

Electrodeposited, dispersion-hardened, lightweight grids for lead–acid batteries

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Abstract

We report a novel processing route to produce battery grids by electrocodeposition of lead with dispersed particles. The grid thickness and design can be chosen within a wide range. This permits us to minimise grid weight and to optimise grid design for current density distribution. The process development has reached a state of maturity permitting us to produce test quantities for battery tests. The grid properties have been investigated thoroughly. Hardness can be adjusted in the range of 4–25 HV units by choice of particle size and volume fraction of dispersoid (oxides or Cu). Creep resistance is excellent. Corrosion tests indicate that grid corrosion is similar to that of Pb–Ca–Sn grids. Such grids were used to make several hundred positive and negative battery plates and eventually test cells and batteries. First test results have been very promising and have shown clearly that the new grid type allows us to make batteries of high specific energy. The process is, also, suitable for the production of lead alloy foil for alternative battery designs. The new manufacturing process can be combined with a hydrometallurgical process for the recycling of battery grids and paste such that a fully integrated processing route from the treatment of battery scrap to the production of new battery grids for batteries featuring significantly higher specific energy is now available. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The lead–acid battery has been improved considerably to reach a specific energy of about 40 W h/kg at 20 h discharge rate in SLI batteries today. Its main shortcoming remains the weight, especially if traction batteries for electric or hybrid cars are considered. Furthermore, alternative battery chemistries with projected specific energies up to about 100 W h/kg are presently being developed which may compete with the lead–acid battery in the long run. But none of these concepts is as well proven, environmentally acceptable and economical as the lead–acid battery, by a large margin.

We have developed a completely new material and manufacturing process for lead battery grids which can reduce battery weight considerably [1–3]. This innovative process involves galvanic deposition instead of casting, a

new hardening mechanism and the potential of improving the grid design beyond the limitations existing for gravity cast and expanded grids, respectively.

Concern has been expressed regarding possible environmental implications due to the production and recycling of lead for batteries by pyrometallurgical processes [4]. It has been shown that this concern was overstated [5,6], but it is true that hydrometallurgical processing and recycling represents a more environmentally friendly route. The combination of these two latter processes, in an integrated production and secondary lead recycling technology, is the aim of our development.

2. The new production technology for lighter lead grids

If lead is deposited electrochemically onto a cathode which is prestructured with conducting lines according to a desired grid shape and from which the lead deposit is stripped after a predetermined thickness is reached, this process lends itself to producing battery grids which are

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thinner and lighter than cast grids. The strength required can be provided by adding to the electrolyte constituents insoluble in lead such as copper or TiO_2 particles which are co-deposited with the lead and give rise to dispersion strengthening.

Our process to deposit electroformed Pb-based grids uses a fluoroborate electrolyte containing phosphate and smoothing additives and operates at about 40°C . For the pilot plant we have designed a diaphragm divided cell with extractable compartments. The anodic reaction is the oxidation of Fe^{2+} to Fe^{3+} which serves as the oxidant necessary to leach the Pb-bearing feed material. The anode is a graphite sheet. The cathode onto which the grids are deposited is a printed circuit board with a copper pattern which is the reproduction of the grid design, i.e., we use a two-dimensional electroforming [7] process. Fig. 1 shows photographs of typical experimental grids produced.

In one variant of the process we add Cu ions to the electrolyte. This leads to a deposit containing Cu particles with a typical average diameter of about 10–20 nm. Fig. 2a shows the total cross-section of the deposit, Fig. 2b shows the size and distribution of the dispersoid particles at high magnification. A volume fraction of 0.3% of these particles suffices to raise the hardness of lead from 4 to 12 HV units as may be seen in Fig. 3. In the present state of the development the positive grids are produced as composite grids consisting of a Pb-dispersoid core and a Pb–Sn alloy coating. Whereas the dispersion hardened core provides the strength and creep resistance required, the coating gives rise to a good grid/mass interface during charge/discharge cycles, and improved corrosion resistance. Fig. 4 shows the cross-section of a composite grid. In our present pilot cell we are producing new grids starting from grid scrap. The cell consists of one cathode between two anodes. The 0.6×0.8 m cathode was designed to produce 12 grids on each side. The Pb-dispersoid core has a hardness of 10–15 HV units.

