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On the behaviour of carbon black in positive lead–acid battery electrodes

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The addition of carbon black to the positive paste led to an alteration in structure of the PbO_2/$PbSO_4$ electrode due to an increase in porosity, in active mass coarsening and in the α/β–PbO_2 ratio. These structural effects are explained as being caused by the ability of carbon black to increase the water-accumulating capacity of the paste, to influence the local formation conditions and to participate in the charge transport within the unformed mass. Oxidative removal of carbon black from the active mass was studied.

1. Introduction

To improve performance and cycle life of the positive lead–acid battery electrode, additives of various types are employed. However, with the exception of a few cases [1–5], there is no detailed information on the effect and mechanism of action of these additives. This especially refers to carbon black which is also of importance for other power sources. Our recent experiments have shown that carbon black, if added to the paste, influences electrical performance only slightly, but does affect the structure of the active material [5]. The aim of this paper is to complete the information on the mode of action of carbon black and to study its removal by oxidation.

2. Experimental details

The paste was formed by mixing 1 kg of lead dust (ball milled; 65% PbO, 35% Pb), 0.2 or 10 g of carbon black (acetylene black P 1250) and 133 ml H_2O with 71 ml H_2SO_4 (1.4 g cm^{-1}) for 25 min. In a subsequent experiment the pure water-accumulating capacity of the paste was examined at intervals by determining the density and consistency. For the latter experiment a simple method involving the penetration of a graduated conical measuring body was used. Unless otherwise stated, curing proceeded at 23° C and at 95% RH. After 1 h of soaking in acid (H_2SO_4, 1.05 g cm^{-3}) formation was carried out at 25° C and at 16 A kg^{-1} for a period of 40 h.

As described previously [5] the formed electrodes were cycled at a current corresponding to the 10-h rate with each cycle involving a discharge for 1 h and a charge for 5 h.

To examine the structure, X-ray diffractometry, Hg-high-pressure porosimetry (Erba-porosimeter) and BET-surface measurements (Erba-sorptomatic) were applied. The carbon content in the active mass was determined by elemental analysis. The electrical conductivity of cured masses (ground; particle size, 63–200 μm) was determined, under pressure, by a.c. measurements (f = 1 kHz).

The investigations with the slurry electrode (gold collector, 60 cm^2) were executed potentiodynamically (sweep rate, 600 mV min^{-1}) in H_2SO_4 (1.05 g cm^{-3}), as described in [6]. All measurements were carried out with the Hg/$HgSO_4$ reference electrodes which were in the same electrolyte solution as the working electrode. The analytical and measured data were obtained by averaging at least two samples of electrode material and two electrodes, respectively.

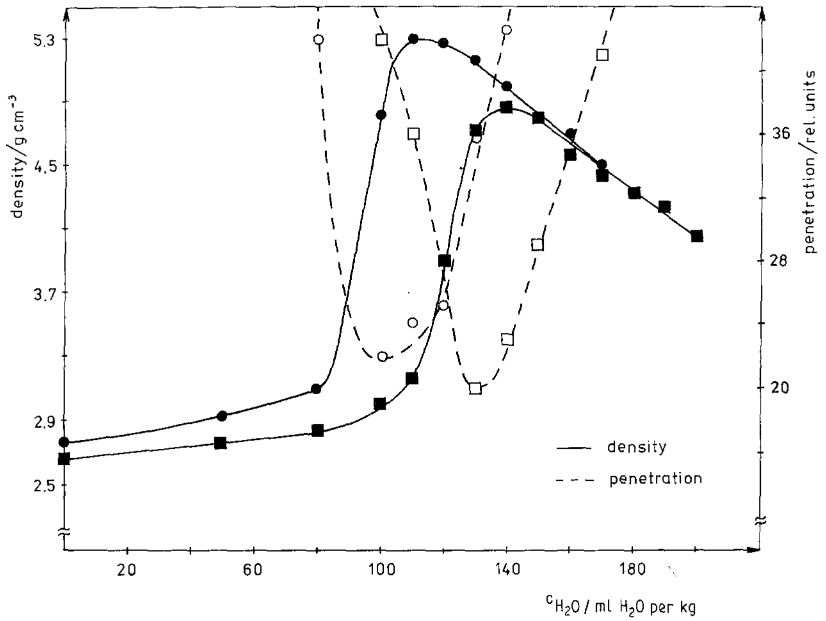

Fig. 1. Density and penetration of lead dusts with 1% carbon black (■, □) and without carbon black (●, ○) as a function of the water content.

