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PLASTIC-BONDED ELECTRODES FOR NICKEL–CADMIUM ACCUMULATORS
IX. OXYGEN RECOMBINATION RATE ON PLASTIC-BONDED CADMIUM ELECTRODES WITH DIFFERENT ACTIVE MATERIALS

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Summary

The rate of oxygen recombination (*i.e.*, reduction) on plastic-bonded cadmium electrodes in sealed Ni–Cd systems can be controlled over a wide range by doping the negative active material with $Ni(OH)_2$, Fe_3O_4 or carbon black. The highest recombination rate was attained by combining all these additives (treatment of CdO with $Ni(OH)_2$ and subsequent addition of Fe_3O_4 and carbon black), allowing the plastic-bonded electrodes obtained to be used without further modifications in sealed Ni–Cd systems.

Introduction

We have shown [1 - 3] that the so-called recombination (*i.e.*, reduction) of oxygen proceeds in sealed Ni–Cd systems at utilizable rates on the metal parts of negative electrodes coated with a thin electrolyte layer easily accessible to oxygen and contacting the electroactive Cd/Cd^{2+} system. The rate of oxygen reduction on plastic-bonded cadmium (PB-Cd) electrodes can be substantially increased by using metal screens applied to their gas side [2], and it can also be influenced to a large extent by the addition of active carbon [3, 4]. In the cited work, PB-Cd electrodes were prepared from powdered active material used in commercial, pressed electrodes, whose active component was cadmium sponge oxidized on its surface in the course of manufacture (during drying). Since certain manufacturers use CdO as a starting material in the manufacture of negative electrodes and suitably modify it, our present work was devoted to the influence on the oxygen recombination rate of modifying admixtures to cadmium oxide.

Experimental

Positive electrodes of dimensions 4.5 × 7.5 cm were of commercial pocket type for prismatic sealed Ni–Cd cells. Their capacity was 2.0 - 2.5

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A h at a 5 h discharge rate. The preparation of PB-Cd electrodes, the electrode assembly, and the test cell have been described in our previous work [1].

Electrochemical measurements were undertaken as follows. The measured cell was charged on the first cycle at a current of 60 mA (approx. 1 mA/cm^2) for 24 h and then discharged with 600 mA to the end voltage of 0.0 V. For the second cycle the cell was charged at 100 mA for 18 h and discharged as before. For the third cycle, the charge current was 150 mA for 18 h, and following discharge it was charged at 200 mA for 18 h. The charging current was then increased to 300 mA and the cell was overcharged until a stationary overpressure was attained (up to 5 - 7 h). The cell was overcharged at 60 mA overnight and then the charging current was increased to 500 mA. This procedure was repeated, the charging current, i, being increased in sequence at one-day intervals to 700, 850, and 1000 mA. After every cell charge the stationary overpressure, Δp — evidence of the equality of the rates of oxygen evolution and recombination — was measured. The measurements were completed as soon as the overpressure, Δp, exceeded 400 kPa or the current attained 1 A. The results were expressed by plotting Δp against i.

The starting material was pure CdO (Lachema, Brno, CSSR) or CdO activated with nickel hydroxide (wetted with a solution of $NiSO_4$ and made alkaline). This was used either as such, or mixed with graphite VA (Rudné doly, Týn/Vlt., CSSR), carbon black P-1042 (Stickstoffwerk Piesteritz, GDR) or technical grade Fe_3O_4 (Lachema, Brno, CSSR). The composition of the active material is given in Table 1.

Results and discussion

The results obtained using different electrode mixes are shown in Fig. 1, from which three groups of these materials can be distinguished:

The first group involves active materials with a very low oxygen recombination rate; these are unsuitable for sealed Ni–Cd cells (CdO, either pure or mixed with Fe_3O_4, graphite or carbon black; curves 1 - 4).

The second group involves active materials obtained by doping CdO with nickel hydroxide without, or with, subsequently added graphite (curves 5 and 6).

The third group shows the highest rate of oxygen recombination. In this case, CdO was doped with $Ni(OH)_2$ and mechanically mixed with Fe_3O_4 and/or carbon black or graphite (curves 7 - 10). The best of these combinations is that of CdO + $Ni(OH)_2$ mixed with Fe_3O_4 and carbon black (curve 10).

