Modern lead/acid battery technology: new materials*

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Abstract

New materials, introduced into the production of lead/acid batteries, have allowed the development of improved technologies and new designs of battery This paper reviews advances in materials for the production of battery plates, separator materials, and materials for battery containers Discussion on plate materials includes grid alloys, materials for non-conventional grids, pure lead for leady oxide for hermetically-sealed batteries, and granulated lead oxide

Introduction

Although many years have passed since the invention of the lead/acid battery, it still represents the most important secondary chemical power source — both in number of types and diversity of application The lead/ acid battery has maintained its leading role for so long due to its competitive electrical characteristics and price, and to its adaptability to new applications Since the inception of the battery, the technology of its production has been changed, more or less rapidly, depending on the requirements of the duty imposed and the existing level of development of science and technology After World War II, efforts to improve the battery were intensified — both from production and application aspects and, more recently, from the need to provide safer environmental conditions. These activities have resulted in the further development of production technologies and the introduction of new types of battery design The greatest achievement in the past 20 years is the realization of a hermetically-sealed lead/acid battery with oxygen recombination This may be classified as one of five greatest advances since the invention of the battery [1] The remaining four notable achievements are the pasted electrode, the use of Pb–Sb alloy for grid manufacture, the development of the expander for negative electrodes, and the introduction of separators made from synthetic material.

The realization of modern production technology, as is obvious from the above-mentioned achievements, has been obtained by the application of new materials and equipment. In both cases, necessary materials and necessary

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equipment have been provided by parallel development in the fields of metallurgy, chemical technology, mechanical engineering, electrical engineering, electronics, and other specialist disciplines

The following items are typical of the progress made in the production of lead/acid batteries (i) the introduction of an increasing degree of automation in order to protect the environment against pollution that may be caused by lead and other harmful agents encountered in the manufacturing process and to cut costs, (ii) improvement of performance characteristics of batteries (e g , starting ability at low temperatures, shelf-life, specific power and energy, etc), (iii) development of new types of battery (e g , maintenance-free, oxygen-recombination, electric vehicle batteries, load-levelling batteries, portable-power batteries, etc.)

This review discusses the series of significant advances in the field of materials for the production of lead/acid batteries during the past 10 to 15 years The materials will be reported in the following order (i) materials for the production of plates, (ii) separator materials, (iii) materials for battery containers The plate materials do not include additives to the active materials as it would be more convenient to present these as part of an analysis of achievements in the production of pastes, due to the specificity of the additives

Materials for plate production

Grid alloys

In the past 15–20 years, a series of new alloys has been proposed for the grids of automotive batteries Most of these alloys (e g , Pb–Sr and Pb–Sb–Cd alloys), however, have not been adopted in industry [2] The alloys now in use (i e , lead–antimony and lead–calcium types) have been improved and adapted according to the fabrication method These alloys are required to have technological properties that are suitable for grid production by one of the following processes conventional casting, continuous casting, die casting, expansion

For automotive batteries in the U S A , it is common practice to use lead–calcium alloys in the negative plates and low-antimony alloys in the positives (so-called 'hybrid' combination of plates) In most other countries, alloys with low antimony contents are overwhelmingly favoured [3]

Table 1 presents the various types of alloys that are presently in use, as well as qualitative estimation of their significant properties, capability of processing, suitability for maintenance-free batteries, and cost factor The conventional lead–antimony alloy (4 to 6 wt % Sb) has been included for comparison purposes, despite the fact that it is no longer employed in automotive batteries Note, however, it is now used for the manufacture of grids for tubular industrial batteries instead of Pb–Sb alloy containing 9 to 10 wt % Sb This replacement has been made possible by the introduction of new casting machines that can handle alloys with lower antimony contents [3]

TABLE 1

Present comparison of the properties of grid alloys [2]

Alloy	Ease of manufacture	Conductivity	Corrosion resistance	Self-discharge	Cycle life	Maintenance-free performance	Cost
Conventional antimony (4–6 wt % Sb)	good	poor	fair	poor	good	poor	fair
Low antimony (1 5–3 5 wt % Sb)	fair/good	fair	fair	fair	fair/good	fair	good
Very low antimony (0 7–1 5 wt % Sb)	fair	good	fair/good	fair/good	fair	fair/good	fair/good
Calcium–low tin	fair	good	good	good	fair	good	fair
Calcium–tin–aluminium	good	good	good	good	fair	good	good
Calcium wrought alloys	good	good	good	good	fair/good	good	good

