

## A lead/acid battery for the new millennium

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### Abstract

Valve-regulated lead/acid battery technology is approaching maturity, but over the next several years many changes will continue to occur and the types of batteries at the beginning of the coming millennium will be considerably different than those of today. The requirements and potential applications for batteries in the year 2001 are reviewed. It is suggested that future development will focus on the power capabilities of lead/acid due in part to the limited improvements possible in specific energy. A technology overview addresses changes and requirements for grids, paste chemistry and processing, separator/electrolyte development, containers and vents, manufacturing innovation and auxiliary systems such as charging, thermal management and monitoring/control technologies. Conclusions are drawn relating to the battery characteristics, critical development areas and market opportunities. It is re-emphasized that the power advantages of lead/acid should be stressed relative to specific energy. Attention is drawn to similarities between nickel/cadmium and lead/acid, and it is noted that inherent weaknesses in lead/acid technology must be addressed and resolved.

### Introduction

Valve-regulated battery (VRB) technology can safely be characterized as being out of its infancy, but not yet to maturity. Technologists have extended flooded lead/acid chemistry and design to valve-regulated analogs, but the transition has not been seamless and there are many improvements being developed now and in the future that will significantly enhance the capabilities of this battery technology.

As we approach the beginning of a new millennium, it is tempting to speculate on what the state-of-the-art will be in the year 2001, i.e., what will lead/acid batteries be like then and what applications will they be slotted into? In general, the batteries will have much higher performance demands placed on them than exist now.

Perhaps the greatest shift will be in the areas of power and energy. To date, the lead/acid battery technology arena has seen most of the effort go into improvements in specific energy. This has steadily pushed specific energy levels up from 20–25 Wh kg<sup>-1</sup> to current development batteries that are approaching 50 Wh kg<sup>-1</sup>; the best mass-manufactured products are at about 40 Wh kg<sup>-1</sup>. The remainder of this decade will see energy raised to 45–50 Wh kg<sup>-1</sup> in what might be called ‘standard’ or conventional designs, while radical new batteries such as the Electrosource Horizon and various true bipolar lead/acid products may crack 50–60 Wh kg<sup>-1</sup>. Such levels are truly remarkable for lead/acid, but the effort and cost required becomes exponentially greater as specific energies are pushed above the current 40 Wh kg<sup>-1</sup>. In terms of energy, lead/acid is inherently limited by the high atomic weight of lead and the relatively poor utilization levels that are operative in the positive-plate chemistry.

Figure 1 graphically illustrates how the theoretical specific energy of the lead/acid system ( $258 \text{ Wh kg}^{-1}$ ) degenerates to the 50–60 range when the complete battery is put together [1]. While there may be some argument over the numbers involved, the overall impact is clear and it is obvious that there is not much room for improvement.

The herculean efforts required to bring lead/acid up to its highest levels become all the more questionable when one looks at systems like nickel/cadmium and nickel/metal hydride, which are at those levels now, and zinc/air, which can realistically achieve levels of  $200 \text{ Wh kg}^{-1}$ , albeit only in primary versions at present. This is not to concede the specific energy arena to other technologies and allow lead/acid to wallow at  $35\text{--}40 \text{ Wh kg}^{-1}$ . Improvements must be made and readily-manufactured lead/acid batteries with energies of  $45\text{--}50 \text{ Wh kg}^{-1}$  will find many new applications and keep existing ones longer than they might have at present levels.

Power has long been the forté of lead/acid in the workhorse automotive-battery products. Very high currents are drawn for short times for starting, lighting and ignition. This is generally done with thin-plate cells that have high active surface areas and close plate-to-plate spacing. Also, because the discharges are so shallow, lifetime is not an issue. This approach can be extended, in principle, to yield batteries with extremely high power levels that will increase present  $150\text{--}200 \text{ W kg}^{-1}$  levels to levels of  $1000\text{--}2500 \text{ W kg}^{-1}$  and possibly more. In applications where appreciable capacities are withdrawn from the cells, achievement of reasonable cycle life will be a development challenge. Figure 2 shows Ragone plots of power versus energy for current lead/acid products and what will be available in batteries in the year 2001.