Thus, it is clear that the presence of $Ni(OH)_2$ on the surface of CdO is a necessary condition for increasing the rate of oxygen reduction on PB-Cd electrodes. This favourable effect is somewhat analogous to that of the catalysis of oxygen reduction on three-phase fuel cell oxygen electrodes

TABLE 1

Composition of the active material used for the preparation of plastic-bonded cadmium electrodes

Electrode number	Composition of electrode	Components (wt.%)					
		CdO	(CdO + $Ni(OH)_2$)	Graphite	Carbon black	Fe_3O_4	Active carbon
1	CdO	100	—	—	—	—	—
2	CdO + graphite	98.8	—	1.2	—	—	—
3	CdO + Fe_3O_4	89.3	—	—	—	10.7	—
4	CdO + carbon black	98.8	—	—	1.2	—	—
5	(CdO + $Ni(OH)_2$)	—	100	—	—	—	—
6	(CdO + $Ni(OH)_2$) + graphite	—	98.8	1.2	—	—	—
7	(CdO + $Ni(OH)_2$) + Fe_3O_4	—	89.3	—	—	10.7	—
8	(CdO + $Ni(OH)_2$) + graphite + Fe_3O_4	—	88.2	1.2	—	10.6	—
9	(CdO + $Ni(OH)_2$) + carbon black	—	98.8	—	1.2	—	—
10	(CdO + $Ni(OH)_2$) + carbon black + Fe_3O_4	—	88.2	—	1.2	10.6	—
11	(CdO + $Ni(OH)_2$) + graphite + Fe_3O_4 + active carbon + carbon black	—	82.0	0.9	2.7	9.0	5.4

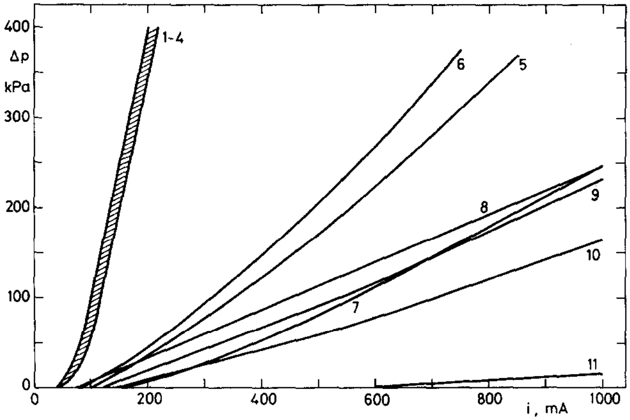

Fig. 1. Influence of the charging current on the steady state oxygen overpressure for PB-Cd electrodes with different active materials given in Table 1.

containing mixed oxides of nickel and other metals [5]. Another similar case concerns the considerable increase in the catalytic activity of carbon electrodes for the reduction of oxygen in alkaline medium observed when silver oxide is mixed with nickel or cadmium oxides [6].

The nickel hydroxide must be present in a finely dispersed form. This can be achieved by activation from solution as mentioned. An additional increase in the rate of oxygen reduction can be achieved by the addition of Fe_3O_4 or carbon black, or better, by the addition of both. The addition of graphite appeared to have no effect.

The favourable effect of magnetite and carbon black can be attributed to an improvement in the structure and conductivity of the PB-Cd electrode. We have in mind an increase of the electrolyte content and its distribution equally over the whole of the electrode body. This is important since plastic-bonded electrodes are semihydrophobic in character. Powdered magnetite is used in pocket cadmium electrodes as an anti-agglomeration agent. Carbon black is known to improve the conductivity and electrolyte distribution in so-called self-breathing air electrodes from active carbon, carbon black and Teflon. The effects of powdered magnetite and carbon black on PB-Cd electrodes are apparently analogous.

Active carbon also has a favourable effect on the oxygen recombination rate, as stated in our preceding work [3]. If active material of optimum composition is mixed with active carbon (Table 1), the resulting electrode shows the highest recombination rate ever recorded in our laboratory (Fig. 1, curve 11), and this not only with PB-Cd electrodes [1 - 3].

Conclusions

(1) The rate of oxygen recombination on PB-Cd electrodes can be considerably enhanced by doping the starting cadmium oxide with $Ni(OH)_2$ in a finely dispersed form.

(2) The addition of Fe_3O_4 and carbon black increases the recombination rate in the case of cadmium oxide doped with nickel hydroxide. The addition of graphite has no effect in this respect.

(3) The addition of active carbon to an optimised active material containing Fe_3O_4, $Ni(OH)_2$ and carbon black leads to a PB-Cd electrode which shows a higher recombination rate than any of the cadmium electrodes of various types hitherto studied.

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