

Lead–acid technology: a look to possible future achievements

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Abstract

The last five years have produced dramatic improvements in understanding lead–acid batteries. Future battery technologies will build on these advances. Battery designs will incorporate more and thinner plates with grids produced from continuous processes using stronger, more corrosion-resistant grid alloys capable of longer life at elevated temperatures. Battery grids will become more sheet-like, producing more uniform discharges and higher utilization of active material. Batteries will be sealed and utilize gel, AGM, or novel separator/acid-retention systems which will apply uniform pressure to the active-material for longer life. Improvements in charging systems will increase life and permit improved active-material utilization via rapid charging, partial state-of-charge operation, and reduction of overcharge. Possible advances are extremely *thin film* batteries to supply high power for vehicle starting or other applications. Advanced batteries for motive power will be rapidly recharged to provide three shift usage with charging between shifts. Robust lead–acid batteries for remote power locations will be continually operated in partial state-of-charge and charged with low currents. Purposely-built lead–acid batteries will drive hybrid or electric vehicles. Improved batteries for standby power applications will yield uniform cell-to-cell performance and longer life. This paper details the improvements in lead–acid battery technology that will permit these achievements to be realized. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Battery grids; Corrosion; Lead–acid batteries; Lead–calcium alloys; Strength; Tin effects

1. Introduction

The last five years have produced dramatic improvements in understanding the electrochemistry of the lead–acid battery system. World-wide battery research, led by breakthroughs sponsored by the Advanced Lead–Acid Battery Consortium (ALABC), has increased dramatically. This research has given rise to improved battery grid alloys which are stronger and more corrosion-resistant than conventional alloys. These new grid materials have initiated many new lead–acid battery designs to take advantage of these new materials.

Recent work on battery charging has yielded a better understanding of the nature of the gradual degradation of capacity in lead–acid batteries and how this can be reduced through improved battery design and construction. Work on rapid charging particularly using controlled pulses of high current has shown that the small crystal morphology of the battery active materials that is produced during formation may be maintained or enhanced. This work has also highlighted the deleterious effects of extensive

amounts of overcharge and how this can reduce battery capacity.

2. Improvements in battery grid materials

There has also been a marked change in the lead alloys used for automotive as well as industrial batteries. New alloys have been developed to replace the traditional lead–antimony alloys which have been used for many years. The demand for maintenance-free batteries, higher demands on batteries via parasitic loads, higher underhood temperatures caused by vehicle aerodynamics, and automation of the plate-making processes have all increased the performance required from the lead alloys used for automotive batteries.

With the need for increased cycling from industrial batteries, as well as the move from wet construction to valve-regulated lead–acid (VRLA) ‘sealed’ batteries, the demands on battery grid alloys for these applications have also increased. Even in cycling batteries where high-antimony alloys have been traditionally used, new grid alloys have been introduced. VRLA batteries with their ease of use, low maintenance, and non-spill characteristics use these new grid materials.

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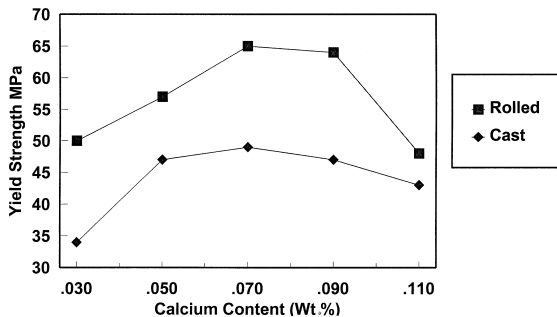


Fig. 1. Effect of calcium content on the yield strength of Pb–Ca–1.5 wt.% Sn alloys.

The major improvement in grid alloys has been the reduction in gassing in the battery caused by a change from the lead–antimony to the lead–calcium system. In addition, these latter alloys have been made more corrosion resistant by the addition of tin and silver as well as by improved processing to control more closely the composition and the grain structure. The alloys have been made stronger and more creep resistant. Combined with the improved corrosion resistance, the stronger materials produce more stable grid materials which can produce longer battery life when the alloys are used in improved grid designs.

