

Active-material additives for high-rate lead/acid batteries: have there been any positive advances?

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Abstract

Low positive mass utilization poses a major problem for lead/acid batteries, particularly at high discharge rates, and is one of the major factors that limits the specific energy of the battery. The reasons for the incomplete discharge at high rates are generally ascribed to a combination of various polarization phenomena including: (i) poor acid transport from the bulk of the solution into the interior of the plate, and (ii) a continuous decrease in the conductivity of the plates due to formation of non-conductive PbSO_4 . One approach to alleviating these problems is to improve the positive-plate porosity and/or conductivity by the incorporation of additives into the positive active-material. The purpose of this paper is to review recent work with such additives, and to appraise their effectiveness towards raising battery performance.

Keywords: Lead/acid batteries; Positive-plate porosity; Electric vehicles; Active-material utilization; Conductivity

1. Introduction

During the past several decades, a great deal of effort has been expended in attempts to develop more powerful and long-life rechargeable batteries. For battery manufacturers worldwide, the impetus driving much of this effort has been the emergence of potentially vast new markets, such as the electric-vehicle (EV) market. Despite the much heralded efforts to develop the so-called 'advanced' battery systems, for example, sodium-sulfur and nickel-metal hydride, lead/acid batteries are still regarded widely as the most practical short- to medium-term solution for powering zero-emission (electric) vehicles. This is due to their reliability, safety and low cost, in addition to the availability of a global network of manufacturers, distributors and recycling facilities. Indeed, most of the several hundred EVs participating in the US Department of Energy test program are based on advanced lead/acid batteries [1].

For lead/acid batteries to become serious long-term contenders in the EV market, gains must be made in the key area of specific energy. The specific energy is defined as the amount of electrical energy that can be delivered per unit mass of the battery, for a particular rate of discharge, in units of Wh kg^{-1} . For the lead/acid system, the practical specific energies are a small fraction of the theoretical maximum; consequently, the EV driving range is severely limited. The factors that limit the specific energy [2] include:

- electrode kinetic limitations that reduce the practical cell voltage
- internal resistance of the cell and its components that also reduce the cell voltage
- low active-mass utilization
- weight of peripheral materials required to produce a functional battery, but which do not contribute to the generation of electric current

Most approaches towards raising the specific energy have addressed the latter three points.

Low positive mass utilization (PMU)¹ poses a major problem for lead/acid batteries, particularly at high discharge rates. A PMU of the order of 20 to 30% is typical. The reasons for the incomplete discharge at high rates are generally ascribed to a combination of various polarization phenomena [3,4]. These may be summarized as follows:

- insufficient supply of ions necessary for the discharge reaction to proceed in the electrode reaction zone; the discharge current then drops to a level that is sustained by diffusion
- rapid coverage of the surface of the electrode with an insulating layer of PbSO_4 and, thereby, exclusion of the bulk of the active material from further discharge

¹ The PMU is defined as the ratio between the actual cell capacity (Ah per g PbO_2), at a particular rate of discharge, and the theoretical capacity (Ah per g PbO_2). It is a measure of the percentage of positive active-material that participates in the discharge process.

- a continuous decrease in conductivity of the positive active-material during discharge due to the formation of non-conductive PbSO_4 ; in some instances, pockets of the conductive PbO_2 can become partially or totally isolated from the current collector

At low discharge rates, ready diffusion of acid into the electrode is less of a problem, and discharge is more uniform through the porous structure.

The positive active-material serves two main functions during discharge: (i) to participate in the electrochemical reaction, i.e., conversion of conductive PbO_2 to non-conductive PbSO_4 , and (ii) to provide conducting pathways from reaction sites in the porous active-mass to the grid. The latter function requires that a certain amount of conductive PbO_2 active-material does not participate in the electrochemical reaction, but acts only to provide structure and conductivity to the plate. Therefore, an active-material utilization of 100% is not achievable practically. For example, it is accepted that the limits are in the order of 70% utilization at $C_{20}/20$ and 55% utilization at $C_3/3$. These limits are not achieved by present commercial batteries.

Attempts to raise the PMU have included the use of very thin plates, decreasing the paste density and the mechanical circulation of acid through the plates. These methods have all been aimed at enhancing the rate of acid diffusion into the porous plates. Whilst significant gains in PMU and specific energy can be made, these are generally at the expense of the battery cycle life; battery durability is diminished through increased grid corrosion and active-material shedding.

Additives that modify the active material, for example, by increasing the plate porosity and/or conductivity, can also increase the specific capacity (Ah g^{-1}). This approach towards enhancing battery performance has received considerable attention in the past decade. The purpose of this paper is to review the efficacy of such paste additives and to judge if any positive advances have been made.

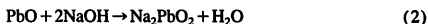
2. Additives: classification and desirable characteristics

Dietz et al. [5] have suggested that active-material additives can be classified according to their mode of function. Additives may enhance the performance of the active material by altering the: (i) porosity; (ii) conductivity; (iii) crystal morphology and geometry, and (iv) mechanical strength. Types (i)–(iii) influence the discharge capacity and active-material utilization, whilst type (iv) affects the cycle life.

Additives to the positive active-material can be introduced to the cell as a soluble species to the paste or electrolyte, or as an insoluble component to the paste. Examples of the first type include phosphoric [6,7], boric [8] and citric [9] acids and numerous soluble sulfate salts [4]. When phosphoric acid or various phosphate salts are added to the electrolyte, there is evidence that phosphate ions are reversibly adsorbed on the PbO_2 particles during charging [7]. It is claimed [6] that this modifies the crystalline structure of PbO_2 and,

thereby, produces crystals that are more difficult to reduce to PbSO_4 . The presence of phosphate ions is believed to improve cycle life by preventing the formation of an insulating PbSO_4 layer at the grid/active-material interface and by inhibiting the self-discharge reaction [6,10–12]. On the other hand, disadvantages include capacity loss, excessive mottling and a decrease in charging efficiency. Boric [8] and citric [9] acids are reported to modify the positive active-material in a similar manner, but with fewer undesirable effects.

Soluble sulfate salts can act upon the positive active-material in a number of ways, as determined by the physicochemical properties of the particular salt, or whether it is added to the electrolyte or during the paste-mixing stage [4]. For example, under the alkaline conditions of the paste, lithium, sodium and potassium sulfate salts are hydrolyzed and can form plumbite species, i.e.:



These may improve adhesion of the paste to the grid and assist plate-formation [4]. During formation, sodium plumbite (Na_2PbO_2) is oxidized to sodium plumbate (Na_2PbO_3), and this is hydrolyzed to PbO_2 and NaOH . Furthermore, the presence of a small amount of a soluble sulfate salt, such as Na_2SO_4 , ZnSO_4 or CdSO_4 , may affect the solubility of PbSO_4 in the electrolyte [4] and improve battery performance. Indeed, a large number of patents have been taken out in this area. Sodium sulfate has also been used as an agent for increasing the porosity of tubular plates that are composed of chemically prepared PbO_2 [13].