As an alternative we have begun to produce Pb deposits dispersion strengthened with TiO_2 particles as shown in Fig. 5a and b. The alloy content, ensuing hardness, microstructure, texture and surface morphology of the de-

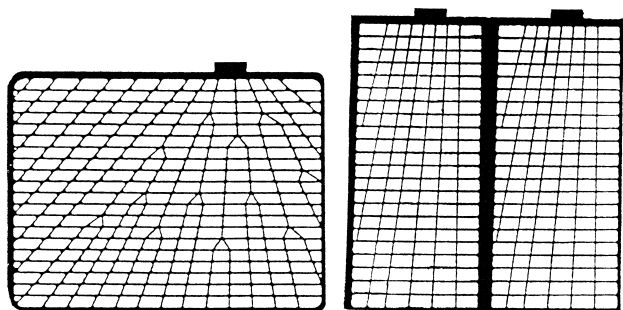


Fig. 1. Experimental battery grids of electroformed, dispersion-hardened lead.

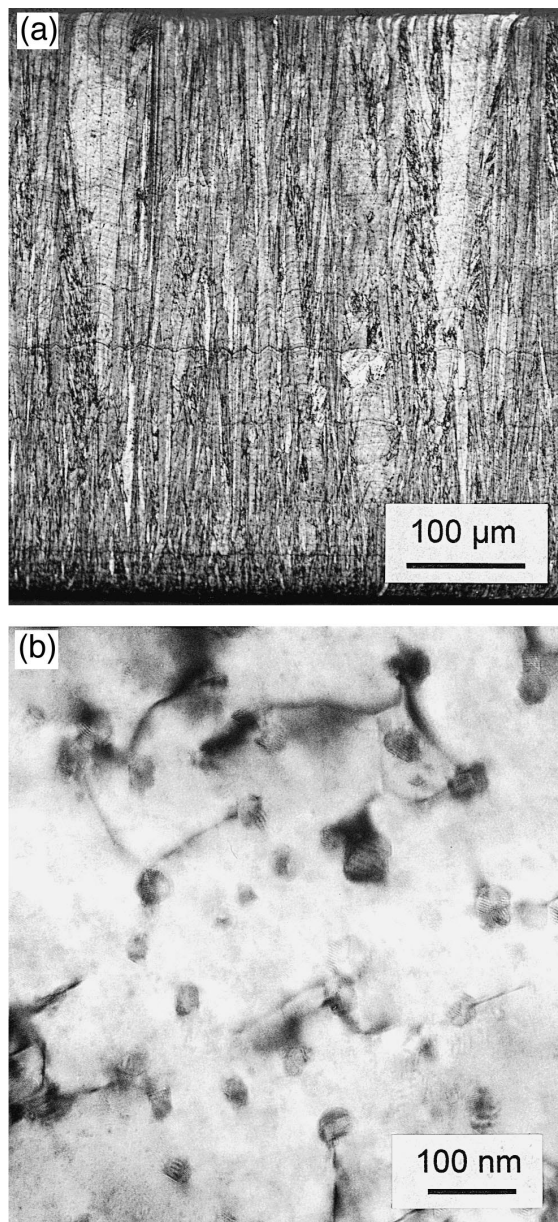


Fig. 2. Microstructures of electrodeposited grids. (a) Pb with Cu dispersion. Light micrograph. (b) Pb with Cu dispersion. Transmission electron micrograph.

