

OPTIMIZATION OF THE PYROLYSIS TEMPERATURE OF ACTIVE CARBON-CoTMPP CATALYSTS FOR AIR ELECTRODES IN ALKALINE MEDIA

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Summary

Catalysts prepared from active carbon impregnated with CoTMPP, and then heat treated in argon at temperatures between 200 and 1200 °C were investigated in air gas-diffusion electrodes.

It was found that heating the catalyst at temperatures between 460 and 810 °C improved the initial polarization characteristics of air electrodes. The activity of the electrodes and the transport hindrances in them were measured during long-term operation with air at 100 mA cm⁻². The results show that the activity of air electrodes with catalysts heat-treated at 750 - 850 °C remains high and stable. The transport hindrances of the electrodes show a minimum in the same temperature range but increase with time of operation.

Introduction

Heat treated catalysts based on active carbon with added N₄-chelates (polymeric Co phthaloyanine, Co dibenzotetraazaannulene, Co tetramethoxyphenylporphyrin and others) display increased activity for the electrochemical reduction of oxygen [1, 2].

More specifically, heat treated catalysts of active carbon with added Co tetramethoxyphenylporphyrin (CoTMPP) show both activity and long-term stability in air electrodes operating in acid electrolytes [3, 4]. Air electrodes with a similar catalyst show a very stable long-term performance, especially at high current discharge in alkaline electrolytes [5, 6].

(It was established [7] that during heat treatment (in argon) above 370 °C the CoTMPP molecule is destroyed and some of its pyrolytic residual products (mainly those from the porphyrin ring) in the porous structure of the active carbon support are responsible for the observed high electrochemical activity of the catalyst.

In this paper an investigation of the influence of the heat treatment temperature of active carbon-CoTMPP catalyst on the long-term performance of air gas-diffusion electrodes in alkaline electrolyte is reported.

Experimental

The catalysts were prepared from active carbon P-33 (G.D.R.) impregnated with CoTMPP from a solution in dioxan. After drying, the product, containing 10 wt.% CoTMPP, was heated for 5 h in an argon flow at temperatures between 200 and 1200 °C. Heating to 200 °C was a preliminary treatment of all the catalysts.

Double-layer air electrodes [8] (with 10 cm² projected area) were prepared with these catalysts. The gas-supply layer consisted of 100 mg cm⁻² of porous hydrophobic material (carbon black wetproofed with PTFE [8]) and the catalytic layer of a 20 mg cm⁻² mixture of the same hydrophobic material and a catalyst in the ratio 1:2.5.

The steady-state polarization curves of the electrodes were recorded in a half-cell arrangement with air and with oxygen in 7 N KOH at room temperature. The electrode potential was measured using an Hg/HgO reference electrode in the same electrolyte.

The long-term behaviour of the air-breathing electrodes was investigated in the same half-cell at a constant load (100 mA cm⁻²). Constant electrolyte specific gravity was maintained throughout the experiment by adding water. After set periods of operation the test was temporarily interrupted for the polarization characteristics of the electrodes with air and with pure oxygen to be measured. This procedure was followed several times during the tests.

Results and discussion

The initial polarization curves of air electrodes with catalysts heat treated at different temperatures are presented in Fig. 1. It can be seen that the heat treatment temperature of the catalyst influences the initial performance of the air electrodes. Heating the catalyst at temperatures between 460 and 810 °C substantially improves the initial polarization characteristics of the air electrodes (lower polarization) compared with those heated at 200 °C. This beneficial effect decreases as 810 °C is exceeded, and the 990 °C and 200 °C polarization curves practically coincide. Heat treatment of the catalyst at higher temperatures (1100 - 1200 °C) has a deleterious effect on the performance of electrodes. The initial performance of electrodes with an unheated catalyst is practically identical with that obtained with catalysts heated to 200 °C.

The best performance (lowest polarization) is displayed by electrodes with catalysts heat treated within the temperature range 460 - 810 °C, when the polarization characteristics are practically identical up to current densities of 150 mA cm⁻².

