

Effect of pyrolysis temperature of the catalytic activity of active carbon + cobalt phthalocyanine in sulfur dioxide oxidation by oxygen

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Structural changes during the pyrolysis of the catalyst 'active carbon+cobalt phthalocyanine' (Ac+CoPc) in the temperature range 500–800°C are investigated using infrared spectroscopy, XRD and DTG analysis. The decomposition products contain organic residues of the phthalocyanine rings and separate phases of CO_3O_4 and $\beta\text{-Co}$. The effect of pyrolysis temperature on: (i) the chemical stability of Co in the pyrolyzed CoPc in 0.5M H_2SO_4 ; (ii) the electrocatalytic activity for oxidation of SO_2 by oxygen; and (iii) the partial electrochemical reactions of SO_2 oxidation and oxygen reduction, has been studied. The rate of electrochemical oxidation of SO_2 is affected only by the active centres formed on pyrolysis of the chelate rings. The presence of Co at lower pyrolysis temperatures decreases the oxygen diffusion limitations. It is shown that the rate of SO_2 oxidation by oxygen is limited by mass transport of oxygen.

1. Introduction

The thermal treatment (in inert atmosphere at 600–900°C) of N-4 chelate complexes of the transition metals, deposited on carbon substrates, bring about a substantial improvement and stabilization of their activity with respect to the electrochemical reduction of oxygen [1–3] and the electrochemical oxidation of SO_2 [4].

There are two basic concepts for the enhancement of the electrocatalytic activity of N-4 chelates after pyrolysis. According to some authors the main role as an active centre in the electrochemical reduction of oxygen is assigned to the metal atom which changes its electronic state, or forms compounds with organic residues of the pyrolysed chelate [5–7]. Others consider that the active centres are formed by the pyrolysed chelate and the carbon carrier, while Co only promotes their formation at lower pyrolysis temperatures [8, 9].

The study of the effect of pyrolysis temperature on the activity and stability of metal phthalocyanines in the electrochemical oxidation of SO_2 is related to the method for purification of SO_2 from waste gases developed in this laboratory. The process takes place at the three phase boundary: catalyst (Ac+CoPc)/liquid phase (H_2SO_4 solution)/gas phase (SO_2 in air). The final product is sulfuric acid. It has been established that this process is basically electrocatalytic and proceeds in short circuited micro galvanic cells [10, 11].

This paper describes a study of the effect of pyrolysis temperature on: (i) the structural changes in CoPc during pyrolysis; (ii) the chemical stability of Co in

pyrolysed catalyst; and (iii) the electrocatalytic activity of the pyrolysed catalyst.

2. Experimental details

The pyrolysed catalyst active carbon modified with phthalocyanine (AC/ H_2Pc) or with cobalt phthalocyanine (AC/CoPc) were studied. H_2Pc and CoPc were synthesized from a melt in urea excess [12]. The degree of conversion of the starting compounds into CoPc was determined by spectrophotometric measurements of pyridine solutions of CoPc. In cases when the catalyst was carbon activated with CoPc or H_2Pc , the necessary amount of active carbon (AC) was added. An experimental brand of AC, produced in the Institute of Organic Chemistry of the Bulgarian Academy of Sciences was used [13]. Pyrolysis of the catalysts was carried out in a tube furnace in Ar atmosphere under the following temperature conditions: one hour of increasing temperature to reach the pyrolysis temperature and four hours at this temperature.

The changes occurring in CoPc during the pyrolysis were followed by the infrared spectra recorded on a Fourier spectrometer Bruker IFS-113 V; XRD spectra were recorded on a Philips APD diffractometer using CuK_α radiation and a graphite monochromator. The differential thermogravimetric analysis was performed on a Perkin–Elmer TGS-2 apparatus.

