

Effect of plate preparation on active-material utilization and cycleability of positive plates in automotive lead/acid batteries

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Abstract

The power demands from automotive lead/acid batteries are rising steadily with the increasing number of electronic accessories that are being fitted to modern vehicles. In order to meet new levels of performance, automotive batteries have been redesigned to use low-ohmic microporous separators, as well as thinner plates (to increase the number of plates per cell) that are made with a low paste density. This approach, however, has led to a separate problem, namely, an appreciable reduction in battery service life. To redress this situation, a research programme has been implemented in our laboratories to examine, in detail, the effect of plate preparation on the active-material utilization and cycleability of automotive positive plates with grids made from low-antimony alloy. The cycleability is evaluated in terms of repetitive reserve-capacity. The results suggest that a paste formula with a combination of high density and low acid-to-oxide ratio is the most appropriate technology for the production of the thin positive plates that are required in advanced designs of automotive batteries.

Keywords: Active-material utilization; Automotive lead/acid batteries; Plate preparation

1. Introduction

Nowadays, automotive batteries are required to supply increasing levels of power to operate not only the conventional starting, ignition and lighting functions but also a wide and growing diversity of electronic accessories, e.g., defrosters, heaters, air-conditioners, powered windows, seat/seat-belt controls, retracting headlights, sunroofs, computerized engine-management systems, security devices, entertainment units and communication devices. The demand from the battery for these auxiliary loads becomes greater when the generator is either not running or is incapable of supplying the entire energy demand. Therefore, it is also necessary for the batteries to have a high reserve-capacity.

Vehicles experience a wide range of driving situations and, consequently, the operating conditions of the batteries are likewise variable. In general terms, the batteries will experience: (i) shallow-discharge cycling and substantial 'rest' (i.e., open-circuit) periods when used in private cars; (ii) frequent stop-start service and repeated shallow and deep-discharge cycling in taxis and urban buses; (iii) continuous overcharge in long-

distance buses. Thus, to cover all of these duty requirements, automotive batteries should have both high active-material utilization and long, deep-discharge, cycle life.

In order to raise the power output (i.e., the active-material utilization), automotive batteries generally use low-ohmic, microporous separators and 'thin' positive plates (0.8–1.8 mm). The plates are produced from low-density paste (i.e., 3.5–4.1 g cm⁻³). It has become commonplace to accept that a decrease in the paste density of the positive plates will increase the active-material utilization, but will reduce the battery cycle life. Conversely, an increase in paste density will prolong the cycle life, but will lower the active-material utilization. Nevertheless, the applicability of this folklore to thin automotive positive plates is questionable, especially with respect to active-material utilization.

It is well established that the active-material utilization is determined, in the main, by the following two factors: (i) slow diffusion of sulfuric acid from the bulk of the solution into the interior of the plates; (ii) continuous decrease in the conductivity of the positive and negative plates during discharge. Thinner plates will minimize the concentration difference between the interior and the outermost parts of the plate. Furthermore, such a design will moderate the otherwise

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adverse effect of an increase in paste density on factor (i), i.e., the diffusion of sulfuric acid. A higher paste density will, however, improve the contact between the individual particles of the active material and this, in turn, will reduce the possibility of deleterious encapsulation by PbSO_4 during discharge. Thus, for thin positive plates, the active-material utilization may remain unchanged over a certain range of paste densities.

The objective of this study is to examine, in detail, the progressive influence of the acid-to-oxide ratio employed in the paste mixing, the resulting paste density, and the subsequent curing procedure on both the active-material utilization and the cycleability of positive plates (with low-antimony grids) in automotive lead/acid batteries.

2. Experimental

2.1. Plate preparation

Pastes were prepared from six different formulae, denoted as P1 to P6 (see Table 1). These formulae yielded three paste densities: (i) 3.5 g cm^{-3} for pastes P1 and P2; (ii) 3.9 g cm^{-3} for pastes P3 and P4; (iii) 4.3 g cm^{-3} for pastes P5 and P6. Two acid-to-oxide ratios¹ were employed for each paste density, namely, 3.9% (for pastes P1, P3 and P5) and 6.6% (for pastes P2, P4 and P6). The procedure involved placing the required amount of leady oxide (Barton-pot variety) in a mixer and adding about three-quarters of the required water as quickly as possible (<2 min) with the mixer kept running. Acid was then introduced at a slow rate (over a period of about 10 min) and with

Table 1
Paste formulae

Ingredient	Paste type					
	P1	P2	P3	P4	P5	P6
Leady oxide (kg)	1.5	1.5	1.5	1.5	1.5	1.5
Water (cm^3)	340	310	261	235	205	175
H_2SO_4 , 1.4 sp. gr. (cm^3)	82.5	142	82.5	142	82.5	142
Acid-to-oxide ratio (%)	3.9	6.6	3.9	6.6	3.9	6.6
Density (g cm^{-3})	3.5	3.5	3.9	3.9	4.3	4.3

Table 2
Phase composition (wt.%) of leady oxide

Ingredient	Pb	α -PbO	β -PbO
Test oxide	27	66	7
Typical Barton-pot oxide	15–27	47–75	10–26

¹ Note, acid-to-oxide ratio (%) = $100 [(0.5 \times 1.4 v_a)/w_o]$ where v_a = volume of 1.4 sp. gr. acid (cm^3) and w_o = weight of oxide (g).

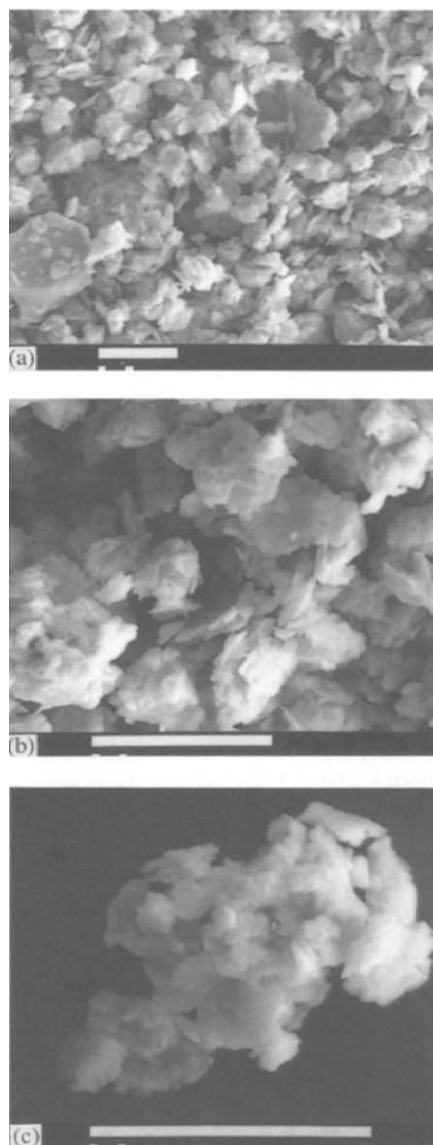


Fig. 1. Electron micrographs of test leady oxide (Barton-pot). Magnification bar: $10 \mu\text{m}$.

good dispersion over the paste. Finally, the remainder of the water was added to the mix and agitation was continued for about 1 min before measurement of the paste density was undertaken. After mixing, the pastes were applied evenly to Pb–1.7 wt.% Sb grids [dimensions: 132 mm (height) \times 105 mm (width) \times 1.8 mm (thick)] by hand application of a polyvinyl chloride (PVC) paddle, and were then compacted under the weight of a purpose-built stainless-steel roller.

The pasted plates were mounted vertically in a stainless-steel rack. The individual plates were allowed to be in contact with their neighbours in order to simulate the curing conditions that are commonly encountered in commercial battery manufacture. The rack was located in a Petri dish that contained a small amount of distilled water. The entire assembly was enclosed by a inverted glass beaker and placed inside an oven.