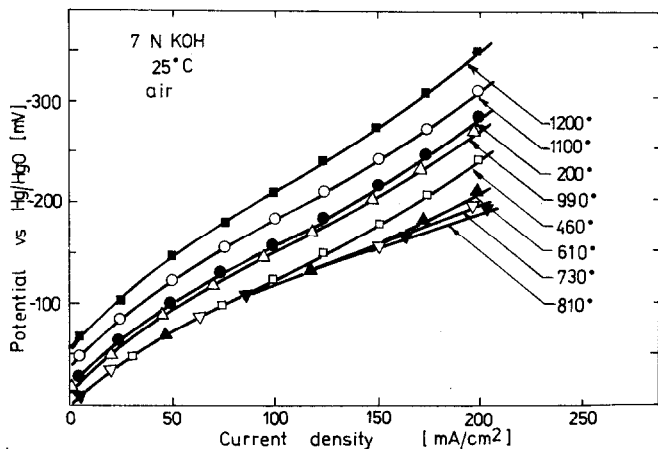


Fig. 1. Initial polarization characteristics of air electrodes with active carbon-CoTMPP catalysts heat treated at 200, 460, 610, 730, 810, 990, 1100 and 1200 °C.

Figure 2 presents the polarization curves (on a semilogarithmic scale) of the electrodes from Fig. 1 operating with oxygen at low current densities ($\leq 30 \text{ mA cm}^{-2}$). In this range of current density there is negligible hindrance to transport in the electrodes, so that Tafel regions in the polarization curves are observed. The straight lines are parallel, with slopes of 40 mV/decade. The intercept of the Tafel portions on the abscissa (at a potential $E = 0$ versus Hg/HgO) is a criterion for an electrode's activity [9]. As can be seen from Fig. 2, electrodes with catalysts heated between 460 and 810 °C have almost identical activities, significantly higher than that of electrodes with a catalyst heated to 200 °C. The electrodes with catalysts treated at temper-

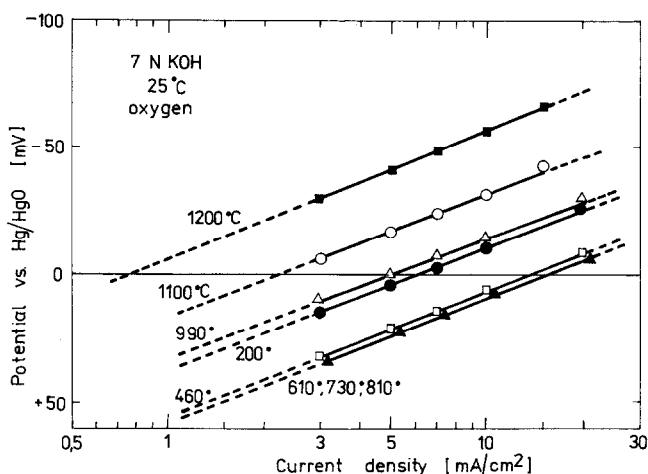


Fig. 2. Polarization curves (in a semilogarithmic scale), at low c.d., of the electrodes from Fig. 1 operating with pure oxygen.

atures above 810 °C show a gradually decreasing activity with increased heat treatment temperature.

The transport hindrances in the electrodes were assessed by the use of $\Delta E = E_{O_2} - E_{air}$ values (obtained from the steady-state polarization curves of the same electrode when operating alternatively with oxygen (E_{O_2}) and with air (E_{air}) at the same current density [10].

ΔE is plotted as a function of the current density, for the electrodes from Fig. 1, in Fig. 3. It can be seen that the transport hindrances in electrodes with catalysts treated at between 460 and 1100 °C are significantly lower than those in electrodes with a catalyst heat treated at 200 °C, whereas they are higher in electrodes with a catalyst heat treated at 1200 °C.

Apparently, the improved initial performance of air electrodes with catalysts heat treated at between 460 and 1100 °C (Fig. 1) are due both to the increased activity and to reduced transport hindrances in these catalysts.

The influence of the heat treatment temperature of active carbon-CoTMPP catalysts on the performance of the air gas-diffusion electrodes is probably connected with the thermal stability of CoTMPP. It is known that by heat treatment in an inert atmosphere at temperatures up to 250 °C CoTMPP remains stable [11]. Heat treatment at higher temperatures results in pyrolysis of CoTMPP. The heat-treatment temperature probably influences not only the type and the catalytic properties of the CoTMPP pyrolytic products, but also affects their distribution in the porous structure of the active carbon carrier.

