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Short Communication

Research on valve-regulated lead/acid batteries for automobiles

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Abstract

This paper introduces design technology for automotive valve-regulated lead/acid (VRLA) batteries, such as grid alloy separator, container, positive and negative plate additives, and grid frame. Compared with conventional flooded-electrolyte lead/acid batteries, automotive VRLA batteries are influenced by high charge voltage and by high temperature. If the voltage of the automotive charging system is reduced and the battery is located outside the engine compartment of the automobile, VRLA batteries will enjoy longer service lives than flooded-electrolyte counterparts. The same assembly line can produce both automotive VRLA batteries and polyethylene envelope batteries. This reduces the production costs for automotive VRLA batteries.

Keywords: Valve-regulated lead/acid batteries; Automotive batteries; Grid alloy; Separator; Electrical tests; Lead/acid batteries

1. Introduction

The lead/acid storage battery was invented 136 years ago. By contrast, valve-regulated lead/acid (VRLA) storage batteries have been developed only during the past 15 years. At present, lead/acid batteries are undergoing a revolutional change, and VRLA batteries are at the centre of this change. Small VRLA batteries are now applied so widely that they are capturing part of the market for nickel/cadmium batteries. Conventional stationary batteries are being replaced extensively by stationary VRLA batteries. Increasing numbers of motorcycles are using VRLA batteries. The technology and performance of small VRLA batteries, stationary VRLA batteries and motorcycle VRLA batteries are well established. By contrast, automotive VRLA batteries are only developing slowly and with difficulty. In the late 1970s the 'Torque Starter' brand of automotive VRLA battery was made in Australia. In the 1980s, Yuasa, GS, Gates, JCI, CEAC and Fiamm researched and field-tested automotive VRLA batteries. The study and the development of automotive VRLA batteries were not, however, undertaken in PR China. Now, Guangzhou Storage Battery Enterprises Co., Ltd. and Evergreen Storage Battery Co., Ltd. of Guangdong Province are able to produce automotive VRLA batteries. They are among the first manufacturers of automotive VRLA batteries in PR China.

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2. Difficulties and key problems for automotive VRLA batteries

Valve-regulated batteries display many advantages, e.g. maintenance-free operation (i.e., no water addition), low self-discharge, etc. Therefore, VRLA batteries are becoming increasingly popular. But there are some disadvantages in automotive service, namely, short deep-cycle life, water loss with high-voltage charging systems, poor performance under the high temperature conditions of engine compartments, poor rechargeability after over-discharge. In the meantime, electrical and electronic functions of automobiles are increasing, e.g. air-conditioning, audio system, electrically-operated window and seat adjustment, automatic locking and unlocking of doors, telephone, alarm system, heated windshield. These may cause appreciable discharge of the battery while the car is stationary. Thus, heavy-duty batteries are required.

Mechanical, electrical and electronic devices are densely packed in the engine compartment [1]. Many of them generate heat. At the same time, the temperatures will rise significantly with the low-profile engine hoods that are being used for improved aerodynamic purposes [2]. Finally, the gas-recombination reaction in a VRLA battery produces heat. Accordingly, the temperature of VRLA batteries can rise to 60–80 °C. Thus, it is necessary for automotive VRLA batteries to operate satisfactorily at elevated temperatures.

Given that engine hoods are becoming lower and engine compartments more densely packed, the battery must occupy a smaller space and be able to work at higher temperatures while, at the same time, have an increased reserve capacity. The best solution to the problem is to remove the battery from the engine compartment. Alternative locations can be under the seat in the passenger compartment or in the trunk compartment.

The voltage of the charging systems of automobiles is a further problem for VRLA batteries. If the charge voltage can be reduced, then automotive VRLA batteries will become practical. Some manufacturers of advanced vehicles are trying to develop a suitable charging method that involves constant low-voltage charge with limited current.

The final problem is the high cost of VRLA batteries. Besides high material costs, fabrication and production processes are expensive because assembly efficiency is too low. This problem can be solved by the automatic assembly of VRLA batteries [3].

