Lead/acid batteries

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Abstract

Lead/acid batteries are produced in sizes from less than 1 to 3000 Ah for a wide variety of portable, industrial and automotive applications. Designs include Planté, Fauré or pasted, and tubular electrodes. In addition to the traditional designs which are flooded with sulfuric acid, newer 'valve-regulated' designs have the acid immobilized in a silica gel or absorbed in a porous glass separator. Development is ongoing worldwide to increase the specific power, energy and deep discharge cycle life of this commercially successful system to meet the needs of new applications such as electric vehicles, load leveling, and solar energy storage. The operating principles, current status, technical challenges and commercial impact of the lead/acid battery are reviewed.

Operating principles

Charge and discharge reactions

The lead/acid battery has the unusual feature that both the positive and negative electrode reactions involve the same elements. At the cathode, or positive electrode, lead dioxide reacts with sulfuric acid to form lead sulfate and water:

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- = PbSO_4 + 2H_2O \qquad (1)$$
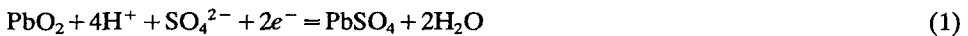
At the anode, or negative electrode, lead reacts with sulfate ion to form lead sulfate:

$$Pb + SO_4^{2-} = 2e^- + PbSO_4 \qquad (2)$$

The net reaction:

$$Pb + PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O \qquad (3)$$

is called the double sulfate reaction [1].

These processes occur by a dissolution/precipitation mechanism in which the Pb^{2+} ion dissolves and reprecipitates on to the surface of the electrode. Since the Pb^{2+} ion is only slightly soluble in sulfuric acid, the product maintains the porous structure of the plate relatively well during charge and discharge. An excellent review of these processes is available [2] and bibliographies of the recent literature are published periodically [3].
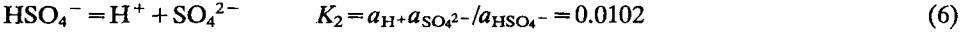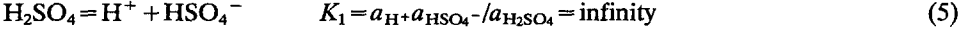
The thermodynamics of these reactions is well characterized [4, 5]. The Nernst equation for the cell potential is:

$$E = E^0 + 2.303(RT/F)(\log a_{H_2SO_4} - \log a_{H_2O}) \qquad (4)$$

where T is the absolute temperature in degrees Kelvin, R is the gas constant, 8.3144 J mol^{-1} K^{-1}, and F is the Faraday constant, 96 487 C per equivalent. The standard

cell potential at 25 °C is 2.048 V. Based on a cell voltage of 2.6076 V for 100% H_2SO_4 going to 100% H_2O, the theoretical energy density of the lead/acid cell is 218 Wh kg^{-1}. If we assume use of 40% H_2SO_4 and include the weight of H_2O, the practical theoretical specific energy of the lead/acid cell drops to 123 Wh kg^{-1}.

Sulfuric acid partially dissociates according to the following equilibria:

$$H_2SO_4 = H^+ + HSO_4^- \qquad K_1 = a_{H^+} a_{HSO_4^-}/a_{H_2SO_4} = \text{infinity} \qquad (5)$$

$$HSO_4^- = H^+ + SO_4^{2-} \qquad K_2 = a_{H^+} a_{SO_4^{2-}}/a_{HSO_4^-} = 0.0102 \qquad (6)$$

Thus, the electrolyte contains a mixture of hydrogen, sulfate and bisulfate ions which varies in composition with concentration and temperature.

The activity of any ion, a, is equal to γm, where γ is the activity coefficient and m is the molality (mol solute/kg solvent). For sulfuric acid:

$$a_{H_2SO_4} = (a_{H^+})^2(a_{SO_4^{2-}}) = (\gamma \pm 2m)^2(\gamma \pm m) = 4\gamma \pm 3m^3 \qquad (7)$$

where $\gamma \pm$ is the mean ionic activity coefficient using the common convention that the acid completely dissociates into hydrogen and sulfate ions. The formula:

$$a'_{H_2SO_4} = a_{H_2SO_4}/K_2 \qquad (8)$$

may be used to adjust the activities of sulfuric acid to the convention that the acid dissociates only partially into hydrogen and bisulfate ions.

The activity coefficient of water is related to the osmotic coefficient, Φ by the formula:

$$2.303 \log a_{H_2O} = -3m\Phi 55.5 \qquad (9)$$

Accurate values for the activity coefficients of sulfuric acid and water are available from 0.1 to 4 M H_2SO_4 at 5 to 55 °C and 0.001 to 8 M at 25 °C [4].

The cell voltage has only a slight dependence on pressure, P, which can be neglected in most normal applications. At 25 °C and an acid concentration of 3.74 M, $dE/dP = -3.32 \times 10^{-5}$ $\mu V/Pa$ (-4.81×10^{-3} $\mu V/psi$). Tables and equations for the pressure dependence have been published [5].
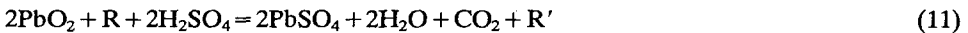
Self-discharge processes

The self-discharge reactions that limit the shelf life of the lead/acid battery were first reported by Gladstone and Tribe in 1882 [1]. Ruetschi and Angstadt [6] studied the reactions in detail in flooded lead/acid batteries. Later, Bullock *et al.* studied these processes in 'valve-regulated' lead/acid or 'recombinant' batteries [7] and batteries stored in a damp rather than a flooded condition [8].