It is intended that the focus of this review be directed towards insoluble paste additives that affect the porosity and/or the conductivity of the active-material, since these types of additives have attracted increasing interest recently. To be effective, a paste additive should possess the following characteristics:

- good stability in sulfuric acid for prolonged periods of time
- electrochemical inertness over the potential range of the positive electrode
- good adhesion to the active material, both cured and formed
- high oxygen overpotential
- light weight
- zero or low toxicity, i.e., recycling should not be problematic
- high conductivity (type (ii) additive)
- low cost²

² As an aside, cost is a much mentioned factor, but is not often quantified. Therefore, it may be of interest to consider the following. If an additive costs $\sim \$0.2 \text{ g}^{-1}$, then for a typical automotive battery, a 2 wt.% loading of this additive will increase the wholesale cost of the battery by around \$5.00. Consequently, the attractiveness of employing this additive will obviously depend on the extent of the performance enhancement. Of course, a battery for a different application, such as an electric-vehicle battery, could perhaps tolerate an additive of this (or greater) cost.

Furthermore, the additive should increase the PMU without adversely affecting the battery cycle life. In practice, however, it can be difficult to meet all of these criteria.

3. Additives that enhance porosity

3.1. Carboxymethylcellulose, carbon black, silica gel and fibres

Dietz et al. [5,14] have investigated the effects of adding carboxymethylcellulose (CMC), carbon black, silica gel (particle size 30–150 nm) or synthetic fibres (Dynel floc) to the positive active-material. The studies were performed mainly on 3 Ah flooded cells, composed of one positive and two negative plates. Capacity tests were performed on 15 Ah cells, and additive loadings of 0.2 and 2 wt.% with respect to leady oxide were investigated. Neither grid alloy composition nor plate thickness were specified.

X-ray diffraction (XRD) phase-analysis of the doped cured material revealed that both CMC and carbon black cause accelerated oxidation of free-lead to PbO, when compared with untreated material [5,14]. The porosity of the cured material was increased by the addition of carbon black, CMC and fibres; this was attributed mainly to an increase in water absorption by the paste. Doping with carbon black produces cured material that contains predominantly large, coarse pores whereas when CMC is employed, additional fine pores are produced at the expense of the percentage of coarse pores. The latter effect is most likely caused by the known swelling and dispersion-stabilizing properties of CMC. Active material doped with CMC showed the largest change in pore volume and distribution, and surface area. Material treated with carbon black exhibited a decrease in surface area.

All additives contribute to an increase in porosity in the formed electrodes; CMC- and silica gel-treated materials possess a more finely grained structure [5]. More than half of the carbon black was lost via oxidation during formation. The energy efficiency of formation was enhanced slightly (2%), presumably due to the conductive nature of carbon black [14].

The low- and high-rate capacity tests were performed at the $C_{20}/20$ and $C_3/3$ rates, respectively [5,14]. Cycle lives were investigated by cycling at the $C_{10}/10$ rate, involving a 1 h discharge and a 5 h charge. The reviewer has deduced these rates from the unorthodox terminology adopted in the work. In fact, failure to provide a clear description of the discharge rate is a common problem with many papers. Accepted practice [15] is to normalize the current (A) during discharge to the rated capacity (C). The current is expressed as C_i/X , where i is the hour rate for the rated capacity, and X is a time specification, in h. For example, the 10 h discharge rate of a 500 Ah cell or battery (rated at the 5 h discharge rate) is expressed as $C_5/10$. Where possible, the reviewer has converted published rates to this format, but in

many cases this has not been possible and the discharge rates are given as quoted in the work.

Little significant improvement in 'mass-related' capacity was observed for cells with a 2 wt.% loading of any additive [5,14]. Cells treated with 0.2 wt.% CMC displayed good initial capacity (5% improvement at the low rate relative to untreated cells, 10% at the high rate), but a poor cycle life was obtained at both rates. This was due to the weakening of the mechanical strength of the active mass by the swelling effect of CMC. It was also reported that CMC is unstable over the potential range of the positive electrode and that most of it is removed during overcharge.

The addition of 0.2 wt.% silica gel [5] resulted in improvements to the low- and high-rate capacities that were similar to those observed with CMC-doped material. The cause of this effect remains unclear, since no significant physicochemical changes were observed in the active-mass structure. One explanation offered by the authors is that silica gel promotes nucleation and, consequently, leads to an increase in the fine-grained porous nature of the active material. Given the good high-rate capacity it was also suggested that the silica gel additive exerts an additional effect, perhaps related to enhanced acid supply. Silica is known to be quite porous, and it may act as a type of acid 'reservoir'. Silica gel was not found to influence battery cycle life. The additive has been patented for use in lead/acid batteries [16].

The addition of carbon black produces little improvement in either cell performance or cycle life [5,14]. Much of the carbon is oxidized during formation, and the remainder is removed during cycling. Cells treated with synthetic fibres showed no increase in capacity [5]. On the other hand, cycle life is significantly prolonged at both the low and high rates, due to strengthening of the active-mass structure by the fibres.

All additives evaluated in these studies [5,14] possess greater specific volumes than the lead components of the active mass. This fact, together with the measured increase in both the surface area and the porosity of the doped active material, will affect the density of the active material, but no details are provided. Moreover, values for active-material utilization, or the average cell voltages during discharge were not given. It is clear from the data presented, however, that neither CMC nor carbon black are suitable additives for enhancing the performance of the positive active-material. Silica gel is worthy of further systematic study, especially at high discharge rates ($C_1/1$ rate or higher, 100% depth-of-discharge (DOD)), and the utility of fibrous materials for promoting long cycle life is noted.

3.2. Glass spheres

Edwards and Srikanth [17] have investigated the addition of hollow glass microspheres to the positive plate. The inert and non-conductive spheres (20–50 μm in diameter) possessed solid surfaces that did not allow electrolyte penetration inside the sphere. Studies were performed on hand-pasted, three-plate flooded cells (Pb–2.75wt.%Sb positive grid

alloy), where the density of the wet, positive paste varied from 1.75 to 4.27 g cm⁻³. These densities correspond to loadings of 6.6 to 0 wt.% glass spheres with respect to leady oxide. Pasted-plate thicknesses were of the order of 0.22 cm.

Microscopic examination of the cured paste revealed that the spheres were distributed uniformly throughout the paste. No data are available concerning the phase compositions of the cured or formed plates. Active-material porosities of the order of 25–30% were reported for both hand-pasted and factory-produced plates, even for those with a high wt.% of glass microspheres. These values appear quite low, possibly due to the method employed for determining the plate porosity (measured by weighing a cured plate both before and after soaking in water). Techniques such as mercury porosimetry are generally regarded as more accurate.

The cycling tests consisted of constant-current discharges to 1.75 V at rates that varied between 0.01 and 0.12 A g⁻¹, followed by constant-current charging to a cell voltage of 2.45 V. Charging was terminated at an overcharge factor of 1.1. Plots of the active-material utilization versus the specific rate (A g⁻¹) were reported for plates containing 0, 2.2, 4.4 and 6.6 wt.% loading of glass spheres. Enormously improved PMUs were obtained for the treated plates at medium and high rates of discharge, where a medium rate appears to be defined as a C₁/1 to C₅/5 rate (C₁/1 rate ≈ 0.07 A g⁻¹). The maximum improvement in utilization, from 5.02 to 33.12% at a specific rate of 0.1 A g⁻¹, occurred for a 4.4 wt.% loading of glass spheres. This corresponded to a paste density of 2.09 g cm⁻³. As might be expected from the low paste densities and the corresponding reduction in the amount of active material present on the plates, the plate capacities were greatly decreased.

