

HEAT-TREATED Co-TETRAMETHOXYPHENYLPORPHYRIN ON DIFFERENT CARBON CARRIERS AS CATALYSTS FOR THE ELECTROCHEMICAL REDUCTION OF OXYGEN IN ACID ELECTROLYTES

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Summary

In this paper it is shown that the type of carbon support used in pyrolyzed TMeOPPCo catalysts modifies their properties in sulphuric acid.

The type of carbon support influences both the catalytic activity for oxygen reduction and their long-term stability. The observed effects are probably due to interactions between the carbon support and the pyrolysis products of the TMeOPPCo compound during heat treatment.

Zusammenfassung

Es konnte herausgearbeitet werden, dass der Typ des Kohleträgers in pyrolysierten TMeOPPCo-Katalysatoren deutlich die Eigenschaften dieser Katalysatoren in Schwefelsäure beeinflusst.

Der Typ des Trägers wirkt sowohl auf die katalytische Aktivität bei der Sauerstoffreduktion als auch auf die Langzeitstabilität. Die beobachtete Beeinflussung durch den Kohleträger wird in einer Wechselwirkung zwischen dem Träger und dem Pyrolyseprodukt des TMeOPPCo während der Wärmebehandlung gesucht.

Introduction

In our previous paper [1] it was shown that tetramethoxyphenylporphyrinato-cobalt-II (TMeOPPCo) precipitated on P-33 active carbon, and subsequently heated in an argon stream, possessed an increased activity for the electrochemical reduction of oxygen in sulphuric acid. A broad maximum of oxygen (or air) electrode activity was obtained when the temper-

ature used for heat treatment was in the range 400 - 800 °C. Electrodes with catalysts treated at 450 °C showed the highest initial activity but this decreased rapidly with time of operation. The initial activity of electrodes with catalysts activated at 800 °C was somewhat lower, but their performance was more stable with time.

The oxygen (air) gas-diffusion electrodes for sulphuric acid investigated in ref. 1 used porous catalysts consisting of an active carbon support onto which TMeOPPCo had been precipitated and heat-treated. The properties of this catalyst therefore depended on the nature of the carbon support.

The aim of the work presented in this paper was to investigate the effect that different substrate materials and activation temperatures (up to 1100 °C) had on the catalytic properties of precipitated TMeOPPCo for oxygen reduction in sulphuric acid. The work is of particular significance for the life of air cathodes used in fuel cells or metal-air batteries.

Experimental

The support materials chosen for these tests were: active carbon Norit NK (The Netherlands), Ketjenblack EC (AKZO-Chemie, The Netherlands), and two acetylene blacks — P 1042 and P 1250 (VEB Stickstoffwerke Piesteritz, G.D.R.). The P 1042 and P 1250 carbon blacks consist mainly of poreless, spheroidal particles with dimensions of about 20 nm. Norit NK is distinctly structured — there are many pores in the BET area.

The particles of Ketjenblack EC are described by Verhelst *et al.* [3] as hollow polyhedra (with a mean radius of about 30 nm) with a very small entrance.

TMeOPPCo (15 wt.%) was precipitated on the particles and subsequently heat-treated in an argon stream for 5 h. Double-layer electrodes were used throughout the experiments. The gas supply layer was a porous hydrophobic material [2] — carbon black wet-proofed with PTFE, while the active layer consisted of a 30 mg/cm² mixture (1:1 by weight) of the same hydrophobic material and the catalyst under investigation. The experimental techniques have already been described elsewhere [1].

Results and discussion

In Fig. 1, the initial room temperature polarization characteristics, with air and with pure oxygen in 4.5N sulphuric acid, of an electrode using the P 1250 acetylene black catalyst with 15% TMeOPPCo (heat treated at 750 °C) are shown. Similar initial polarization curves were obtained for catalysts consisting of the described supports and 15% TMeOPPCo, treated at different temperatures ranging from 300 to 1050 °C. The current density (i_{650}) of the oxygen electrode at 650 mV *vs.* a hydrogen electrode in the same solution was used as a measure of the activity of the catalysts.

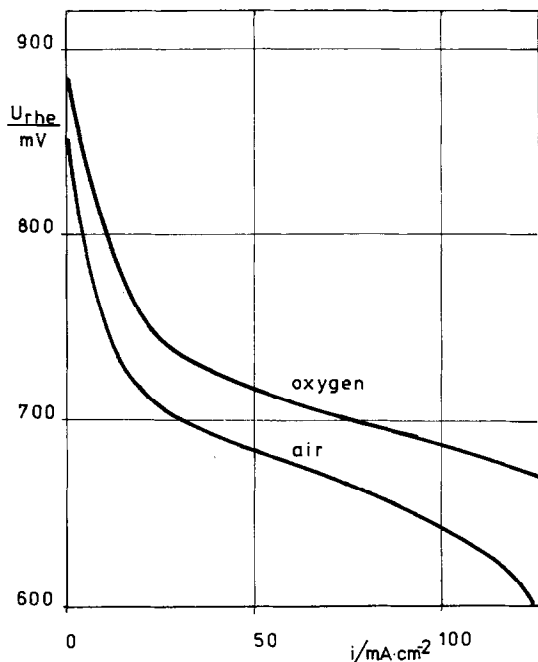


Fig. 1. Polarization curves of two-layer electrodes in air (bottom curve) and oxygen (top curve) with catalyst P 1250, 15% TMeOPPCo, heated at 750 °C in an argon stream, and measured at room temperature in 4.5N sulphuric acid.