On open circuit, the following reactions can take place at the positive electrode:

(i) oxygen evolution:

$$PbO_2 + H_2SO_4 = PbSO_4 + H_2O + 1/2O_2 \qquad (10)$$

(ii) oxidation of organics, R:

$$2PbO_2 + R + 2H_2SO_4 = 2PbSO_4 + 2H_2O + CO_2 + R' \qquad (11)$$

(iii) sulfation of residual PbO (primarily in newly formed cells):

$$PbO + H_2SO_4 = PbSO_4 + H_2O \qquad (12)$$

(iv) corrosion of the lead current-collector:

$$Pb + PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O \qquad (13)$$

(v) oxidation of alloying metals in the lead current collector, for example, antimony:

$$5PbO_2 + 2Sb + 6H_2SO_4 = (SbO_2)_2SO_4 + 5PbSO_4 + 6H_2O \qquad (14)$$

The reduction of hydrogen by PbO_2, which can occur at very high voltages and temperatures [9, 10], is negligible on open circuit [11].

At the negative electrode, two additional reactions can occur:

(i) hydrogen evolution:

$$Pb + H_2SO_4 = PbSO_4 + H_2 \qquad (15)$$

(ii) oxygen recombination:

$$Pb + H_2SO_4 + 1/2O_2 = PbSO_4 + H_2O \qquad (16)$$

The latter reaction is limited only by the diffusion rate of oxygen to the negative plate and can be very fast in valve-regulated lead/acid battery designs. Accordingly, these designs must be rigorously sealed to prevent self-discharge of the negative plate by atmospheric oxygen. The rates of the hydrogen- and oxygen-evolution reactions are primarily determined by the acid concentrations [6, 7]. Grid corrosion is accelerated at low acid concentrations, where the positive electrode potential drops into a region where Pb(II) compounds can form rapidly.

Overcharge and reactions

As the cell approaches 85 to 90% state-of-charge, the recharge reactions become less efficient, and the positive electrode begins to evolve oxygen:

$$H_2O = 2H^+ + 2e^- + 1/2O_2(g) \qquad (17)$$

At the negative electrode, hydrogen ions react to form hydrogen gas:

$$2H^+ + 2e^- = H_2(g) \qquad (18)$$

The net reaction is water electrolysis:

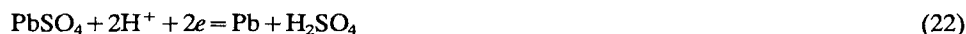$$H_2O = H_2(g) + 1/2O_2(g) \qquad (19)$$

Thus, hydrogen and oxygen are released from the cell in stoichiometric proportions.

A valve-regulated lead/acid battery, however, is designed to promote the chemical recombination of the oxygen at the negative electrode to minimize water loss. In the oxygen cycle, the reactions are as follows:

(i) positive electrode:

$$H_2O = 2H^+ + 2e^- + 1/2O_2(g) \qquad (20)$$

(ii) negative electrode:

$$Pb + 1/2O_2 + H_2SO_4 = PbSO_4 + H_2O \qquad (21)$$

$$PbSO_4 + 2H^+ + 2e = Pb + H_2SO_4 \qquad (22)$$

In this cycle, the oxygen chemically discharges the negative plate, preventing it from reaching a potential where hydrogen will evolve. Since the plate is simultaneously on charge, the discharge product is immediately reduced to lead, restoring the chemical balance of the cell. The net sum of these reactions is thus zero. Since no chemical change is occurring, the electrical energy input into the cell is converted to heat which must be dissipated from the cell to prevent overheating and overcharging. Some lead/

acid designs operate at up to 99% oxygen-recombination efficiencies, releasing only very small quantities of hydrogen and carbon dioxide under normal charging conditions [12]. The most efficient designs can sustain the oxygen cycle at charge rates up to between $C/4$ and $C/3$, where C is the rated capacity.

A number of papers have been published that discuss the charging and gas-recombination characteristics of lead/acid batteries. Hills and Chu [13] first studied gas recombination as a function of cell design and concluded that the oxygen cycle could be used to minimize water loss in lead/acid cells. Oxygen- and hydrogen-recombination rates in both gelled and absorptive glass mat (AGM) cells have been measured under a variety of conditions [11, 12, 14–16].

