An investigation on the suitable battery system for marine applications

Dr. S. Sathiakumar

School of Electrical and Information Engineering
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Executive Summary

Due to extreme weather conditions during the *1998 Sydney Hobart Yacht Race* (SHYR), the electrical systems failed in a number of yachts that were flooded due to rolling, flipping or capsizing. The survey from the crew indicates that in some cases the engine could not be started again due to insufficient cranking power from the batteries that were used. The communication equipment could not work properly and in some cases there was a complete block out. It has also been reported in different occasion that the acid in the batteries used has drained out when the yacht remain inverted for a length of time and in some cases causing toxic fumes to permeate through the cabin.

In order to investigate the matter an inspection of a typical yacht was done and it has lead to an understanding that the most popular battery system used in yachts is of lead acid type. This type of flooded (or wet) battery system causes safety concerns in the tough marine environment. During its operation, this type of battery emits hydrogen and oxygen gases while charging and they could cause explosion when the conditions are favourable. Some types of lead-acid batteries can also release small quantities of toxic gases; stibine and arsine, which are extremely dangerous and can cause serious illness.

A study has been undertaken on different battery technologies in order to find a suitable battery system for marine application that will meet the following requirements.

The battery system used should

- have both starting (cranking) capability as well as sufficient reserve capacity to power the electronic equipment continuously.
- be able to operate in any position without the risk of leaking or spilling.
- be able to operate in extreme weather conditions.

- be vibration proof.
- provide safe environment during its operation.

Considering different prevailing battery technologies, it is concluded that the conventional flooded type lead-acid batteries are not suitable for marine applications. They rise many safety concerns and do not meet most of the requirements listed above. The recent advancement in battery technology for marine application gives other choices to consider.

- For small yachts designed with one battery a 'dual marine battery' using the *gel technology* is the right choice.
- Yachts designed with two batteries are very common and in such vehicles at least one of the batteries should be of *gel type* for reliability and safety. The second battery could be of sealed maintenance free type.
- It is a good practice to separate the starting battery circuit and other deep cycle battery using *diode isolator*, which will connect both in the charging circuit when the engine is running.
- The safety and reliability of the electrical system can be ensured only when the system is wired with the right cables and connectors. Marine grade cables and connectors have better resistance to corrosion and provide proper electrical connections in this applications.
- Periodic inspection and certification of the electrical system, by qualified personnel is essential to ensure the safety and reliability of the system.

Introduction

A battery is an electrochemical device that stores energy in chemical form. When connected to an electric circuit, chemical energy is transformed in to electrical energy. Since its discovery in the 19th century, the battery has gone through different stages of development to suit different applications. Being a portable power resource, it finds application in all mobile vehicles and mobile equipments. It is also used as a storage medium of electric power. The power demand characteristics are not the same for different applications and therefore can not be met by a common battery design. Numerous designs of battery exist in the market having different electrical and mechanical characteristics. New type of batteries also evolves as demanded by ever growing applications.

Batteries for marine application are an evolving technology and continuous development is taking place in this field. Stringent requirements are being placed on the batteries, taking into consideration, the operating conditions and other safety issues. This report explains the battery technology, reviews different types of battery system and their characteristics. The requirements for marine application are discussed and a suitable battery type is recommended.

Principles of Battery

All batteries are similar in construction and are made up of a number of electrochemical cells. Each cell consists of a positive and negative electrode and a separator. The electrodes are placed in the midst of an electrolyte in the liquid or in other forms. Different types of material can be used to store energy and the names of batteries often identify the active material used in their construction. Other batteries are named after the type of material found in the electrodes and the type of electrolyte used. The active material used determines the voltage of the cells and the number of cells determines the total voltage of the battery. Most common are lead acid batteries. A lead acid battery has a nominal voltage of about 2 V. A typical yacht battery has six cells giving 12 V output.

The action of the lead-acid storage battery is determined by the chemicals in it.
The active materials in the lead acid battery are:

- lead oxide (PbO_2) in its positive plate,
- pure spongy lead (Pb) in the negative plate and
- diluted sulphuric acid (H_2SO_4) as electrolyte.