Figure 4 presents the long-term performance at 100 mA cm⁻² of air electrodes with catalysts heat treated at 460, 610, 730, and 810 °C. It can be seen that the polarization of the electrodes with catalysts heated at 460 and at 610 °C increases significantly during the first 200 h, whereas the performance of electrodes with catalysts treated at 730 and at 810 °C is much more stable.

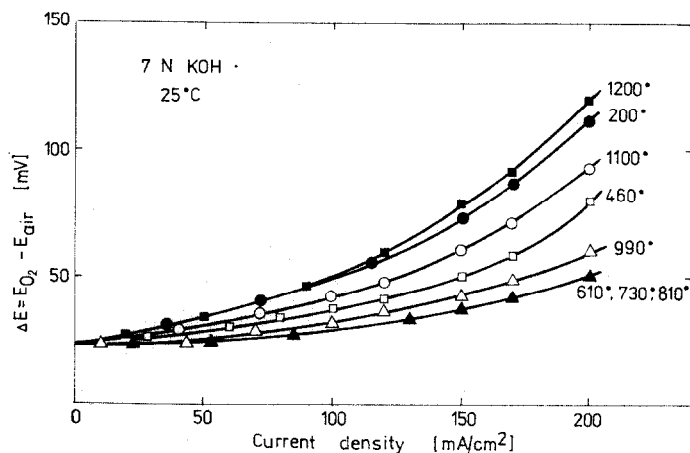


Fig. 3. ΔE - I curves for the electrodes from Fig. 1.

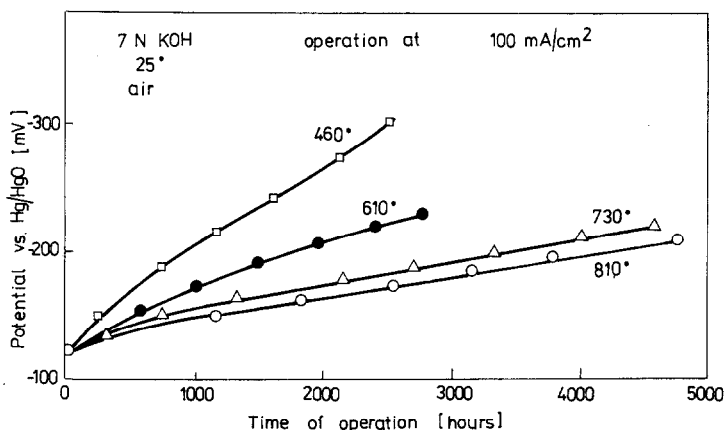


Fig. 4. Potential as a function of the time of operation at 100 mA cm^{-2} of air electrodes with active carbon-CoTMPP catalysts heat treated at 460, 610, 730, and 810 °C.

The degradation in the performance of the air electrodes could be ascribed either to a loss of activity or to increased transport hindrance. Figure 5 shows the electrochemical activity of the electrodes from Fig. 4 as a function of the duration of operation. The initial activity of all four electrodes was the same and remained practically unchanged during the first 2000 h of operation in the case of electrodes with catalysts heat treated at 810 °C. The activity of the electrode with catalyst heated at 730 °C was stable during the initial 1000 h of operation and fell slightly during the following 1000 h. The electrodes with catalysts treated at 460 and 610 °C started to lose their activity after 500 h and after 2000 h it has fallen to nearly half of its initial value.

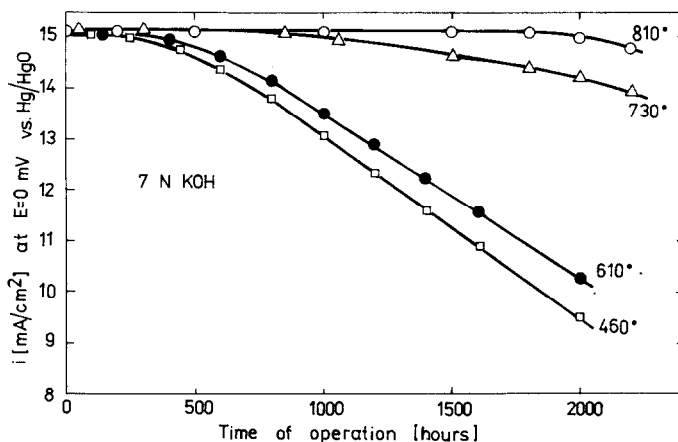


Fig. 5. Electrochemical activity (expressed with the c.d. at $E = 0$ vs. Hg/HgO) as a function of the time of operation at 100 mA cm^{-2} of the air electrodes from Fig. 4.

