

# Improvements to active material for VRLA batteries

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## Abstract

In the past several years, there have been many developments in the materials for lead–acid batteries. Silver in grid alloys for high temperature climates in SLI batteries has increased the silver content of the recycled lead stream. Concern about silver and other contaminants in lead for the active material for VRLA batteries led to the initiation of a study by ALABC at CSIRO. The study evaluated the effects of many different impurities on the hydrogen and oxygen evolution currents in float service for flooded and VRLA batteries at different temperatures and potentials.

The study results increased the understanding about the effects of various impurities in lead for use in active material, as well as possible performance and life improvements in VRLA batteries. Some elements thought to be detrimental have been found to be beneficial. Studies have now uncovered the effects of the beneficial elements as well as additives to both the positive and negative active material in increasing battery capacity, extending life and improving recharge.

Glass separator materials have also been re-examined in light of the impurities study. Old glass compositions may be revived to give improved battery performance via compositional changes to the glass chemistry. This paper reviews these new developments and outline suggestions for improved battery performance based on unique impurities and additives.

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## 1. Introduction

The lead–acid battery has always suffered from poor utilization of the active material. During discharge, the positive and negative active materials react with the sulfuric acid of the electrolyte to form lead sulfate. Lead sulfate is an insulator, which increases the resistance of the active material as the discharge reaction continues. The active material also experiences an expansion as the positive  $\text{PbO}_2$  and negative sponge lead are converted to  $\text{PbSO}_4$ . The expansion can interfere with the integrity of the active material and its adherence to the grids. In addition to the expansion, the active material must undergo a dissolution and precipitation reaction at each charge–discharge cycle. The active material is altered in its reactivity as the structure changes shape and conductivity during the cycling of the battery leading to lower capacity.

As the battery ages, accumulations of  $\text{PbSO}_4$  and impurities in the active material, as well as those leached from the grids in the corrosion process, can hinder the recharge process

and decrease the ability to be fully recharged. Since impurities can influence the recharge process by modifying the oxygen and hydrogen gassing currents, attempts have been made to understand the effects of impurities on the discharge and recharge process. The concern about gassing in VRLA batteries has increased the need to understand the effects of impurities and additives to the active material on life, capacity, recharge, and stability of the batteries.

Over the past 10 years there has been a tremendous amount of research into grid alloys to reduce positive grid corrosion particularly at elevated temperatures for both SLI and cycling batteries. These batteries use non-antimony lead alloys. Silver additions to lead calcium tin alloys have dramatically decreased the rate of corrosion of the positive grids particularly at elevated temperatures. Silver introduced into the grid alloys has dramatically increased the silver content of the recycled lead stream. As the amount of recycled lead used for the active material has increased, the concern about its effect on the performance and life of the battery has increased.

In 1998, the ALABC decided to perform research into the effects of not only silver, but also 16 different impurities on the oxygen and hydrogen gassing currents of both wet and VRLA batteries on float service. These results as well as other ALABC projects related to partial-state-of-charge cycling have led to an improved understanding of the effects of not only impurities, but also additives to the active materials of the lead–acid battery. There have been a number of new additives and modifications to the active material over the past several years, which offer the benefits of higher capacity, longer life, improved recharge, and improved uniformity in the performance of the active material from plate to plate.

Based on these studies, additional research has indicated the benefit of additives to the active material and plate surface, which increase the capacity of the active material from the use of glass fibers, pasting papers, and graphitic carbon.

## 2. Impurities studies

There have been several investigations about the effects of impurities on the gassing characteristics of lead–acid batteries. Pierson et al. [1] described the effects of various impurities added to the electrolyte on gassing. The research collected the gases generated from a cell held at a temperature of 51.7 °C and subjected to a constant potential of 2.35 V for 4 h. The electrolyte was doped with various impurities at levels of 0.1–5000 ppm or until the electrolyte became saturated with the impurity. The most deleterious elements toward gassing are tellurium, antimony, arsenic, nickel, cobalt and magnesium. Tin, zinc, cadmium, calcium, lithium, and mercury had no discernable effect at the maximum concentrations. Silver,

bismuth, copper, cerium, chromium, and molybdenum were acceptable at levels of 500 ppm or less in the electrolyte.

Prengaman [2] and Rice et al. [3] have proposed pure lead specifications from recycled and primary lead, which reduce the levels of gas-causing impurities to very low levels. While these limits were accepted for SLI batteries, many manufacturers required 99.99% lead for the active material of traction and stationary batteries. In 2000, the advanced lead–acid battery consortium (ALABC) commissioned a study at CSIRO in Australia. [4]. The study ALABC Project N 3.1 “Influence of Residual Elements in Lead on the Oxygen and Hydrogen-Gassing Rates of Lead-Acid Batteries” examined the effects on VRLA batteries as wet cells.

The study systematically evaluated the influence of the 17 elements considered to be of the most immediate significance to the production of oxygen at the positive and hydrogen at the negative plates in VRLA batteries on float charge. As expected, some elements aggravated the problem of gas generation at the electrodes, while other elements were found to suppress the production of gas. Fig. 1 shows the effects of the various elements studied in the project. The table shows the effect of the increase or decrease in the oxygen or hydrogen gassing current in mA Ah<sup>-1</sup> of battery capacity per 1 ppm of the impurity element. It is interesting that only bismuth and zinc suppress gassing, while cadmium, germanium, and silver have virtually no effect.

