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Lead–acid batteries with polymer-structured electrodes for electric-vehicle applications

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Abstract

Some years ago a consortium of enterprises and a university from different European countries and industrial sectors was established to work together in the development of lighter lead–acid batteries for electrical and conventional vehicles with new innovative materials and process techniques, with the final goal of increasing the energy density by means of a battery weight reduction. Its main idea was to substitute the heavy lead alloy grids (mechanical support of the active masses and collectors of the current produced during the charge and discharge reactions) by lightweight metallised polymeric network structures (PNS) with reduced mesh dimensions in comparison to conventional grids. The network was then coated with conductive materials and corrosion resistant layers to conduct the current flow. In this paper, the electrode characteristics and the design features of the batteries prepared in the project will be described and their electrical performance presented. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Lead acid batteries; Electric vehicle; Polymeric support; Electroplated materials; Manufacturing processes; Electrode and cell testing

1. Introduction

The increasing concern for the environment and the pollution problems caused by the ICE vehicles, specially in the big cities, have led to a worldwide interest for the development of efficient electric and hybrid vehicles. The battery, as autonomous energy storage system, is a key element in the operation of the electric vehicles, due to its great influence on the final cost, range and performance of the vehicle. The characteristics of the batteries available in the market today impose hard restrictions to the performance of the electric vehicles.

Most of the electric vehicles in the market are tractioned by lead–acid batteries, although they store less energy per unit weight than the other systems. This fact is due to the main advantages of this system: availability, low cost, satisfactory power density, safety and the established infrastructure for battery manufacturing and recycling. However, its main disadvantages are its low specific energy and cycle life, when compared to other battery systems (alkaline, lithium, etc.).

Some years ago, a consortium of enterprises and a university from different European countries and industrial sectors was established in order to work together in the development of lighter lead–acid batteries for electrical and conventional vehicles. The project has been partially funded by the European Commission and the Swiss Federal Office for Education and Science (OFES) under the Brite-EuRam II Programme.

The objective of the project was to develop advanced lightweight lead–acid batteries with new innovative materials and process techniques, with the final goal of increasing the energy density by means of a battery weight reduction, and continuous processes for electrode manufacturing to allow the achievement of a cost competitive product.

The main idea was to substitute the heavy lead alloy grids (mechanical support of the active masses and collectors of the current produced during the charge and discharge reactions) by the best-suited material for each function: high strength fibre material for the support of the active mass and copper for the current collector function. The new grid has therefore been developed as a lightweight metallised polymeric network structure (PNS) with a high surface area due to the reduced mesh dimensions in comparison to conventional grids. The network was then coated with conductive materials and corrosion resistant layers to conduct the current flow.

Fig. 1 shows a cross-section of the polymeric network structure electrode, with indication of the partners involved in the development of the different layers.

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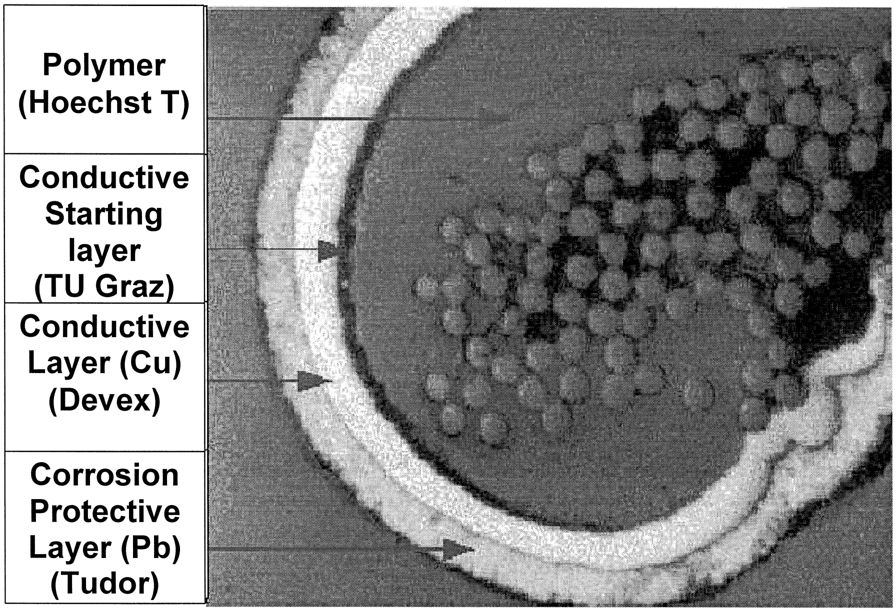

Fig. 1. Cross-section of PNS electrodes.

This paper covers a part of Tudor's work in the project, dealing with the testing of PNS grids and electrodes and the modification of the battery manufacturing processes.

2. Grid testing

Different open mesh polymer network structures have been developed during the project, and, after copper and lead plating, tested mechanically and electrically as battery grids, in comparison with conventional gravity casted and expanded lead grids.