To test the chemical stability of Co in sulfuric acid, samples pyrolysed at various temperatures were washed in 0.5M H_2SO_4 at 20°C (for 50–100 h). The amount of cobalt dissolved in H_2SO_4 was assessed by titration. The washed samples were subjected to

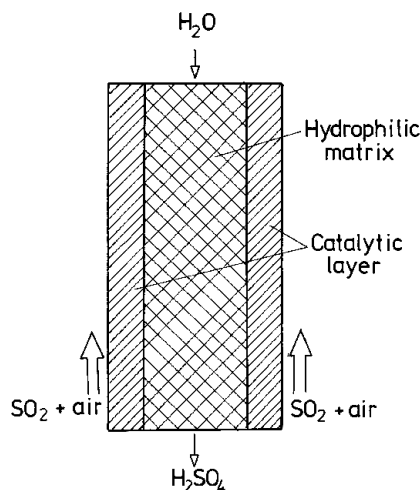


Fig. 1. Cross section of the catalytic sheet.

EPR analysis using an ERS 220 Q apparatus and subsequently treated in HCL + HNO₃ (3:1) at 60°C to estimate the amount of Co undissolved in 0.5M H₂SO₄.

The electrocatalytic activity of pyrolysed catalysts with respect to the reduction of oxygen and the oxidation of SO₂ was assessed by voltammetry of two-layer gas-diffusion electrodes (g.d.e.) developed in this laboratory [14]. The catalytic layer contains the catalyst and acetylene black hydrophobized with Teflon in a ratio 1:1. The measurements were carried out in air, oxygen, SO₂, and a mixture of 14% SO₂ and 86% Ar (vol.) in 0.5M H₂SO₄ at constant current. The potential was measured with respect to a Hg/Hg₂SO₄ reference electrode and the values are referred to the potential of a reversible hydrogen electrode in the same solution (RHE).

The catalytic activity in the SO₂ oxidation by atmospheric oxygen was evaluated with catalytic sheets [11] in an atmosphere containing 14 vol % SO₂ and 86 vol % air. The catalytic sheets were polyester (fibrous material) strips on both sides of which the

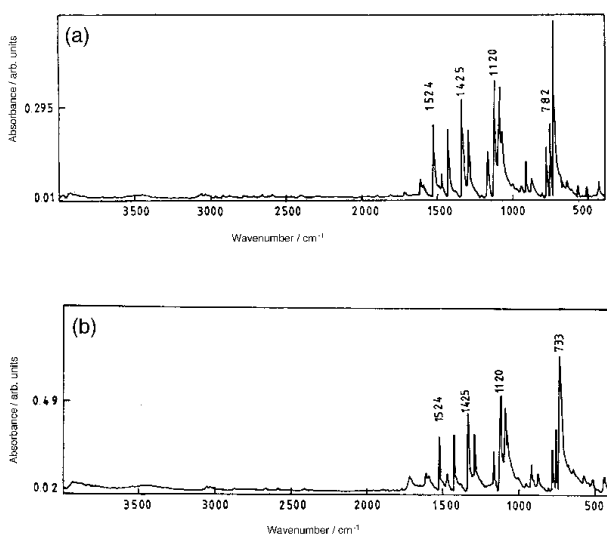


Fig. 2. Infrared spectra of CoPc samples: (a) Fluka standard; (b) synthesized from a melt according to reference [12].