2.1. Mechanical properties

The structural parts of the battery (grids, straps and terminals) must have sufficient strength to maintain the

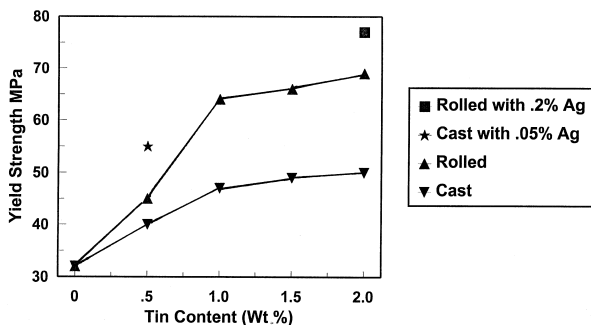


Fig. 2. Effect of tin content on the yield strength of Pb–0.07 wt.% Ca–Sn alloys.

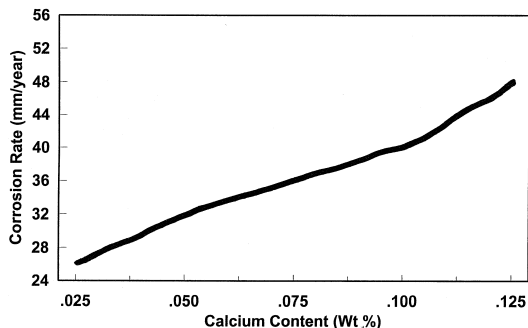


Fig. 3. Effect of calcium content on rate of corrosion of Pb–Ca alloys.

Tin Content (Wt %)	Corrosion Wt. Loss (mg/cm ²)			
	0.6	1.2	1.5	3.0
0.1 Ca	126	80	76	54
0.08 Ca	75	37	33	32
0.08 Ca + 0.05 Ag	39	22	--	--

Fig. 4. Effect of tin and silver additions on the corrosion resistance of Pb–Ca alloys.

integrity of the active material under the corrosive conditions within the battery. The effect of calcium on the yield strength (YS) of cast and rolled lead–calcium–tin alloys containing 1.5 wt.% tin is shown in Fig. 1. The mechanical properties reach a peak at about 0.07–0.09 wt.% calcium, and then decrease. Rolling the material increases the yield strength. For lead–calcium alloys, the yield strength is a more important parameter than ultimate tensile strength (UTS) because a low yield strength combined with a high tensile strength will often lead to growth of the grids in service of the material, while a slightly higher yield strength closer to the tensile strength will be less subject to growth. The effects of calcium and tin on the YS, UTS, and creep characteristics of cast and rolled Pb–Ca–Sn alloys has been detailed [1,2].

Tin increases the mechanical properties. For example, Fig. 2 shows the effects of increasing the tin content on the yield strength of Pb–Ca–Sn alloys. The effects of tin on the yield strength are dramatic and increase as the tin content is increased up to a peak of 1.5–2 wt.% and subsequently decrease as the tin is increased further [3]. Rolling the material increases the yield strength at all tin levels, but is particularly effective at higher tin contents.

The addition of silver to a cast or rolled material enhances the mechanical properties and makes the material more resistant to deformation or creep and growth [4,5].

2.2. Calcium content

The rate of corrosion of lead–calcium alloys increases as the calcium content is increased [6,7]. Positive grid corrosion is one of the major causes of reduced battery

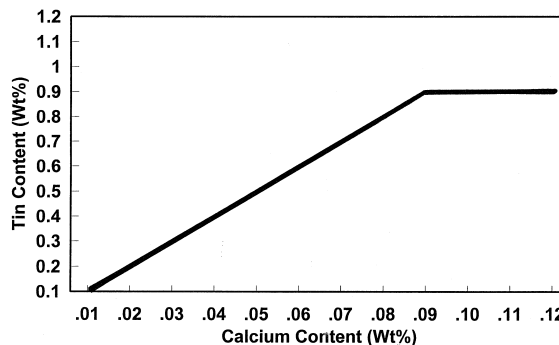


Fig. 5. Amount of tin required to form Sn₃Ca as a function of calcium content.