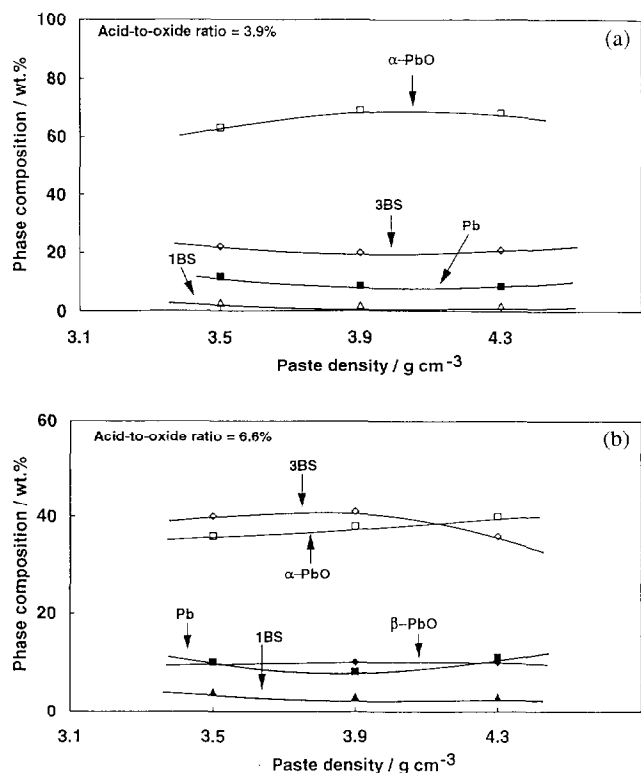


Fig. 2. Effect of paste density and acid-to-oxide ratio on paste composition.

Curing was conducted at either 50 or 90 °C with 95% relative humidity (r.h.) for 48 h. The high humidity was achieved by evaporation of distilled water from the reservoir. After curing, the plates were dried at 75 °C until the moisture content fell to below 0.1 wt. %.

The dried plates were grouped into 2 V cells. Each test cell comprised four positive plates (enclosed in Daramic envelope separators) and five negative plates. The negative plates were produced under factory conditions. Sulfuric acid solution (1.235 sp. gr.) was introduced and then a constant current of 5 A was applied for 20 h at 25 °C. After formation, the specific gravity of the acid had increased to ≈ 1.270 sp. gr.

2.2. Material characterization

Samples of leady oxide and paste, cured and formed materials were subjected to X-ray diffraction (XRD) phase-analysis (Philips PW1710 diffractometer). The phase compositions were determined by an advanced XRD method developed in the CSIRO laboratories [1]. The morphology of the materials was examined with a JEOL JSM-25S III scanning electron microscope [2]. The surface areas of both the internal pores and the internal surface of leady oxide and cured/formed samples were determined by the BET method [3,4]. The procedure involved the adsorption of a mixture of nitrogen and helium (30% N₂, 70% He) at the temperature of liquid nitrogen. The measurements were

performed with a continuous-flow Quantachrome (model Monosorb) instrument. The porosity and pore volume of the cured and formed materials were obtained by mercury intrusion porosimetry with a Micromeritics model 9200 instrument [4].

2.3. Cell performance

After formation, all the cells were kept at open circuit for 15 min at 25 °C. A constant current of 2.5 A was applied until both the terminal voltage and the acid density exhibited no appreciable change (i.e., within $\pm 3\%$) between three consecutive hourly readings. This condition was taken as the fully-charged state and was achieved prior to each performance test.

Five-hour discharge capacity

After full charging of the cells, the acid density was adjusted to lie between 1.265 and 1.275 g cm⁻³ at 25 °C. The cell was then discharged at a constant current of 5.5 A and the time for the terminal voltage to fall to 1.75 V was determined. The product of the current and the time yields the five-hour discharge capacity. The battery was returned to full charge. This charge/discharge sequence was repeated until the measured capacity reached a maximum value.

Twenty-hour discharge capacity

The procedure followed that described above for the five-hour capacity test, except that the cell was discharged at a constant current of 1.7 A.

Repetitive reserve-capacity

The cell temperature was maintained at 25 °C and the acid density was adjusted to lie between 1.265 and 1.275 g cm⁻³. The cell was discharged at 25 A until the terminal voltage fell to 1.75 V. The time, in minutes, taken for the terminal voltage to reach this limit is the reserve-capacity. The test was repeated until the measured reserve-capacity had fallen to 50% of the rated value (40 min).

3. Results and discussion

3.1. Leady oxide

Phase-analysis data for the leady oxide used in this study, together with the range of compositions expected for a typical Barton-pot oxide [4] are given in Table 2. The results show that the phase composition of the test oxide falls within the values normally expected for the Barton-pot variety. It should be noted, however, that the high free-lead (Pb) and low β -PbO contents suggest that the process temperature used in the manufacture of this oxide was on the low side. In the

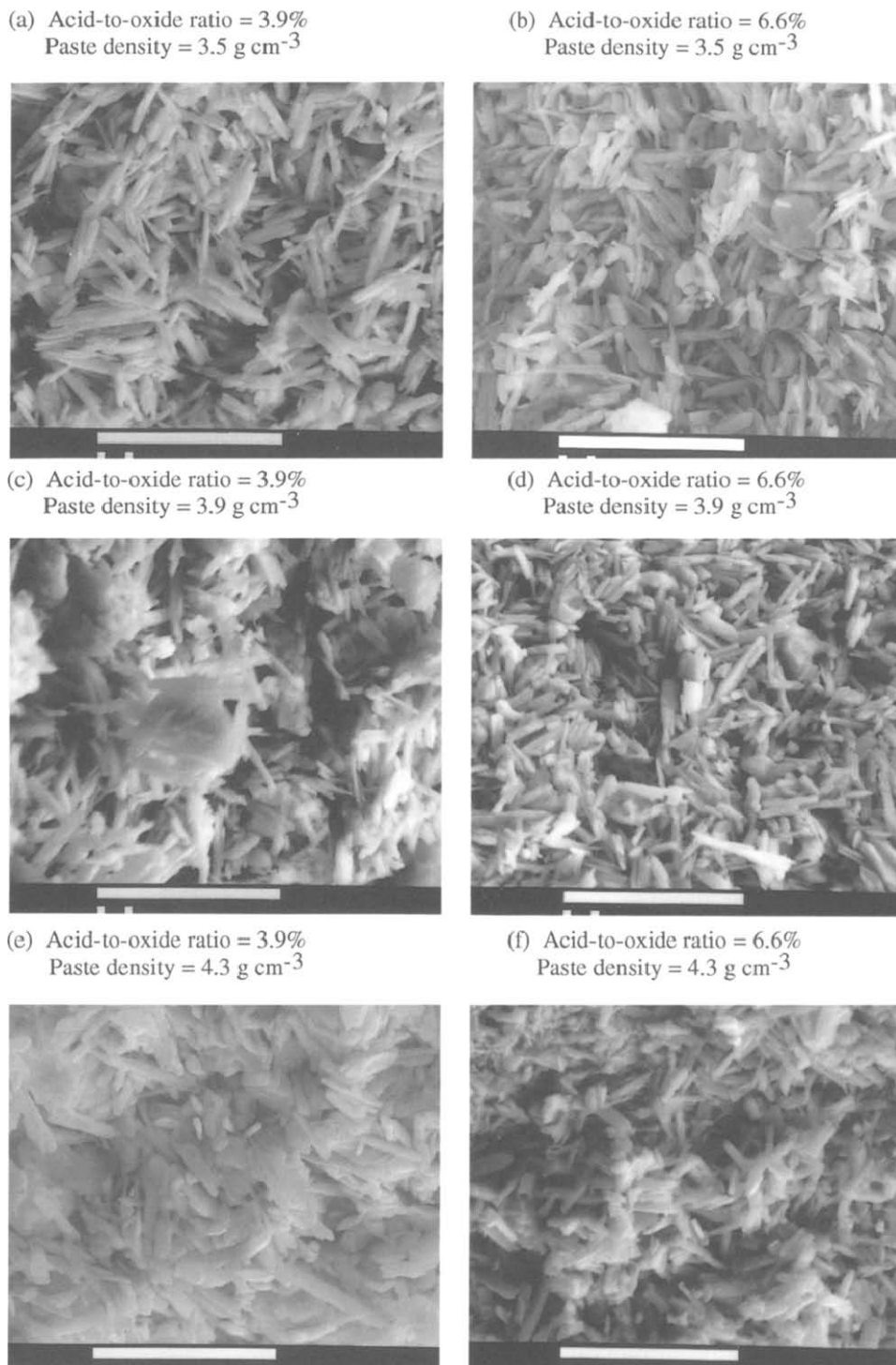


Fig. 3. Electron micrographs of paste material prepared from different acid-to-oxide ratios and paste densities. Magnification bar: 10 μm .