A complete schematic of the overcharge reactions that can occur in a valve-regulated lead/acid cell is shown in Fig. 1 [11]. It is assumed that metallic impurity levels are minimal. In addition to the oxygen-cycle and water-electrolysis reactions described above, several additional reactions occur on the positive plate that must be balanced either by hydrogen evolution or formation of the negative plate. These reactions include grid corrosion, formation of any residual lead oxides or sulfates in the positive plate and oxidation of organic materials such as soluble lignins. Thus, even if all of the oxygen produced at the positive on overcharge were recombined at the negative, some hydrogen evolution would still occur on overcharge when the negative plate is fully formed. This fact precludes the development of hermetically sealed lead/acid cells. Under float-charge conditions at room temperature in which the oxygen cycle is normally at least 99% efficient, the primary failure modes are water loss and grid corrosion. These are interrelated by the following cycle:
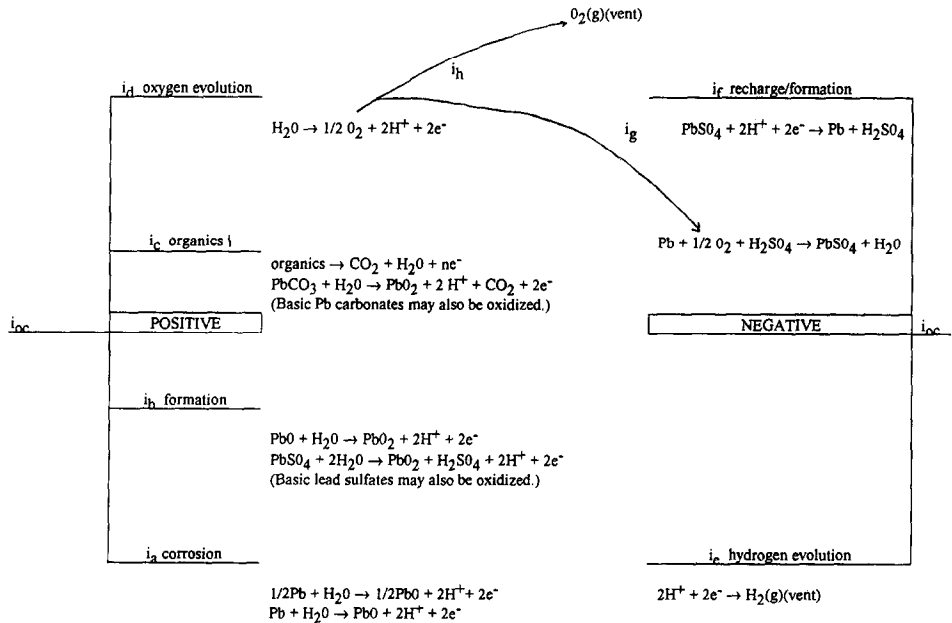
(i) positive:

$$Pb + H_2O \longrightarrow PbO + 2H^+ + 2e^- \tag{23}$$

Fig. 1. Schematic of reactions in a valve-regulated lead/acid cell on float or overcharge.

or,

$$1/2Pb + H_2O \longrightarrow 1/2PbO_2 + 2H^+ + 2e^- \tag{24}$$

(ii) negative:

$$2H^+ + 2e^- \longrightarrow H_2(g) \text{ (vented)} \tag{25}$$

The net reactions that account for most of the remaining 1% of the float current are thus:

$$Pb + H_2O \longrightarrow PbO + H_2(g) \tag{26}$$

and,

$$1/2Pb + H_2O \longrightarrow 1/2PbO_2 + H_2(g) \tag{27}$$

Fiorino [17] has accurately measured the rate of lead corrosion under float conditions.

Reviews of the literature on the kinetics of oxygen evolution on lead electrodes [18] and oxygen recombination in lead/acid cells [19] are available. Atkin *et al.* [20] studied and compared the recombination kinetics of oxygen on lead and cadmium.

Current status

Lead/acid batteries are produced commercially in a broad range of sizes and designs. These are categorized both by the electrode construction and by the electrolyte/separator configuration.

Electrode types

Electrodes are classified as Planté [21], Fauré or pasted [22], and tubular. Planté plates are made by cycling a high surface-area lead electrode in acid to form a thick corrosion layer of lead dioxide on the surface. These designs are used exclusively in industrial applications where very long life is desired and a high specific energy is not required.

Fauré plates are made by applying a lead paste on to a lead or lead alloy grid. The grid [23] is typically made either by casting molten lead in a book mold or by slitting and expanding or perforating a lead sheet. Because pure lead is a very soft material, antimony has been added since the 1880s to strengthen the lead and reduce grid growth. Unfortunately, antimony also accelerates water loss by poisoning the negative plate. Lead–calcium alloys were developed by Haring and Thomas in 1935 [24] to minimize gassing and grid corrosion. The use of lead–calcium alloys led to the introduction in the 1970s of low-maintenance batteries that do not require water addition.

The lead paste that is applied to the grid is prepared by mixing a powdered lead oxide with sulfuric acid and water, and then 'hydrosetting' the plate at high temperatures and humidities to form a hardened porous structure composed of lead oxide and basic lead sulfates. Both positive and negative plates are made in the same manner. When opposing positive and negative plates are charged or 'formed' in sulfuric acid, PbO_2 is formed at the positive and Pb at the negative electrode.