In addition, some important synergistic effects were found where several of the elements were present together. For hydrogen gassing, the combined action of bismuth, cadmium, germanium, silver, and zinc gave the greatest benefit. Bismuth, silver, and zinc give the greatest single element suppression of gassing, while nickel, selenium, and tellurium ac-

Elements	Upper Level	Rate of Change (mA Ah <sup>-1</sup> per ppm)			Level		
		<i>I</i> float	<i>I</i> hydrogen	<i>I</i> oxygen	<i>I</i> float	<i>I</i> H <sub>2</sub>	<i>I</i> O <sub>2</sub>
	(ppm)						
Ni	10	+0.03772	+0.00019	+0.03772	4	16	4
Sb	10	+0.01860	+0.00059	+0.01828	6	5	6
Co	10	+0.04332	+0.00109	+0.04252	4	7	4
Cr	5	+0.01782	+0.00016	+0.01774	7	16	7
Fe	10	+0.01958	+0.00014	+0.01951	6	19	6
Mn	3	+0.04643	+0.00080	+0.04543	5	5	5
Cu	10	+0.00625	+0.00038	+0.00583	33	13	34
Ag	20	+0.00097	+0.00006	+0.00103	76	165	66
Se	1	+0.10410	+0.00500	+0.09950	2	1	2
Te	0.3	+0.10167	+0.00933	+0.11233	1.5	0.5	1.4
As	10	+0.00887	+0.00030	+0.00881	15	15	14
Sn	10	+0.00393	+0.00002	+0.00399	49	150	48
Bi	500	-0.00026	-0.00001	-0.00026	500?	500?	500?
Ge	500	+0.00041	+0.00001	+0.00042	673	250	658
Zn	500	-0.00003	-0.00002	-0.00001	500?	500?	500?
Cd	500	+0.00027	+0.00001	+0.00026	901	706	903

Fig. 1. Rate of change of gassing currents of impurity elements [4].

celerate the gassing markedly. For oxygen gassing, bismuth, antimony, and iron gave the greatest suppression of gassing while nickel, selenium, and tellurium were found to enhance gassing, but not to the same extent as found in accelerating the hydrogen gassing current.

When synergistic elements were added at high levels, the total gassing currents—even at high impurity levels—were reduced to levels below that of the high purity refined lead used as a standard. The reduction of gassing was maintained at higher potentials as well as higher temperatures. Gassing reactions play an important part in the failure mode of both SLI batteries with regard to water loss, and VRLA batteries with regard to poor recharge of the negative plate and production of insoluble PbSO<sub>4</sub>. The study is of such significance that it can now be used to explain many divergent results and be used to formulate new theories to improve the performance of the active materials.

### 3. Silver

#### 3.1. Silver in grid alloys

Silver was one of the elements most studied in the ALABC Project N 3.1 described above because of its importance to the lead supply to North America and Europe as more batteries are recycled and the supply of mined lead decreases. Silver has been added to lead alloys for grid and post alloys for lead–acid batteries for many years. In the past 10 years, the positive grids of SLI batteries have used the addition of 125–500 ppm silver to lead–calcium–tin alloy positive grids to reduce corrosion particularly at elevated temperatures. The benefits have been described by Prengaman [5,6] and Rao et al. [7,8].

#### 3.2. Silver in recycled lead

The silver from these batteries has entered the recycling stream in Australia, Europe and North America, which continues to grow as more silver-containing batteries are produced. Prengaman [9] has described the increase in silver in the pure lead stream in the last 10 years, and predicts that

Silver Content (ppm)	Rate of Oxidation Kg/h	Increase or (Decrease)	
		Silver only	Zero Silver
0	863.6	----	
43	814.3	(6%)	
80	708.3	(18%)	
43+Mg	881.1	8.2%	2%
80+Mg	780.3	11%	(10%)

Fig. 3. Rate of oxidation of lead in Barton pots with silver [9]. In the last two rows be first percentage change figure compares with the silver-only rate, while the second figure compares with the zero silver rate.

the average silver in recycled lead will reach about 60 ppm by 2008 in the US, and expects levels of 50 ppm or more in recycled lead in Australia, with somewhat lower levels expected for Europe. The increase in average silver content of recycled lead for active material in North America is shown in Fig. 2.

Understanding the effects of the silver content on the performance of batteries utilizing active material produced from silver-containing lead is important. There are benefits as well as negative aspects to the silver content. Silver decreases the rate of oxidation of lead in Barton pot reactors for the production of lead oxide for active material. Ball mill oxide reactors do not seem to be as sensitive to silver contents of the lead as Barton pots. Fig. 3 shows the effect of silver additions on the rate of oxide production. An increase to a level of 43 ppm reduced oxide production by about 6%, while higher levels further decrease the rate of production.

The reduced rate of oxidation can be overcome by the introduction of antimony into the metal. This has been described by Hoffmann [10] and has been utilized by many battery companies to overcome the negative effects of the higher silver contents. In applications where antimony is not desired, such as for VRLA batteries, Prengaman [9] has discovered that the addition of small amounts of magnesium to the lead will dramatically overcome the reduced rate of oxidation caused by silver as seen in Fig. 3. The magnesium also increases the rate of oxidation of lead in the curing process, leading to lower free lead levels even in the presence of high silver contents.

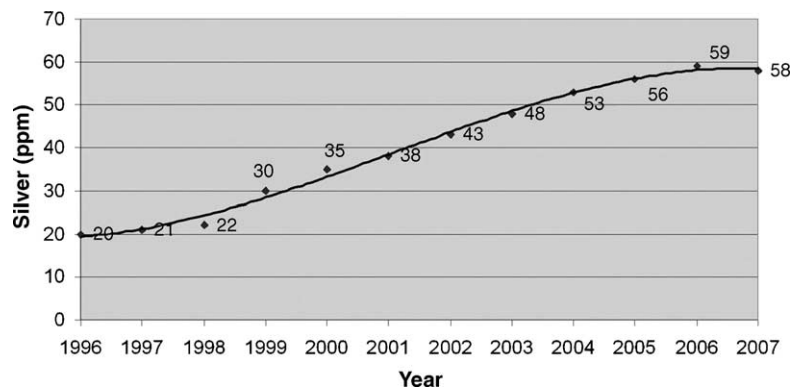


Fig. 2. Annual silver average of pure lead in North America [9].

Initial Silver Content AM (ppm)	Final Silver Content Positive (ppm)	Final Silver Content Negative (ppm)
0	1.0	32.8*
50	1.8	117.0
100	2.1	183.0
450	10.2	899.0

\* Pb-Ca-Sn-Ag Positive Grids

Fig. 4. Distribution of silver in active material after J240 75 °C cycling [11].