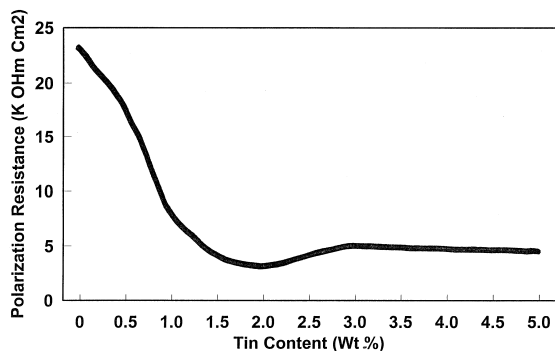


Fig. 6. Effect of tin content on the polarization resistance of Pb–0.08 wt.% Ca–*x* wt.% Sn alloys.

life. Elevated temperatures increase the rate of grid corrosion. It is estimated that for every 20°C increase in temperature, the corrosion rate doubles. With both automotive and industrial batteries now operating at higher temperatures, it is important to decrease the rate of corrosion of the positive grid. As seen in Fig. 3: the lower the calcium content, the lower is the rate of corrosion. Thus, there is a world-wide movement to reduce the calcium content of positive grid alloys to improve the resistance to corrosion.

2.3. Tin content

Perhaps more important than their effect on mechanical properties, tin additions to lead–calcium alloys reduce dramatically the rate of corrosion [8–10]. The reduction in corrosion rate is believed to be due to the formation of tin-doped PbO₂ passive layers [11,12], much like chromium additions in stainless steel inhibit corrosion of this material. The effect of tin additions on the corrosion rate of

lead–calcium alloys with two different calcium contents are shown in Fig. 4 [13]. The rate of corrosion drops dramatically as the tin content is increased to levels of 1 wt.% or more. There seems to be a threshold level for tin content to protect the lead–calcium alloy by formation of the passive film.

The corrosion rate, as well as the level of tin required to form the passive layer, decreases as the calcium content is decreased (Fig. 4). Two mechanisms contribute to this decrease. Tin reacts with calcium in lead–calcium–tin alloys to form Sn₃Ca intermetallic compounds [1,2]. For each 0.01 wt.% calcium in the alloy, 0.09 wt.% tin is required to react stoichiometrically to form the Sn₃Ca intermetallic compound. The amount of tin which is required to react with the calcium to form Sn₃Ca intermetallic compounds in lead–calcium–tin alloys is shown in Fig. 5. If all the tin is consumed to react with calcium, there is no extra tin available to assist in forming the passive, protective tin-doped PbO₂ layer. The maximum reactivity of tin with calcium is clearly illustrated in Fig. 5. The line bends where Pb₃Ca is formed in the melt during solidification and no additional calcium is available to react with tin despite the higher calcium content.

For lead–calcium–tin alloys in which the calcium content is less than 0.10 wt.%, decreasing the calcium not only decreases the rate of corrosion caused by the calcium but also increases the amount of tin available to form the passive film on the surface of the grid alloy.

The effects of tin on the polarization resistance of Pb–0.08 wt.% calcium alloys as a function of tin is presented in Fig. 6 [8]. The polarization resistance decreases until the tin reaches a level of about 1.5 wt.%, and then remains uniform. Moreover, the resistance of the corrosion film decreases markedly at a calcium content of about 1.5 wt.%. At a calcium content of 0.08 wt.%, about

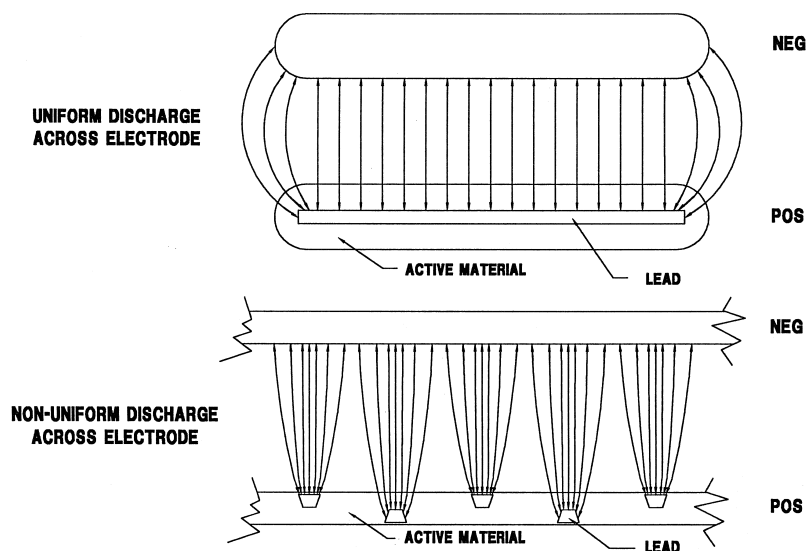


Fig. 7. Effect of grid geometry on discharge characteristics.

