

New materials for current-conducting components in lead/acid batteries*

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Abstract

A review is presented of the substitution of lead by alternative materials in the grids and other non-active current-carrying components of lead/acid batteries. The use of such materials is aimed at improving the specific electrical properties of the batteries, i.e. gravimetric energy and power densities. The materials discussed include copper, aluminium, titanium, and lead-plastic composites.

Introduction

During the 130 years that the lead/acid battery has been in existence its technology has been continuously improved and perfected. Notable advances have included the use of plastic monoblocks, terminal connection through the cell walls of the monoblock, the development of grids with radial ribs, optimization of the design of the separate cells and the battery as a whole.

Progress in the manufacturing processes of lead/acid batteries has been equally successful, e.g., leady oxide production by the Barton-pot method, the design of mixers for obtaining pastes with stable and consistent composition, high-speed pasting machines characterized by minimal differences in plate weight, continuous casting of grids, use of low-antimony and antimony-free alloys, improvements in the curing of newly-pasted plates, programmed formation of plates, perfection of assembly lines, etc.

Recent fundamental research into the morphological and phase transformations taking place during the production of leady oxide and the preparation of paste has allowed active materials to be obtained with pre-assigned properties. Investigations are being also conducted into the use of new materials in the manufacture of the current-conducting components of cells and batteries, i.e., grids, busbars, connectors, and terminals. This paper reports studies and achievements in the U S S R concerning the use of copper and aluminium.

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Copper-based components

The non-active parts of a lead/acid battery (e.g., grids, terminals, container, separators, etc.) account for a considerable share of the total weight of the unit. Obviously, the application of materials of lighter weight for the current-conducting components will give rise to an increase in the gravimetric energy density of batteries. In this respect, copper is a most promising material. From thermodynamics considerations, copper is rather stable in sulfuric acid solution. Hence, copper can not only be used for the manufacture of current-conducting parts, but also as an active electrode material. At the author's Institute during the 1960s, there was created a lead-copper current source, the current formation process can be represented by the following reaction



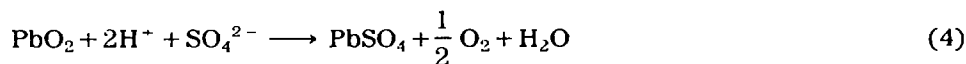
The Nernst equation for this reaction is

$$E = E_0 + \frac{2 \cdot 303RT}{2F} \lg \frac{a_{\text{H}_2\text{SO}_4}}{a_{\text{H}_2\text{O}}} - \frac{2 \cdot 303RT}{4F} \lg a_{\text{CuSO}_4} \quad (2)$$

At the same time self-dissolution of copper in the sulfuric acid might occur via reaction with oxygen, i.e.,



The oxygen source might be either oxygen from the atmosphere (especially, when the battery employs air stirring of the electrolyte), or oxygen formed as a result of spontaneous reduction of lead dioxide according to



The speed of reaction (3) depends upon the conditions under which oxygen dissolves in the electrolyte and the access of the gas to the surfaces of the negative electrodes. Thus, despite the fact that copper is not directly soluble in the sulfuric acid electrolyte, its dissolution is indeed possible and gives rise to the formation of copper oxide and, later, copper sulfate. In addition, bivalent copper deposits (both electrolytically and by contact) on the surface of negative electrodes and, thereby, promotes self discharge of the electrodes and gassing. For these reasons, the surfaces of copper components should be reliably protected against contact with the electrolyte. This can be achieved by application of a thick layer of lead by hot dipping, electric vacuum spraying, or electrolytic deposition. The results of many investigations indicate that the electrolytic method, incorporating the deposition of an intermediate sub-layer of tin, is the most reliable. The precursor leading is necessary in order to ensure good electrical and mechanical contact between the spongy deposited lead and its smooth surface of the copper substrate.

In prototype designs, the copper current-conducting components were manufactured by the method of thin strip stamping. Later, the process was improved and a completely mechanized waste-free technology for the manufacture of copper grids of the notching-stretching type was developed (Fig 1). An example of a grid is shown in Fig 2. The processes of notching, stretching and advancing of the strip take place simultaneously. At the same time, the edges are curled to form tube-shaped rims. The only additional operation involves welding of the bottom edges.

This technology eliminates copper waste and reduces consumption by 40%. Further improvements of the technology might result in the replacement of the copper edges (rims) by plastic versions.

In the U.S.S.R., copper negative grids are used for the manufacture of high-capacity storage batteries. Such batteries find service in applications in storage, floating and periodic charging duties, e.g., in telephone exchanges, electrical substations, atomic power stations, etc. In case of final voltage control, the batteries can also be successfully used in battery-powered carts and trucks.