Barton-pot method, lead is melted and introduced into a chamber where an agitator atomizes the molten mass to produce fine droplets. The latter are oxidized to α -PbO by a stream of air at temperatures between 330 and 400 °C. Further heat is generated during the oxidation so that the temperature at the surface of some of the lead particles can reach up to 500 °C. This brings about the conversion of α -PbO to β -PbO.

The leady oxide will contain a higher amount of free-lead, and a lower level of β -PbO, when the pot is operated at a lower temperature, and vice versa.

Scanning electron microscopic studies show that the oxide phase consists mainly of individual 'particles' of varying shape and with diameters in the range 2–10 μm (Fig. 1(a)). At higher magnification, however, micrographs reveal that the 'particles' are, in fact, ag-

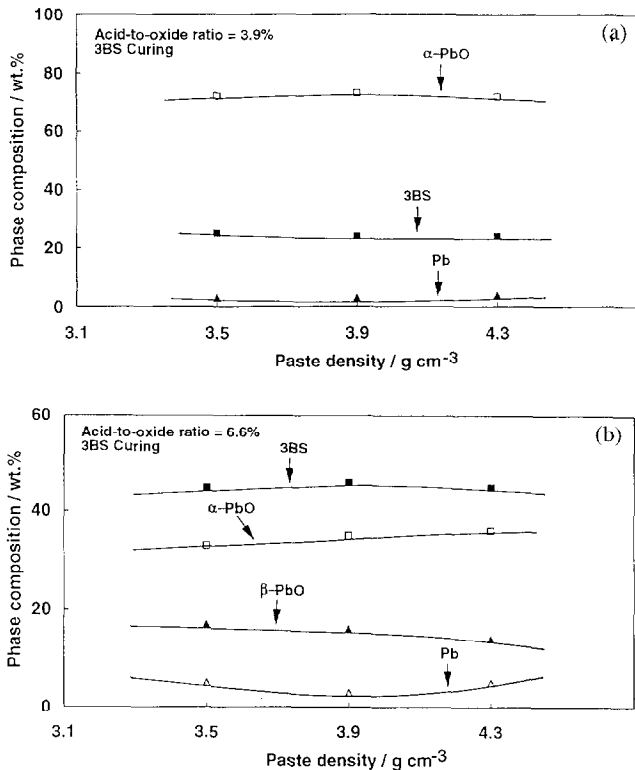


Fig. 4. Effect of paste density and acid-to-oxide ratio on phase composition of 3BS-cured plates.

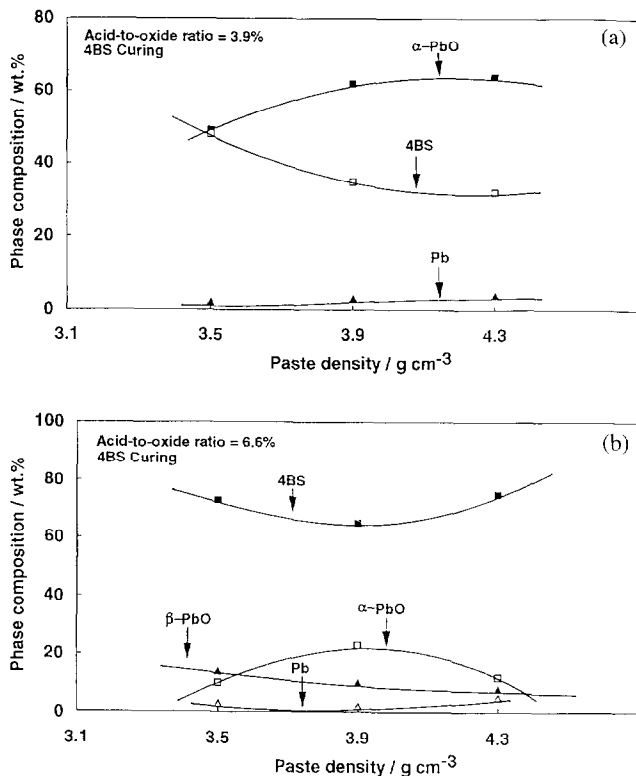


Fig. 5. Effect of paste density and acid-to-oxide ratio on phase composition of 4BS-cured plates.

gregates of various tiny grains with sizes less than 2 μm (Fig. 1(b), (c)). Furthermore, the aggregates are found to contain numerous small pores (Fig. 1(c)). The latter serve to increase the surface area and, hence, the reactivity of the oxide.

A value of $0.90 \pm 0.05 \text{ m}^2 \text{ g}^{-1}$ was obtained for the specific surface area of the test leady oxide. The reactivity was found to be 158 mg H_2SO_4 per gram of leady oxide. These properties show that the leady oxide used in this work is of good quality.

3.2. Paste materials

Phase-analysis data for pastes produced from various acid-to-oxide ratios and densities are given in Fig. 2(a), (b). The data clearly indicate that, at a given acid-to-oxide ratio (3.9 or 6.6%), a change in paste density does not influence greatly the phase composition of the paste. By contrast, at a fixed paste density, the acid-to-oxide ratio exerts a significant effect on the paste composition. In particular, the level of tribasic lead sulfate ($\text{PbO} \cdot \text{PbSO}_4$, 3BS) is enhanced on increasing the ratio from 3.9 to 6.6%.

Density is one of the parameters that is used to characterize the paste; it determines the degree of bonding between the active-material particles under static conditions. The concept of paste density implies a solid-liquid system in which the solid particles are separated by the liquid phase. The greater the quantity of liquid, the lower the paste density and the greater the porosity of the active mass. Therefore, paste density determines the main physical characteristics of the finished plates, i.e., porosity, surface area, and the contact between particles.

Reaction between sulfuric acid and the oxide results in the formation of basic lead sulfates. During paste mixing at temperatures $< 60^\circ\text{C}$, 3BS and monobasic lead sulfate ($\text{PbO} \cdot \text{PbSO}_4 = 1\text{BS}$) can be formed. The relative proportions of these two species depend upon the acid-to-oxide ratio [5]. The 1BS variety is harmful to battery performance [6]. For the range of acid-to-oxide ratios used in this work (i.e., 3.9–6.6%), however, only relatively small amounts of 1BS develop in the paste. These are unlikely to cause any serious detrimental effects during subsequent cycling duty. As expected, the yield of 3BS increases with increase in the acid-to-oxide ratio (compare Fig. 2(a) with 2(b)).

Scanning electron micrographs show clearly that the morphology of the paste changes from the spherical shape of the precursor oxide to the needle-like form of 3BS crystals (Fig. 3). The size of the 3BS crystals is affected markedly by the acid-to-oxide ratio: the needles become smaller when a high acid-to-oxide ratio is used.