Edwards and Srikanth [17] also provide details of a series of calculations that attempt to estimate the relative contributions of the pore and bulk electrolyte utilizations to the total utilization at a high specific rate. The sum of the pore and bulk electrolyte utilizations compare reasonably well with most of the measured utilizations, and reflect the trend of increasing utilization with increasing loading of glass spheres. For the untreated active material of high density, the calculations illustrate that the utilization at high specific rates is dominated by the contribution from the electrolyte in the pores. For the doped active material, in addition to the contribution from the pores, a much bigger bulk electrolyte utilization is estimated. This improvement in utilization is attributed to the low paste density and, therefore, the smaller current density experienced by the active material. The authors assert that for smaller current densities, more of the bulk electrolyte is able to diffuse into the plate and participate in the electrochemical reaction, which leads to higher utilization.

At the highest loading of glass spheres (6.6 wt.%; 1.75 g cm⁻³ paste density), it is clear that an additional factor influences utilization, since there is a large discrepancy between the calculated (50.57%) and measured values (19.94%). The authors logically suggest that at this loading, electrical

isolation of portions of the positive material occurs due to the high volume ratio of glass spheres to active material. This causes a decrease in the electrical conductivity of the active material and, hence, a decrease in PMU.

No information regarding the service life or specific energy of these cells was provided, but it seems likely that the cycle life for the cells with very low paste densities would be drastically reduced due to rapid loss of interparticle contact in the active material during extended cycling [18]. It is also unlikely that the addition of glass spheres to plates that otherwise display a high PMU, such as thin automotive plates, would enjoy the same startling degree of improvement reported in this study. Nevertheless, glass microspheres are an attractive option in terms of their stability and cost.

3.3. Graphite: a porosity enhancer?

Tokunaga and co-workers [19,20] have published several detailed studies of the effect of anisotropic graphite addition to both flooded [19] and valve-regulated [20] lead/acid (VRLA) batteries. For the flooded cells, loadings of 0.1 to 2 wt.% graphite (with respect to leady oxide) were examined, with Pb–5wt.%Sb–0.15wt.%As positive grids (135 mm × 140 mm × 3.2 mm) and a wet positive paste density of 4.2 g cm⁻³. The cell capacity was tested at three rates, namely, 0.2C (18 A); 0.5C (45 A) and 1.0C (90 A), to final cutoff voltages of 1.70, 1.70 and 1.00 V, respectively. Discharge times were not quoted.

The PMU was observed to improve markedly with increasing loadings of graphite for all discharge rates; the largest increase (from 27 to 40%) was found for the lowest rate and the highest loading of graphite. XRD analyses of the PbSO₄ content at various DODs at this 0.2C rate showed that the distribution was fairly uniform in the graphite-doped positive plates, even at the end of discharge. Conversely, for the untreated plates the level of PbSO₄ distribution increased near the surface of the plate as discharge proceeded. These results demonstrate that graphite addition allows the discharge reaction to proceed to a much greater extent in the interior of the plate, particularly at the 0.2C (18 A) rate.

Following several cycles, the active mass showed an increase in porosity from 50% to more than 60% when treated with a 2 wt.% loading of graphite. Analysis of the pore-volume distribution revealed that the increase in porosity was due to a greater number pores with diameters of 2 μm or more. The increase in porosity correlated with an observed increase in active-mass thickness, and porosity was also found to rise linearly with PMU at all discharge rates. Consequently, the improvement in PMU for the graphite-treated cells was attributed to an increase in porosity of the active mass. No mention was made of the possible contribution to plate conductivity by the graphite. The greater porosity and thickness of the active mass were linked to graphite intercalation, and XRD patterns of the graphite obtained from the formed plates confirm that some intercalation had occurred. It is well known that at potentials greater than 0.9 to 1.2 V

(versus saturated calomel electrode (SCE)), HSO_4^- intercalation compounds are formed with graphite [21]. During intercalation, HSO_4^- ions are inserted between the carbon planes, and the interlayer spacing between the planes increases from 3.35 to 8–10 Å.

Cycle-life tests were performed for a single loading of graphite (0.5 wt.%) and employed a regime consisting of a 3 h discharge at the 0.25C (22.5 A) rate, followed by a 5 h charge at the 0.18C (16.2 A) rate. Cell failure was defined as 80% of initial cell capacity. The cycle lives for the treated and untreated cells were both around 500 cycles, but the treated cells exhibited a 10% higher capacity throughout the test. The maintenance of good cycle life for the treated cell was ascribed to compressive effects of the thicker plates that prevented the active material from shedding. Although the beneficial effects of compression on positive-plate cycle life are known [18,22], no data were provided to support this contention.

Tokunaga et al. [20] have also investigated the addition of graphite to the positive plate of absorptive glass mat (AGM) valve-regulated batteries, where the diffusion of acid is quite restricted compared with flooded cells. Conventional Pb–Ca–Sn grids (60 mm \times 40 mm \times 3.0 mm) were employed and the positive active-mass was treated with 0.1 to 2 wt.% loadings of graphite. The results were presented in terms of the relative capacity; this is the ratio of the capacities of the treated cell to the untreated cell. The relative capacities of the graphite-treated VRLA cells improved by 5 to 10% at the lower rates (e.g., 0.05C and 0.2C), but larger increases were observed at the higher rates. For example, at the 5C discharge rate (30.0 A, 1.00 V cutoff voltage, 3 to 4 min duration) the relative capacity of the cell containing 1 wt.% graphite improved by 60%. Furthermore, when discharging at the 5C rate at temperatures of 25 °C and –30 °C, both the cell voltage and duration time were higher for the graphite-treated cells. Hence, it appears that addition of graphite to this type of VRLA cell may have resulted in some improvement in specific energy, although this is difficult to verify without more information. Unfortunately, cycle-life studies were not reported.

For VRLA cells treated with graphite, the largest increases in capacity [20] were observed at the highest discharge rates; the opposite was true for flooded cells [19]. The authors suggested that this was due to differences in the amount of electrolyte and its distribution within the cell. A series of measurements were made of the VRLA active-mass porosity, pore-volume distribution and plate thickness, as well as variation of the electrolyte volume within the positive and negative plates and the glass-mat separator. The authors asserted [20] that the increase in plate thickness resulted in compression of the glass-mat separator, and this caused the small changes in electrolyte volume measured in the separator (decrease) and the positive plate (increase). Nevertheless, no measurements of separator compression were provided to support the theory.

