Chapter 17
Lead-Acid Batteries

17.1 Introduction

Over many years, the most common use of the word "battery" was in connection with the rechargeable energy source that was used to start automobiles. These were almost always what are generally called *Pb-acid batteries*, and were often a source of aggravation. A considerable amount of progress has been made in recent years, so that the SLI (starting-lighting-ignition) batteries now used in autos are actually quite reliable, assuming that they are not abused. Different types of Pb-acid batteries are used for a number of other applications, both mobile and stationary, and ranging from quite small to very large. The greatest fraction of the total battery market worldwide is now based upon this technology.

There are several reasons for the widespread use of lead-acid batteries, such as their relatively low cost, ease of manufacture, and favorable electrochemical characteristics, such as high output current and good cycle life under controlled conditions.

Pb-acid cells were first introduced by G. Planté in 1860 [1], who constructed them using coiled lead strips separated by linen cloth and immersed in sulfuric acid. By initially passing a dc current between the two lead strips, an oxide grew on the one on the positive side, forming a layer of lead dioxide. This caused the development of a voltage between them, and it was soon found that charge could be passed reversibly through this configuration, so that it could act to store electrical energy.

Significant improvements have been made over the years. One of the most important was the invention of the pasted plate electrode by C. Fauré in 1881 [2]. This involved the replacement of solid metal negative electrodes by a paste of fine particles held in a lead, or lead alloy grid. By doing this, the reaction surface area is greatly increased.

Another significant improvement has been the development of sealed cells during the last several decades. This is sometimes called *valve-regulated lead-acid* technology. These matters are discussed in the following sections.

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There are two general types of applications that are commonly considered for Pb-acid cells, and they impose quite different requirements. One type involves keeping the cell essentially fully charged so that it maintains a constant output voltage. This is sometimes called *float charging*. Such cells are generally stationary, and are expected to have high reliability, long life, a low self-discharge rate, and a good cycling efficiency with low loss under cycling and overcharge. They are often used in telecommunication and large computer systems, railroad signaling systems, and to supply standby power as uninterruptible power sources (UPS). They are generally not optimized for energy density or specific energy, but are attractive because of their low cost.

The other general type is targeted toward applications that may involve deeper discharging, such as in load leveling systems and traction applications. In these cases, the specific energy and/or specific power can be very important, in addition to the cost, cycle efficiency, and lifetime. Periodic, rather than continuous, charging is more common in these cases.

Although hydride/"nickel" and lithium-ion cells are generally used in smaller portable applications, some sealed Pb-acid cells are now also used for such applications where the lowest cost is particularly important.

17.2 Basic Chemistry of the Pb-Acid System

The pb-acid cell is often described as having a negative electrode of finely divided elemental lead, and a positive electrode of powdered lead dioxide in an aqueous electrolyte. If this were strictly true and there were no other important species present, the cell reaction would simply involve the formation of lead dioxide from lead and oxygen:

$$\mathrm{Pb} + \mathrm{O}_2 = \mathrm{PbO}_2 \tag{17.1}$$

The open-circuit voltage of such a cell would be determined from the Gibbs free energy of formation of PbO_2, $\Delta G_f^0(\mathrm{PbO}_2)$, by

$$E = -\left(\frac{\Delta G_f^0(\mathrm{PbO}_2)}{zF}\right) \tag{17.2}$$

in which z is 4, the number of charges involved in reaction (Eq. (17.1)), and F is the Faraday constant. The value of $\Delta G_f^0(PbO_2)$ has been measured as −215.4 kJ/mol [3]. Thus the cell voltage would be 0.56 V. However, this is far from what is actually observed, so that the reaction that determines the cell voltage must be quite different from Eq. (16.1).

Instead of the reaction in Eq. (17.1), the overall chemical process involved in the discharge of Pb-acid cells is generally described [4], in accordance with the *double-sulfate theory* [5–8] as

$$Pb + PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O \tag{17.3}$$

This reaction proceeds to the right-hand side during discharge, and toward the left side when the cell is recharged. This has been demonstrated by observations of morphological changes in both the negative [9, 10] and positive electrodes [11].

Using values of the standard Gibbs free energy of formation, ΔG_f^0, of the phases in this reaction, it has been shown that the equilibrium voltage of this reaction under standard conditions is 2.041 [12].