As it can be seen from the data in Table 1, alloys with low antimony contents (1 5 to 3 5 wt %) are highly valued for their cost, while other features are close to good (fair/good) or satisfactory (fair) With regard to suitability for maintenance-free batteries, it should be noted that the 'fair' estimation refers, in fact, to batteries with *low* maintenance This ambiguity results from incomplete and inconsistent distinction between the terms maintenance-free' and 'low maintenance'

Alloys with very low antimony contents (0 7 to 0 5 wt % Sb) have a good advantage with respect to electrical conductivity, and close to good for corrosion resistance, self discharge and cost The latter estimation also holds for maintenance-free application, in which case it should be noted that alloys containing $\leqslant 1$ wt % Sb can be used for the positive plate batteries with oxygen recombination The eutectic at the grain boundaries in these alloys does not contain antimony The whole of the antimony is located in a solid solution, or is deposited sub-microscopically during ageing of the alloy Under these conditions, the amounts of antimony that may be extracted from the positive grid by anodic corrosion is minimal and, consequently the undesirable transfer of antimony to the negative grid is negligible [4]

All three classes of calcium alloys are suitable for recombinant batteries Among cast-type alloys, those with a low-tin content (Ca–low Sn) and those with tin and aluminium have good characteristics except for cycle life for which the estimation is satisfactory The ease of production and cost of low-tin alloy are also only satisfactory Calcium alloys containing tin and aluminium are used for grid manufacture by rolling and expansion (wrought alloys) and are characterized by high values for all characteristics

Decrease in antimony content has caused difficulties in the process of grid casting Meanwhile, improvements in the technology of casting (e g , the Wirtz Cast Master machine) have made it possible to lower the content of antimony from 2 75 wt % to approximately 1 wt % [3] In order to obtain grids with a fine-grain structure, and resistance to cracks and corrosion, from very-low antimony alloys, it is necessary to use nucleating agents such as sulfur, selenium and copper in very low concentrations For alloys with < 2 wt % Sb, selenium is the major choice of nucleating agent and is applied in combination with sulfur and copper Casting of such alloys requires higher temperatures (from 460 to 500 °C) that must be rigidly maintained in order to avoid losses of nucleating agents via deposition in the molten metal before casting of the grids has been completed To improve other properties (e g , mechanical strength, passivation resistance), small quantities of As (0 2 wt %) and Sn (0 2 to 0 4 wt %) should be added

When first used in lead/acid batteries, lead–calcium grid alloys contained 0 08 to 0 11 wt % Ca In addition, tin was added to prevent the formation of a passivating layer at the grid/positive active material interface This layer interfered with the charging process of positive electrodes after deep discharge, and this decreased battery cycle life Initially, the tin content ranged from 0 5 to 0 7 wt % but has now been reduced to 0 3 to 0 4 wt %, tin is added only to the alloy for positive grids There was another problem to be solved,

namely, the high reactivity of calcium in the molten alloy. This resulted in the formation of large quantities of intermetallic compounds as well as oxide drossing This behaviour adversely influences alloy quality and decreases productivity Inclusions of calcium oxide in the grids, or its deposition on the grid surface, cause serious corrosion problems To solve these problems, aluminium has been added to the alloy [6] through optimization of the process The aluminium content has been reduced from 0 03 to 0 05 wt % to 0 015 to 0 025 wt % The action of aluminium is to form an aluminium-oxide-rich surface film that prevents contact between the molten metal and air and, hence, deters calcium oxidation

The two most important classes of alloys — low antimony and calcium types — may be further improved by the introduction of low concentrations of other alloying elements, optimization of alloy content, and optimization of the conditions under which grid manufacture is conducted

Materials for non-conventional grid production

In the past few years, two new metallic materials for non-conventional grid production have been developed These are (i) copper-stretch-metal (CSM) [3, 7], (ii) lead-coated wire produced by the process developed by the Electrosource company [3, 5] The use of either material gives rise to a significant reduction in the impedance (internal resistance) of the battery

Copper-stretch-metal (CSM)

This material is manufactured by the stretching of copper strip The width of the strip is the length of the resulting grids Stretched strip is subjected to the following operations

(i) the strip is electrolytically coated with lead–tin alloy (which may contain selenium as well), and afterwards with pure lead,

(ii) the length of grid is cut to the dimensions required,

(iii) a plastic bar is applied to the bottom part of the grid by injection moulding,

(iv) bars made of lead alloy are automatically cast onto the upper part of grid, this renders the grid suitable for further conventional production of electrodes

The grids produced by the above process are used only for negative electrodes in combination with tubular positive electrodes Such combination of electrodes has been applied in traction, submarine and load-levelling duties