These high power levels must also be sustained throughout the majority of the discharge, i.e., the products must exhibit long, flat plateaus, much like those seen in nickel/cadmium. The electric-vehicle goal of sustained power to at least 80% DOD

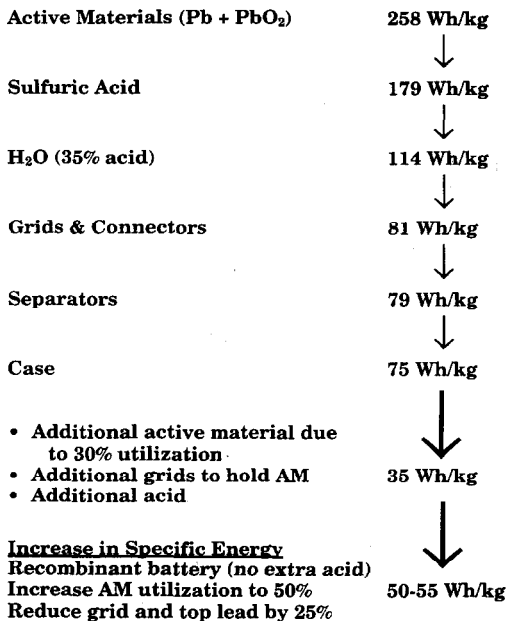


Fig. 1. Sources of specific energy reductions and improvements from theoretical active-materials level for the lead/acid electrochemical couple.

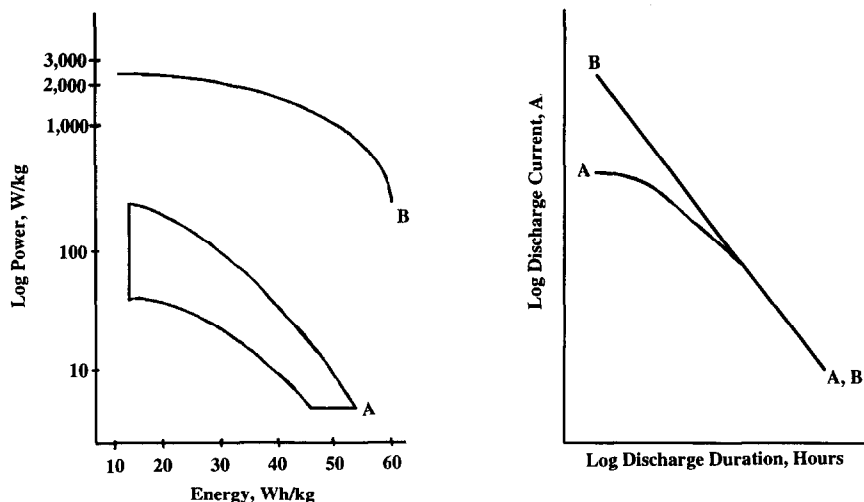


Fig. 2. Ragone plots for: (A) typical existing lead/acid batteries; (B) those projected for the year 2001.

Fig. 3. Peukert curves for: (A) typical existing lead/acid battery products; (B) those in the year 2001.

appears to be a realistic one. Such performance may also translate into more linear Peukert curves for these new batteries than for current products and, in the process, may extend useful discharge times up to much higher power levels than those presently available, as shown in Fig. 3.

Such power levels will be accomplished by developing radically new lead/acid cells with novel design features. Moderate improvements can be realized through the use of conducting additives in the positive plate, but the quantum leap anticipated must be accomplished by building products with impedances at least an order of magnitude lower than those seen in current products. This can be achieved through bipolar or pseudo-bipolar designs, and also by building conventional batteries with ultra-thin plates.

All of this must be accomplished with no compromise in cycle life. In fact, conventional stand-by batteries will be required to have float lives of at least ten years, even under realistic, abusive conditions common in many applications, and cycling batteries will possess the capabilities of furnishing at least 800–1000 deep-discharge cycles, even in the types of high-power batteries described above. In all products, premature capacity loss will have been eliminated through new developments and understanding of the roles of materials, processing and control of applications conditions.

### Applications

What types of applications will we see? Many will be the same as today, particularly in stand-by and traction applications. Stand-by batteries will have much better uniformity and longer life, in the drive to achieve the status of the battery as just another electrical component. This will be accomplished through improved manufacturing techniques, but also by developing versatile, inexpensive monitoring and control systems for large battery arrays.