17.2.1 Calculation of the MTSE

It is interesting to calculate the maximum theoretical specific energy of Pb-acid cells. As discussed in Chap. 9, this can be expressed as

$$\mathrm{MTSE} = 26,805\left({}^{xE}\!/_{W}\right) \tag{17.4}$$

in which x is the number of elementary charges, E the average cell voltage, and W the sum of the atomic weights of either the reactants or the products. In this case, x is 2, E is 2.05 V, and W is 642.52 g. Inserting these values, the maximum theoretical specific energy, calculated from these reactions, is 171 Wh/kg. This is fallacious, however, for it is necessary to have additional water present in order for the cell to operate. This increases the weight, and thus reduces the specific energy. But in addition, other passive components add significant amounts of weight, as is always the case in practical batteries. Values of the practical specific energy of lead-acid batteries are currently in the range of 25–40 Wh/kg. Higher values are typical for those optimized for energy, and lower values for those designed to provide more power.

17.2.2 Variation of the Cell Voltage with the State of Charge

From Eq. (17.3) it is obvious that the electrolyte changes, the amount of sulfuric acid decreases, and the amount of water present increases, as the cell becomes discharged. This causes a change in the electrolyte density. It is about 40 % by weight H_2SO_4 at full charge, but only 16 % when the cell is fully discharged. The corresponding values of equilibrium open circuit voltage are 2.15 V and 1.98 V at 25 °C. These density and voltage variations are illustrated in Fig. 17.1. Whereas it may take some time to reach the equilibrium voltage because of temporary structural and compositional inhomogeneities in the electrodes, the electrolyte density can be readily measured, and is often used to indicate the state of charge of the cell.

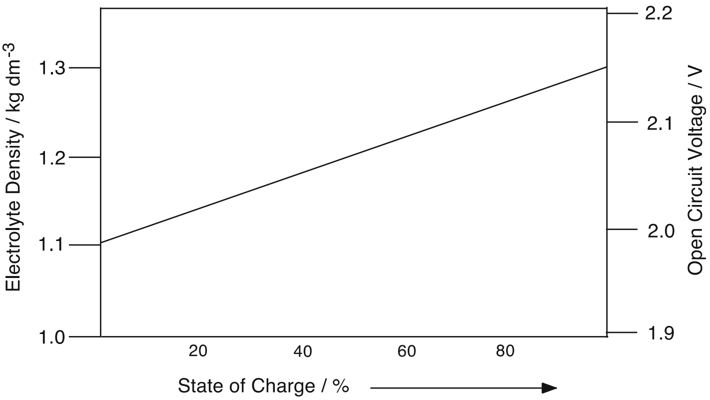

Fig. 17.1 Variations of the electrolyte density and open-circuit voltage in Pb-acid cells as functions of the state of charge

17.3 Potentials of the Individual Electrodes

It is clear that the cell voltage in pb-acid cells is significantly greater than the theoretical stability range of water, which is 1.23 V under equilibrium conditions. This is often attributed to (unspecified) kinetic factors in the literature.

However, this really means that the electrolytic stability window is extended by the presence of at least one additional ionically-conducting phase in series with the aqueous electrolyte [13].

Whereas it is easy to measure the cell voltage with a voltmeter, such a measurement does not give any information about the potentials of either electrode, just the difference between them. To get information about the individual potentials it is necessary to use reference electrodes.

This was done by Ruetschi [12, 14, 15], who used this information to determine the potential-determining microstructure in each electrode. He found that the surface of the lead in the negative electrode reactant is covered by a completely formed membrane layer of $PbSO_4$. He described this layer as perm selective, for it is essentially impermeable to the SO_4^{-2}, HSO_4^-, and Pb^{+2} ionic species in its vicinity, whereas H^+ ions can pass through it. This phase can thus be considered to be a selective ionic conductor for H^+ ions that extends the electrolytic stability window of the system. As a result, the negative electrode potential is determined by the Pb, $PbSO_4$ equilibrium, which he found to be −0.97 V relative to the Hg/Hg_2SO_4 reference electrode potential. This reference potential is + 0.65 V relative to the standard hydrogen reference potential, the SHE. PbO cannot play a role in this electrode potential, for it is only stable at potentials above −0.40 V vs. the Hg/Hg_2SO_4 reference.

