INSIDE THE LEAD ACID CELL

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With the ever increasing use of stand-by power and consequently lead acid storage cells, the need for a clearer understanding of this device and it's components is necessary. No one battery is universal. Therefore, a basic knowledge of cell constructions and their corresponding performances are required. With this, one can then appreciate the manner in which batteries respond when exposed to various charge and discharge parameters. This paper will deal with the design and application characteristics one should be aware of when called upon to make a choice of today's available products.

A brief look back shows that in response to research conducted during the years 1859 to 1879 by Gaston Plante, considered to be the father of the lead acid cell, a wealth of ingenuity and imagination was illustrated by a rapid growth of design and application variations of early products thru the turn of the century. Since that time, the improvements have been essentially refinements of these basic designs using more modern materials and techniques.

However, even yet there is no ideal battery. The ideal battery, were it available, would exhibit infinite energy, handle all power levels, operate over a full range of temperatures, have an infinite shelf life and be consumer proof. Since this is not the case, we must approach this device with its many factors in mind.

In the design of a lead acid cell, the function of the various components must be considered in relation to the actual requirements of each application. It is worth noting that any design is a compromise. Each function has been considered in terms of its importance in the particular application. Thus, there will be different optimized designs depending on the use into which the cell will ultimately be placed. Cells that are designed for example for optimum capacity at relatively low or moderate discharge loads contain maximum quantities of active material. On the other extreme, cells capable of high-rate, large current delivery performance, are designed with reaction surfaces and other features to minimize internal resistance. The later is done often at the expense of total capacity. It will be found that cells designed for high-rate service will exhibit a more constant performance, ie: current output, to those of the greater capacity category.

The typical lead acid battery is comprised of three basic elements. The positive plate, the negative plate and the electrolyte. There are, of course other nonreactive components such as the separators, connecting straps and case. We will only consider the active components and there interrelated effects.

PLATES AND GRIDS

The plates should be considered as a compound element in that they are a combination of two items. First, a grid is formed in one of several methods. The most popular, for a vertical plate design, being a casting process where the lead is poured into a mold to form the basic structural component. The second most popular process employed today is a wrought technique where a solid lead sheet is drawn through an expander which places slots in the sheet and then stretches these slots into openings much like the common expanded mesh sheets available from most hardware suppliers. This system reduces the cost of manufacture as there is less energy required to process a continuous sheet of lead as opposed to that of maintaining supplies of molten lead for the casting operations. The advantage of individual casting is that in process changes can be made in the lead mixture at any time where as in the wrought process the entire lead supply must be reworked. The claimed advantage of lower gassing rates in the wrought process, due to a more consistent and finer grain structure in the lead, will most likely not be a factor of concern in CATV applications as this reduced gassing is such a low value of change that other factors in the electrochemistry and particularly the application will serve to overshadow these gains.

After the grid is prepared, a mixture of highly reactive sponge lead for the negative electrode, (anode) or lead dioxide for the positive electrode, (cathode) is mixed with sulfuric acid to form a paste. Included in this mixture are sufficient expander materials to achieve and maintain a high level of porousity. This is necessary so as to achieve an optimum ion conductivity in and out of the plate active material. The paste is then spread onto the grid which will provide the necessary support structure and electrical conductivity.

There are, however, several points regarding the lead which should be addressed here. If pure lead were attempted to be used for the grid structure, which by far is the most desirable, it would not exhibit enough rigidity to withstand handling during manufacture, not to mention the actual in service requirements. This then dictates that an alloy be introduced into the pure lead to add strenght. Historically an antimonial alloy was used as this strength adding agent. The presence of this compound though, exhibited two major down side effects. The first to be discussed is that of excessive gas production.

The gassing is a direct result of electrolysis depletion of the water at the end of charge. This electrolysis produces hydrogen at the negative plate and oxygen at the positive plate. The main contributor to this activity is the presence of this antimony alloy. In the past, low cost vertical plate design batteries were routinely maintained therefore frequent watering intervals were not of great concern. It is interesting to note that the production of oxygen starts as soon as the recharge cycle is commenced and continues through full charge. The evolution of hydrogen at the negative plate does not start until it has reached 90 to 95% recharge. An interesting point is that the negative plate accomplishes it's recharge must faster than the positive. This is why the "End of Charge Rate" must be closely controlled to achieve total recharge of the positive plate without excessive over charge of the negative which would result in excessive hydrogen evolution.

