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Advanced technologies in VRLA batteries for automotive applications

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Abstract

This paper discusses battery temperature limits as a challenge to be answered when using valve-regulated lead-acid (VRLA) batteries in motor vehicles, and then describes the results obtained in road tests on VRLA batteries used in an idling-stop (stop and go) vehicle.

In general, using lead-acid batteries at high-temperature increases grid corrosion and water loss, and accelerates deterioration. VRLA batteries are more susceptible to the effects of temperature than flooded batteries, but that is largely due to their structure. Water loss is fatal to VRLA batteries because water replenishment is impossible. At high temperature not only does the electrochemical decomposition of water increase considerably, but a substantial amount of water also evaporates due to the increased vapor pressure. This requires control to keep batteries from exceeding their maximum temperature. The low-temperature limit of lead-acid batteries is at least −50 to −60 °C, and that temperature is higher at a low SOC. This is dependent on change in the solidification point of the sulfuric acid electrolyte.

From an environmental perspective there are expectations that idling-stop systems will find wide use as simple systems to improve fuel economy. We studied the performance of a conventional flooded battery, a conventional VRLA battery, and an improved VRLA battery in road tests with an idling-stop vehicle, and found that the improved VRLA battery is suited to idling-stop applications because it had a smaller capacity loss than the conventional flooded battery.

Keywords: VRLA; High temperature; Low temperature; Idling stop

1. Introduction

Major changes have come to automotive systems in recent years, and it is no overstatement to call this the second industrial revolution for motor vehicles. This new wave includes the transition to hybrid vehicles, 42 V mild hybrid systems, idling-stop systems, X-by-wire systems and fuel cell vehicles. Secondary batteries are the key to all these next-generation automotive systems. For example, there are two types of batteries in hybrid vehicles, which are the only such automobiles to have been commercialized. One type is Ni–MH batteries for the power train, and the other is lead-acid batteries for auxiliaries control.

Idling-stop systems, which shut down the engine when a vehicle is stopped, are the simplest way to improve fuel efficiency. There is a growing need for these systems in Japan to cut automobile exhaust emissions and improve fuel efficiency [1]. Thus, far these systems have been developed for delivery trucks and buses to shut down their engines when parked or stopped, but recently efforts are being directed at their use in passenger cars when they are stopped for short time periods such as at traffic signals and in congested traffic. Lead-acid batteries are likely candidate because wide use will require low cost.

Lead-acid batteries offer the best cost/performance ratios of all batteries, and for that very reason they have been used to supply automobile cranking power for over a half century. Lead-acid batteries in particular have a wider operating temperature range than other batteries, and conventional flooded batteries have been used without any special temperature control under the harsh conditions of automotive applications, from below freezing to near boiling temperatures. Features of VRLA batteries are that unlike flooded batteries they do not need water replenishment, and that there are few limitations on their installation orientation. They eliminate fluid electrolyte by absorbing and retaining the sulfuric acid electrolyte with mat separators made of glass fiber unwoven cloth. Batteries can be closed because oxygen evolved from water decomposition during charging is reduced to water on negative plate surfaces. Battery elements are closed by a safety valve that keeps internal pressure below a certain level by releasing pressure when it rises, which is the reason for calling them "valve-regulated lead-acid batteries" (VRLA). One must take the effect of temperature into sufficient consideration when using VRLA batteries in automotive applications.

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Generally, they cannot be used at temperatures as high as flooded batteries can withstand due to increases in water loss and grid corrosion. Water loss especially is fatal to VRLA batteries due to the inability to replenish it. Moreover, battery temperature must be monitored during high-temperature use to prevent thermal runaway.

Because engines shut down when idling-stop vehicles are stopped, batteries must cover the entire electrical load at that time, and they must be capable of quick restoration charging. As these vehicles have more frequent battery discharges than conventional automobiles, the batteries are more often used in a partial state of charge (PSoC). Therefore, even if a battery has not deteriorated, it might not be able to restart the engine at a low state of charge. As such, batteries are expected to have plenty of endurance even under conditions in which they are apt to be undercharged.

