both cases.

α -Cobalt occurs only with substrate-free cobalt acetate (The evidence for β -cobalt is doubtful, rather negative.) Thus, radiographic statements are only of limited validity concerning the active structure of the pyrolysed material on which TMeOPPCo has been previously precipitated. Various hypotheses concerning the active structure of the catalyst material have been proposed by us [22]. The formation of β -cobalt in the pyrolysis of cobalt porphyrin without substrate can be considered as a definite fact. That β -cobalt could not be proved to be present after the pyrolysis of the substrate-containing material could be due to a superposition on the first cobalt reflection of a carbon reflection or, on the other hand, it could result from suppression of the formation of crystalline cobalt by the substrate or from an interaction with this substrate. Other cobalt phases cannot be proved either.

The occurrence of cobalt–nitrogen or cobalt–carbon compounds can also be excluded. It is remarkable for the spectra of pure TMeOPPCo, as well as for the corresponding activated material, that β -cobalt, if the peak at 26° really can be traced to β -cobalt in the activated material, occurs only at temperatures at which the catalytic activity of electrodes made therefrom has already begun to decrease (Figs. 2 and 5).

When comparing Fig. 7 with the current density–pyrolysis temperature curve (Fig. 5, 510°C) it must be pointed out that the carbon formation is at first in a finely divided form. This corresponds to the rise of the i – U curve from 300 to 450°C . By pyrolysis at about 550 to 650°C a product is obtained which, besides carbon and cobalt, still contains nitrogen and hydrogen (Fig. 1). This product is not decomposed until above 650°C when, finally, only cobalt and carbon are present.