In the mid 1970s, the maintenance-free lead acid battery became popular. This design featured a grid alloy that basically was a nonreactive component. The antimonial alloy, being a reactive component, and as stated before, elevated the gassing rate and contributed to plate corrosion which also results in increased water depletion as the cell ages. By using a nonreactive strengthening agent, a more nearly pure lead grid could be achieved. This resulted in a dramatically reduced end of charge gassing rate. This marked the introduction of the Lead-Calcium battery. The inclusion of calcium resulted in a reduction of the antimony to generally no more than 2%. A maximum strength yield is achieved with about .11% calcium content.

The inclusion of calcium brought on it's own set of problems mainly related to the manufacturing process. It seems that while maintaining the lead in the molten stage rapid loss of calcium through oxidation would result. Many attempts to control this were tried. Floating lids of various types were tried by placing them on the surface of the molten lead. One attempt of a floating layer of dross was even attempted. None of these were successful. It was then found that by adding Aluminum to the mixture that this condition could be controlled effectively. Along with the inclusion of AU it has been found that by utilizing nucleating agents such as copper and selenium a very uniform and fine grain structure results. This allows for a superior active material to grid adhesion there by reducing loss of the active material through sheadding. This also reduces the ill effects of corrosion as the corrosion tends to be more uniform on the grid wires rather than forming pits and fractures as a result of inconsistency in the lead crystallization.

The second ill effect of using antimony for grid alloy is a high self discharge rate. The self discharge rate (loss of battery capacity on storage) is dependent on a number of factors, including the type of lead alloy used, the concentration of electrolyte, the age of the battery and storage temperature. The greatest contributor to this activity however is the antimony lead alloy. Self discharge is caused by local reaction of the plate materials and occurs almost entirely in the positive electrode. The rate of self discharge is about 15% per month for antimonial-lead batteries at 25'C. Batteries using lead-calcium grids have substantially lower rates of self discharge. A reduction in this activity by 50% or more is not unrealistic. For best practice, a battery on stand should be recharged every 3 to 6 months, since prolonged storage can cause irreversible damage and make recharging difficult, owing to sulfation of the plates. (Fig-1)

Stationary batteries utilize a thick plate design that reflects the lack of need for high energy and power as in the case of starting, lights, and ignition (SLI) types. The typical overcharge operation of stationary batteries requires a large electrolyte volume and non-antimonial grids, all to maximize intervals between waterings. This over or constant recharging, by any of the various on-off, dual-rate or closed loop methods used today, causes some positive grid corrosion. This is manifested a "growth" or expansion of the grid structure and must be allowed for during the design of the cell so as to provide room for this normal expansion to take place during the useful life of the battery. Excessive overcharging can accelerate this activity to a point where, if allowed to continue over time, it may cause case rupture to occur. The normal tolerated growth is calculated to be about 10% over the life of the cell. (Figure 2)

ELECTROLYTE AND SPECIFIC GRAVITY

The selection of a specific gravity used for the electrolyte depends on the application and service requirements. The concentration must be high enough for good ionic conductivity and to fulfill electrochemical requirements, but not so high as to cause separator deterioration or corrosion of other parts of the cell which would shorten life and increase self discharge. In some cases where a battery is required to operate in high ambient temperatures, the electrolyte concentration may be deliberately reduced to off set the effects of temperature elevated chemical activity resulting in accelerated plate corrosion and lowered overvoltage gassing potential. The concentration for most lead acid batteries to be used in temperate climates is usually between 1.26 - 1.28 sp.gr. Higher concentrations tend to attack the separators and other components. Lower concentrations tend to be insufficiently conductive in a partially charged cell and freeze at low temperatures. In standby and or stationary cells with larger proportional electrolyte volumes and no high rate demands, concentrations as low as 1.12 sp.gr. are used.