We used an idling-stop vehicle to determine how well lead-acid batteries perform. An improved VRLA battery, which we enhanced through use in a 42 V mild hybrid vehicle also performs excellently in idling-stop applications.

2. Use of lead-acid batteries in high- and low-temperature environments

It is anticipated that VRLA batteries will find growing use in automotive applications. These batteries cannot be used at such high temperatures as flooded batteries, but they can operate at slightly lower temperatures, which is mainly because VRLA batteries have higher sulfuric acid density and less fluid electrolyte. This section will discuss VRLA battery behavior under high- and low-temperature conditions.

2.1. Lead-acid battery behavior at high temperatures

Some causes underlying lead-acid battery deterioration are positive grid corrosion, positive active material softening, and negative plate sulfation. In VRLA batteries an additional cause is dryout from water loss.

2.1.1. Relationship between temperature and water consumption

Roughly there are two reasons for water loss at high battery temperatures.

(1) *Higher gas evolution*: Fig. 1 is an example of overcharging VRLA batteries at four different temperatures. The charging current is all used for the electrolysis of water because overcharging started at a fully charged state. In VRLA batteries the current causes the reactions of these formulas, and thus no water is lost (oxygen absorption reaction). In addition, there are reactions of positive grid corrosion and hydrogen generation at negative plate, though the current can be neglected.

$$\text{Positive plates}: H_2O \rightarrow \tfrac{1}{2}O_2 + 2H^+ + 2e$$

$$\text{Negative plates}: \tfrac{1}{2}O_2 + 2H^+ + 2e \rightarrow H_2O$$

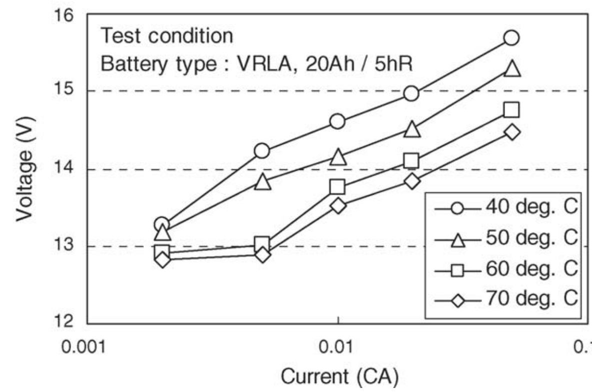

Fig. 1. Overcharge characteristics of VRLA battery at high temperatures.

The larger the current, the more gas evolves, and the oxygen absorption reaction cannot keep up, leading to the evolution of oxygen from positive plates and hydrogen from negative plates in a 1:2 ratio. The higher the temperature, the more gases these reactions produce.

$$\text{Positive plates}: H_2O \rightarrow \tfrac{1}{2}O_2 + 2H^+ + 2e$$

$$\text{Negative plates}: 2H^+ + 2e \rightarrow H_2$$

(2) *Water loss from evaporation*: The vapor pressures of water and sulfuric acid appear in Fig. 2. Vapor pressure soars when temperature rises, signifying that water is also lost by evaporation when battery temperature is high.

Fig. 3 plots water loss during high-temperature, constant-voltage charging when 40 °C has a value of 1. Oxygen and hydrogen produced by electrolysis are the main constituents in the normal temperature range. Although very little water is lost to evaporation in the low-temperature range, that proportion rises quickly when the temperature exceeds about 60 °C.

2.1.2. Cycling behavior under high-temperature conditions

Fig. 4 shows the behavior of terminal voltage, battery surface temperature, and internal pressure change in a VRLA battery during continuous high-temperature cycling. This test assumed use in HEVs and therefore had a very short cycling period.

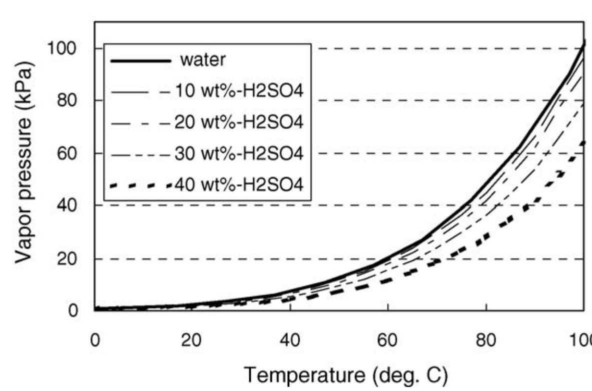

Fig. 2. Vapor pressure of sulfuric acid.