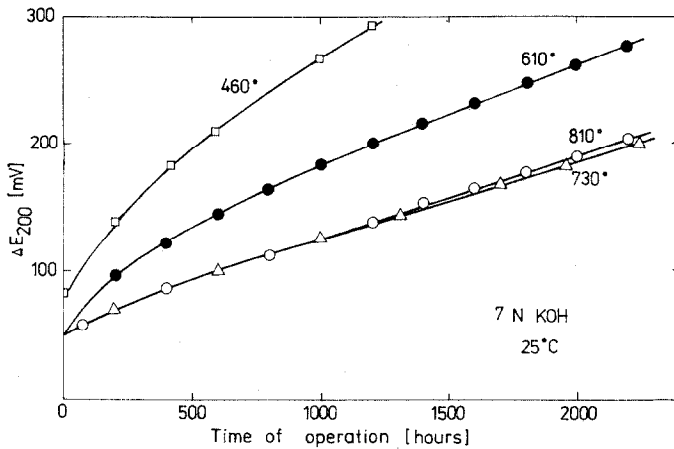


Fig. 6. Transport hindrances (expressed with the values of ΔE_{200} — at c.d. 200 mA cm^{-2}) as a function of the time of operation at 100 mA cm^{-2} of the electrodes from Fig. 4.

Figure 6 gives the ΔE values, obtained at a current density of 200 mA cm^{-2} as a function of the duration of operation of the electrodes from Fig. 4. It can be seen that the transport hindrances of all the electrodes increase with time. This effect is much more pronounced for electrodes with catalysts heat treated at 460 and 610 °C than for electrodes with catalysts processed at 730 and 810 °C.

From the results presented in Figs. 5 and 6 it can be concluded that the degradation with operation time in the performance of the electrodes with catalysts heated at 730 and 810 °C is mainly caused by the increased transport hindrances in the catalysts. For electrodes with catalysts treated at

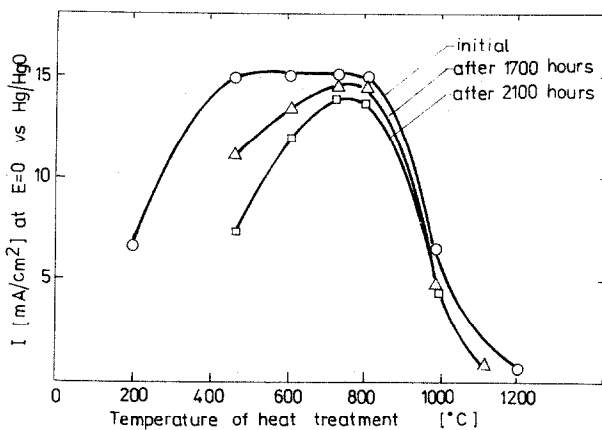


Fig. 7. Electrochemical activity of air electrodes with active carbon-CoTMPP catalysts as a function of the heat treatment temperature of the catalyst (initial and after 1700 and 2100 h of operation at 100 mA cm^{-2}).

460 and at 610 °C the degradation is due to both decreased activity and increased transport hindrances in the catalyst.

The activity of the electrodes as a function of the heat treatment temperature of the active carbon-CoTMPP catalysts is plotted in Fig. 7: curves for the initial activity and the activity after 1700 and 2100 h of operation are presented. The initial activity of the catalysts shows a broad maximum within the temperature range 460 - 810 °C. During long-term operation the activity of the electrodes with catalysts heat treated at temperatures below 700 °C decreased, while the activity of the electrodes with catalysts heat treated at 700 - 850 °C remained high and stable. The activity of the electrodes with catalysts heat treated at temperatures above 900 °C also remained stable with time but was very low.