posits are functions of the deposition parameters such as composition of the electrolyte, diameter and volume fraction of dispersoids [2,3], additives [3,8], cathodic current density, temperature and mode and degree of stirring. As an example for the influence of decisive variables, Fig. 6 shows the dependence of the hardness on the crystal size and the volume fraction of TiO_2 powders used. It should be noted that the average crystal size varied from about 10 nm to about 150 nm while the actual particles in the deposit consist of aggregates of TiO_2 crystals about 100 nm to about 300 nm in diameter. Whereas low-cost powders with 220 nm particle size have a somewhat lower, but sufficient, hardening efficiency, experimental powders with

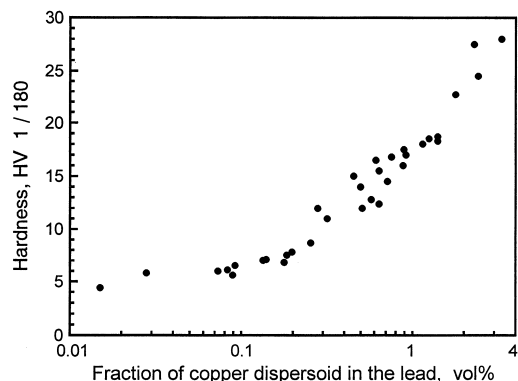


Fig. 3. Vickers hardness of electrodeposited Pb with Cu dispersion. The average Cu particle size is constant at about 10–20 nm.

10 nm particle size are more potent hardening dispersoids but they are less economical due to higher cost.

With the pilot cell we were able to prepare more than 1000 grids to be tested for corrosion behaviour and to build test cells and batteries.

Fig. 7 shows the results of corrosion tests comparing electrodeposited grids with conventional gravity cast Pb–Sb and Pb–Ca–Sn book mould grids. The current density due to both oxygen evolution and metal oxidation was measured as a function of continuous exposure to a high positive polarisation. The polarisation voltage and bath temperature were chosen according to common practice

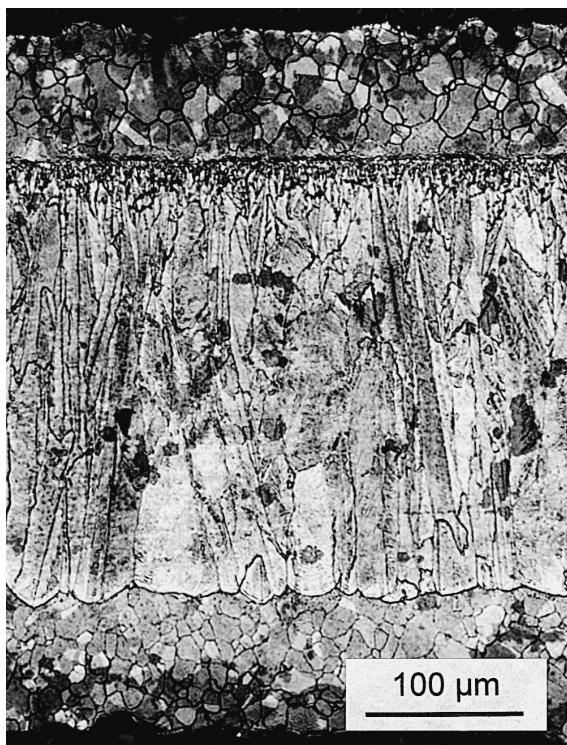


Fig. 4. Microstructure of a composite grid. Core: Pb with Cu dispersion; coating: Pb–Sn alloy. Light micrograph.