Tubular plates are formed in a similar way. The plate is constructed, however, by packing the lead oxide powder into porous vertical tubes made from chemically stable fibers. Lead rods or spines are inserted down the center of each tube and are connected together in parallel at the top of the plate. The oxide is soaked or 'pickled'

in acid to form basic lead sulfates prior to the formation charge. Tubular plates are generally used only as positive electrodes with pasted negative electrodes. The tubular structure has the advantage of good deep cycle life, but is not as versatile as the pasted plate. Thus, pasted plates are used where low cost, high specific energy or power, or special grid or plate structures are required.

Electrolyte types

In most automotive and industrial lead/acid batteries, the cell stack is flooded with 30 to 40% aqueous sulfuric acid. Excess acid is found above and below the plates to provide additional capacity at low discharge rates. An electrolyte pump has been introduced in at least one commercial automotive battery to enhance performance and extend life [25].

Beginning in the late 1960s, small portable lead/acid batteries with immobilized electrolyte were introduced. The electrolyte is immobilized in two ways. In gelled lead/acid batteries [26, 27], the acid is mixed with finely divided silicon dioxide to form a thixotropic gel. AGM batteries, on the other hand, use a highly porous glass mat to absorb a limited volume of acid [28, 29]. Both the gelled and AGM batteries operate on the oxygen cycle during overcharge to minimize water loss. Because their pressures are regulated with a one-way pressure relief vent, they are also known as valve-regulated lead/acid (VRLA) or sealed batteries.

Over the past decade, these small VRLA batteries have been scaled to sizes up to 3000 Ah for industrial applications such as uninterruptable power supplies (UPS), telecommunications and load-leveling [30–32]. Although the original designs were made with pasted plates, commercial tubular designs are now available using gelled electrolyte [30] and development of tubular AGM batteries in ongoing. Valve-regulated batteries have also been scaled down to smaller sizes for portable power applications, such as stereo headphones and laptop computers. For example, a 2 V, 0.28 Ah per AGM battery is now available in a thickness of only 6 mm [33, 34].

The largest market for lead/acid batteries today is in starting, lighting, ignition (SLI) or automotive applications, which require high power. During the past two decades, significant increases in the specific power and energy of automotive batteries have been achieved by reducing battery weight, increasing material utilization and minimizing internal resistance [35, 36]. Efforts to increase specific energy even further by developing bipolar lead/acid battery designs are described below.

Lead/acid batteries have been designed with a 70-year float life [37], more than a thousand deep-discharge cycles [16], a specific energy of 40 to 50 Wh kg^{-1} [38] and power of 150 to 200 W kg^{-1} [39]. It is important, however, to understand that not all of these are achieved in the same battery design. Batteries must be optimized for a specific application by considering numerous possible performance trade-offs.

In addition to the battery design itself, the battery environment and electronic system have a strong effect on battery behavior and life. Improved approaches to charging, control and monitoring, thermal management, and maintenance are continually under development. Some of the challenges inherent in pushing out the limits of lead/acid battery technology are described below.

Technical challenges

Increasing specific power

Bipolar batteries have several advantages that make them attractive for high-power applications [40, 41]. In a typical bipolar design, shown in Fig. 2(b), the cells
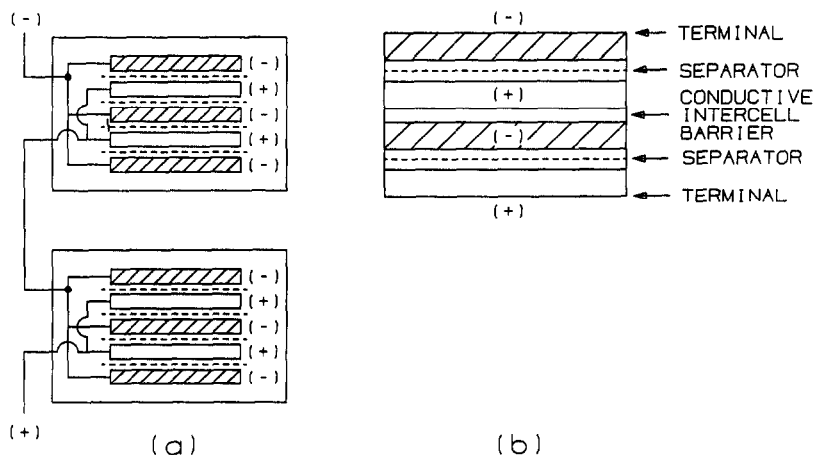
Fig. 2. (a) Comparison of monopolar (high capacity/low power) and (b) bipolar (high power/low capacity) battery designs.

are stacked to produce a high voltage in a small volume. The straps and posts that are required to carry the current in the monopolar design, shown in Fig. 2(a), are eliminated in bipolar batteries, reducing both weight and ohmic resistance. Since the poles in the bipolar design are at each end of the battery stack, the electron flow is perpendicular to the plate, ensuring a uniform current and potential distribution. The resistive losses that occur across the plate in the monopolar design are thus virtually eliminated. Consequently, the bipolar design can have a significantly higher peak power compared with a traditional monopolar design. A disadvantage of bipolar batteries is that the capacity (Ah) is low because each cell has only one set of relatively thin positive and negative plates. Because several plates can be connected in parallel in a monopolar cell, these designs have the advantage in low-power, high-capacity applications.