The significant improvement in relative capacity at high-rate discharges for graphite-treated VRLA cells was attributed by Tokunaga et al. [20] to enhance acid diffusion and greater participation of the interior of the active mass in the discharge reaction. Although this was supported by an analysis of the PbSO_4 distribution through cross sections of selected plates after discharge, any possible contribution made by graphite on plate conductivity was not discussed. Furthermore, it was established in these studies, and subsequently in others [23], that during formation and cycling significant amounts of the graphite additive are lost from the active material via oxidation to CO_2 . By virtue of this instability, the utility of graphite as an effective additive during prolonged service seems doubtful.

A more recent study [23] has reported that the addition of graphite positive active-material reduces premature capacity loss (PCL) and helps to recover capacity during 'reactivation', but that these effects are not very strong. The VRLA (AGM) cells utilized active material obtained from tribasic lead sulfate ($3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O} = 3\text{BS}$), tetrabasic lead sulfate ($4\text{PbO} \cdot \text{PbSO}_4 = 4\text{BS}$) and 4BS doped with 0.45 wt.% graphite. Typical Pb–Ca–Sn grids (66 mm \times 96.5 mm \times 4.2 mm) were employed. Note, other studies mentioned thus far have used active material derived from 3BS. The cells, of nominal capacity 4.5 Ah, were subjected to float operation under constant voltage charging at 2.25 V.

A post-mortem study [23] of the graphite-treated cells revealed that the active material was weakly bonded and very brittle. This was ascribed to the degradation of the graphite. XRD studies provided evidence of HSO_4^- intercalation, and showed the average size of the graphite crystallites to be 28.8 Å at the end-of-life, compared with 1000 Å initially. It was clear that oxidation of the graphite had occurred. Tokunaga and co-workers [19,20] reported a similar effect upon prolonged cycling (see above).

Wang et al. [24] have also investigated the effects of graphite, carbon fibre and needle coke addition to the positive plate. The tests were performed on flooded cells with low-antimony alloy grids (63 mm \times 26 mm \times 3 mm) and loadings of 0.5 wt.% graphite with respect to leady oxide. Discharge rates of 3–4 h were employed (1.65 V cutoff voltage), but no information on the charging regime, paste densities or active-material porosities were provided. Plots of PMU versus cycle life suggested that the cells were insufficiently formed, since maximum cell capacity was not achieved until around cycle 20. An initial increase ($\sim 10\%$) in PMU was observed for the treated cells, compared with that of the untreated cells but the cycle life was reduced. The cells were removed from service after 60 to 70 cycles; examination of the graphite-treated cell revealed severe softening and shedding of the active material.

These studies may be contrasted with the work of Tokunaga et al. [19] who observed that the cycle lives of cells treated with 0.5 wt.% graphite were very similar to those of untreated cells. Although this may be due to the harsher duty employed by Wang et al. [24] (100% DOD), it is difficult

to ascertain precisely why the performance was different, since full details on the cycling regimes and cell construction are not reported. It is also possible that there were differences in the graphite used in each study.

Wang et al. [24] also examined the effects of organic additives on the positive active-mass, and claimed improved utilization for a 'certain nitrogenous heterocyclic additive (AS)'. When 'AS' was mixed in a 1:1 ratio with graphite, an increased PMU was obtained and cycle life was unaffected. Similar improvements were obtained when an unspecified amount of LiSO_4 was added to the electrolyte. It is unclear exactly how the composite additives act upon the positive material, as detailed analyses of their effects (e.g. by XRD, scanning electron microscopy (SEM), porosity studies, cycling regime, etc.) were not given. Results were presented, however, of some standard battery tests, such as the reserve capacity, cold-cranking current and C_{20} capacity, for factory-produced automotive batteries (12 V, 60 Ah) treated with 1 wt.% of the composite graphite-AS additive. The doped batteries performed comparably with untreated counterparts for all tests, but gave a slightly reduced 'cycling durability'. Notably, the wet paste density for the treated positive active-material was 3.6 g cm^{-3} , and 14% less active material was required to produce a similar performance to that of untreated cells in terms of, for example, C_{20} capacity and cycle life. A more systematic and detailed study of the effect of this composite additive could be warranted, provided its use in batteries is affordable.

3.4. Graphite: an electro-osmotic pumping agent?

There appears to be sufficient evidence to suggest that the improvement in utilization observed when graphite is added to the positive active-material may be due to more than one factor. In addition to affecting porosity and conductivity, graphite may also contribute to enhanced acid flow via electro-osmotic pumping. Enhancing the acid flow in the active material without substantially increasing its porosity is an attractive option from the point of view of cycle life and volumetric energy density, which are both adversely affected if the porosity of the positive active-material is increased drastically.

Baker et al. [13] have examined the effect of graphite addition to tubular positive plates that contain chemically prepared PbO_2 . Studies were performed at loadings of 0, 1, 5 and 12 wt.% graphite with respect to the weight of PbO_2 . The cells were cycled at a constant current; details of the cycling duty were not supplied. The highest utilization of active material was obtained at the lower concentrations of graphite, and the authors could not ascertain whether the improvement was due to the greater electrical conductivity of the plate, an assisted packing density or enhanced acid diffusion.

The authors [13] concluded that the graphite enhances the transport of electrolyte through the porous electrode via electro-osmotic pumping. Electro-osmosis relates to the flow of

liquid in thin capillaries under the action of an applied voltage [25,26]. It is the reverse of electrophoresis, i.e., in electro-osmotic pumping, the particles (in this case the porous material) are stationary and the liquid moves. It is well known that a surface electric charge is generated when a polar liquid, such as H_2SO_4 , is brought into contact with a solid surface such as an electrode. Each solid component of the active material possesses a characteristic zeta potential, and Baker et al. [13] proposed that if a compound with a high zeta potential of the correct polarity is incorporated into the active material, electro-osmotic pumping of H_2SO_4 through the porous mass might occur. The flow rate of the electrolyte due to electro-osmosis is inversely proportional to the electrolyte concentration, hence as discharge proceeds the flow rate should increase, thus the pores are 'irrigated' more effectively than by acid diffusion alone.

For electro-osmosis to contribute to the flow of electrolyte in the positive plate during discharge, it was advocated [13] that a material with a high negative zeta potential is required. The zeta potentials of each solid component of the doped tubular-plate active mass were measured and it was found that after contact with H_2SO_4 , graphite was the only material present that possessed a substantial negative zeta potential. This was thought to be due to HSO_4^- intercalation between the carbon planes. Experiments with a purpose-built tubular cell showed that the volume of electrolyte expelled during discharge was very close to the theoretical amount predicted by electro-osmotic pumping. Other experiments illustrated that graphite may also assist in the wetting of the porous mass when it is initially immersed in the electrolyte. The authors [13] also suggest that electro-osmotic pumping may be of benefit in preventing acid stratification.

Since graphite is not stable over the potential range of the positive electrode, it is clear that alternative agents must be investigated. For example, Baker et al. [13] have speculated that species such as polymers that contain pendant benzene sulfonate groups may satisfy the requirements for a suitable electro-osmotic additive, since these are relatively stable in 5 M H_2SO_4 , and might be expected to possess a high negative zeta potential. Recently, the Advanced Lead-Acid Battery Consortium (ALABC) embarked upon a research project that is evaluating several potential electro-osmotic pumping agents in terms of their ability to enhance the specific energy of batteries at high-rate discharges.

