

# An account of the development of the first valve-regulated lead/acid cell

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## Abstract

In 1967 work was begun on the research and development of small, cylindrical lead/acid cells containing spirally-wound electrodes. Four years later the resulting products were offered for sale: a cell equivalent in size to the conventional manganese dioxide D-cell, and another having twice the capacity. These cells were the first to use a separator material consisting of microfiber glass paper, now generally termed 'absorbent glass mat' (AGM). The sulfuric acid electrolyte incompletely saturates this separator, permitting oxygen gas transport directly through the separator to react with the sponge lead negative plate during overcharge of the cell. Thus, a recombination reaction is achieved which is analogous to that used in the sealed nickel-cadmium cell. A number of technical developments were incorporated, including substantial compression of the plate-separator assembly. This greatly lengthened the service life of these first 'valve-regulated' cells. In the following years, many sizes of rectangular batteries, using the principles described, have been manufactured throughout the world.

*Keywords:* Valve-regulated lead/acid batteries; Lead/acid batteries; D-cell; Microfiber glass separator

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## 1. Introduction

The valve-regulated lead/acid battery has rapidly become an important component of the worldwide battery industry. Today, both absorbent-glass-mat (AGM) and gelled-acid types are produced in large numbers for an ever-growing list of applications. The AGM type was the first to be produced commercially in a design intended to provide controlled oxygen recombination by gas transport directly through the separator, as had been done previously in the sealed nickel-cadmium cell. This commercial product was the D-cell, introduced in 1971 by Gates Energy Products (Denver, CO, USA.) This paper is a brief recounting of the development of that cell.

## 2. The project proposal

The beginning is found in a memorandum written by the writer to the management of Gates Corporation on 13 April 1965, entitled 'Lead-Acid Sealed Cells'. Briefly, the proposal recommended the development of a cell which would perform in a manner similar to that of the nickel-cadmium cell. The proposed cell would provide high-rate discharge capability and thus would employ a spirally-wound electrode configuration. The commercial significance of the cell was understood to be: (i) a cycle life adequate for many applications, combined with (ii) very low material costs — as

little as one-tenth that of the nickel-cadmium cell. It could thus be made in larger sizes and thus open up new application areas. Prospective markets included engine starting, portable medical and electronic equipment and power tools.

The list of development problems to be solved was never changed after this initial presentation. The most serious ones were felt to be: (i) provision of an adequate volume of acid, yet preventing any escape of acid; (ii) need to reduce or eliminate water loss during the life of the cell, and (iii) reduction or elimination of cell damage during prolonged storage in the discharged state. A quote from the memo: '...the oxygen recombination reaction used in alkaline cells appears to have no direct counterpart in the lead/acid system'. The crucial advantage of the alkaline cell, wherein no electrolyte component is quantitatively consumed during discharge, was recognized. The sealed nickel-cadmium cell operates very well with very little electrolyte. So the oxygen cycle potential of the proposed cell was viewed as unlikely, but nonetheless desirable. No plans were made at that time for achieving it.

At the time the memo was written there were two historic lead/acid products which were felt to indicate paths the development work might take: (i) the Willard low discharge (LD) cell, and (ii) the Willard electrolyte-retaining (ER) battery. It was recognized that the proposed D-cell would need to have a very low self-discharge rate because of the practical impossibility of recharging inventories of these cells periodically. The LD cell was a development of Rose and Zachlin

[1], first used in navigation buoys. Its features and characteristics are fascinating: (i) grids were pure lead and about 24 mm thick; (ii) design discharge rates were between 2000 and 9000 h; (iii) tests showed self-discharge rates of about 1% per month at 27 °C, and (iv) the largest cell, in a hard rubber container, yielded a specific energy of 46 Wh/kg. The cell used a high ratio of acid to active material, providing a flatter voltage–time curve. While the proposed cell was to have some very different attributes, the use of pure-lead grids was very appealing.

The ER battery was based closely on the familiar motor-cycle battery design, but used a very absorbent separator material: a fluffy cardboard made of redwood fibers. If inverted, the battery would not leak or spill. The memo proposal expanded a bit upon this idea, suggesting that the D-cell separator ‘should extend into all portions of the interior so that no electrolyte becomes permanently inaccessible to the cell processes’.

The manufacture of a spirally-wound cell element was viewed as solvable by hard work and ingenuity.

Estimates of development costs for the D-cell were very much too low.