Lead-coated wire

The composite wire for grid manufacture is produced by computer-controlled application of coatings of pure lead, lead–tin alloy, and lead–antimony (1 5 wt % Sb) or lead–calcium alloy on to a fine wire of copper (e g , 0 20 mm dia), glass fibre or other material The processing is performed in a special design of extruder The mechanical properties of the coatings are not important as the mechanical load is carried by the basic (core) wire The core and coating materials are selected according to the

battery application Purpose-designed processes are required to prepare grids from the coated wires

Lead feedstock for leady oxide

The introduction of maintenance-free, hermetically-sealed batteries into the market has initiated a re-evaluation of the maximum amount of impurities permissible in pure lead for the production of leady oxide In the first place, this relates to impurities able to cause gassing, i e , Sb, As, Se, Te, Ni, Co and Mn The maximum allowed concentrations for Bi, Ag, Sn and Cu have not been reduced, because these impurities in the 'normal' concentrations encountered to date in pure lead do not influence the rate of gassing To obtain lead of satisfactory purity, it is necessary to develop a more efficient process of purification and to introduce sensitive analytical methods of control Table 2 shows the typical requirements for lead purity for sealed automotive batteries

Granulated lead oxide

Manufacturers of tubular batteries have to meet very strict regulations regarding the content of lead (lead dust) in air Factory shops in which tubular electrodes are charged with dry oxide material are the major problem areas Therefore, new processes are being developed and introduced to prevent pollution exceeding the allowed limits One of these processes is the so-called 'wet-fill' process, in which the tubular electrodes are charged with a paste of adequate consistency An alternative approach is to use granulated lead oxide [8]

Granulated oxide has good free-flowing properties and creates little dust during handling Thus, the application of this material decreases significantly the air-borne content of lead in factory shops. On account of the free-flowing nature of granular oxide, electrode tubes can be charged considerably more rapidly (~ 5 times) than when using conventional oxide powder The typical chemical composition and properties of granulated oxide are given in

TABLE 2

Maximum allowed concentrations of impurities in pure lead for leady oxide to be used in the manufacture of hermetically-sealed automotive batteries [5]

Element	Maximum allowed concentration (wt %)
Sb	0 0001
As	0 0001
Co	0 0001
Mn	0 00005
Ni	0 0002
Se	0 00005
Te	0 00003

TABLE 3

Comparison of properties of granular oxide [8] and conventional (blended) oxide

Parameter	Granular oxide		Blended oxide[a]	
Chemical composition				
PbO_2	8–10%		9–14%	
PbO	<2%		9–14%	
Sulfate	7%		nil	
Pb	balance		balance	
Oxide density (g ml^{-1}) (JEL volumeter)	3 3–3 8		3 3–4 0	
BET surface area (m^2 g^{-1})	1 7		0 84	
Particle-size distribution	%	Size range (μm)	%	Size range (μm)
	100	<1500	99	<20
	40	<500	7	10–15
	18	250–500	10	8–10
	13	125–250	18	6–8
	9	63–125	25	4–6
	12	<63	38	<4

[a]Proprietary blends of red lead and leady oxide

Table 3. The granulated oxide is prepared from a mixture of red lead (specified as PbO_2 in Table 2), and leady oxide, using sulfuric acid as a binding material

The data given in Table 3 clearly show that although granular oxide has a wide distribution in particle size there are few small particles (<63 μm). Such distribution in particle size allows the possibility for uniform filling of electrode tubes, with only a small risk of blockage In addition, there is good accessibility to acid to the active material Dry filling with granular oxide apparently has advantages over the alternative wet-fill process

Materials for separators

Separators have two basic roles First, being electrical isolators, separators prevent the occurrence of short-circuits between electrodes of different polarity Second, the separators serve as mechanical spacers between the electrodes and decrease the rate of shedding of active material Separator materials should have the following important properties
● good wettability with regard to the electrolyte
● high porosity, as characterized by small pore dimensions
● low electrical resistance
● high resistance to oxidation

- good mechanical properties (these are important in battery assembly as well as for operation of the batteries under vibrational conditions and at high/low temperatures)
- low consumption of electrolyte as a consequence of small thickness

Separators for automotive batteries

The most important types of separators in use today for automotive batteries may be classified in four groups [9], according to the material These are

(i) cellulosic separators in a form of leaves made of cellulosic fibers (wood or cotton), mechanically fixed and chemically protected with phenol-formaldehyde resin,

(ii) separators obtained by sintering polyvinylchloride (PVC) powder,

(iii) separators made from fine glass microfibre paper, which may contain synthetic polymeric fibers as well, connected firmly in one piece by means of binding material based on latex,