3.5. Other agents

A survey of recent abstracts in the patent literature has revealed that a wide variety of materials that purport to increase the active-material porosity have been patented for use in lead/acid batteries. The addition of poly(vinylformyl) particles [27] or the sodium, potassium or lithium salts of cross-linked poly(acrylic acid) [28] are claimed to increase both PMU and cycle life. Polyester and polypropylene fibres, of differing melting points, are said to improve the high-rate discharge [29]. Acid-resistant microporous synthetic fibres

[30] are also claimed to promote long cycle life in conjunction with high energy density. Hollow additives that can store electrolyte and act as a type of 'reservoir', such as SiO_2 beads [31], porous microspheres [32] and 1–10 μm fibres (aspect ratio of 1:{2–20}) [32] have also been reported.

One method of increasing the plate porosity that has attracted popularity is to add an agent to the paste mix that can be subsequently removed during formation. One patent reports cooling the pasted grids to less than 0°C , in order to freeze the water in the paste [33]. Subsequently, the electrodes are 'aged' and then thawed, leaving a supposedly more porous paste of increased capacity. Cycle life is reported to be unaffected.

Similarly, when metal sulfates such as $\text{Al}_2(\text{SO}_4)_3$ or MgSO_4 [34] are added to the positive paste during preparation, the following reaction occurs [4]:



The bulky oxide remains in the paste until formation, when it is dissolved out of the paste, to leave a more porous plate. Clearly, the distribution of the metal sulfate needs to be controlled very carefully, to avoid generating very large voids within the positive active-material and causing a decrease in utilization and mechanical strength through the loss of inter-particle contact.

Calcium sulfate has also been reported to improve significantly the high-rate performance of commercial automotive batteries with flat or tubular plates [35]. For loadings of 0.25–2 wt.% in the positive active-material, the cell voltage was increased at all discharge rates, including the 7 min rate. Cycle-life studies were not reported, but from a visual examination of the plates, it was claimed that cycle life is unaffected. The author asserted that porosity changes were not responsible for the improved cell performance, but detailed porosity and pore volume measurements were not provided. Clearly, further studies are required to establish why calcium sulfate appears to enhance high-rate cell performance.

4. Additives that enhance conductivity

An alternative approach to raising PMU is to incorporate highly conductive additives into the porous mass. It was mentioned earlier that as the discharge reaction proceeds, the conductivity of the active mass continuously decreases due to the formation of non-conductive PbSO_4 . In some locations, PbSO_4 can completely encapsulate pockets of crystalline PbO_2 and, in effect, can remove them from the electrochemical reaction (Fig. 1). Thus, the utilization is lowered. If the 'islands' of PbO_2 could be connected via a conductive matrix (Fig. 1), then the discharge reaction could continue unhindered and utilization would be raised. Such a network might also provide some cohesive structure and strength to the positive active-material and, thereby, would also enhance cycle life. Moreover, a conductive additive might also serve to increase formation efficiency and assist rechargeability.

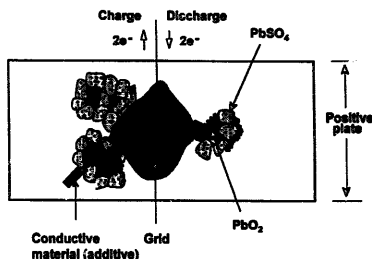


Fig. 1. Schematic representation of the cross section of a lead/acid positive plate during discharge. (Reproduced from [36].)

In addition to the physicochemical requirements listed earlier, conductive additives should:

- be inert and not participate in the electrode reactions
- have a conductivity comparable with PbO_2
- show good adhesion to both the cured and the formed materials
- be of suitable geometry to form a conductive network within the active material

Surprisingly, few reports concerning conductive additives have been published in the literature, although there has been considerable activity within the patent literature. Accordingly, the ALABC has embarked upon a program that is evaluating a wide range of compounds in terms of their ability to enhance the specific energy of batteries at high-rate discharges. The ALABC hope to identify a stable conductive additive that will be of benefit to EV and other high-rate applications.

4.1. Carbon fibres

In an early report, Weininger and Morlock [37] introduced carbon fibres into the positive grid of a lead/acid battery in a structure that 'resembled a grid of pipe-cleaners'. An expanded $\text{Pb-0.065wt.\%Ca-1.0wt.\%Sn}$ grid was used, and the fibres (3–10 μm in diameter, derived from polyacrylonitrile) were interlocked with each other and the grid. The fibres had a conductivity in the range 1 to 2.5 mS cm^{-1} (cf., 1 and 4 mS cm^{-1} for α - and β - PbO_2 , respectively). A positive grid in which the carbon fibres were replaced by glass fibres was also constructed. The grids were pasted with active material, and cured and formed in the normal manner; neither plate thicknesses nor paste densities were specified. Surprisingly, no mention was made of improvements in formation efficiency.

The flooded cells were cycled at constant current to cutoff voltages of 2.70 V on charge and 1.75 V on discharge. An untreated cell and a carbon fibre/lead alloy cell were cycled at the $C_2/2$ discharge rate. Their initial utilizations were identical (49%); the untreated cell failed after less than 10 cycles, whilst the carbon fibre/lead alloy cell failed after 30 cycles.

A carbon fibre/lead alloy cell and a glass fibre/lead alloy cell were cycled at the $C_4/4$ rate for 40 cycles, and then subsequently at the $C_6/6$ rate, in an attempt to prolong cycle life. Their initial utilizations were $\sim 60\%$, but both cells also lost capacity rapidly; the glass fibre/lead alloy cell failed after about 40 cycles, and the carbon fibre/lead alloy cell after 90 cycles. It should be noted that the service limit was set arbitrarily at $\sim 30\%$ of initial capacity. If a more usual definition of failure had been used, for example, 50% of initial capacity, then for all cells service would have been terminated within less than 30 cycles.

Post-service examination of the plates revealed that whilst gross shedding had occurred in the untreated cell, it was less severe for the carbon fibre/lead alloy grids due to superior adhesion of the active material. SEM studies illustrated that the active material was distributed uniformly between individual carbon fibres, and that the fibres acted as nucleation sites for growth of the active material. Typically, the carbon fibres were heavily encrusted with active material. This was cited as evidence that the carbon fibres had formed a true conductive network. By contrast, although the glass fibres appeared to contribute to structural support, they did not provide a substrate for crystal growth.

Based on evidence from the SEM studies, the large decreases in utilization found for the first few cycles were tentatively assigned to passivation of the grid. It is also likely that cell design problems contributed to the poor performance of the cells, as corrosion of the grid at the carbon fibre/lead alloy interface was observed for at least one cell. The authors also mentioned that there was excessive weight in the construction of the cell, and this would account for the minimal changes in specific energy that were calculated. Whilst some increases in utilization were observed for the cells that incorporated carbon fibres into the positive grid structure, and longer cycle lives were claimed, studies with a better cell design are needed to confirm that the improvements are significant. Measurements of the plate conductivity would also be informative.

