Lead−acid battery research and development—a vital key to winning new business

Kathryn R. Bullock

C&D Technologies Inc., 1400 Union Meeting Road, Blue Bell, PA 19422, USA

Abstract

Battery strings are operated in a partial-state-of-charge mode (PSoC) in several new and changing applications for lead–acid batteries, in which the battery is seldom, if ever, fully charged or discharged. The lead battery industry faces new challenges as additional failure modes become evident in these PSoC applications. Without overcharge, cell imbalances caused by variations in cell temperature will cause premature failures. Valve-regulated lead−acid batteries are especially susceptible because of the heat generated by oxygen recombination at the negative plate. Improved thermal properties are shown by a proprietary battery design that combines absorptive glass mat and gelled acid technologies. Well-designed power systems are also required to reduce cell-to-cell temperature variations and, thereby, increase battery life.
© 2002 Published by Elsevier Science B.V.

Keywords: Battery design; Partial-state-of-charge; System design; Temperature effects; Valve-regulated lead–acid batteries

In the past, lead–acid battery designs have been optimized in several different directions for major industrial and automotive markets. Batteries for uninterruptible power supply (UPS) systems and telecommunications applications are designed to withstand a continuous charge at a low level with only occasional discharges at relatively moderate rates. Starting batteries are optimized to deliver short-term, high-power pulses with only rare deep discharges. Cycling batteries for vehicle propulsion are designed for regular discharges down to 20% of rated capacity and recharges at moderate rates to a full state-of-charge.

New opportunities and changes in use modes in traditional battery markets present new challenges in the design of batteries and power systems. The increasing use of computer networks requires better power grid reliability and, therefore, more batteries in the system. Standby-power batteries may be subjected to more deep discharge because of the decreasing reliability of the electric power grid. Discharge rates are increasing as back-up times decrease from the traditional 8 h to as low as 1 h.

Starting batteries are powering so many new electronic devices in vehicles that the automotive industry is developing a 42 V electrical system and is looking for a 36 V battery of higher power [1]. This new system will be used in the next decade to increase fuel economy and add new features for

comfort and safety. Valve-regulated lead–acid (VRLA) batteries and nickel–metal-hydride batteries are being considered to replace flooded lead–acid batteries. If another battery chemistry successfully replaced all automotive batteries, about 75% of the lead–acid battery market would be lost. This would have a profound effect on lead suppliers and recyclers and, consequently, would impact the economics of the industrial battery market. For this reason, the entire lead–acid battery industry should have an interest in the outcome of this shift in technology.

New utility applications, such as residential fuel-cell systems and solar systems, are emerging. Environmental constraints on the building of electrical generation and transmission systems, the need for increasingly reliable power, and security concerns are increasing the use of energy storage [2]. Batteries that are connected to the central utility grid have been designed up to 40 MW. Smaller, off-grid, fuel-cell systems that generate power close to the user site can reduce dependence on the transmission system. Fuel cells run more efficiently at a nearly constant load, but homes have high peak-power requirements as appliances are turned on and off. Thus, lead–acid batteries are used in conjunction with the fuel cell for peak shaving. The batteries provide about half the power for these peaks to minimize equipment costs and fuel usage.

Both flooded lead–acid and VRLA batteries are being used in solar energy systems. Successful commercialization

requires optimizing the system to maximize battery life and minimize the total system cost. Most systems are not grid-connected. These remote-area power supply (RAPS) systems are typically only 0.1–10 kW, but require a battery storage capacity of 1–100 kWh [3].

Operation of larger batteries and placement of batteries in remote sites and harsh environments introduce new challenges in the design of energy-storage systems. High maintenance costs are driving the development of remote monitoring capabilities. Methods of monitoring and controlling the battery state-of-charge and evaluating the battery state-of-health are improving. In the telecommunications industry, interactive electronic controls that adjust the charge voltages for temperature or limit the charge current have increased substantially the life and safety of VRLA batteries in harsh environments [4]. Similar optimization of the total power system will be required as new applications evolve.

