ELECTROCHEMICAL ACTIVITY OF SOME DIFFERENT IRON POLY-PHTHALOCYANINES FOR THE OXYGEN REDUCTION REACTION IN ACIDIC MEDIUM

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Summary

The electrochemical activity of iron polyphthalocyanines (pPcFe) synthesized from pyromellitic dianhydride (PMDA) or tetracyanobenzene (TCB) and dicyanobenzene (DCB) or TCB and dicyanonaphthalene (DCN) or by condensation of octamethoxyphthalocyanine has been examined for the oxygen reduction reaction in 4N sulphuric acid.

It was found that pPcFe derived from PMDA has the highest activity and that the temperature dependences of electrical conductivity in vacuum and oxygen of the polyphthalocyanines studied are different. A linear dependence of electrochemical activity on electrical conductivity and on conductivity activation energy has been stated to exist. From the experimental data it was deduced that negatively charged adsorption centres exist, and that the electrochemical properties of pPcFe are determined by its electrical conductivity The system support — iron polyphthalocyanine of higher electrical conductivity — shows a lower potential drop than that with pPcFe of lower conductivity.

Introduction

Among the known phthalo- and polyphthalocyanine complexes of transition metals, those of iron and cobalt [1 - 4] show the greatest electrochemical activity for the oxygen reduction reaction in acidic medium. It has been stated also that, apart from the central ion, the activity of phthalocyanines is particularly affected by the chemical character of the substituents [5] This influence is of importance in the case of both low molecular weight compounds and of polymers. In the latter case, the influence can be strongly masked by other factors, *e g* , the change of molecular weight. In a previous work [6] , we observed that copper polychlorohydroxyphthalocyanine was considerably more active than copper polyhydroxyphthalocyanine. However,

that compound, despite a small change of activity with time, is of no practical value because of the low current density obtained.

After Frumkin [7] and Bagotzki *et al* [8], the process of oxygen reduction can be written in the form of the following equations:

$$O_2 \; + \; e \; \rightleftharpoons \; O_2^- \tag{1}$$

$$O_2^- \; + \; H^+ \; \rightleftharpoons \; O_2H \tag{2}$$

$$O_2H \; + \; e \; \rightleftharpoons \; O_2H^- \tag{3}$$

$$O_2H^- \; + \; H^+ \; \rightleftharpoons \; H_2O_2. \tag{4}$$

Equations (1) and (3) represent acceptor type reactions. This means that the higher the electron concentration in the catalyst the more rapid is the reaction. Reactions of this type take place at a rapid rate in n-type semiconductors. Iron polyphthalocyanine (pPcFe) is a semiconductor of this type. The value of the electrical conductivity of pPcFe varies within a wide range, depending on the method of synthesis and the degree of polymerization.

Dabrowski *et al.* [9], Kretzschmar *et al* [10] and Meier *et al.* [11] state that the electrochemical activity of pPcFe depends on the value of the electrical conductivity. However, to date these parameters have not been connected by any dependence which would allow the properties of the catalyst to be selected with the aim of obtaining high catalytic activity.

Investigation of the influence on their electrocatalytic activity of different factors related to their structure is, therefore, very interesting for the compounds under consideration.

The aim of the present work was to examine the influence of factors other than the central ion on the electrocatalytic activity of pPcFe and also to determine the relation between the electrical properties of pPcFe and its electrochemical activity for oxygen reduction in sulphuric acid.

We prepared several iron polyphthalocyanines from pyromellitic dianhydride (PMDA), from tetracyanobenzene (TCB) and dicyanobenzene (DCB) or from tetracyanobenzene (TCB) and dicyanonaphthalene (DCN) and finally, by polycondensation of iron octamethoxyphthalocyanine. The latter compound, as with phthalocyanine, is characterized by a spread of the π electrons' coupling system limited to one macroring. The remaining polymers have a coupling system encompassing the whole macromolecule.