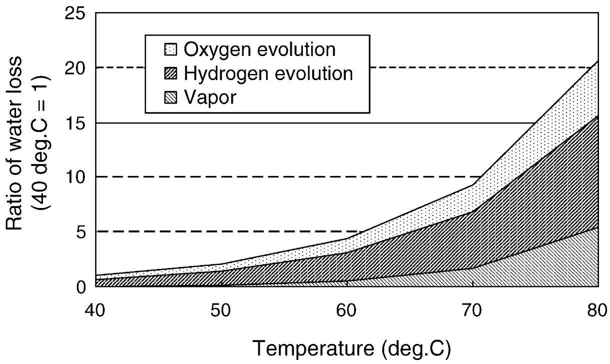

Fig. 3. Water loss of VRLA batteries at high temperatures.

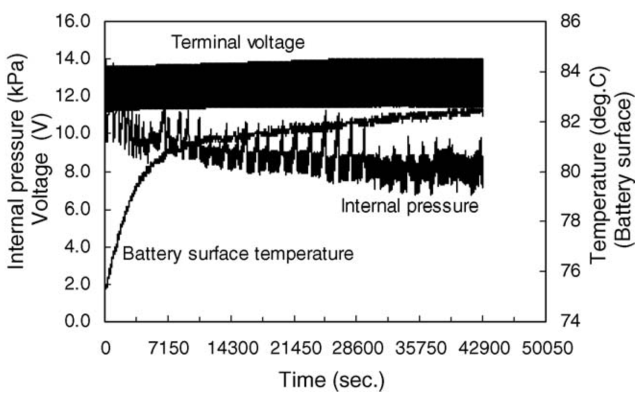

Fig. 4. Behavior of VRLA battery under continuous cycling at high temperature.

Discharge-1: 1.7 CA for 58 s.
Discharge-2: 5 CA for 4 s.
Charge: 4 CA for 30 s.
Rest: 50 s.
Ambient temperature: 75 °C.

Under these conditions, battery temperature rose to over 80 °C due to heat generation. It is evident that internal temperature changes in response to cycling. Fig. 5 shows the change occurring per cycle. Internal pressure rises when charging, and falls when resting and discharging, which indicates that gas evolves when charging, and that gas absorption occurs when resting and discharging. Apart from this, there are also large changes in internal pressure, which gradually increases as cycling proceeds, and then drops. This rise and fall is caused by safety valve operation. The rubber safety valves in VRLA batteries are designed to open when pressure rises, and close when pressure drops. Generally, they are set to open when pressure reaches about 10 kPa. When safety valves open they release the oxygen and hydrogen inside, but at high temperatures they also release water vapor, which considerably diminishes the amount of water. Battery dryout raises internal resistance and is one cause underlying shortened battery life.

Temperature control as practiced with conventional flooded batteries is inadequate for VRLA batteries, making it essential to control charging and discharging while constantly monitoring battery temperature. Battery makers feel it is desirable to keep battery temperature below 60 °C.

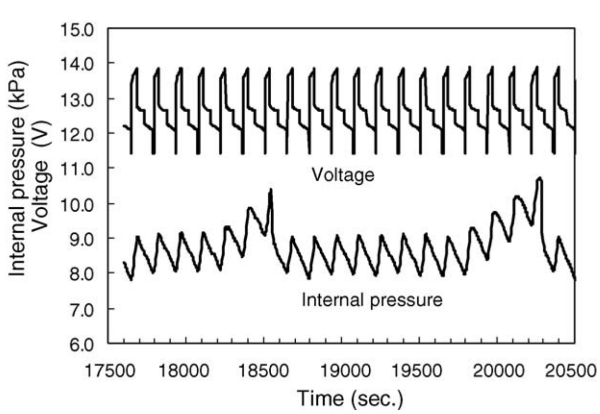

Fig. 5. Transition of terminal voltage and internal pressure of VRLA battery.