Experience with copper negative grids has shown that the specific capacity and energy of batteries can be increased by at least 20%. By comparison,

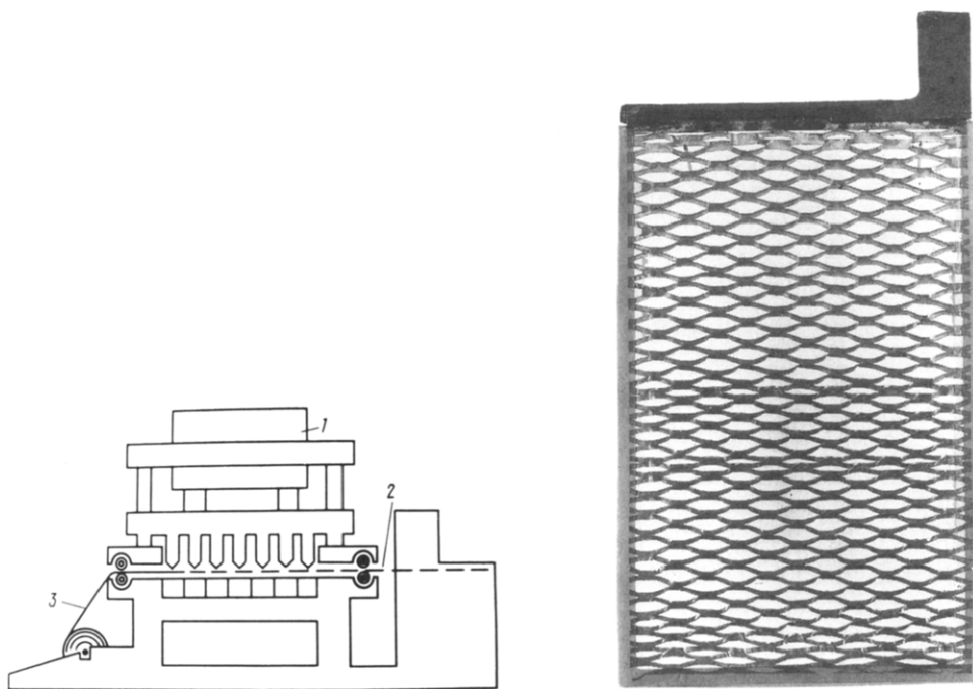


Fig 1 Schematic of method for fabricating expanded mesh copper grids (1) press, (2) mesh, (3) strip

Fig 2 Copper grid manufactured by procedure shown in Fig 1

Kiessling [1] has reported that the corresponding increase in energy for traction batteries with Exide ironclad positive electrodes and copper based negative electrodes is 172, 142 and 129% at discharge rates of 0.5, 2 and 5 h, respectively

The improved performance of lead/acid batteries using copper-based grids is due to the fact that copper has a much higher electrical conductivity than lead. Thus, ohmic losses are reduced. At equal discharge current density, batteries using copper are characterized by greater power. This advantage becomes greater with increase in the discharge current. Copper-based grids also ensure higher utilization of the electrode material on account of an improvement in the current distribution within the electrodes. This feature is particularly important in the case of large storage batteries. Copper grids are considerably lighter than lead counterparts because thinner strip can be employed. Finally, copper technology is environmentally less-polluting than that using grids made from lead alloys.

Aluminium-based components

A further approach to improving the gravimetric energy and power of lead/acid batteries involves the use of aluminium and its alloys in the manufacture of the current-conducting components. This metal has a high electrical conductivity and a low density. As with copper, the employment of aluminium is only possible on condition that reliable protection against attack by sulfuric acid is achieved. Attempts to protect aluminium by means of hot or electrolytic leading have proved ineffective since the adhesion of lead to aluminium is prevented by the formation of an oxide film on the aluminium surface.

A new thermo-diffusion method of aluminium leading and tinning has been developed in the author's Institute. The basic operation involves removal of the oxide film from the aluminium surface, and simultaneous leading, during treatment in a melt of lead chloride, i.e.



This reaction is possible due to the penetration of the melt through the pores of the oxide film. The aluminium surface, cleaned of oxides, is covered with lead. The reliable adhesion of aluminium and lead is only possible when solid-state mutual solubility exists. The phase diagram for lead and aluminium indicates, however, that the metals are characterized by very low mutual solubility, even in the liquid state. Thus, due to the extremely limited solubility of lead in solid aluminium, pure lead is not used but rather its alloys with silver and calcium. In the liquid state, aluminium and silver exhibit unlimited mutual solubility, in the solid state, solid solutions and intermetallic compounds are formed. Silver and lead also provide unlimited mutual solubility in the liquid state, in the solid state, the solubility of silver in lead is 0.1%. Thus, the main role of silver, or calcium, is to form a transition (diffusion) layer of significant thickness (up to 50 μm) on the aluminium surface.