Experimental

Preparation of polyphthalocyanines
Polyphthalocyanines from pyromellitic dianhydride (PMDA)

Iron polyphthalocyanines were synthesized from pyromellitic dianhydride and anhydrous iron(II) chloride in the presence of urea at 570 K and in an ammonia atmosphere. The crude product was purified in acetone, hydrochloric acid, DMF, and finally it was precipitated several times from sulphuric acid. The degree of polymerization was determined from Eley's

formula [12], according to which the degree of polymerization is determined from the relation

$$E = 38/N \qquad (5)$$

where E is the conductivity activation energy (eV) determined from the temperature dependence of the electrical conductivity. Relation (5) served for the calculation of the total number (N) of π electrons in the polyphthalocyanine system. The ratio of N to the number of π electrons in the phthalocyanine (38) is the degree of polymerization. The iron polyphthalocyanines studied have a degree of polymerization of from 3 to 8. To obtain iron polyphthalocyanines with different electrical properties, the polyphthalocyanines were synthesized at constant temperature (570 K) and the duration of the synthesis was varied from one to several hours. The polyphthalocyanine obtained in this way is denoted as polymer I.

Polyphthalocyanines from TCB, DCB and TCB, DCN

These polymers were prepared from TCB and DCB (polymer II) or TCB and DCN (polymer III), in both cases in a 1:2 molar ratio, in the same way as for copper polyphthalocyanine, described in ref. 6. In an identical way, iron 1,2-naphthylocyanine (polymer IV) was prepared starting from 1,2-dicyanonaphthalene.

The iron octamethoxyphthalocyanine (polymer V) was obtained in the following way [13] · a mixture of 15 g of free octamethoxyphthalocyanine and 22.5 g of ferrous acetylacetonate in 300 ml of DMF was heated under reflux for 5 h. The contents of the flask were then diluted with water and the precipitate was filtered and extracted with H_2O and CH_3OH. To obtain iron polyhydroxyphthalocyanine (polymer VI) 5 g of iron octamethoxyphthalocyanine was mixed with 100 g of $AlCl_3$, 50 g of $AlBr_3$, 29.6 g of NaCl and 8 g of $FeCl_2$, and heated at 493 K for 2 h and at 523 K for 1 h. After cooling, 10% hydrochloric acid was added and the precipitate, i.e., iron polyhydroxyphthalocyanine, was washed with water and ethanol.

Supporting material

The support was prepared from active carbon, Carbopol N (980 m^2/g), acetylene black (140 m^2/g) or active carbon obtained from saccharose. The methods of polyphthalocyanine deposition on the supporting material and of the oxygen electrode production were both analogous to those described in ref. 6. Polyphthalocyanines were deposited in amounts of 5, 10, 20 and 30% by weight with regard to the supporting mass.

Investigation of electrochemical activity

The electrochemical activity of the polyphthalocyanines was determined on the basis of the current–voltage characteristics of oxygen electrodes as described previously [6].

Measurements of the electrical conductivity of pPcFe

The electrical conductivity at 303 K and its dependence on temperature were determined for pPcFe preparations in the form of cylindrical pellets of 6 mm dia. and 0.3 - 0.4 mm thickness, pressed at 430 MPa. Good electrical contact was obtained by partially covering the surfaces of the samples with gold (vacuum evaporated) and placing them between the measuring electrodes in a vessel connected to a vacuum system. The conductivity was measured under vacuum, and in oxygen at a pressure of 200 kPa, keeping a constant heating rate of 1 °C/min. The activation energy of the dark conductivity was determined from the formula

$$\sigma = \sigma_0 \, e^{-E/kT} \tag{6}$$

where E is the activation energy (eV), T the temperature, k the Boltzmann constant, σ the conductivity and σ_0 the pre-exponential factor.