3. Results and discussion

3.1. *Carbon black as a water-accumulating and catalytically active additive*

The electrochemically effective porosity can be enhanced by increasing the total interstitial volume during paste preparation. This produces a higher 'water value at the density maximum' of the paste during water take-up [7]. The maximum density, corresponding to a penetration minimum, is attained for complete filling of the void volume. Further added water, decreasing the paste density, only increases the particle mobility and is not conductive to the formation of the desired pores [7].

In Fig. 1 it is shown, via the shift of the density maximum, that the water-accumulating capacity of the paste is increased not only by addition of H_2SO_4 [7] but also by carbon black. Obviously, the surface area and volume of the grain interstices increase due to the different shape of lead dust and carbon black particles. In addition, it is concluded from the results that

(i) the packing of lead particles is expanded by the high elasticity of the chain-like coordination of the carbon crystallites,

(ii) water can be embedded into the caves formed by carbon black chains (see also [8]).

The increased water accumulation of the paste consequently results in higher porosity of the cured mass.

Table 1 shows that when 0.2% carbon black is added, additional active mass pores are formed.

Table 1. Pore volume in the range of fine and coarse pores of cured masses with and without carbon black

Type	*Pore volume* (10^{-3} cm^3 g^{-1})	
	r_p: *4 to* 10^2 *nm*	r_p: 10^2 *to* 2×10^3 *nm*
Without carbon black	9	77
With 0.2% carbon black	12	95

At a higher concentration there is a further increase in pore volume mainly due to the intrinsic porosity of carbon black [9].

The lead oxidation proceeding in the paste during curing can be interpreted as the local cell reaction (Reaction 3) of the subprocesses of lead oxidation (Reaction 1) and oxygen reduction (Reaction 2), and is controlled by the kinetic limits of the latter process (Reaction 2) [5].

$$\mathrm{PbO} + 2\mathrm{OH}^- \longrightarrow \mathrm{PbO} + \mathrm{H_2O} + 2e \quad (1)$$

$$\mathrm{H_2O} + \tfrac{1}{2}\mathrm{O_2} + 2e \longrightarrow 2\mathrm{OH}^- \quad (2)$$

$$\mathrm{Pb} + \tfrac{1}{2}\mathrm{O_2} \longrightarrow \mathrm{PbO} \quad (3)$$

As carbon surfaces for the cathodic oxygen reduction have electrocatalytically active centres which can even be present when carbon black is used [10], it was supposed that this additive in lead masses also contributes to a reduction in transfer polarization. However, Reaction 2 and consequently Reaction 3 can only be accelerated when the diffusion polarization becomes so low that it can reach the level of the transfer polarization.

This is the case when the grain interstices are not completely filled by water [11], i.e. at the beginning of the paste preparation and towards the end of the water removal. In fact, such tendencies are reflected by Fig. 2.

Table 2. Powder resistivity of cured masses with and without carbon black and of carbon black alone. Pressure = 51 MPa

Type	*Electrical resistivity (S^{-1} cm)*
Cured mass	
Without carbon black	7.06×10^{6a}
With 1% carbon black	6.92×10^{6a}
Carbon black	0.11

[a] Correct to ±0.02.

3.2. *Carbon black as an electrically conductive additive*

Previous measurements showed that the electrical conductivity of carbon black is about 10^8 times higher than that of the cured mass (see Table 2). We therefore supposed that carbon black is able to act as an electrically conductive additive within the unformed mass. By measuring the powder conductivity of the mass containing carbon black, however, this was not definitely proved (Table 2). It is only at the mixture composition enabling the more conductive component to form continuous conductive strings that, according to the Percolation theory [12] as shown by Metzendorf [13], a distinct rise in conductivity can be measured.