### 3. The development process

Gates’ interest in battery manufacturing was based upon advice from a consultant who had been charged with the task of finding diversification opportunities. Work on nickel–cadmium and nickel–zinc battery systems was recommended. One result was that the writer began a serious nickel–zinc sealed-cell development project in 1965. But only a small feasibility study was authorized for the lead/acid cell. This latter opportunity, however, was exploited unmercifully. Vendor contacts were established and much library work was done. Grids were planned to be made of longitudinally-expanded lead sheet purchased from vendors. This decision was based upon the writer’s only previous battery experience: twelve years in the development and manufacture of silver oxide zinc primary and secondary batteries. Expanded silver and copper sheet materials were used in those batteries. Grid material and oxides were procured in 1965, but used only in relatively few preliminary experiments.

All of the early work was devoted to learning ‘The Art of Lead Batteries’, almost none of it being recognizable in terms of silver–zinc technology. Valuable advice was obtained from Everett Ritchie of Eagle Picher and John Nees of National Lead. Both oxide vendors were then valuable sources of battery design and processing information.

We continued to look for competing commercial products. The only viable battery appeared to be the Sonnenschein Dryfit battery, a gelled-acid product. It employed a soft rubber check valve (retaining little or no pressure inside the battery) and detailed charging instructions which provided for a careful limitation of on-charge voltage to prevent gassing. In that period of time there appeared to be no expectation of achiev-

ing an oxygen cycle in the battery. In our work we had made the permanent decision to use the usual liquid acid, primarily because of the desire to achieve high discharge rates.

We could find no literature directed toward a practical lead/acid oxygen cycle. However, in 1966, an excellent review of the situation was presented by Ruetschi and Ockerman [2]. They proposed the use of a third electrode in the cell for oxygen reaction purposes. We were greatly interested in this paper, but did not feel that it led us toward a practical solution. Later, in August of 1969, Hills and Chu [3] reported experiments in which the oxygen recombination capability of a vertical, partially-immersed negative plate was measured, with and without a flooded microporous rubber separator in contact. They did not recommend using any sort of direct gas path from positive to negative surfaces, and thus we did not find value in terms of a practical design. (And we had by that time begun to verify oxygen recombination in our D-cells, see below.)

By mid-1967 a clear go-ahead had finally been received from Gates’ management and we moved rapidly. The first D-cells which cycled well were made in October 1967, by Marvin Walker, a technician, and the writer. They were housed in polystyrene pill containers. Their design included expanded lead–calcium grids and paste recipes based upon Ritchie’s recommendations. The separators were a special phenolic-treated cellulosic paper which was flexible enough to wind up. The cells were sealed as well as tape and glue would permit. As sometimes happens, their performance was not significantly exceeded by cells made during most of the following year.

Also in 1967 we became aware of the unspillable miners lamp batteries which used a latex-bound diatomaceous earth separator. This design did not yield usable ideas.

During late 1965 the writer became acquainted with Donald McClelland, whose battery experience had also been limited to work on silver–zinc cells. Months later he joined our group and was assigned to the nickel–zinc project. Then in early 1968 he was transferred to the lead/acid work. He conceived and tested some hydrophobic material approaches to a recombination construction, but these did not work. (It is interesting to note at this point that the original D-cell development was carried out by McClelland and the writer, neither of whom had any previous experience with lead/acid cells, together with some technicians who had no battery background.)

By this time the D-cell capacity specification had been established at 2.5 Ah, a value still used today. The writer had also conducted the first exploration of the market for this product, with a very positive result.

The year 1968 was occupied with (necessarily simultaneous) work in optimizing formulations, processing parameters and mechanical details. A 960-cell computerized cell-cycling and data-recording installation was planned and implemented. Every cell could be cycled individually. Our pilot plant began operating in early 1969. It could, on short notice, transform an idea into enough test cells to be placed

on the big tester to give a meaningful answer. This combination of pilot plant and large tester was a key factor in our realizing the relatively-short total D-cell development time of less than four years.

But the separator was still a problem. A large number of synthetic non-wovens and treated papers were tried, in many combinations. By the end of 1968 McClelland was directing the D-cell project on a full time basis. The writer was now in the role of general manager of both development projects, both lead/acid and nickel–zinc (stopped in 1971).

During the first half of 1969 D-cell cycle life was still limited by water loss. Further design optimization was done, including grid alloy experiments. Because of our use of expanded grids, alloy choices depended more on their successful passage through the expanding machine, and our ability to paste and wind the electrodes, than on such important considerations as corrosion and growth in the positive.

In the middle of 1969, the scene began to change fast. Some cells containing a layer of treated cellulose paper and a layer of Whatman GF83 filter paper (microfiber glass) began to exhibit abnormally low water loss. As 1970 proceeded it became obvious that we were at last on the road to a true starved electrolyte, recombination design. A company the writer had used as a supplier of absorbent cellulose paper for silver–zinc cells (tea-bag paper!), C.H. Dexter Company, had mentioned its expertise in making various types of fiber glass paper, including those grades made of microfibers. Inquiries led to their furnishing us with a Type 225, which, as was our habit, was first used in combination with other materials. At last it was used alone. Many test cells later it was apparent that our cells now failed, at a life of hundreds of cycles, from grid corrosion and growth, with little or no readily-measurable water loss.