In many of these new applications, strings of lead–acid cells are operated in a PSoC mode. Batteries are discharged to about 50% of their capacity but are seldom fully recharged. Battery designers face new challenges as additional failure modes become evident in these use modes. Without repeated equalization, cell imbalances caused by variations in cell temperature and manufacturing variables will cause premature failures. VRLA batteries are especially susceptible because of the heat generated by oxygen recombination and cell-to-cell variations in electrolyte volumes. Overheating in part of a cell string causes dry-out with grid corrosion and, in some systems, thermal runaway. Without improvements in life, the lead–acid cell could lose its dominant position in these new markets. To succeed, the battery industry must approach these challenges on several fronts. In addition to improving battery materials and design, ways must be found to reduce processing variables and manage total power systems [5].

Reducing variations in temperature is critical to success. Most battery failure modes are accelerated by high temperature. A good example is the premature sulfation of the negative plate in VRLA batteries used in hybrid electric vehicles (HEV) [5]. The batteries are typically charged and discharged at high rates in a narrow range around 50% SoC. Sulfation cannot be overcome because the batteries are not fully charged and the strings are not equalized. Rates of sulfate formation and re-crystallization are controlled by the solubility of the lead sulfate, the rate of oxygen evolution,

Table 1
Solubility of lead sulfate in sulfuric acid as function of temperature [6]

H_2SO_4 (mass%)	Solutions saturated with $PbSO_4$ ($PbSO_4$ mass% $\times 10^3$) (°C)			
	0	25	35	50
10.00	0.12	0.16	0.38	0.96
20.00	0.05	0.12	0.28	0.80
30.00	0.04	0.12	0.20	0.46
40.00	0.04	0.12	0.18	0.28

the rate of positive grid corrosion, and the rate of self-discharge. All of these processes are accelerated by temperature.

The solubility of lead sulfate as a function of acid concentration and temperature is given in Table 1 [6,7]. Acid concentration in a VRLA battery will vary between about 40 and 10 mass%. The increasing solubility of lead sulfate with temperature has also been well documented in pure water. Little, if any, study of the effect of temperature on lead sulfate morphology has been undertaken.

Zachlin [8] and Bullock et al. [9] have measured the effect of temperature on the rates of self-discharge in flooded and VRLA batteries, respectively. Temperature influences the rate of self-discharge in VRLA batteries significantly, as shown in Table 2 [9] for 2.5 Ah, D-size, cylindrical cells. This will be a significant issue in automotive applications if the battery is left on open-circuit or at a low discharge rate for long periods of time. Another application where self-discharge could affect the health of batteries is in solar systems, where discharge rates are typically very low. The data in Table 2 also show that addition of 0.1–0.8 wt.% phosphoric acid to the electrolyte of VRLA cells decreases the self-discharge rate at all temperatures. This may be because phosphoric acid additions reduce the surface area of the positive active-material [10].

Positive grid corrosion is one component of the self-discharge process that also occurs on charge. The corrosion rate varies with the positive-plate potential, as shown in Fig. 1 for pure-lead and lead–tin–strontium grids corroded in 5.1 M (39 mass%) acid at 49 °C [11]. The peak rate occurs at open-circuit, where a non-protective corrosion film composed of both lead(II) and lead(IV) compounds will form.

The effect of temperature on the corrosion rates of a lead–tin–strontium alloy at 1.10 V in 5.1 M (39 mass%) sulfuric acid is shown in Fig. 2. The voltage range in the passive region

Table 2
Rate constants for self-discharge of production 'D' cells [9]

H_3PO_4 (wt.%)	50 °C	55 °C	60 °C	65 °C
0	0.049[a] (0.002)[b]		0.10 (0.007)	0.16 (0.096)
0.1	0.045 (0.003)	0.049 (0.002)	0.089 (0.008)	0.13 (0.004)
0.8	0.036 (0.009)	0.041 (0.002)	0.063 (0.003)	0.12 (0.010)