With respect to the stability of carbon fibres in acid at high positive potentials, Weininger and Morlock [37] reported that carbon fibres were stable when held at 1.40 V versus $\text{Hg}/\text{Hg}_2\text{SO}_4$ at ambient temperature in 1.28 sp. gr. H_2SO_4 for 10 days. This was based upon visual examination (SEM) of the fibres and a lack of measurable weight loss. By contrast, 50% of the carbon 'whiskers' added to the positive paste of a VRLA cell [38] were found to be oxidized during formation of the positive active-material. Moreover, there were increases in the charging efficiency during formation, the porosity and the average pore size in the positive active-material.

Kamenov and Leonov [39] have also investigated the stability of carbon fibres, derived from cellulose and polyacrylonitrile, at the potential of the PbO_2 electrode. Current-time curves were obtained over the range 0.9 to 1.2 V (versus $\text{Hg}/\text{Hg}_2\text{SO}_4$), and during the reduction of oxidized fibres, a delay was observed in the curve at 1.0 V. The authors sug-

gested that a CO_n sub-species may have formed on the fibre surface, and that it passivates the surface and offers stability at high anodic potentials. There have been other reports in the literature of carbon-fibre passivation [40]. Kamenov and Leonov [39] also found that at low current densities the oxygen overpotential of the positive electrode was lowered for carbon fibre loadings of up to 2 wt.%. At high current densities ($10^{-2} \text{ A cm}^{-2}$), there was no influence due to passivation of the fibre.

Several different types of conductive carbon materials have been patented for use in the positive electrodes of lead/acid batteries. These include carbon and graphite whiskers [41], hollow carbon-black shells [42], graphitized hollow carbon fibres [43] and spherical carbon particles with a lamellar (intercalated) structure [44] and graphite with fluoropolymer fibres [45]. Naturally, all inventors have claimed increased PMU and long cycle life. The utility of carbon fibres and related materials as effective conductive additives for raising PMU seems doubtful, however, due to the many reports of oxidation during prolonged service. These materials may play a role in improving the formation efficiency.

4.2. Barium metaplumbate

Barium metaplumbate, BaPbO_3 , is a conductive ceramic that possesses a perovskite structure. Several reports have appeared recently concerning its utility in lead/acid batteries [1,46,47], and Bullock and Kao have patented the use of BaPbO_3 and a range of other conductive ceramic perovskite materials for bipolar lead/acid battery substrates [48,49].

The addition of conductive BaPbO_3 to positive plates in a conventional 50 Ah automotive battery improves the formation efficiency and current acceptance of a deeply-discharged battery [46,47]. The improvement in formation efficiency is more pronounced in the early stages of formation and, for a 1 wt.% loading, formation is up to three times faster with 12% less input charge [47]. For plates composed of material that is difficult to form (e.g., $\alpha\text{-PbO}$ and tetrabasic lead sulfate), the degree of improvement is even greater [46].

A detailed study has demonstrated [47] that BaPbO_3 is most stable at the discharge potential of the positive plate, and least stable at the high temperatures and positive potentials encountered during formation and charging. The products of decomposition of BaPbO_3 include PbO_2 and BaSO_4 ; the latter is found to reduce deep-discharge cycle life at levels of greater than 0.3 wt.% in the positive plate. Plots of the reserve capacity (current density 13.3 mA cm^{-2}) versus number of 100% DOD cycles for various loadings of BaPbO_3 illustrate that a loading of 1 wt.% is optimum. At these levels, the BaSO_4 content in the plate after formation is less than 0.1% and does not affect cycle life. There is little difference in reserve-capacity performance between the untreated and 1 wt.-%-doped cells.

These studies illustrate the efficacy of BaPbO_3 as a conductive additive for enhancing formation in lead/acid batteries if the loading level and formation temperature are

controlled. It does not appear, however, to be an effective agent for raising the PMU at high discharge rates, due to its instability over the potential range of the positive electrode. Barium metaplumbate has proven useful for inhibiting grid corrosion when it is coated on to the grid and then plated with an outer layer of lead [1]. This protects it from decomposition in the electrolyte.

4.3. Conductive transition metal oxides and other agents

Several reports [1,50] in the recent literature have mentioned the Magnelli phases of titanium oxides, Ti_nO_{2n-1} , and their potential employment in a number of electrochemical applications. These highly conductive materials have been patented for use as electrode materials [51] and are reported to be highly resistant to oxidation and corrosion. Among the oxides, Ti_2O_3 has a conductivity similar to graphite and may be well suited as a conductive additive in the positive plate. These oxides have high oxygen and hydrogen overpotentials, and are stable over the potential range of the PbO_2 electrode. Importantly, they are reported to be chemically stable in H_2SO_4 and show good adhesion to the active materials. Magnelli phases of titanium oxides can be obtained in a wide variety of forms, e.g., solid ceramics, reticulate structures, powders and fibres [1]. Whilst no detailed investigations of their application to lead/acid batteries have yet been published (but see Section 5), it is envisaged that a fibrous oxide might prove to be useful at the very least for increasing formation efficiency for some active materials.

A range of conductive metal oxides have recently been patented for use in lead/acid batteries for the purpose of both enhancing formation and as bipolar substrates [48,52]. These include TiO_{2-x} , WO_{3-x} , MoO_{3-x} , OsO_{3-x} , V_2O_{5-x} and Nb_2O_{5-x} , where $0 \leq x \leq 1$. Another patent reports that the addition of 3.0 wt.% TiO to the positive active-material increases the relative capacity of the battery by 6% when discharged at the 0.25C rate [53]. Titanium nitride-coated porous silica powder or beads have also been patented as the additives to the positive electrode [54]. A wide range of interstitial transition metal nitrides, carbides and borides are known to exist, and these characteristically possess great hardness, high melting points and metallic conductivity [55]. Some of these compounds may also be suitable for conductive additives in the positive plate.

4.4. Tin dioxide

A number of groups have investigated the effect of conductive tin dioxide on the performance of lead/acid positive plates [36,56–65]. Lam et al. [36] have incorporated a novel tin dioxide-coated glass flake into the positive active-material of typical automotive (NS40) plates in an effort to raise the utilization without affecting service life. The addition of a 2 wt.% loading of two proprietary additives was investigated; both particulates had a nominal 0.3 μm coating of SnO_2 , but differed in length (1/64 in versus 1/8 in) and weight (the

shorter flakes are lighter in weight). Tin dioxide is known to be stable over the potential range of the positive electrode, and in fact has been used as a corrosion protection coating for lead/acid battery grids [58]. The amount of tin leached into the battery electrolyte from the coated glass flakes was found to be minimal over long periods of time and at elevated temperature.

Lam et al. [36] employed a wide range of plate-processing conditions, and the plate performance was evaluated in terms of PMU, cold-cranking capability, repetitive reserve capacity, and life endurance under the Japanese Industrial Standard (JIS) procedure. For typical automotive plates treated with the coated glass flakes (3BS curing, acid-to-oxide ratio of 6.6%, paste density of 3.9 g cm^{-3}), the PMU increased by 7–14% at the $C_2/5$ rate, and 8–12% at the $C_{20}/20$ rate, when compared with untreated plates. Measurements of the BET surface area and total pore volume of the plates demonstrated that the PMU does not depend on either of these parameters and, therefore, it was concluded that the improvement in PMU was due to an increase in plate conductivity. It was also found that the improvement in PMU was much greater when the paste density was decreased to 3.5 g cm^{-3} .