The following parameters have been studied, defining in some cases special testing procedures:

- Average grid weight and weight distribution.
- Electric conductivity by means of the resistance map of the grids, in comparison with conventional grid designs, gravity cast and expanded.
- Distribution of conductive materials, by means of the chemical analysis of different positions in the grid samples and the observation and measurement of the metallic layers with a metallographic microscope.
- Adherence of the metallic layers to the polymeric substrate when the grid is subjected to an external stress and deformation. No variation of the grid electrical resis-

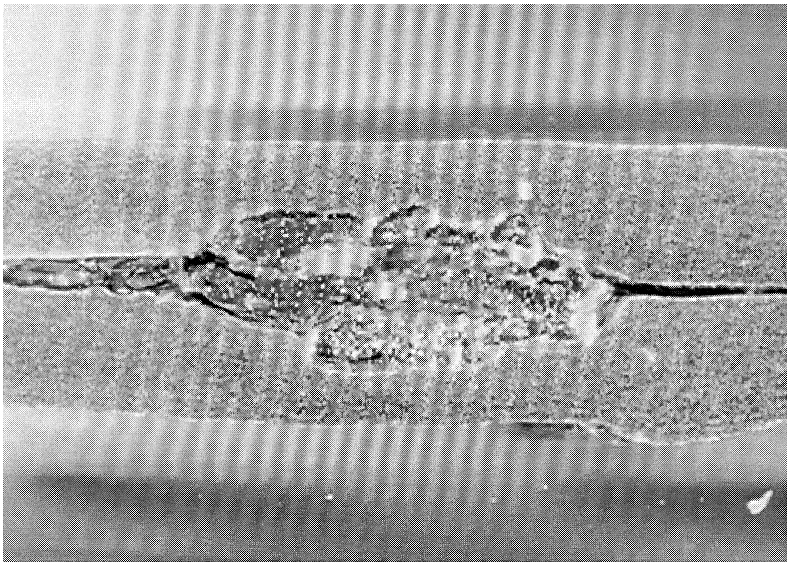

Fig. 2. Poor welding connection lug-substrate.

Fig. 3. Optimised lug-substrate connection with pre-tinned welding.

tance has been observed after winding the samples around glass cylinders with different diameters. These results indicate that the copper layer is ductile and shows enough adherence to the substrate, to avoid the formation of cracks which would reduce the grid conductivity.

- Mechanical strength: Tensile strength tests have shown the improved behaviour of the PNS grids when compared with conventional samples, and the high quality of the lug welding process.
- Thermal stability of electrodes under low pressure conditions, by the measurement of the elongation and thickness decrease when the grids are subjected to compression under extreme battery working temperatures (up to 80°C).
- Chemical stability of the lead protective layers by immersion of the grids in sulphuric acid solutions with different specific gravity values.

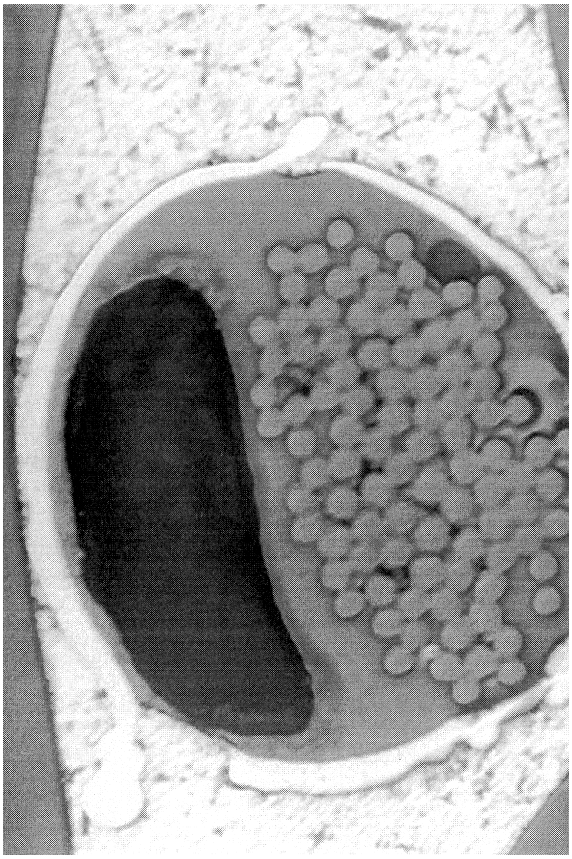

Fig. 4. Pretinning of PNS grids: long immersion time.

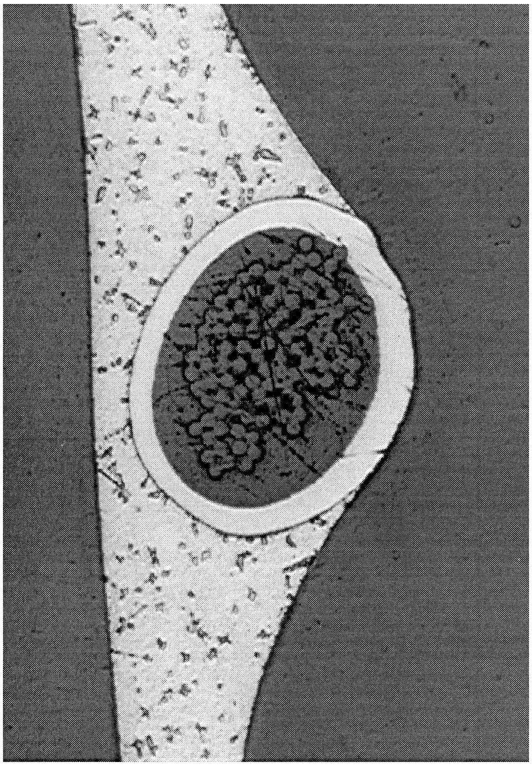

Fig. 5. Pretinning of PNS grids: optimised conditions.