The iron polyphthalocyanines studied are n-type semiconductors. The type of conductivity was determined from Seebeck effect measurements

Discussion of results

Figure 1 presents polarization curves for cathodes containing iron poly-phthalocyanines prepared by us. It is seen from Fig. 1 that the highest activity is shown by one of the iron polyphthalocyanines (polymer I) prepared from PMDA. Iron polyphthalocyanines prepared from TCB and DCB (polymer II) and from TCB and DCN (polymer III), show a little lower activity. The lowest activity is shown by iron 1,2-naphthylocyanine (polymer IV) and iron polyhydroxyphthalocyanine (polymer VI), i e , by compounds with coupling spread limited to one porphyrin system. Octamethoxyphthalo-cyanine (polymer V) shows a medium activity. Polymers in which the bond coupling involves the whole macromolecule are more active. However, donor substituents (CH_3-O groups) considerably influence the activity of low molecular weight compounds. The activity of 1,2-naphthylocyanine at a concentration of 20% with regard to the weight of carbon black support, measured as the value of the cathode current, does not exceed 9 mA/cm^2 at 700 mV and an oxygen pressure of 100 kPa at 318 K, as compared with 27 and 45 mA/cm^2 for iron polyphthalocyanines from TCB and DCB, and from PMDA, respectively.

Figure 2 shows the same current–voltage characteristics IR-corrected. As is seen from Fig 2, the current densities obtainable from individual poly-phthalocyanines are much higher than those shown in Fig. 1. The current densities obtained for the most active polyphthalocyanines at 800 mV and 318 K are 30 and 87 mA/cm^2 for polyphthalocyanines from TCB and DCB, and from PMDA, respectively. This is in agreement with the observations of ref 14, where the introduction of highly conducting acetylene black into the electrode composition was found to lead to a considerable increase in the current density.
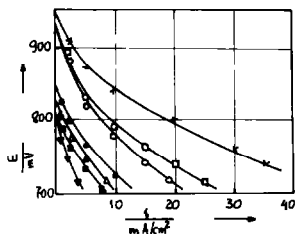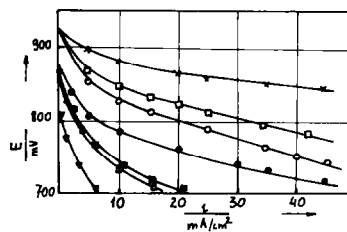
Fig 1   Fig 2

Fig 1 Dependence of current density on polarization potential for electrodes containing × , polyphthalocyanine from PMDA, □, polyphthalocyanine from TCB and DCB, ○, polyphthalocyanine from TCB and DCN, ●, octamethoxyphthalocyanine, ■, 1,2-naphthylocyanine, △, hydroxypolyphthalocyanine, ▼, carrier Temperature, 318 K, electrolyte, 4N H_2SO_4, concentration of pPcFe, 17 mg/cm^2, oxygen pressure, 100 kPa

Fig 2 Dependence of current density on polarization potential (IR-corrected) for electrodes containing × , polyphthalocyanine from PMDA, □, polyphthalocyanine from TCB and DCB, ○, polyphthalocyanine from TCB and DCN, ●, octamethoxyphthalocyanine, ■, 1,2-naphthylocyanine, △, hydroxypolyphthalocyanine, ▼, carrier Temperature, 318 K, electrolyte 4N H_2SO_4, oxygen pressure, 100 kPa, pPcFe concentration, 17 mg/cm^2

TABLE 1

Comparison of electrochemical activity of different iron polyphthalocyanines, at polarization potentials of 700 and 800 mV
Temperature 318 K, oxygen pressure 100 kPa, electrolyte 4N sulphuric acid

Active phase derived from	Polarization potential (mV)			
	800		700	
	IR-corrected (mA/cm^2)	IR-uncorrected (mA/cm^2)	IR-corrected (mA/cm^2)	IR-uncorrected (mA/cm^2)
PMDA	87 5	20 0	150 0	45 5
TCB + DCB	29 5	9 2	80 3	27 4
Octamethoxy-phthalocyanine	6 0	2 1	51.3	14 0
TCB + DCN	20 0	7 5	60 0	19 2
Hydroxypoly-phthalocyanine	2 1	1.5	19 5	10 0
1,2-Napththylo-cyanine	2 1	1.0	21 5	8.5