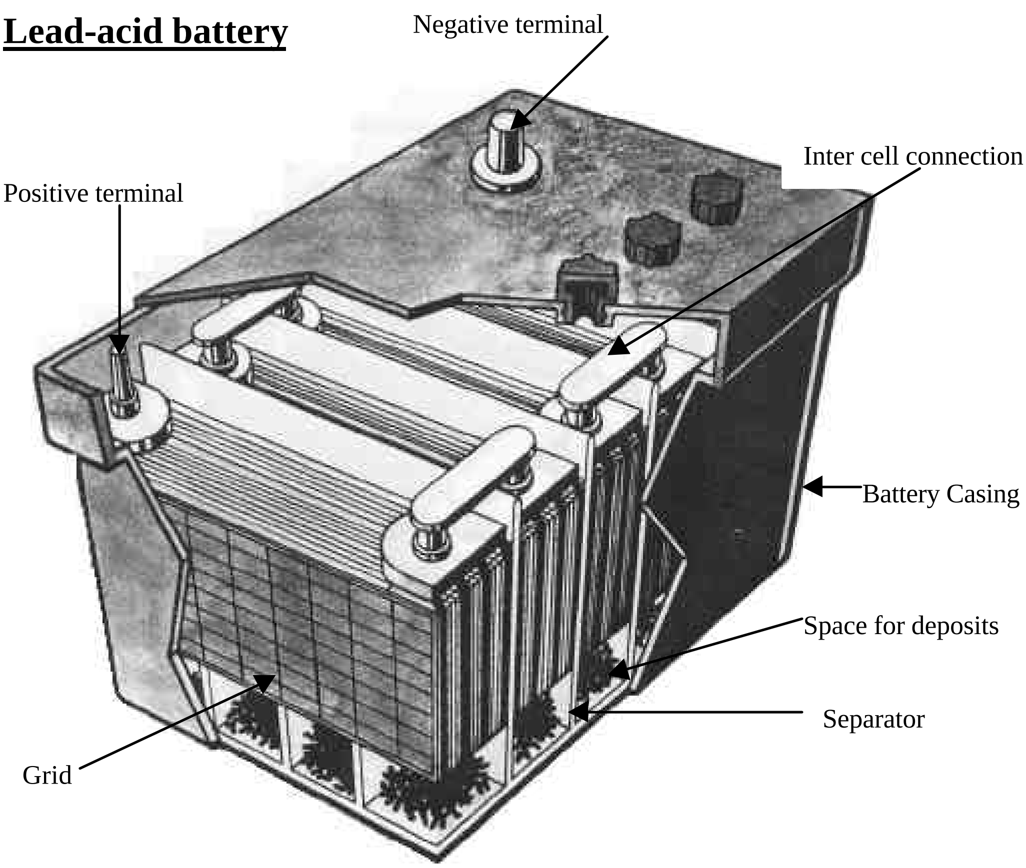

Figure 1 Cut view of the conventional Lead-acid battery

A separator is usually introduced between electrodes (Figure 1) to avoid short-circuiting of the electrodes.

Discharge Cycle

When the battery is loaded (i.e. connected to an external circuit), an electrochemical exchange takes place between the different materials in the two electrodes. Electrical energy is produced by the chemical action between the metals and the electrolyte.

Electrons are transported between the positive and negative electrodes via an external circuit and this process is known as discharging.

The material in the negative electrode is oxidised and releases electrons to the electrode, which as a result becomes more negative (an anodic reaction) represented by the following chemical equation.

$$PbO_2 + 2H_+ + H_2SO_4- + 2e- \leftrightarrow 2\ H_2O + PbSO_4 \qquad (1)$$

At the same time the material in the positive electrode is reduced and the electrode becomes more positive (a cathodic reaction).

$$Pb + H_2SO_4 \leftrightarrow PbSO_4 + H_{2+} + 2e- \qquad (2)$$

The electrons flow from anode, which is oxidised, through external load to the cathode where the electrons are accepted and the cathode material is reduced. The process produces lead sulphate ($PbSO_4$) on both the negative and positive plates. Hydrogen and oxygen gases are set free from the battery.