Battery models have been used to simulate the performance of bipolar lead/acid batteries and compare them with other battery types. As in all battery designs, power and capacity are complex functions of many design parameters, as well as the discharge rate and temperature. The peak power and sustainable current density depend strongly upon the discharge time. Table 1 summarizes the predicted performance of bipolar lead/acid batteries at high rates.

LaFollette and Bennion [42, 43] compared the power density of various rechargeable aqueous battery systems in bipolar configurations using a planar electrode model at current densities from 0 to 60 A cm^{-2}. They concluded that the lead dioxide/lead system has the highest power density over this range. The silver–zinc battery has the second highest power density.

Kao [44] used the porous electrode model developed by Tiedemann and co-workers [45–47] to simulate performance of bipolar lead/acid designs discharged at a 30 s rate, with a goal of achieving 4.4 kW kg^{-1} and a total power of 50 kW. (For comparison, a monopolar automotive battery will deliver a specific power of about 0.2 to 0.5 kW kg^{-1} at a 30 s rate at room temperature [44].) Kao [44] concluded that achieving this goal would require a plate porosity of 70% or higher to increase the material utilization. Subsequently, he developed a high porosity plate with Bullock and Petersen [48].

TABLE 1

Estimated power of bipolar lead/acid batteries as a function of discharge rate

Discharge time	Current density (A cm^{-2})	Power density (W cm^{-2})	Specific power (kW kg^{-1})	Ref.
<100 μs	10–40		100–800	41–43
1 ms	10	7.7		43
2 ms			10–20	67
10 ms			6	84
1–10 s	1.5		1.6	85
16 s			3.6	44
30 s	0.6	1.08	50	86
135 s	0.28	0.5		49

Using the Tiedemann–Newman model, Wruck et al. [49] compared simulations of a monopolar automotive battery in a standard Group 58 size with a bipolar design of the same size at 25 °C and a cranking current density of 280 mA cm^{-2} to a 1.2 V cutoff. Figure 3 shows this comparison, along with the predicted performance of the alkaline zinc/manganese dioxide system under the same conditions. A 48 V automotive battery could have as much as 2.5 times the cold-cranking rate of a standard monopolar design [49, 50].

It is apparent from these simulations that bipolar lead/acid batteries could provide improved power densities in a variety of applications, including very high pulse-power discharges, capacitor charging, and aircraft and automotive starting [50]. Increasing use of electronic equipment in automobiles is demanding more and more power and energy from the automotive battery. For example, electrically heated catalysts can reduce automobile exhaust emissions by as much as 90% but require very high power and up to forty times the energy required to start the engine. Consequently, higher voltage (24 to 48 V) batteries are of interest to power automotive electronics, and bipolar designs are becoming more attractive [51]. They may also be useful in hybrid electric vehicles to provide peak power capability for acceleration [51, 52].

High-voltage bipolar batteries may also have advantages in stationary applications. Arias et al. [51] have pointed out that a higher voltage battery could reduce the weight and cost of small UPS by eliminating the power transformer. In telecommunications applications, it is conceivable that a single 48 V bipolar lead/acid battery could provide instantaneous power backup while alternative power sources such as fuel cells were automatically activated.

Bipolar batteries have not yet been commercially successful because of significant technical challenges which limit their life. As Bennion [41] noted, side reactions are greater than in monopolar designs because the thickness of the active material is much less relative to the current-collector area. This impacts on both shelf life and cycle life. He also noted that, although gas evolution is significant, bipolar designs need to be completely sealed to eliminate electrolytic short circuits which form when gases carrying acid spray are vented. Other major challenges in developing a bipolar design are finding a stable conductive substrate and removing heat from the battery interior during high-rate discharges and overcharge.

