Journal of Applied Electrochemistry **33**: 1057–1061, 2003.

Lead-coated glass fibre mesh grids for lead–acid batteries

J. WANG, Z.P. GUO*, S. ZHONG, H.K. LIU and S.X. DOU
Institute for Superconducting & Electronic Materials, University of Wollongong, Wollongong, NSW 2522 Australia
*(*author for correspondence, fax: +61 242215731; e-mail: jiazhao@uow.edu.au)*

Received 24 December 2002; accepted in revised form 7 May 2003

Key words: corrosion resistance, cycle life, lead–acid battery, lead-coated glass fibre grid, material utilization

Abstract

A lightweight lead-coated glass fibre mesh grid was tested for use in valve-regulated lead–acid (VRLA) batteries. Plates made with these new grids show a higher material utilization over a wide range of discharge rates (i.e., 20–200 mA g^{-1}) and temperature (i.e., −15–25 °C) compared with conventional gravity-caste plates. The results also suggest that the lead-coated glass fibre grid can replace the conventional gravity-cast grid without causing any deleterious effects so far as the cycle life is concerned.

1. Introduction

Conventional lead–acid batteries are relatively heavy and thus have a low specific energy. The heavy weight of the battery is a direct consequence of the use of large amounts of lead in the electrodes, both in the grid and in the active material. The lead grid in a lead–acid battery has two functions: as a current collector and as an active material supporter [1, 2]. Most of the lead in a conventional electrode grid does not participate in the electrochemical reaction, but merely provides the strength and stiffness needed for the grid to survive its environmental and manufacturing stresses. In fact, the conventional grid has cross-sectional dimensions that are much larger than what is required for actually conducting the currents [3].

To improve the energy density, a lighter grid has been proposed. Recently, a novel processing route to produce lightweight grids involving the electrodepositing of lead with dispersed particles has been reported by Barkleit et al. [4]. Their results show that the new grid production process is likely to be compatible with a continuous, expanded grid technology. Using this new grid, an increase in specific energy by more than 10% over that of conventional batteries has been achieved.

Soria and his coworkers have developed another new grid material [5], which is a lightweight metallized polymeric network structure with a high surface area. As the weight of the grid is reduced and the active material remains relatively constant, the specific energy of the battery is increased.

It is well known that glass fibres are lightweight and have extremely high strength, highly desirable flexibility and good acid-corrosion resistance characteristics, which make them of particular advantage for many applications such as reinforcing materials. Methods for applying metal coatings to a high tensile strength glass fibre to form a composite, continuous wire were patented long ago [6], and this technique has been applied for covering telegraph cables. The technique has been further developed in recent years and applied successfully in the manufacture of lead acid batteries [7]. The use of lightweight, fibreglass filaments yields a specific energy (energy per unit weight) as much as twice that of most conventional lead–acid batteries [8].

The work presented here is to investigate this new composite glass fiber mesh as a battery grid to replace the conventional gravity-cast grids for valve-regulated-lead acid (VRLA) batteries. Although glass fibre mesh grids for lead–acid batteries have been studied, and relevant patents have been published, to our knowledge the detailed preparation of the battery plates has not yet been reported. We chose to study glass fibre mesh because it is a very promising method for improving the specific energy of lead–acid batteries. Besides its scientific interest, understanding the preparation procedures may be of practical interest in designing lead–acid batteries.

2. Experimental details

2.1. *Corrosion test*

Since grid corrosion is one of the important factors which affects the performance of the lead–acid battery, an accelerated corrosion test was performed on glass fibre wires coated with either pure lead or lead −1.5 wt % tin alloy. This test was also tried to determine which metal coating would be more effective in terms of corrosion resistance. The test was performed in 1.28 r.d. (relative density) H_2SO_4 under a constant oxidation potential of +1.30 V for five days at 50 °C. The potential used here is similar to the value found for positive plates in VRLAs on float-charging. The constant potential was maintained by a potentiostat (model 362, EG & G Princeton Applied Research). The constant temperature was provided by a thermostat controlled water bath (JULABO (Germany), refrigerated, circulated model F10-MH). The pure lead coated and lead–tin alloy coated glass fibre wires were cut into 15 cm lengths. The weight of each sample was recorded prior to the test. A basic three-electrode system with a 'multiple' working electrode was used [9]. The counter electrode was a pure lead sheet and the reference electrode was Hg/Hg_2SO_4 (K_2SO_4 saturated solution). After each test, specimens were removed from the test cell, washed free from acid and dried. The corrosion layer was dissolved in a 'stripping solution' [10] in an ultrasonic cleaner for 30 min. The individual weight loss was then measured.