The total cell reaction shown in Figure 2 and may be represented by the following chemical equation.

$$PbO_2 + Pb + 2H_2SO_4 \leftrightarrow 2\ PbSO_4 + 2\ H_2O + \text{electrons} \qquad (3)$$

In the above equations the symbol $\leftrightarrow$ means that the equation is reversible.

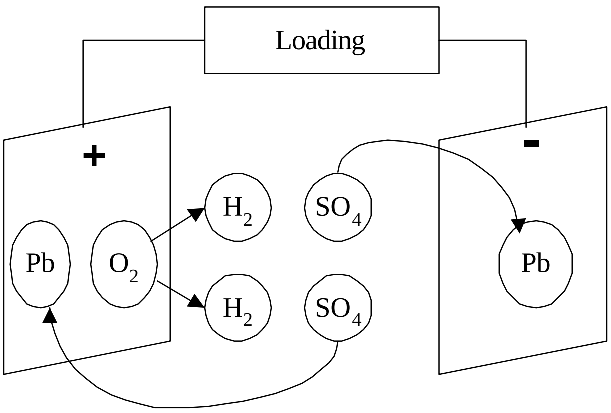

Figure 2 Discharging process

During the discharge, the active material of both plates is changing to lead sulphate ($PbSO_4$). The plates are becoming more alike and the acid is becoming weaker. Therefore the voltage is lower, since it depends on the difference between the two plate materials and the concentration of the acid. Eventually the battery can no longer deliver electricity at useful voltage and it is said to be discharged.

When the battery is subjected to a high discharge rate, such as cranking an engine near freezing temperature, it becomes discharged quickly. This is due to the fact that the acid circulation into the pores of the plates and diffusion of water from the pores of the plates is too slow to sustain the discharge. A very small percentage of the electrolyte and plate active materials in the cell can be utilised during the relatively short duration of a high rate of discharge. Only the material on or near the plate surfaces takes part in the chemical action. That is why the starting batteries must have large plate surface area per cell to deliver a large current.

On the other hand for a slow discharge rates the material near the centre of the plates has more opportunity to take part in the chemical reaction.

Charge cycle

The lead acid storage battery is chemically reversible. A discharged storage battery can be charged by passing electrical current through it in the direction opposite to the direction of discharge (Figure 3). This will restore the active material to a charged state and the battery will be ready to deliver full power. All equations (1-3) are reversible; they go from right to left (discharging) or from left to right (charging).

The sulphate in both plates ($PbSO_4$) is split into its original form of lead (Pb) and sulphate (SO_4). The water is split into hydrogen (H_2) and oxygen (O). As the sulphate leaves the plate it combines with the hydrogen and is restored to sulphuric acid (H_2SO_4). At the same time the lead of the positive plate chemically combines with oxygen to form lead dioxide (PbO_2). The specific gravity of the electrolyte increases since sulphuric acid is being formed.

A battery will evolve gas when it is being charged. Hydrogen is given off at the negative plate and oxygen at the positive. These gases result from the decomposition of water (H_2O). A battery is gassing because it is being charged at a higher rate than it can accept. Generally, a battery will gas near the end of a charge because the charge rate is too high for the battery to accept all of it. A charger, which automatically reduces the charge rate as the battery approaches fully charged state, eliminates most of this gassing.

