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F CTO AFFECTING C P CITY.

<u>Capacity</u>. The capacity of a storage battery - its ability to delivers energy - is usually expressed in ampere - hours, which is simply the product of the discharge in amperes over a number of hours. However, a simple figure of - say - 200 ampere hours has very little significance unless it is qualified by the many factors which customary usage of the application in which it is applied. The principal factors that effect the capacity of lead - acid battery are as follow :

- The amount of active material within the cell.
- The concentration and quantity of electrolyte.
- Practical limit of final voltage.
- The previous history of the plates.
- The temperature.
- The Rate of discharge.

The Amount of Active Material within the Cell.

The electrical energy that a battery delivers during discharge is derived from the electrochemical reactions taking place between the electrolyte and the active material of lead dioxide and spongy lead. The greater the amounts of these materials, the greater will be the capacity of the battery.

According to Faraday's law, 96500 coulombs transform 1 equivalent of lead. Since the atomic weight of lead is 207.2 and the valence 2, the equivalent weight of lead is 103.6 grams. From this we may readily calculate the number of grams of lead, on the negative plate, that are transformed into lead sulphate during the passage of 1 ampere - hour.

As 96,500 coulombs are equivalent to 26.80 ampere - hours, we have 3.866 grams of lead corresponding to 1 ampere - hour. Similarly, 4.463 grams of the dioxide, or active material of the positive plate, take part in the reaction per ampere - hour.

Two molecules of sulphuric acid in the electrolyte are transformed for each molecule of lead or lead dioxide, in accordance with the equation

$$PbO_2 + Pb + 2 H_2SO_4 = 2 PbSO_4 + 2 H_2O$$

The molecular weight of sulphuric is 98.076, and, since the valence is 2, there are 98.076 grams of acid reacting for each equivalent of the lead. This amounts to 3.660 grams per ampere - hour. The net change in the weight of the electrolyte during charge or discharge differs from 3.660 grams per ampere - hour because of the formation of 2 molecules of water during discharge for each 2 molecules of the acid that take part in the reaction. When the battery is on charge the reverse takes place; that is, 2 molecules of water disappear for each 2 molecules of acid that are formed. The net change on discharge is, there fore,

 $-2 H_2 SO_4 + 2 H_2 O \rightarrow -2 SO_3 + Other non - chemical reaction elements$

This education shows that the actual change in weight is 160.12 grams for every 2 gram - molecules taking part in the reaction. This loss in weight of the electrolyte is balanced by a corresponding gain in weight of the plates.

The mass of the electrolyte reacting at the positive plates during discharge is slightly greater than at the negative plates. This may be seen from the formula for the chemical reactions taking place at the positive and the negative plates as follows :

> At Pos; Pb 0_2 + H_2 + H_2S0_4 = PbS0_4 + 2 H_20 At Neq; Pb + $S0_4$ = PbS0_4

- 15 -

The actual consumption of sulphuric acid at the two plates differs more than the formula indicates, because it is necessary to take into account also the concentration changes caused by the migration of the hydrogen (H⁺) and the sulphate (SO_L^{∞}) ions.

during discharge sulphate ions are consumed at both the positive and the negative plates. Sulphate ions migrate toward the negative plates and away from the positive plates. Hydrogen ions, on the other hand, migrate away from the negative plate toward the positive plate, where part of them are consumed in the formation of water. The net change taking place is therefore a greater loss of acid at the positive plate than at the negative. If this is considered together with the amount of water formed at the positive plate, it is found that the positive requires about 1.6 times the amount of acid that the negative plate required during the discharge period. This fact is a reason for placing the corrugated side of separators next to the positive plate in order to allow more space for acid. It is sometimes noticed, when separators are renewed in old batteries, that the capacity of the battery is considerably increased. This is undoubtedly due in part to the additional acid space provided next to the positive plates by new separators, since the ribs of the old separators are generally worn down almost to the web of the separator by the time that they required renewal.

Limitation to the Use of the Materials.

The foregoing figures showing the relation of lead, lead diexide, and sulphuric acid consumed per ampere - hour are based entirely upon theoretical considerations. The practical amounts of the active materials required are considerably greater than these calculated from theory.