2.2. *Grid preparation*

Conventional gravity-cast grids with dimensions of 40 mm × 40 mm × 1.5 mm were obtained from the Shenyang Battery Co., China. Two types of lead-coated glass fibre mesh (pure lead coated and Pb–1.5 wt % Sn alloy coated) with wire diameter of 1.0 mm were provided by Powertronic Corp., China. Within a given distance, two Pb–3.0 wt % Sn alloy bars were cast onto the mesh to serve as current connectors and to form the two-end supporters of the mesh. A specially designed cast mould was prepared for this purpose. The lead-coated glass fibre grid is shown in Figure 1. The properties of the lead-coated glass fiber grid and the gravity-cast grid are compared and listed in Table 1. For the same dimensions, the weight of the composite grid is only about 70% of that of the conventional cast grid. This type of grid is flexible, nonself-supporting and nonreinforced structure.

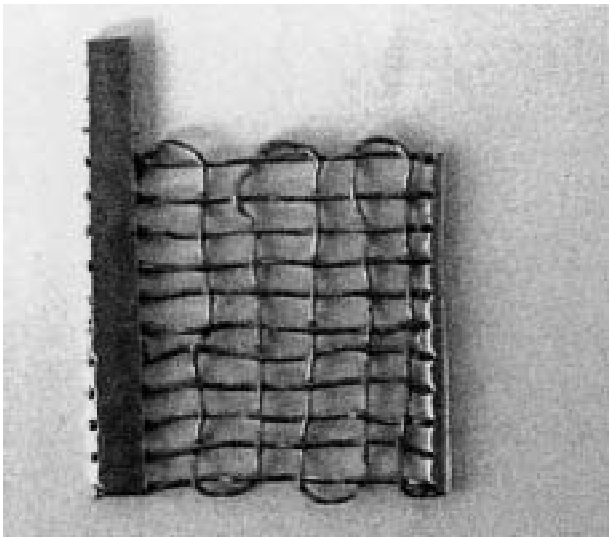

Fig. 1. Illustration of the lead-coated glass fibre grid.

Table 1. The properties of the lead-coated glass fibre grid and the cast grid

Sample	Grid type	Mesh size /mm	Grid size /mm	Grid weight /g
1	Conventional cast grid	10 × 5	40 × 40 × 1.5	12.5
2	Lead-coated glass fibre grid	5 × 3	40 × 40 × 1	9.19

2.3. *Positive plate preparation*

Two groups of plate were prepared with the two different types of grid. For group one, plates were prepared with the conventional gravity-cast grids. These plates were used as control plates in the experiment. For group 2, plates were made with the pure lead-coated glass fibre mesh as the grids.

The positive paste was prepared by mixing leady oxide (Guangzhou Battery Co., China) with water and sulfuric acid (r.d. 1.40). The apparent density of the paste was about 3.8–4.0 g cm^{-3}. The paste was then manually applied onto the grids with a plastic scraper. The dimensions of the grids were 40 mm × 40 mm. The thickness of all the plates was controlled to 2.0 mm for the mesh grids and 2.5 mm for the gravity-cast grids, respectively. The pasted plates were cured at 50 °C with a relative humidity over 95% for 48 h in an autocontrolled water bath and then dried at 60 °C for 24 h in an oven.

A dried plate prepared with a mesh grid is shown in Figure 2.

2.4. *Battery assembly and testing*

Each positive plate was sandwiched by two conventional commercial negative plates (negative plates were taken from commercial batteries) with microglass fibre separators inserted between them. The individual plate-groups were then inserted into the cells of a battery case. In each cell, two separate polycarbonate sheets were added to provide high plate-group compression. The cells were filled with H_2SO_4 (r.d. 1.28) electrolyte to such a degree that similar total volume of plates, separator and electrolyte was achieved. The cell were sealed and a rubber valve was fixed to each cell. After 2 h of soaking in H_2SO_4 (r.d. 1.28) electrolyte, the cell formation was conducted with a constant formation current density of 25 mA g^{-1} for 24 h (with 1 h step and 10 min rest). After formation, the reserve capacity of each cell was tested with different discharge rates at different temperatures until the cell voltage fell to 1.75 V.