It is important to maintain not only the correct sp.gr. at full charge per the manufacturers specifications, but also, especially in the case of calcium alloyed grids, not to contaminate the acid solution. A preventative measure, from the manufacturers standpoint for automobile batteries, has been to permanently attach the vent caps. This is done understanding that under normal conditions the electrolysis of the water will be at a rate far lower than the overall aging of the cell. Therefore, cell failure due to other factors will occur prior to damage caused by water loss. If the electrolyte is allowed to become contaminated , as in the case of replenishment with other than distilled water, an increase of the gassing rate will result. This obviously will increase watering intervals and if at these times the same practice of using non-distilled water is employed, the gassing rate will again be increased. This practice , if allowed to continue, will most likely result in premature failure of the cell as it is highly unlikely that the watering schedules will be adjusted to compensate for this increased loss.

VOLTAGE AND SPECIFIC GRAVITY

The nominal voltage of the lead acid cell is 2 V. The open circuit potential is a direct function of the sp.gr. ranging from 2.12 V for a cell with a sp.gr. of 1.28 to a potential of 2.05 V at 1.21 sp.gr. Figs. (C,D & E) present typical discharge curves for the lead acid cell. The end voltage is typically 1.75 V but can be as low as 1.0 V at extremely high rates such as in automotive starting service. The 1.75 V point is the standard cut-off voltage which manufacturers design too. During discharge the sp.gr. decreases about 0.125 to 0.150 points from a fully charged to a fully discharged condition. The change is proportional to the ampere-hours discharged. The sp.gr. is thus an excellent means for checking the state of charge of the battery.

A short period should be allowed prior to measurement after completion of the discharge for equalization of the concentration throughout the cell. On charge, the change in sp.gr. should similarly be proportional to the ampere-hours accepted by the cell. There will be a lag in the sp.gr. change if the cell incorporates a high concentration electrolyte as complete mixing of the concentration will not occur until overvoltage gassing occurs and is sustained at the end of charge.

The variation of the performance of the lead acid cell at different temperatures and loads is given in Figures 6 and 7. Although the battery will operate over a wide range of temperatures, continuous operation at high temperatures may reduce cycle life as a result of the aforementioned increased rate of chemical activity and subsequent corrosion.

It should be understood that in applications where the battery will be housed outside, subject to very low temperatures for long periods of time (dissipating the internal heat needed for full capacity delivery), some form of warming provision should be considered. If long-term storage is going to take place, an area should be chosen that will provide a low mean temperature but will not fall below freezing as this could damage a flooded free electrolyte battery which is only partially charged.

PHOSPHORIC ACID EFFECTS

The utilization of phosphoric acid as an electrolyte additive has been patented as far back as 1929 for the claimed purposes of strenghtening of the positive active material and preventing harmful sulfation during long discharged stand conditions. In the case of cell designs using tubular positive plates, a reduction in active material shedding and in the rate of positive grid corrosion have been claimed.

It has been demonstrated that cycle life of lead acid batteries using plates with lead-calcium grids is increased when the electrolyte contains small amounts of phosphoric acid, at the cost of some reduction in the positive plate capacity, of the order of 5 to 10%. The mechanism by which phosphoric acid increases cycle life is one of modification of the pattern of the lead sulfate as it forms on the plate active material surface. The result is a more conductive interface, with less of a sulfate barrier and less interference with the discharge process.

There are also chemical and or electrochemical reactions which occur between the phosphoric acid and the positive plate active material, with phosphoric acid incorporation during charge and release during discharge. However, the formation of lead phosphate compounds in the positive plate during charge is the likely candidate for responsibility of the observed reduction in capacity in such cases. Other effects due to the presence of phosphoric acid in the electrolyte solution are lead "Mossing" and dendrite formation, both of which are factors which tend to reduce capacity.

DISCHARGE LOADS

A battery can be discharged under different modes depending on the equipment load. Three typical modes are constant resistance (the equipment resistance remains constant during discharge), constant current, and constant power (the current load on the battery increases as the voltage drops to maintain a constant power,I x V). Assuming that the discharge current is the same at the start of the discharge, the current will be different during the discharge under different discharge modes as shown in Fig.(G-a). The constant resistance curve reflects the drop in the battery voltage. Fig.(G-b) shows the voltage vs. time discharge curves for the three modes. Under the conditions shown, the service time is longest in the constant resistance mode.