2.2. Lead-acid battery behavior at low temperatures

As the charge–discharge reaction of lead-acid batteries proceed with dissolution–precipitation mechanism, the performance declines severely at low temperatures [2]. Other causes of performance decline include decreased sulfuric acid conductance and acid solidification.

2.2.1. Characteristics of sulfuric acid

(1) *Sulfuric acid conductance*: As shown in Fig. 6, the conductance of sulfuric acid changes in response to its concentration [3]. While the concentration in lead-acid batteries in a charged state is about 40%, conductance is at about its highest value when fully charged, and at a low value in a deep-discharged state. It is also quite low at low temperatures.

(2) *Sulfuric acid solidification point*: The solidification point of sulfuric acid depends on concentration. Fig. 7 shows its solidification curve [3]. Because sulfuric acid concentration changes when cycling, the solidification point of battery electrolyte depends on the state of charge. The

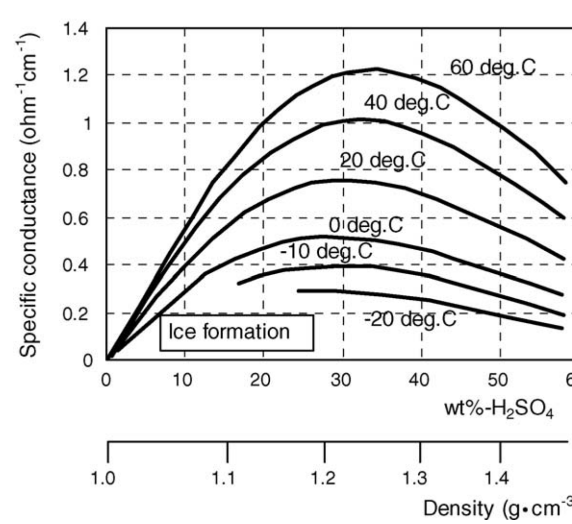

Fig. 6. Specific conductance of sulfuric acid solution.

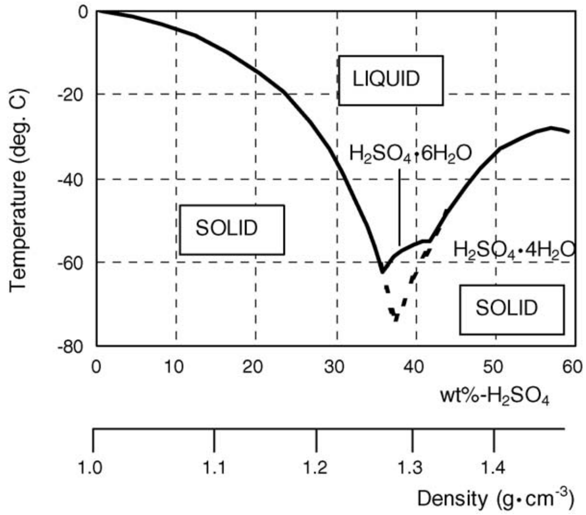

Fig. 7. Solidification curve of H_2SO_4/H_2O system.

usual sulfuric acid concentration of a lead-acid battery in a charged state has a low solidification point (−60 to −50 °C), but as the concentration decreases the solidification point quickly rises, becoming 0 °C when electrolyte is water. When a battery is discharged at low ambient temperature, ice sometimes forms inside. When that happens the electrolyte becomes a slurry with very poor conductance, thereby raising internal resistance and impeding cycling.

2.2.2. *Discharge behavior under low-temperature conditions*

Fig. 8 plots the discharge curve at −30 °C. The battery can discharge normally up to about 40% DOD, but voltage plummets once that point is passed, which indicates that sulfuric acid concentration gradually declines owing to discharging, finally attaining the point at which it solidifies.