Table 1 presents the current densities actually obtained and the resistance-free values at potentials of 800 and 700 mV. It is apparent from these data that the differences between the current densities are considerable. This is, first of all, due to the properties of the support–active phase–electrolyte system. Moreover, when using the same support for the deposition of the polyphthalocyanines studied it is not always possible to have the most advantageous combination from the point of view of electrochemical activity.
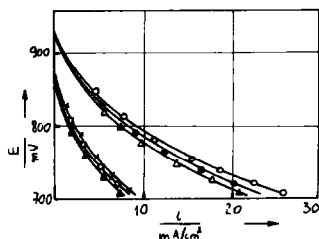
Fig 3 Dependence of current density on polarization potential at different temperatures for electrodes containing polyphthalocyanine from TCB and DCB ▲, □, ×, 5%, △, ●, ○, 20% Electrolyte, 4N H_2SO_4, oxygen pressure, 100 kPa, temperature, ▲, △, 298 K, □, ●, 308 K, ×, ○, 318 K

Figure 3 shows the dependence of electrochemical activity of electrodes containing polyphthalocyanine II on the amount of polyphthalocyanine deposited on the support and on the temperature. An increase of polyphthalocyanine content from 5 to 20% causes a rise in the current density per unit surface area of electrode. Electrochemical activity per gramme of pPcFe on the other hand, is not increased but, on the contrary, decreases. This behaviour is similar for other phthalocyanines including that from PMDA.

Iron 1,2-naphthylocyanine and octamethoxyphthalocyanine are considerably less active than the polymers, even those with a low degree of polymerization. One of the reasons for this is certainly their lower electrical conductivity. It has been proved by Kretzschmar *et al.* [15], by Dabrowski *et al* [16] and Meier *et al* [17], that the electrical conductivity of polyphthalocyanines has a fundamental influence on their electrochemical activity. We have obtained further proof of such a dependence. The lowest activation energy (0 23 eV) and the highest electrical conductivity (at room temperature) are shown by polyphthalocyanine I (from PMDA) which is the most active.

Figure 4 shows the dependence of electrical conductivity on the reciprocal of the temperature for polyphthalocyanine I and polyphthalocyanine II (from TCB and DCB) and for iron polyhydroxyphthalocyanine (polymer VI). These three polyphthalocyanines show different properties, especially those referring to the changes of dark conductivity in contact with oxygen. In the case of polyphthalocyanine I of highest conductivity, the latter property, as well as the activation energy decrease in contact with oxygen. The conductivity of polyphthalocyanine II also decreases in contact with oxygen, but the activation energy rises as compared with that under vacuum, and consequently the conductivity in an oxygen atmosphere at higher temperature is higher than under vacuum. In the case of polyhydroxyphthalocyanine, the conductivity in oxygen is higher than that under vacuum in the whole range of temperatures investigated and the activation energy of the conductivity also rises. The polyphthalocyanines considered show n-type conductivity at 298 K. This means that electrons are the predominating carriers or that, at least, they have higher mobility. In the case of polymers I and II the
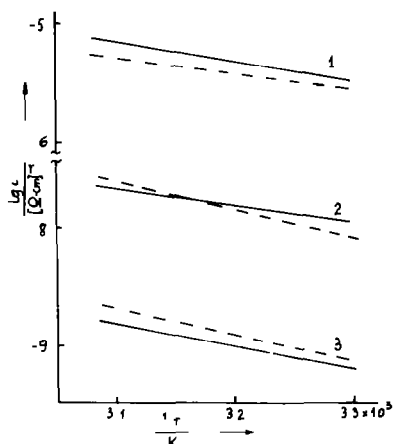
Fig 4 Dependence of electrical conductivity on the reciprocal of the temperature for 1, polyphthalocyanine from PMDA (polymer I), 2, polyphthalocyanine from TCB and DCB (polymer II), 3, hydroxypolyphthalocyanine (polymer VI). Oxygen pressure 20 kPa, - - - - oxygen, ——— vacuum

conductivity decrease under the influence of oxygen is in agreement with expectation for that type of conductivity, and this is due to the trapping of free electrons during chemisorption of the oxygen molecules. It can be seen from Fig. 4 (polymer I) that the conductivity in oxygen is lower than that under vacuum. This is in accordance with earlier observations by Jahnke *et al* [18] and Dabrowski *et al* [9]. They explain the conductivity decrease in oxygen atmosphere as being due to electron trapping by oxygen adsorbed on the surface.