Final design optimization included many plate-compression experiments. In the 1960s it was commonly said that ‘lead–calcium batteries do not cycle well’. But the batteries in question did not typically incorporate any significant retention of the positive active material. Early in the project the writer had formed a (simplistic?) opinion: An abnormally-large pressure applied to the active material surface might accomplish two things: (i) it might reduce the electronic resistance in the interface between the grid and lead dioxide to such a level that there would be no inclination for a sulfate or oxide layer to form, and (ii) at the same time, ‘shedding’ of material would be impossible, and, again, electronic contact between particles of active material might prevent their becoming either detached or inactive. Accordingly, we employed that most ideal of dimensionally-stable structures, the cylinder, as our retention device. One has only to vary the length of the spiral electrodes and separators to obtain any degree of initial compression desired. This technique proved to be a vital element in the design of a long-lived cell.

As experience was gained in pilot-plant production of the D-cell a number of processing difficulties were recognized. The element winder was a persistent mechanical problem. It is no exaggeration to say that the formation of a starved cell

was by far the most troublesome operation. But deliveries to customers were going well in 1971. Larger cell sizes were introduced. In the early 1970s the grid form was changed to the use of a punched configuration. This avoided the dimensional instability of the expanded grid, which passed through the machinery only with great difficulty. The punched grid also could be made of pure lead, or a low-tin alloy, without losing its ability to be processed, as the punched configuration is inherently mechanically stable. Lastly, the plate lugs could be made solid, for much-improved terminal connections.

The present D-cell construction is shown in Fig. 1, furnished by Hawker Energy Products. The only significant change from the 1971 product is the grid. The following lead/acid cell design elements are believed to have been first commercially introduced in the Gates’ D-cell: (i) expanded grids; (ii) spirally-wound cell elements; (iii) plate compression for increased cycle life; (iv) glass microfiber separators; (v) direct oxygen transport across the separator; (vi) internal-expansion ‘Pop-Rivet’ terminals, and (vii) rubber-cap Bunsen valve. Hawker acquired the Gates Energy Products business, and now produces the original Cyclon (cylindrical) line, as well as the SBS batteries in Wales, UK, and the Genesis line in Warrensburg, MO, USA. Optima Batteries, of Denver, CO, produces a very long-lived SLI battery using the spiral construction. All of these batteries are direct, close relatives of the original work.

The basic patent on the Gates’ recombination technology, *US Patent No 3 862 861* [4], to D.H. McClelland and J.L.

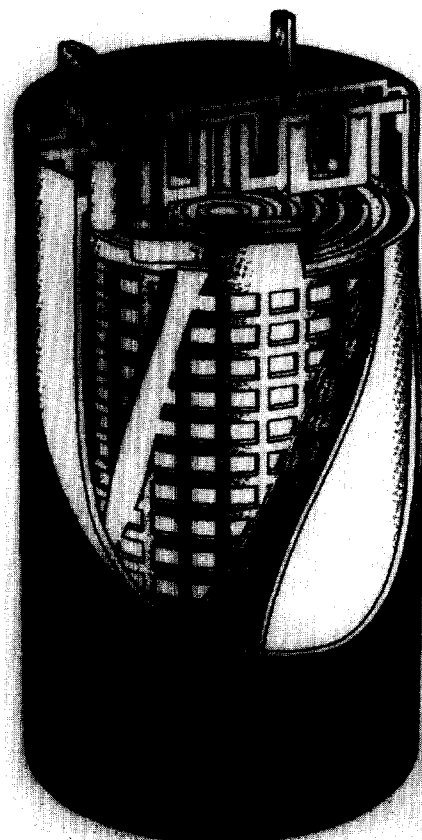


Fig. 1. The Gates’ D-cell, 1975.

Devitt, has been licensed throughout the world, and forms the basis for AGM technology. In addition, the Research Award of the Battery Division of the Electrochemical Society, for 'Research and Development of Lead/Acid Batteries using the oxygen cycle' was awarded jointly to the two above inventors.

Contributions of the following individuals are gratefully acknowledged, in alphabetical order: Willard Bundy, Curt Castleman, Lee Gillman, Karl Matthes, Barbara Papp, Tosh Uba, Doug Walker and Marvin Walker. It is with sadness that

we must acknowledge the death of Don McClelland in October of 1992. His contributions, particularly in the latter phases of the original D-cell development, were crucial to its success.

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