In Fig. 2 the activities of the investigated electrodes (i_{650}) are plotted as a function of the pyrolysis temperature for different supports. It can be seen that maximum activity of all the catalysts investigated, falls between 400 and 900 °C. The highest activity was obtained for catalysts heat-treated at about 450 °C. The shapes of the maxima are apparently different for the different supports, but differences in the amplitudes of the maxima are not significant as the contents of the active layers were not always optimum.

In Fig. 3 the potential at a constant current density (20 mA/cm²) is plotted for air electrodes with different catalysts (different supports) but all heat treated at 450 °C, corresponding to the maxima in Fig. 2. Their performance deteriorated markedly during the first 300 h of operation.

After 900 h polarization was lowest for the electrode with the catalyst supported on P 1250 acetylene black (curve 1). The polarization of electrodes with Ketjenblack (curve 3) and P 1042 acetylene black (curve 2) were higher, but the differences are not significant.

Figure 4 shows the long-term behaviour of air electrodes with the same catalysts as in Fig. 3, but heat-treated at 750 °C, well above the maxima in Fig. 2. In this case the potentials of the electrodes with catalysts supported on Ketjenblack (curve 3) and P 1250 acetylene black (curve 1) did not change so drastically: their long-term performance was more stable than when they had been treated at 450 °C. This beneficial influence of the heat

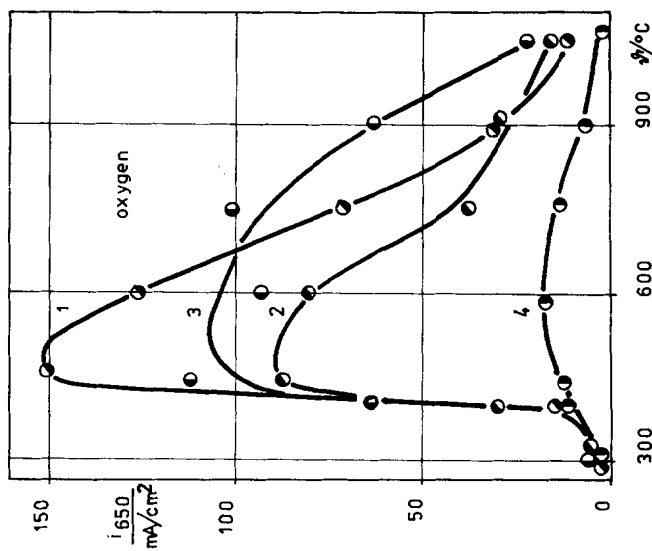
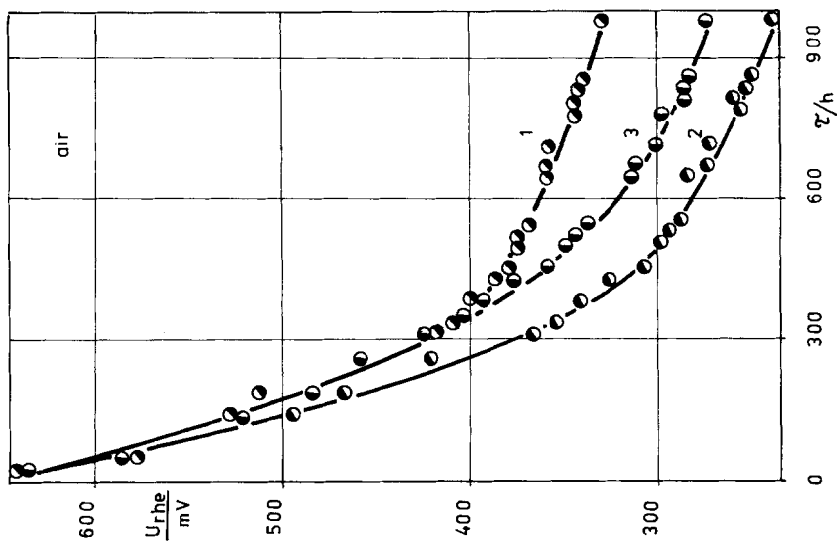


Fig. 2. Current densities at 650 mV vs. reference hydrogen electrode as a function of the pyrolysis temperature, measured at room temperature in 4.5N sulphuric acid. 1, P 1250 with 15% TMeOPPCo; 2, P 1042 with 15% TMeOPPCo; 3, Ketjenblack with 15% TMeOPPCo; 4, Norit NK with 15% TMeOPPCo.