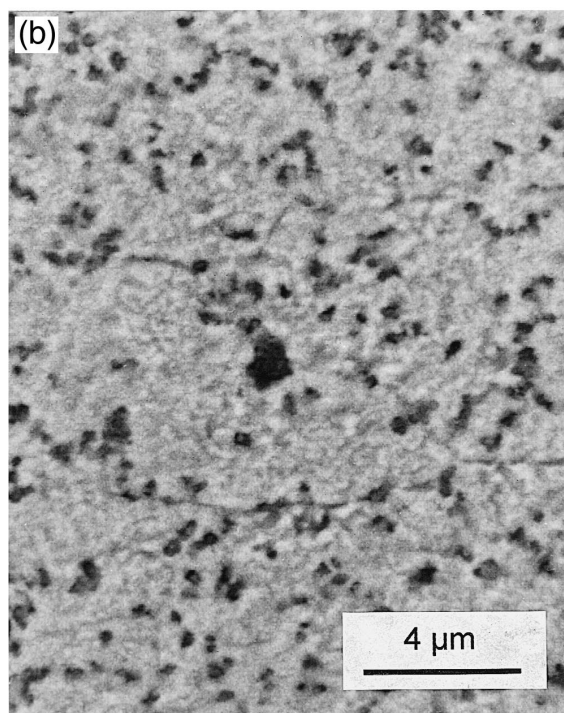
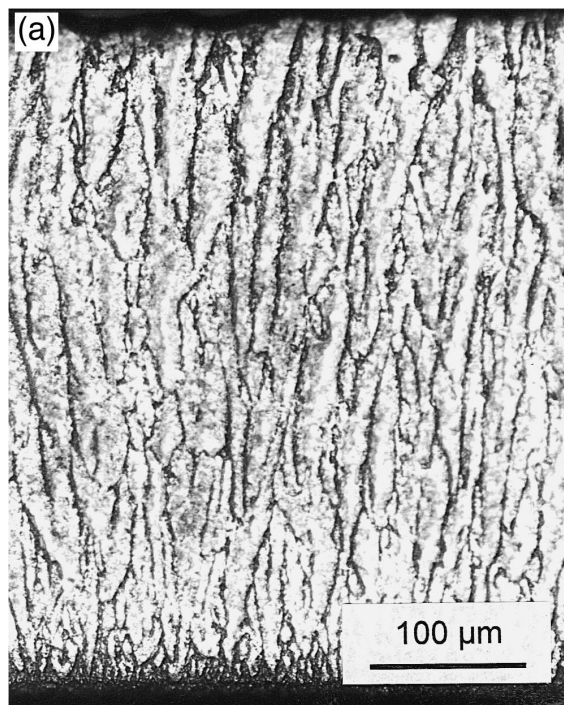


Fig. 5. Microstructures of electrodeposited grids. (a) Pb with TiO_2 dispersion. Light micrograph. (b) Pb with TiO_2 dispersion. Scanning electron micrograph.

for accelerated corrosion testing of grids. The weight loss determined accounted for less than 5% of the current density measured. The results for the electrodeposited grids compare favourably with those of the conventional gravity cast Pb–Ca–Sn grids, all being greatly superior to conventional cast Pb–Sb grids.

Several hundred positive and negative battery plates were made by using electrodeposited grids with a thickness of about 0.5 mm. The overpasting was varied to obtain plates with different thickness ranging between 1.1 and 0.8 mm for the positive plates and 1.0 and 0.7 for the negative plates. Pasting and handling of the plates were possible in all cases and did not pose serious problems.

Some of the positive plates were used for an accelerated corrosion test at 55°C. In parallel the same test was performed with standard starter plates (lead calcium tin alloy with 0.09% Ca) of the same size (length and width) but with a plate thickness of 1.7 mm. The test on plates was performed in addition to the corrosion tests on grids in order to take the influence of the active mass on the corrosion resistance of the grids into account.

For both types of plate the test was completed after about 20 weeks. The plates with standard grids were fully damaged after 20 weeks (as an average of four samples) and the plates with electrodeposited grids were fully damaged after 18 weeks (as an average of four samples). The results for plates with active mass fit well with those for grids without active mass, where the corrosion resistance of the electrodeposited grids was similar to that of gravity cast lead–calcium grids (Fig. 7).