Likewise, Ruetschi found that the positive electrode microstructure consists of three phases. $PbSO_4$ and PbO_2 are on top of the underlying lead structure. Again, there is a perm-selective layer of $PbSO_4$ on top of the PbO_2, which is an

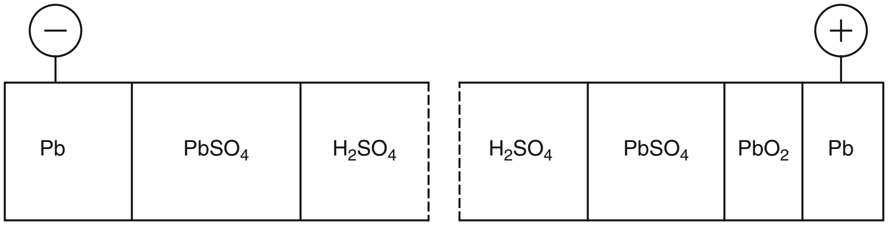

Fig. 17.2 Schematic structures of the potential-determining portions of the electrodes in Pb-acid cells

Table 17.1 Potentials relevant to the Pb-acid battery

Equilibrium	Potential vs. Hg/Hg_2SO_4 reference/V	Potential vs. SHE reference/V
Hg/Hg_2SO_4	0.00	+0.65
$PbSO_4/PbO_2$ (unit activities)	+1.03	+1.68
$PbSO_4/PbO_2$ (5 m H_2SO_4)	+1.08	+1.73
$PbSO_4/PbO_2$ (1 m H_2SO_4)	+0.91	+1.56
Ag/Ag_2SO_4	+0.04	+0.69
$Pb/PbSO_4$	−1.01	−0.36
Lowest potential at which PbO is stable	−0.40	+0.25

electronic conductor. Thus the potential is determined by the $PbSO_4$, PbO_2 equilibrium in that case.

Based upon this quantitative work on their potentials and local corrosion films, the potential-determining parts of the Pb-acid battery system can be understood by considering the compositions of the two electrodes, as schematically illustrated in Fig. 17.2.

It was found that the PbO_2, $PbSO_4$ positive electrode potential depends upon the acid concentration in the same way as the voltage of the total Pb-acid cell. This is consistent with the Gibbs phase rule discussed earlier, It can be written as

$$F = C - P + 2 \tag{17.5}$$

For a fixed temperature and total pressure, it becomes simply

$$F = C - P \tag{17.6}$$

And since the PbO_2, $PbSO_4$ system has three components, Pb, S, and O, and only two phases, there is one degree of freedom left. Thus the potential is composition-dependent.

Table 17.1 shows the values of the relevant potentials in the lead-acid system, including two different liquid electrolyte compositions.

17.4 Relation to the Mechanisms of the Electrochemical Reactions in the Electrodes

The electrochemical reaction at the negative electrode is generally expressed as

$$\mathrm{Pb} + \mathrm{HSO_4^-} = \mathrm{PbSO_4} + \mathrm{H}^{'} + 2e^- \tag{17.7}$$

and that at the positive electrode as

$$\mathrm{PbO_2} + 3\mathrm{H}^+ + \mathrm{HSO_4^-} + 2e^- = \mathrm{PbSO_4} + 2\mathrm{H_2O} \tag{17.8}$$

It can be seen that both of these reactions involve H^+ ions. These are the species that, as protons, move in and out of the electrodes by transport through the $PbSO_4$ solid electrolyte surface layers. As they move into and out of the local aqueous environment they cause the pH to vary, changing the solubility of the $PbSO_4$ in solution in the negative electrode structure, and that of both PbO_2 and $PbSO_4$ in the positive electrode structure. These solid phases are caused to precipitate and/or dissolve as the cell reaction takes place. This is generally called a dissolution—precipitation mechanism.

Thus the overall reaction in this type of battery is a composite of ionic transport of protons through a dense solid electrolyte layer of $PbSO_4$ that causes changes in the local pH, and thus of the solubility of $PbSO_4$ and PbO_2, in the adjacent liquid electrolyte. This results in their dissolution or precipitation within the multiphase electrode structure. Although the electrode potentials are determined by the two-phase equilibria under the $PbSO_4$ layer, the electrode capacity is determined by the amounts of the precipitate phases that react within the liquid electrolyte portion of the electrodes.