Thus, the broad maximum in the initial activity becomes narrow around the optimal temperature of heat treatment (750 - 850 °C). The transport hindrances in the electrodes investigated are shown in Fig. 8 as a function of the heat treatment temperature of the active carbon-CoTMPP catalysts. The initial curve shows a broad minimum of the transport hindrances in the electrodes. From the curves obtained after 500, 1700, and 2750 h of operation it can be seen that the minimum becomes sharper and its position shifts towards a higher temperature. After 2750 h operation the optimal heat treatment temperature of the active carbon-CoTMPP catalysts is about 800 °C.

Figures 7 and 8 show that after long-term operation there is a coincidence in the position of the maximum of the activity and the minimum in the transport hindrances for electrodes with a catalyst heat treated at 800 °C. It is possible that the active carbon-CoTMPP catalyst, heat treated in an inert atmosphere at this optimal temperature (800 °C), is also an effective catalyst for the decomposition of hydrogen peroxide. In this case

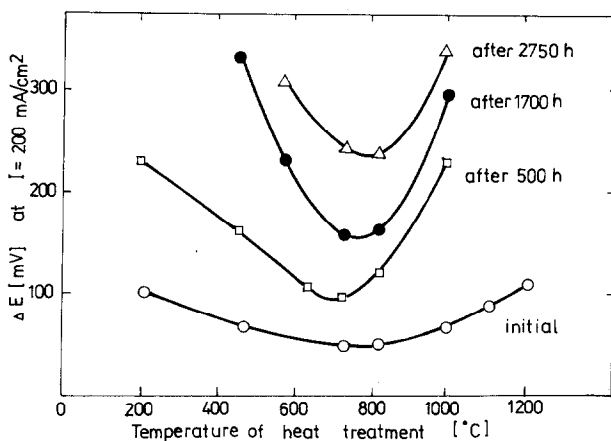


Fig. 8. Transport hindrances of air electrodes with active carbon-CoTMPP catalysts as a function of the heat treatment temperature of the catalyst (initial and after 500, 1700, and 2750 h of operation at 100 mA cm^{-2}).

the catalyst surface (especially its hydrophobic properties) is protected against the harmful influence of hydrogen peroxide, which results in low transport hindrance in the catalyst after long-term operation.

References

- 1 H. Jahnke, M. Schoenborn and G. Zimmermann, *Topics in Current Chemistry* 61, Springer, Berlin, 1976, p. 133.
- 2 B. Becker, H. Jahnke and M. Schoenborn, *DOS* 232 667 (1973).
- 3 V. S. Bagotsky, M. R. Tarasevich, K. A. Radyushkina, O. A. Levina and S. I. Andruseva, *J. Power Sources*, 2 (1977/78) 333.
- 4 K. Wiesener and A. Fuhrmann, *Z. Phys. Chem. (Leipzig)*, 260 (1980) 441.
- 5 S. Gamburgzev, A. Kaisheva and I. Iliev, *29th ISE Meeting, Budapest, Hungary, Aug. 28 - Sept. 2, 1978, Ext. Abstr. Part II*, p. 106.
- 6 R. J. A. van Veen and C. Visser, *Electrochim. Acta*, 24 (1979) 221.
- 7 I. Iliev, S. Gamburgzev and A. Kaisheva, *31st ISE Meeting, Venice, Italy, Sept. 22 - 26, 1980, Ext. Abstr. Vol. 1*, p. 286.
- 8 I. Iliev, S. Gamburgzev, A. Kaisheva, E. Vakanova, J. Muchovski and E. Budevski, *Izv. Otd. Khim. Nauki, Bulg. Akad. Nauk*, 7 (1974) 223.
- 9 A. Kaisheva, I. Iliev and S. Gamburgzev, *J. Power Sources*, 13 (1984) 181.
- 10 I. Iliev, S. Gamburgzev, A. Kaisheva and J. Mrha, *J. Appl. Electrochem.*, 5 (1975) 291.
- 11 E. S. Brodsky, K. A. Radyushkina, G. A. Kalinkevich, I. M. Lukashenko and O. A. Levina, *Dokl. Akad. Nauk SSSR*, 257 (1981) 139.