Fig.(G-c) and (G-d) show the same relationships assuming the same average current during the discharge. Under these conditions, the service time is about the same, but the voltage regulation for the constant resistance mode is best. The constant power mode has the advantage, however, of providing the most uniform equipment performance throughout the life of the battery and, hence, makes most effective use of the battery's energy. It is worth noting at this point that standby equipment powering line equipment will regard this load as a more nearly constant power load. In the case of a pulsed discharge load, these conditions will exhibit the recovery effects that occur when the cell is left open circuit for a period of time after discharge. This sawtooth type of response will, in some cases, lead one to thinking that a battery has sufficient charge to operate when in fact it has reached cutoff under load but has had time to recover above the specified exhaustion voltage. See Fig.(8)

BATTERY CHARGING

Proper recharging is important to obtain optimum life from any lead acid battery under any condition of use. Some rules for proper charging are given here and apply to all types of lead acid batteries. The charge current at the START of the recharge can be of ANY value that does NOT produce an average cell voltage in the battery string greater than the gassing voltage which is typically 2.39 V/cell. During the recharge and until 100% of the previous discharge has been returned, the current should be controlled to maintain a voltage lower than the gassing voltage. If one wishes to minimize charge time, this voltage should be just below the gassing point which is directly related to the sp.gr. and cell electrolyte temperature. When 100% recharge is accomplished, the charge rate will have to decay to the "Finish" rate. This rate is described as a constant current no higher than 5A per 100 ampere hour of the rated capacity at the 5 hour rate. As a result of testing done at temperatures of 80' on new cells, a finish rate for batteries available to the cable television industry of no more than 100ma float current will overcome the effects of self discharge and keeps the end-of-charge gassing to a tolerable limit.

Some of the more popular methods to achieve recharge are listed here.

1. Constant current
2. Constant potential, modified constant potential
3. Taper
4. Pulse
5. Trickle
6. Float

1) CONSTANT CURRENT

Constant current recharging at one or more rates is not widely used for lead acid batteries. This is because of the need for current adjustment unless the charging current is kept at a low level throughout the charge cycle. This would, however, result in an extremely long recharge time.

2) CONSTANT POTENTIAL, MODIFIED CONSTANT POTENTIAL

In normal industrial applications, the modified constant potential is employed. In this case the charging circuit has a current limit, and this value is maintained constant until a predetermined voltage is reached. Then the voltage is maintained constant until the battery is called upon to discharge. It has been found that more than 50mv positive negative over potential is necessary to prevent self discharge. So that .005a float current per 100 ampere hour of capacity is required for lead calcium batteries. Lead antimony cells require at least .06a per 100 ampere hour, but this increases to about .6a per 100 ampere hour as the battery ages. This higher current also increases the water electrolysis depletion rate. This can be attributed to plate grid corrosion and accelerated sulfation. Decisions must be made regarding the current limit and the constant voltage value in accordance with the manufactures specifications.

3) TAPER

The taper charging is a variation of the modified constant potential method using less sophisticated controls to reduce equipment costs. The initial rate is limited, but the taper is such that, if special precautions are not taken, the 2.39 V/cell at 25§C may be exceeded prior to the 100% return of charge. This method could result in gassing at the critical point of recharge. The degree of gassing is a variable depending upon the charger design. Battery life can be degraded from excessive gassing. the gassing voltage decreases with increasing "Electrolyte", not ambient, temperature. A correction factor for the actual temperature of the electrolyte should be employed. The end of charge is often controlled by a fixed voltage rather than a fixed current. therefore, when a new battery, which has a high counter EMF is used, this battery often does not receive sufficient charge. Conversely, an older battery who's CEMF is low, will now receive a higher than normal finishing rate resulting in excessive gassing.

4) PULSE

A pulse system periodically disconnects the batteries from the charge circuit and performs a high impedance, no load, voltage check. If the open circuit voltage is above a preset value, depending on the reference "Electrolyte" temperature, the charger is not called upon. When the open circuit voltage decays below that limit, the charger delivers a dc pulse for a fixed period of time. The duration of the open circuit and charge pulses are chosen so that when the battery is fully charged the time for the open circuit voltage to decay is exactly the same as the charge pulse duration. When the charger senses this condition, it is automatically switched over to the finish rate current and short charging pulses are delivered.