Many of the bipolar batteries that have been tested have used lead sheet as the substrate material. Although lead is a good conductor, the thickness of the lead is
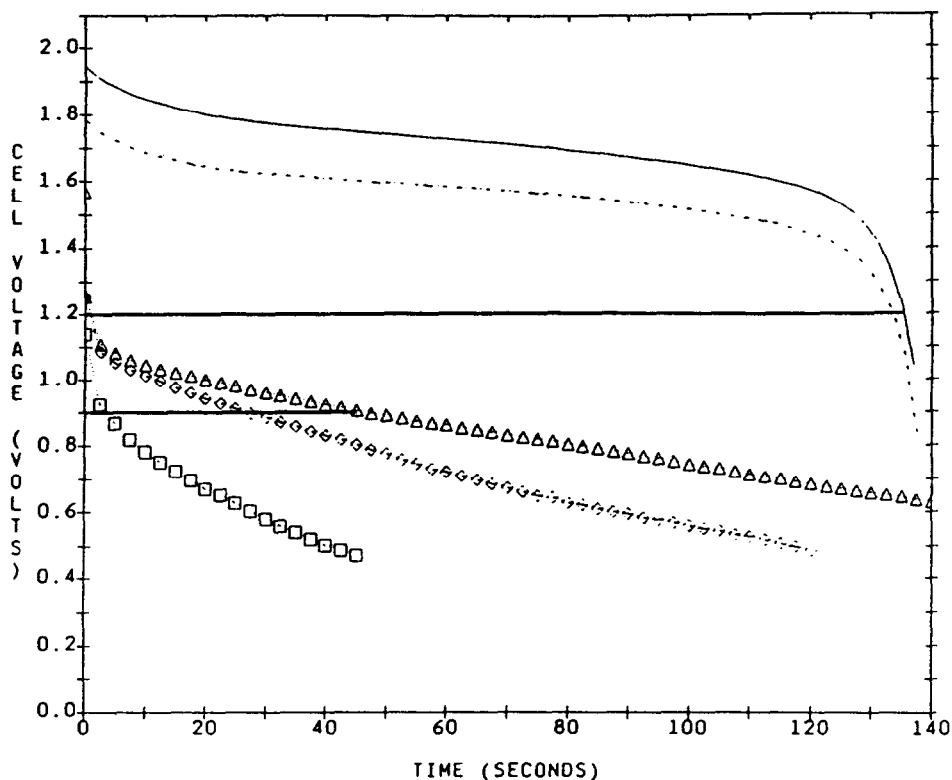
Fig. 3. Manganese dioxide compared with lead/acid for 25C high-rate discharges (280 mA cm^{-2}, 0.030 in thick). Manganese dioxide discharges are shown for a (□) bipolar design with present D cell cathode technology parameter values, (◇) doubled proton diffusivity and solution phase conductivity, and (△) quadrupled proton diffusivity with doubled solution conductivity. Lead/acid discharges are shown for (– · –) a present monopolar design and a (——) bipolar design. Reproduced with permission from *J. Electrochem. Soc., 138* (1991) 3560.

limited by its weight. On the other hand, the thinner the lead becomes, the faster it will corrode through and form an electrolytic path between cells, producing a short in the bipolar stack. Another problem is that self-discharge rates increase by an order of magnitude when only thin layers of lead dioxide are applied to a lead substrate [40, 53]. But in spite of these limitations, a number of bipolar battery designs that use lead substrates are presently under development with both pasted [54–56] and tubular [57] constructions.

In addition to the true bipolar designs under development, work on pseudo-bipolar designs is also ongoing [50, 58–61]. This type of design eliminates the top lead and posts. Nevertheless, since the electrons flow in a direction parallel to the plate surface in these designs, ohmic losses across the plate are not eliminated and the conductivity of the substrate is more important. Pseudo-bipolar batteries have cycled more than 600 times at a 2.25 h discharge rate to 1.75 V/cell [59].

Much of the research into bipolar designs has focused on finding alternative materials for the bipolar substrate that would reduce the weight and minimize the

side reactions in the bipolar battery. Alternative substrate materials must satisfy a number of criteria, including stability over the more than 2 V range of the lead/acid battery, high oxygen and hydrogen overvoltages, and good conductivity. In addition, the active materials must adhere well to the substrate and the substrate must be able to withstand, without cracking, the changes in the volume of the active material that occur during charge and discharge.

A number of conductive materials have been suggested as direct substitutes for the lead current collector, as fillers for plastic composite materials and as protective films that would protect current collectors made of lead or other metals from corroding. These materials include carbon [62–68], conductive ceramics such as the Magnelli phases of titanium oxide [69–73], transition metal oxides [74] and barium metaplumbate [75–79], as well as glass fibers coated with conductive tin oxide [80, 81].

Carbon is insoluble in acid and is stable in the negative plate, but it tends to decompose in the positive plate at potentials above 1.5 V versus a standard hydrogen electrode [82]. Rao *et al.* [83] evaluated the stability of a carbon–polypropylene substrate in 1.21 sp. gr. sulfuric acid under conditions found in the positive electrode on both open circuit and during charge. They reported slow evolution of oxygen and carbon monoxide even at open-circuit potentials. They estimated a life of years at 20 °C but only hours at 70 °C.

A variety of conductive ceramic materials has been investigated for bipolar battery substrates. Some of these materials have good stability and conductivity and adhere well to the active materials. The brittleness of ceramics is a disadvantage that can lead to cracking and shorting when they are stressed by the volumetric changes that occur in the active materials during charge and discharge. Hayfield [69] has patented the use of the conductive Magnelli [70] phases of titanium oxide as electrode materials. These phases range from Ti_4O_7 to Ti_5O_9 and are chemically stable in sulfuric acid [71, 72]. They have high hydrogen and oxygen overpotentials [73] and are electrochemically stable over the potential range of the lead dioxide electrode, but not over the potential range of the lead electrode. Unlike many ceramic oxides, lead dioxide and lead adhere well to these materials. Their narrow range of non-stoichiometric compositions, however, makes bulk preparation of these compositions a challenge. At higher oxidation states, titanium oxide is not conductive, while at lower oxidation states the material dissolves in acid. One method used is to form titanium dioxide into the desired structure and reduce it with hydrogen to form the Magnelli phases. Although this is a commercially attractive approach, uniform conversion of the material becomes more difficult as the thickness of the titanium dioxide increases and its porosity decreases. Alternative processes are under development [73].