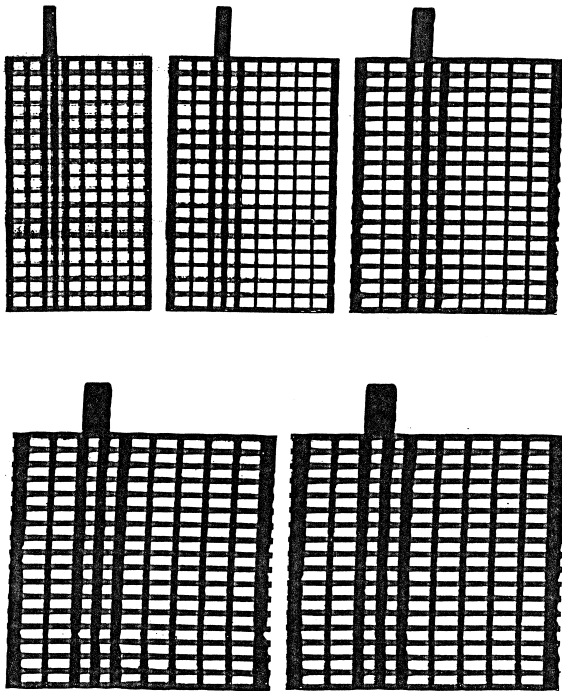


Fig. 8. Wirtz con-roll/East Penn/ALABC grid-production process.

0.72 wt.% tin is tied up as Sn_3Ca . The remaining tin is available to form rapidly a conductive corrosion product enriched in tin and deficient in PbO . At a level of 0.08 wt.% calcium and 1.5 wt.% tin in the positive grid alloy, it can be calculated that about 0.78 wt.% tin is available to form the corrosion-resistant conductive film. This is in good agreement with grid materials used in some lead–acid batteries which do not contain calcium. These grid materials normally use 0.6 to 0.8 wt.% tin and have unusually low rates of corrosion.

Grid materials with calcium contents below 0.08 wt.% calcium in the above example should require less tin to achieve the threshold conductive layer. Decreasing the resistance of this corrosion layer by the addition of tin improves recharge. It also reduces the PbO in the corrosion film, which decreases the resistance of the grid/active-material layer.

Based on these discoveries that tin reduces the rate of corrosion and promotes the formation of a conductive corrosion film, many battery companies have increased the amount of tin in the grid materials so that non-conducting

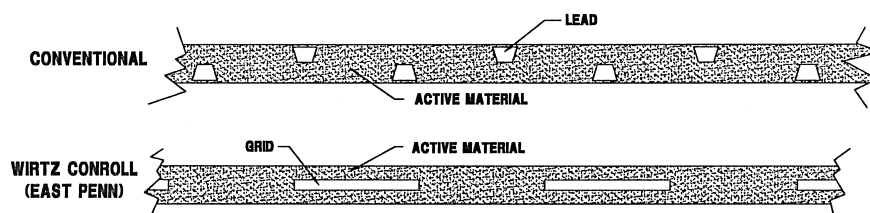


Fig. 9. Wirtz con-roll/East Penn/ALABC battery plate.