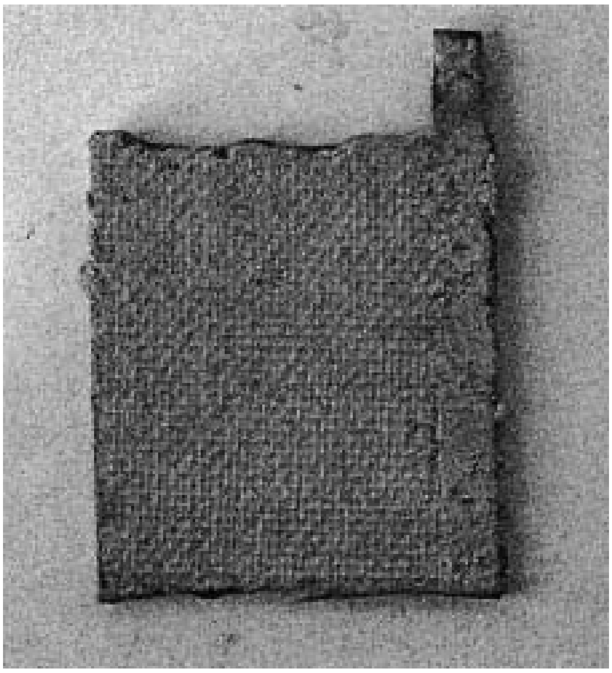

Fig. 2. Illustration of a pasted plate prepared with a mesh grid.

3. Results and discussion

3.1. *Corrosion test results*

The purpose of the accelerated corrosion test was to compare the corrosion properties of the pure lead and the lead–tin alloy coating on the composite wires before using them as battery grid. The coating of either pure lead or lead–tin alloy on the glass fibre is based on a 'coextrusion process' [7]. This process applies a high compression and a low temperature (below the melting point of the pure lead) to coat the lead layer on a continuous filament of lightweight glass fibre. With this procedure, a very fine and compact grain structure is obtained. More importantly, the microstructure of the coating layer is different to that of the conventional gravity-cast grid and thus this layer is highly corrosion-resistant. Results from the accelerated corrosion tests are given in Table 2. The weight loss for the pure lead coated glass fibre wire is much lower than that of the lead–tin alloy coated counterpart. This result indicates that the corrosion rate of the lead–tin alloy is higher than that of the pure lead. Figure 3 shows the corrosion morphologies of the pure lead and the Pb–3 wt % Sn alloy after an accelerated corrosion test. The edge of the pure lead coated glass wire is still almost smooth, while obvious chips can be observed at the edge of the Pb–Sn alloy wire. This phenomenon is consistent with the description above, that is, the corrosion resistance of the pure lead coating is higher than that of the Pb–Sn alloy coating. Therefore, the Pb–Sn alloy is not suitable for the coating layer in term of its corrosion properties.

Table 2. Results of the accelerated corrosion test

Sample	Weight loss /%
Pure lead-coated glass fibre grid	10.4%
Lead–tin alloy coated glass fibre grid	13.5%