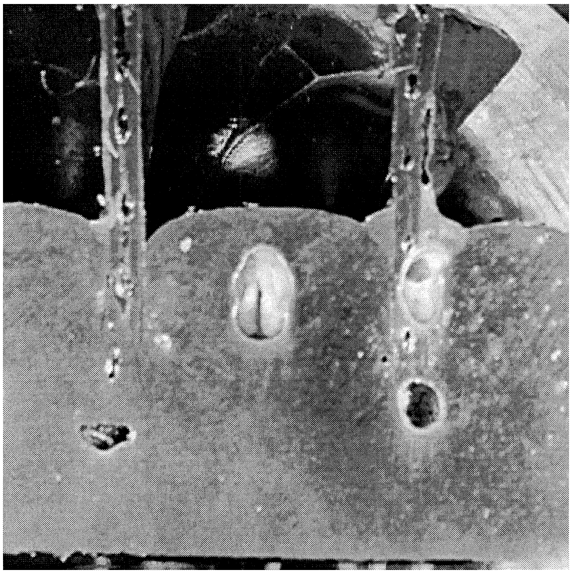

Fig. 6. COS welding of PNS grids under high temperature conditions: partial melting of PNS substrate.

During the project, new grids including modifications in the polymer substrate, knitting design and copper and lead electrodeposition conditions, copper content and improved electrical characteristics through the insertion of conductive filaments have been characterised. In general, an important weight reduction has been achieved, with an improvement in conductivity and mechanical properties through a better distribution of the metallic layers and the knitting designs.

The optimised PNS grids developed in the project show lower weight than standard grids (approximately 1/3) with the same conductivity properties, proper weight homogeneity in the same batch and metal distribution on the grid surface, good adhesion of the metallic layers, enough thermal stability under pressure for the application and higher mechanical strength than standard grids.

3. Modification of the manufacturing processes

Several battery manufacturing processes had to be adapted to the characteristics of the new grid materials.

A *lug fixing process* has been developed to provide the PNS grid with a compact metallic contact for good current transfer without damaging the polymeric structure during the welding process. The lug is a critical part of the electrode because it works as collector for the current flowing from the electrode to the battery terminals. The development of a proper lug fixing process was important for the whole performance of the battery, in order to provide the lowest voltage drop under high current drains.

The whole process was characterised by the following features:

- A pre-tinning step of the copper plated PNS electrodes with a low-melting alloy, which favours the welding process carried out subsequently.

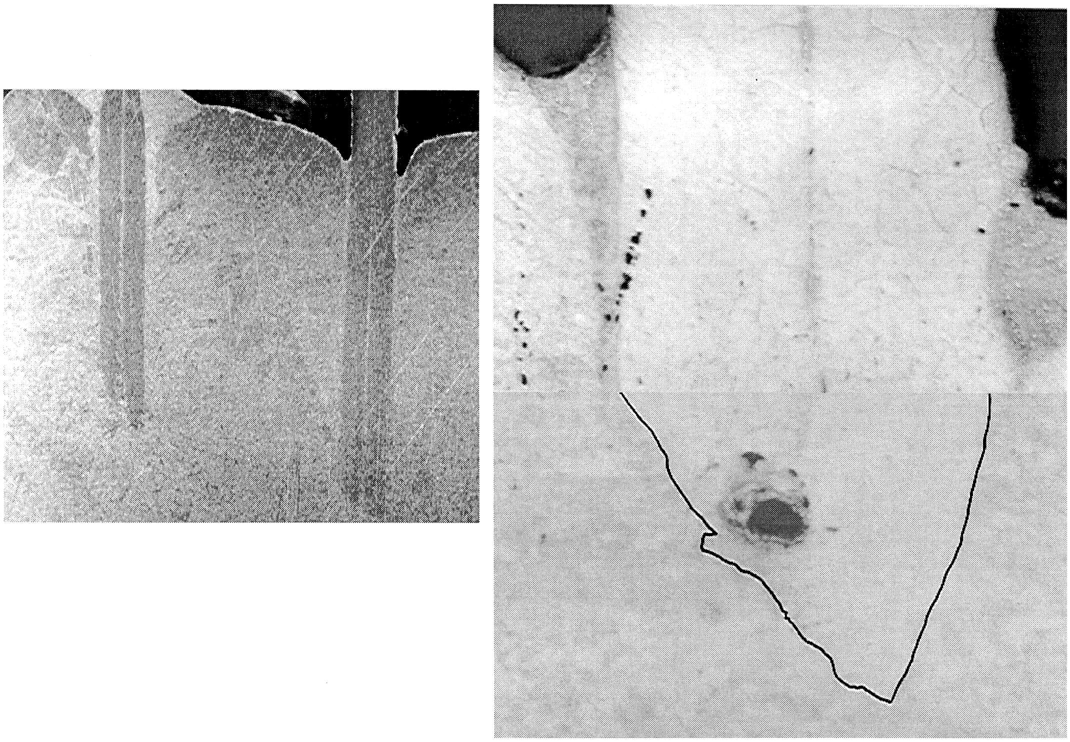

Fig. 7. Strap-lug welding under optimised conditions: general and detailed view.

Table 1
Characteristics of the different grid designs

PNS type	Mesh size	Co-knitted Cu filament	Observations
A	1 mm × 1 mm	No	
B	3 mm × 1 mm alternating 1 mm × 1 mm	Yes	
C	3 mm × 3 mm	Yes	Knitting T-1
D	3 mm × 3 mm	Yes	Enhanced Cu density in the lug region
E	3 mm × 3 mm	Yes	Knitting T-2

- The lug material was a low melting point lead alloy strip.
- A special lug design was used to avoid the polymer deterioration during the plate group completion.
- Lug welding under high pressure and low temperature conditions.

The quality of the lug fixing has been studied by means of metallographic observation and conductivity measurements. Figs. 2 and 3 show, respectively a poor welding connection between the lug and the substrate, without the pre-tinning step, and the high welding quality obtained with the optimised process conditions defined in the project.

The process conditions of the pre-tinning step are also critical: Fig. 4 shows that long immersion times can lead to the partial melting of the polymer and Fig. 5, the proper process conditions.