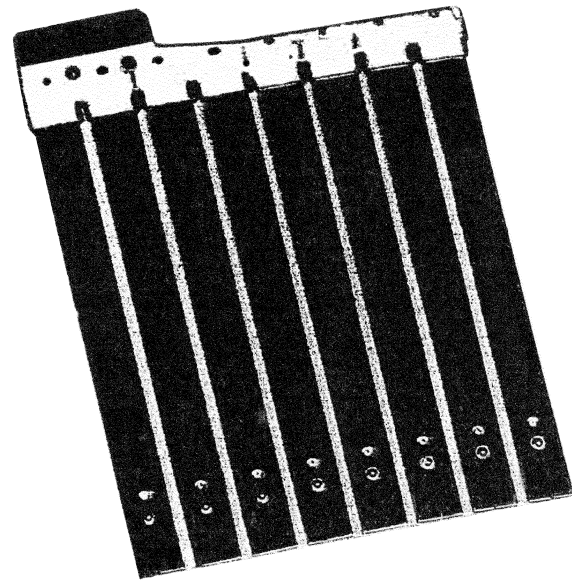


Fig. 10. Yuasa/ALABC improved, flat, tubular, positive grid.

layers at the grid/active-material interface can be eliminated and recharge of the battery is improved [14].

2.4. Silver content

Silver is added to lead–calcium–tin alloys to decrease further the corrosion rate [13,15]. Silver in combination with tin has been shown to decrease dramatically the rate of corrosion of these grid alloys. For example, the effects of silver on the rate of corrosion of such alloys with 0.08 wt.% calcium are presented in Fig. 4. Silver decreases the rate of corrosion of each alloy by about the same amount.

In addition to increasing the resistance of lead–calcium–tin alloys to corrosion, silver dramatically increases the creep resistance of the alloys. The increased creep resistance makes the alloys more stable at the elevated temperatures which are now being encountered much more frequently in automotive and industrial batteries.

2.5. Barium

Barium additions to lead–calcium–tin alloys have been shown to increase dramatically the mechanical properties [16,17]. In addition, barium serves to stabilize the grain

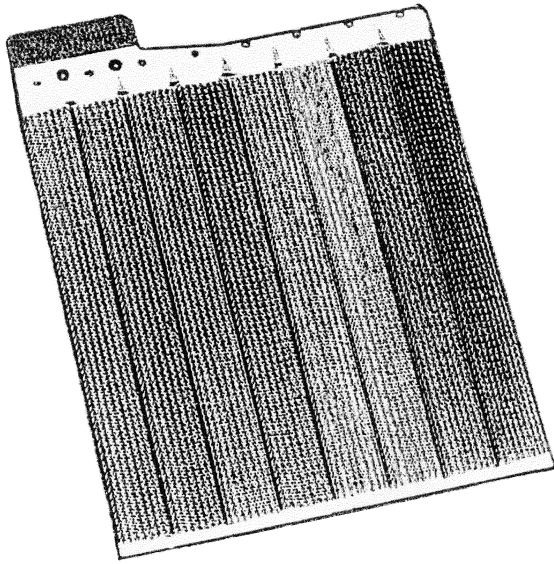


Fig. 11. Yuasa/ALABC improved, flat, tubular positive plate.

structures of the alloys so that they are less susceptible to over-ageing or are prevented from over-ageing completely. Thus, barium additions may serve to prevent completely recrystallization or grain boundary movement in the alloys, and to reduce the effects of high-temperature corrosion caused by loss of mechanical properties and microstructural instability. If barium does not cause softening or shedding of the active material, it may serve as a positive additive to grid alloys for improved batteries.

The addition of tin for improved corrosion resistance, enhanced conductivity of the corrosion interface and increased mechanical properties indicates a tin content of between 1 and 2 wt.% for modern positive-grid alloys. Lower tin contents do not provide adequate mechanical properties, greater stability by reacting with the calcium in the alloy, improved corrosion resistance, or enhanced conductivity of the corrosion layer. Higher tin contents may provide improved corrosion resistance but may result in decreased mechanical properties. A low calcium content combined with adequate tin and a small amount of silver

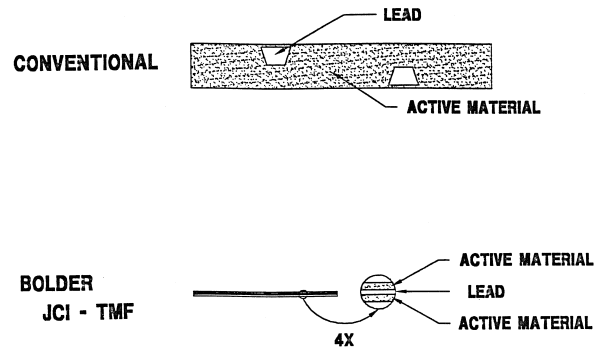


Fig. 13. BOLDER/JCI thin metal foil battery plate.

appears to be the best-performing material for positive grids. Barium may enhanced the effect.

