

## PLASTIC-BONDED ELECTRODES FOR NICKEL-CADMIUM ACCUMULATORS.

### VIII. STUDY OF OXYGEN RECOMBINATION RATE ON PLASTIC-BONDED CADMIUM ELECTRODES PROVIDED WITH ACTIVE CARBON CATALYST\*

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#### Summary

The oxygen recombination (reduction) rate on plastic-bonded cadmium electrodes in sealed Ni-Cd systems can be controlled by the use of a catalytic mix consisting of active carbon and carbon black either in the pure state or mixed with PTFE. This catalytic mix is either rolled onto the gas side of the plastic-bonded cadmium electrode or added to the active material prior to the preparation of the electrode by a rolling technique. The highest oxygen recombination rate, which surpassed that obtained with commercial pocket-type electrodes, was obtained in both cases by the use of an active carbon, carbon black and PTFE catalytic mix. In this case an optimum three-phase boundary, well known from oxygen electrodes for fuel cells, was established.

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#### Introduction

It was shown in our preceding communication [1] that the recombination (*i.e.*, reduction) of oxygen is drastically reduced when plastic-bonded cadmium (PB-Cd) electrodes are used in the sealed Ni-Cd system. In our previous work [2], we showed that the recombination rate of oxygen on PB-Cd electrodes can be substantially increased by using metal screens applied to the gas side of the PB-Cd electrode. The use of such screens causes,

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on the other hand, some obstacles when assembling multi-electrode cells, and it was therefore necessary to develop a PB-Cd electrode with an appreciable oxygen recombination rate without using additional metal screens.

Active carbon is a reliable, cheap, and effective electrocatalyst for oxygen reduction in alkaline solution [3 - 5] and it has therefore been used in PB-Cd electrodes. The influence of active carbon, applied in different ways, on the oxygen recombination rate is the subject of the present work.

## Experimental

The positive nickel oxide electrodes were of commercial pocket type used in prismatic sealed Ni-Cd cells. Their dimensions were  $4.5 \times 7.5$  cm and their capacity was 2.0 - 2.4 A h at the 5 h discharge rate.

The mode of preparation of the PB-Cd electrodes containing 5% of Teflon was described in our previous work [2] together with the electrode assembly (two positive and one PB-Cd electrode of dimensions  $4.0 \times 7.5$  cm), test cell design, and the method of electrochemical measurements.

Two types of catalytic electrode were prepared, A and B. In type A, the electrode consisted of two layers, the usual layer of the PB-Cd electrode mix (95% active material and 5% Teflon) and a relatively thin catalytic layer on the gas side [6]. The catalytic layer consisted of a catalytic mix (active carbon, carbon black, Teflon) and the PB-Cd electrode mix. Type B electrodes consisted of a single layer of a mixture of the PB-Cd electrode mix and the catalytic mix (see Table 2). In the former case, the catalytic layer was rolled onto the gas side of a finished PB-Cd electrode, (about  $50 \text{ mg/cm}^2$ ), while in the latter case the electrode was prepared in a single operation by rolling the mixture onto a current collector [7].

The catalytic mix was either HS-4 active carbon (Moravské chemické závody, Ostrava) of BET surface area  $915 \text{ m}^2/\text{g}$  and grain size below  $60 \mu\text{m}$ , or a mixture of this with P-1042 acetylene black (Stickstoffwerk Piesteritz, GDR) and powdered Teflon (Fluon CD-1, ICI, Great Britain). In some cases Teflonised acetylene black (35 wt.% Teflon) was used [8] instead of acetylene black and Teflon.

## Results and discussion

### *Type A electrodes*

The measured  $\Delta p(i)$  characteristics obtained with catalytic layers of the composition given in Table 1 are shown in Fig. 1 (curves 2 - 11) together with curve (1) for a non-catalytic PB-Cd electrode and curve (12) for a pocket electrode containing the same active material. The oxygen recombination rate increases according to the order beginning with the non-catalytic PB-Cd electrode (curve 1) and ending with the electrode with a catalytic layer on both sides (curve 11). It is also apparent that the oxygen recombina-

TABLE 1

Composition of type A PB-Cd electrodes

Catalytic mix (parts by weight)				Catalytic layer	Fig. 1
Active carbon	Carbon black	Teflon	Teflonised carbon black	Mass ratio of cat. mix/elect. mix	Curve no.
5	0	0	0	2:5 or 3:5	2, 3
2	3	0	0	1:1 or 3:2	4, 5
2	0	0	3	1:1 or 3:2	6, 7
2	2	1	0	1:1 or 3:2	8, 9
2	0	0	3	only catal. mix	10
2	0	0	3	1:1	11

Curves 2 - 10: catalytic layer on one side, 11: on both sides.