New active masses with lower density and higher penetration values, adapted to the closer mesh structure, have led to a higher active material efficiency, taking advantage of the three-dimensional structure of the new grid. Curing and formation conditions have also been tested, in order to achieve a satisfactory performance in the cycle life test, together with improved capacity and high rate performance due to the higher porosity.

Cast on strap welding of the plates has been adapted for the group completion. As the thermal characteristics of PNS and conventional lugs are different, it has been necessary to study the process conditions in order to obtain a good welding quality for both types of plates simultaneously.

The temperatures of both the mould and molten lead turned out to be critical: a too low temperature leads to a bad welding, with poor contact between the strap and the plate lugs and a too high temperature produces the melting and fracture of the PNS lug due to its polymeric core (Fig. 6). The optimised process conditions were finally established and used in the preparation of plate groups for electrical testing. Fig. 7 shows a general and detail view of the welding area of PNS grids.

4. Test of single electrodes and plate groups

Electrodes prepared along the project with the different PNS materials and conductive layers developed have been

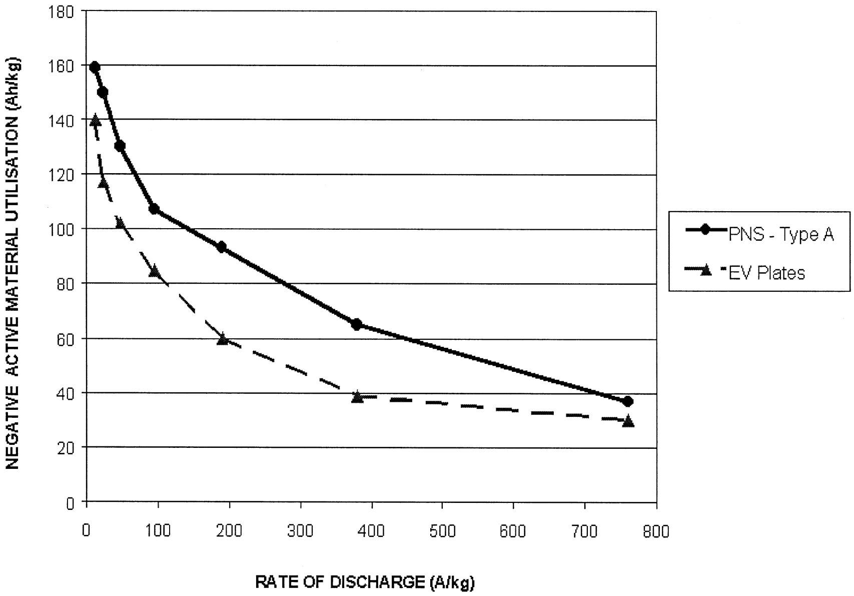

Fig. 8. Negative mass utilisation at different discharge rates.

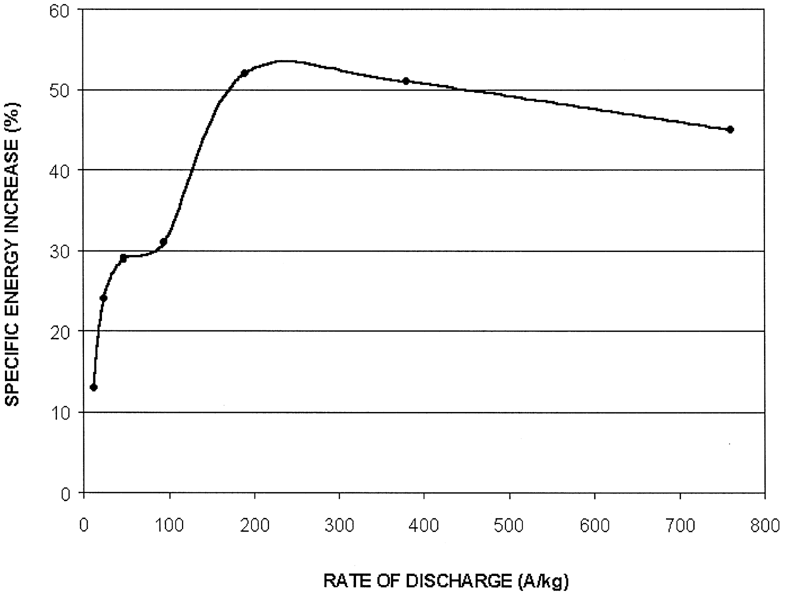

Fig. 9. Specific energy increase: PNS vs. conventional EV.

mechanically and electrically tested. Mechanical testing showed good active material retention after a strong vibration test.

Electrical testing was aimed to study the effect of the mesh size and the copper distribution on the active material utilisation at different discharge rates and temperatures. Tests have been performed with single electrodes and as plate groups and real cells, comparing the performance of PNS grids with standard plates for EV applications.

Table 1 shows the characteristics of the different PNS materials tested along the project. In all cases the total copper content per grid was 10 ± 0.5 g and the lead content was calculated according to a layer thickness of 50 μm.

4.1. Electrode testing

The performance of negative electrodes has been tested in single cells with two positive plates and one negative plate (PNS and conventional grids for EV application). In all cases, the cell was flooded, and the positive plates were conventional EV plates. In these conditions, the cell performance would be limited by the negative plates under study.