There are several reasons for the limited used of the materials in actual service.

- The lead sulphate that is formed during the process of discharge is a non - conductor and increases the resistance of the active material of the plates. Then the active material contains 50 percent of sulphate, the resistance has risen to a very high value.

- 16 -

- Another reasons is the stoppage of the pores of the plates by the lead sulphate, which hinders the diffusion of the electrolyte.

- ' third reason is the increasing resistance of the electrolyte itself, the minimum resistivity of the electrolyte occurs at a specific gravity of approximately 1.225. As the specific gravity decrease below this point the resistivity increases, slowly at first, and then more rapidly as the concentration fall below 1.100

- / fourth reason, which involves the design of the plate it self, is the limited contact between the active material of the plate and its support.

The ratio of the amount of active material taking part in the reactions to the total amount of active material present in the plates is called " The coefficient of use."

This coefficient differs markedly with the thickness and porosity of the plate, the rate of discharge, and the temperature. I cell of good quality will have normally a coefficient of 0.25 or more. Lower values are to be attributed to deficient amount of electrolyte, lack of porosity of the plates, or improperly designed separators.

<u>Design of cell</u>. For a cell to give the maximum output for a given weight of active material it is essential for the active material to be readily accessible to the electrolyte. This is achieved by using a large number of thin plates, with a high weight ratio of active material to grid, compatible with maintaining the grid sufficiently strong for good conductivity and retention of pasts. The same weight of active material distributed in a few thick plates containing a dense or hard pasts would result in a cell of much lower capacity.

A plate with porous active material is capable of producing a greater output, particularly at high rates of discharge, than a plate with a dense, hard, active material. Porosity is produced by adding small amounts of carbon, barium sulphate or other org nic or inorganic expanders during the mixing of the paste. Too high a perosity is avoided for plates which are to be subjected regularly to cycles of discharge and charge, as this is conductive to short life by premature shedding of the active material. The formation of lead sulphate durin the normal discharge of a cell reduce the percenty of the plate, because the lead sulphate occupies more space than the original active material. Normally this expansion is taken up by the pores of the plate being compressed, and no harm results. If, however, the sulphation is excessive, owing to the cell being persistancely overdischarged and undercharged or left for a long periods in a discharged condition, the sulphate expands beyond the absorbing capability of the pores. The active materil is then subjected to pressure which results eventually in fracture of the grid frame or less of active material from the plate, and if the condition is not remedied the cell loses capacity and will not accept a charge.

<u>Thickness of the Active Material</u>. The capacity of a storage cell increases with the thickness of the active material of the plates at moderate rates of discharge, assuming that the plates have sufficient perosity for the electrolyte to reach the inner recesses. The effect of thickness cannot be considered apart from the rate of the discharge, because the faster the discharge the more nearly is the total output of the cell confined to the layers of active material that are in immediate contact with the free electrolyte. At excessively high rates of discharge, the output of the cell becomes practically a surface phenomenon. This is because there is insufficient time for the electrolyte to diffuse into the pores of the plates, and the sulphate forming at the surface clogs the pores. It low rates of discharge, on the other hand, almost any depth of the active material may become effective.

The reactions of discharge penetrate into the plate only a pertion of the way. For this reason, cells, that contain thin plates are found to have greater capacity than cells of similer size containing thicker plates. This is particularly true at high discharge rates. Thin plates do not have a greater capacity per plate than thick plates. Is a matter of fact, the capacity per plate is some what less, but, owing to the large number of plates that can be used in a cell of given size, the capacity of the cell as a whole may be considerably greater. The negative plates are more sensitive to changes in thickness than the positive plates. This means that, if the capacities of the positive and negative plates are equal at any high rate of discharge, the negative will exceed the capacity of the positive at any lower rate of discharge.

Concentration of the Electrolyte.

Specific gravity range. The specific gravity of the electrolyte for the main types of lead - acid cell at 60°F (15.6°C.) varies as shown:-

Stationary cells 1.210 Portable cells -Temperate climate 1.270 - 1.285 Tropical climate 1.230 - 1.250

The specific gravity falls during discharge and increases during charge. It is least when the cell is fully discharged, and greatest when the cell is fully charged.