Bullock and Kao [75, 76] patented the use of barium metaplumbate ($BaPbO_3$) and other conductive oxides in bipolar lead/acid battery substrates. They used this material as a conductive filler in a composite conductive polymer, as a ceramic substrate, as a film in a lead–barium metaplumbate laminate, and as a non-corrosive coating on lead and other metals. They demonstrated that grids coated with barium metaplumbate and then plated with an outer layer of lead have reduced rates of corrosion and growth under high temperature float conditions [77]. Barium metaplumbate is electrochemically stable but decomposes very slowly in sulfuric acid to form barium sulfate and lead dioxide. The half-life of this material in 1.265 sp. gr. sulfuric acid at 20 °C was estimated to be 3.4 years. Lead dioxide stabilizes the material, however, and the lead coating protects it from acid attack [78]. Corrosion is inhibited because the barium metaplumbate sandwiched in between layers of lead provides a barrier to the solid-state transport of oxygen through the lead corrosion film to the underlying lead metal.

Another material that has been patented for use in batteries is glass fibers coated with tin oxide that has been doped with fluoride ion to make it conductive. A conductive composite material has been formed by filling a thermoset resin (such as epoxy) with these fibers [80]. A thin foil of lead is then attached to this composite with a graphite-filled epoxy adhesive to form a bipolar substrate. The fiber-filled plastic is coated with positive paste and the lead sheet with negative paste. Electric-vehicle batteries are under development using this bipolar plate [81].

Although much progress has been made in developing substrate materials and designs for bipolar lead/acid batteries, commercial products are not yet proven. Other problems such as sealing and heat removal need to be addressed to maximize the safety, life and performance of these designs. Bennion et al. [66] have shown that gas recombination can be enhanced by adding small quantities of polytetrafluoroethylene powder to a fibrous separator. Use of non-corroding substrates may also minimize hydrogen evolution, which is driven by positive grid corrosion, and reduce self-discharge rates. Because the materials and designs are radically different from conventional monopolar lead/acid batteries, development of low-cost, high-volume processes for manufacturing bipolar batteries will also require substantial effort and investment. But the need for smaller, lighter, more powerful batteries for applications such as electric vehicles is presently providing the incentive to continue the search for the elusive bipolar lead/acid battery.

Increasing specific energy and deep-discharge cycle life

Another major area of investigation is improving the specific energy and the cycle life of monopolar battery designs. These areas are coupled together because they are inseparable and often mutually exclusive. Automotive batteries will cycle thousands of times at a cranking rate, but the energy delivered per cycle is very small. On the other hand, batteries that are deeply discharged at low-to-moderate rates, may cycle only a few hundred times, because the material utilization is about an order of magnitude higher.

Potential new markets for batteries, such as load leveling, solar and wind energy storage, and electric-vehicle propulsion demand high specific energy and long cycle life. In the automotive market, the need to reduce vehicle weight and improve efficiency to increase gas mileage has also created a need for batteries of lighter weight and with higher specific power and greater reserve capacity. These requirements are providing an incentive for much of today's research and development.

Efforts to increase specific energy over the past decade have achieved 40 to 50 Wh kg^{-1} at moderate discharge rates [38, 39]. Nevertheless, the designs that yield these improved specific energies have not been mass produced for two main reasons. First, increased material utilization has uncovered new failure modes which must be overcome before long cycle lives can be achieved. Second, users have demanded low-maintenance, valve-regulated designs. Inherently, these have lower specific energy and typically do not cycle as well as the traditional flooded batteries made with antimonial lead alloys.

The main limitation to better material utilization is the transport of acid into the porous electrode. Acid transport can be enhanced by making thinner or more porous electrodes or by enhancing acid convection. Extensive studies have been done on cells where the acid is forced through the electrodes [87–89]. If this approach proves to be successful, then energy densities of 50 to 60 Wh kg^{-1} could be achieved. Unfortunately, such high material utilizations stress the elecroactive materials severely and destroy

the structure and conductivity of the plate. These effects are particularly severe in the positive electrode, but appear to be less so in the presence of additives such as antimony, arsenic and bismuth [90]. Two models proposed to explain these effects are under active investigation: (i) the gel–crystal model proposed by Pavlov [91–93], (ii) the Kügelhaufen or agglomerate-of-spheres model proposed by Winsel and co-workers [94, 95] and Meissner [96]. It is hoped that by better understanding these phenomena, new ways of overcoming them can be found.

Another failure mode in deep-discharge applications is formation of resistive corrosion products on the positive grid. If the positive plate potential is driven too low by deep discharge, lead oxide and lead sulfate barrier layers can form and isolate the active material from the current collector. Electric-vehicle driving cycles show this phenomenon particularly clearly. The acceleration phase of the driving cycle forces the positive potential to very low voltages at the end of the discharge and this reduces cycle life compared with a constant-current discharge cycle [16]. Batteries constructed of pure lead or lead–calcium grids are particularly susceptible to this problem. Use of tin in the grid alloy improves the performance of low-maintenance or valve-regulated designs [97–100]. Addition of phosphoric acid to gelled electrolyte batteries also improves cycle life [27]. Phosphate promotes the formation of dense lead dioxide corrosion films that resist discharge to lead sulfate [101].

