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Latest developments in super high rate lead-acid batteries from India

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Abstract

The application of lead-acid batteries for automobile applications has to meet stringent specification guidelines. Design engineers are more concerned to meet the high rate discharge (HRD) performance of a battery, particularly for automobile applications. The required HRD is to be tested to the full satisfaction of the ultimate user. This paper gives a review on lead-acid batteries manufactured in India with special focus on their HRD performance.

Basically, there is a cut-off voltage (which is 7.20 V for a 12 V battery system) down to which the battery shall be able satisfactorily to deliver current to the starting mechanism of a vehicle at the low critical temperature of −18°C.

For determination of HRD performance under simulated conditions a high rate discharge tester is used to draw a constant discharge current from the battery, kept and conditioned in a cold chamber. It uses a built-in data acquisition system for logging of current and voltage values at an interval of 5 s.

Keywords: Lead-acid batteries; Testing/high-rate; Applications/automobiles

1. Introduction

India is now producing super high rate lead-acid batteries to meet global standards. These batteries are achieving the stringent International requirements of battery performance in sub-zero as well as in high ambient temperatures.

The rate of discharge of a lead-acid battery (or any other storage type) is usually expressed in terms of current flow (amperes) and the duration (hour/minute) obtained to a certain cut-off voltage. The quantity of electricity, which can be delivered during discharge of the battery at a constant current to the cut-off voltage, is the capacity of the battery.

The capacity obtained from a lead-acid battery is strongly dependent upon the rate of discharge. Increasing the rate from nominal to a high rate value results in voltage depression, shortening of the discharge time and a discharge characteristic having a slope of steeper gradient (as against that of a nominal rate). During rapid discharge, the electrochemical reactions take place mainly on the surface of the plates, because of the limited time available for adequate diffusion of acid into the pores of the active material. Moreover, the reaction product ($PbSO_4$) tends to block the pores, a process that further restricts the even percolation of acid throughout the volume of the plates and so the capacity is severely reduced at high rate discharge [1].

Tables 1 and 2 summarise the performance of a 12 V, 100 Ah battery and show that the final voltage and the available capacity is depressed at high rates.

For this reason, various International as well as Indian standards have been introduced in order to compare the performances of different batteries. Attempts have also been made throughout Europe to unify the requirements through a battery section of the International Electrotechnical Commission (IEC) using SAE and BS specifications.

Japanese Industrial Standards have drawn up specification JIS D5301 for batteries compatible for SLI (starting, lighting and ignition) applications, which is different from other International standards in some respects.

As indicated by the SAE/BSI specifications, the primary function of the SLI battery is to provide power to crank the engine during starting [2]. With the increase in the compression ratio of internal combustion engines, this duty has become more and more difficult especially at sub-zero temperature owing to the increased viscosity of the engine oil. Therefore, SAE/BSI standards declared SLI performance as the current, in amperes, delivered at a temperature around −17.8°C (0°F) for not less than 30 s to a voltage, not less than 1.2 V per cell or 7.2 V for a 12 V battery. This value is referred to as CCA (cold cranking ampere) of the battery.

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Table 1
Voltage limits at normal temperature, 25°C

Discharge rate	Final voltage (V)
20 h to 1 h	10.50
30 min to 1 min	8.00

Table 2
Capacity at normal temperature of 25°C, expressed as % of 20 h rate

Discharge rate	Capacity (Ah)	Current (A)	% Capacity
20 h	100	5.0	100
10 h	89.5	8.95	89
5 h	78	15.6	76
3 h	70	23.3	68
1 h	53	53.0	51
30 min	45.8	91.5	43
20 min	42.3	127.0	39
10 min	34.6	208.0	30
5 min	27.2	327.0	22
3 min	20.5	410.0	16
1 min	8.8	528.0	6

The corresponding IEC requirement, also at −18°C, is a minimum duration of 1 min to not less than 1.4 V per cell or 8.4 V for a 12 V battery. The current delivered under SAE condition is greater than that specified by IEC by a factor of 1.6–1.8. The German DIN specification also has the cold start test at −18°C down to a cut-off of 1 V per cell, i.e. 6 V for 12 V battery with a minimum duration of 150 s. A 30 s voltage with a minimum requirement of 9 V is also mentioned.