3. Novel battery designs

With improved battery grid materials which are stronger, more corrosion resistant, more creep resistant, more stable at elevated temperatures, and provide improved conductivity between the grid and active material, novel battery concepts have been developed that take advantage of these improvements and offer the possibility of improved battery performance in smaller and lighter packages.

3.1. Movement to sheet-like electrodes

The benefits of a sheet-like electrode are many. The concept is illustrated in Fig. 7. The sheet-like positive electrode offers much more uniform discharge and recharge characteristics for the positive active-material compared with those for conventional cast or expanded-metal grids. The discharge and recharge currents across the surface of the electrode are very uniform. In addition, the corrosion is reduced because the grid has a high surface area and therefore gives lower corrosion currents ($A\text{ cm}^{-2}$) than conventional materials.

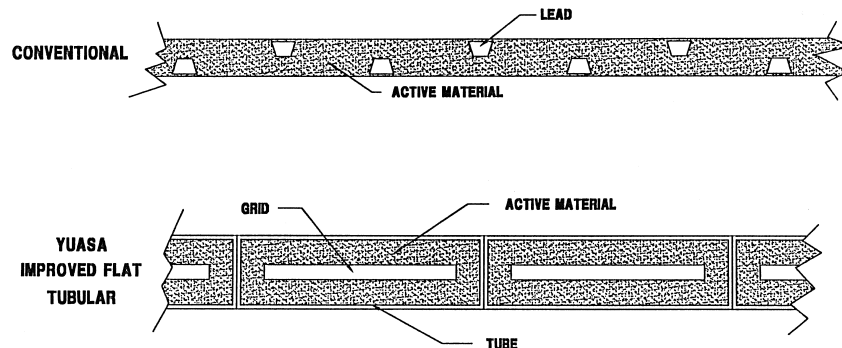


Fig. 12. Cross-sections of conventional positive plate and Yuasa/ALABC improved, flat, tubular positive plate.

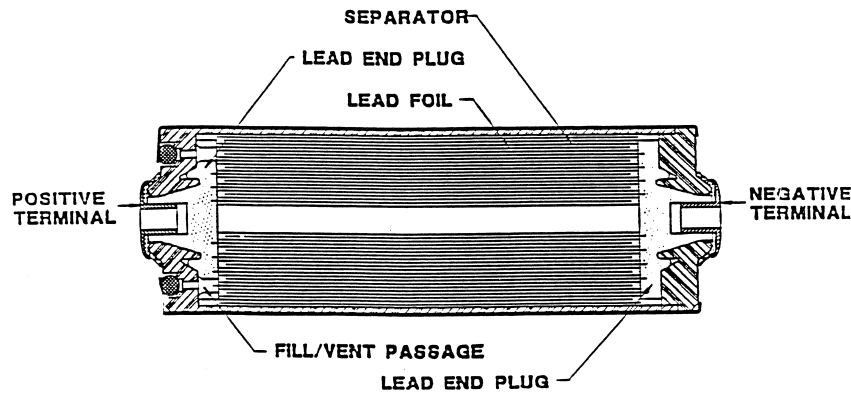


Fig. 14. BOLDER/JCI thin metal foil battery.

The development of the flat concept of electrodes can be seen in conventional electrodes which utilize the Wirtz con-roll process, in flat tubular grids and, ultimately, in the BOLDER TMF/JCI-TMF battery.

3.2. Flat conventional electrodes

The Wirtz con-roll process is shown diagrammatically in Fig. 8. In the process, a grid shape is continuously cast from a machined drum. The grid shape is rolled in a series of mills to the final grid thickness, i.e., the grid wires become flattened and elongated. The sheet-like characteristics of the material of these electrodes are compared in Fig. 9 with those of conventional plate [18]. This material is currently being evaluated as light weight grids in an ALABC project at the East Penn.