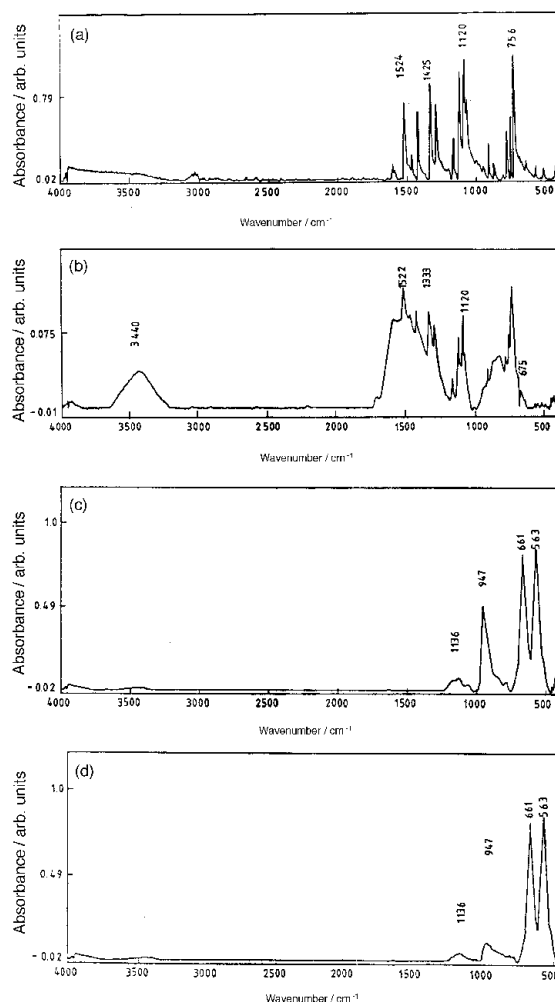


Fig. 3. Infrared spectra of CoPc samples after pyrolysis at: (a) 400°C; (b) 500°C; (c) 700°C; (d) 800°C.

catalysts with the same composition as the active layer of g.d.e. were applied, Fig. 1. The sheets were packed in glass columns into which sulfuric acid (0.025–0.5M) flowed freely over the polyester strips. The gas mixture was introduced in counterflow mode from the bottom of the column and the oxidation of SO₂ by oxygen occurred at the three-phase boundary catalyst/electrolyte/gas. The activity was determined by the difference between the initial and final sulfuric acid concentration (M), from which the yield of sulfuric acid per kilogram of the catalyst for 24 h was estimated.

3. Results and discussion

3.1. Effect of the pyrolysis temperature on the structural changes in CoPc

Figure 2 juxtaposes the i.r. spectrum of CoPc prepared in a melt by the method described in [12] against a standard sample supplied by Fluka (cat. no. 60855/1990–1991). The similarity in the spectra indicates that their structures are identical.

Figure 3 shows the i.r. spectra of the investigated CoPc after thermal treatment at various temperatures: 400°C (a), 600°C (b), 700°C (c) and 800°C (d). The phthalocyanine was applied on SiO₂. After the

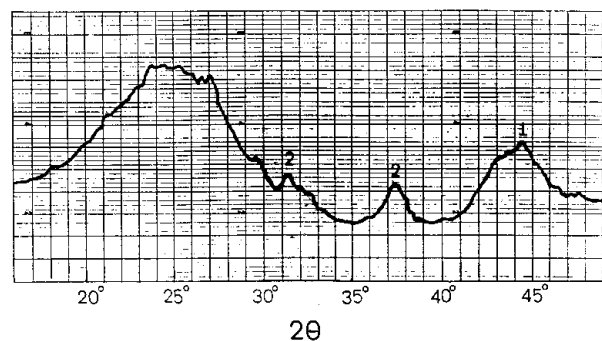


Fig. 4. XRD patterns of AC/30% CoPc pyrolysed at 700°C: (1) β -Co; (2) Co_3O_4 .

pyrolysis, SiO_2 was dissolved in 30% KOH [15]. It can be seen that no changes occur in the sample treated at 400°C, while at 600°C some changes are evident. The basic bands are still present, but some are broad; these appear as a background upon which the narrow bands of Pc are visible. This shape of the spectral patterns occurs in cases of mixed monomer and a polymer in the investigated compound. It is well known that phthalocyanines show a tendency to polymerize and this process is initiated at about 600°C. From the spectrum recorded after the pyrolysis at 700°C it may be concluded that the destruction of the phthalocyanine ring is complete. Besides the bands at 661 and 563 cm^{-1} ,