The dynamic process of oxygen adsorption occurring on the surface can be presented in the form

$$O_2 + e \xrightleftharpoons{K_I} O_{2ads}e \xrightleftharpoons{K_{II}} O_2^- \tag{7}$$

$$\underbrace{\qquad\qquad}_{I} \underbrace{\qquad\qquad}_{II}$$
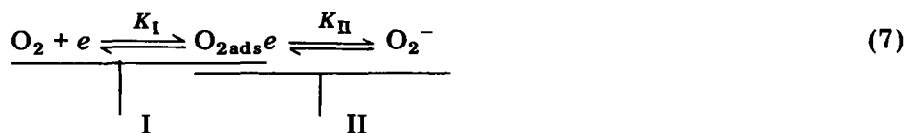
Equation (7) shows the steps in the process controlling the electrochemical activity. Depending on the surface properties, the rate of the electrode process is determined by the equilibrium constant K_I or K_{II} in eqn. (7). At stage I of eqn. (7), a localization of an electron on the oxygen molecule occurs, so the electron does not participate in the conduction of current. This is a direct cause of a decrease of electrical conductivity.

From the analysis of eqn. (7) it follows that, when the equilibrium constant for stage I–K_I is equal to that of stage II–K_{II}, then the concentration of the molecular ion O_2^- can be written in the following form:

$$O_2^- = K \cdot pO_2 \cdot N_e / N_p \tag{8}$$

where N_e and N_p are the mean concentrations of electrons and holes in the iron polyphthalocyanine catalyst, respectively, $K = K_I \cdot K_{II}$, and pO_2 is the oxygen pressure.

From eqn. (8) it follows that, at constant oxygen pressure, the concentration of the molecular ion O_2^- which can react in the electrode process is a function of the ratio of the concentrations of electrons to holes As the electrochemical activity is a function of the molecular ion concentration then it also is a function of the ratio of the concentrations of electrons to holes. Holes probably do not participate directly in the electrode process, however, they prevent the binding of oxygen with the polyphthalocyanine surface from being too strong.

In Fig. 5 the dependence of the electrochemical activity on the electrical conductivity of iron polyphthalocyanine is shown It is a linear dependence, which can be presented by the formula

$$\lg \iota = a + b \lg \sigma \qquad (9)$$

where a and b are constants dependent on temperature. Similar linear dependence between electrochemical activity and conductivity was observed by Kretzschmar and Wiesener [10] who synthesized iron polyphthalocyanine from phthalonitrile and pyromellitic dianhydride, taken at different molar ratios. Probably because of the lower degree of polymerization [1 - 3] the observed activation energies of conductivity are higher than those presented in this paper.
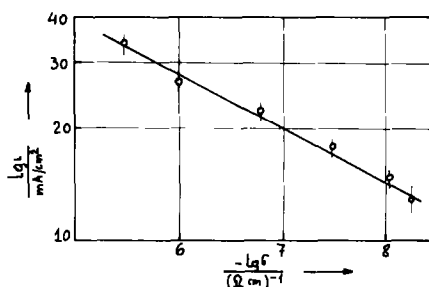

Fig 5 Dependence of current density on conductivity of pPcFe for electrodes activated with 20% (by weight) at constant polarization potential, 700 mV Temperature 298 K, oxygen pressure 100 kPa, support, acetylene black

From these investigations it can be seen that there is also a linear dependence between electrochemical activity and conductivity activation energy. Expressing eqn. (9) as a dependence of current density on activation energy of conductivity, and using relation (6) one can derive the following equation·

$$\lg \iota = C - \frac{b}{2.3kT} E \qquad (10)$$

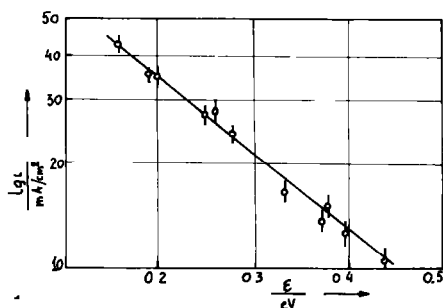where ι is the current density, and C and b are constants.