3. Technical data and processes

Materials, structure, dimensions, hold method and additives are compared in Table 1. The batteries are divided into four groups: groups 1 and 2 are VRLA batteries; groups 3 and 4 are conventional flooded-electrolyte batteries.

3.1. Container

The overall dimensions of the container are the same, but the designs are different. The end wall of the VRLA battery is thicker and is strengthened with ribs. The cover is fitted with a low internal-pressure, cap-type, rubber valve. A lifting handle is provided, see Fig. 1. Talcum power ($CaCO_3$) is added to the polypropylene construction material in order to prevent deformation of the container [4]. The deformation is less than 1 mm under an internal pressure 70 kPa. The water vapour permeability of polypropylene is 1.5 to 3 g m^{-2} compared with 30–40 g m^{-2} for acrylonitrile/butadiene/styrene (ABS) (24 to 100 h) [5]. Polypropylene is suitable for heat welding. Therefore, polypropylene is chosen to be the container material for VRLA batteries.

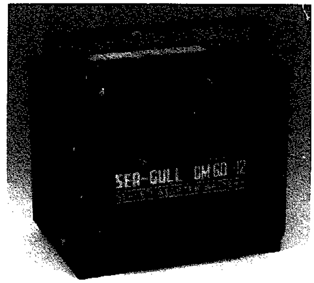

Fig. 1. Photograph of automotive VRLA battery.

3.2. Grid

The automotive VRLA batteries have adopted a new type of grid frame (Fig. 2), while the conventional flooded-electrolyte batteries return the old type grid frame (Fig. 3). The

Table 1
Comparison of designs of different batteries

Item	Group 1	Group 2	Group 3	Group 4
Battery type	VRLA battery QM 60-12 (12 V, 60 Ah)	VRLA battery QM 60-12 (12 V, 60 Ah)	Flooded battery 6QW-60 (12 V, 60 Ah)	Flooded battery 6QW-60 (12 V, 60 Ah)
Grid alloy				
Positive	Pb–Sn–Ca–Al–others	Pb–(0.6%)Sb–others	Pb–(2%)Sb–others	Pb–(2%)Sb–others
Negative	Pb–Ca–Sn–Al	Pb–Ca–Sn–Al	Pb–(2%)Sb–others	Pb–(2%)Sb–others
Separator	AGM	AGM	10-G+	Polyethylene
Overall dimensions				
Length (mm)	247	247	247	247
Width (mm)	173	173	173	173
Height (mm)	224	224	224	224
Wet weight (kg)	18.50	18.56	18.55	18.55
Container	Polypropylene + talcum + strong ribs	Polypropylene + talcum + strong ribs	Polypropylene	Polypropylene
Hold method	Up and down	Up and down	Up	Up
Positive paste additives	Graphite (different in nature) + sulfate + polypropylene fibre	Graphite (different in nature) + sulfate + polypropylene fibre	Polypropylene fibre	Polypropylene fibre
Negative paste additives	Agent N + other	Agent N + other	Agent N	Agent N
Electrolyte additive	Sulfate + other	Sulfate + other		
Electrolyte density (g cm^{-3})	1.30	1.30	1.28	1.28

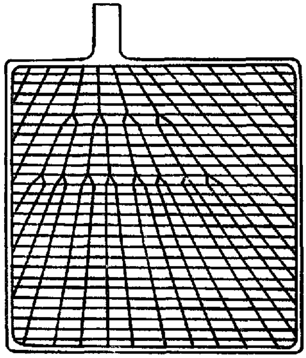

Fig. 2. Grid design of automotive VRLA battery.

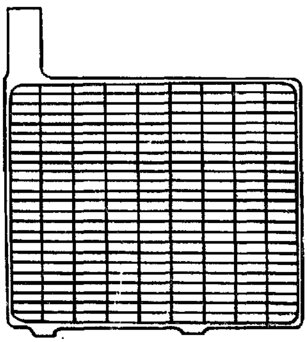

Fig. 3. Grid design of conventional flooded battery.

new grid has the advantages of uniform current and increased active-material utilization. Moreover, high-rate discharge is improved.