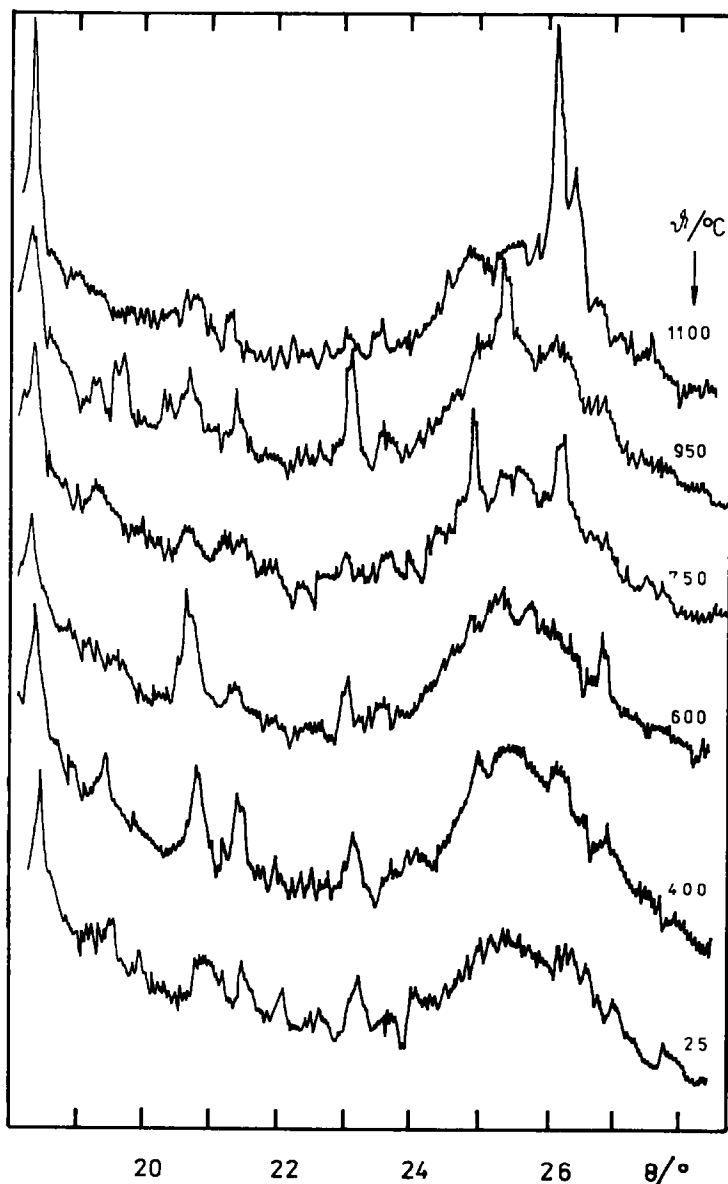


Fig 12 X-ray spectra of active charcoal P 33 treated for 5 h in an argon stream at the temperatures listed, and angles measured between 18 and 30° and drawn to the original scale

This decomposition gives a product having a somewhat lower initial activity but a substantially better stability, established by measurements at higher temperature and current density. Parallel to the chemical alteration of the catalyst a change of the surface area with rising pyrolysis temperature can be seen also (Fig. 14). With the beginning of decomposition at about

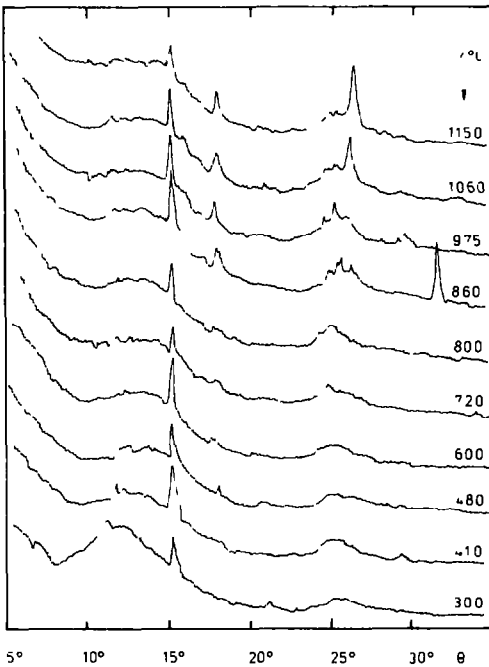


Fig 13 X-ray spectra of activated material (10% TMeOPPCo precipitated from a 1,4-dioxane solution and treated 5 h in an argon stream at the temperatures listed)

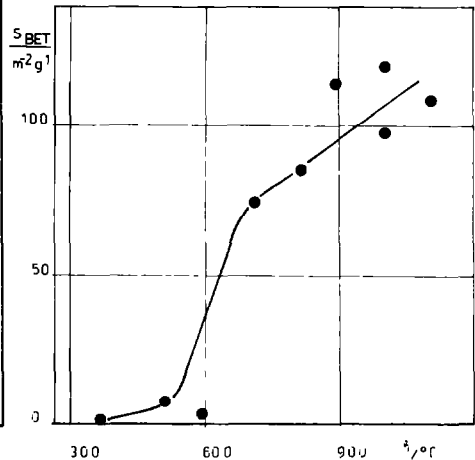


Fig 14 The BET-surface area of pure TMeOPPCo treated 5 h in an argon stream at the temperatures ϑ

450 °C, an amorphous product arises from the crystalline TMeOPPCo which contains a large number of micropores due to the loss of low-molecular pyrolysis fragments. The BET-surface suddenly rises to values of about 100 m²/g. The increase in temperature above 600 °C has no further detectable influence upon the BET-surface of the catalyst.

Conclusions

Evidently, since cobalt is only effective for the formation of a catalytically active surface when in connection with the N₄-chelate ligand, the conclusion must be drawn that the bonding conditions of the cobalt in nitrogenous complexes are responsible for the formation of active carbon. By a thermal treatment of active charcoal P 33 on which TMeOPPCo has been precipitated previously an activated material can be prepared by an optimum temperature treatment (800 °C, argon stream, 5 h) which enables considerable current densities to be attained when employing it in oxygen diffusion electrodes. The active centres formed in the pyrolysis probably consist of carbon of a specially-ordered arrangement, whilst the pyrolysis itself has to proceed in the presence of finely-distributed bonded cobalt.

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