3.3. Flat tubular electrodes

In an ALABC programme at Yuasa [19], flat tubular grids are being evaluated for electric vehicle (EV), hybrid electric vehicle (HEV), and other cycling applications. The use of flat tubular grids produced via casting or by punching from strong wrought lead–calcium–tin alloys has been described [20–22]. An example of the grids produced by Yuasa is shown in Fig. 10, the material is a rolled Pb–0.07 wt.% Ca–1.5 wt.% Sn alloy. It is sufficiently strong that spines as thin as 0.75 mm can easily be handled. An improved tubular plate for lower weight and higher specific density is shown in Fig. 11, and in cross-section in Fig. 12. Note the uniformity of the active material around the grid members to produce uniform charge and discharge across the entire electrode. These flat tubular plates have given improved active-material utilization compared with conventional electrodes of the same dimensions.

3.4. True sheet electrodes

The BOLDER TMF/JCT TMF spiral, wound, thin metal sheet electrode [23,24] offers extremely high power and excellent rechargeability. The grids for this battery are

rolled sheets of only 0.05 to 0.08 mm in thickness and have an active-material layer of about the same dimensions. As seen in Fig. 13, these thin sheet electrodes offer the ultimate design for uniform charge and discharge of the active material. Moreover, the novel method of having the positive ‘terminal’ at one end and the negative at the other end of the cell improves the high-rate performance of the electrodes (Fig. 14). These cells are being evaluated for use in power tools, automobile starting, and other applications, such as HEVs, where high power and rapid recharge capability is required.

3.5. Minimal grid weight

Highly corrosion-resistant materials combined with lightweight strong fibre cores, have led to the development of the Horizon, a battery with high specific energy from Electrosorce. The cross-section of the pasted electrodes of this novel battery is presented in Fig. 15. The battery takes the opposite approach to sheet electrodes by minimizing grid weight.

4. Rapid recharge and partial-state-of-charge cycling

One of the most important areas in on-going battery research, particularly for cycling batteries, EVs and remote-area power supplies, is control of the charging pro-

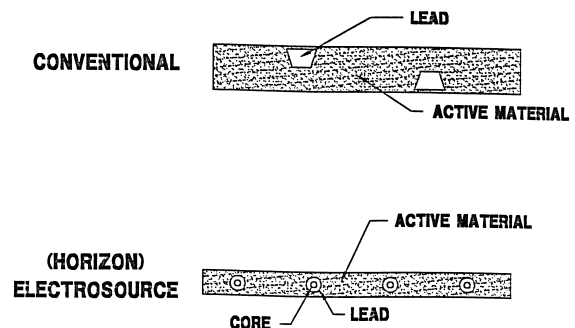


Fig. 15. Electrosorce Horizon battery plate.

cess. Work in ALABC projects at Cominco have shown that virtually all lead–acid batteries can be rapidly recharged [25]. In addition VRLA batteries can be rapidly charged and discharged in the undercharged condition to give greatly improved lifetime ampere–hour capacity compared with batteries fully charged at each cycle [26]. A major part of the decrease in life of batteries is the positive grid corrosion caused by overcharge required for complete conversion of the active material. Ageing of the electrodes and impurities increase the amount of overcharge required. By not fully recharging at each cycle, grid corrosion can be avoided except when the battery is fully charged. Cycling VRLA batteries between 20 and 70% state-of-charge has resulted in almost 100% recharge efficiency [27,28]. Rapid recharge with high initial charging current in this less than 100% state-of-charge regime keeps the active-material crystal size small and dramatically increases life.

To cycle effectively in a reduced state-of-charge condition, batteries must have no stratification of the electrolyte. VRLA batteries with immobilized electrolyte offers the opportunity to operate in the partially discharged condition without major stratification problems.

5. Summary

Novel battery designs have been spawned by the research into battery grid alloys conducted over the past six years in the ALABC programmes. The ALABC projects have initiated research programmes which should produce even more novel battery designs which will offer lower internal resistance and provide short, uniform conduction paths between positive and negative electrodes. The batteries will be constructed from strong, creep-resistant, conducting, corrosion-resistant lead alloys. They will not only be able to be rapidly recharged and discharged, but will also provide long life when charged properly.

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