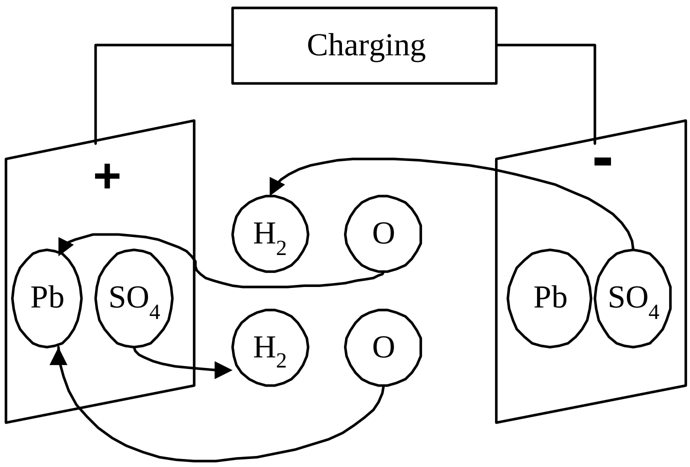

Figure 3 Charging process

It is extremely important not to charge low water loss batteries for a long period of time at rate, which cause them to gas because this means they are using water which, in sealed batteries, can not be replaced.

Electrolyte and specific gravity

The specific gravity of the electrolyte in a fully charged lead-acid battery is 1.265 corrected to 26.7^{o} C and it contains approximately 36% of suphuric acid by weight or 25% by volume. The remainder of the electrolyte is water. The specific gravity of the electrolyte is an indication of the state of charge. The table1 gives a typical open circuit voltage and the specific gravity values. It is possible to tell the state of the battery by measuring the specific gravity of its electrolyte.

Table 1 Charge level and the specific gravity of the electrolyte

Charge level	Specific gravity	Open circuit voltage
100%	1.265	12.7
75%	1.225	12.4
50%	1.190	12.2
25%	1.155	12.0
DISCHARGED	1.120	11.9

Grids

The electrode is formed by pasting a mixture of lead oxide, water and sulphuric acid on a grid casted out of lead alloy. The grid is a supporting structure for active material and most batteries use a small amount of antimony or arsenic in the grids to strengthen and stiffen the soft lead. This is necessary so that the grids can be handled during the battery manufacturing process without bending or other damage. Now there is a trend towards lower antimony content with manufacturers producing batteries which require less frequent water addition as a result of the reduced gassing experienced with lower antimony content. Batteries using grids containing other materials such as calcium or strontium for strength in place of antimony also reduce the gassing, water usage and self-discharge rates of batteries. These alloys in the lead increase corrosion, self-discharge, internal resistance and promote shedding of the active material. Small quantities of additional alloys such as tin, cadmium, and selenium are added to counteract these effects.

The lead-acid battery is rechargeable and it is classified as a secondary type. There are primary batteries (or cells) which are not capable of being easily recharged electrically and hence are discharged once and discarded. The electrolyte in this cells is not of liquid type but is contained by an absorbent or separator material. For this reason they are known as ‘*dry cells*’.

Alkaline Batteries

There are other conventional secondary batteries, which use an aqueous alkaline solution (KOH or NaOH), as the electrolyte and are known as alkaline batteries. The electrode materials in alkaline batteries are less reactive with the alkaline electrolyte than with acid electrolyte. Furthermore the charge/discharge cycle in the alkaline electrolyte involves only the transport of oxygen or hydroxyl ions from one electrode to the other and hence the concentration of the electrolyte does not change. There are different electrode systems in this type.

<u>Nickel-cadmium</u>:
Nickel-cadmium is the most popular alkaline battery available in wide range of sizes. They have very long life and require very little maintenance. This type is used in heavy-duty industrial applications like mining vehicles, diesel engine starting, railway signaling and standby power.

<u>Nickel-Iron:</u>
The Nickel-Iron battery is noted for long life and ruggedness, but has only small energy density advantage over lead-acid. Other disadvantages include poor peak power, very high self-discharge rates and poor low temperature performance.

<u>Nickel-Zinc</u>:
The nickel-zinc battery displays better energy and power performance than either the lead-acid or nickel/iron system, but suffers from short cycle-life due to the tendency of the zinc electrode to form dendrites, which cause internal shorting.

<u>Silver-Zinc</u>:
The silver-zinc battery is noted for its highest energy density available commercially, low internal resistance and flat discharge profile. Due to high cost, limited cycle life and poor performance at low temperature, the silver-zinc system is not used for general storage applications. This system is popular where high energy density is a prime requisite, such as portable electronic equipment, submarine and other military and space applications.