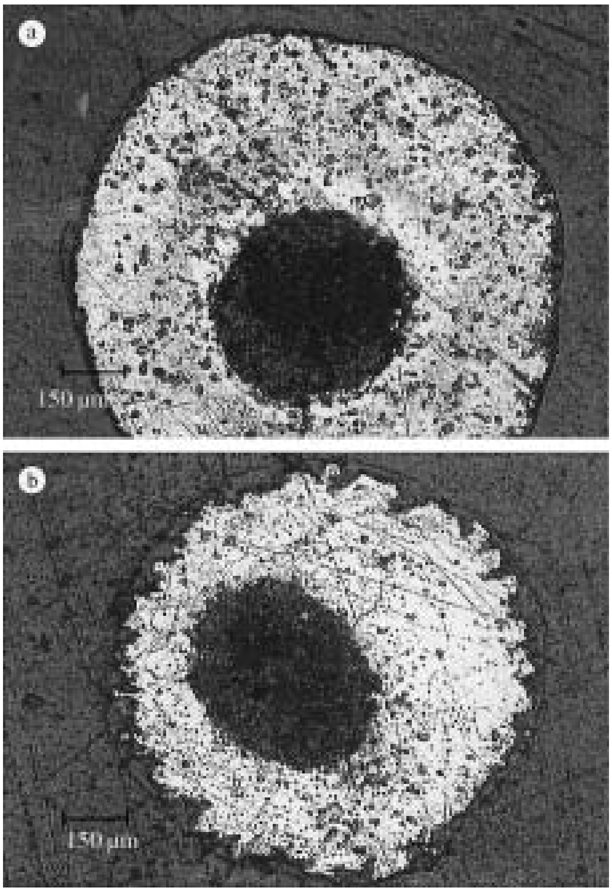

Fig. 3. Corrosion attack of the cross-section of: (a) a pure lead coated glass fibre; (b) a lead–tin (3%) alloy coated glass fibre.

3.2. *Material utilization*

To compare the electrochemical performance of the lead-coated glass fibre grid and the gravity-cast grid, test cells with the two types of grid were assembled and formed under identical conditions, as described above. Tests were performed at room temperature under variable rates of discharge. The results were calculated in terms of the active material utilization and are given in Figures 4 and 5. Compared with conventional plates, the plates prepared with lead-coated glass fibre grids give higher active material utilization. The reasons for this increase can be explained as follows. Low utilization of active material is a major disadvantage with the present designs of the lead–acid battery. This limitation in performance is promoted by two factors: (i) slow diffusion of sulfuric acid from the bulk of the solution into the interior of the plates; (ii) continuous decrease in the plate conductivity of the positive and negative plates during discharge [11]. It is obvious that thinner plates produced from grid with smaller mesh size will reduce

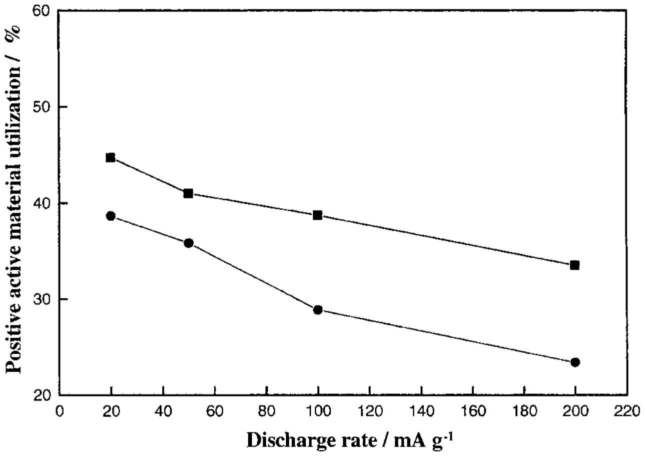

Fig. 4. Positive active material utilization of cells using lead-coated glass fibre grid and conventional gravity-cast grid at 25 °C.

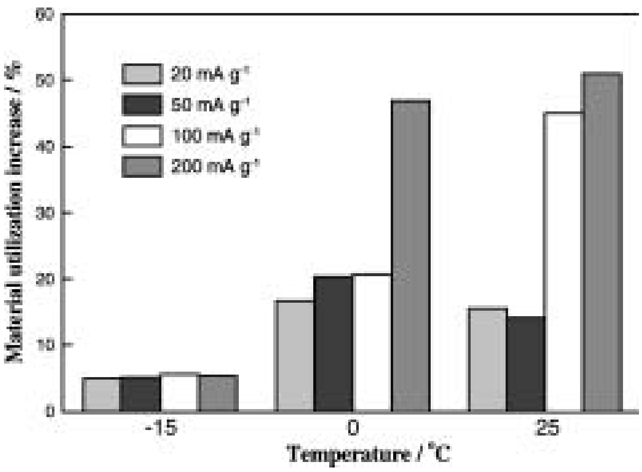

Fig. 5. Percentage material utilization improvement of plate using lead-coated glass fibre grid when comparing with plate using conventional gravity-cast grid.

both the diffusion pathway of sulfuric acid and the electrical resistance of the plate and, therefore, can raise the level of the material utilization. Since the thickness and mesh size of the plate using lead-coated glass fibre mesh are thinner and smaller than those of the plate using conventional cast grid, the former has higher material utilization than the latter. It is understood that the mesh size of conventional gravity-cast grid can be reduced without causing manufacturing problems, but the weight of the grid will be increased substantially. By contrast, it is possible to reduce the size of the mesh, while still maintaining a small increase in weight of the lead-coated glass fibre grid.