High-rate discharging at very low temperatures could cause ice formation when sulfuric acid is diluted in positive plate pores, even when the average acid concentration is still high. Ice formation severely hinders discharging and decreases cranking voltage. Fig. 9 shows discharge characteristics at −30 °C at four states of charge, and plots the voltage at the 5th second of discharge. Voltage drops to zero at 40% SOC and 400 A discharge, thereby losing all discharge capacity.

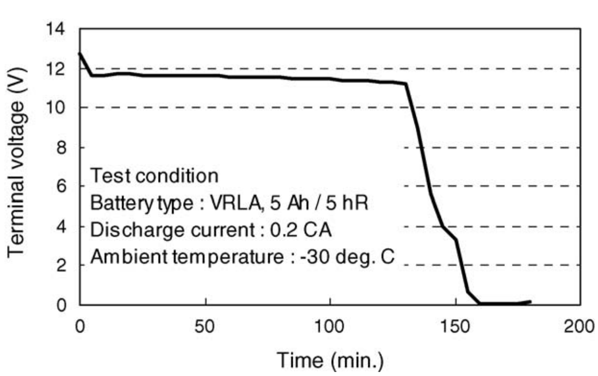

Fig. 8. Discharge *V–t* characteristics of VRLA at −30 °C.

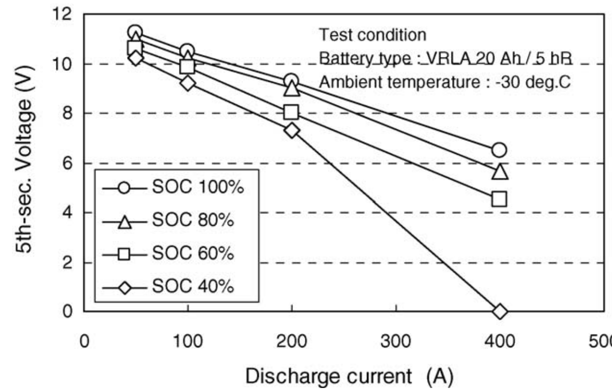

Fig. 9. Discharge *I–V* characteristics of VRLA at −30 °C.

As the lower temperature limit of lead-acid batteries depends on when solidification occurs, the limit is about −50 °C even at a high SOC, and a higher temperature when the SOC is lower.

3. Lead-acid batteries for idling-stop applications

We have conducted vehicle field tests to develop a battery suited to idling-stop systems. We used three types of lead-acid batteries: a flooded battery like those presently used for most automotive applications; a VRLA battery that does not need water replenishing, which is mainly used for backup; an improved VRLA battery. We installed these in vehicles and evaluated them under a variety of conditions. The improved VRLA type incorporated the technologies of 36 V VRLA batteries for mild hybrid applications.

3.1. *Improved VRLA battery*

Hybrid-vehicle batteries are used in a partial state of charge to efficiently accept the vehicle's regenerated power, but even under these conditions they are expected to have high-power characteristics and to be highly reliable under the conditions in which automobiles are used. The main technical elements of this improved VRLA battery are described below.

(1) *Positive plates*: To decrease the active material deterioration, we employed a paste of even greater density than that used in conventional cycling applications. Usually, the use of high-density paste decreases active material utilization, but the use of new additives improved utilization for high-current discharges [4].

(2) *Negative plates*: We used high-density active material with much added carbon to prevent sulfation occurring in PSoC use. This forms a conductive network of carbon and lead in the active material and makes it possible to suppress the formation of lead sulfate, which acts as an insulator.

Because automotive applications require tolerance to high temperatures, we optimized the negative active material additive to improve the activity of reaction sites on negative plates, thereby bettering the acceptance of regenerative charging.

3.2. Experiment

3.2.1. Relationship between alternator voltage and SOC

Idling-stop vehicles frequently discharge their batteries, which could therefore become undercharged during vehicle operation. We conducted road tests at different alternator voltages to determine the charging voltage needed for SOC maintenance and to investigate the effects of battery differences.