Figure 4 compares the energy density of different types of battery. The silver-zinc system has a higher energy density while the nickel-cadmium and lead-acid system have lesser energy density

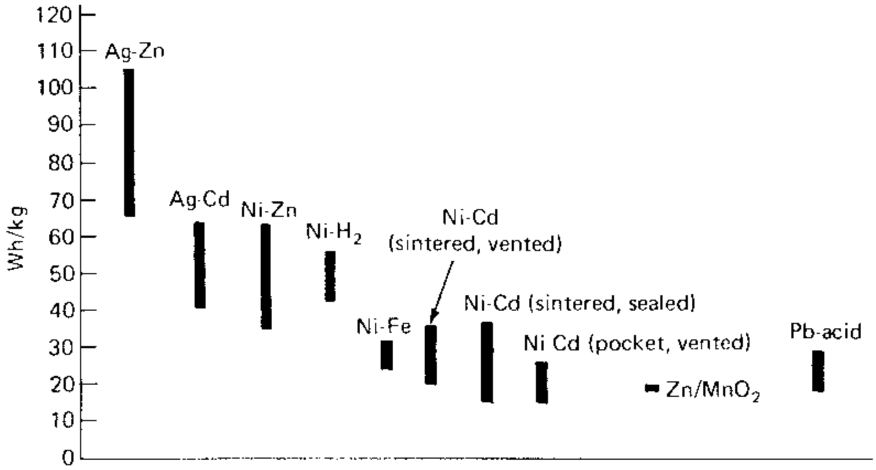

Figure 4 Energy density of the secondary battery system

Despite a great deal of research into different types of material, lead acid batteries have been found to be unsurpassed for a wide range of applications. Lead is available abundantly and it is therefore possible to mass-produce good batteries at low cost. This type is popular in automobile, heavy vehicles, marine and similar applications.

Limitations of lead-acid Battery

There are many limitations of the flooded type batteries and in particular the lead-acid batteries, which restrict their applications in certain area.

Shelf-life

Like all batteries, lead-acid battery also deteriorates as a result of chemical reaction that proceeds during storage. The type of cell design, electrochemical system, temperature, and length of storage period are factors which affect the shelf life of the battery. Self-discharge proceeds at low rate at reduced temperature and therefore refrigerated or low-temperature storage extends the shelf life. Figure 5 shows the charge retention property of different secondary battery systems. There are wide variations in performance depending on design and many other factors and the figure shows a general comparison only. It can be seen from the figure that the batteries lose their capacity rapidly at elevated temperature.