In summary, a change in paste density exerts little influence on either the phase composition or the morphology/grain-size of the paste. By contrast, the acid-

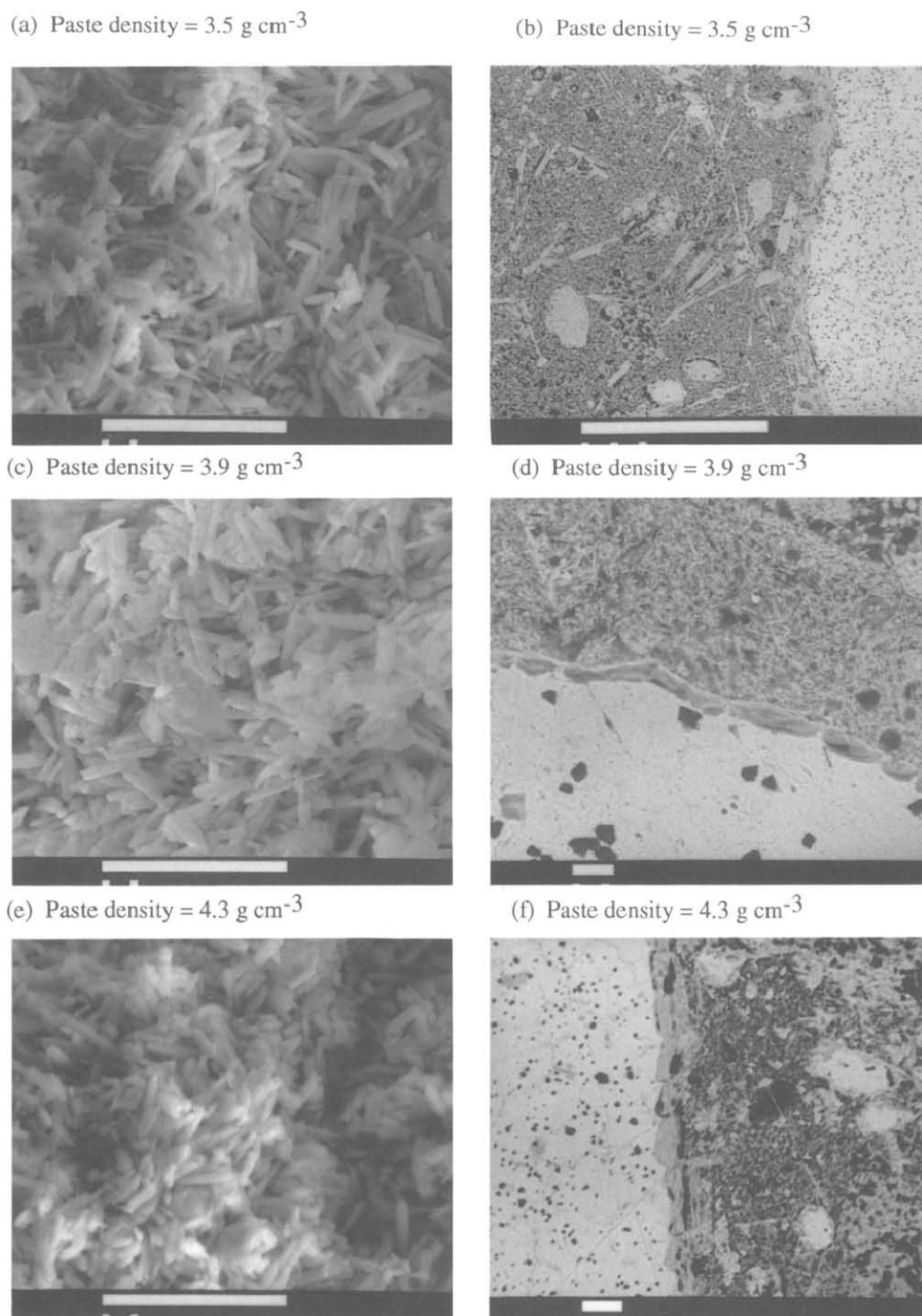


Fig. 6. Electron micrographs of 3BS-cured material produced from 6.6% acid-to-oxide ratio and different paste densities. Magnification bar: (a), (c), (d), (e), (f) 10 μm ; (b) 100 μm .

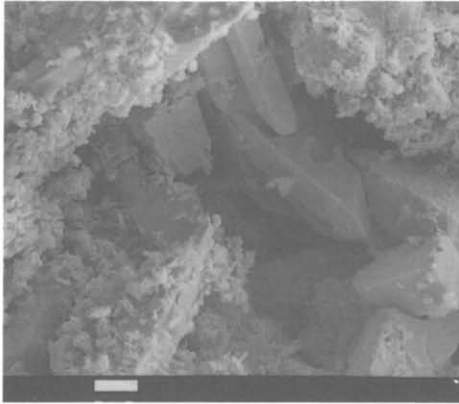
to-oxide ratio determines both the level and the crystal size of the 3BS in the paste. The yield of 3BS becomes greater, and the size becomes smaller, when a high acid-to-oxide ratio is used. Similar phenomena were also observed in our earlier studies [7].

3.3. Cured materials

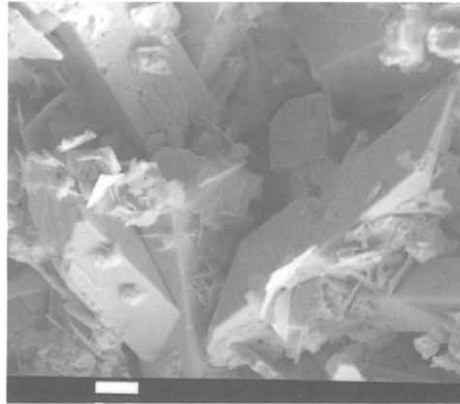
Investigations have shown that the following processes generally occur during the curing of pasted plates [5,8–10]:

- (i) oxidation of free lead (i.e., $\text{Pb} \rightarrow \text{PbO}$) with liberation of heat
- (ii) conversion of lead monoxide to basic lead sulfates (to promote binding between the individual particles of the material)
- (iii) recrystallization and interconversion of basic lead sulfates
- (iv) paste consolidation by evaporation of moisture from the plate
- (v) mild corrosive attack of the metal grid (to promote an interlock between the grid and the active material).

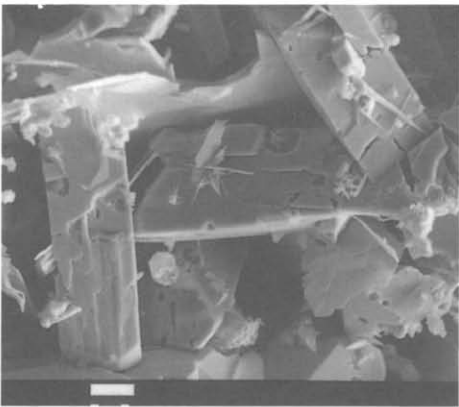
(a) Acid-to-oxide ratio = 3.9%
Paste density = 3.5 g cm^{-3}



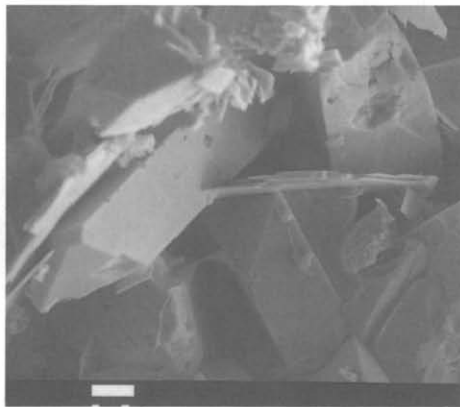
(b) Acid-to-oxide ratio = 6.6%
Paste density = 3.5 g cm^{-3}