Temperature effects on the battery performance are also of concern for many applications. In this study, two types of cell were also tested at different temperatures with different rates of discharge. Figure 5 shows the percentage increase of positive active material utilization for the lead-coated glass fibre plate over that of the conventional plates. There is a slight increase (~5%) in material utilization of positive plate using lead-coated glass fibre mesh at 15 °C and the degree of increase is virtually unchanged, irrespective of the increase in discharge rate. Nevertheless, the improvement of material utilization becomes significant (>15%) and increases with the increase in discharge rate when the cells were tested at 0 °C and 25 °C. The highest increase in material utilization (~50%) is obtained when the plate was discharge at 200 mA g^{-1} at 25 °C. These results demonstrate that material utilization can be further improved when the cells are used under high-rate discharge and high-temperature conditions.

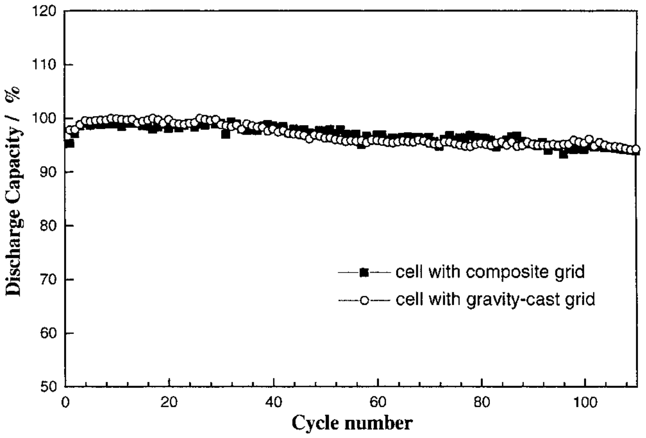

Fig. 6. Percentage of discharge capacity against cycle number for lead–acid cells discharged at 50 mA g^{-1}. Key: (■) lead-coated glass fibre grid; (○) conventional gravity-cast grid.

3.3. *Cycle life*

Figure 6 shows the percentage of discharge capacity against cycle number for the cells using lead-coated glass fibre grids and cast grids. Although both types of cell are still under evaluation, no difference in the percentage discharge capacity is observed up to about 108 cycles. This indicates that the fibre grid can replace the conventional gravity-cast grid without causing any deleterious effect on cycle life while providing other beneficial properties.

4. Conclusions

A lead-coated glass fibre mesh has been tested as a grid for lead–acid batteries. The grid is thin, lightweight, strong, flexible, and is found to be highly corrosion-resistant and conductive. It can also be shaped into various configurations. The active material utilization has been improved for cells using lead-coated glass fibre grids over a wide range of discharge rates and temperatures compared with conventional cast grids. Importantly, the cycle life of the cell is not impaired when using lead-coated glass fibre mesh as the battery grid.

Acknowledgements

This work was financially supported by the Australian Research Council under an ARC-SPIRT project (C89805127). The authors also thank Dr T. Silver for critical reading of the manuscript.

References

1. M. Torralba, *J. Power Sources* **1** (1976/77) 301.
2. R.D. Premgaman, *J. Power Sources* **67** (1997) 267.
3. *US Patent 5 952 123* (1999).
4. G. Barkleit, A. Grahl. M. Maccagni, M. Olper, P. Scharf and R. Wagner. *J. Power Sources* **78** (1999) 73.
5. M.L. Soria, J. Fullea, F. Seaz and F. Trinidad, *J. Power Sources* **78** (1999) 73.
6. *US Patent 275 859* (1883).
7. *US Patent 6 027 822* (2000).
8. *US Patent 4 865 933* (1989).
9. N. Papageorgiou and M. Skyllas-Kazacos, *J. Power Sources* **36** (1991) 57.
10. S. Zhong, H.K. Liu, S.X. Dou and M. Skyllas-Kazacos, *J. Power Sources* **59** (1996) 123.
11. B.D. McNicol and D.A.J. Rand, 'Power Sources for Electric Vehicles' (Elsevier, New York, 1984).