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Enhanced performance of VRLA batteries with a novel spirally-wound electrode design

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Abstract

A spirally-wound electrode has been designed, constructed and applied to VRLA cells. Because of its unique construction: high strength, light-weight lead-coated glass fibre mesh as the grid, comparatively thin plates and sufficient internal compression, this new design provides significant advantages over the conventional prismatic type of VRLA battery. The total weight of grids and top lead used in a battery can be reduced by 40% compared with conventional cast grids. There was no positive active-material softening and expansion until after over 300 deep cycles. Substantial improvement in sustaining the cycleability has been achieved. This technique also provides a convenient process for manufacturing a spirally-wound VRLA battery in a simple and cost competitive way.

Keywords: Lead–acid battery; Spirally-wound electrode; Cycle life; Active material utilisation

1. Introduction

In spite of extensive and continued efforts aimed at developing new light-weight, low-cost secondary electrochemical power sources, the old lead–acid battery system still is often chosen as the most suitable power source. This is because lead–acid batteries offer several advantages over other advanced battery systems. These include availability, low cost, satisfactory power density, safety, and an established infrastructure for battery manufacturing and recycling. The main drawbacks of the current technology of the lead–acid system are its relatively low energy density and short cycle life under depth discharge. Both drawbacks have always been incompatible with electric vehicle applications. The limitations arise from the theoretical specific energy density of the system, the properties of the electrode material employed, and current design of the battery [1–5].

Although the spirally wound cell configuration appeared as the earliest model of the lead–acid system, it was not commercialised until recent years. Compared with the conventional flat plate configuration, the spirally wound construction provides the following advantages [6,7]:

(1) a uniformly high plate compression for extending the cycle life;
(2) the use of comparatively thin plates for improving the specific power;
(3) the use of pure lead or soft lead alloys for reducing gassing;
(4) simpler and cost competitive manufacturing techniques.

With these advantages, the new spirally wound VRLA cells are well able to provide many benefits not available with conventional lead–acid construction.

In this paper, we report the advantages of a novel spirally wound electrode design and the improved performance of the prototype cells.

2. Experimental

2.1. Material preparation

A custom-made ABS tube with a diameter of 4.4 cm was used as the case for VRLA single column spirally wound prototype cell. Lead-coated glass fibre mesh [8] with thickness of 0.8 mm was used as the electrode substrate (grid) for both positive and negative plates. ‘‘Barton oxides’’ having a free lead content of 12 wt.% were used for the paste. An AGM separator was used (provided by AXOHM Industries, France). Conductive $BaPbO_3$ powder and high conductive carbon fibre were added to the oxide during the paste preparation in order to enhance the paste strength and improve formation efficiency.

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1. terminal
2. top cap
3. terminal seal
4. positive current connector
5. positive plate.
6. press cap
7. rubber valve
8. negative current connector
9. negative plate
10. separator (AGM type)
11. case

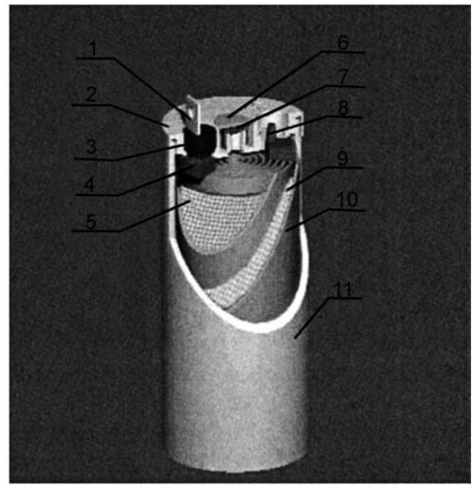


Fig. 1. Schematic structure of a spiral wound cell.

2.2. *Spirally wound electrode preparation and cell construction*

Spiral wound cells with a nominal 10 Ah capacity were fabricated. The positive and negative electrodes were pasted manually. One positive plate was covered by an AGM separator sheet, and one negative plate was placed on top of the separator layer. The negative plate was longer than the positive plate, so the capacity of the cell is restricted by the capacity of the positive electrode. The sandwiched electrodes were then wound tightly with a homemade spiral-winding machine and inserted into a custom-made ABS cylindrical case under compression. The cell was sealed but with the valve open, and then dried at 70 °C for 48 h. The resistance of the cell was continually monitored with an ohmmeter during the drying process. When the measured resistance become very large (i.e. $\Omega \to \infty$) the drying was essentially complete.