This is a good result considering that the amount of grid lead was markedly higher in the case of the standard version (55 g) than in the case of the electrodeposited grids (33 g). Furthermore, it should be pointed out that this was a test with plates taken from an early stage of the development of an appropriate pasting process for such a kind of thin grids. Also, there appears to be room for optimisation of the grid production process with regard to improving the corrosion resistance. Therefore it can be expected that in the end the corrosion stability can be even superior to that of standard gravity cast lead calcium grids although the grids are so much thinner.

In order to investigate the performance of the plates, 2 V test cells were made with both standard plates and plates with electrodeposited grids. For the standard version the test cell comprised five positive and five negative plates,

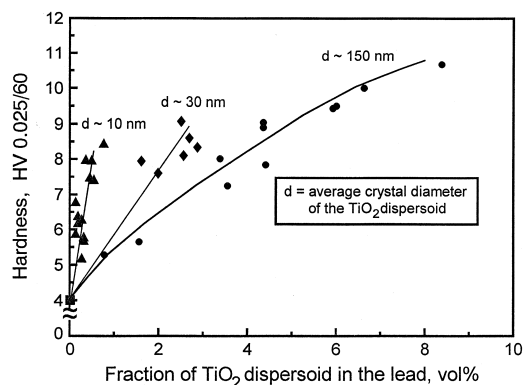


Fig. 6. Vickers hardness of electrodeposited Pb with TiO_2 dispersion.

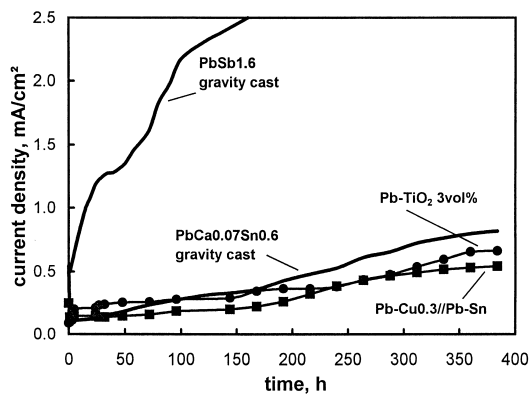


Fig. 7. Polarisation current density as a function of exposure time comparing the corrosion behaviour of new electrodeposited and conventional gravity cast grids. $U = +1420$ mV ($\text{Hg}/\text{Hg}_2\text{SO}_4$), 40°C.

whereas for the new version with electrodeposited grids it accommodated seven positive and eight negative plates. The volume of the cell was identical and nearly the same total amount of active positive and negative mass as well as electrolyte were used in both cases. Capacity tests gave virtually the same result at the 20-h discharge rate but markedly better results for the version with electrodeposited grids at 5 h rate (+10%) and 1 h rate (+16%). This shows, as expected, that the use of thinner grids and plates has markedly increased the high rate discharge performance.

Further tests are presently underway leading up to field tests of prototype batteries. It should be noted that full exploitation of the weight reduction potential requires a redesign of the grid structure and of practically all components of the battery. A minimum lead weight can be realised by using a specially designed composite grid [9].

3. The combined process of production and recycling

As mentioned above an ideal combination of electrochemical production and recycling can be realised if the new grid manufacturing process is employed.

In recent years, several electrochemical processes to recycle lead compounds from spent batteries have been developed to the point of testing in industrial pilot plants. These processes were described and analysed by R.D. Prengaman recently [10]. Although different in some aspects, the more advanced processes are based on a common concept that includes: (i) conversion of insoluble lead compounds such as PbSO_4 and PbO_2 into leachable products, (ii) leaching by a suitable electrolyte to put the lead ions into solution, (iii) electrowinning via an insoluble anode with oxygen evolution. Certain deficiencies of these processes such as short anode life, undesirable by-products and high operating costs have been overcome to a large extent by a processing variant named CX-EWS [11]. It consists of several operations: reaction of the lead paste