[a] Rate constant in days^{-1}.
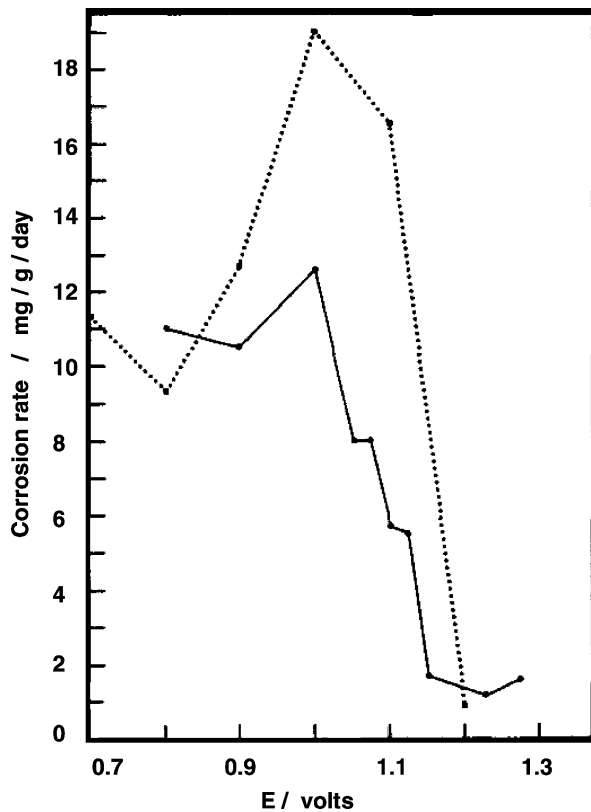[b] Estimated standard deviation, 1 s.

Fig. 1. Effect of potential on corrosion rate at 49 °C in 5.1 M H_2SO_4 [11].

corrosion rate is controlled primarily by the level of tin when the calcium or strontium contents are similar. Improved alloys have since been developed to reduce corrosion and negative sulfation, but reduced corrosion has caused poor adhesion of the positive active-material to the grid. Many of these failure modes are now understood [12] but more work will be needed as new applications and failure modes emerge.

The rate of oxygen evolution also increases with temperature. Oxygen evolution in flooded batteries that are routinely 'watered' is not detrimental. In VRLA batteries, however, higher rates of oxygen evolution cause both more rapid sulfation at the negative plate and faster loss of the electrolyte.

In some cells, greater internal heat generation and dry-out at high temperatures is tied to the increased equilibrium vapor pressure of the acid. Overheating thus causes dry-out with excessive grid corrosion and, in some systems, thermal runaway. Data for the standard fill gravity and a more concentrated acid, indicative of dry-out at the end-of-life, are shown as a function of temperature in Table 3. Vent pressures in large rectangular VRLA batteries are low compared with those in small cylindrical VRLA cells. This is necessary to prevent excessive bulging of the battery container. At high temperatures, the vapor pressure of acid can exceed the valve pressure in some designs and this leads to more rapid dry-out. A low-pressure vent, operating at 2–2.5 psig, will open when the temperature rises to 65–70 °C. Better case materials and improved valves are needed to prevent dry-out at high temperatures.

Improved VRLA cell materials and designs are being developed to increase battery life in new markets. The two VRLA technologies—absorptive glass mat (AGM) and gel—have been combined in a patented hybrid technology [13] that has the higher power density of AGM designs with the
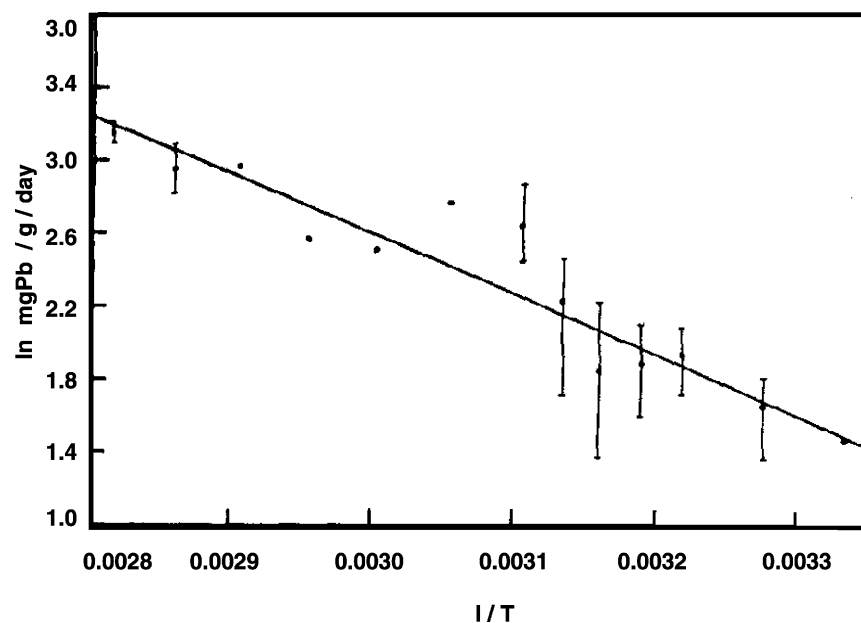
of the curve, where batteries are typically floated in standby applications, narrows as the temperature increases. This indicates that the lead dioxide film that forms during charge is less protective at higher temperatures. Lead–tin–calcium alloys behave similarly under equivalent conditions. The