17.5 Construction of the Electrodes

Although descriptions of Pb-acid cells always say that the negative electrodes are primarily lead, and the positive electrodes primarily PbO_2, during manufacture they are both initially made from the same material, a paste consisting of a mixture of PbO and Pb_3O_4 [16]. It can be considered to be lead powder that is 70–85 % oxidized, and is traditionally called “leady oxide.” Measured amounts of water and a H_2SO_4 solution are added, along with small polymer fibers to influence the mechanical properties, under carefully controlled temperature conditions. This results in the formation of basic lead sulfates, 3 $PbO{\cdot}PbSO_4{\cdot}H_2O$ or 4 $PbO{\cdot}PbSO_4$. Various other materials are sometimes added to this mix. An example is the use of lignin, a component of wood, as a spacer, or “expander,” in the paste that is used in negative electrodes [17]. Its presence reduces the tendency to form large Pb_2SO_4 crystals upon cycling those electrodes.

The paste is inserted into the electrodes by spreading it into an open grid structure. In addition to mechanically holding the paste material in place, the grid, which has better electronic conductivity than the fine-particle paste, also serves to carry the current throughout the total electrode structure.

Following this process, during which the paste is inserted into both electrode structures, generally before their final insertion into the battery case, a process called *formation* is undertaken. This process converts the materials in the two electrodes into the different compositions and structures required for the fully charged state of the cell.

This forming process is equivalent to an initial electrochemical charge. It is carried out under carefully controlled conditions, typically at a very low current density, so that the total structure in the two sets of electrodes is converted into the desired chemical species without disruption of the physical state of the paste-impregnated electrodes. This is essentially what Plante [1] did, for he made his battery using sheet lead electrodes, and cycling them in dilute H_2SO_4.

The variation of the potentials of the two electrodes during the formation process is shown in Fig. 17.3.

In an increasing number of cases, formation is followed by a carefully controlled drying process, and the batteries are supplied to the user in the dry state. The acid electrolyte is inserted into the cell at the time of the first use.

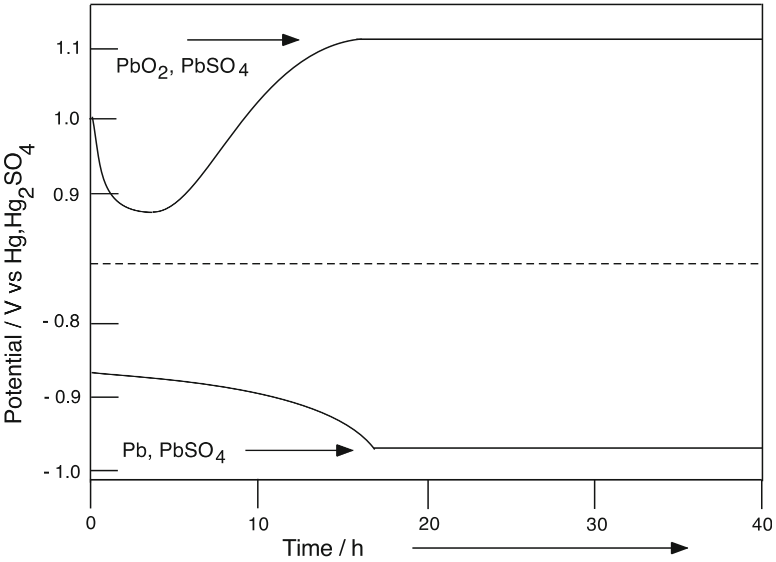

Fig. 17.3 Variation of the potentials of positive (*top*) and negative (*bottom*) electrodes during low rate formation process. After [12]

17.5.1 Volume Changes and Shedding

As is the case with a number of other battery systems, significant volume changes can occur in the electrodes as the result of the reactions that take place during charging and discharging. $PbSO_4$ has a substantially greater volume than both PbO_2 and elemental lead. The conversion of PbO_2 to $PbSO_4$ results in an increase of 92 %, whereas the change in volume from Pb to $PbSO_4$ is 164 %.