### 3.3. Silver in active material

Despite the information of Pierson et al. [1], silver has been considered to be a negative element for lead–acid batteries and was believed to increase the rate of hydrogen evolution. Many specifications restrict it to less than 10–15 ppm. The ALABC Project N 3.1 study indicated, however, that silver had virtually no effect on the hydrogen evolution current. There was, however, a small increase in the rate of oxygen evolution when silver was present in the positive active material. The most definitive work on the effects of silver on the performance and gassing in batteries has been performed by Lawrence [11]. The result of the investigation is shown in Fig. 4. During formation and cycling, the silver, regardless of the concentration, is transferred to the negative active material. The study used a lead–calcium–tin–silver alloy for the positive grids. The silver from the corrosion layer was also transferred to the negative material during the cycling of the batteries. In the ALABC Project N 3.1 work, the gassing current for the negative is more than 100 times lower than for the same amount of silver in the positive active material. The work also shows a beneficial effect of silver on the DIN cycling of the batteries. The results are shown in Fig. 5.

As the silver level was increased, there was a corresponding increase in the number of DIN cycles, which could be achieved. The maximum benefit seems to occur at between 50 and 100 ppm silver in the active material. The beneficial

Silver Content (ppm)	DIN Cycles	Water Loss (ml)
0	180	30
50	204	25
100	228	30
450	276	35

Silver	Transfer (ppm)	
	Initial	After Cycling
Start	Positive	Negative
0	1.6	37.7
50	2.3	117.0
100	2.9	210.9
450	18	795.4

Fig. 5. Effect of silver on DIN cycling [11].

effects may be due to the higher conductivity of the silver in the negative active material. Silver may enable the active material to conduct current even in a deeply discharged state, improving battery recharge.

## 4. Bismuth

### 4.1. Bismuth as an impurity in lead

Bismuth is a common impurity in lead. It is the most common impurity, which must be removed to reach high purity lead. Bismuth is difficult to remove by pyrometallurgical processes. The Betts electrolytic process was found to effectively remove bismuth to low levels and has been utilized around the world particularly in Asia. Bismuth must be removed from lead to reach the high purity designated 99.99%. Lower purity grades of lead permit higher levels of bismuth and silver.

### 4.2. Bismuth in active material

A study of the literature on the effects of bismuth on the active material shows conflicting results. Some results indicate that bismuth increases the rate of gassing while others indicate a reduction in the gassing currents. Pavlov et al. [12,13] have shown that bismuth in the grid alloy or in the electrolyte restores the capacity of tubular electrodes produced from bismuth-free pulverized positive active material. The bismuth doped the positive active material and formed bridges between the PbO<sub>2</sub> particles, thus forming conductive interconnecting acicular crystals, which strengthen the porous mass of the positive active material. Fig. 6 shows the beneficial effects of the bismuth in increasing the capacity of the active material in the early life cycles in both pure lead and lead 6% antimony grids. The bismuth was more effective in the pure lead grids.

In similar work, Lam et al. [14] produced cells from high purity oxide containing 500 ppm bismuth by compacting previously produced PbO<sub>2</sub>. At any compression, the bismuth containing cells gave higher initial capacity and increased the rate at which the cells increased in capacity upon cycling. This phenomenon is shown in Fig. 7. In a parallel investigation Lam et al. [15] found that batteries containing active material manufactured from lead oxide containing 0.05% bismuth and cycled in the Japanese industrial standard (JIS) or IES protocols had increased cycle life of 18–32% compared to those with high purity oxide.

The control cells failed by positive active material shedding in the JIS tests while, the active material in the bismuth-containing cells was sound. In the IES tests the control cells failed by an increase of PbSO<sub>4</sub> in the negative active material. The 32% longer life of the bismuth-containing cells indicates that bismuth improves recharge of the negative. This is shown in Fig. 8. Lam et al. [16] showed improved recharge of cells with active material containing 600 ppm bismuth cycled in a narrow partial-state-of-charge window.

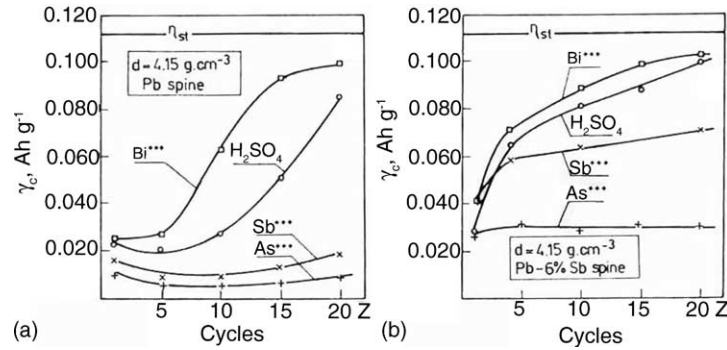


Fig. 6. Influence of bismuth ions in the electrolyte capacity [12].

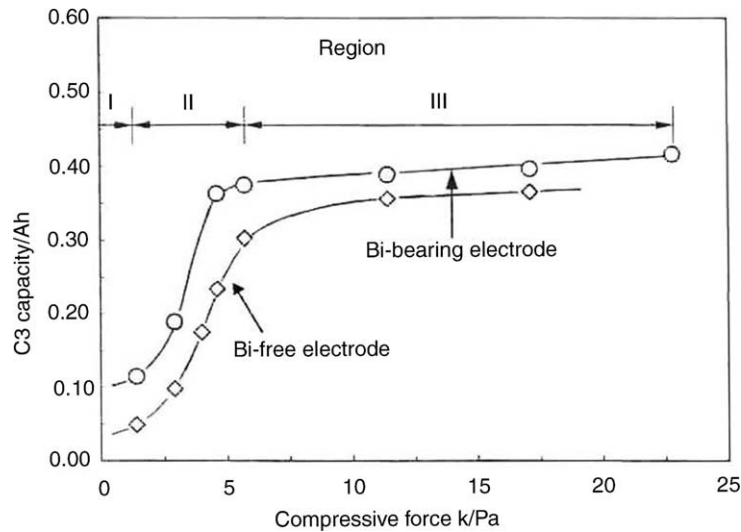


Fig. 7. Capacity of Bi-free and Bi-bearing electrodes with compression [14].

The ALABC N 3.1 study showed that lower rates of both positive and negative gassing currents could be obtained by incorporating bismuth in amounts up to 500 ppm in the active material. Combined with silver and zinc, bismuth shows synergistic benefits to lower float currents. Additional work is now being conducted in PSOC to determine the upper beneficial levels of bismuth. There is less risk of selective discharge

of the positive or negative plates, lower float currents, lower self discharge rates, improved recharge, and improved adhesion of the positive active mass. Bismuth, which has been considered a negative for many years for lead–acid batteries, must now be considered a beneficial additive—not a deleterious impurity.