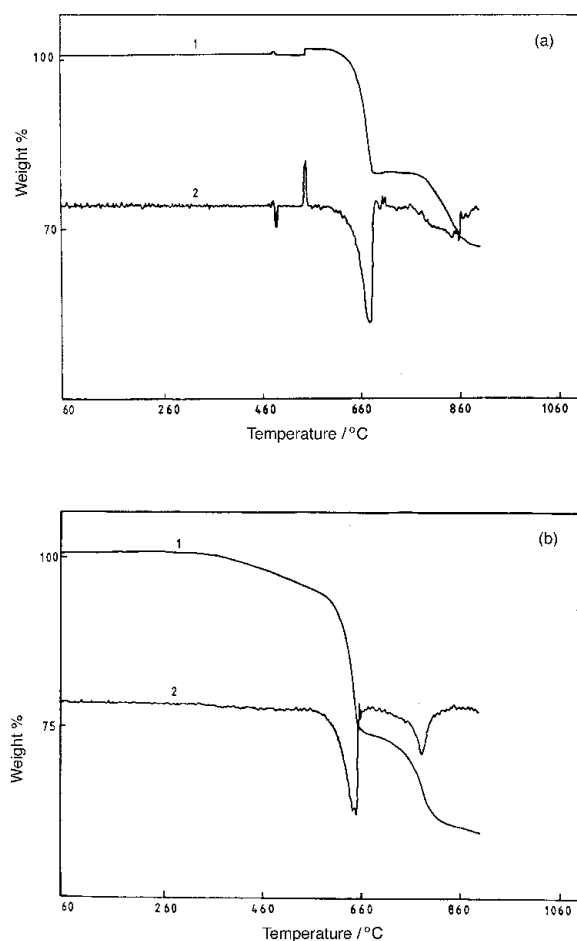


Fig. 5. TGA (1) and DTGA (2) plots of: (a) AC/30% CoPc (Fluka), 6.94 mg; (b) AC/30% CoPc synthesized from a melt, 11.42 mg. Rate: 5.0°C min^{-1} .

which can be identified as Co_3O_4 , two more bands are observed in the last spectrum: one at 947 cm^{-1} and a second one with a complex profile and low intensity at 1136 cm^{-1} . These probably originate from undecomposed products which have lost their hydrogen content. The spectrum of CoPc after pyrolysis at 800°C is similar to that after pyrolysis at 700°C, the only difference being the intensity of the bands related to the undecomposed products of the chelate ring.

Along with the lines of Co_3O_4 ($2\theta = 31.27^\circ$ and 37.25°) the XRD patterns of the samples pyrolysed at 700°C, feature, though partly hidden by a broad halo, a peak at $2\theta = 44.5^\circ$ (Fig. 4). This is an indication of the presence of β -Co as a separate phase in the pyrolysed samples, although the halo is probably due to the crystallites formed after the pyrolysis of the chelate ring. Similar overlap of the line of β -Co over the halo of carbon is observed also in the spectrum of pyrolysed CoTAA [8].

Figure 5 demonstrates the results of the thermogravimetric analysis of CoPc with (b) deposited on active carbon (AC) and (a) a standard CoPc sample (Fluka). The curves are similar in shape: the weight losses, respectively the decomposition, begin at 600°C and, after a slight retention at 660°C, stop at 800°C. These results are in good agreement with the IR spectral data, which indicates that the carbon carrier has no effect in the range of pyrolysis temperatures studied. The relationships (Fig. 5(a) and (b)) show two differences: (i) the investigated CoPc, synthesized in a melt also undergoes thermal alterations in the temperature range 360–560°C, which is accompanied by a 6% weight loss; (ii) the standard sample loses 30% of its weight after the thermal treatment, while that synthesized in a melt loses 40%. The different weight losses may be explained by the formation of intermediate products of the phthalocyanine in the melt synthesized sample. This was confirmed by the spectrophotometric data which show that the amount of CoPc in the product obtained in the melt does not exceed 75%. The intermediate products do not exhibit separate i.r. bands, because their structure is similar to that of the final product of the synthesis, but they have lower thermal stability (Fig. 5(b)).

It follows from the above results, that melt synthesized CoPc undergoes major thermal changes in the 600–800°C range, similar to CoPc synthesized in a solution. The intermediate products of the melt synthesized CoPc are also subjected to alterations in the range 360–600°C.