The positive grid alloy of the VRLA batteries is Pb–(0.12–0.15) wt.%Ca–(1.0–2.0) wt.%Sn–(0.02–0.04) wt.%Al–other (proprietary) component. The negative grid alloy is Pb–(0.12–0.15) wt.%Ca–0.03 wt.%Sn–(0.02–0.04) wt.%Al.

3.3. Separator

The VRLA batteries use absorptive glass-mat (AGM) separators. They are made from microfibre glass (the most common), synthetic fibres, some large and long fibres, etc. In Japan, this separator is made from glass fibre, polyester fibre and inorganic powder [6]. This type of AGM has sufficient strength for passing through an automatic, high-speed, envelope/stacker machine. Because there are synthetic fibres in the mix, it is possible to seal the edges with supersonic or heat-welding technology. If AGM separators consist of pure microfibre glass, they will pinch when pulled into the envelope/stacker machine, and their edges cannot be welded. AGM, PE and 10-G+ separators are imported from France and the USA.

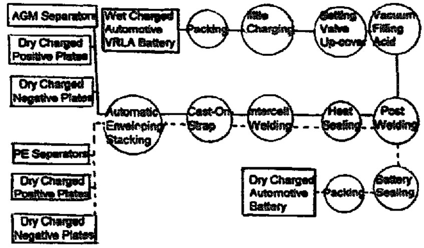

Fig. 4. Technical process of assembly line.

3.4. Assembly process

Guangzhou Storage Battery Enterprises Co. Ltd., manufactures automotive VRLA batteries and conventional flooded-electrolyte batteries (PE envelope separator) in the same automatic assembly (Sea-gull) plant. Only after post welding VRLA and PE separator batteries are treated separately. The technical process of the assembly is shown in Fig. 4.

4. Test results

4.1. High-rate discharge

The VRLA batteries are discharged with a current of $9C_{20}$ (540 A), and conventional flooded-electrolyte batteries with a current of $5C_{20}$ (300 A). The temperature is −15 °C. The voltages after 5 and 30 s are listed in Table 2. The high-rate discharge performance of the VRLA batteries is excellent. The electrical resistance of the AGM separators is low, and the VRLA cells have more plates than the conventional flooded-electrolyte cells.

4.2. Cycle life

Automotive VRLA batteries are influenced by both charge voltage and environmental temperature. This is confirmed by the results of cycle-life tests with different charge voltages

Table 2
Performance under high-rate discharge (−15 °C)

Program	Battery			
	1	2	3	4
Discharge current (A)	540	540	300	300
V_{5s} (V)	9.10	9.02	8.88	8.97
V_{30s} (V)	8.78	8.77	8.79	8.89

Table 3
Effect of charge voltage and temperature on cycle life

Condition	Cycle life	Battery			
		1	2	3	4
Discharge: 15 A × 1 h	Temperature: 40 °C	6	4	7	8
Charge: 14.8 V × 2 h	(GB5008-1-91)				
I_{max}: 30 A	Temperature: 75 °C	4	3	5	7
Discharge: 15 A × 1 h	Temperature: 40 °C	9	6	8	9
Charge: 14.4 V × 2 h					
I_{max}: 15 A	Temperature: 75 °C	6	4	6	7
Discharge: 15 A × 1 h	Temperature: 40 °C	11	7	9	9
Charge: 14.0 V × 2 h					
I_{max}: 15 A	Temperature: 75 °C	9	5	7	9

Table 4
Electrical test results (GB5008.1-91, Chinese National Standard)

Battery	First starting (≥1V)	Cold cranking at −18 °C (≥1.40V)	Charge acceptance $I_{ca}/(C_e/20) \geq 2$	Reserve capacity (≥94 min)	Cycle life (≥4 units)	Water loss (≤6 g/Ah)	Actual lead weight (kg)
1	1.48	1.60	3.95	105.02	6	0.01	14.21
2	1.65	1.61	4.31	103.34	4	0.15	14.25
3	1.39	1.51	5.23	109.28	7	2.11	13.83
4	1.41	1.53	5.30	111.13	8	1.96	13.74

and temperatures, see Table 3. A low charge voltage and a low temperature improve the cycle lives of VRLA batteries. At a charge voltage of 14.00 V and a temperature of 40 °C, VRLA batteries made of lead–calcium alloy display longer cycle lives than conventional batteries. At the end of cycle life, it is found that the VRLA battery group 1 failed through electrolyte drying out and some corrosion at the negative grid/top–bar connection. The positive and negative plates were in a good condition. VRLA battery group 2 failed through electrolyte 'drying out', severe corrosion of the positive grids and some corrosion at the negative grid/top–bar connection. By contrast, conventional battery group 3 failed through short circuits from positive-paste shedding, together with positive-grid corrosion. Conventional battery group 4 failed through positive-grid corrosion.