(1) Test vehicle: our vehicle was a modified gasoline-powered car with 1.1-L displacement and a continuously variable transmission (CVT). The idling-stop system kills the engine when speed is 0 km h^{-1}, and automatically starts it with an ordinary starter when the driver depresses the accelerator. The CVT ensures the car will not accelerate suddenly. Alternator voltage is continuously variable. Maximum battery load for engine ignition is 500 A, and the engine starts in about 0.7 s.
(2) Test batteries:
 A. conventional flooded automotive battery;
 B. conventional VRLA automotive battery;
 C. improved VRLA battery using hybrid technology:
  Capacity: 27 Ah/5 h rate (*Note*: Each battery has same capacity).
(3) Test description:
  alternator voltage settings (battery voltage): 15.0, 14.4, 13.8 and 13.2 V;
  test period: one week;
  test course: commuting road, 15 km one way.

3.2.2. SOC after two months driving

The same vehicle was used under the following conditions to study battery behavior during relatively long-term road testing.

(1) Test batteries:
  A: conventional flooded automotive battery;
  C: improved VRLA battery using hybrid technology.
(2) Test description:
  alternator voltage settings (battery voltage) (*Note*: Based on the results of Section 3.3.1, we chose voltages resulting in about the same SOC);
  battery A: 13.4 V;
  battery C: 13.2 V;
  test period: two months.

3.3. Results and discussion

3.3.1. Driving pattern example

Fig. 10 shows vehicle speed, engine revolutions, battery voltage, and battery current for one instance. When vehicle speed is 0 km h^{-1} idling-stop kicks in and the engine stops. A current is discharged from the battery and voltage gradually drops. A large current flows at the next engine ignition, and there is a charging current when the engine starts. In this instance alternator voltage was held at 13.2 V.

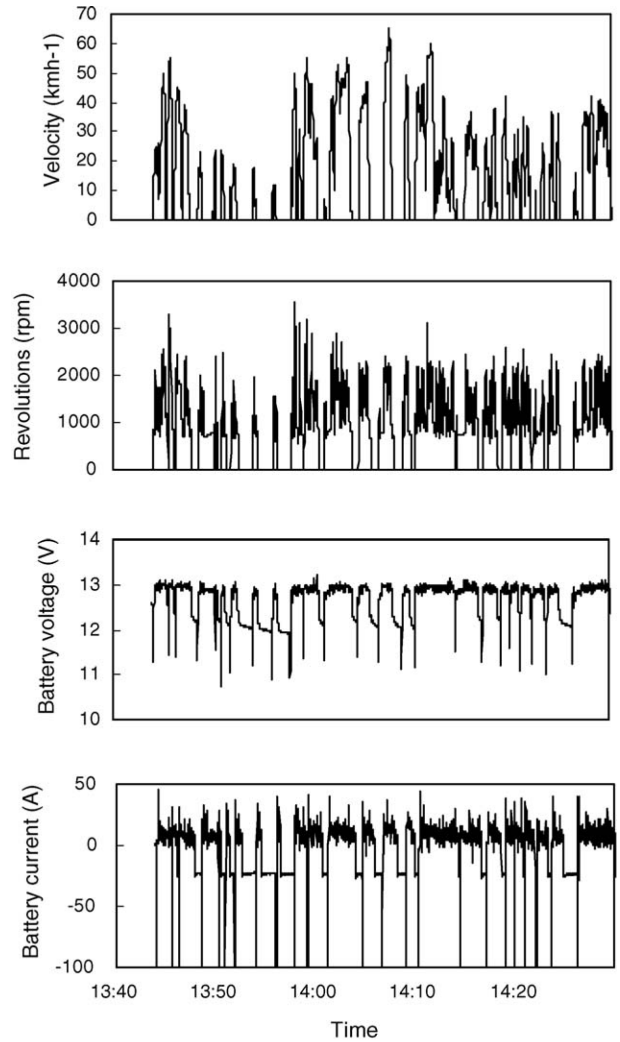

Fig. 10. Example of commuter driving data with idling stops.

Table 1 presents the analysis results of idling-stop frequency and the average discharge current. The return-trip average discharge current was 29 A, or 13 A higher than when going to the office, which was because while the blower fan was always used, headlights were used only on the return trip. Idling-stop frequency per kilometer was 1.1 events to the office and 1.5 events from the office, accounting for 29.5 and 20.5% of driving time, respectively.