Both additives were found [36] to assist the plate-formation process and to increase the BET surface area, but produced no significant improvement in porosity or pore volume. Under repetitive reserve-capacity cycling conditions, a small deterioration in performance was observed for plates treated with either additive (3BS curing). For JIS endurance test conditions, cells doped with one of the additives yielded better performance than untreated cells. Cold-cranking currents were not diminished for positive-limited cells. The authors concluded that further benefits could be gained if elongated, conductive flakes of less weight were employed. A number of tin oxide materials have been patented for use in lead/acid batteries. These include tin oxide whiskers with 0.01–2 wt.% antimony oxide [62], tin dioxide-coated glass fibres, flakes or powder [63], fluoride-doped tin oxide powders [64] and glass or polymer fibres coated with a layer of fluoride-doped tin oxide, to aid conductivity [65].

Several studies have reported the effects of addition of tin (II) compounds such as SnO or $SnSO_4$ to the positive paste [56] or the electrolyte [57]. Voss et al. [57] found that the addition of small quantities of $SnSO_4$ to the electrolyte in Planté cells can reverse capacity loss. The strength of the effect is dependent upon the type of charging duty that is employed. The improvement was discussed in terms of the 'Kugelhaufen' theory of plate conductivity [66] and was attributed to increased conductivity of the positive active-material.

Wei and Wang [56] studied the effect of a 1.5 wt.% addition of $SnSO_4$ to the electrolyte of a flooded industrial-type cell, and reported a 20% increase in capacity at the $C_{12}/12$ rate at 100% DOD. Material utilizations were not quoted, nor were cycle-life studies performed. Cyclic voltammetric studies confirmed that Sn^{2+} was oxidized to Sn^{4+} at positive-plate potentials. Although Sn^{4+} is soluble at low pH, it could

precipitate as SnO_2 in the positive active-material [58]. The improvement in capacity was explained in terms of the 'gel crystal' theory [67], and attributed to the incorporation of SnO_2 in the gel zones of the positive active-material that, thereby, increased in conductivity. More physical evidence is required, however, to support this contention. It has also been suggested that SnO_2 and $\beta\text{-PbO}_2$, which both exhibit a rutile structure, could form a mixed oxide of general formula $\text{Pb}_x\text{Sn}_{1-x}\text{O}_2$ that may influence conductivity [58].

4.5. Theoretical studies and conductive additives

Recently, Appel and Edwards [68] have derived a model to predict the discharge capacity of positive plates doped with conductive and non-conductive particles over a wide variety of discharge rates. The model combines Fick's laws of diffusion with a 'critical volume fraction' parameter, derived from percolation theory. The 'critical volume fraction' is defined as the ratio of conductive material to non-conductive material at which the active material becomes non-conductive. Many of the parameters employed in this model are measured directly from the plate, e.g., porosity, plate thickness, etc.

Capacity predictions were made for plates that contained 19, 34 and 54% by volume of particles [68]. For the plates with conductive particles, the predicted ratios of reacted to unreacted material were higher than those with non-conductive particles and untreated plates for all rates of discharge. The degree of improvement with respect to the plates with non-conductive particles was less as the discharge rate was increased. These results point towards the decreasing importance of conductivity at high discharge rates, and where the predominance of acid diffusion is thought to limit the reaction. Nevertheless, a 34% addition of conductive particles (20–50 μm in diameter) was predicted to double the capacity at the $C_1/1$ discharge rate (0.07 A g^{-1}). The authors do stress that this is assuming the positive active-material is stable and retains mechanical integrity throughout the life of the battery, a factor that is obviously critical. Practically, this could be very difficult to achieve for such high loadings of additive, since the paste density will be drastically reduced and perhaps cycle life as well. Furthermore, it is not clear if the predicted doubling in capacity will compensate for the substantial decrease in the plate capacity due to the lesser amount of active material per plate.

The capacity predictions for the plates containing conductive particles were unable to be validated, since a suitable stable additive could not be found [68]. The particle types under test included carbon black, graphite, titanium-coated glass microspheres and titanium powder. The experimental and predicted low-rate capacities for plates doped with 2.2–6.6 wt.% of non-conductive hollow glass microspheres showed reasonable agreement [69]. Experimental results for plates with higher loadings of glass spheres were not quoted.

5. Increase in PMU=increase in specific energy?

Although many of the reports reviewed in this paper have commented on the role of additives in enhancing the battery specific energy, few have provided any details on possible gains made. An increase in the cell specific capacity, for example, does not necessarily correspond to an increase in the cell specific energy. A vital piece of information is the average cell voltage during discharge. For gains in specific energy, the average cell voltage should be at least unchanged, and preferably increased.

To determine what sort of improvements in specific energy *might* be achieved from some of the more stable additives, some calculations have been performed with results obtained in the CSIRO laboratories. Lam et al. [36] have recently investigated the effects of the addition of tin dioxide-coated glass flakes and powdered Ti_4O_7 [70] to the positive active-material. The latter compound was prepared and characterized at the CSIRO laboratories [70]. XRD phase-analysis demonstrated that this material consisted of pure Ti_4O_7 . Both additives are highly conducting and are reported to be stable in battery electrolyte over the potential range of the positive electrode.

Typical flooded automotive cells were employed (NS40 type) in both studies, with Pb–1.7wt.%Sb grids, and identical processing conditions were used. The positive active-material was doped with a 2 wt.% loading of each additive, and the wet paste densities were adjusted to 3.9 g cm^{-3} . The addition of two proprietary tin dioxide-coated additives was investigated; both particulates had a nominal 0.3 μm coating of SnO_2 , but differed in length (1/64 in versus 1/8 in) and weight (the shorter flakes are lighter in weight). For the tin dioxide studies, the 3BS-cured plates were grouped into 2 V cells that consisted of four positives and five negatives. The cells were discharged at a constant current of either 25 A, for the determination of reserve capacity (~50 min), or 5.5 A for the $C_5/5$ rate. Further details of experimental conditions are given in Ref. [36]. Only a small amount of powdered Ti_4O_7 was prepared and, thus, this cell consisted of one positive and two negative plates. The Ti_4O_7 -treated cells were discharged at a constant current of 6.25 and 1.4 A for the reserve capacity and $C_5/5$ rates, respectively.