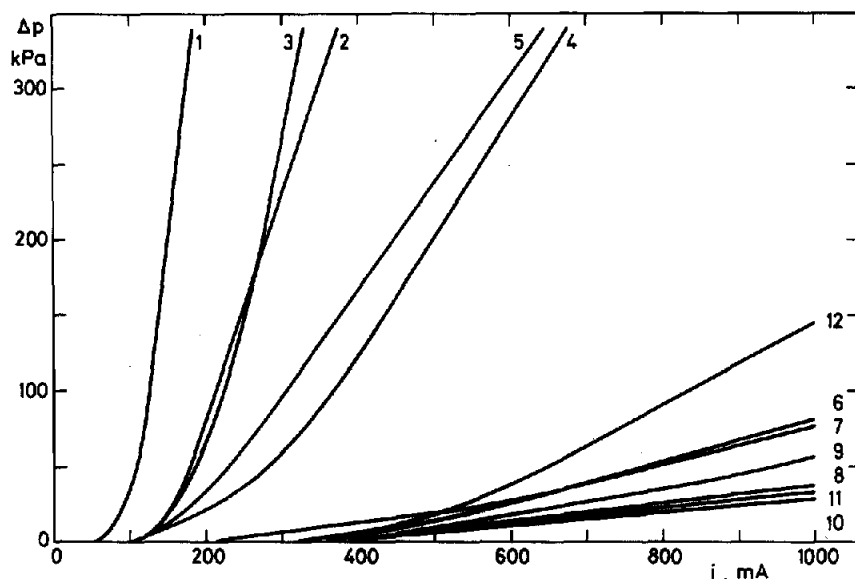


Fig. 1. Influence of the charging current on the steady state oxygen overpressure for type A PB-Cd electrodes with catalytic layers given in Table 1. 1, pure PB-Cd electrode; 12, pocket Cd electrode.

tion rate at a current load higher than 0.5 A (curves 6 - 11) in some cases exceeds that obtained with the pocket electrode (curve 12).

Based on the positions of the  $\Delta p(i)$  characteristics (Fig. 1), it is possible to divide the studied electrodes into three groups:

The first group comprises those cases where the catalytic mix was pure active carbon only (curves 2 and 3) and where the recombination rate was lowest, *i.e.*, not much higher than with the non-catalytic PB-Cd electrode (curve 1). The concentration of the added active carbon was without influence over the range investigated.

The second group of catalytic electrodes (curves 4 and 5) is characterised by an elevated oxygen recombination rate; the catalytic mix here was a mixture of active carbon with carbon black in the ratio of 2:3. The amount of the catalytic mix was again without significant influence over the range investigated.

The third group (curves 6 - 11) consisted of electrodes with a high recombination rate which at current loads over 0.5 A surpassed that for the pocket electrode. The catalytic mix was a mixture of active carbon with carbon black and Teflon (curves 8, 9), or a mixture of active carbon with Teflonised carbon black (curves 6, 7, 10 and 11).

It is seen by comparison of the curves that the oxygen recombination rate is increased moderately by the addition of carbon black to the active carbon (curves 4 and 5); however a substantial increase is caused by the addition of Teflon (curves 6 - 11). This finding substantiates the conclusions of our previous work where the reduction of oxygen in sealed Ni-Cd cells was discussed in terms of an electrochemical process proceeding under a thin electrolyte film on a metal (steel, Ni, Ag) on which oxygen reduction takes place at the potential of the Cd/Cd(OH)<sub>2</sub> electrode. Since active carbon is hydrophilic, its pores become drowned with the electrolyte, whereby the reduction of oxygen is hindered. Carbon black is hydrophobic and assists in the formation of gas pores; however the best hydrophobicity is achieved by the addition of Teflon to the active carbon. In this way, an active layer is formed analogous to that in double-layer carbon fuel cell electrodes operating in oxygen.

If the catalytic mix is blended with the electrode mix, then the effectiveness of the resulting catalytic layer is lowered, as can be seen by comparing curves 6 and 7 with curve 10 (Fig. 1 and Table 1). This can be attributed both to the lowered amount of the catalytic mix in the catalytic layer and to a higher content of hydrophilic (drowned) pores. On the other hand, the presence of the electrode mix improves the ease of rolling of the catalytic layer. The reduction in the effectiveness of the catalytic layer can be counterbalanced by applying this layer to each side of the PB-Cd electrode (curve 11). In the cases of curves 8 - 11, the oxygen recombination rates are generally very high and therefore the differences between the single curves are not significant.