The process of thermo-diffusion leading takes place at a melt temperature of 450 °C within a period of 3 to 4 min. The thickness of the diffusion layer increases with temperature, but the latter results in a marked acceleration of the rate of aluminium dissolution.

For the process to occur at lower temperatures, the pickling is performed in a melt of mixed chloride salts rather than in pure lead chloride. The quality of the thermodiffusion coating depends upon the flux composition and the pickling regime. The flux is required to have minimal viscosity and melting temperature as well as an increased content of lead chloride. From studies in the author's laboratories of several three-component salt mixtures are recommended: 81% PbCl₂-9% LiCl-10% KCl, as well as the eutectic PbCl₂-KCl-NaCl.

Examination of the phase diagram for aluminium and tin shows that tin (as compared with lead) dissolves readily in aluminium and is quite soluble in lead both in the liquid and solid states. Thus, it is concluded a tin coating on aluminium is capable of forming, on its surface, a transition layer in which lead can dissolve. For practical use, the following systems are recommended: Pb alloy + 3.0% Sn, 90% PbCl₂, salt flux, 5.3% KCl-4.7% NaCl. The temperature of the process is 460-490 °C.

It is also possible to undertake a tinning process (i.e., without the need for a metallic Pb-Sn alloy) directly in a melt of lead-tin, and sodium and calcium chlorides. The tinning is performed within 2-3 min after the commencement of the reaction of the flux with the sample surface. The following interaction is possible:



The abovementioned regimes for thermo-diffusion leading and tinning make it possible to use aluminium and its alloys for the manufacture of current-conducting components, e.g., inserts for connectors and terminals. These reduce considerably the ohmic losses in voltage, especially at very high discharge rates. Such inserts are suitable for large stationary batteries, as well as for traction types.

The problem of materials selection for current-conducting components in positive electrodes is complicated by the fact that, under the encountered conditions of high potential in sulfuric acid solution, many metals and alloys undergo intensive anodic attack.

Other materials

Titanium is one of the more-promising metals for positive electrodes. During anodic polarization, a protective passive film is formed on the titanium surface and this prevents the metal from dissolving. Indeed, it is for this reason that titanium is used in the manufacture of insoluble anodes for certain electrochemical industries. Nevertheless, the titanium dioxide film possesses semiconductor properties, and thus tends to insulate the current-conducting substrate from the lead dioxide active material. Thus, the primary

task in the further development of titanium-based grids concerns the search for current-conducting coatings for the metal. Such coatings might involve various metal oxides of variable composition.

Considerable attention has also been paid to the use of plastic grids coated with lead. In the author's opinion, such grids will be primarily used in negative plates since their ohmic resistance (due to the high conductivity of spongy lead) is substantially lower than that of positive electrodes. Several methods are known for making plastic-based conductive grids, e.g., reinforcing with metal strips or ribs, plasma lead spraying, chemical leading, etc. In summary, the use of metal-plastic composite grids is a promising approach to increasing the life and gravimetric electrical characteristics of lead/acid battery plates.

It is known that optimum electrode life can be achieved when tubular positive electrodes are used. Modern tubular-plate design reliably prevents the softening and shedding of positive active material, as well as reduces the corrosion rate of the current-conducting spines. On the other hand, tubular plates are much thicker than their pasted counterparts and thus lowers the number of plates per block, i.e., reduces the capacity at high discharge rates. Furthermore, it is known that the internal resistance of tubular-plate batteries is slightly higher than that of batteries using pasted plates. Thus, it is difficult to use tubular-plate designs for pulsed-discharge duties.

Recently, some firms have begun to use electrodes of the 'single-armour' type. The design of such electrodes is as follows. Plastic nets are welded to both sides of conventional cast alloy grids. The thickness of the metal part of the grid is approximately one-third that of a conventional cast grid. The total thickness of the central metal part and the outer two plastic nets is equal to the thickness of a cast grid. Such an arrangement reduces by approximately one-third the weight of the grid, thus making it possible to increase the specific energy of the battery. After the pasting, an 'armour' is applied to the plate surface. The latter is then welded to the plastic nets and connected along the edges of the plates. Thus, a single-armour plate is created with the combined advantages of a pasted design, with respect to high discharge characteristics, and of a tubular variety, with respect to durability. Such plates can be used effectively in traction, stationary and diesel-locomotive service.

Summary

The above discussion of the substitution of lead in grids by alternative materials has highlighted the advantages to be gained in terms of improved battery performance. Additional fundamental and applied research is necessary to maximize the effect of these materials.

Reference

- 1 R. Kiessling, *J. Power Sources*, 19 (1987) 147