However, even if present in low concentration, carbon black should participate in the charge

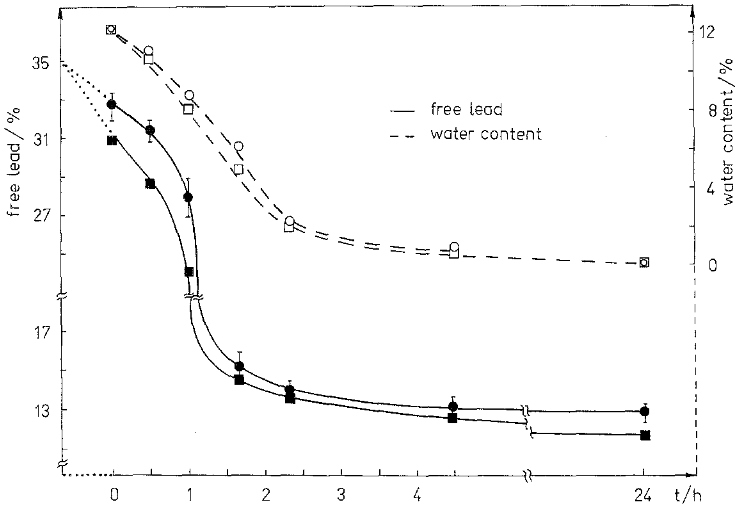

Fig. 2. Contents of free lead and water of pastes with 1% carbon black (■, □) and without carbon black (●, ○) as a function of the curing time. Temperature, 23° C; relative humidity, 75%.

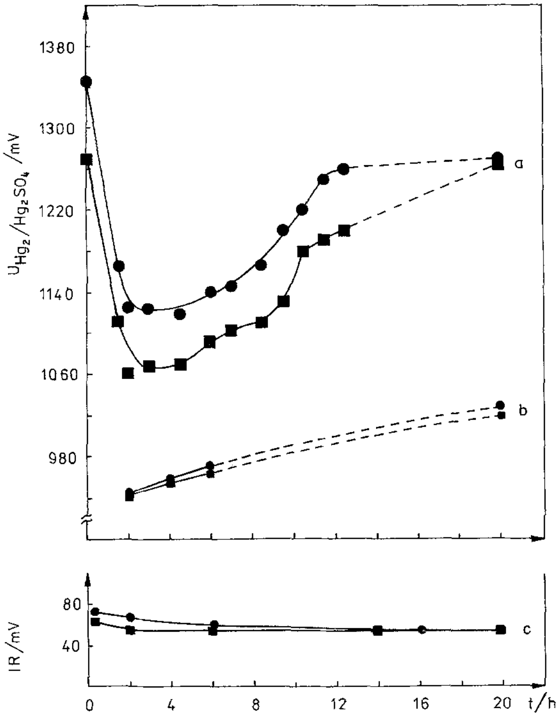

Fig 3. (a) Formation potential, (b) open circuit potential and (c) ohmic potential drop of electrodes with 1% carbon black (■) and without carbon black (●) as a function of the formation time.

transport during formation. As the formation is a dynamic process, the conductive carbon chains within the unformed mass become 'active' one by one as soon as they are overtaken by the growing PbO_2 zone and begin to contact with it. This conclusion, which is supported by the lower ohmic potential drop of the electrode with carbon black at the beginning of formation, enables us to explain satisfactorily the influence of carbon black on formation.

The first period of formation is known to be determined by the electrochemical conversion of the PbO components of the unformed mass into α-PbO_2. Evidently, as this reaction proceeds more easily the better the ability of the electrons to migrate from the collector to the PbO phase, i.e. the larger the contact area between the conductive (formed) α-PbO_2 and PbO.

At the beginning of formation the contact area is very small, causing high polarization (Fig. 3). This results from the fact that primary PbO_2 is always formed at the grid bars [14], due to the extremely low electronic conductivity of the electrode compared to its ionic conductivity [15, 16]. With increasing formation time, due to progressive α-PbO_2 formation and improvement in electronic conductivity, the PbO/α-PbO_2 contact area increases and advances in space, as described in [17]. Thus both the polarization and the formation potential are decreased (Fig. 3).

However, in the course of formation the consumption of PbO occurs to an increasing extent. As soon as PbO components are no longer available, the potential-determining process changes and the oxidation of $PbSO_4$ to β-PbO_2 begins. This, according to Pavlov *et al.* [18], is reflected by the rapid increase in formation potential.