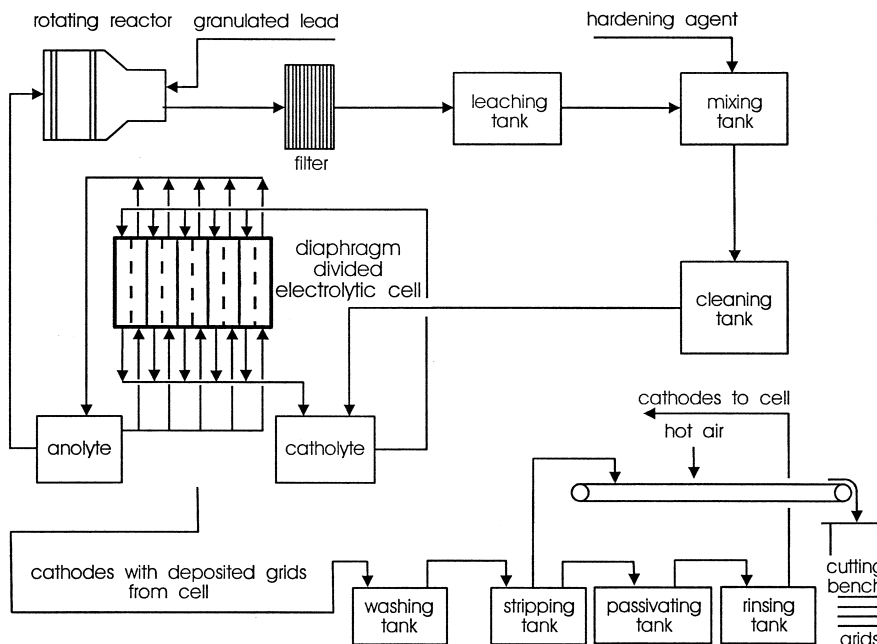


Fig. 8. A conceptual flow sheet for the electroforming of dispersion-hardened lead grids combined with the recycling of spent batteries.

obtained by breaking and screening the spent batteries with a solution of sodium sulfide and sulfuric acid such that lead sulfide and sodium sulfate solution are obtained; leaching of the lead sulfide with a ferric fluoroborate electrolyte yielding ferrous fluoroborate in solution and elemental sulfur in an insoluble residue [12]; electrolysis, after adding hardening agents, of the lead fluoroborate and ferrous fluoroborate in a cell yielding lead grids in the cathodic compartment and the formation of ferric fluoroborate in the anodic compartment. The CX-EWS process avoids the use of desulfurization chemicals as well as the need to market sodium sulfate. Due to the reduced consumption of chemicals and to the energy savings by using just one electrolytic process to both convert scrap and produce new grids, the total process is projected to be highly cost effective. A conceptual flow sheet of the plant is shown in Fig. 8.

4. Conclusions

Even if the concept presented here has not yet been fully proven to be viable many intermediate results are promising. The electrochemical recycling part of the process has been tested successfully in a demonstration plant of one of the main lead producers in the USA. Cycling tests of first laboratory type batteries containing electroformed, dispersion hardened grids should be completed by the end of 1998. After a redesign which fully optimises the battery for maximum energy density based on the new grids, we expect an increase in specific energy by more than 10% over that of comparable batteries.

It should be noted that there are several alternative battery concepts which provide a significantly higher specific energy than such an improved lead-acid battery as proposed here. On the other hand incomplete proof of technical reliability, high cost, recycling problems and, in some cases, operating temperatures above room temperature are still hampering their introduction into the market.

An important advantage of the new grid production process is the possibility to use it in conjunction with a continuous plate production line similar to expanded metal technology. Moreover, rather thin grids and plates can be manufactured and this makes the electrodeposited grids interesting for all kinds of high power application such as UPS, starter, EV and hybrid vehicles.

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