Fig. 2. Effect of temperature (T) on corrosion rates of strontium–lead alloy grids at 1.100 V in 5.1 M H_2SO_4: mg Pb in corrosion film/g Pb in grid sample per day vs. 1/T for 4-day, constant-potential, corrosion test [11].

Table 3
Partial pressure of water vapor above sulfuric acid as function of temperature and acid concentration (mass%)

Temperature		Water (mm @ satn)	40% H_2SO_4		Equiv. r.h.[b] (%)	45% H_2SO_4		Equiv. r.h. (%)
°C[a]	°F		mm	psi		mm	psi	
25	77	23.756	13.5	0.26	56.83	10.9	0.21	45.88
35	95	42.175	24.3	0.47	57.62	19.7	0.38	46.71
45	113	71.88	41	0.79	57.04	33	0.64	45.91
50	122	92.51	53.9	1.04	58.26	44.7	0.86	48.32
55	131	118.04	69	1.33	58.45	57.5	1.11	48.71
60	140	149.38	87.3	1.69	58.44	73	1.41	48.87
65	149	187.54	110	2.13	58.65	92.3	1.79	49.22
70	158	233.7	138	2.67	59.05	116	2.24	49.64
100	212	760						

[a] Computed from data published in Chemical Engineers' Handbook, McGraw-Hill, 1973, Tables 3–3.
[b] Relative humidity: r.h.

improved thermal properties of gel designs. The cell stack has a compressed AGM separator between the plates and the area between the cell stack and the case is filled with gel electrolyte. This provides improved thermal transport and reduces cell dry-out. Cycle tests for a six-cell hybrid battery to 74% depth-of-discharge at room temperature are shown in Fig. 3 [14]. The battery delivered 930 cycles with minimal overcharge. The charging efficiency decreased at the end-of-life with the result that the cell temperature increased from about 30–40 °C. This is not as severe as the temperature rise that is often seen in commercial AGM designs. The performance of the hybrid design is being evaluated at a solar home in New Mexico under a typical PSoC duty cycle.

Although cell design is important, it is not sufficient to assure the success of the lead–acid battery in new applications. The battery industry must work closely with users to develop a power system that protects the battery from abuse and assures that power requirements are met. Historically, this has been the industry's greatest challenge. The telecommunications industry, for example, learned important lessons in making VRLA batteries more reliable by controlling the electronics and temperature of the system. Central office systems with controlled environments and flooded lead–acid batteries were introduced in 1939. Today, lead–acid battery lives of up to 30 years have been demonstrated in such environments.

Significant problems occurred when VRLA batteries were put in uncontrolled outdoor cabinets, especially in hot climates such as those experienced in southern parts of the USA. In 1968, Willihnganz [15] showed that the float life of stationary batteries is a function of temperature and used the resulting data to develop an accelerated life-test.
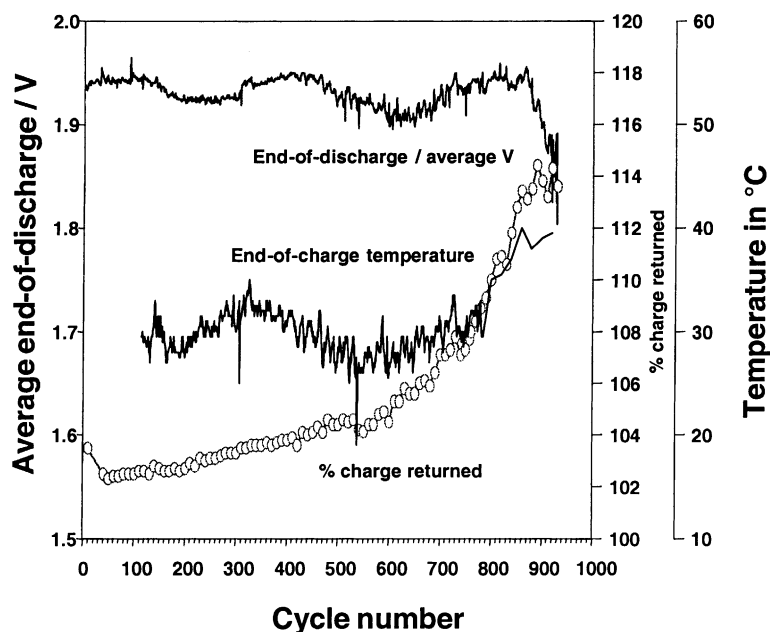