(iv) separators based on polyethylene of high molecular mass and containing purified deposited silica to provide mechanical strength and to maintain constant wettability of the separator

All the above separator types are used in a form of leaves ('leaf' separators), while the polyethylene versions can also be used successfully in the form of an envelope that can be sealed on three sides ('envelope' separators) In batteries with grids based on antimony alloys, both leaf and envelope separators can be employed On the other hand, only envelope designs can be used in batteries with lead–calcium alloys The latter is due to the inadequate adhesion of the paste to the grids and the need to prevent dendrites at the positive electrode boundary from causing short-circuits

The most important properties of the above four groups of separators are listed in Table 4 [9] It can be seen that glass and polyethylene separators have the best properties Due to the low electrical resistance of these separators, higher power values can be attained on automotive discharging at low temperatures, as indicated by low values for the voltage drop at -18 °C These two types of separators are also characterized by low values of acid displacement These allow the attainment of higher values for reserve capacity compared with cellulose and PVC separators Polyethylene separators are noted for their puncture resistance (on wrapping of the electrodes in separator material) and resistance to penetration of dendrites, due to the very low mean pore diameter ($<0 1$ μm) Glass and polyethylene separators have been on the market for more than 10 years and efforts to improve their performance are still in progress

Trends in the utilization of the various types of separators for automotive batteries in the U.S.A. for the period 1980–1996 are given in Fig 1 [10]

The scope of utilization of polyethylene separators (designated as polymeric in Fig 1) has been in progress since 1980, while the ratio of utilization of cellulosic separators has decreased Utilization of glass separators increased in the period from 1984 to 1987 Meanwhile, since 1987 the utilization of

TABLE 4

Properties of separators made from various materials [9]

Property	Cellulose	PVC	Glass	Polyethylene
Electrical resistance (Ω cm^2)				
25 °C	0 22	0 16	0 08	0 08
− 18 °C	0 67	0 49	0 24	0 24
Voltage drop[a] − 18 °C (V/cell)	0 137	0 098	0 049	0 049
Acid displacement[b]				
ml cm^{-2}	0 02	0 08	0 01	0 01
ml/cell	39 10	58 65	19 55	19 55
Mean pore diameter (μm)	25 00	13 00	24 00	<0 1
Puncture (g)				
Dry	350	500	320	
Corrosive	100	450	300	

[a]400 A, 11-plate automotive battery with 10 separators and 1 280 sp gr acid
[b]Separator with an overall thickness of 1 04 mm and dimensions 133 × 148 mm
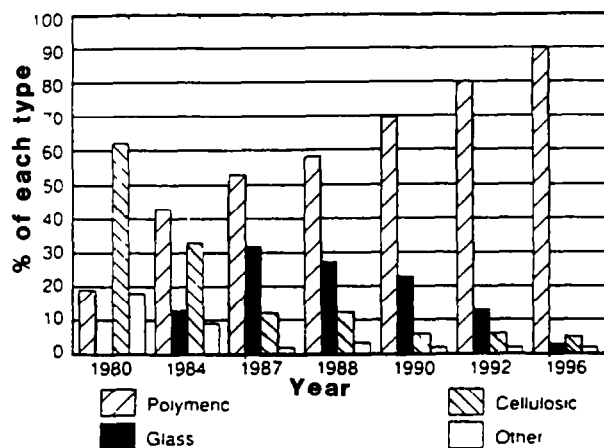

Fig 1 Utilization of various types of separators for automotive batteries in the USA [10]

glass separators has decreased, while the utilization of polyethylene separators increased In the USA market in 1990 the percentage of polyethylene separators used out of the total quantity of all types of separators was 70% It is predicted that the share of these separators will be 90% in 1996

In Europe, inexpensive cellulosic separators in the form of leaves are mainly used, while the utilization of the separators based on sintered PVC is less frequent To date, glass separators have not been accepted in the European market, due to the high price Meanwhile, even in Europe, poly-

ethylene separators in the form of envelopes are beginning to take over from leaf separators Although the introduction of these separators is slower than in the U S A , the market share in 1990 was 54%, with a predicted increase of up to 70% in 1992 [10]

Improvement in the properties of polyethylene separators and the development of new types have been achieved by choosing the most appropriate basic materials (e g , polyethylene of high molecular mass, silica of very fine grain structure and adequate mineral oil), optimization of the separator composition, and advances in the manufacturing process By application of one improved technological process, high quality separators of 0 125 mm thickness have been produced, these are 50% thinner than those manufactured previously

It is worth noting the suggestion [11] that the separators be manufactured in a form of coating at the electrodes themselves This could be achieved by immersion in a solution of a suitable polymer This idea is presently being extended to the manufacture of a micro-tubular construction active material is applied to an alloy spine by immersion into a paste of adequate composition and consistency, the applied paste is dried, after which the spine and attached paste is immersed in a solution of separator material.