To cater for the lowest temperature met in USA or elsewhere, the SAE specification includes a second low temperature requirement, i.e. current in amperes delivered at −29°C (−20°F) for not less than 90 s to a voltage of 1 V per cell or 6 V for 12 V battery. The IEC adopted the duration at −29°C as 1 min and 8.4 V minimum for 12 V battery in the CCA test.

The JIS differs more. JIS D5301 specifies temperature of −15°C and currents of 150, 300 and 500 A, to a voltage of 6 V for 12 V battery for a period of 1.4–4.3 min depending upon the size of the battery. Certain minimum voltages of 7.1–8.9 V after 5 s and 7.6–8.2 V after 30 s are also mentioned, depending on the battery size.

However, in India, the ambient being quite on the high side, performance of the battery at sub-zero temperature is not a dominant factor. Indian standards (IS), therefore, concentrate on specifying the performance of an SLI battery at 27°C. The current requirement in IS is 3 times the C_{20} rate for normal type batteries and 4.5 times of C_{20} rate for heavy duty type batteries down to 1.33 V per cell. Gulf countries normally follow IS condition as the atmospheric environment is more or less similar to that in India.

The high rate discharge performance obtained from the above-mentioned specifications is determined by several factors such as:

1. Materials/components used
2. Construction/design
3. Method of production/processes
4. Maintenance and life of the battery
5. Temperature

2. Battery materials

Raw material, like lead, should be 100% pure. Impurities cause depression of over voltage and resist a full recharge after a discharge, leading to sulphation and drop in HRD performance within a short period.

For active material or paste, the oxide used should be tetragonal in character. Above 1% ortho-rhombic oxide leads to scaling during formation that hinders HRD performance to some extent.

Various types of separators have been developed for various International and Indian battery types.

The resistance values in Table 3 show that the batteries with microporous thin polyethylene type and also LEWK glass mat type separators give better performance in comparison with PVC to obtain a good high initial voltage (IV), i.e. at 5 or 30 s on HRD.

3. Battery construction

3.1. Grids

In a lead-acid battery, the grid is not only for holding the active material, it also acts as a good conductor of current. Traditional rectilinear grid structures with a lug at one corner perform the structural function well, but are not so efficient from the conductivity point of view. Ohmic losses in the current collecting grid are inversely related to HRD performances. In terms of % utilisation in current conduction, different types of grid are described in Table 4.

From above discussion, it is evident that a radial grid with the lug at the centre is the best design so far as HRD performance character is concerned.

3.2. Plate pitch

The batteries required for engine cranking are designed with minimum plate pitch. Low internal resistance depends on the number of plates per element. Plates of the same

Table 3
Types of separator

Type of separator	Resistance of surface area ($\Omega\ cm^{-2}$)
Sintered poly vinyl chloride (PVC) sheet	0.32
Poly ethylene (PE) envelope	0.075
Bonded glass mat (LEWK)	0.09

Table 4
Relative merits of various grid designs

Type of grid	Utilisation
Rectilinear grid with lug on one corner	10% of grid area
Radial grid with lug on one corner	19% of grid area
Radial grid with lug at centre	34% of grid area

polarity in a group are in parallel and act as a parallel resistance. Higher the number of plates, greater will be the deliverable current from a given contact volume of electrolyte and smaller will be the internal resistance. Thus, larger numbers of thin plates per element in a given volume increases the surface area and delivers more current from a battery, thereby showing better HRD performance.

3.3. Electrolyte

At the time of discharge, positive and negative plates, as per the double sulphate theory, consume equal amounts of H_2SO_4. During discharge, sulphate ions migrate towards the negative and hydrogen ions towards positive. A good part of these hydrogen ions reacts to form H_2O at positive electrode. So, near the positive plate, there is always a dilution caused by this water. Thus, the volume of acid required is 1.6 times higher in positive plates than in negative plates for complete reaction.

Therefore, separator design is such that near to the positive plate more space is given for quick discharge, such that vigorous gassing and formation of water can easily take place in this excess space.

3.4. Group bars

Group bar thickness has also to be designed properly for optimum high current discharge.

3.5. Assembly design

In some cases, reverse ratio assembly design is made so that end plate is positive instead of negative to improve the initial voltage during high rate discharge.

4. Manufacturing processes

4.1. Grid alloys

High antimony (Sb) increases electrical resistances and lowers CCA/HRD performance. Lowering of Sb to 1.6% improves the CCA value to a large extent.