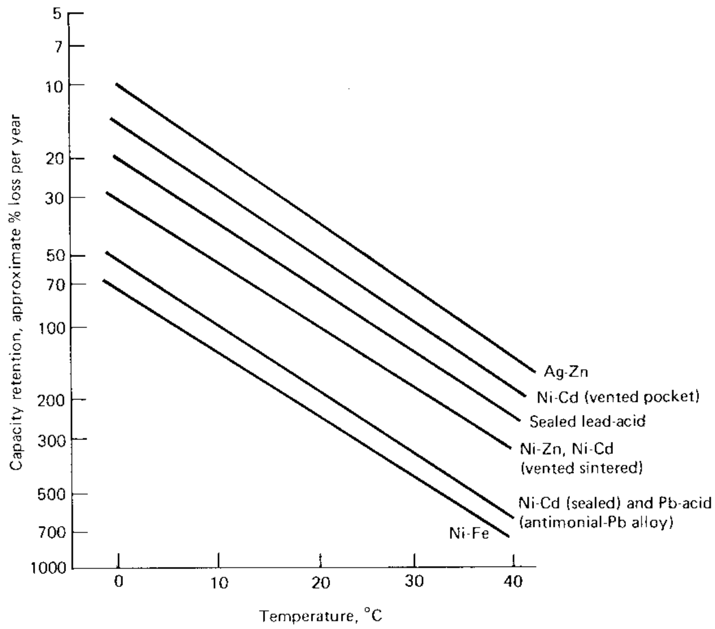

Figure 5 Capacity retention of secondary battery system

Sediment buildup and Sulphation

Normally a battery "ages" as the active plate material sheds (or flakes off) due to the expansion and contraction that occurs during the discharge and recharge cycles. Heat and vibration accelerate this "aging" process. Eventually, the sediment builds up and can short the cell out. Sufficient space is required between the plates in the cell for shedding of the active material to prevent electrical shorts and at the bottom of the battery for these materials to accumulate. This spacing requirement results in a battery that is larger in size, with lower energy density and higher internal resistance.

Another major cause of faulty batteries is sulphation. When batteries are stored discharged or for over six months, lead sulfate makes the plates very hard and dense and the battery less capable or unable to be recharged. The active material in the plates can no longer sustain a discharge current and therefore the battery "dies".

Gassing

During charging of the battery, hydrogen and oxygen gases evolve and get collected in the space provided above the plates. The gassing increases due to the fact that the battery is fully charged, that its plates are sulphated or that it is too cold to accept a charge. In the conventional flooded type battery design these gases are ultimately vented out through the vent holes. This could cause corrosion to the battery cables and connector.

Safety Issues

Spilling of sulphuric acid through the vent holes, potential explosions from the generation of hydrogen and oxygen, and the generation of toxic gases such as arsine and stibine are the highest safety concerns.

For the cells to remain active, electrolyte (sulphuric acid) must always completely cover the grids so that they may not dry out. The acid could escape through the vent holes provided in the conventional battery design, if the battery is tipped over or tilted. When the battery case is cracked or ruptured, the acid could leak out causing battery to fail and posing a risk to people, equipment and environment.

Precautions must be taken to prevent explosions from ignition of the flammable gas mixture of hydrogen and oxygen formed during overcharge of lead-acid cells. Often, batteries will he charged, off the vehicle, for long periods of time with an unregulated charger. In spite of the fact that the charge currents can be low, fair volumes of gas can accumulate. The gas mixture is explosive when hydrogen in air exceeds 4% by volume. Good air circulation should be maintained around batteries and electrical sources of arcs, sparks, or flame must be mounted in explosion-proof metal boxes to prevent ignition of the gases. It is good practice to refrain from smoking, using open flames, or creating sparks in the vicinity of the battery.

Some types of batteries can release small quantities of the toxic gases, stibine (SbH) and arsine (AsH). These batteries have positive or negative plates, which contain small quantities of the metals antimony and arsenic in the grid alloy to harden the grid and to reduce the rate of corrosion of the grid. Arsine and stibine are generally formed when the arsenic or antimony alloy material comes into contact with nascent hydrogen, usually during overcharge of the battery, which then combines to form these colorless and essentially odorless gases. They are extremely dangerous and can cause serious illness. When the batteries are used in an enclosed atmosphere proper air circulation, preferably fan forced ventilation should be maintained.

Effect of heat, cold and vibration

Heat increases the rate of evaporation, which causes a loss of water from the electrolyte. Extreme heat also increases the rate of self-discharge and promotes the corrosion of the positive plate grids. Extreme cold dramatically reduces the speed at which chemical reaction can occur and increases electrolyte resistance leading to poor cranking capability. The heat and vibration accelerate the aging process of the battery.

Prevailing battery technologies

The lead-acid batteries are now available in different designs to suit different operating conditions.

Conventional batteries

The conventional lead acid batteries are of open type and require constant maintenance because hydrogen and oxygen gases escape from the battery resulting in loss of water. They have filling covers so that they can be refilled. This technology may suit well for stationary batteries but poses problems in other applications. There has been a continuous development for the past two decades to improve the technology and make it suitable for other applications.