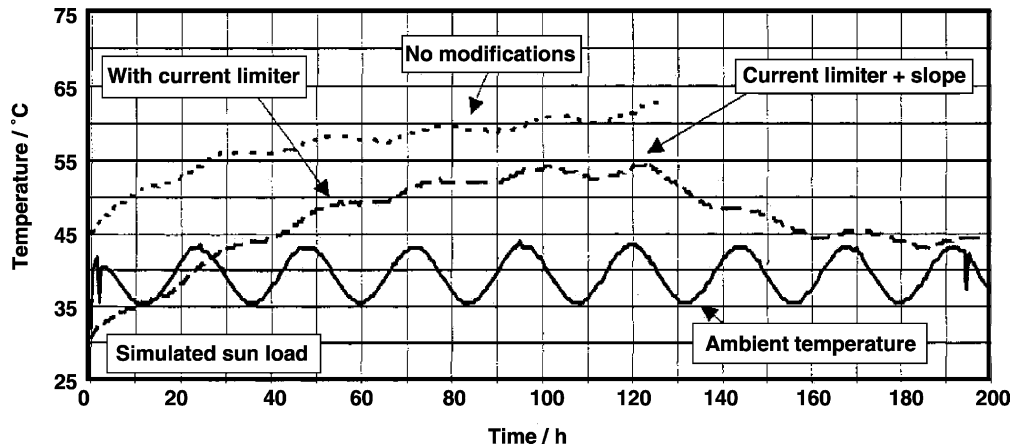Fig. 3. Cycle-life of VRLA battery with hybrid AGM + gel acid retention.

Fig. 4. Battery temperature with/without modifications [4].

It was found that for normal float operation, 1 year at 71 °C is equivalent to 36 years at 25 °C. The industry soon learned, however, that the lives of VRLA batteries in hot cabinets were even shorter than the predicted values. This is because the oxygen cycle in VRLA technology causes internal heating and thus the batteries are more susceptible to high ambient temperatures than are flooded batteries.

When the electronic architecture was changed from constant-current trickle charging to constant-voltage float charging, the float current was allowed to increase as higher temperatures reduced the battery internal resistance. The practice of including a redundant rectifier in each cabinet meant that the currents that could be produced were much higher than any battery could sustain. The result in hot climates was often thermal runaway, which occasionally became catastrophic.

The best efforts of the battery industry to develop improved battery designs could not eliminate all failures. Improvements in the outdoor cabinets were required to control the battery temperature. The batteries were installed at the base of the cabinet instead of on top of the hot electronics. Reduction in the float voltages as a function of the battery temperature was introduced. Modification of the battery charging profiles reduced the risk of thermal runaway. The effects that some of these system changes had on the battery temperature are illustrated in Fig. 4 [4]. The outdoor cabinet environment was simulated by cycling the temperature between 32 and 44 °C. Heaters outside the door of the cabinets simulated a solar load. Four strings of 48 V, 125 Ah, VRLA batteries were placed in the cabinet and float charged at 2.27 V/cell. The dotted line shows the temperature of a battery in the center of one string with no current-control device. The dashed line indicates the temperature of the same battery with a current limiter up to about 120 h. At this point, a patented [16] temperature compensation device (slope) was also added to the system. With the (slope) limiter alone, the battery temperature is significantly cooler than with no modifications to the system. At 55 °C, where temperature-compensation is added, the rectifier output voltage is controlled at the low-voltage limit. As the temperature begins to fall, the rectifier output voltage increases at a rate of 3 mV/°C per cell of battery temperature. The temperature levels off at about 44 °C, which is close to the maximum ambient temperature.