The specific capacities, specific energies and mass utilizations for the treated and untreated cells are summarized in Table 1. The relationship between the specific capacities and the specific energies at the reserve capacity and $C_5/5$ rates is shown in Figs. 2 and 3, respectively. The specific capacity is the product of the current and the time, divided by the number of kg of positive active-material. Calculations of the specific energy are based on standard 12 V automotive batteries. The total weight of components are estimated as a ratio of the weight of positive active-material. For example, for a positive active-material weight of 250 g per 2 V cell, the total weight of components in a 12 V battery is estimated to be $0.250 \times 6 \times 6.6 = 9.9$ kg. Whilst the specific energy values may not be entirely accurate, all data are treated in the same

Table 1

Specific capacities, specific energies and positive active-material utilizations for cells with and without 2 wt.% loadings of conductive additives [36,70]

Additive	Specific capacity (Ah kg ⁻¹) (2 V cell)		Specific energy (Wh kg ⁻¹) (12 V battery)		Positive mass utilization (%)	
	Reserve capacity	C ₃ /5	Reserve capacity	C ₃ /5	Reserve capacity	C ₃ /5
Untreated	89.8	110.0	24.9	32.4	38	48
SnO ₂ -coated flakes, 1/64 in	90.8	124.9	25.6	35.5	39	55
SnO ₂ -coated flakes, 1/8 in	83.8	119.2	24.3	34.9	36	52
Powdered Ti ₄ O ₇	105.1	125.8	33.3	38.6	46	55

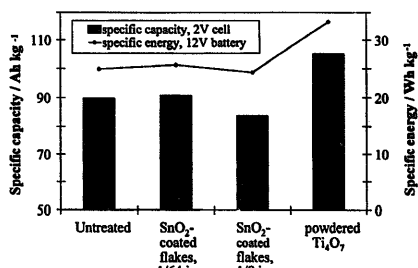
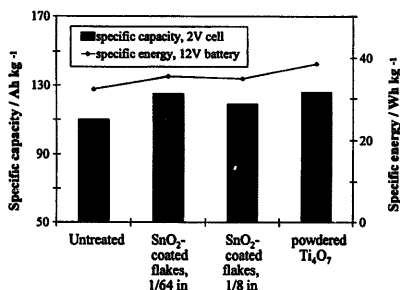


Fig. 2. Schematic representation of the change in specific energy and specific capacity at the reserve capacity rate, for cells with and without a 2 wt.% loading of conductive additives.

Fig. 3. Schematic representation of the change in specific energy and specific capacity at the C₃/5 rate for cells with and without a 2 wt.% loading of conductive additives.

manner and they are sufficient for the purposes of relating trends in specific capacity, specific energy and PMU.

The results displayed in Table 1 demonstrate that, in general, for a typical automotive cell treated with either of the conductive additives, an increase in PMU or specific capacity does correlate with an increase in specific energy. For the cells doped with tin dioxide-coated glass flakes, the gains in specific energy are greater at the lower rate, whereas for

powdered Ti₄O₇, the gains are more substantial at the higher rate. Note, the improvements in specific energy for the Ti₄O₇-treated cells appear to be unusually good, when compared with the specific capacities and mass utilizations obtained for these cells. The voltages during discharge for the Ti₄O₇-treated cell were on average slightly higher than those observed for the other cells, and this could be related to differences in the cells employed for the Ti₄O₇ (three-plate cells) and other studies (nine-plate cells). Further studies that incorporate Ti₄O₇ into identical nine-plate cells are required to enable direct comparison between the effects of these additives. Nevertheless, Ti₄O₇ appears to be a promising candidate for improving battery capacity at high rates of discharge. Under repetitive reserve-capacity duty, few differences were observed between the cycle lives of the treated and untreated cells [55,70].

At C₃/5, the target for specific energy set by the ALABC is 50 Wh kg⁻¹. Clearly, if automotive-type cells are to achieve this target, not only does the PMU need to be raised further, but improvements must also be made in other key areas that affect specific energy, such as cell weight. Additives that enhance conductivity and/or porosity could have significant impact on industrial batteries with thicker plates, where the levels of PMU are appreciable lower than in automotive cells. Relatively larger gains in PMU and specific energy might be achieved for these cells through the use of additives, depending on the total weight of the battery. Many of the papers discussed in this review have employed cells with thick plates, and lend support to this view.

6. Concluding remarks

Considerable emphasis has been placed on increasing the high-rate discharge capability of lead/acid batteries due to the emergence of new markets, such as electric vehicles and portable power supplies, that require significantly better performance. The discharge reaction is known to proceed from the active-material surface to the grid, and at high rates of discharge, conversion of PbO₂ to PbSO₄ takes place mainly in the outer regions of the porous material, close to the bulk electrolyte. For healthy plates, most of the active material is

still highly conductive, and the capacity of the battery is thought to be limited predominantly by: (i) slow acid transport to the interior of the plate due to pore blockage, and (ii) the subsequent decrease in surface area available for reaction. Therefore, additives that enhance acid transport, via increasing porosity or possibly electro-osmotic pumping, can assist in raising the positive active-material utilization. More careful study is required in the area of porosity agents and their effect on the balance of macro- and microporosity within the plate, in order to obtain the optimum proportion of pore volumes for good high-rate performance and cycle life. The concept of electro-osmotic pumping shows promise, if successful agents can be developed.

When a battery is subjected to very harsh operating conditions, such as EV duty, premature failure often occurs, due to a rapid loss of discharge capacity. This is known as 'premature capacity loss' (PCL) [71]. The exact causes of premature capacity loss are still the subject of much debate, but several recent theories have linked conductivity and connectivity problems within the active mass with PCL [18,66]. Unfortunately, few conductivity measurements on active materials doped with additives have been reported [14]; clearly such measurements would be very useful for determining the optimum loading of an additive. For high loadings of conductive additives, problems such as decreasing paste densities and lower volumetric energy densities could arise, depending on the geometry and specific volume of the additive. It has been suggested [72] that elongated, fibrous additives will produce the most efficient conducting networks in the PbO₂ electrode. Further research is required to establish optimum aspect ratios for conductive fibres. Several workers [44,45] have shown that conductive additives can play a significant role in increasing the formation efficiency of the positive plate.

In addition to forming an effective conducting network, fibrous additives may also assist in maintaining the mechanical integrity of the active mass and, therefore, promote good cycle life. Hollow or porous additives have the potential to act as 'acid reservoirs' and enhance acid supply. Possibly a combination of the two geometries may be of some benefit, and further improve additive performance.

A number of recent studies [73,74] have suggested that at some stages during typical EV duty, the battery is, in fact, limited by the performance of the *negative* electrode. Clearly, this issue must be addressed, since it raises the question of whether doping the positive active-material with porous/conductive additives will enhance battery performance during EV duty. No reports have appeared that examine the effects of conductive/porosity additives in the positive active-material under, for example, the Simplified Federal Urban Driving Schedule (SFUDS duty).

In conclusion, a variety of additives have been added to the positive active-material in an effort to increase the porosity and/or conductivity of the active mass, and thereby raise the positive active-material utilization. Only a handful of materials tested to date can withstand the strongly oxidizing

conditions encountered during formation and charging, e.g. silica gel, glass spheres, SnO₂ and the Magnelli phases of titanium oxides, but it is encouraging that some gains in PMU and specific energy at high rates of discharge can be achieved through the use of such additives. Further research is required to improve the cycle lives of these doped active materials, particularly at high rates of discharge. Therefore, although some positive advances have been made, there is scope for greater improvement.

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