Table 1
Frequency and duration time of idling stops and the average discharge current of the lead-acid battery during the full driving course

Items	From office	To office	Full-day total
Driving time (min)	67	73	140
Driving distance (km)	15	15	30
Average discharge current (A)	29	16	22
Number of idling stops (times)	22	16	38
Accumulated idling-stop duration (min)	13.7	21.5	35.2
Idling stops per kilometer (times)	1.5	1.1	1.3
Idling stops per minute (times)	0.33	0.22	0.27
Total idling-stop rate[a] (%)	20.5	29.5	25.1

[a] Accumulated idling-stop duration time/driving time.

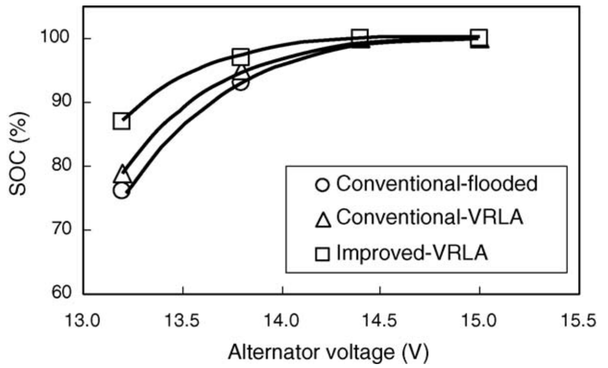

Fig. 11. Effect of alternator voltage on remaining SOC after one-week field test.

3.3.2. *Relationship between alternator voltage and SOC (after one week of driving)*

Fig. 11 plots the battery SOC measurement results after one week of road testing. All batteries more or less maintained 100% SOC at a charging voltage of at least 14.4 V, while below that voltage the SOC dropped. When setting the voltage at a very low 13.2 V the SOC was 76% in the flooded battery and 79% in the VRLA battery. By contrast, the improved VRLA battery tended to be high at 88%, showing that this improved battery's SOC declines little even at a low charging voltage.

3.3.3. *Road test results (after two months of driving)*

We conducted testing at a low voltage setting with a flooded battery and improved VRLA battery to accelerate undercharging. Voltages were chosen to yield the same SOC, with reference to the results in Fig. 11. They were 13.4 V for the flooded battery, and 13.2 V for the VRLA battery. Batteries were removed after two months of testing, tested for capacity, and disassembled for study.

(1) *Residual capacity*: We measured the capacities of both batteries after removing them from the vehicle and after a complete charge. Results appear in Fig. 12. Residual capacity was 43% in the flooded battery, while the improved VRLA battery had declined little because it was 67%. Even after a complete charge the flooded battery recovered to only 85%, but the improved VRLA battery was 102%, having recovered its total capacity.

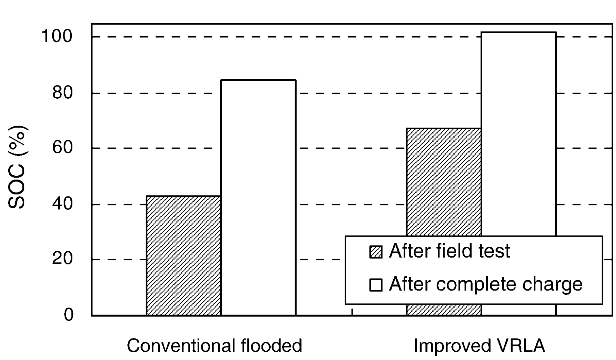

Fig. 12. Remaining SOC of conventional flooded battery and improved VRLA battery after two-month field test.