## 5. Zinc

### 5.1. Zinc as an impurity in lead

Zinc is found and mined together with lead worldwide. During smelting a small amount of zinc will dissolve in the furnace bullion, but this is easily removed. Zinc as an impurity in lead has been a concern since the development of the silver removal process known as the Parkes process. The lead is saturated with zinc to produce AgZn crystals, which rise to the surface to separate the silver from the lead. About 0.06–0.2% zinc remains in the metal, which must be removed to produce high purity lead. The residual level permitted by most specifications is 10 ppm.

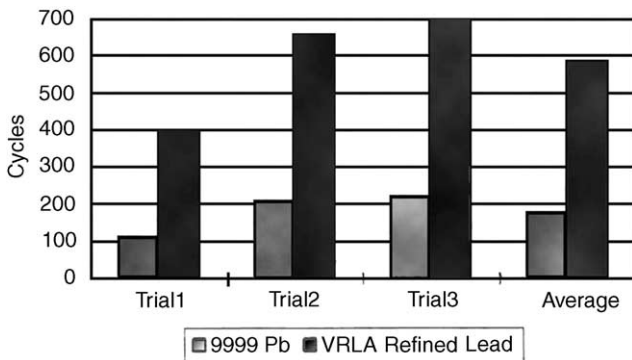


Fig. 8. Cycle life improvements with VRLA lead containing 500–600 ppm bismuth [16].



Zinc Additive to the electrolyte		Gassing current after 60 minutes float at 2.35 V / Cell 25°C	
ZnSO <sub>4</sub> (g)	Zn (g)	mA	mA/Ah
0	0	200	2.15
6	1.35	150	1.61
10	2.25*	108	1.16

\*Equivalent to 340 ppm addition to AM  
93 Ah Battery

Fig. 9. Effect of zinc on the gassing current of SLI batteries [17].

## 5.2. Zinc as a beneficial element in batteries

Zinc has been shown to be a beneficial element in reducing the float current of lead batteries. Mao and Rao [17] have shown that the addition of a small amount of zinc to the electrolyte (6 g of ZnSO<sub>4</sub>·7H<sub>2</sub>O per battery) decreases the float current of SLI batteries by almost 50% when floated at 51.6 °C and 2.35 V. Fig. 9 shows the reduction of gassing currents as a function of zinc added to the electrolyte. The addition gave the maintenance-free battery even lower water usage than that which could be attained with lead–calcium–tin alloy grids. There was no description of the impurity content of the oxide used for the active material. The authors, however, indicate that the critical nature of the impurities in the grids, which might leach during corrosion, could be lessened.

In another example, the zinc was added to the positive and negative active material in an amount of 340 ppm. This is even more effective than additions to the electrolyte. The float current at 51.6 °C is reduced by 49% at the high float voltage of 2.76 V per cell. Smaller amounts were less effective but still reduced the oxygen and hydrogen evolution float currents. Zinc additions above 340 ppm were not evaluated.

ALABC Project N 3.1 [4] revealed that zinc was the only element other than bismuth, which was effective in reducing both the positive and negative gassing currents. Based on the amount of zinc added to the active material in the Mao and Rao work, the reduction in gassing currents results are what would be predicted from the ALABC work. While the exact mechanism is not known, zinc seems to stabilize the plate potentials upon float and reduces the effects of other impurities, which might be present particularly on the negative active material. These stabilized currents should permit improved recharge and ultimately higher capacity and longer life. Higher levels of zinc are currently being evaluated.

## 6. Tin as an additive

### 6.1. Additions of tin oxide

Tin has been added to the positive active material as SnO<sub>2</sub>, or as SnO<sub>2</sub>-coated glass and carbon fibers. Atiak et al. [18]

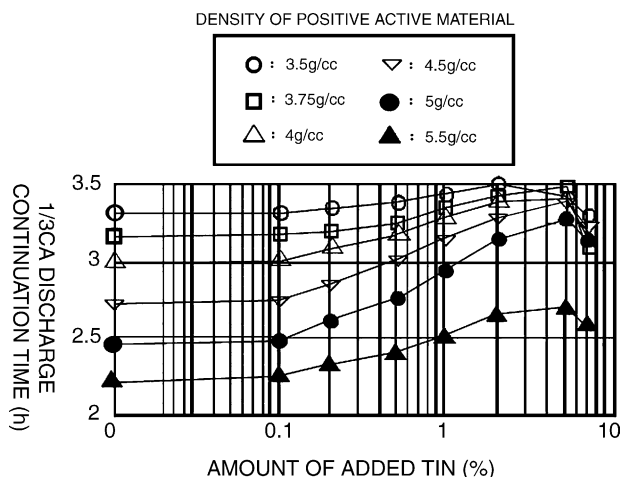


Fig. 10. Effect of tin additions to positive active material [21].

have shown that such additions improve formation efficiency and plate performance by improving the conductivity of the active material and providing improved utilization at high rates.

### 6.2. Additions of tin sulfate

Recently Shiomi et al. [19] have shown dramatically improved capacity in high density active materials with the addition of SnSO<sub>4</sub> to the positive active material paste. When the formation is performed correctly, the SnSO<sub>4</sub> is oxidized to SnO<sub>2</sub>, which dopes the newly formed PbO<sub>2</sub> and gives substantially higher capacity. Fig. 10 shows the benefits of SnSO<sub>4</sub> additive to the positive active material. Even very high density active material can yield much higher capacity than some lower density active material when doped with 1–2% of SnSO<sub>4</sub>.

The effect is not seen immediately, but requires several cycles to achieve the desired beneficial effect. The effect may be similar to that of alloying the positive grid with sufficient tin. At levels of 1–2%, the PbO<sub>2</sub> corrosion product is doped with SnO<sub>2</sub>. This provides stability to the thin corrosion product, which does not discharge to PbSO<sub>4</sub>. Stable, highly conducting doped PbO<sub>2</sub> permits improved active material utilization as well as improved recharge. Fig. 11 shows the cycling of a traction battery containing 1% SnSO<sub>4</sub> added to the positive active material. As predicted by Shiomi et al., this leads to a capacity increase of about 20%. The batteries are cycled over 200 cycles with no loss of the improved capacity. Such an additive can lead to lighter batteries or higher capacity batteries with improved active material utilization.