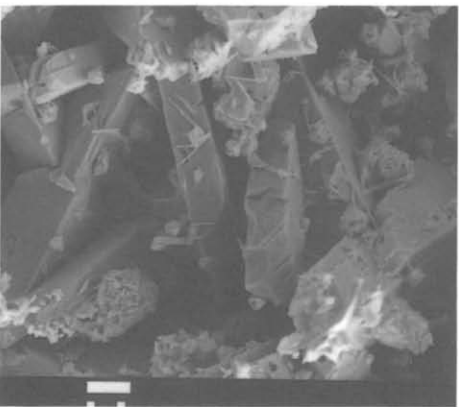
(c) Acid-to-oxide ratio = 3.9%
Paste density = 3.9 g cm^{-3}



(d) Acid-to-oxide ratio = 6.6%
Paste density = 3.9 g cm^{-3}



(e) Acid-to-oxide ratio = 3.9%
Paste density = 4.3 g cm^{-3}



(f) Acid-to-oxide ratio = 6.6%
Paste density = 4.3 g cm^{-3}

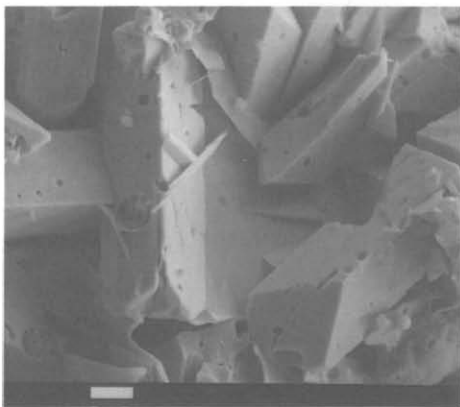


Fig. 7. Electron micrographs of 4BS-cured material produced from different acid-to-oxide ratios and paste densities. Magnification bar: $10 \mu\text{m}$.

Collectively, these reactions cause the plate material to harden and form a strong bond with the grid.

The chemical composition of the cured plate is largely dependent on the temperature and humidity conditions that are applied during the process [10]. At low temperature (below $\approx 70 \text{ }^\circ\text{C}$) and high humidity (95% r.h.),

3BS is the dominant species. At high temperature (above $\approx 70 \text{ }^\circ\text{C}$), 3BS converts to tetrabasic lead sulfate ($4\text{PbO}\cdot\text{PbSO}_4 = 4\text{BS}$), given that adequate water is present and sufficient time is allowed for the chemical reaction to develop. In this study, curing was performed at either low temperature ($50 \text{ }^\circ\text{C}$) or high temperature ($90 \text{ }^\circ\text{C}$), with 95% r.h.

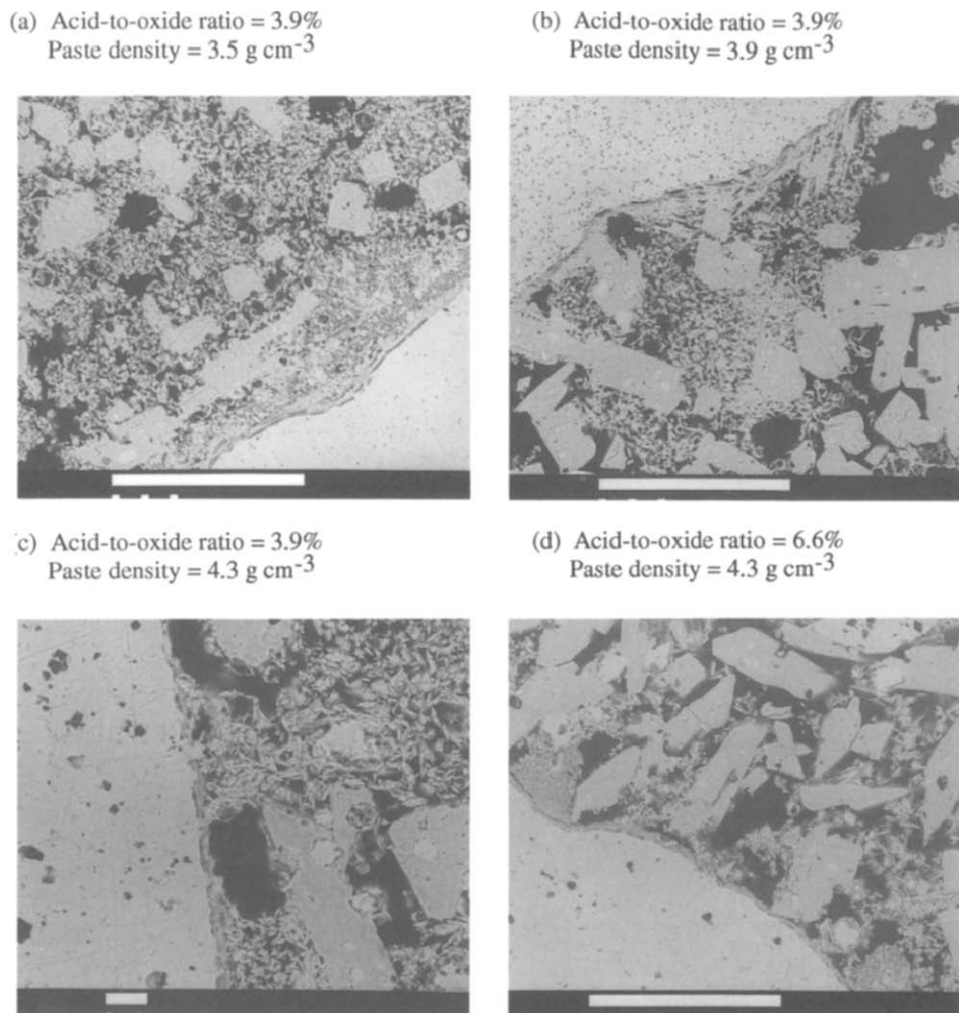


Fig. 8. Electron micrographs of cross sections of 4BS-cured plates produced from different acid-to-oxide ratios and paste densities. Magnification bar: (a), (b), (c) 10 μm ; (d) 100 μm .

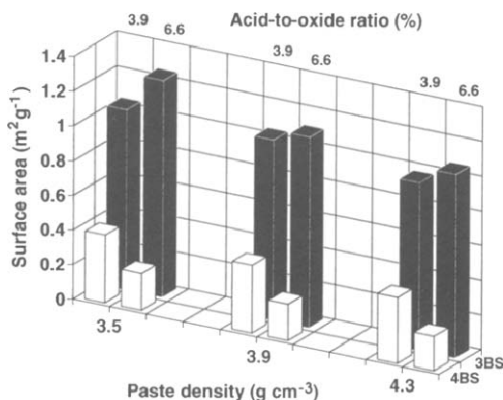


Fig. 9. Effect of acid-to-oxide ratio and paste density on surface area of 3BS- and 4BS-cured plates.

Phase-analysis data for materials produced from pastes cured under either low-temperature/high-r.h or high-temperature/high-r.h are presented in Figs. 4 and 5, respectively. At a low curing temperature, the phase composition is close to that of the precursor paste, except for the further reduction of free-lead (due to

the conversion of this material to PbO) and the disappearance of 1BS (compare Fig. 4 with Fig. 2). Curiously, with a high acid-to-oxide ratio, the free-lead is converted mainly to β -PbO rather than to α -PbO. At a given acid-to-oxide ratio, a change in paste density does not induce any major differences in phase composition (Fig. 4(a), (b)).

When the plates are cured at 90 $^{\circ}\text{C}$ (Fig. 5(a), (b)), the levels of both free-lead and α -PbO decrease from those registered in the paste, while the 3BS content disappears due to the formation of 4BS. For a fixed acid-to-oxide ratio, the yield of the latter material remains virtually constant with increasing paste density, except in the case of plates produced from a 3.9% ratio and a 3.5 g cm^{-3} density. In the latter case, the level of 4BS is higher than that in a paste with a density of 3.9 or 4.3 g cm^{-3} .