These volume changes can cause material to fall to the bottom of the cell, sometimes causing electrical shorting between adjacent electrode plates. In the past, when battery construction was different, it was sometimes found that apparently dead batteries could be "cured" by simply extracting this electrically conductive material from the bottom of the cells.

Whereas the electrodes in these batteries are generally flat, and assembled in stacks, a different configuration is also sometimes employed, in which the active electrode reactants are enclosed in porous tubes of an inert material, which serve to contain the active material, and reduce the shedding problem. Some manufacturers now encase each electrode in a porous plastic bag to prevent the results of shedding from shorting out the electrodes.

17.6 Alloys Used in Electrode Grids

The grid is generally considered to be the most critical passive component of lead-acid cells. It has two functions. One is to physically contain the active materials in the electrodes, and the other is to conduct electrons to and from the active materials. Both (relatively) pure lead and several lead alloys have been used in the manufacture of the grids in lead-acid batteries. There are two basic considerations, their mechanical, and their corrosion, properties.

Pure lead is quite soft, and although this might be an advantage in a mechanical manufacturing process, most grids are currently manufactured by casting liquid lead alloys.

Several lead alloys were developed in order to increase the mechanical strength of grids without significantly changing their electrochemical properties. Lead-antimony alloys were initially preferred. The phase diagram for this system is shown in Fig. 17.4. Compositions not far from the eutectic, which is 17 atom% antimony, are quite fluid, making it relatively easy to cast grids with relatively complex shapes. After freezing, the solid contains two phases, relatively pure lead containing a precipitate of finely divided antimony particles. The fine precipitate particles act to increase the mechanical strength of the lead.

Partly because of concern regarding the health issues related to the use of antimony—SbH_3 gas, which can form in the presence of moisture, is poisonous—attention was given to reductions in the antimony content from up to 11 wt% down to some 6–9 wt%. But with less Sb, they are not so readily cast, have

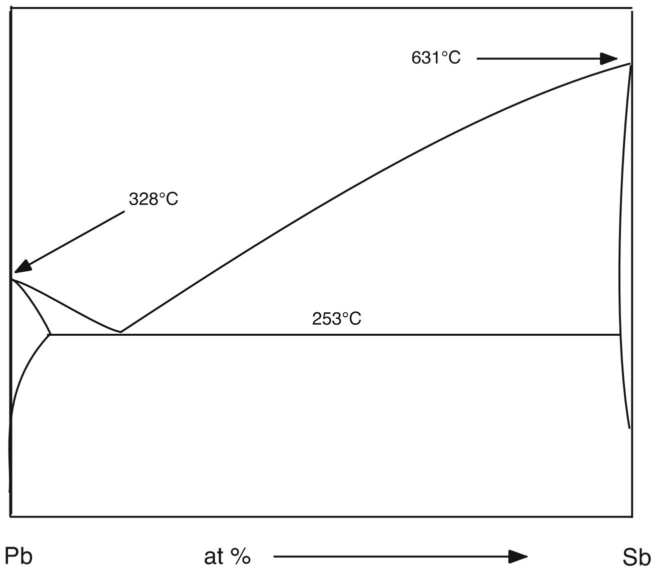

Fig. 17.4 Lead-antimony phase diagram

reduced mechanical strength and are less resistant to corrosion—especially if less than 6 % Sb.

Several other alloys were introduced subsequently. One direction that was followed by a number of manufacturers was the use of lead-calcium alloys, particularly in batteries to be used in float applications.

The phase diagram for this alloy system is quite different. Instead of having a eutectic reaction and appreciable solid solubility, as in the lead-antimony system, there is a peritectic reaction at low calcium contents at a temperature quite close to the melting point of pure lead. This is shown in Fig. 17.5. Since the solid solubility of calcium in lead is quite small and rather temperature dependent, it is possible to form fine precipitate particles of the phase $CaPb_3$. The microstructure of these alloys changes gradually after they are cast, resulting in age hardening, that increases the resistance to mechanical deformation by creep.

In addition, alloys in this system have good corrosion resistance at the potentials of the positive electrode. Their use in negative electrodes is generally thought to result in reduced hydrogen gas evolution.

A number of ternary alloys have also been explored. The presence of a small (0.5 %) amount of As increases the rate of age hardening, and provides better creep resistance, which is important for positive plates during deep discharging. Small amounts of Sn (2.5 %) increase the fluidity, making the grids easier to cast, and also give better cycle life.