Small VRBs will continue to be used in portable devices, toys, emergency lighting, etc., where flooded lead/acid products cannot be used. Products with high-power characteristics will continue to displace nickel/cadmium and nickel/metal hydride batteries in areas such as power tools and remote-control racing cars and planes.

Batteries in vehicles will not even remotely resemble the single 12-V automotive unit of today. Because of ever-increasing requirements for vehicle electronics and innovations such as electrically-heated catalysts (EHCs), 24- or 48-V batteries may be employed, or there may be a move to dual-battery systems, one a small power VRB for starting and the other a larger deep-cycling battery for electronics support. A single battery may be used for starting and the EHC; if possible, a 'do-everything' battery would probably be welcomed with open arms by automotive manufacturers. It is likely that most, or all, of these batteries will be valve-regulated and weight reduction will be vital.

Probably the most difficult applications for lead/acid batteries will be electric vehicles (EVs), partly because of the energy restrictions discussed above, but also due to the nature of the usage patterns. In large vehicles such as buses, trucks and even vans, flooded batteries may continue in use, but there will likely be pressure to develop VRBs in order to reduce weight and maintenance costs. The 'final frontier' will be passenger vehicles, in both pure electric zero-emission (ZEV) and hybrid ultra-low emission (ULEV) forms. These will, of necessity, be VRBs, and probably in long strings. Design innovation will be required to achieve specific energy levels of 50–60 Wh kg<sup>-1</sup> for ZEV applications. Lead/acid is ideally suited for hybrids, where power is the primary need, not only for acceleration and hill climbing, but for taking up regenerative braking energy. In addition, full recharge within 5–10 min appears to be an achievable goal with ultra-thin plate designs.

High-power lead/acid designs will also open up military and commercial applications based upon providing extremely high pulses of short duration to power lasers and other devices requiring intense, short energy inputs. For 2001, the development of high-power lead/acid batteries will probably be the most striking new applications area for our technology. The capability is inherent in the chemistry; all that is required is design and manufacturing innovation to package it.

### **Technology overview**

The keys to developing these types of products will be significant advances in materials, process and design technologies. The following is a brief overview containing personal views on what areas might be most amenable to development within the next 5 to 10 years. Some of these will doubtless lead to improvements which will go into the batteries that will be available in 2001.

### **Grids, current carriers**

While these components are 'inert' with regard to energy production from the cell, they have processing/performance characteristics such as mechanical strength, castability, corrosion resistance and conductivity that impact greatly on their selection for a particular battery. Cost and recycleability are less obvious, but nevertheless important, attributes. It will be important for the chosen grid material to have paste

bonding and 'controlled corrosion' properties that are similar to those of high-antimony alloys – but without the deleterious gassing properties of the latter.

Grid and top-lead alloy grain-structure may be at least as important as composition, as corrosion along grain boundaries may be an effective method of minimizing the effects of premature capacity loss that occurs through build-up of a passivating  $\text{PbSO}_4/\text{PbO}$  layer at the grid/active-material interface.

In summary, then, the materials used may be of the following compositions and/or have the following properties:

- thin, lightweight, but strong lead alloys: (i) Pb–Ca–Sn–Ag; (ii) composites (Pb/glass,  $\text{Al}_2\text{O}_3$ , fly ash, etc.)
- non-gassing alloys that mimic the paste bonding and corrosion properties of 6 wt.% antimony alloys: (i) Pb–Ca–Sn–Al, 2–3 wt.% tin; (ii) composites; In, Ge grid coatings
- sheet electrodes for ultra-thin plates (low current densities, low corrosion rates, therefore grid corrosion is not limiting)
- minimization of grid and top-lead weight through novel designs (Electrosorce, bipolar, etc.)