### *Type B electrodes*

From a practical point of view, combining the catalytic mix directly with the PB-Cd electrode mix prior to the rolling process seems to be advantageous. The catalytic mix is thus evenly distributed in the bulk of the electrode. The composition of the catalytic mix and of the mixtures used is given in Table 2. The  $\Delta p(i)$  characteristics obtained from the resulting PB-Cd electrodes are shown in Fig. 2, where the effect of different components of the catalytic mix can be readily seen. Carbon black alone (curve 2) is without influence on the recombination rate owing, apparently, to its low catalytic activity. On the other hand, the addition of active carbon alone

TABLE 2

Composition of type B PB-Cd electrodes

Catalytic mix (mass percent. in electrode)			PB-Cd electrode mix (mass percent. in electrode)		Fig. 2
Active carbon	Carbon black	Teflon	Active material	Teflon	Curve no.
10.0	0.0	0.0	85.5	4.5	3
0.0	2.0	0.0	93.1	4.9	2
9.76	0.0	2.44	83.41	4.39	4
4.88	4.88	2.44	83.41	4.39	5

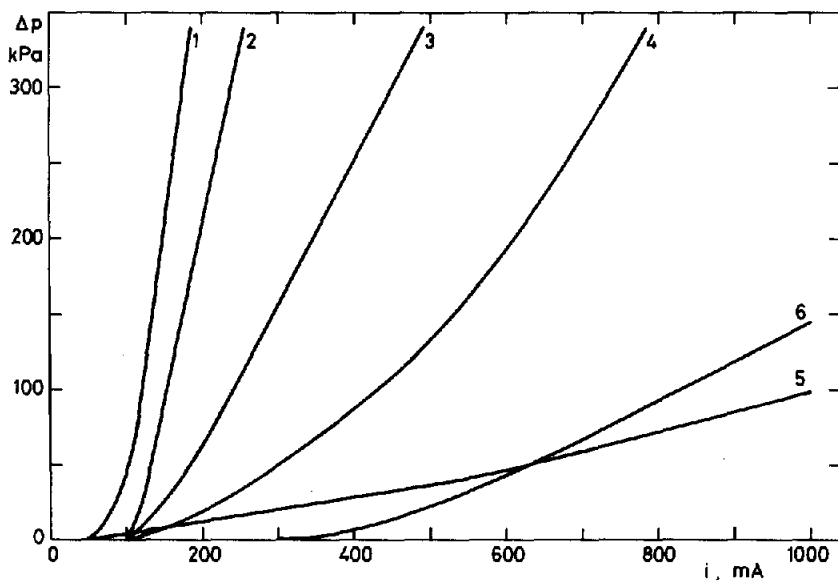


Fig. 2. Influence of the charging current on the steady state oxygen overpressure for different type B PB-Cd electrodes (see Table 2). 1, pure PB-Cd electrode; 6, pocket Cd electrode.

enhances the recombination rate of oxygen (curve 3), and its effect is larger than with electrodes of type A (Fig. 1, curves 2 and 3). This difference can be attributed to the fact that oxygen can react on both sides of type B electrodes, but only on one side of type A electrodes.

If the active carbon is blended with Teflon and then added to the PB-Cd electrode mix, its catalytic effect is much more pronounced (curve 4), since drowning of the carbon particles is more or less prevented. A still higher catalytic effect was obtained with a mixture of active carbon, carbon black and Teflon (curve 5), as was also the case with electrodes of type A (Fig. 1, curves 8 and 9). In this case, the distribution of the electrolyte in the catalytic component, and the electrical contact between the active carbon and the cadmium electrode material are obviously optimised; good electrical

contact of the carbon particles ensures a sufficiently high negative potential and thus a high rate of oxygen reduction. Thus the oxygen recombination rate for the PB-Cd electrode with the active carbon-carbon black-Teflon catalytic mix surpasses (Fig. 2, curve 5), at high current loads, even the pocket electrode (Fig. 2, curve 6). The different and reproducible shapes of curves 5 and 6 probably reflect the different oxygen recombination mechanisms of the two types of electrode.

The beneficial effect of the presence of the catalytic mix (active carbon or active carbon + carbon black) in the electrode mix was confirmed with multi-electrode 6 A h cells (four PB-Cd electrodes of type B and three pocket nickel oxide electrodes). The capacity and overpressure characteristics of these cells after 155 - 186 accelerated cycles were comparable with those of a commercial 6 A h cell (only pocket electrodes). In the absence of the catalytic mix in the PB-Cd electrodes it was not possible to cycle the 6 A h cells because of the extremely high values of overpressure and a low cell capacity, even in the early cycles, caused by the negative electrodes.

## Conclusions

(1) The oxygen recombination (reduction) rate on plastic-bonded cadmium electrodes in sealed Ni-Cd systems can be controlled by the use of a catalytic mix of active carbon and carbon black with or without Teflon.

(2) The catalytic mix can be either rolled onto the gas side of the PB-Cd electrode or directly blended with the PB-Cd electrode mix.

(3) The highest oxygen recombination rates are obtained in either case when a mix of active carbon, carbon black, and powdered Teflon is used; they surpass those obtained with commercial pocket-type electrodes, especially at high charging rates.

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