## 7. Antimony

Antimony has been shown to dope the positive active material during corrosion of lead antimony alloy grids. The PbO<sub>2</sub> corrosion product on lead–antimony alloys has been shown

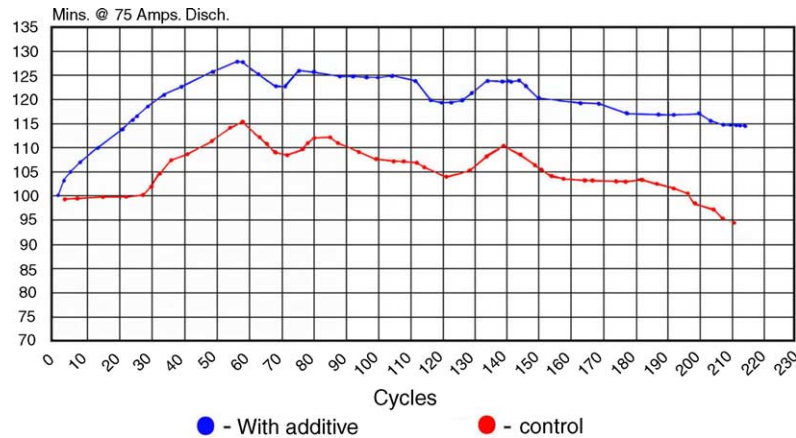


Fig. 11. Effect of 1% SnSO<sub>4</sub> on the capacity of a battery [21].

to resist discharge to lead sulfate and provides a conductive path from the grid to the active material, which does not degrade with cycling. The major problem with the use of lead antimony alloys in grids has been the transfer of the antimony to the negative plate during cycling where it increases the rate of gassing. ALABC Project N 3.1 indicated that antimony might be beneficial in reducing the oxygen evolution currents in float applications.

### 7.1. Antimony metal additions to active material

Giess [20] studied the structural effect of antimony on the growth of PbO<sub>2</sub> during the formation process. Very small metallic antimony particles (less than 100 μm) were added to the active material by imbedding the particles into the surface of the wet paste. The plates were cured and formed in a conventional manner using 1.10 g ml<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> at 40°C.

The areas of the active material in the region of the antimony particles showed a marked modification of the electrocrystallization structures of the newly formed PbO<sub>2</sub>. The PbO<sub>2</sub> particles in this region appeared to be fused together in a smooth glass like structure. As the antimony concentration was reduced, there was a subsequent decay in the number of welded particles. There were antimony accumulations, or doping of the glassy or welded PbO<sub>2</sub> particles.

When the electrodes containing the antimony doped positive active material were cycled at high rates, the glassy or fused PbO<sub>2</sub> particles did not discharge to PbSO<sub>4</sub> and retained the glassy morphology for many cycles. The PbO<sub>2</sub> maintained its integrity and did not change shape or orientation during discharge. During cycling, the antimony was not transferred to the negative active material but remained in the positive PbO<sub>2</sub>. This work implies that antimony doped into the active material may bond PbO<sub>2</sub> particles together and prevent degradation during cycling, thus extending life. The doped PbO<sub>2</sub> should also improve the recharge of the positive plate by providing a conductive stable structure, which does not discharge to PbSO<sub>4</sub>, and thus maintains conductivity to the discharged active material.

### 7.2. Antimony additions to the positive active material

Shiomi et al. [21] has shown that small amounts of antimony added to the positive active material paste mix can substantially increase the cycle life of batteries. Fig. 12 shows that the antimony is most effective at active material densities at or above 3.75 g cm<sup>-3</sup>. The most effective antimony contents are between 100 and 1000 ppm. Addition of 100 ppm antimony to the positive active material can result in an increase in cycle life of even low density active material by as much as 30%. The material can be added as antimony sulfate, antimony oxide, or antimony metal particles.

If the batteries are formed soon after filling, the antimony remains in the positive active material and is not leached into the acid and transferred to the negative active material. This can be seen in Fig. 13. At paste densities of about 4 g cm<sup>-3</sup>, no antimony is transferred at a 50 ppm addition. At higher paste density, more antimony can be utilized before it is transferred. If the antimony is added to the lead and subsequently oxidized in a ball mill or Barton pot, the antimony is more uniformly distributed and is more effective.

Kosai et al. [22] added up to 1% antimony to the positive active material. The high antimony content of the active

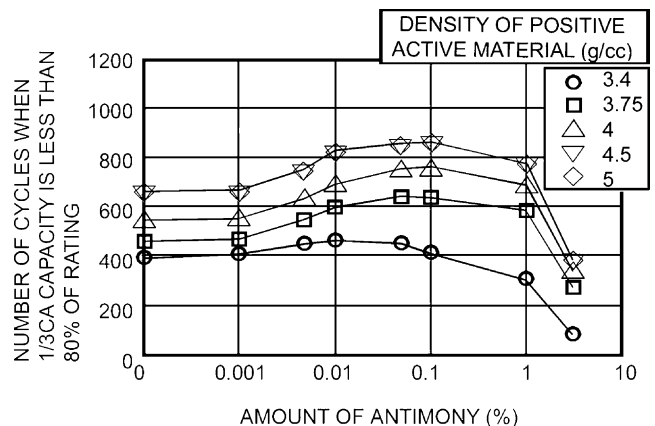


Fig. 12. Effect of antimony addition to positive active material [21].

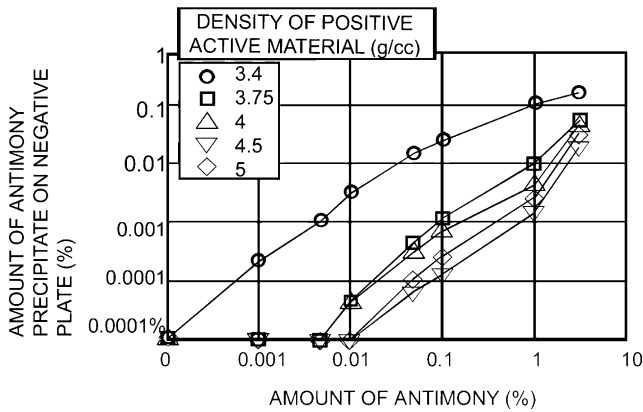


Fig. 13. Antimony transfer to negative plate [21].

material improved the cycle life of batteries with antimony-free grid materials to levels similar to those of lead antimony containing grids. They found that even though the antimony was uniformly distributed throughout the active material when the plates were produced, the antimony was segregated to the grid corrosion layer after the cycling test. Corrosion layers containing antimony discharge only with difficulty, and thus doping the newly produced PbO<sub>2</sub> layer with antimony prevents the creation of insulating layers and improves cycling performance of the positive active material.