Electron micrographs of materials produced from a paste with a high acid-to-oxide ratio (6.6%) and cured at low temperature are shown in Fig. 6. The 3BS crystals are slightly larger than those in the precursor paste

Table 3
Phase analysis (wt.%) of formed materials

Experimental conditions	Phase composition			
	α -PbO	β -PbO ₂	PbSO ₄	4BS
Paste P1: acid-to-oxide ratio = 3.9%; density = 3.5 g cm ⁻³				
3BS	21	52	27	
4BS	33	28	29	10
Paste P2: acid-to-oxide ratio = 6.6%; density = 3.5 g cm ⁻³				
3BS		84	16	
4BS	6	18	56	20
Paste P3: acid-to-oxide ratio = 3.9%; density = 3.9 g cm ⁻³				
3BS	26	62	12	
4BS	39	22	21	18
Paste P4: acid-to-oxide ratio = 6.6%; density = 3.9 g cm ⁻³				
3BS		48	52	
4BS		13	87	
Paste P5: acid-to-oxide ratio = 3.9%; density = 4.3 g cm ⁻³				
3BS	15	85		
4BS	45	13	20	22
Paste P6: acid-to-oxide ratio = 6.6%; density = 4.3 g cm ⁻³				
3BS	4	69	27	
4BS		22	34	44

(compare Fig. 6 (a), (c), (e) with Fig. 3 (a), (c), (e)). This indicates that recrystallization of 3BS has occurred during the curing process. Furthermore, the degree of crystal aggregation increases with the paste density. The cross sections of these cured plates reveal clearly that there is good contact between the active material and the grid member, and that a corrosion layer has developed during curing. Similar phenomena are also observed for cured plates produced from paste with a low acid-to-oxide ratio, except that the size of the 3BS crystals is slightly larger.

Electron micrographs of materials produced from either a high or a low acid-to-oxide ratio and cured at high temperature are presented in Fig. 7. The cured plates now contain large, rectilinear 4BS crystals. At a given acid-to-oxide ratio, the morphology/size of these crystals does not change appreciably with paste density (compare (a) with (c), (e), and (b) with (d), (f) in Fig. 7). By contrast, at a given paste density, the size of the 4BS crystals increases when a high acid-to-oxide ratio is used (compare (a) with (b), (c) with (d), (e) with (f) in Fig. 7). Again, there is a good contact between the cured material and the grid member (Fig. 8).

The BET surface areas of the cured materials prepared from different acid-to-oxide ratios and different paste densities are presented in Fig. 9. For each acid-to-oxide ratio, the surface area of 3BS-cured material decreases slightly with increase in paste density, while the surface area of 4BS-cured material remains largely unchanged. For the same paste density, the 3BS-cured plates produced from a low acid-to-oxide ratio have a

lower surface area than those prepared from a high ratio. This is because the size of 3BS crystals is larger when the cured plates are obtained from a paste with a low acid-to-oxide ratio (see Fig. 3). By contrast, the 4BS-cured plates produced from a low acid-to-oxide ratio display greater surface area than plates prepared from a high ratio. This is because the cured plates made from a low ratio contain a lower yield of 4BS with smaller crystals.

3.4. Formed materials

Phase-analysis data for the formed materials produced from different acid-to-oxide ratios and paste densities are given in Table 3. The results show that the formed plates derived from 4BS-rich material still contain appreciable levels of unoxidized residues, i.e., PbO, PbSO₄, and 4BS itself. Furthermore, the amount of β -PbO₂ in formed 3BS plates is greater than that in formed 4BS varieties. This indicates that the 4BS-cured plates are more difficult to convert. A change in either the acid-to-oxide ratio or the paste density does not exert a consistent effect on the phase composition of the formed 3BS or 4BS plates.

The 3BS-formed plates, produced from different acid-to-oxide ratios and paste densities, exhibit similar morphology. The material consists of a mixture of large, shapeless agglomerates of individual crystals in the form of tiny anhedral and needle-like grains (Fig. 10(a), (b)). By contrast, the inherent interlocking structure of the 4BS-cured plates is not destroyed completely during the subsequent formation stage (Fig. 10(c), (d)). The surface of the 4BS is converted into a large number of fine PbO₂ crystals, but the interior of the 4BS remains unoxidized. Unconverted PbSO₄ particles are also observed in the active mass. Examination of polished cross sections of 3BS- and 4BS-based plates (Fig. 11(a), (b) and Fig. 11(c), (d), respectively) reveal that there is a strong bonding between the active material and the grid member.

The BET surface areas of formed materials prepared from different acid-to-oxide ratios and different paste densities are presented in Fig. 12. For the same paste density, the surface areas of both 3BS- and 4BS-based materials increase with increase in the acid-to-oxide ratio. Furthermore, with a low acid-to-oxide ratio, the surface area of both types of material decreases with increase in the paste density. This trend, however, does not follow for both 3BS- and 4BS-formed materials that are produced from paste with a high acid-to-oxide ratio. The surface area remains virtually unchanged when the paste density is increased from 3.5 to 3.9 g cm⁻³, but decreases significantly with further increase in density. In all cases, the surface areas of the 3BS-formed plates are appreciably larger than those of 4BS varieties.

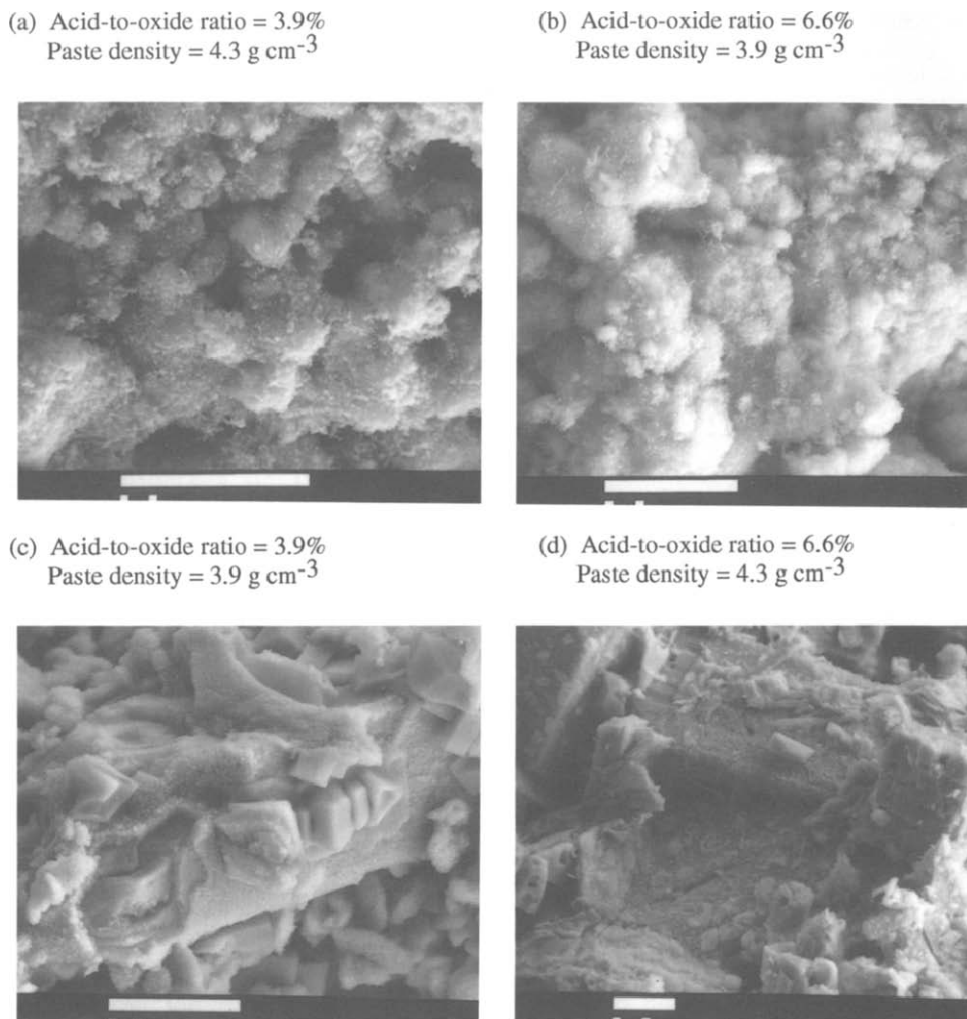


Fig. 10. Electron micrographs of: (a), (b) 3BS-formed plates; (c), (d) 4BS-formed materials. Magnification bar: $10 \mu\text{m}$.