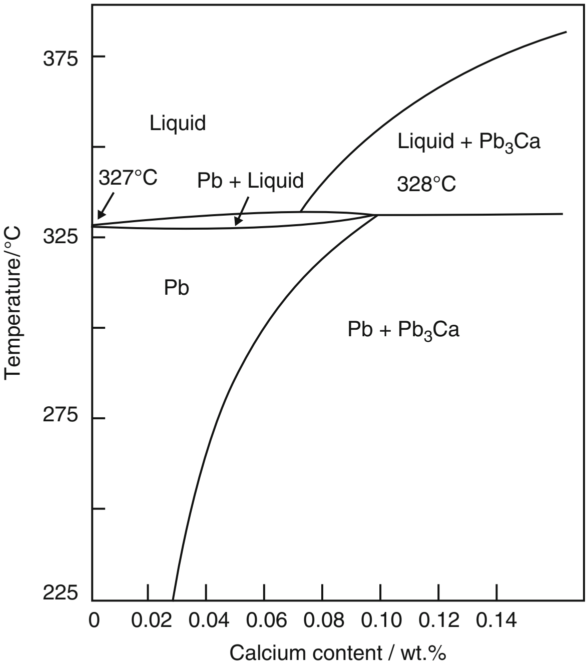

Fig. 17.5 Lead-rich region of lead-calcium phase diagram

17.7 Alternative Grid Materials and Designs

There have been several other approaches to the design and materials used in electrode grids. One of these involves strengthening the lead by the inclusion of fine glass fibers, or polymers.

An alternative that has also been explored somewhat is the use of partially reduced titanium oxides for the construction of grids for positive electrodes [18]. This material, which is primarily TiO_x, where x is between 1.75 and 1.8, is called by the trade name *Ebonex*.

17.8 Development of Sealed Pb-Acid batteries

For more than 100 years Pb-acid batteries were designed as “flooded” open cells, so that the hydrogen and oxygen products that are developed upon overcharge could escape into the atmosphere. To compensate for these losses, water (preferably distilled) had to be periodically added to the electrolyte.

The technology has now changed significantly, and most common batteries do not require water replenishment. In addition, the electrolyte is immobilized, so that these products are essentially "spill-proof," and can be used in any physical orientation, upright, on the side, or even upside-down [19].

There are two general approaches that are used. One of these is generally called "*gel*" *technology*, and was first developed by Sonnenschein in Germany [20]. The other is known as *"glass mat" technology*, and was initially developed by Gates Energy Products in the United States [21]. Both are now described by the general term: *valve-regulated lead-acid (VRLA) cells*. This name is related to the fact that a small pressure valve must be present in such sealed cells for security purposes. It reversibly opens if the interior gas pressure exceeds about 0.5 bar above atmospheric.

In the case of the gel technology, the addition of fumed silica, a very fine amorphous form of silicon dioxide that has a very high surface area, to the sulfuric acid electrolyte causes it to thicken, or harden, into a gel. Upon the loss of some water, this mechanically stable structure develops cracks and fissures that can allow the passage of gaseous oxygen across the cell from the positive electrode to the negative electrode upon overcharge.

The other approach involves the use of a highly porous microfiber glass mat between the electrodes. This mat functions as a mechanical separator, and also as a container for the electrolyte, which adsorbs on the surface of the very fine—e.g., 1–2 μm diameter—glass fibers. If the mat is only partially filled with the liquid electrolyte, there is also space in this structure for gas to move between the positive and negative electrodes.

In both cases, the cells are designed to be positive electrode-limited. This means that the capacity of the positive electrode is less than that of the negative electrode. The cells operate by means of an *internal oxygen cycle*, or *oxygen recombination cycle*. When the positive electrode reaches the limit of its capacity, further charging causes the decomposition of water and the formation of neutral oxygen gas:

$$H_2O = 2H' + 1/2O_2 + 2e^- \tag{17.9}$$

This gas travels through the gel or glass mat electrolyte to the negative electrode, where it reacts with hydrogen in the negative electrode to again form water, which can be written as

$$O_2 + 4H^+ + 4e^- = 2H_2O \tag{17.10}$$

The result is that the cell suffers self-discharge as the negative electrode loses capacity.