The specific gravity reading therefore provides an excellent indication of the state of discharge of a lead - acid battery, as the fall in specific gravity during discharge is directly proportional to the number of aspers - hours supplies by the battery.

The difference between the values of specific gravity with the cell fully charged and fully discharged varies according to the amount of electrolyte in the cell. The usual working ranges of specific gravity for the main types of cell are approximately

 Stationary
 1.210 to 1.30 - 1.180 (30 to 80 points)

 at the 10 - hr rate.

 Automotive
 1.280 to 1.110 (170 points)

 at the 20 - hr rate.

 Traction
 1.280 to 1.210 - 1.150 (130 to 160 points)

 at the 5 - hr rate.

It will be seen that the range of specific gravity can vary from 30 points (0.030), for the large stationary cells with heavy plates, to 170 points (0.170) of more for portable cells.

<u>Change in capacity with concentration</u>. The concentration of the acid in the porce of the plates is a vital factor in determining the voltage and capacity of a cell. Unless a sufficient amount of sulphuric acid can be maintained in the porces during discharge the voltage at the terminals of the cell will decrease rapidly and the cell will become exhausted.

The concentration affects the capacity because

- it determines the potential of the plates.
- it affects the resistance of the electrolyte to the passage of the electric current.
- it affects the viscosity of the electrolyte and there by the rate of diffusion.
- it affects the rate of diffusion because of differences in the concentration of the electrolyte in the pores of the plates and outside.

Practical Limit of Final Voltage.

The capacity can be related to any practical limit of voltage, and the higher the final voltage the lower will be the capacity available. This can be demonstrated for a typical duty where a 24 - cell battery supplies a load to a minimum working voltage of 46 V., or 1.92 V. per cell. The current drown from the battery during peak loading might be the equivalent of the 6 - hr rate to the standard final voltage of 1.71 V. per cell, but when related to the permissible working voltage of 1.92 V. per cell, the battery would supply the current for only 4 hr.

The final voltage is determined partly by the nature of the duty which the battery performs and partly by the discharge voltage characteristic of the battery. I lighting load requires a fairly high stable voltage, whilst a heavy engine starting load requires a high power output from the battery, that is high current at a lower working voltage and to a lower final voltage.

- 20 -

When final voltage is determined by the discharge voltage characteristic of the battery, it is usually fixed to allow a fall of 0.3 V. per cell from the initial voltage. The cell voltage on discharge falls sharply beyond this end point, which is known as the knee of the voltage curve. Continuing the discharge beyond the knee does not produce any worth - while increase in available capacity, because of the sudden collapse of cell voltage.

The Previous History of the Plates.

<u>Porosity of the Plates.</u> The importance of porosity of the plates in facilitation the access of electrolyte to the active material has been treated in connection with other factors previously discussed. The porosity of the finished plate varies with the expansion of the material from which it was made and with its state of charge.

The aggregate porosity of the plate is a matter of 50 percent of the entire volume of the plate, but the individual peres are probably little more than molecular in size.

Although the term porosity is generally understood to indicate the possesion of absorption qualities similar to those of a sponge, it is desirable to establish a definition for it.

The porosity = 1 - The apparent density of the active material from this definition the percentage of porosity of the plates may be obtained in any case by multiplying the factor 100.

Veriation of perosity with state of charge.

The perosity of the plate varies with the state of charge. Lead sulphate, which is formed as a product of the discharge of the cells, is less dense than either lead or dioxide of lead. It therefore occupies more space than the active materials, yet the apparent volume of the plate doesnot charge. The reason for this is that the expansion is taken care of by the pores of the plates. Effect of previous discharge. The capacity of the plates is affected by the discharges immediately preceeding. For this reason it is desirable to run a few preliminary cycled at the same rate of discharge as is to be used in a formal test.

The capacity is lower if the discharge has been preceded by a discharge at a higher rate, and it is higher if preceded by a discharge at a lower rate.