The failure modes that limit the cycle life of lead/acid batteries may be summarized as follows:
• shorting
• shedding of PbO_2 from the positive plate
• loss of positive plate and/or negative plate surface area, porosity or chemical conductivity
• contamination of the lead/electrode and, thereby, reduction of its charging efficiency
• corrosion of the positive plate current collector, sometimes with the formation of a resistive barrier layer between the grid and active material

Various battery designs have overcome these sources of degradation and, consequently, have pushed cycle life out farther. With each new advancement, a new failure mode appears and must be overcome.

The greatest problem in developing batteries with long cycle lives is the time required to cycle the batteries to failure. When a large battery cycles deeply over a thousand times, the testing of a new design will take at least a year. For this reason, accelerated tests are needed to minimize the development time. Unfortunately, accelerated tests are notoriously difficult to develop because degradation in performance must be accelerated without changing the failure mode. Proving that an accelerated test has achieved this also takes a long time. Developing a theoretical understanding of failure modes and a model that allows a simulation of the cycle life may be the best approach. Little has been done in this field because of the complexity of the problem and the computer resource required. Pattern recognition methods are being used, however, to study and predict failures in large battery strings [102, 103].

Battery design is only one aspect of making the technology work in new applications. The environment and electronic system strongly affect any battery's life and performance. The development of improved, lower cost electronics and microprocessors has opened up many new opportunities to improve battery systems. Battery charging, control and monitoring systems, and regulation of the environment are under active development. Although these efforts are beyond the scope of this review, their importance to the development of new applications should not be underestimated.

Commercial impact

The lead/acid battery is one of the most successful electrochemical systems ever developed. Although it was first demonstrated by Planté in 1859 [104] and many other storage battery systems have been developed since, the lead/acid battery is still the most widely used storage battery.

Lead/acid batteries are manufactured on every continent and in nearly every country. More than three-quarters of these products are used for automotive applications. In 1991, 238.3 million automotive batteries were shipped worldwide [105]. Other major applications include stand-by motive and portable power.

In spite of its success, the lead/acid battery is plagued by over capacity, commodity markets, niche markets, industry consolidation and the market's seasonal nature. Major new markets such as electric vehicles, load leveling and solar energy storage are still uncertain.

The average growth rate in the automotive market from 1983 to 1991 was 0.7% per year in Western Europe, 1.3% per year in North America and 5% per year in the Asian-Pacific region. The total annual growth rate for the Western World is only 2.6% [105]. In Eastern Europe, the average annual growth rate from 1991 to 2000 is estimated at 1.2 to 3.7% [106].

The average annual compound growth rate of industrial battery production is 4.0, 4.3 and 5.6% in the USA, Western Europe and Japan [107], respectively. The annual average growth rate for industrial batteries in Eastern Europe from 1991 to 2000 is estimated to be 5 to 10%. This is higher than in Western Europe because of the need to expand the infrastructure in these countries [106].

Of the industrial, markets, telecommunications and UPS have the highest growth rates. By 2001, stand-by batteries will be 55% of total industrial lead/acid battery production. Valve-regulated lead/acid batteries are becoming increasingly important; they account for more than 52% of total US stand-by power production and more than 60% of Japanese and European production [107].

Portable markets such as power for laptop computers and portable telecommunications are growing rapidly. In these markets, however, storage battery systems such as nickel/cadmium, nickel/metal-hydride, lithium and lithium-ion batteries are favored because of their higher energy densities.

The industry's principal hope is the environmental legislation driving the introduction of zero-emission vehicles. In the USA, California and New England are expected to force introduction of 116 000 vehicles by 1998. By 2001, 850 000 vehicles are projected nationwide. If 50% of these have lead/acid batteries, lead consumption will grow from 3000 tons in 1995 to 208 200 tons in 2000.

In Japan, MITI plans 200 000 electric vehicles by the year 2000 with 100 000 annual production. Projected worldwide sales, one-third of them in the USA, are shown in Table 2. In the next decade (and possibly longer), these vehicles will be powered primarily by lead/acid batteries [107]. Nearly all of the 181 electric vehicles presently in the US Department of Energy test program, as well as those scheduled for testing into 1996, are based on advanced lead/acid batteries [108]. This new market would require a substantial increase in battery production, and would give both the lead and battery industries a significant boost.

Lead/acid battery design and manufacturing technology will also certainly improve even more. When high power is required, the lead/acid battery has very little competition but research into alternative, higher energy density battery systems will continue. Because battery research is a highly specialized, difficult and slow evolutionary process,

TABLE 2

Projected world sales of electric vehicles

Year	Number of vehicles
1993	0
1994	5000
1995	15000
1996	75000
1997	140000
1998	275000
1999	480000
2000	850000

it is easy to forget that batteries are not stand-alone devices. History tells us that it is the battery system that succeeds or fails [109]. When battery technology meets the needs of the system, as in the case of automotive starting, it is a tremendous success. Key issues which in the past have made the lead/acid battery fail are high cost, short life and high maintenance. Other issues in some applications have included inadequate energy density and shelf life. Additional issues such as safety, environmental impact and material recycleability are becoming more critical then they have been in the past. Thus, many new challenges will have to be met in developing the distribution and recycling systems and the support infrastructure required for new markets.

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