The latter reaction is exothermic, whereas the oxygen formation reaction is endothermic.

Upon charging, part of the electrical energy is consumed by the oxygen-recombination cycle and converted into heat.

17.9 Additional Design Variations

There have been several new approaches to the design of Pb-acid cells in addition to the standard parallel flat plate and tubular configurations. One of these is the bipolar concept, which involves the construction of a stack of cells that are connected in series. To do this, it is necessary to have an electronically- conducting bipolar plate that acts as a separator between the electrodes in adjacent cells. The negative electrode of one cell is on one side of the bipolar plate, and the positive electrode of the adjacent cell is on the other side. An example of such a configuration is shown in Fig. 17.6.

It is necessary to have seals to separate the electrolytes in adjacent cells in order to prevent current flow between them. It would also be advantageous to get rid of one of the current collectors, with one layer serving as the positive electrode for one cell, and the negative electrode for the other.

The simplest case is to have a metal sheet or foil act in this way. However, this requires that this metal be stable in contact with these two electrode materials and the potentials at which they both exist, e.g., reducing on one side, and oxidizing on the other side. Alternatively, one could have an electronically conducting nonmetal serve this function. One example could be graphite. Other materials might also be considered, such as oxides, nitrides, and borides, but they also have to meet the same requirements.

Another approach would be to use a bimetallic sheet, fabricated with one material on one side, and a different one on the other side. Such double-layer sheets could be produced by electrodeposition, sputtering, or other such processes. Simply rolling the two materials together might well be the best, and least expensive, method for modest to large scale applications.

A further approach would be to put metallically-conducting layers on both sides of a mechanical support material—perhaps a polymer or ceramic. These two conducting layers could be electronically connected by the use of holes through