Fig 6 Dependence of current density at a polarization potential of 700 mV on the activation energy of the electrical conductivity of iron polyphthalocyanine at 308 K under vacuum Temperature, 308 K, oxygen pressure, 100 kPa, support, acetylene black activated with 20% pPcFe
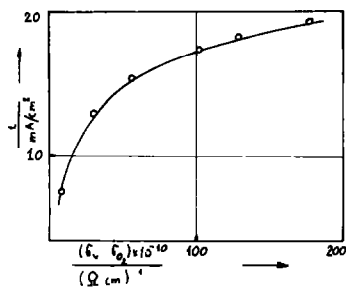
Fig 7 Dependence of current density on the difference between conductivities under vacuum and in oxygen Temperature, 303 K, polarization potential, 800 mV, oxygen pressure, 100 kPa, electrolyte, 4N H_2SO_4

From this equation, a linear relation between electrochemical activity (current density) and activation energy of conductivity results. The experimental data are plotted in Fig. 6 using this equation which, as can be seen, shows a linear relationship.

Figure 7 presents the electrochemical activity of the examined polyphthalocyanines, in terms of the cathode polarization current density I_{800}, as a function of the difference between the conductivities under vacuum and in oxygen The dependence is logarithmic in character and the increase in activity is initially fast and then slower. If we assume that the conductivity differences are related to the number of trapped (chemisorbed) oxygen molecules, then we can suppose that only some of them undergo reduction, and that this part decreases with the rise in the polymer conductivity. This is probably due to the fact that the chemisorption energy necessary for active complex formation must have an optimum, but not too low, energy of oxygen bonding to the surface.

The energy gap in polyphthalocyanines and phthalocyanines which is decisive for their intrinsic conductivity is determined according to ref. 19 by the equation·

$$E_g = 2E_T = I_c - A_c \tag{11}$$

where I_c is the ionization potential of the molecule, and A_c the electron affinity.

In polymers with a coupling system such as in polyphthalocyanines the I_c values decrease and the A_c values increase with increasing molecular weight, which ensures higher electrical conductivity. On the other hand, in the case of the polyphthalocyanines, I_c and A_c can be changed by introducing suitable substituents, mainly those capable of decreasing the ionization potential, e.g , methoxy substituents and the like However, these changes are not so large as in the case of the polymers.

Adsorption of oxygen on the polyphthalocyanine surface can be regarded as the formation of a *CT* complex between the oxygen molecule and polyphthalocyanine. In the complex, some dislocations of an electron from the polyphthalocyanine molecule to the oxygen are observed and under favourable conditions polyphthalocyanine can ionize forming a positive, free or trapped, current carrier according to the scheme

$$\text{pPcMe} + \text{O}_2 \; \rightleftarrows \; \text{pPcMe}....\text{O}_2 \; \rightleftarrows \; \text{pPcMe}^{\cdot+} + \text{O}_2^{\cdot-} \qquad (A)$$

Such a complex will be formed more easily if the polyphthalocyanine molecule (pPcMe—metal polyphthalocyanine) has a trapped electron or if it can trap an electron from the lattice.

$$\begin{array}{l} \text{pPcMe}^{\cdot-} + \text{O}_2 \\ \text{pPcMe} \quad + \text{O}_2 \end{array} \rightleftarrows \text{pPcMe}....\text{O}_2^{\;-} \; \rightleftarrows \; \text{pPcMe} + \text{O}_2^{\cdot-}. \qquad (B)$$
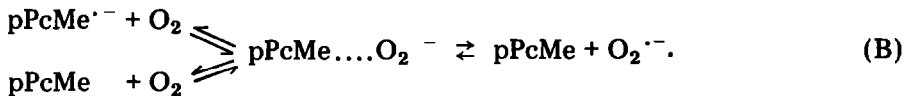
This mode of interreaction does not lead to the generation of carriers but, on the contrary, to their consumption.