Maintenance-free (or Valve regulated) batteries

This type of closed batteries is usually maintenance free. Reduced water loss has been achieved primarily through improvements in battery plate alloys. In conventional battery grids, antimony has been used as an alloying element to enhance castability and hardness. However the presence of significant quantities of antimony can greatly increase the rates of water loss and self-discharge. The grids of low water loss batteries or low maintenance batteries contain little or no antimony. In the maintenance free batteries the grids use other metals such as calcium, cadmium and strontium to provide the necessary mechanical strength, while reducing gassing and self-discharge.

These batteries have more acid when they are manufactured. Of course they are better sealed than open batteries, but they often have hidden values or openings. They gradually loose liquid through gassing but can not be refilled.

Gel / Recombination (sealed) batteries

This type of batteries is relatively a new design, the individual cell of which is in a cylindrical form and is completely sealed. The battery is completely maintenance free since there is no need to refill. The batteries of this type are constructed to convert hydrogen and oxygen gases, which evolve during charging to water.

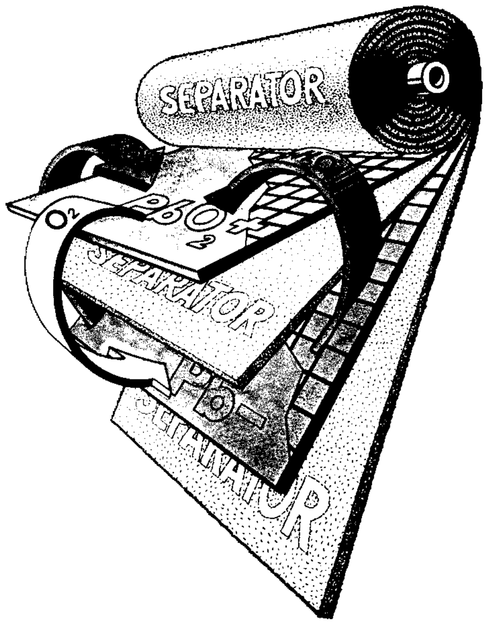

Figure 6 Gel battery technology

Both the positive and negative plates are made of pure lead and are extremely thin (Figure 6). The electrolyte used is in gel form or absorbed into some form of separator. This type of battery has high resistance to vibration, better shelf life and there is no risk of electrolyte spill as in the case of flooded type. Their greatest disadvantage is the high initial cost (two to three times), but could have an overall lower cost due to a longer lifetime.

Classification of Batteries based on applications

The lead-acid batteries are traditionally used for starting, lighting and ignition in automobiles and other vehicles with internal combustion engines. The new applications of lead-acid batteries are mainly associated with sealed maintenance free type or the one using electrolyte in gel form.

Starter Battery

The starter battery, whose main function is to start (crank) an internal combustion engine, discharges briefly at a higher current. Once the engine starts running, an alternator system recharges the battery and then supposed to maintain it on ‘float’ at full charge. The cranking ability of the starter battery is directly proportional to the geometric area of the grid surface. To maximise the cranking ability the grids need to have minimum electrical resistance, thin plates in higher concentration of electrolyte. The cranking ability decreases with lower temperature. The Cold Cranking Ampere (CCA) rating is measured in accordance with the American SAE standard. It is the battery current that can be delivered for 30 seconds at -18^{o} C with final voltage of 7.2V or above.

Deep Cycle Battery

Deep cycle batteries are designed for prolonged discharges at lower amperage. How deep a battery is discharged is termed "depth of discharge." In this type up to 80% of the battery capacity is discharged and then recharged. Batteries designed for deep cycling are built with thicker plates of active material, which have less overall surface area. These batteries resist the damage caused by repeated draining, but don't produce as much cranking power. Due to the reduced surface area available for chemical reaction, these batteries yield just as much power relative to their size, but do so over a longer period of time. The deep cycle batteries are characterised by its reserve capacity. The reserve capacity is measured in accordance with an SAE standard approved by the Battery Council International. It is measured in minutes, while at room temperature. 25 A is drawn from the battery for as long as the voltage does not drop below 10.5 V.