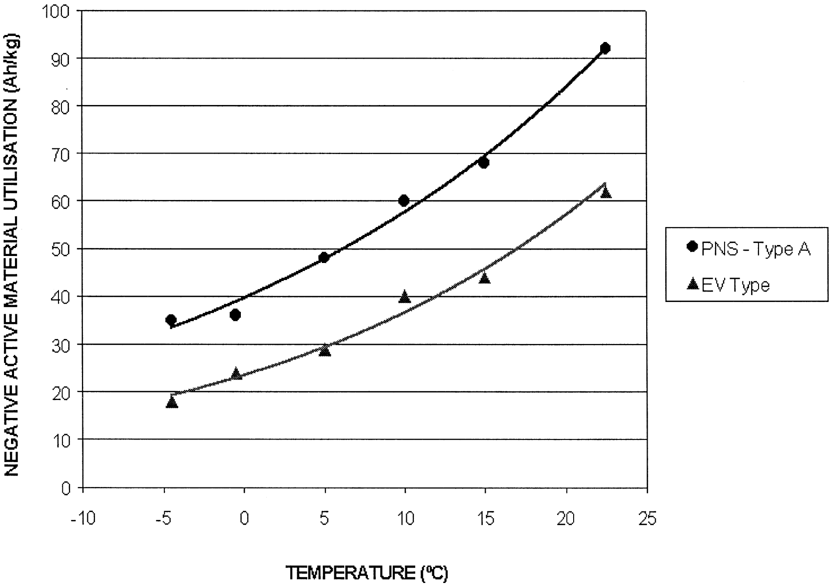

Fig. 10. Negative active material utilisation of PNS and standard plates at 190 A/kg.

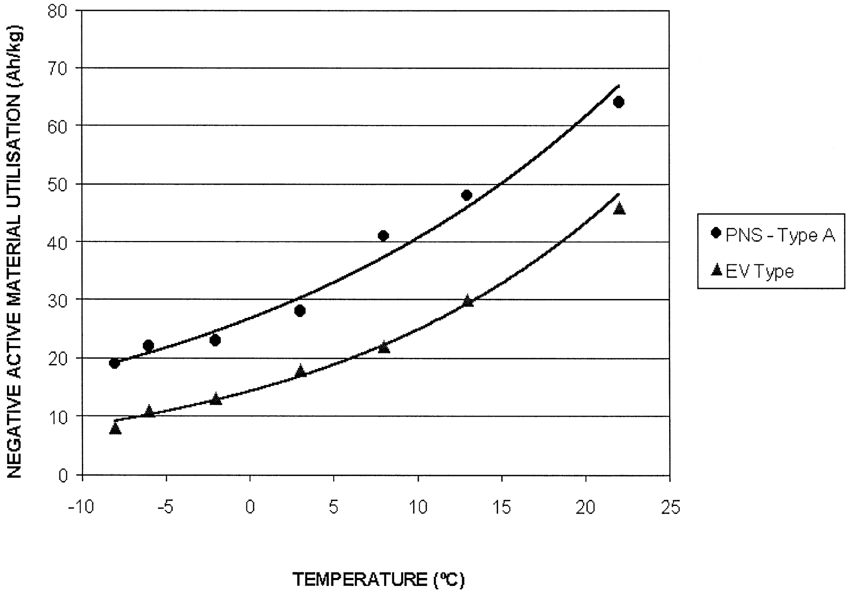

Fig. 11. Negative active material utilisation of PNS and standard plates at 380 A/kg.

Six cells were assembled with conventional negative plates, and six with PNS type A negative plates. All of them had the same grid weight and dry paste weight, so that they were directly comparable. The cells were tested at different discharge rates (from C/8 to 8C) and different temperatures, obtaining the following results.

■ Evolution of voltage vs. duration of the discharge: The shape of the voltage evolution curve is very similar for both types of plates, but the duration time for PNS type A plates is larger than for conventional grids in the same conditions.

■ Negative active material utilisation vs. discharge rate (Fig. 8): The PNS type A plates show a better active material utilisation in the whole range from C/8 to 8C discharge rates in discharges down to 1 V/cell.

■ Specific energy increase (Fig. 9): The highest increase in energy for the PNS type A grids vs. the conventional grids is in the high discharge rate area (2C, 4C and 8C) with a 50% increase.

■ Influence of temperature: Another important parameter tested was the influence of temperature in the specific energy. The increase in negative active material utilisation energy for PNS type A plates with respect to the conventional plates is higher at temperatures under 0°C, obtaining the better results at the higher discharge rates. The evolution of negative active material utilisation vs. temperature

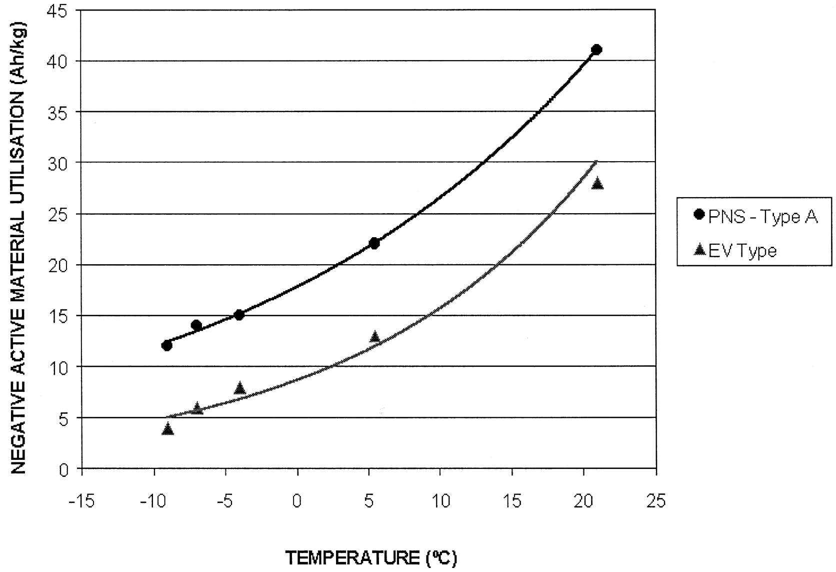

Fig. 12. Negative active material utilisation of PNS and standard plates at 760 A/kg.