### **Paste/curing**

Paste composition and morphology need considerable work to take the 'black art' aspect out of the equation. In most applications, the positive active material (PAM) remains the limiting factor and, thus, the one that requires major attention. Put simply, PAM utilization levels must be pushed to 55–60% with maintenance or extension of cycle life; this may be accomplished via the following approaches:

- use of inert and/or conductive additives in the positive paste
- advances in curing technology to create better paste bonding to the grid, and a more 'open' pore structure that is maintained during cycling
- cell designs that promote constant, substantial compression
- proper paste porosity through optimal material balance (pastes:electrolyte:separator)

In applications that demand high power, and as the positive-plate efficiency increases, optimization of the negative paste will eventually become an issue, particularly in hostile usage conditions. The following areas of research may thus be fruitful:

- development of synthetic expanders tolerant of elevated temperatures
- electrolyte management that promotes formation of the negative and also optimizes discharge capacity
- development of paste morphology and cell design to allow efficient electrolyte access to the negative pores
- use of additives to create deeper open pores and/or improve the conductivity of the paste as the plate discharges

### **Separator/electrolyte development**

In valve-regulated products, the role of the separator is a critical one as it relates to distribution of electrolyte between the two plates and topographically into and across the plate surfaces. This is particularly true when cells/batteries are filled and formed *in situ* with the separator stack under compression. Depending upon the wicking action of the separator and the relative plate/separator porosities, as well as the surface areas employed, electrolyte will distribute unevenly to some extent, both within a given

cell and from cell to cell. As the separator void volume and plate pore film thicknesses have a direct bearing on the oxygen recombination process in VRBs, each cell will behave somewhat differently. The cells will go through and down from the voltage: time recombination 'hump' at different times. In batteries, this can lead to some cells being overcharged and others undercharged, particularly so in a large string such as in an EV battery.

It may be the case that a more uniform separator is the key to more uniform cell-to-cell behavior on charge/overcharge. Thus, an 'engineered' separator is necessary, i.e., one that has a more reproducible structure than the currently available random glass microfiber mats, gels, or even granular silica. It is relatively easy to have the same weights of pastes, electrolyte and separator in the cells of a VRB, but it is not always the case that identical electrolyte distribution follows. Separator composition, mass and structure should be given at least as much consideration as the other materials in the plate stack; the separator in the batteries of 2001 may be viewed as an 'active material', as it has a great deal to do with electrolyte distribution, and hence discharge capacity and even lifetime.

The composition and properties of the separator will be foci for intense research activity through the remainder of this decade. The separators used in 2001 will probably be silica-based (though not necessarily so), but because the surfaces can be chemically modified with ease (but at a cost) they may serve functions not now envisaged. Overall, the following areas of separator technology will be better defined, if not fully elucidated, by the year 2001:

- characterization of electrolyte distribution and movement
- effects of surface area, mass, chemical composition and compression on performance and cycle life
- development of a uniform, reproducible separator structure in the compressed, wetted state
- development of chemically modified glasses to solve important electrochemical problems

Recent publications [2, 3] have gone a long way towards characterizing the properties and functioning of VRB separators, but much more needs to be done on this most critical cell component.

### **Containers/vents**

The battery box (and, in the case of VRBs, the vent) can have a considerable impact on cell performance and life. In some situations, there can be a cancelling out of the advances in cell chemistry that have been painstakingly won. For the container itself, a wide range of considerations come into play in selecting a suitable material. In 2001, at least the following factors will be important in container selection:

- moldability, cost
- imperviousness to strong acid
- flame retardancy/oxygen index
- rigidity, low creep to maintain shape with high internal cell pressures (banding/metal sleeve?)
- good heat-transfer properties, ribbed to ensure air gaps between modules
- recyclability

The pressure-relief vent is a tiny part, often costing only a cent or two, but one that can have an enormous effect upon battery performance and life. Rigorous standards

will be applied to VRB vents in 2001. They will have to possess characteristics such as:

- resistance to chemical attack from materials such as persulfuric acid, ozone, H<sub>2</sub>S, SO<sub>2</sub> and SO<sub>3</sub>
- ≥ 1 000 000 operations
- capability to function as a flame arrestor (or flame arrestor furnished in the case design)
- operation as a true one-way valve

The issue of vent pressure is one that is often given scant attention in VRB design. A vent release pressure of several psi is often designed in, but it has been demonstrated [4] that too low a release pressure can result in oxygen ingress and resultant passivation of the negative plate, even on float if the ingress rate is sufficiently high and/or the float current very low. At the high end, it has also been shown [4] that elevated vent pressures can have a beneficial effect upon weight losses in valve-regulated cells, particularly at high overcharge rates. In applications where proximity to personnel is a problem, the resultant lower levels of gassing can also be a benefit. An optimal range for vent pressures will depend to some extent upon the vent design. For example, for the commonly used Bunsen valve, a minimal pressure of about 10 psi is advisable. The upper limit will usually be dictated by what the cell design can handle without distortion. The product design engineer of 2001 may find that efforts put into case design and material selection will pay off handsomely in an improved battery performance.