Table 1. Co content in AC/CoPc after 100 h extraction in 0.5M H_2SO_4 (initial Co content in AC+30% CoPc, 32 mg)

Pyrolysis, temperature T /°C	Co content after 100 h /mg Co	Co vs the initial Co content/%
500	5	16
600	9.8	32
700	11.5	37
800	3	9.6

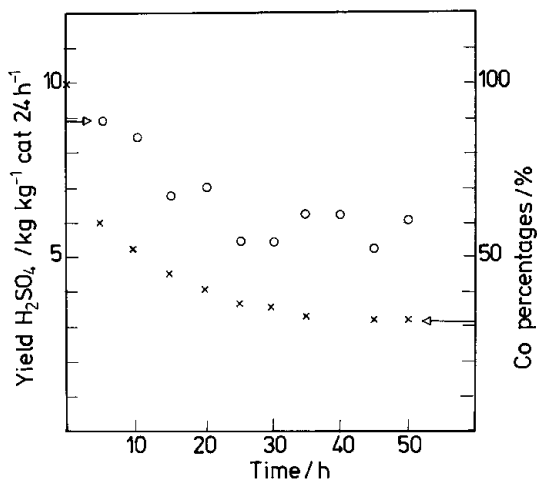


Fig. 6. Evolution of the activity of the catalytic sheet and decrease in the content of Co (%) in AC/20% CoPc pyrolysed at 700°C with the time of testing in the gas mixture of 86 vol % air and 14 vol % SO₂. $C_{H_2SO_4} = 0.05\text{--}0.6\text{ M}$; $t = 20^\circ\text{C}$.

3.2. Influence of the pyrolysis temperature on the stability of Co in 0.5 M H₂SO₄

Table 1 illustrates the effect of the pyrolysis temperature on the stability of Co in 0.5 M H₂SO₄. The data in the table indicate, that: (i) the stability of Co in the pyrolysed catalyst is low (the undissolved Co does not exceed 40% of the initial amount); and (ii) Co is more stable in the samples pyrolysed at 600 and 700°C.

The decrease of Co in the samples pyrolysed at 500°C is probably due to the dissolution of CoPc in H₂SO₄, since no pyrolysis of CoPc proceeds at this temperature, see Fig. 2. After the test in 0.5 M H₂SO₄, XRD and EPR analyses of the samples were performed. There are no lines of $\beta\text{-Co}$ and Co₃O₄ in the XRD patterns of the samples pyrolysed above 700°C. The EPR spectra evidence the presence of Co²⁺ in a low symmetry field, that is, this Co is not in hexagonal or octahedral coordination characteristic

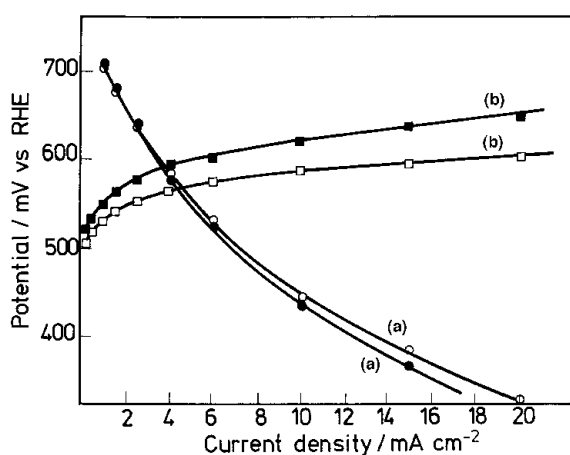


Fig. 7. Voltammograms of a gas diffusion electrode catalysed with AC/20% CoPc pyrolysed at 700°C. $C_{H_2SO_4} = 0.5\text{ M}$; $t = 20^\circ\text{C}$. Oxygen reduction: (○) air, first VA; (●) air, steady state VA. (b) SO₂ oxidation, 86 vol % air and 14 vol % SO₂: (□) first VA; (■) steady state VA.

for spinels (Co₃O₄). This implies that, as a result of the extraction in H₂SO₄, both $\beta\text{-Co}$ and Co₃O₄ are dissolved, while the undissolved Co is stabilized in the form of compounds with the pyrolysed residue of the chelate ring. The i.r. spectra and the thermal analysis (Fig. 5) show that polymerization of the chelate rings begins at 600°C, followed by destruction of the chelate ring at 700°C. Therefore, in this temperature range (600–700°C), both the polymer structures and the destruction products of the chelate rings stabilize the Co in them.