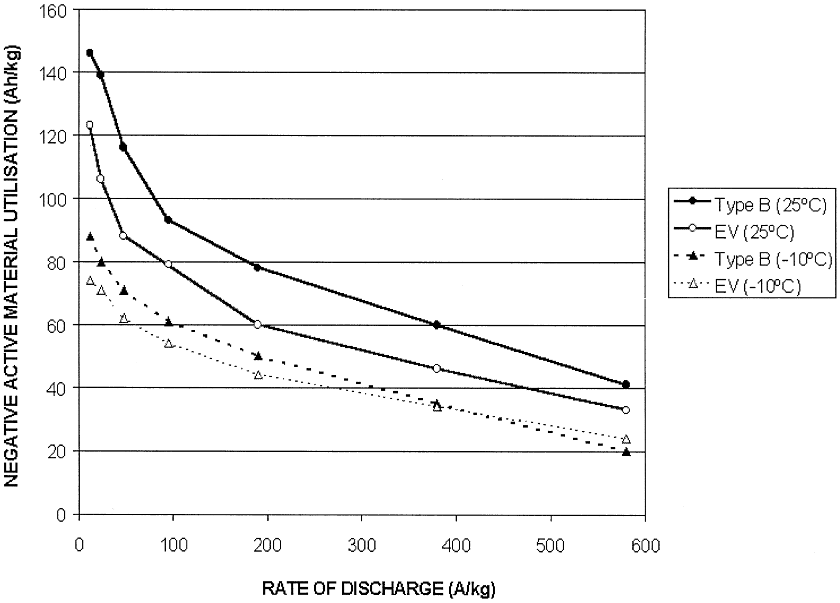

Fig. 13. Negative active material utilisation of PNS and EV plates at different temperatures.

is represented in Figs. 10–12, for discharges at 190, 380 and 760 A/kg, respectively.

The great difference observed between PNS type A and conventional grids is attributed to the mesh size: 1 mm × 1 mm for the former and 11 mm × 8 mm for the latter. The influence of the grid geometry on the active mass utilisation follows a well-known pattern [1]: the smaller the mesh size, the higher the active mass utilisation. But, on the other hand, with conventional lead grids, a small mesh size involves an important increase in the grid weight. In the present case, with polymeric electrodes, it is possible to reduce the size of the mesh while maintaining a low grid weight.

4.2. Test of electrodes as 3/2 groups

Cells with negative PNS type B plates and with negative conventional plates were assembled with similar total weights. In Fig. 13, the negative active material utilisation vs. the rate of discharge for two temperatures (25°C and −10°C) is represented. In all conditions tested, the PNS type B plates showed better results than conventional plates.

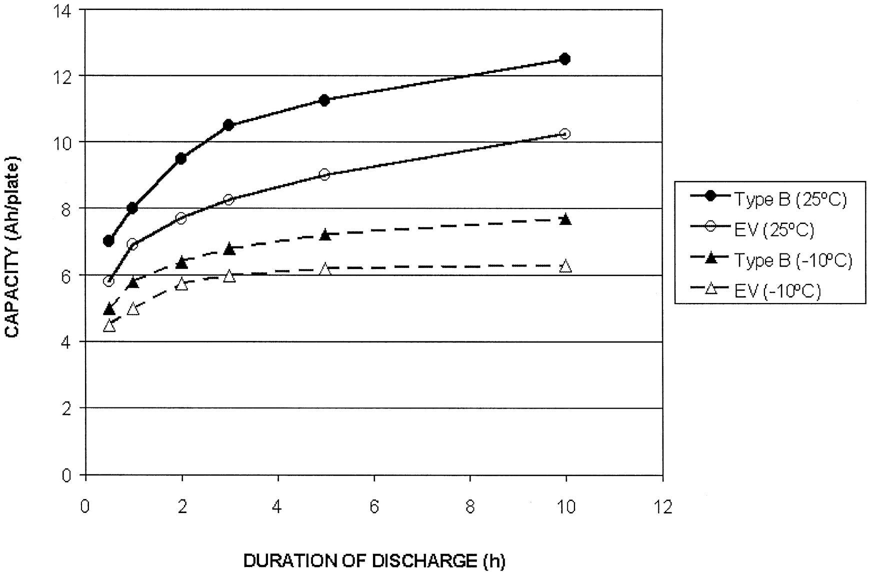

Fig. 14. Capacity of PNS and EV negative plates at different discharge regimes.

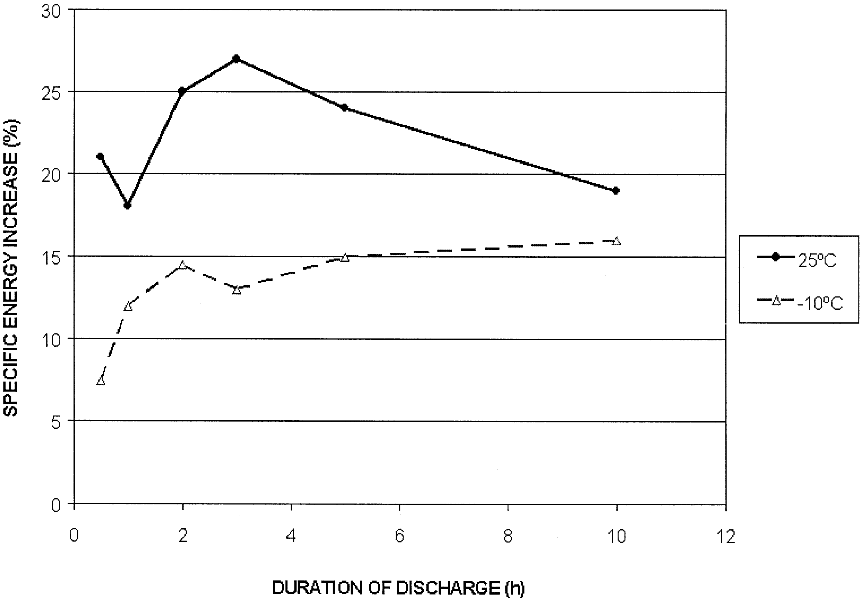

Fig. 15. Specific energy increase of PNS vs. conventional EV at different discharge rates and temperatures.