### **Manufacturing innovation**

The best-designed battery, if poorly manufactured, will be a disaster. In the push to overcome the intrinsic chemical variability of the VRB and to have the unit achieve the status of 'just another electronic component', the battery manufacturer must be innovative and flexible. This is particularly true in some of the emerging applications that involve long strings of cells such as UPS, Telecom and EVs. Uniform manufacturing will lead to more uniform performance. Given the above-mentioned chemistry of the VRB system, however, complete uniformity may not be as achievable as with flooded lead/acid systems. Some variation may be inevitable, but the 'zero defects' approach of largely eliminating obvious infantile failure sources will go a long way towards raising the image of the lead/acid industry and towards improving battery system reliability. Particularly in the EV arena, manufacturing cost will be a constantly moving target (always downward!), as this is a principal advantage of lead/acid over most other battery technologies. The enviable record of the lead/acid industry on recycling will have to be improved from its remarkable current level of 95–98% in the USA to virtually 100%, worldwide, even for small VRBs, which are now usually discarded. For larger batteries in applications such as EVs, manufacturers may have to focus on changing existing and creating new product designs to facilitate recycling. Standardization of case material may also become a reality.

In general, the manufacture of lead/acid products in 2001 may be recognizable by today's guidelines, but with concepts such as Total Quality and achievement of standards such as ISO 9000, as well as user pressure for ever-higher quality and regulatory pressure for ever-lower pollution levels, it may only be narrowly so. It is likely that lead/acid will be a truly 'high-tech' industry by the turn of the century, much more so than it is now.

## Auxiliary systems

Building a good cell or battery is no longer sufficient, and in the year 2001, with evermore sophisticated and demanding applications, it will be even less so. Many applications now being developed in Telecom, UPS and EVs, in particular, will require close monitoring of thermal and electrical conditions, and proper charging of large battery arrays is always difficult. In addition, for EVs the use of very fast charging will put an additional stress on the battery system.

In 2001, the batteries in use and applications may require specialized charging as used now for nickel/cadmium systems. In addition, charging is likely to be different for various uses and battery types. Whatever the situation, it is not likely that the relatively simple and inexpensive taper-current or constant-voltage (CV) charging now in use will be very prevalent then at that time. The following approaches may be in wider application, as determined by the battery type and cycle:

- multi-step constant current
- low-levels constant current in thermal runaway situations
- pulse charging
- intermittent charging with extended rest periods on float to extend life
- individual module charging for equalization

Thermal management of the battery environment will be of greater concern than it is today, and battery design will be done with hostile end uses in mind. Table 1 shows heat capacities and thermal conductivities for common battery materials [5]. Except for the electrolyte, a lead/acid battery is not a very good heat sink and transmission of heat out of the battery and to the surrounding environment is hampered by the poor heat-transfer characteristics of the plastic case. Thermal management,

TABLE 1  
Thermal properties of cell/battery materials

Material	Heat capacity (cal g <sup>-1</sup> °C <sup>-1</sup> )	Thermal conductivity (10 <sup>-4</sup> cal cm <sup>-1</sup> s <sup>-1</sup> °C <sup>-1</sup> )
Pb	0.032	832
PbO	0.052	67
PbO <sub>2</sub>	0.085	76
PbSO <sub>4</sub>	0.067	105
Water	1.00	13.5
20% aqueous H <sub>2</sub> SO <sub>4</sub>	0.843	13.4
30% aqueous H <sub>2</sub> SO <sub>4</sub>	0.760	12.7
40% aqueous H <sub>2</sub> SO <sub>4</sub>	0.685	12.0
Air	0.24	0.82
Oxygen	0.22	0.64
Hydrogen	3.41	4.5
Polyethylene		8.7
Polypropylene	0.46	2.8
Polyallomer (Tenite)		3.0
Acrylonitrile/butadiene/styrene	0.35	3.6–5.1
Polycarbonate		4.6
Polystyrene	0.30	



even in normal battery environments, is challenging [6], and in others its absence can have dire consequences [7]. Battery design and the complete system configuration will be critical in many applications as larger power levels are put into and withdrawn from ever-smaller batteries. Many of these applications will require some form of passive or active thermal management. It is likely that heat-transfer theory and techniques such as thermal imaging will be everyday items in the battery technologist's repertoire.