The importance of cooling cells in batteries both evenly and actively was demonstrated [17,18] for deep-cycling battery packs in early studies of electric vehicles. Forced air convection at 30 ft^3/min and 23 °C reduced the average cell temperature of flooded batteries from 45 to 36 °C. Nevertheless, the total temperature spread across the cells increased from 8 to 12 °C. In another experiment, the sides of the end cells and the terminal posts were insulated to maintain uniform cooling across all of the cells in a flooded battery module with circulating acid. At an average cell temperature of 33 °C, the temperature spread across the cells in a six-cell module decreased from 6 to 1.5 °C when the posts and cell end-walls were insulated. Maintaining even cell temperatures will extend the life of the battery significantly by maintaining electrical and chemical balances across the cells.

There are many such examples of the importance of good power system design in the quest for the reliable battery. Many of the market successes of the lead–acid battery have been due to improvements in battery materials and designs. On the other hand, improvements in the system design have been equally critical to success. The battery industry must work very closely with systems and electronic engineers to develop reliable battery applications in utility, automotive, telecommunications, UPS, and other industries. It must be remembered that battery reliability can only be achieved when the battery is well designed for the application and the power system is well designed for the battery.

Acknowledgements

References

[1] G. Iemmi, B. Dilecce, D. Macerata, P. Rena, J. Power Sources 105 (2002) 103–109.

[2] C.D. Parker, J. Power Sources 100 (2001) 18–28.

[3] R. Dell, D.A.J. Rand, J. Power Sources 100 (2001) 2–17.

[4] K. Bullock, D. Fent, P. Ng, in: Proceedings of the 17th International Telecommunications Energy Conference, IEEE Paper 95CH35824, 1995.

[5] P.T. Moseley, J. Power Sources 95 (2001) 218–223.

[6] H.D. Crockford, D.J. Brawley, J. Am. Chem. Soc. 56 (1934) 2600–2601.

[7] J.W. Lorimer, K.R. Bullock, in: Proceedings of the Paper Presentation at IUPAC Solubility Data Conference, Newark, NJ, USA, August 1986.

[8] A.C. Zachlin, Trans. Electrochem. Soc. 82 (1942) 365.

[9] K.R. Bullock, D.H. McClelland, Extended Abstract No. 17, vol. 75–71, Electrochem. Soc. Meeting, May 1975, J. Electrochem. Soc. 123 (1976) 327.

[10] K.R. Bullock, J. Electrochem. Soc. 126 (1979) 360.

[11] K.R. Bullock, W.H. Tiedemann, Extended Abstract No. 53, vol. 79–72, Electrochem. Soc. Meeting, October 1979, J. Electrochem. Soc. 127 (1980) 2112.

[12] R.D. Prengaman, J. Power Sources 95 (2001) 224–233.

[13] S. Misra, T. Noveske, U.S. Patent 4,863,816 (5 September 1989) and U.S. Patent 4,889,778 (12 December 1989), S. Gerner, U.S. Patent 5,376,479 (27 December 1994).

[14] S. Misra, A. Williamson, T. Noveske, K. Bullock, in: Proceedings of the 24th International Telecommunications Energy Conference, 2001, in press.

[15] E. Willihnganz, Electrochem. Tech. 6 (1968) 338.

[16] N.K. Bullock, D.G. Fent, T.V. Nguyen, U.S. Patent 5,623,195 (22 April 1997).

[17] B.L. McKinney, G.L. Wierschem, E.N. Mrotek, in: Proceedings of the Presentation at International Congress and Exposition, SAE Technical Paper 830229, Detroit Michigan, 28 February to 4 March 1983.

[18] W.C. Delaney, B.L. McKinney, E.N. Mrotek, C.E. Weinlein, in: Proceedings of the 19th Intersociety Energy Conversion Conference, vol. 2, Technical Paper 849446, San Francisco, CA, 19–24 August, 1984, p. 779.