The influence of carbon black on the formation process is also to be understood from Fig. 3. It is clear that adding carbon black decreases the ohmic potential drop and, above all, polarization, thus indicating an increase in the PbO/α-PbO_2 contact area at the beginning of formation. Obviously, carbon black enhances the PbO availability by providing for the bridging of $PbSO_4$ layers and the formation of conductive paths into and within the unformed mass. This implies an opening up of additional internal PbO portions to electrochemical attack. As a consequence, more PbO is oxidized direct to α-PbO_2 and less PbO, after being chemically converted to $PbSO_4$, is oxidized to β-PbO_2.

Table 3. Influence of carbon black on the phase composition of active masses after formation and after 216 cycles (end of cycle life)

Type	*After formation*			*After 216 cycles*
	α-PbO_2 (%)	*β-PbO_2 (%)*	*α/β-PbO_2*	*α/β-PbO_2*
Without carbon black	47	36.5	1.29	0.95
With 0.2% carbon black	65	32.5	2.00	1.34

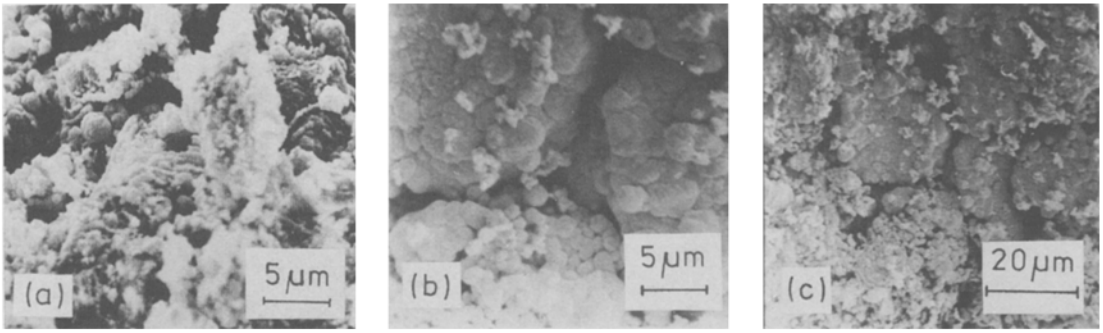

Fig. 4. SEM photographs of PbO_2 active mass. (a) Without carbon black; (b, c) with 0.2% carbon black.

Therefore, as indicated in Fig. 3, the α-PbO_2 formation lasts for a longer time. This is confirmed by the higher α-PbO_2 content of electrodes with carbon black (Table 3).

3.3. *Influence of carbon black on the active mass morphology*

The effect of adding carbon black on the active material morphology can be seen from Fig. 4. The Scanning electron micrographs of the formed mass containing carbon black show the exclusive appearance of spherical particles, the majority of which grow together thereby forming cauliflower-like agglomerates. The regular shape of the particles and their agglomeration indicates that crystal growth has occurred under moderate conditions at low supersaturation. The approximately uniform size of the particles formed initially seems to suggest that the degree of supersaturation was relatively constant and the local current density was low [19, 20].

Such conditions may be preferentially created in the mass containing carbon black since

(i) the additional formation of large pores promotes both decrease and levelling of concentration gradients and, for example, facilitates the transport of formed H_2SO_4 away from the pores, thereby limiting pore acidifying.

(ii) carbon black enables the PbO/α-PbO_2 contact area to increase, thus making the current density decrease.

3.4. *Oxidation resistance of carbon black*

Oxidative removal of carbon black from the active mass was studied by carbon analysis (Table 4). The results show that

(i) during formation about 60% of the additive amount was lost by oxidation (there was no carbon to be identified in the electrolyte),

(ii) carbon black was completely removed at the end of cycle life.

In addition, the oxidation resistance of carbon black suspended in H_2SO_4 ($1.05\,g\,cm^{-3}$) was potentiodynamically investigated (Fig. 5). The anodic peak at about 860 mV, for the background solution, is due to the collector material oxidation [6]. The additional anodic process, which occurs when carbon black is present, can be explained by partial oxidation of the additive, beginning at $U_{Hg/Hg_2SO_4} \approx 300\,mV$, on the surface groups [21].