The capacity of the cells vs. the duration of discharge is represented in Fig. 14. The cells with PNS electrodes show a higher capacity than the conventional cells. Finally, the energy increase of PNS vs. conventional plates is represented in Fig. 15. Values of 20–27% increase of the specific energy are obtained in the typical rates of electric vehicle working conditions (discharge rates around 1–2 h).

In order to compare the electrical performance of grids with different mesh sizes, cells with plates prepared with PNS grids types B, C, D and E were assembled. Tests of single cells were carried out on plate groups made with three expanded positive plates, and two negative PNS plates. The plates were carefully selected in order to have the same weights in all the plate groups. A wide excess of both the amount of electrolyte and the positive active material was foreseen, in order to assure that the negative plates limit the test results. The cells were tested at different rates and two different temperatures (+20°C and 0°C). Test results are represented in Figs. 16 and 17.

The results showed that PNS type D electrodes lead to better results than type E or type C at all the discharge rates and temperatures tested. Therefore, the following conclusions could be obtained:

- PNS grids types C and E, with similar mesh dimensions, copper content and copper distribution, lead to very similar results in all cases.

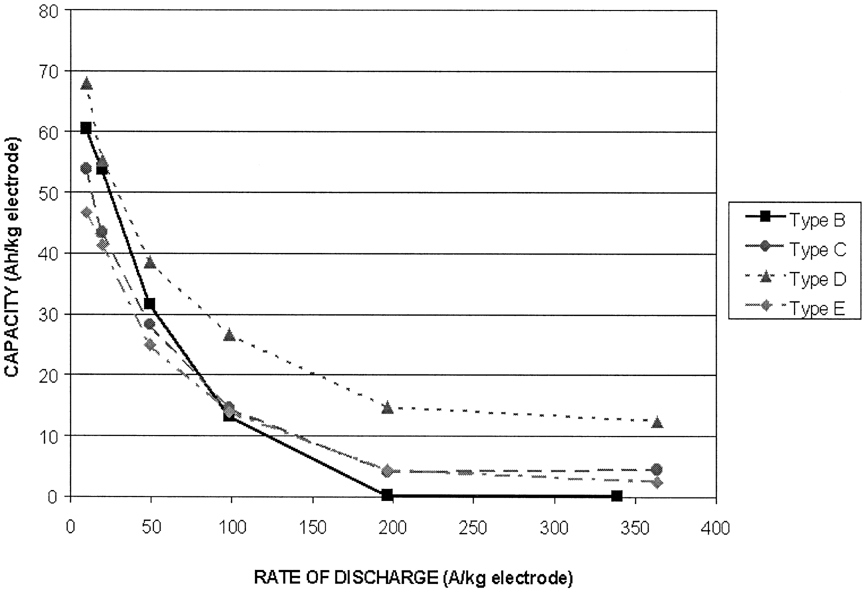

Fig. 16. Test of electrodes with different PNS grid types ($t = 20°C$).

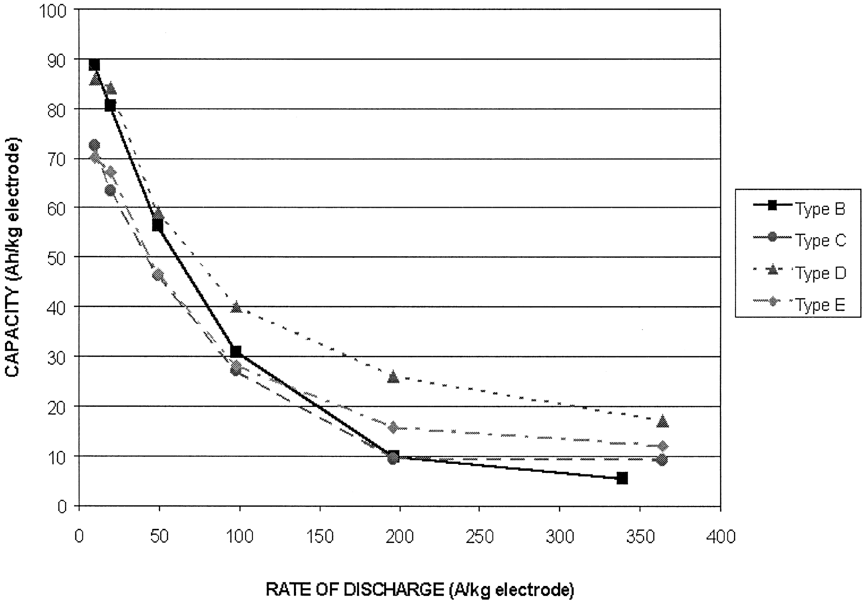

Fig. 17. Test of electrodes with different PNS grid types ($t = 0°C$).

- Grids types D and E, with similar copper content but different copper distribution produce quite different results, showing type D between a 15% and a 65% increase in active material utilisation depending on the discharge rate.
- In relative terms, PNS type B, with a smaller mesh size than types C, D or E, has a satisfactory performance at low rates, but shows a high decrease in performance at high discharge rates.
- The best ratio 'performance/grid weight' for all the solutions developed during the Project is achieved with type D electrodes, i.e., a 3 mm × 3 mm mesh, a co-knitted copper filament and enhanced copper density in the lug region.