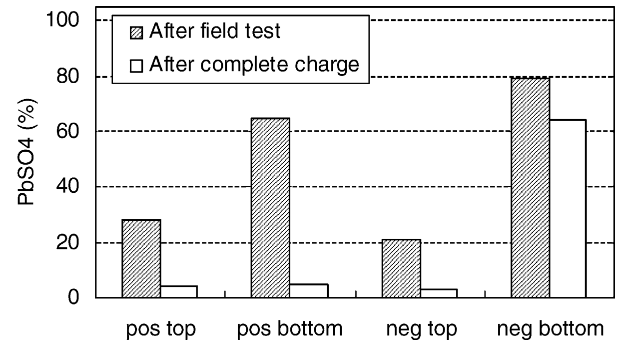

Fig. 13. Accumulated $PbSO_4$ in plates of conventional flooded battery after two-month field test and after complete charge.

(2) *Disassembly results*: We found no positive grid corrosion at all in either battery, which was probably because low-SOC use presented little opportunity for exposure to the high voltages that induce grid corrosion.

Fig. 13 graphs the results of analysis for lead sulfate in the positive and negative active material of the flooded battery. Positive active material had softened at the plate tops in this battery, which happened because continued use in a discharged state caused lead sulfate to accumulate at the bottom, thereby hindering charging and discharging reactions and causing the reactions to concentrate near the top. Complete charging almost completely eliminated the lead sulfate in the positive plates, while that at the bottom of the negative plates could not be eliminated.

Fig. 14 shows the lead sulfate analysis results for the improved VRLA battery. Although there was a lead sulfate accumulation of about 20% in both the positive and negative plates just after road testing concluded, there was no large top–bottom difference as in the flooded battery, and no positive plate softening. The lead sulfate was eliminated by charging.

3.3.4. *Discussion*

The results of this test suggest that using the following kind of management for the lead-acid batteries in idling-stop vehicles will further improve battery endurance.

(i) *Using PSoC condition*: Positive grid corrosion can be prevented by controlling overcharging.

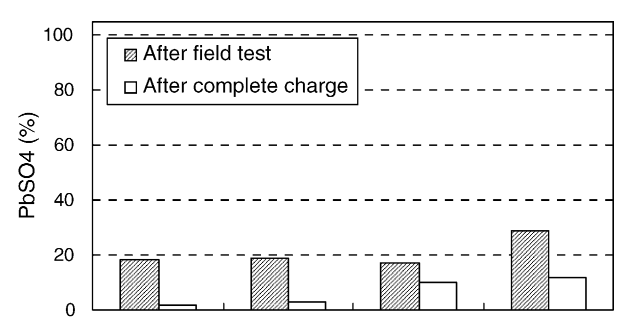

Fig. 14. Accumulated $PbSO_4$ in plates of improved VRLA battery after two-month field test and after complete charge.

(ii) *Periodically equalizing charge*: Undercharging can be limited by periodically eliminating the accumulation of lead sulfate. Adequate performance cannot be elicited from conventional flooded batteries even by these types of management. In contract, the improved VRLA battery can maintain a higher SOC than flooded batteries or conventional VRLA even at a low voltage setting, and it does not suffer active material deterioration. Moreover, accumulated lead sulfate can be eliminated by charging.

The success of idling-stop systems depends greatly on a combination of battery management and the improved VRLA battery.

4. Conclusion

This paper has described the high- and low-temperature behavior of VRLA batteries, and an example of their use in an idling-stop application.

- When using VRLA batteries at quite high temperatures, the valve will open during cycling operation and release an increased amount of water vapor along with evolved gas, which makes batteries susceptible to dryout. It is recommended that VRLA batteries be used at temperatures under 60 °C.
- The lower temperature limit depends on the solidification point of sulfuric acid. Even when the SOC is high, this limit is probably −50 °C. A lower SOC raises the lower temperature limit, and in the worst case acid will solidify in the battery during discharging.
- We tested flooded batteries, VRLA batteries, and improved VRLA batteries in idling-stop use, and found that performance improves substantially when incorporating technologies for hybrid-vehicle batteries into VRLA batteries.

References

[1] http://www.eccj.or.jp/sub_05.html.
[2] E.J. Casey, J. Power Sources 8 (1982) 83.
[3] D. Berndt, Maintenance-Free Batteries, second ed., Research Studies Press Ltd./John Wiley & Sons Inc., Taunton/New York, 1997.
[4] K. Yamanaka, et al., GS News Techn. Rep. 60 (2) (2001) 8.