Due to the low gas-recombination efficiency under high charge voltage and elevated temperature, water in the electrolyte is decomposed into hydrogen and oxygen. The corrosion products also require some water. Grid corrosion becomes serious when the temperature increases. Thus, water is lost in VRLA batteries by gassing and corrosion. The corrosion resistance of a super-low antimony (0.6 wt.% Sb) alloy is inferior to that of lead–calcium alloys, and this causes serious drying out of the electrolyte. VRLA batteries made from a mixed structure of super-low antimony alloy and lead–calcium alloy exhibit short cycle lives. Therefore, VRLA battery group 2 was abandoned.

4.3. Electrical testing

The four groups of batteries were tested by Digatron UBT equipment according to the Chinese National Standard: GB5008.1-91. The results are reported in Table 4. Usually, VRLA batteries display poor reserve capacity compared with conventional flooded-electrolyte batteries. This is because of their acid-starved design. The reserve capacity can be improved, however, by adding positive-paste additives, and by adopting special AGM separators which include hydrophobic organic fibres that provide sufficient pore passages for oxygen even though the separators are fully saturated with electrolyte. A high content of tin in the positive grid prevents the growth of a passivation film on the grid surface. Nevertheless, the charge-acceptance capability is not as good as that for a low-antimony alloy grid. The tin content of the negative grid is not important, it can be reduced to as low as possible, especially to save on costs (tin is a relatively expensive metal). The initial starting and cold-cranking abilities of VRLA batteries are superior to those of conventional batteries. This results from the low electrical resistance of AGM and the large plate surface area. According to electrical test results, battery group 1 is regarded as an ideal automotive VRLA battery.

5. Conclusions

The choice of design and materials is very important for automotive VRLA batteries, for example, the new grid-frame proposed here improves both high-rate discharge and active-material utilization. High tin contents in the positive-grid alloy avoid passivation films and ensure good charge-acceptance. Special AGM separators are fitted for automatic enveloping stacking. These separators absorb more electrolyte and provide sufficient oxygen passages. The container is made from polypropylene with added talcum powder. Additives to the positive paste and the electrolyte are necessary for increasing capacity and preventing short circuits.

Both automatic VRLA batteries and conventional flooded-electrolyte batteries with PE separators can be manufactured on the same automatic assembly line. This lowers production costs.

The cycle-lives of automotive VRLA batteries with lead–calcium grids are greater than those of VRLA batteries with super-low antimony (positive) and lead–calcium (negative) grids. At a charge voltage of 14.00 V and a temperature of 40 °C, automotive VRLA batteries with lead–calcium exhibit longer cycle-lives than conventional flooded–electrolyte batteries.

Because the cycle-life of automotive VRLA batteries is influenced by the charge voltage and the temperature, it is best to adjust the charge voltage to less than 14.40 V and to locate the battery outside the engine compartment.

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References

[1] J.R. Pierson and R.T. Johnson, *J. Power Sources*, *42* (1993) 237–246.
[2] W. Böhnstedt, *J. Power Sources*, *42* (1993) 211–220.
[3] D. Johnson, *Batteries Int.*, *23* (1995) 44–45.
[4] D. Calasanzio, G. Cecchinato and M. Marchetto, *J. Power Sources*, *42* (1993) 247–260.
[5] J. Wang, *Xudianchi Jixu*, *38* (1994) 27–29.
[6] K. Takahashi, H. Yasuda, H. Hasegawa, S. Horie and K. Kanetsuki, *J. Power Sources*, *53* (1995) 137–141.