The observed changes in the electrical properties of the examined polymers can be easily explained with the help of these two mechanisms of oxygen adsorption. If the crystal lattice contains a large number of more or less free electrons, *e g* , as in polymer I, then oxygen adsorption leads to the formation of a type B surface complex. This process can be treated as trapping of free electrons which, consequently, leads to the lowering of the conductivity. These traps do not, however, lie very deep. They are probably placed below the bottom of the conduction band at a depth less than $E_g/2$, *i.e* , above the Fermi level. Thus, the energy of liberation of such a trapped electron is lower than the activation energy of intrinsic conductivity and, in consequence, the activation energy observed in an oxygen atmosphere, which is a result of the electron transfer from the valency band and liberation from traps, is lower than that observed under vacuum. When the traps lie deeper, the activation energy of conductivity observed in oxygen can be higher than that under vacuum. This occurs for polymer II. In polymer IV of low intrinsic conductivity, and therefore with a small number of free electrons, the predominating process will then be the formation of type A complexes leading to the increase of the conductivity as a result of polymer ionization. In the light of the above considerations, the relation between the electrocatalytic activity of polyphthalocyanines and the changes of their electrical properties after oxygen adsorption becomes clear. The mechanism of the initial stage of oxygen electroreduction on the polyphthalocyanine catalyst seems to be a little different from that proposed by Savy *et al.* [20]. Savy considers the ionization of the adsorption center (phthalocyanine molecule) to be the first stage

$$\text{PcMe} \; \rightleftarrows \; \text{PcMe}^+ + e \qquad (12)$$

In the second stage the center interacts with oxygen yielding a π type complex

$$O_2(g) + PcMe^+ + e \rightleftarrows PcMe^+ + O_2^-. \qquad (13)$$

It seems that the positively charged adsorption center is not so important here as the negative center which can be formed as a result of selfdissociation or electron capture

$$2PcMe \rightleftarrows PcMe^- + PcMe^+ \qquad (14)$$

or

$$PcMe + e \rightleftarrows PcMe^-. \qquad (14a)$$

The electrocatalytic activity of polyphthalocyanines in the oxygen reduction reaction depends therefore on the ability to form negative adsorption centers.

Figure 8 shows the dependence of the potential drop on time at a constant current density of 20 mA/cm^2 for iron polyphthalocyanines from PMDA (polymer I) of different electrical conductivity deposited on carbon Carbopol N and acetylene black. This dependence shows two stages, an initial one of large potential drop followed by one in which the fall is less rapid. A similar dependence of potential drop with time was observed also by Johanson *et al* [21], by Kretzschmar *et al.* [14], and by Meier *et al* [17]. This potential drop seems to be connected with a change in the pPcFe concentration in the electrode material. The potential drop depends, as shown in Fig. 8, on the type of support and on the value of the electrical conductivity of pPcFe, the higher the conductivity, the lower the potential drop.
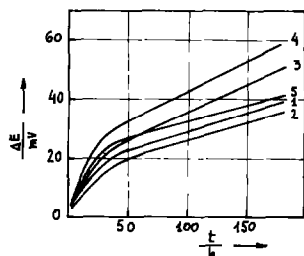

Fig 8 Dependence of potential drop on time at a constant cathode current density of 20 mA/cm^2 for pPcFe of different electrical conductivities, deposited on carbon Carbopol N and acetylene black 1, acetylene black, 30% pPcFe of electrical conductivity 5 5 × 10^{-5} (Ω cm)$^{-1}$, 2, acetylene black 30% pPcFe of electrical conductivity 8 4 × 10^{-5} (Ω cm)$^{-1}$, 3, Carbopol N, 30% pPcFe of electrical conductivity 5 8 × 10^{-6} (Ω cm)$^{-1}$, 4, Carbopol N, 30% pPcFe of electrical conductivity 2 3 × 10^{-6} (Ω cm)$^{-1}$, 5, direct synthesis of pPcFe on the acetylene black (about 10% pPcFe)

Conclusions

The electrocatalytic activity of iron polyphthalocyanine for the oxygen reduction reaction depends, *inter alia*, on its electrical properties and on the ability to form the negative centers for oxygen adsorption. The effect of

other factors, *e.g.*, substituents, can be considered in terms of changes taking place in the electrical properties.

These observations lead to the practical conclusion that pPcFe production should be directed towards the production of material with the highest possible electrical conductivity, because the higher the electrical conductivity, the higher the electrochemical activity and the smaller the potential drop with time.

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