It may therefore be concluded that oxidation

Table 4. Residual amount of carbon black in the active mass after formation and after 216 cycles (end of cycle life). Elemental analytical amount correct to ±0.05

Type	*Nominal content of carbon black (%)*	*Element analytical content of carbon (%)*	
		After formation	*After 216 cycles*
Without carbon black	–	0.07	0.05
With carbon black	1.0	0.40	0.05

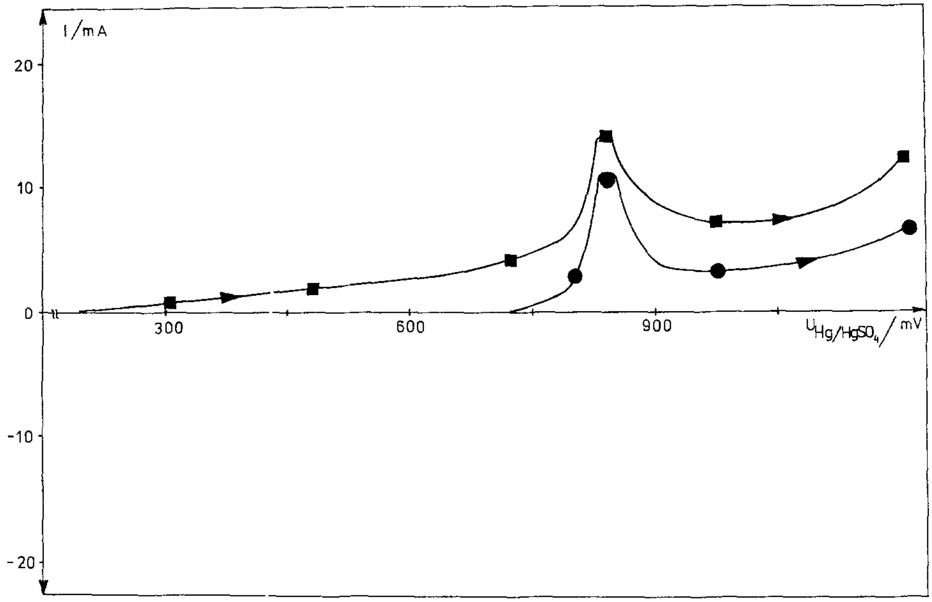

Fig. 5. Influence of carbon black suspended in H_2SO_4 (1.05 g cm^{-3}) on potentiodynamically generated *I–U* characteristics at a gold collector using the suspension electrode technique [6]. ■, with carbon black (100 mg per 150 ml); ●, without carbon black.

of carbon black already occurs under open circuit conditions of the $PbO_2/PbSO_4$ electrode, i.e. by electrochemical oxidation with PbO_2, as also indicated in Table 5.

4. Conclusions

Before being oxidized, the carbon black added to the mass leads to alterations in electrode structure during active material manufacture.

The increase in porosity of the cured mass, which is based on the additional formation of coarse pores, is due to better water accumulation of the paste in the presence of carbon black. The increase in the α/β-PbO_2 ratio should be attributed to the participation of carbon black strings, within the unformed mass, in the charge transport. As a result,

(i) the PbO availability and the PbO/α-PbO_2 contact area increase, thus leading to a higher α-PbO_2 content,

(ii) the energy efficiency of formation enhances slightly (maximally 2%) due to the decrease in polarization and ohmic drop.

As recently shown [5], the addition of carbon black, though causing increase in porosity, did not lead to marked improvement in performance. This can be attributed not only to the larger amount of α-PbO_2 [22, 23] but particularly to structure coarsening by the agglomeration of PbO_2 particles.

During formation, about 60% of the carbon black added initially was lost by oxidation, with the oxidative removal apparently beginning at the open circuit potential of the $PbO_2/PbSO_4$ couple. The additive was completely removed during cycling. However, as adding carbon black did not affect cycle life [5], the influence of the consequent structure loosening seems to be compensated by that of the permanently higher amount of α-PbO_2, the utilization of which, in contrast to β-PbO_2, does not decline [23].

Table 5. Influence of PbO_2 on the oxidation of carbon black at 25° C. Tablets were pressed from PbO_2 powder with 2% carbon black at a pressure of 60 MPa; values correct to ±0.1

Storage time (days)	*Storage medium*	*Analytical content of carbon (%)*
14	Dry	1.7
56	Dry	1.7
56	Wet	1.4

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