The pore characteristics of the formed materials produced from various acid-to-oxide ratios and paste densities are shown in Fig. 13. For formed plates derived from 4BS-cured plates, the percentage of pores (i.e., the porosity) and the total pore volume are both lower than those for the 3BS counterparts, except in the case of plates made from paste with a 3.9% acid-to-oxide ratio and a 3.5 g cm^{-3} paste density. In the latter plates, the respective magnitudes of the two pore characteristics are reversed (Fig. 13(a), (b)). For the same paste density, the porosity and the total pore volume of 3BS-formed plates both tend to increase when the acid-to-oxide ratio is increased from 3.9 to 6.6%. The situation is not so clear cut with 4BS-formed plates. The data show that the porosity and total pore volume increase with increase in the acid-to-oxide ratio for 4BS plates produced from a 3.5 g cm^{-3} paste density, but that both parameters decrease in plates made from the two higher densities.

In general, two kinds of pores exist in formed plates, namely, macropores and micropores [7,11,12]. Macropores contribute mainly to the pore volume and provide

a transport pathway for reaction species from the bulk of the solution to the reactive sites. Micropores give rise to a high surface area that allows the electrochemical reactions to proceed at useful rates during charge and discharge. The volume generated by the macropores (i.e., pores with diameter $>0.1 \mu\text{m}$) in each of the 3BS- and 4BS-formed plates is presented in Fig. 13(c). Unlike the total pore volume, the macropore volume is generally larger for plates derived from 4BS-cured material. This is because the formed plate still retains the open and interlocking structure of the precursor 4BS-cured plate

3.5. Active-material utilization

The active-material utilization represents the percentage of material that participates in the discharge process. It is defined as the ratio between the measured capacity, taken at a particular rate of discharge, and the corresponding theoretical capacity. The latter capacity is equivalent to discharging the total amount of PbO_2 in the formed plates to PbSO_4 at 100% efficiency.

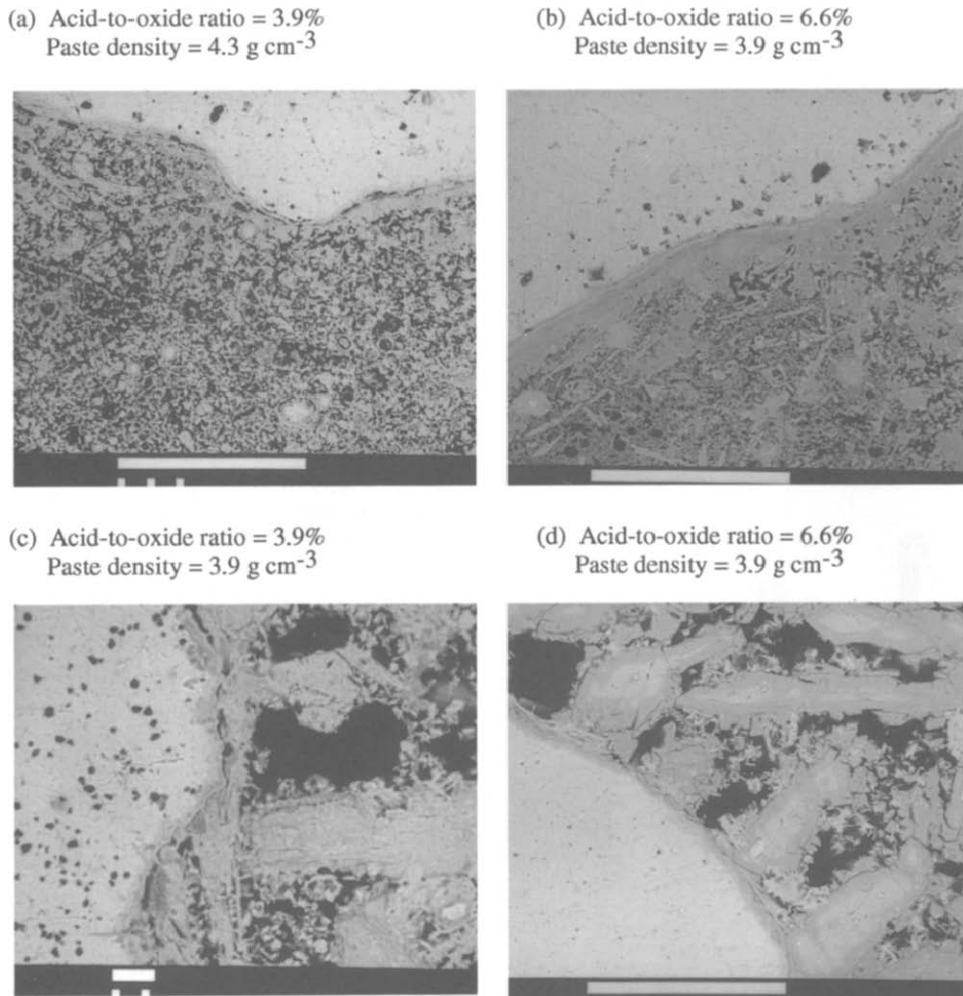


Fig. 11. Electron micrographs of cross sections of: (a), (b) 3BS-formed plates; (c), (d) 4BS-formed plates. Magnification bar: (a), (b), (d) 100 μm ; (c) 10 μm .

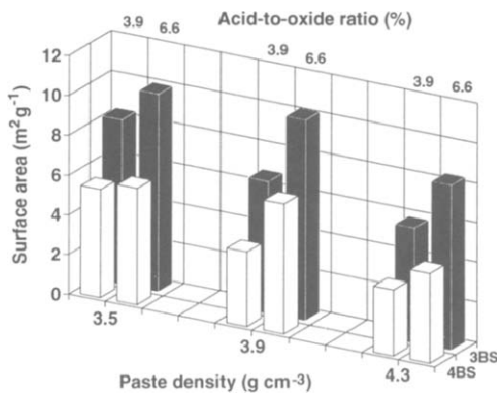


Fig. 12. Effect of acid-to-oxide ratio and paste density on surface area of 3BS- and 4BS-formed plates.

The value is calculated to be 0.229 Ah per gram of cured material.

Active-material utilization in cells prepared from different acid-to-oxide ratios and paste densities is given in Fig. 14. As expected, the active-material utilization of all cells increases as the rate of discharge is decreased from 5-h to 20-h rates. For a paste density of either

3.9 or 4.3 g cm^{-3} , the level of active-material utilization in 3BS cells is similar at both rates, irrespective of a change in the acid-to-oxide ratio. By contrast, the active-material utilization in 4BS cells with a paste density of 4.3 g cm^{-3} is increased at either rate when the acid-to-oxide ratio is increased from 3.9 to 6.6%. With a paste density of 3.5 g cm^{-3} , the active-material utilization in both 3BS and 4BS cells increases with an increase in the acid-to-oxide ratio. In general, cells produced via the 4BS-curing route exhibit higher active-material utilization than their 3BS counterparts. Surprisingly, the effect of a progressive increase in paste density on the active-material utilization in both types of cells at either rate is relatively small.