Superiority of Pb–Ca alloy over Pb–Sb alloy is due to low electrical resistivity, being very close to that of pure lead. As a result, CCA is maximum for this alloy. Ca alloy has also other advantages including maintenance-free characteristics. Presence of Sn above 0.1% increases conductivity and reduces oxidation loss.

4.2. Grid quality

No breaks in radial/vertical wires are allowed. No weakness in lug or frame is acceptable. These factors reduce conductivity.

4.3. Paste

High paste density (above 4.2 g ml^{-1}) in the positive plate causes degradation of HRD performance. Paste densities in the order of 3.8–4.0 g ml^{-1} for positive plates improve plate porosity and decreases internal resistance (IR) and thereby helps HRD performance.

Carbon black used in negative plates increases conductivity to some extent and improves cold performances.

Vanisperse is the lignin sulphonate used in negative plates for improving cold performance. It contains 50% humic acid, has ion exchange properties and retains hydrogen ions around negative plates. Some conducting fibres that adhere to pastes are used today for better HRD performances.

Residual Pb below 3% is ideal, so that formation will be satisfactory and internal resistance will be less.

4.4. Terminal posts

The quality of terminal building is advancing day by day, to avoid any incipient cracks or shrinkage or holes that lead to failure during HRD. A cold forging system has been applied to terminal post building, resulting in significant improvement in strength of terminals and their current carrying capacity and longer life.

BCI type terminals, however, ensure firm contact with connecting bolts. They reduce heating and voltage drop at the connection/contact surface.

4.5. Miscellaneous factors

Apart from other factors, it should be mentioned here that the processes of pasting and formation of plates are affected by high temperature. So, a temperature controlled method for chilling improves the process for production of good plates, particularly in India where the environmental temperature is high.

Drying of positive plates should not be above 80–90°C so that the positive plate will not be passivated and give poor HRD performance.

For SLI systems with more and more usage, the life and HRD performance decreases and to maintain longer life and better performance, the following points must be avoided:

1. Overcharging
2. Undercharging
3. High ambient temperature
4. Keeping idle for a long period
5. Addition of concentrated acid when topping-up

6. Abuse, allowing impurities inside the battery
7. Hammering on terminals

5. Model analysis

The generic representation of a battery circuit is shown in Fig. 1. The metallic internal resistance which includes the terminal posts, straps, grids and grid-paste is R_m, R_e the resistance of the electrochemical path, comprising electrolyte and separator and depends on acid concentration, separator resistance, presence of impurities and temperature, C_P the capacitance of the parallel plates. This is shunted by a non-linear resistance contributed by the contact resistance of plate and electrolyte (R_I).

Overcharge current results in water loss which reduces electrolyte volume and increases electrolyte concentration. Higher concentrations, due to volume loss or addition of acid from outside, leads to rapid sulphation of negative plates. Undercharging leading to sulphation of plates and may cause similar situations. Overheating, improper topping up and overcharging may lead to plate corrosion. Loss of active material in contact with electrolyte increases the value of R_I.

Hammering, or hammering after wrong fixing of terminal cables (negative clip to positive and vice versa) may create fine cracks leading to an increase of the R_m value.

At sub-zero temperatures, the viscosity of electrolyte increases and diffusion of electrolyte in plates become more difficult. In other words, R_e and R_I are increased. The viscosity has found to increase 2-fold from $+30^\circ$C to 0°C and about 8 times at -30°C. The internal resistance of H_2SO_4 (R_e) increases 3.5–3.8 times at -18°C and 2.8–3 times at -15°C depending upon the acid concentration.

However, the value of C_P which is responsible for good HRD, is perfectly maintained by selecting a correct alternator voltage to keep the battery always in a completely charged condition at the respective ambient. So, the HRD performance for starting a car will always then be satisfactory irrespective of a cold atmosphere.

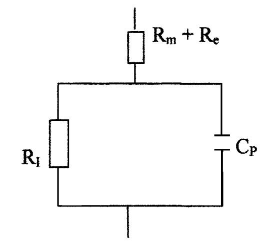

Fig. 1. The battery circuit.

6. Conclusion

In India, a wide portfolio of automotive and industrial batteries are manufactured to cope up with various requirements and different geographical characteristics. As such, batteries are designed for high temperature zones like SE Asia, Sri Lanka, etc. and also very low ambient zones found in parts of Europe, USA and the Scandinavian countries. Quality and technical up-grading are the focus areas to survive the globalisation of economy. New paradigm is, therefore, is the motto of the battery manufacturers of India.

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