5) TRICKLE

This is a constant current simplistic system which delivers a very low current to the battery and is used mainly to overcome the effects of self discharge. There are no provisions for any compensation techniques.

6) FLOAT

This is a system used to deliver a low rate, constant potential charge. In it's purest form it will be found in applications where stationary batteries are used in constant temperature environments.

CONCLUSIONS

As can be seen from the information given here, wise application of the proper battery for a specific need is of most importance. The cable television industry has basically three cell configurations to choose from. The traditional flooded lead acid battery, the gelled flooded battery and now the SLA configuration. Of the three mentioned, list price comparisons will show that the traditional flooded type has the lowest cost, with the gelled and SLA being competitive with each other. The obvious disadvantage of the flooded type is the need for water replenishment and the overhead cost there of. The gelled types can be thought of as a can't maintenance cells as replenishment of dissipated moisture is impossible. They do have however very low gassing rates so as to provide an improved life performance before replacement is required. The SLA technology, as applied to catv uses, would seem to indicate the best of all available performance characteristics. It can be spoken of as the only true no maintenance product. It's inability to vent the internal gases obviously will prevent it from dissipating the electrolyte moisture. Improved internal resistance characteristics provide for greater capacities at lower temperatures as well as more desirable recharge results. Another interesting feature is in the case of freezing of the cell. This type of treatment will not effect the cell adversely as in the case of flooded types. The only result will be that the cell will not operate until the internal temperature has been raised above the electrolyte freezing point allowing ion activity to resume.

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Martin de Alminana is head of Lectro's Field Eng. Dept. He is known for his very thorough and informative lectures and seminars on the many aspects of stand-by power.

He comes to Lectro with background in computer based automated test systems for the aviation industry, system design and application of rf communication equipment and having served as an instructor on military microwave communication installations.

Figure 1: Capacity/power loss during storage at 25°C

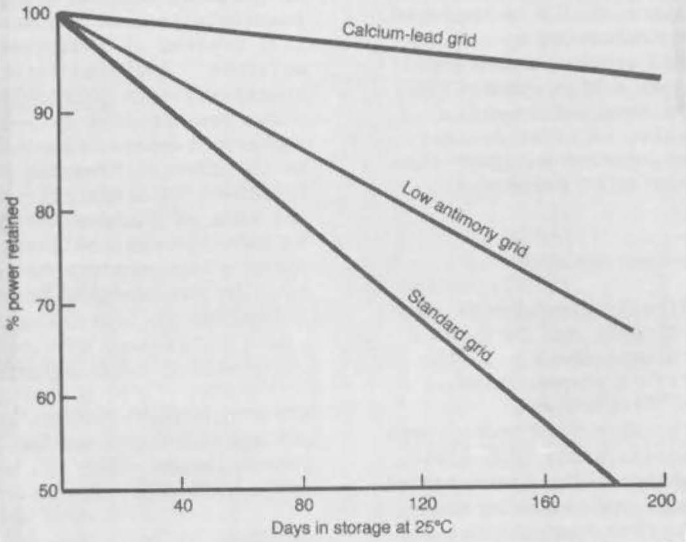
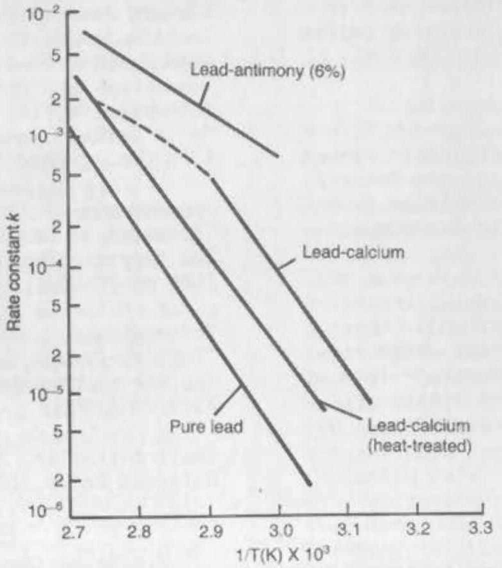


Figure 2: Plate corrosion rate chart



Corrosion rate constant *k* on log scale vs, 1/t (*K*) for different lead-alloy grids.