3.6. Repetitive reserve-capacity

The cycle life of cells produced from different acid-to-oxide ratios and paste densities was evaluated in terms of repetitive reserve-capacity. The results are presented in Fig. 15. At a given acid-to-oxide ratio, the cycle life of the cells increases significantly with

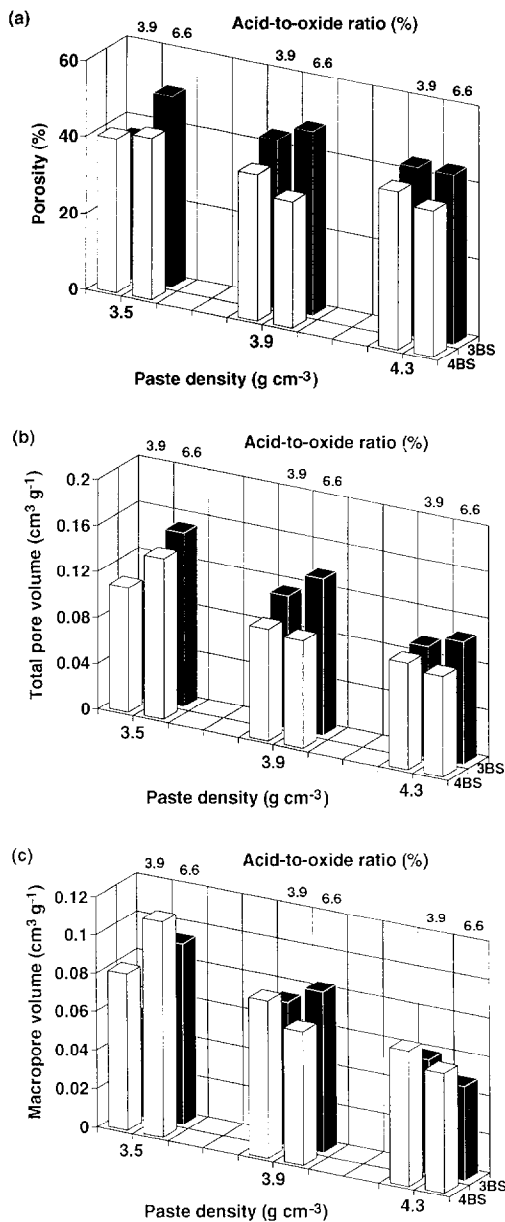


Fig. 13. Effect of acid-to-oxide ratio and paste density on the pore characteristics of 3BS- and 4BS-formed plates.

increase in paste density. For the same paste density, a further increase in cycle life is observed when the acid-to-oxide ratio is reduced from 6.6 to 3.9%. The cells produced from 4BS-cured plates display inferior cycle life compared with 3BS varieties. This finding is opposite to that usually observed with motive-power batteries and argues the case for an improved 4BS-curing technique over the traditional method that has been adopted here [10].

Despite wide differences in electrical loads and driving conditions, certain 'standard' tests have been correlated with in-car battery service. Thus, if the tests are satisfactory, there is every assurance that the battery design will be capable of performing well on the road. As

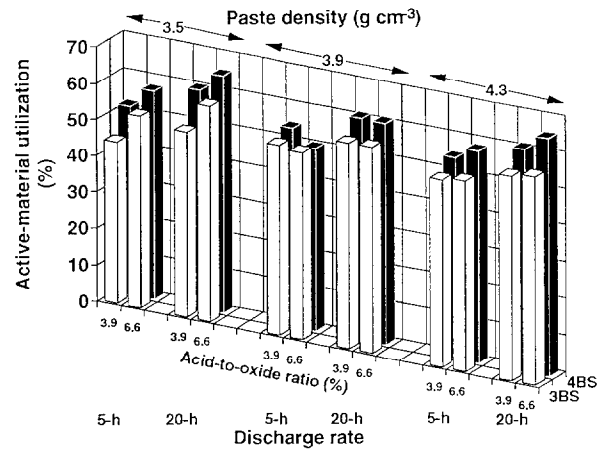


Fig. 14. Effect of acid-to-oxide ratio and paste density on active-material utilization in 3BS- and 4BS-based cells.

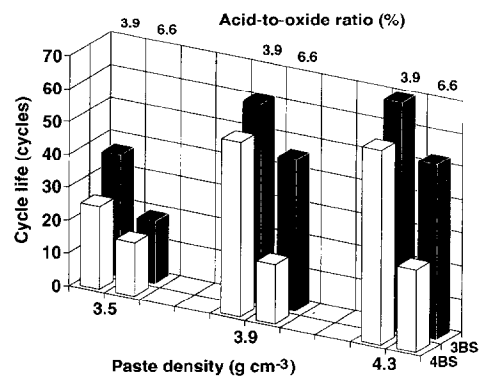


Fig. 15. Effect of acid-to-oxide ratio and paste density on cycle life (repetitive reserve-capacity) of 3BS- and 4BS-based cells.

mentioned above, the main function of the battery in a vehicle is to start the engine in all weather conditions and to ensure operation in the event of failure of the electrical recharging system. Having this in mind, two specifications have been formulated for the evaluation of automotive batteries, namely, cold-cranking and reserve-capacity performance tests. The first procedure characterizes the starting ability of a battery at cold temperatures, while the second is a capacity test at a discharge rate that is approximately equal to the electrical load of the auxiliary equipment in the car.

The cold-cranking performance of automotive batteries is 'negative-potential limited' [7]. During discharge, the potential of the negative plate is the first to reach the cut-off value, even though the total weight of negative material in the battery is greater than that of the positive material. This behaviour is due to the much lower surface area of the negative plate compared with that of the positive plate, i.e., 2–3 versus 6–10 m² g⁻¹. Thus, the cold-cranking ability of a battery is governed by the characteristics of the negative plates and, consequently, is not affected by a change in paste density of the positive plates. In order to raise the cold-cranking ability, manufacturers usually increase

the respective numbers of positive and negative plates per cell through reduction of the plate thickness. This approach will, however, decrease the cycle life of batteries.

4. Conclusions

This study has provided a detailed evaluation of the influence of both the density and the acid-to-oxide ratio of the paste, as well as the conditions of the subsequent curing process, on the active-material utilization and cycleability of positive plates (with low-antimony grids) in automotive lead/acid batteries. The following conclusions can be drawn.

(i) A change in paste density produces little effect on either the phase-composition/morphology of the paste, cured and formed materials, or the capacity performance of the resulting cells. It does, however, exert a significant impact on the cycleability of the batteries: the cycle life is enhanced by an increase in paste density, especially for paste prepared with a low acid-to-oxide ratio.

(ii) The acid-to-oxide ratio used in the paste formulation is found to be the main determinant of the yield/size of 3BS and 4BS crystals in both the paste and the cured material. The levels of 3BS and 4BS both increase, the size of 3BS decreases, and the size of 4BS increases when using a high acid-to-oxide ratio.

(iii) Formed plates derived from conventional 4BS-cured material display lower surface area, porosity and total pore volume, but higher macropore volume, than those produced from the 3BS counterpart.

(iv) At low paste density (3.5 g cm^{-3}), the active-material utilization generally increases with increase in the acid-to-oxide ratio. By contrast, an increase in paste density has little effect on the capacity performance of the batteries. Overall, 4BS-based cells display better active-material utilization than 3BS varieties.

(v) At all paste densities, cycle life (repetitive reserve-capacity) increases with a decrease in the acid-to-oxide ratio, irrespective of curing conditions. The cycle life of 3BS-based cells is superior to that of 4BS-based types.

5. Summary

A paste with a 4.3 g cm^{-3} density and a 3.9% acid-to-oxide ratio, and cured to give 3BS, is particularly appropriate for the production of thin automotive positive plates that use low-antimony alloys. Such processing will provide the battery with both a high cold-cranking ability and a good reserve-capacity (by increasing the number of plates), together with a long service life.

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