7.3. Combination of antimony and arsenic

The addition of a small amount of arsenic to the lead along with the antimony prior to oxidation further increases the cycle life of the batteries. This is seen in Fig. 14. An antimony addition of 100 ppm combined with an arsenic content of 100 ppm in the lead used to produce the oxide results in an almost doubling of the cycle life of the battery. The battery is a 63 A h VRLA battery tested at the C/3 rate to a depth of discharge of 80% at 40 °C. The antimony and arsenic enter the positive active material and give significantly improved life without excessive gas generation.

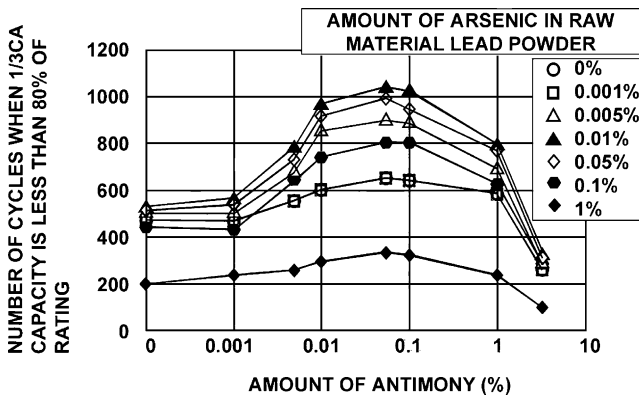


Fig. 14. Effect of arsenic combined with antimony on cycle life [21].

Element	1975	1989	2002
Al	120	62	8
Ba	600	60	0.2
Ca	190	60	28
Fe	10	6	0.6
K	270	90	3
Mg	47	24	12
Na	1290	2140	65
Si	2340	1400	110
Zn	400	22	0

Fig. 15. Amount of material leached from AGM separators in water [23].

8. Separators

8.1. Leaching of impurities from separators

The glass used as the base for separators has changed significantly over the past 30 years of VRLA battery construction. Battery cycling performance was reported to be better many years ago than is currently experienced. The batteries use the same high purity lead for both grids and active material. The separators have become significantly more resistant to degradation and leaching of the glass components than was the case years ago. Prengaman [23] compared the leaching of impurities from separators from 1975, 1989, and 2002 in both water and 20% H<sub>2</sub>SO<sub>4</sub>.

8.1.1. Leaching in water

Fig. 15 shows the amount of glass components leached from the glass in water. A sample of separator was leached by treating it with ultrasonic vibrations in distilled water for 20 min. The extract was analyzed on an ICP to determine the amount of the material leached from the separator. The character of the glass separators is markedly different. The 1975 glass leached substantial amounts of silica, sodium, potassium, zinc, and barium, as well as smaller amounts of calcium, magnesium and aluminum. The 1989 glass separator showed significantly lower rates of leaching with only sodium and silicon at significant levels. The glass separator of 2002 had virtually no extraction of the components.

8.1.2. Leaching in H<sub>2</sub>SO<sub>4</sub>

Fig. 16 shows the leaching characteristics of the glass separators in 20% H<sub>2</sub>SO<sub>4</sub>. The 1975 glass leached significant amounts of sodium. Zinc, silicon, potassium, and aluminum were leached at levels of about 2000 ppm. Calcium and magnesium were leached at about 2–3 times higher levels than with water. Barium was not leached as expected. The 1989 glass samples had lower extracted levels of virtually every component except sodium, which was at the same level as that of the 1975 separator sample. The 2002 sample leached virtually nothing even in the acid solution.



Element	1975	1989	2002
Al	2400	1250	10
Ba	.10	.10	.10
Ca	470	1000	40
Fe	110	57	.4
K	1840	1360	5
Mg	195	250	15
Na	6400	6800	105
Si	1800	400	35
Zn	2200	520	15

Fig. 16. Amount of material leached from AGM separators in 20% H<sub>2</sub>SO<sub>4</sub> [23].

8.1.3. Composition of separators

Fig. 17 shows the composition of the separators used in the study. Today’s separators contain virtually no barium or zinc, much lower potassium and significantly more magnesium than separators of 15 or 30 years ago. The chemistry has been optimized to resist dissolving the components of the separator in acid. The separators of 30 years ago leached significant amounts of sodium. The sodium at the surface of the active material may have had the effect of sodium sulfate additions to prevent formation of soluble lead ions and subsequent dendrite shorts. Dendrite short circuits were unknown in early VRLA batteries. Potassium serves the same function as sodium.

Zinc has been shown to reduce gassing, and thus the zinc leached into the electrolyte would have reduced gassing and enhanced stability of the potentials. Barium leached from the separator during filling might have applied finely divided BaSO<sub>4</sub> precipitates onto the surface of the negative plate, which may have retarded surface sulfation during recharge. Silicon leached from the separator may have served as a gel around each glass strand to more efficiently convey oxygen from the positive active material to the negative for improved recombination.

8.1.4. Glass compositions

Zguris [24] has also shown that the glass chemistry used today for separators is significantly different from earlier

Element	1975	1989	2002
Al	19,400	8,800	20,000
Ba	41,200	15,000	400
Ca	27,000	30,000	43,000
Fe	750	580	600
K	22,000	16,000	6,000
Mg	5,000	18,000	19,000
Na	87,000	114,000	84,000
Si	226,000	160,000	260,000
Zn	25,000	10,000	450

Fig. 17. Composition of AGM separators dissolved in HBF<sub>4</sub> [23].