Figure 3: Self-discharge

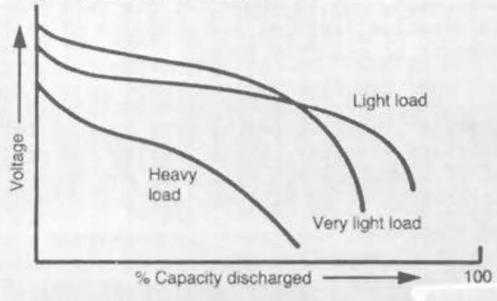


Figure 4: Discharge curves at hourly intervals

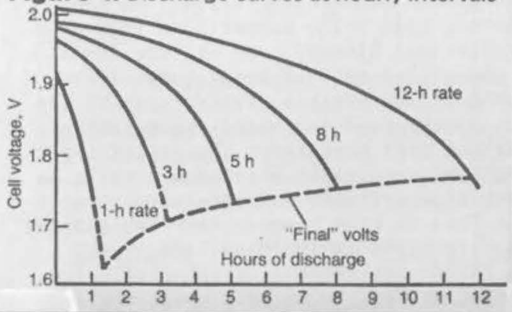


Figure 5: Discharge/charge characteristics

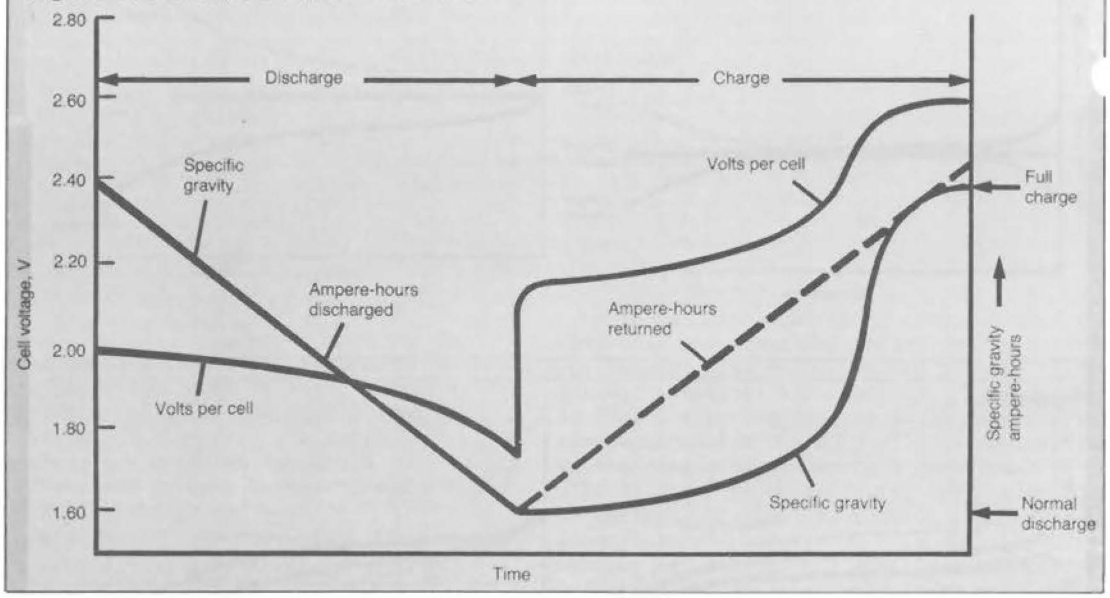