Variation of capacity during life. Most batteries are designed to give at least their nominal capacity in the first few discharges. Batteries in the early part of life, particularly those which are cycled (given regular cycles of discharge and charge), increase in capacity, and the increase may be as much as 10 - 20 percent more than nominal. This higher capacity is maintained for a considerable period, followed by a gradual decline. battery is usually considered worthless when its capacity has fallen to about 80 percent of nominal. This plates reach their maximum capacity after a smaller number of cycles than thick plates, but beyond this point their decrease in capacity is more rapid.

Loss of capacity during the life of portable batteries largely results from deterioration of the positive plate by shedding or softtening of the active material and corrosion of the grid. The negative plates loss some capacity by hardening of the paste, usually caused by the gradual formation of insoluble lead sulphate.

Temperature.

The temperature plays an important part in determining the capacity that can be delivered by a storage cell under any specified conditions of rate and final voltage.

Chemical reactions do not take place readily at extremely low temperature, and much below O^OF. it becomes impossible to charge the batteries.

Low temperatures increase the viscosity of the electrolyte, impairing its circulation in the pores of the plates. The increase in viscosity becomes very rapid at temperatures below 0°C. Normal temperature for storage batteries is generally accepted as falling within the range from 60° to 80°F. (15.6 to 27°C.) Low battery temperatures temporarily reduce the available ampere - hour capacity and discharge voltage. Capacity and voltage are restored with a return to normal temperature, even without a charge. An increase in battery temerature results in an increase in capacity, particularly at high rates of discharge.

Both these effects of temperature on capacity are mainly a result of the change in the viscosity and resistance of the electrolyte. At low temperature the viscosity and resistance are increased, especially below $32^{\circ}F$ ($0^{\circ}C$). The increased viscosity reduces the rate of diffusion or circulation of electrolyte into the pores of the active materials. As high temperatures the viscosity and resistance are reduced and the battery capacity is increased.

The effect on battery capacity of changes in the viscosity and resistance of the electrolyte are most noticeable at high rates of discharge, where electrolyte diffusion is the main factor in limiting the available capacity.

Comparison of effects of concentration and temperature on positive and negative plates.

Although a high concentration of the electrolyte is favorable for the Positive plates, it may be detrimental to the negative plates. The capacity of the negative plates in an electrolyte of 1.315 sp.gr. is less than in an electrolyte of 1.140 sp.gr., particularly at high rates of discharge and low temperatures. The negative plates may thus become the limiting factor.

The reduced concentration may reduce slightly the capacity at normal rates and temperatures when the positives limit the capacity, but this is more than offset by the gain in capacity under more severe conditions that result in limitations imposed by the negatives.

The Rate of Discharge.

The higher the discharge rate in amperes, the less total ampere hours a battery will deliver under other wise similar conditions.

- 23 -

This relationship will vary somewhat with different types of plate and cell construction.

This is due to two causes. The primary one is the lack of immediate diffusion of the electrolyte. During discharge, the only portion of the electrolyte which is "useful " is that in the pores of the plates in actual contact with the active material. As the acid in this portion becomes depleted or exhausted, the electrolyte must diffuse or circulate in order to bring more acid to the active material where it is needed. The higher the rate of discharge, the more rapid this circulation must be to maintain normal cell voltage. As the rate increases, however, this circulation or diffusion does not increase in the same proportion, with the result that the electrolyte in the pores of the plates is less dense and the cell voltage decreases more rapidly, thus limiting the total capacity.

Another result of higher current rates is to increase the voltage drop within the cell. All cells have a certain internal ohmic resistance. The higher the current, the greater the voltage drop or loss in this resistance within the cell, thus reducing its external or useful voltage which supplies the load.

The rate most commonly used as a standard is the 10 hour rate which can be expressed, for example, either as " 100 h at the 10 hour rate " or as " 10 amperes for 10 hours ". There are exceptions, however, the principle ones being automotive batteries which are customarily rated at the 20 hour rate and Motive Power (Industrial Truck) types rated on a 6 hour basis. Any correct rating is quite proper to use as long as it is properly specified or understood. Manufacturers usually list several hourly ratings, nearly always, including the 10 hour, for the convenience of users in making comparisons and conducting tests.