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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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Keywords: Lead–acid batteries; Active material; Impurities; Additives; Glass; Separators

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 PbO_2 and negative sponge lead are converted to $PbSO_4$. 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 $PbSO_4$ 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.

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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^{-1} 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-1 per ppm)			Level		
	(ppm)	*I float*	*I hydrogen*	*I oxygen*	*I float*	*I* H_2	*I* O_2
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].

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