After drying, the cell was filled with electrolyte of specific gravity 1.30 and a rubber valve was fixed. Fig. 1 shows the cross section of a spiral wound cell. In order to compare the spiral wound cell with a prismatic mode, one prismatic cell was fabricated and tested under identical conditions to the spiral one. However, the flat plates were treated under a conventional process (cured at 70 °C with relative humidity of 99% for 24 h, and then dried at 70 °C for 24 h).

2.3. *Cell formation and test*

Two hours after filling the cell with electrolyte, cell formation was applied with a constant formation current density of 25 mA g^{-1} for 27 h with a 1 h step and 10 min rest programmed. Since the cell capacity was designed to be restricted by the positive electrode, the total input capacity was always kept at 600 mAh g^{-1} with respect to the positive active material (PAM). That was 2.5 times the theoretical value for converting PbO to PbO_2. After cell formation, the reserve capacity was recorded with a 2 h discharge rate to a cut-off voltage of 1.60 V per cell, and then the charging and discharging cycle test immediately followed. During charging a constant current was maintained until the cell voltage reached 2.45 V and then the charging was held at this voltage for 6–8 h, or until 110% of the previous discharge capacity was reached. The formation and the cycle life tests were carried out by a self-designed, home made program controlled battery cycler.

2.4. *Material characterisation*

The free lead content of the samples before formation was analysed using a gravimetric method. The PbO_2 content of the samples after formation was analysed using a titrimetric analysis method. The morphology of the non-cured spiral wound plate and the cured flat plate were both examined with a scanning electron microscope (SEM, Lexica, Model 44).

3. Results and discussion

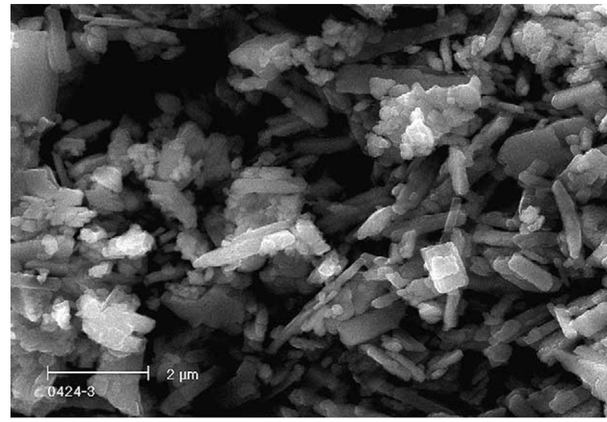
3.1. *A new one-step drying process to replace the conventional two-step plate curing/drying process*

The new process provides many benefits which are not available from the conventional flat plate manufacturing process. Only two single electrodes are needed in a spiral wound cell, and there is no need for a conventional connector to connect each plate. Since the plate drying is performed inside the cell case directly after pasting, there is enough moisture (from the fresh paste) inside the case during the early stage of drying to supply the function of the conventional ''plate curing''. As drying proceeds, the moisture eventually evaporates and the dried plate is then obtained. The free lead content for the non-cured plate was 1.5%, only slightly higher than that of the cured plate (1.0%), which indicates that the free lead in the plate can be well oxidised through one-step drying. The conventional two-step curing/drying process can thus be replaced by the one step drying process for production simplicity and cost effectiveness.

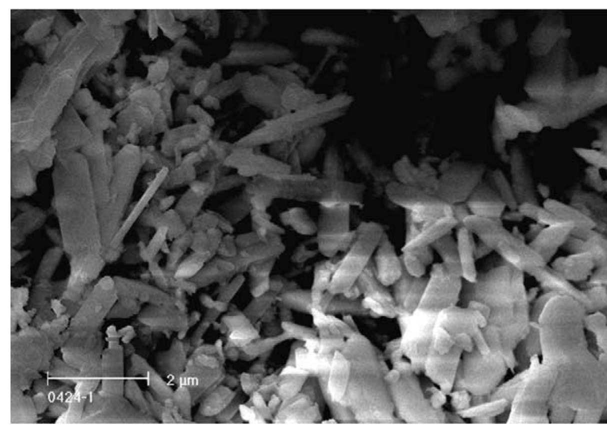
The PbO_2 content of the samples after formation was analysed. Results showed that the PbO_2 contents of the two samples were all over 70%. This means that the formation process can proceed properly in the plates without the curing process as well as in the cured plate. SEM images of the two types of plates are given in Fig. 2. Both of the plates contain large, rectilinear 4BS crystals. The 4BS crystals in the non-cured plate are slightly smaller than in the cured one. These SEM images also show that using the new one-step drying process can produce similar crystal structure and size as using the conventional two-step curing/drying process.