Test Condition	Control (No Paper)	Glass Pasting Paper	Percent Change
10C Discharge at -29° C [s]	52	60	+15
C/5 Discharge at 25° C [Ah]	5	5.2	+4
10C Discharge at -29° C [s]	57	63	+11
Cold Crank (-18°C) 1.5V [s]	11.2	18	+61
Cold Crank (-18°C) 1.2V [s]	25.3	31.3	+24

Fig. 18. Improved performance of gates spiral-wound cells using glass pasting paper [25].

chemistries. Today’s glass fiber is very resistant to materials leaching from the fiber in H<sub>2</sub>SO<sub>4</sub>. The high sodium solubility may have been beneficial in reducing dendrite short circuits. Zinc is beneficial to the glass fibers because it reduces the tendency for the fibers to become brittle when exposed to hot, humid climates, thus reducing handling and manufacturing problems particularly with thinner separators. The ALABC projects and other sources have indicated that increasing the surface area of the glass fibers used in a separator will increase cycle life. The high surface area may increase the leaching of sodium and other materials from the glass, which may improve battery performance by doping the active material.

8.1.5. Glass pasting papers

Nelson and Juergens [25] have shown that a thin sheet of glass, when pressed into the surface of the wet active material prior to curing and formation, can increase the capacity of the active material particularly at high rates of discharge and low temperatures. The experiments use a pasting paper to contain the active material on the plate during pasting. The glass fibers of 5 μm in diameter are embedded deeply into the surface area of the wet active material. They bond to the active material to form a laminate at the plate surface. The pasting paper remains on the plate and becomes part of the

Group	Deep Cycle SLI Gr. 34 VRLA-Spiral Wound			
	SAE J537 (Spec. 24 A)		EN50432 (Spec. 9.6A)	
Std +/-	36.8 A		8.8 A	
Std +/-HV-	43.4 A	(+18%)	11.2A	(+27%)
Std +/-SG-Graphite	44.4 A	(+21%)	10.7A	(+22%)
HV+/Std-	50 A	(+36%)	12.3A	(+40%)

Fig. 19. Charge acceptance (A) of batteries with and without VRLA glass fibers [26] additives. In the chart, HV indicates an additive to either the positive (+) or negative (-) plate, or both. Std indicates no additive in the designated plates.

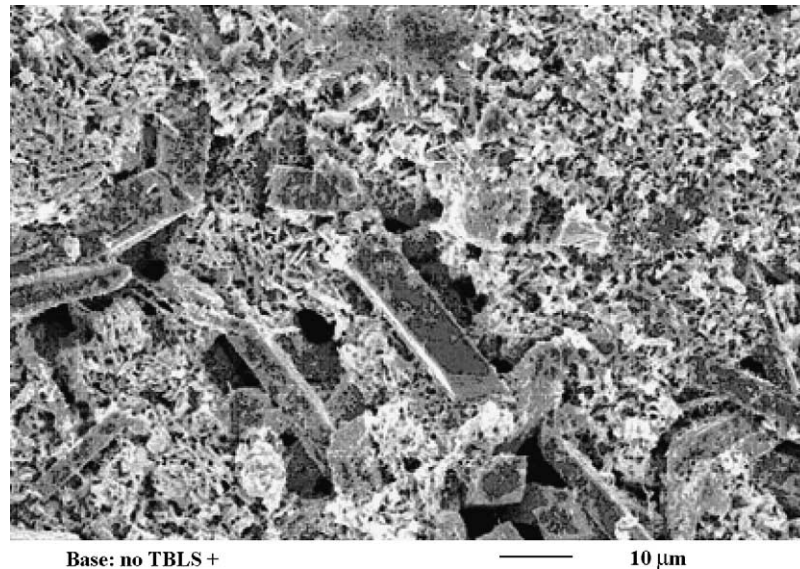


Fig. 20. Conventional tetrabasic lead sulfate cured paste [27].

battery. Fig. 18 shows the improvement in the performance of the cells using the fine fiber glass pasting paper compared to cells without the pasting paper.

The glass composition used is not discussed, but it may have been the older composition glass. Materials from the glass could have leached and had a beneficial effect on the battery performance. The additives would have been directly applied to the positive and negative plate surfaces for optimum effect. An additional benefit would have been the incorporation of higher water content of the paste, which may have improved attachment of the active material to the grid.

#### 8.1.6. Glass fibers as an additive to active material

The use of fine glass fibers as an additive to the active material has been described by Ferreira [26]. The fiber addition

to either the positive or the negative increases the capacity of the batteries by 15–40% in deep cycling tests, as shown in Fig. 19. The mechanism is not yet known. The fine glass fibers permit higher water content of the active material, which promotes improved curing and adhesion of the active material to the grid surface. The glass fibers, depending on the surface area and composition, may leach beneficial elements into the active material. The fibers, which are hydrophilic, can wick water and electrolyte into the active material and promote improved active material utilization during discharge.

### 9. Addition of tetrabasic lead sulfate

One of the most promising areas of research into improving the performance of the active material has been

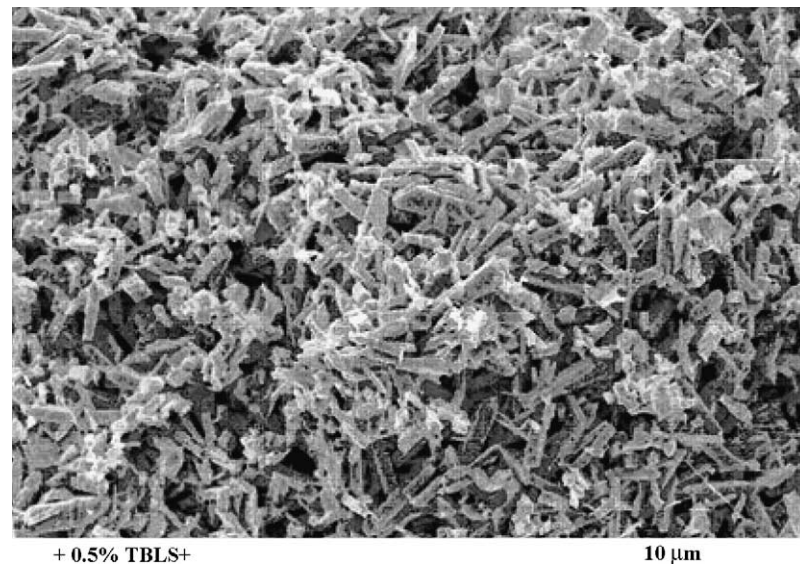


Fig. 21. Cured paste modified with 0.5% tetrabasic lead sulfate [27].