The considerable dissolution of Co from the sample pyrolysed at 800°C is probably related to the high level of destruction of the phthalocyanine and the release of Co. This is supported by the lower bands associated with the products of the pyrolysed chelate ring in the i.r. spectrum of samples pyrolysed at 800°C (Fig. 2(d)).

3.3. Effect of the pyrolysis temperature on the catalytic activity

To estimate the role of $\beta\text{-Co}$ and Co₃O₄, studies of catalytic activity against SO₂ oxidation by oxygen were performed with AC/CoPc pyrolysed at 700°C, where Co is most stable (Table 1). The catalyst was applied on polyester sheet and tested in a column, as shown in Fig. 1. Figure 6 presents the plots of the activity (yield of H₂SO₄) and the Co content against the time of operation of AC/20% CoPc. It can be seen that 50 h of operation about 70% of the Co is extracted from the catalytic sheet. Its activity drops by about 40%. However, this is not unambiguous evidence that decay in the activity is related solely to the decrease in Co content in the catalyst. A similar decay could also be due to changes in the hydrophobic/hydrophilic structure of the catalytic sheets, which could possibly change both the diffusion conditions of the gas and the surface area of the three-phase boundary.

These assumptions may be checked by investigation of the partial electrochemical reactions, that is, the oxidation of SO₂ and the reduction of oxygen. Figure 7 presents the first partial and the steady state voltammograms. The analysis showed that 85–90% of $\beta\text{-Co}$

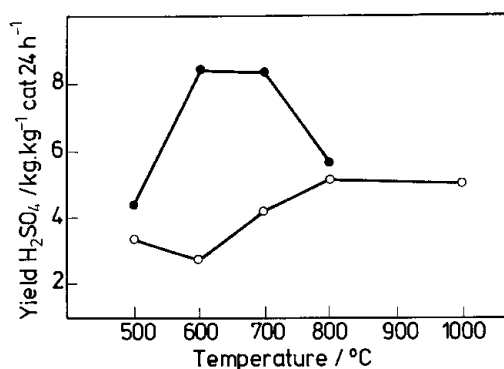


Fig. 8. Dependence of activity for the overall process of SO₂ oxidation on the pyrolysis temperature: (●) AC/30% CoPc; (○) AC/30% H₂Pc. Gas mixture: 86 vol % air and 14 vol % SO₂. $C_{H_2SO_4} = 0.05\text{--}0.5\text{ M}$; $t = 20^\circ\text{C}$.