Finally, Fig. 18 compares the grid weight of all the types of electrodes tested during the project.

4.3. Cell testing

Type B and type D electrodes have been compared in cells simulating real battery conditions: plate groups comprised six positive conventional electrodes and five nega-

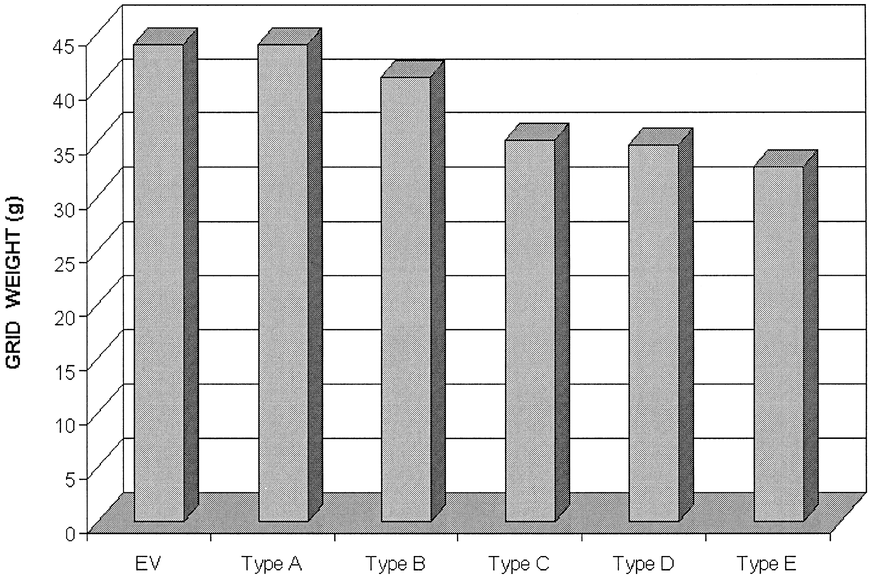

Fig. 18. Comparison of grid weights.

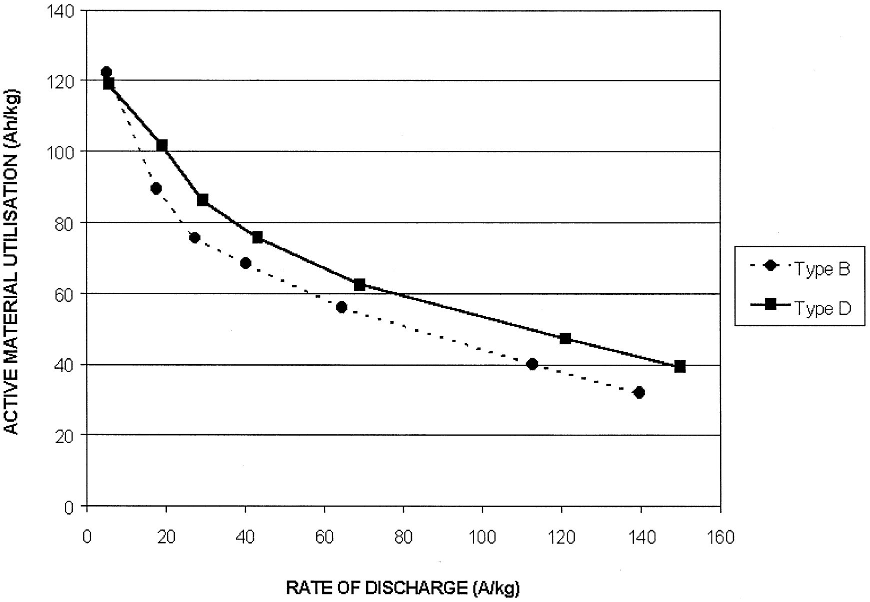

Fig. 19. Cell testing of optimised PNS electrodes.

tive electrodes, and an AGM design with glass microfibre separators. The cells were formed with 1.240 g/cm^3 density acid. After the formation, all the cells were submitted to a series of discharges at different rates. The maximum rate applied to the cells was 150 A/kg (maximum current output of the testing equipment = 100 A).

The results are represented in Fig. 19, as average performance at each discharge rate for both types of cells with PNS type B and D electrodes. If these results are compared with those from Fig. 16, it is observed that the values obtained with real cells are somewhat lower than in previous group tests, due to the acid limitation of the present conditions, in contrast to the wide excess of acid used in the tests with 3/2 cell design. Therefore, as typically found in recombination batteries, the acid is limiting the test results. Nevertheless, the acid concentration cannot be increased much above the actual levels without a deleterious effect on the cycle life.

It can be concluded that at very low discharge rates (10 A/kg) there is no significant improvement for type D PNS grids, but, at higher discharge rates, type D electrodes perform between a 15 and a 20% better than type B electrodes.

5. Conclusions

New materials and process techniques have been defined in order to substitute the heavy lead grids used nowadays in commercial lead–acid batteries by the polymeric structure with a high conductivity due to the copper content and the higher active material utilisation due to the optimised three-dimensional electrode structure.

The results obtained in the mechanical and electrical characterisation of grids and electrodes have allowed an optimisation of the mesh size and composition of the PNS grid to provide the best compromise performance/weight/cost.

The forecast applications are:

As **starter batteries** for conventional vehicles, to reduce the fuel consumption.

As **traction batteries for electric vehicles**, with an increased range for the same total weight, or a higher payload for the same range.

Exploitation of results depends strongly on the final production costs, once the achievement of lifetime and quality and reliability levels similar to standard batteries could be demonstrated.

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