Batteries for Marine Applications

Batteries were used in early times of boating only for starting the engine with starter motor. Now the modern yachts are designed with powerful trolling motors, bilge pumps and a host of electronic instruments on board. Some even have satellite GPU receivers that tell precisely where the yacht is located even in the thickest fog or the darkest night. The depth finder is also popular and used all day very frequently.

The yacht engine is started using a starter battery. The power demand from it is only called on for a brief time and could loose about 20 % of its capacity for every starting operation. Although this battery sits idle for the rest of the time it is not capable of meeting the power demand for all other items on a modern yacht.
Deep cycle (and marine) batteries are designed for this purpose and is capable of prolonged discharges at lower amperage but has inadequate CCA rating to start the engine. A dual marine battery is now available in the market, which is a compromise between a starter and deep cycle battery and is used to start small engines and to provide deep cycle discharge capability.

Two battery systems are very common among the present day yachts. A starter battery is used to start the engine and a deep cycle battery is to supply power to the accessories. The starter battery is normally isolated from the deep cycle battery, which power the radio and other communication equipments. The batteries are connected through a diode isolator and both are automatically recharged by the charging system when engine is running. In some arrangements mechanical switches are used to isolate the starter battery from the deep cycle battery.

The batteries used in marine application have to withstand the tough environment and provide reliable service in every emergency situation. The use of traditional flooded type lead-acid battery can not withstand the constant pounding and vibration from the surf. In rare but probable situations like the one experienced in the 1998 Sydney to Hobart yacht race, some of the yachts were over turned and remained in that position for a prolonged length of time. In such conditions the electrolyte (sulphuric acid) in the flooded type battery could drain out completely and become totally out of service. The electrolyte can find its passage through the vent holes provided for the gases to escape. Another possibility is that the battery cap became loose due to excessive vibration and overturning.

Some type of batteries, which contains small quantities of antimony (Sb) or arsenic (As) in the grid produce small quantities of toxic gases Stibine (SbH) and Arsine (AsH). When the batteries are not properly ventilated these gases cause safety concerns for the people.

It is a trend now to reduce the antimony content to reduce gassing and substitute with calcium, strontium or some other metal. Use of recombinant technology minimises the gassing and having the electrolyte in the gel form absorbed in the separator material eliminates the possibility of any spill. The gel technology uses pure lead to manufacture the grids, which extends the life of the battery and protects against corrosion of the grid. It is vibration resistant and ideally suited for marine applications.

For the batteries to be reliable, they must be kept clean and dry particularly the top surface between the terminals. When the yacht takes in large amount of seawater, it is possible that the battery terminals are covered with seawater providing a discharge path across the terminals. The discharge current will not be as high the starting current of the motor since the resistance of the seawater is much higher than that of the copper winding of the motor. The battery can sustain this condition for a reasonable length of time. This problem can not be completely overcome but could be minimised by properly covering at least one of the terminals of the battery with insulating watertight cap.

Due to vibration and high temperatures, damaged wiring on and around engines is one of the most common causes of stray current damage, i.e. true electrolysis. It is always safe to connect the starter motor circuit directly to the battery power. It is not uncommon to use the body of the motor as one of the conducting path. This method of connection increases the possibility of stray current damage.

It is extremely important to consider the routing of the wiring so that it is not in contact with hot surface, or vibrating on sharp edges or rough surfaces. The cables and terminals used should be of marine grade, which are less susceptible to corrosion. Wiring of the electrical system should be inspected regularly for signs of damage. It should be done by qualified personnel for certification, and it should also be made as a condition of entry to the race.

Conclusion

The incidents recorded of the 1998 Sydney to Hobart Yacht Race has prompted a study of current technologies for rechargeable batteries in order to find a safe and reliable battery system for yachts. It is found that the conventional flooded type lead-acid batteries are not quite suitable and the batteries using the recent gel technology are safe and reliable for marine application. In order to ensure reliable operation of the electrical system it is also recommended that an inspection and certification of the electrical wiring system by qualified personnel is essential to ensure safe yachting race.

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