Figure 6: Temperature effects on electrolyte

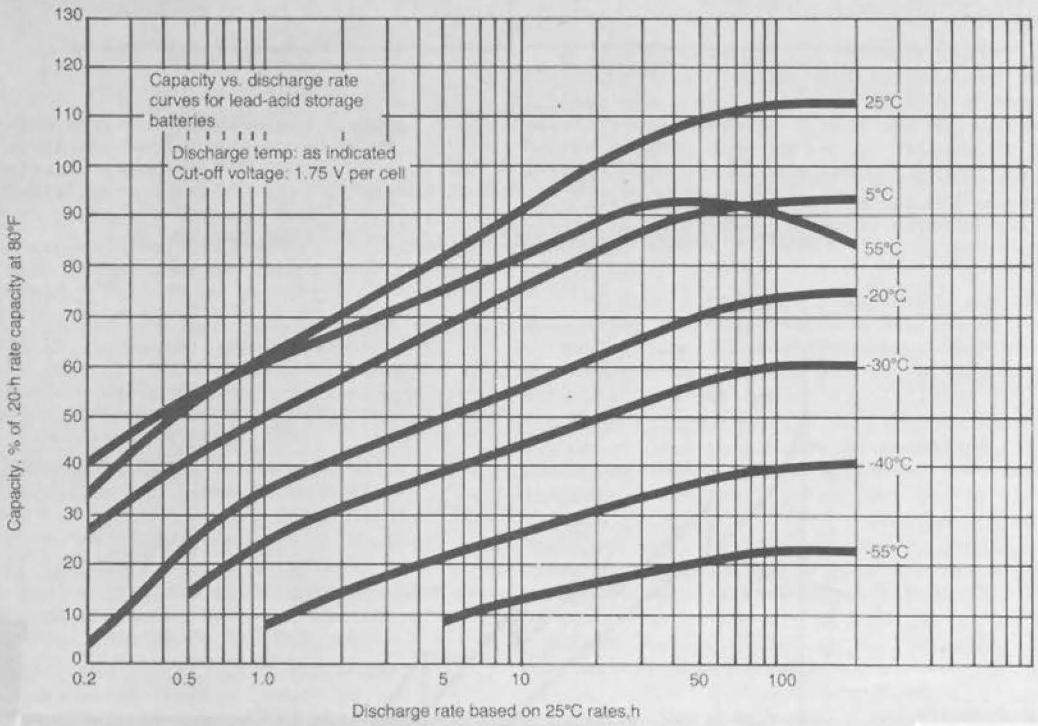
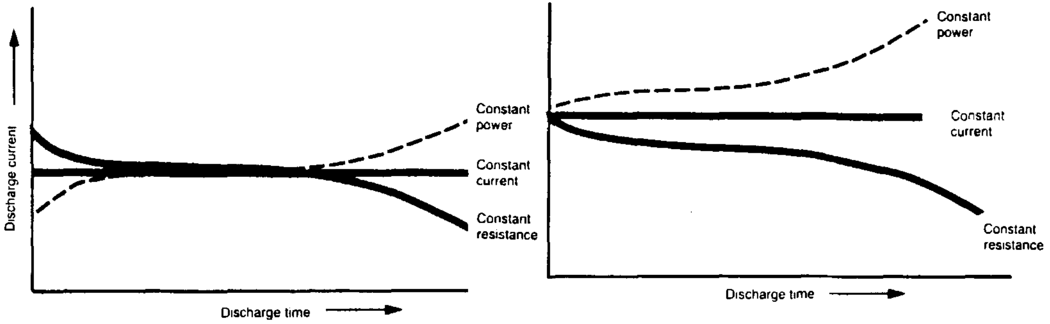
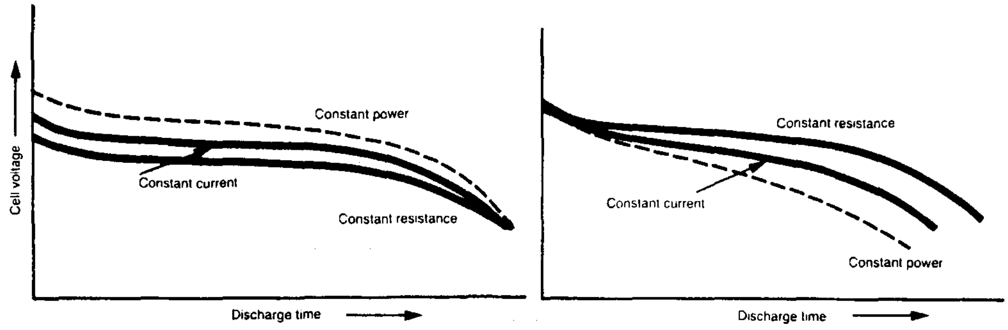


Figure 7



(c) (a)

Figure 7



(d) (b)

Figure 8: Effects of intermittent discharge on battery capacity