Separators for other types of batteries

In the U S A , polyethylene separators have been used almost exclusively (>99%) for traction batteries These have replaced separators made from microporous rubber as the latter exhibit inferior properties (e g , higher thickness, higher electrical resistance, poorer mechanical properties) Separators based on either microporous rubber or polyethylene have been used in stationary batteries in the U S.A Again, it is is only a question of time before separators made of microporous rubber are completely replaced by polyethylene counterparts

Compared with Europe, the production of tubular-plate industrial batteries in the U S.A is rather small. Microporous rubber separators or microporous non-sintered PVC (commercial designation PORVIC 1) separators, together with wave-shaped perforated leaves (made from an appropriate polymer) as spacers between the separator and positive electrode, have been built into European batteries This is because separators made from the materials specified cannot be produced with a high thickness In the past few years, however, polyethylene separators of necessary thickness have been used in Europe for industrial batteries, with elimination of the need for the spacers [12]

In the case of recombinant batteries, the electrolyte is either in a gelled condition or has been absorbed in an absorptive glass material (AGM) Gelled technology uses conventional types of separators, while the AGM separator completely fills the space between the electrodes and plays the triple role of electrolyte carrier, separator, and a diffusive passage for oxygen

In the manufacture of AGM separators, a combination of fibres of boron-silicate glass of various thicknesses (ranging from 0 7 to 4 μm) [13] is used,

with or without binding material In order to combine good properties for both modes of electrolyte immobilization, addition of colloidal silica into glass separator has been suggested [14]

Container materials

Intensive development of the organic chemical industry after World War II allowed the production of a wide variety of polymeric materials that were suitable for various technical applications and for the manufacture of consumer products This included materials that, according to their physical, chemical and technological properties, exceeded the value of hard rubber, that, for a long period, had been used exclusively for the manufacture of battery containers The replacement of hard rubber by suitable polymeric materials has been in progress for more than a decade and is still increasing The introduction of new materials has enabled both the wall thickness and the container weight to be reduced In addition, the mechanical properties have been improved (e g , impact resistance)

In the manufacturing process of monoblock containers for automotive batteries, the most frequently used materials are polypropylene, co-polymer of ethylene and polypropylene, polyethylene (reinforced with glass fibres or with kaolin as a filler), acrylo-nitrile-butadiene-styrole (ABS), and polystyrole Although these materials are more expensive than ebonite, their attendant advantages completely justify their application [15] Among these materials, the most popular is polypropylene A battery container made from this material, compared with the equivalent hard rubber version of the same outer dimensions, is 3 3 times lighter [15], has good mechanical properties (both at high and low temperatures), and is characterized by high chemical resistance Thinner intercellular walls allow the placement of a large number of active components (e g , electrolyte, electrodes) in the cellular space, and this contributes to an increase in energy density per mass and volume From the technological point of view, this material enables the cells in mono-block to be electrically connected via the process of welding short lead couplings through the cell walls, so-called 'through-the-partition connection' As a result, the electrical resistivity of the intercellular junctions is reduced significantly A single lid made of polypropylene may be connected to the body of the monoblock through the process of thermal welding The two specified technological operations are performed on automatic devices It should also be pointed out that the introduction of polymeric materials has made it possible to manufacture coloured, translucent and transparent cases and lids In this way, the image of the lead/acid battery as a 'black box' — the term used because of the colour ebonite — has been eliminated

In recent years, there has been an increasing application of foam plastic as a structural material This material is noted for its cellular structure and monolithic non-porous outer surfaces By virtue of the cellular structure which, in fact, represents a porous body with enclosed pores, foam plastics

are very good heat and electrical insulators, and in products manufactured from foam plastic there is no residual strain With these materials, it is possible to obtain components of lower weight, satisfactory mechanical properties, and high accuracy in dimension Foam plastics are also used for the manufacture of battery containers, e g , for batteries to be operated at very low temperatures [16] For these purposes, foam polyethylene is used Containers made from this material with a wall thickness of 5 mm have exhibited excellent mechanical properties, even at temperatures down to − 60 °C Furthermore, the containers do not change their dimensions significantly (1%) over long periods of storage

In the above discussion, attention has been drawn to the application of polymeric materials for automotive battery containers Meanwhile, the same polymeric materials have also been used successfully in the manufacture of containers for other types of lead/acid batteries, e g , traction, stationary, portable, etc

Acknowledgements

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