Fig. 3. Potential-time curves of two-layer electrodes with catalysts heat treated at 450 °C in an argon stream. 1, 2, 3, as for Fig. 2.

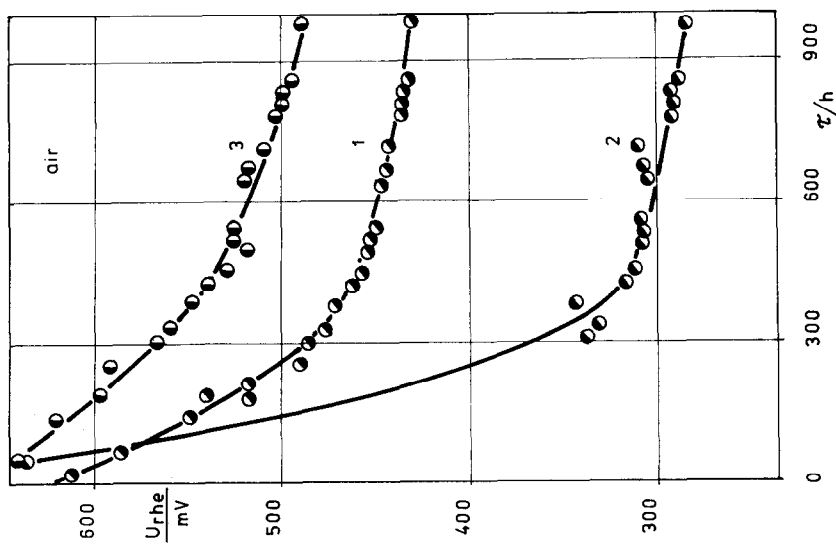


Fig. 4. Potential-time curves of two-layer electrodes with catalysts heat treated at 750 °C in an argon stream. 1, 2, 3, as for Fig. 2.

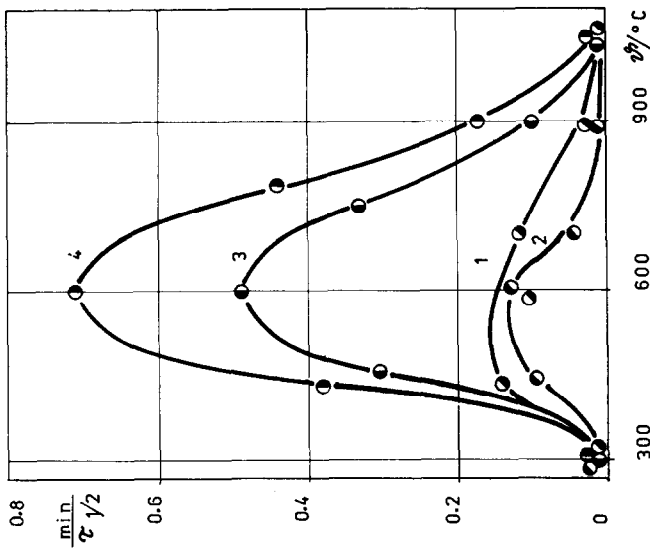


Fig. 5. Reciprocal half-life periods for hydrogen peroxide decomposition as a function of the pyrolysis temperature, measured at 25 °C (1 g/l catalyst, powdered and screened taking all fractions below 0.15 mm dia.; 0.04 mol/l H_2O_2 ; 2.25 mol/l H_2SO_4), curves 1, 2, 3, 4, as in Fig. 2.

TABLE 1

Surface area, S_{BET} , of Norit NK active carbon without, and with, 15% TMeOPPCo, and subsequently heated 5 h in an argon stream

Material	Temperature (°C)	S_{BET} (m ² /g)
Norit NK	not heated	610
Norit NK		
+ 15% TMeOPPCo	300 (vacuum)	360
+ 15% TMeOPPCo	440	335
+ 15% TMeOPPCo	600	332
+ 15% TMeOPPCo	780	364
+ 15% TMeOPPCo	900	256
+ 15% TMeOPPCo	1070	235

treatment temperature was not observed for the catalyst supported on P 1042 acetylene black (curve 2 in Figs. 3 and 4). Apparently the carbon support material influences the long-term performance of the heat-treated catalysts with TMeOPPCo in sulphuric acid.

Results from measurements of the catalytic decomposition of hydrogen peroxide in sulphuric acid are presented in Fig. 5. The half-life periods $\tau_{1/2}$ for hydrogen peroxide decomposition are plotted 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.: 0.4 mol/l H₂O₂; 2.25 mol/l H₂SO₄). Curves 3 and 4 (for catalysts with Ketjenblack and Norit NK) have well defined maxima at about 600 °C, while the positions of the maxima for curves 1 and 2 (P 1042 and P 1250 acetylene blacks, respectively) are not so well defined. The heights of these maxima are probably influenced by the porous structure of the catalysts, which differ significantly in their BET surface areas.

References

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