3.2. Reducing the weight of non-capacity-contributing components and increasing the specific energy

A total weight reduction of 40% could be achieved for the new electrode by using a light weight lead-coated glass fibre grid to replace the conventional cast grid (which includes the top lead). A cast grid from a commercial VRLA battery (Panasonic 12 V/10 Ah) was used for this comparison. The new spirally wound electrode provides high active material



(1)



(2)

Fig. 2. SEM images of pastes prepared by the two methods. (1) Non-cured plate. (2) Cured/dried plate.

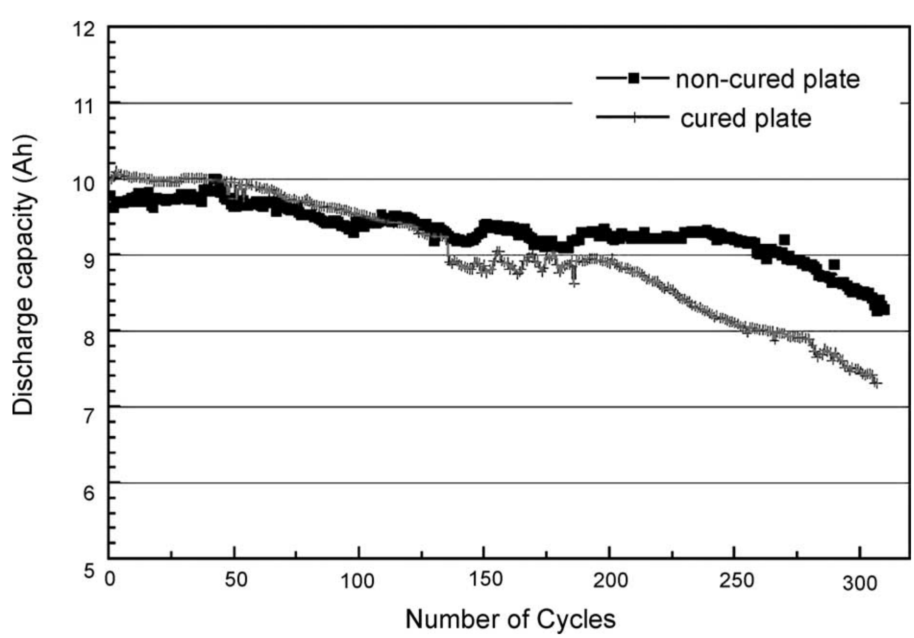


Fig. 3. Discharge capacity vs. cycle number.

utilisation, and a specific energy over 40 Wh kg^{-1} under a 3 h discharge rate can be reached with this new design compared with ~30 Wh kg^{-1} for the conventional model.

3.3. Improvement of cycle life

Fig. 3 shows the cycle behaviours for the two types of cells. The conventional cured/dried plates present a higher reserve capacity in the early cycles while the non-cured plate shows a slightly lower initial reserve capacity. However, this difference substantially disappears after 100 cycles, and the cycle stability of the spiral wound cell proved to be superior to that of the flat plate cell as the test proceeded.

The improvement in cycle life indicates the beneficial effects of the spiral wound electrode construction, which can be attributed partially to the uniformly high plate compression, together with the high open valve pressure, specifically designed and only suitable for the spirally wound cell. After over 300 cycles, each of the two types of cells was disconnected and then disassembled for evaluation. Both positive and negative plates were in a good condition, and no electrolyte dry-out was found for either type of cell. Positive material softening was observed for both cells. The capacity decline was thus attributed to the softening of the positive plate for both cells.

4. Conclusion

(1) A new manufacturing process for spiral wound VRLA cells is more efficient and cost competitive compared with the conventional manufacturing processes.

(2) The spirally wound VRLA batteries can use less "dead" lead for plate connection and thinner plates than the conventional prismatic battery, which results in a weight reduction of non-capacity-contributing components and a significant increase in the specific energy.

(3) These beneficial results have been recognised and proved by the collaborating battery manufacturing company, and a pilot production line for commercialisation of the new processing technique has been built.

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