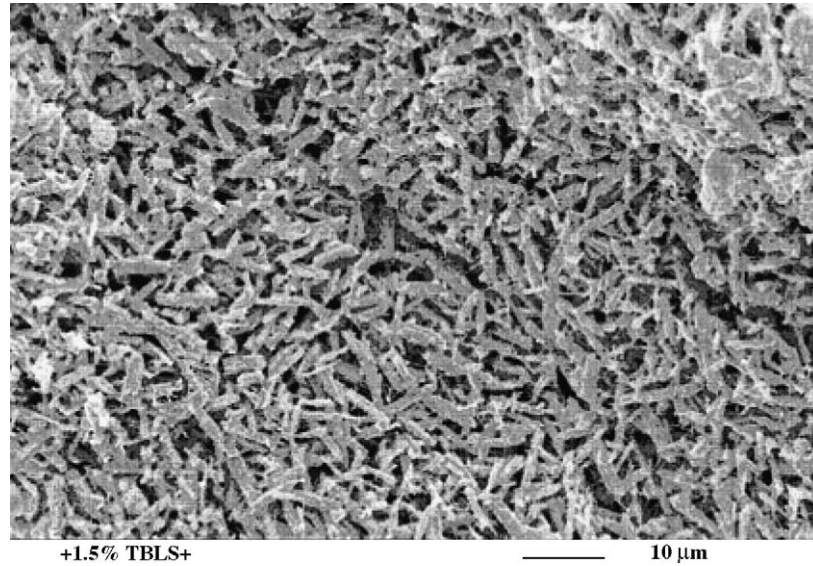


Fig. 22. Cured paste modified with 1.5% tetrabasic lead sulfate [27].

the modification of the crystal size and morphology of the basic lead sulfates, and subsequent  $\text{PbO}_2$ , upon formation. Tetrabasic lead sulfate (4BS) crystals give the active material improved cycle life. The curing processes for (4BS) produce large crystals, which are difficult to form and require significantly more energy than the smaller tribasic lead sulfate (3BS) crystals. These large crystals are often mixed with smaller crystals as seen in Fig. 20. New processes have been developed to produce 4BS with the desired crystal size. In addition, the crystals can be produced with uniform size and shape to better control the discharge and recharge of the active material. The process involves the addition of very

small seed crystals of 4BS to the positive active material paste mix.

Nitsche et al. [27] described the use of extremely small wet ground seed crystals added in various amounts to the paste mix and the subsequent crystal size and uniformity. The addition of as little as 0.5% of the additive produced a uniform 4BS particle size of 10–15  $\mu\text{m}$  merely by steaming the pasted plate for 2 h. This crystal size is designed for cycling batteries and is shown in Fig. 21. Higher amounts such as 1.5–3% can produce even smaller crystal sizes of 3–8  $\mu\text{m}$  for VRLA and SLI batteries as seen in Figs. 22 and 23. The smallest sizes are in the same range as 3BS particles. Several producers of

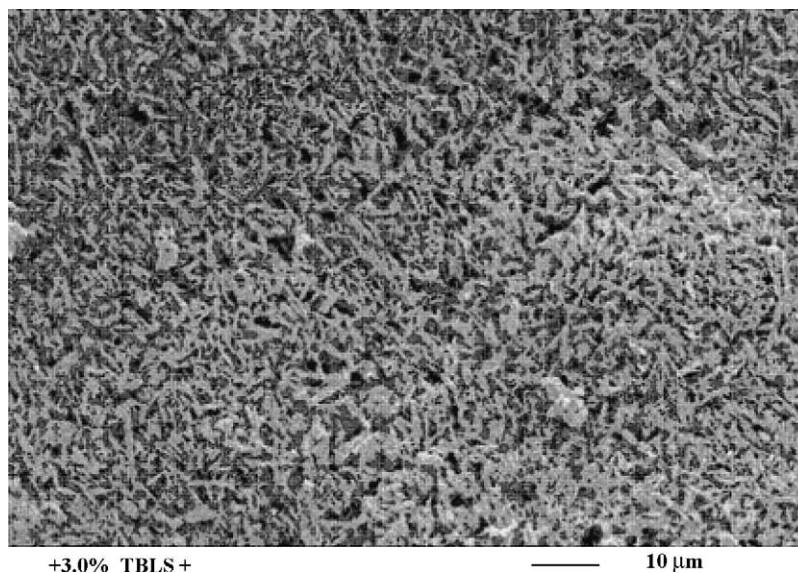


Fig. 23. Cured paste modified with 3.0% tetrabasic lead sulfate [27].



lead oxides and lead chemicals offer the additive. Control of the structure of the active material by 4BS seed crystals may yield significant improvements in capacity as well as cycle life.

## 10. Conclusions

Recent work by the ALABC has indicated that some of the impurities, which were thought to be harmful for batteries, may in fact be beneficial. Bismuth, one of the primary elements removed to produce high purity 99.99 lead, not only can reduce gassing but also can improve recharge and capacity of the active material at levels of 500–600 ppm. Zinc, which is removed to low levels in lead used for active material, can stabilize the potential of the active material, and reduce the float currents, which cause gassing, and reduce water usage when added to the active material in amounts of about 350 ppm or more. Silver, thought to contribute to gassing, is transferred to the negative active material during formation and cycling where it may improve cycling and recharge of the active material at levels of 100 ppm.

Additions of  $\text{SnSO}_4$ , antimony, and arsenic to the positive active material can substantially increase capacity and cycle life by doping the positive active material to make it more conductive and more resistant to disintegration during cycling. Added properly, the elements remain in the positive and do not contribute to gassing. AGM separators using glass compositions of 30 years ago leached substantial amounts of zinc, sodium, barium, and silica, which may have been beneficial to the performance of the active material by directly doping its surface with these additives. Even more beneficial may be incorporating fine glass fibers directly onto the surface of the active material in a pasting paper, or adding fine, chopped glass fibers directly into the active material.

Lead–acid performance in the near future may be improved by the use of unconventional additives, which will introduce beneficial impurities into or directly onto the surface of the active material. The active material crystal structure may be tailored to produce improved properties in different applications by the addition of controlled amounts of 4BS seed crystals to the positive paste mix.

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