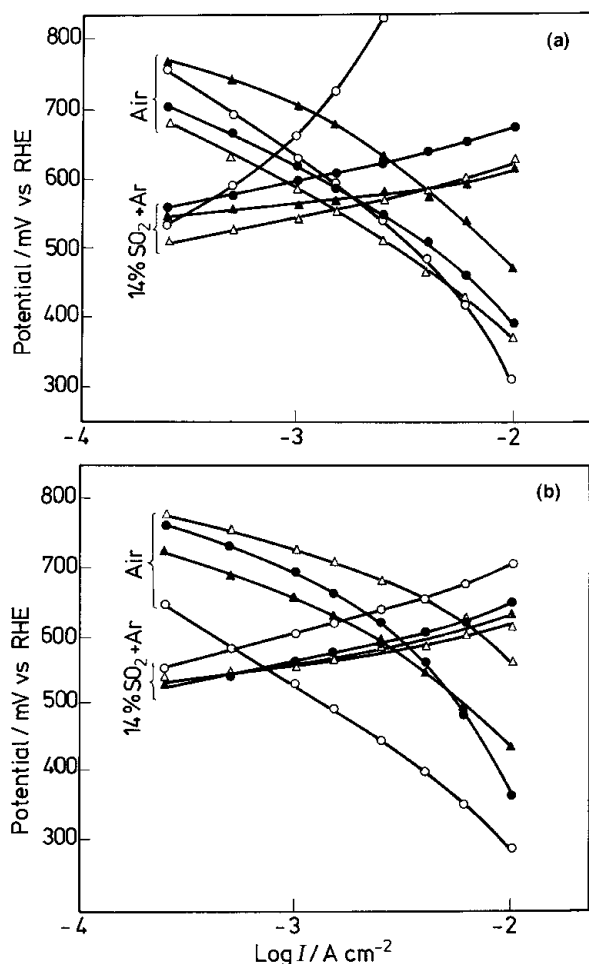


Fig. 9. Tafel plots of a gas diffusion electrode catalysed with (a) AC/30% H_2Pc and (b) AC/30% CoPc at different pyrolysis temperatures: (○) 500°C; (●) 600°C; (△) 700°C; (▲) 800°C. Gas mixture: 86 vol % air and 14 vol % SO_2 . $C_{\text{H}_2\text{SO}_4} = 0.5 \text{ M}$; $t = 20^\circ\text{C}$.

and Co_3O_4 dissolved during the recording of the first oxygen (air) voltammetric curve. This is probably the reason for the similarity between the first and the steady state curves. Although recording the SO_2 voltammograms the dissolution is slower, which is probably due to the considerably more negative steady state potentials of the sulfur dioxide reaction. Some 55–60% of $\beta\text{-Co}$ and Co_3O_4 are dissolved after the recording of the first SO_2 voltammogram, which differs considerably from the steady state voltammetric curve. It follows that the Co and Co compounds soluble in sulfuric acid play the role both of active centres in the electrochemical oxidation of SO_2 and also affect the gas transport. Naturally, they could also play the same role in the oxygen reduction reaction although their fast dissolution does not allow this effect to be disclosed.

To understand the role of cobalt stabilized by the pyrolysis products of the chelate ring, AC/CoPc and AC/ H_2Pc catalysts pyrolysed at temperatures above 500°C were investigated. The effect of pyrolysis temperature on the rate of H_2SO_4 production was studied. The soluble Co was preliminarily extracted. The gas mixture was 14 vol % SO_2 + 86 vol % air. The results are represented in Fig. 8. There is a big difference between the two curves due to the

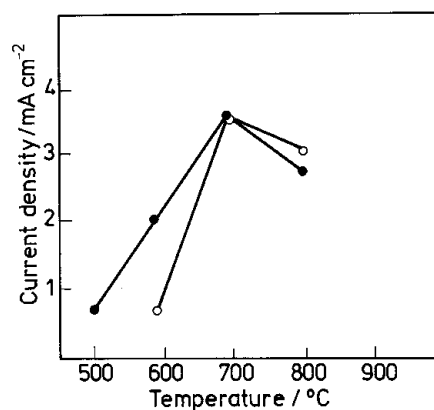


Fig. 10. Dependence of the current density (rate of SO_2 oxidation) on the pyrolysis temperature at constant potential, $E = 580 \text{ mV}$ vs RHE: (○) AC/30% H_2Pc ; (●) AC/30% CoPc . Gas mixture: 86 vol % air and 14 vol % SO_2 . $C_{\text{H}_2\text{SO}_4} = 0.5 \text{ M}$; $t = 20^\circ\text{C}$.

electrochemical activity, transport limitations, or due to both.