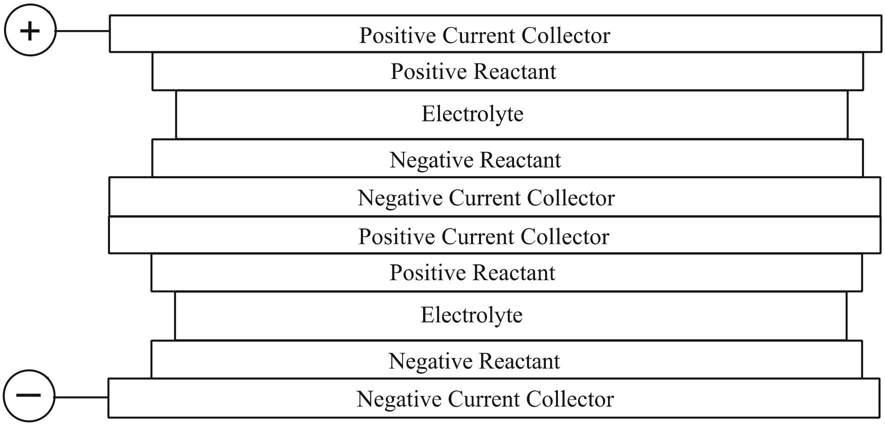

Fig. 17.6 Simple bipolar arrangement

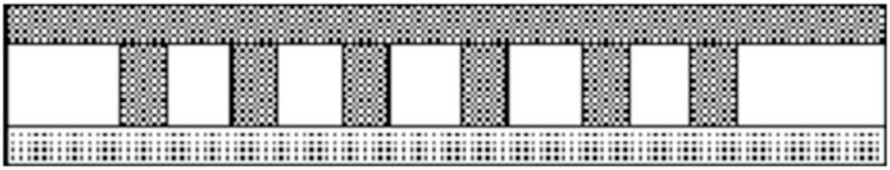

Fig. 17.7 Simple model of mechanically-supported three-layer bipolar plate

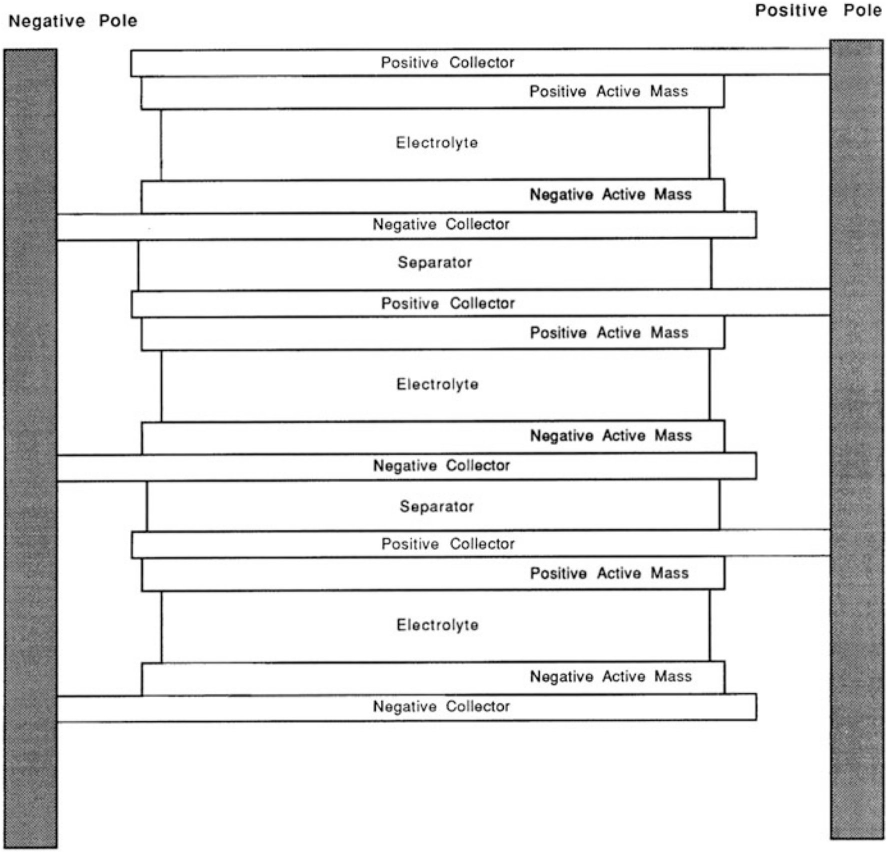

Fig. 17.8 Schematic representation of the Bolder thin-layer wound system

the support material. This might be represented schematically as shown below. In this case, one conductor is both on the top and in the holes, and the other is on the other side. This is shown schematically in Fig. 17.7.

Another design variant would be to enhance the power output, rather than the voltage. One approach to this was developed by Bolder Technology [22]. It involves the use of a spiral-wound thin layer concept that essentially places a large number of local cells in parallel. This is represented schematically in Fig. 17.8. But the construction is unique. Thin film electrodes, separated by a separator are wound into a spiral. They protrude out of opposite ends of a cylindrical can, and are electrically connected by melting and freezing caps on the two ends of the container. This provides a very large contact area, and produces a configuration with very low internal impedance. Such a design does not store much energy, but can operate at very high power for short times. In one application, starting power was supplied for internal combustion engines by a cell that is only 1/8 to 1/10 times the size and weight of conventional lead-acid cell designs.

17.9.1 Other Improvements

In addition to these innovative design changes, a number of improvements have been made in lead-acid cell components. One area involves the improvement of the mechanical properties, or the reduction in weight, of grid materials. One approach involves the use of mechanically expanded metal, rather than cast, grids. Another has been the development of extruded lead-covered glass fibers for grid structures.

Also, both polymer fibers and graphite particles have been introduced into the active materials in some cases to increase the mechanical strength or electronic conductivity.

17.10 Rapid Diffusion of Hydrogen in PbO_2

Experiments [23, 24] have shown that the chemical diffusion of hydrogen in PbO_2 is very fast, with a diffusion coefficient in the range of 0.4 to about $5 \times 10^{-7}\ \mathrm{cm}^2\mathrm{s}^{-1}$, varying with the potential, and thus with the hydrogen content. These values are some six orders of magnitude greater than hydrogen diffusion in MnO_2, which is the positive electrode reactant in the common alkaline Zn/MnO_2 cells. This very rapid diffusion explains why Pb-acid cells can provide such very high values of initial current, which is useful when they are used as starter batteries. The quantity of this proton-related charge is relatively small, however, only about 1 % of the total capacity of the positive electrode. Thus this effect does not last very long during a starting operation.

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