Monitoring and control of various battery and environmental parameters will be necessary in large systems such as EVs and load-levelling facilities. With the ever-increasing sophistication and decreasing cost of electronic components such as microprocessors, the use of battery management systems (BMSs) may be extended to relatively small batteries by 2001.

Monitoring of parameters such as voltage and impedance will be done routinely and readouts will be available for operators and/or maintenance personnel. Fault detection software will identify bad connections, weak modules, etc. Microchips may be built right into cells/modules and the monitoring and control functions will be controlled by a master microprocessor — all for the cost of only a few hundred dollars!

Control functions will also be exercised on charge/overcharge and discharge in order to equalize out-of-balance modules with the rest of the battery. This will extend both discharge performance and battery life, probably well beyond the relative costs of these benefits versus the price of the BMS. Batteries will not be replaced; rather, individual modules/cells will be exchanged during routine maintenance checks as they fail. The concept of 'x cycles per cell failure' will be used to characterize a battery rather than its overall life. Prompt removal of weak cells/modules will extend the life of the battery and reduce overall costs to the point where a BMS is more than justified. Obviously, chargers and vehicle/system electronics will have to be compatible with these BMSs (and vice versa) and the development of software algorithms to oversee battery systems will become a part of lead/acid technology.

## Conclusions

In summary, what will these batteries in the year 2001 look like? Clearly, they will be almost exclusively valve-regulated (or totally sealed?!) and they will be smaller, lighter and more powerful than today's lead/acid products — all this at reduced cost in terms of \$ per Wh. In addition, they will be more consistent, more reliable, and thus longer lived. They will, of necessity, be fully recyclable and 100% recycled.

Development efforts will focus on critical areas such as manufacturing consistency, 'engineered' separators, superior grid alloys, and totally new designs such as bipolar and ultra-thin-plate approaches now in the early stages of development. Auxiliary systems for thermal management and monitoring/control will receive increased attention; microelectronics will become an integral aspect of battery technology.

The specific energy range for 'conventional' deep-cycling products will approach, and possibly exceed, 50 Wh kg<sup>-1</sup>; novel designs will be at even higher levels. In 2001, it is likely that lead/acid will remain the dominant technology in zero-emission vehicles, or EVs. Hybrids will almost exclusively utilize lead/acid as the power battery.

In general, new markets will largely be created in the area of high-power applications. Lead/acid will be dominant in power tools and remote-controlled racing cars, and will be used exclusively in electrically-heated catalysts in automobiles. Some combination of VRBs will be used in internal combustion engine vehicles, both for engine starting and electronics support. Large stationary batteries for load levelling and spinning

reserve will be routinely used by utilities to increase the flexibility of their transmission and distribution systems. Lead/acid will be widely used in Telecom and UPS applications, but not without BMSs to achieve the longer lifetimes and reliability demanded by users at this time.

The relatively low cost and proven performance record of lead/acid will ensure that it remains a force in applications featuring high specific energies, but its dominance will slowly be eroding unless novel designs such as Electrosource and sealed bipolar are in large-scale production. Huge growth potential will be a reality at this time in high-power applications, and for very high-power uses ( $1000 \text{ W kg}^{-1}$  or greater) lead/acid will have a virtual monopoly among the various chemical battery couples available.

In the intervening seven years or so, lead/acid battery technologists will have to address and resolve weaknesses in VRB products (such as PCL, thermal runaway and sustained high-temperature operation) so that the technology can penetrate the majority of battery markets.

The long-heralded demise of lead/acid will not only be held at bay, but will be pushed to the back-burner. VRB technology will be in its ascendancy and approaching maturity, with most major problems resolved. Lead will have become virtually a one-product metal — batteries — but what a class of products! Markets will be expanding, profits will be rising and the lead/acid industry will be working in concert to solve common technical problems, but, simultaneously, will compete for market shares. As the new millennium dawns, life will be good for the lead industry.

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