The electrochemical activity was elucidated by partial voltammograms on the g.d.e. with oxygen (air) and a mixture of 14 vol % SO_2 + 86 vol % Ar, presented in semilogarithmic mode, see Fig. 9 (a) and (b). The structure of the active layer of the g.d.e. was the same as on the polyester sheets used in Fig. 8. Figure 9 shows that the Tafel plots are linear for SO_2 oxidation for both catalysts, AC/ H_2Pc (Fig. 9(a)) and AC/CoPc (Fig. 9(b)), except for the catalyst AC/ H_2Pc pyrolysed at 500°C. Tafel slopes are $b = 50\text{--}70 \text{ mV}$ per decade. The current density at $E = 580 \text{ mV}$ (Fig. 10) is taken as the magnitude characterizing the rate of electrochemical SO_2 oxidation. It follows from Fig. 10 that the activities of AC/CoPc and AC/ H_2Pc become equal after treatment in the temperature range where the destruction of the chelate ring has been completed (700–800°C). This shows that the cobalt stabilized in the remnants of the chelate ring has no impact on the rate of electrochemical SO_2 oxidation. The decisive factors are

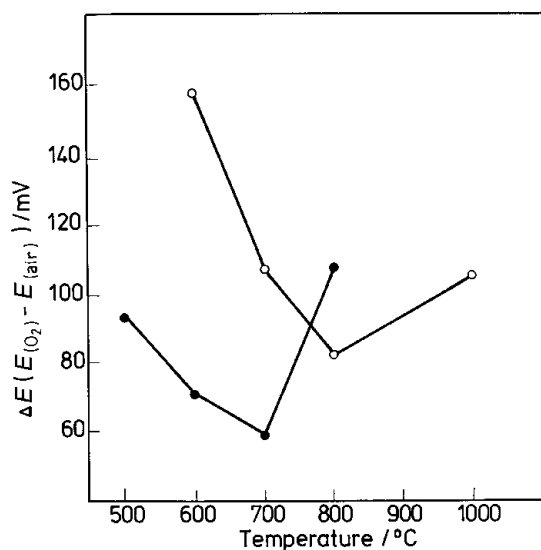


Fig. 11. Dependence of $\Delta E (E_{\text{O}_2} - E_{\text{air}})$ at $i = 5 \text{ mA cm}^{-2}$ on the pyrolysis temperature: (○) AC/30% H_2Pc ; (●) AC/30% CoPc .

the active centres formed after the pyrolysis of the chelate ring.

The Tafel plots of the oxygen reduction reaction (Fig. 9(a) and (b)) are curved, implying that this reaction is diffusion limited. The transport hindrances were estimated from ΔE ($E_{O_2} - E_{air}$) against i relations [16]. Figure 11 shows the plots of pyrolysis temperature against ΔE at constant current density ($i = 5 \text{ mA cm}^{-2}$). The differences in ΔE for AC/CoPc and AC/H₂Pc show that the transport hindrances are reduced in the presence of cobalt. On the other hand, this decrease depends on the amount of cobalt remaining firmly bound in the AC/CoPc (see Table 1). Similar results have been obtained by other investigators [17] who have studied the oxygen reduction reaction on electrodes catalysed with AC/CoTMPP. The juxtaposition between the two plots in Fig. 11 also shows that at 800°C the diffusion limitations in AC/H₂Pc are smaller than those with AC/CoPc. Hence, the pyrolysed residue may lead to the formation of an optimum structure with respect to low diffusion limitations. Cobalt decreases the diffusion limitations at lower pyrolysis temperatures.

Similar conclusions have been drawn by Grunig *et al.* [8] in the study of the activity of pyrolysed AC/CoTAA and AC/H₂TAA with respect to the rate of the electrochemical reduction of oxygen. Van der Putten *et al.* [7] studied the same reaction on AC doped with pyrolysed CoPc, H₂Pc, CoTA and H₂TAA. According to [7], Co plays an important role in the formation of active centres. The conclusions of van der Putten *et al.* [7] are based on potentiodynamic measurements on a rotating disc electrode, under conditions where Co is still not dissolved and the diffusion limitations can be reduced.

A comparison between Fig. 8 and Fig. 11 shows that the rate of SO₂ oxidation by oxygen is higher when the diffusion hindrances of the partial oxygen reaction are smaller, which means that transport of oxygen is the limiting stage in the SO₂ oxidation.

This suggests that the pyrolysis temperature affects the rate of the overall process through the formation of different diffusion limitations for oxygen.

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