

EVOLUTION OF GAS-RECOMBINATION LEAD/ACID CELLS AND BATTERIES

R. F. NELSON

Gates Energy Products, Sealed Lead Division, Warrensburg, MO 64093 (U.S.A.)

Introduction

From the first work by Gaston Planté in 1859, flooded lead/acid batteries were the workhorse in the portable energy field for the 100 or so years following their inception. Although many significant improvements and modifications were made over the years, the basic technology for flooded lead/acid chemistry/technology remained intact. In general, these advances were directed towards enhancements in energy density, cycle life, high-rate discharge performance, and the like, as well as towards improvements in processing and materials such as separators and grids. Parallel developments in grid materials led to improvements in castability and pasteability and, in the performance area, reduced gassing levels.

Two fundamental drawbacks of flooded lead/acid batteries were their heavy gassing levels on overcharge and their tendency to leak electrolyte. These restrictions limited the range of application and meant that the batteries could only be used in an upright position. The former shortcoming was greatly ameliorated by the development of lead-calcium and low-antimony grids, but gassing was still substantial and the presence of free electrolyte restricted their use.

In 1912, Thomas Edison was issued a patent [1], whereby he demonstrated that gases could be retained within a battery via combustion using a heated platinum wire. Several modifications of this approach followed, but it was not until the 1950s that anything of a practical value for the development of a sealed lead/acid battery system requiring no maintenance, capable of being used in any position, and having relatively modest levels of gassing during overcharge, emerged. Many methods were employed to recombine the hydrogen and oxygen gases given off during overcharge in a lead/acid battery during the 1950s and 1960s, and the success enjoyed by the practical application of oxygen recombination chemistry in the nickel/cadmium battery system lured electrochemists to the task of developing a similar technology for lead/acid batteries. In the past 20 years, this goal has been realized in a variety of commercially-viable products from a number of countries. This paper chronicles the history of the development of valve-regulated, recombinant lead/acid batteries from Edison's first demonstration of gas recombination to the present, when it is clear that the technology for

building recombinant batteries, while not fully understood, is approaching maturity.

Early studies on gas recombination

Most batteries, on overcharge, will produce gas(es) due to the overcharge reactions at one or both of the plates. In vented cells, these gases are liberated and the material consumed is periodically replaced, *e.g.*, watering in flooded lead/acid batteries. In order to develop a sealed battery that would not leak electrolyte, some method of consuming these gases would have to be found. Ideally, they would be re-converted to the material from which they were generated and thus there would be no net change in the cell chemistry, and the starting material would not have to be replenished.

Over the years, there have been many ingenious methods patented to accomplish gas recombination, starting with Edison in 1912 [1]. He proposed the use of a platinum wire or sponge in the head space of the cell. The platinum would be heated by the unit during the passage of current and thus would recombine hydrogen and oxygen gases generated during overcharge in either alkaline- or acid-based secondary cells. Thus, the water that had been decomposed from the electrolyte is regenerated and the need for periodic topping up is obviated. This approach was not converted into practice, at least partially due to the non-stoichiometric nature of gas evolution and the rapid deactivation of the platinum catalyst, as well as the possibility of explosions! Much later, Tichenor [2] augmented the platinum approach by proposing the use of auxiliary electrodes and sensing circuitry to maintain the proper stoichiometry by enhancing overcharge at one of the electrodes via independent charging. System complexity and cost, along with the aforementioned problems associated with the use of heated platinum catalysts for gas recombination, precluded commercialization of Tichenor's method.

In 1938, Dassler was issued two patents that specifically addressed the recombination of H_2 and O_2 gases in alkaline or lead/acid secondary cells using auxiliary electrodes [3], and exposed lead [4] approaches. The use of auxiliary electrodes was an extension of Edison's work, again to deal with the problem of non-stoichiometric gas quantities. Dassler [3] used high-surface-area electrodes of Pt, Pd, Ir, Rh or Ru held at potentials sufficient to ionize the hydrogen or oxygen and/or chemically recombine them catalytically on the electrode surfaces. The principles of the oxygen cycle were not laid out, but Dassler's work was important in establishing clearly the possibility of using one or two auxiliary electrodes to maintain low gas pressures in a secondary cell.

Using exposed top lead or auxiliary chambers, Dassler [4] extended this work and began laying the groundwork for elucidation of the oxygen cycle in alkaline and lead/acid cells. He focused, correctly, on the generation and recombination of oxygen by chemical reaction with negative active material housed in the cell head-space or in an adjacent chamber. Once spent, this

electrode portion would be immersed in electrolyte and electrochemically regenerated. In this paper, Dassler laid down the following principles upon which present-day sealed Ni/Cd and lead/acid cells operate:

- oxygen gas is generated by the overcharge reaction at the positive electrode
- this gas can then diffuse to the negative electrode with which it reacts chemically
- the negative active material is then re-converted electrochemically to its reduced metallic state.

Dassler's methods for recombining oxygen were cumbersome and impractical for large-scale production, but he did postulate several of the basic requisite ideas related to gas recombination and sealed-cell operation.

What is apparently the first complete explanation of the oxygen recombination chemical principle was proposed by Rublee [5] in 1942 for a $\text{PbO}_2/\text{Cu}/\text{H}_2\text{SO}_4$ electrochemical cell. He envisioned reaction of oxygen with the copper negative electrode at the surface of the electrolyte as the gas bubbled to the liquid/head-space interface. This approach was therefore another example of an 'exposed negative' system similar to that of Dassler [4]. Rublee's contribution was nevertheless unique in that he provided the following key elements for a complete picture of the oxygen cycle (in addition to those duplicating Dassler's hypotheses):

- provision for excess negative electrode (Cu/CuSO_4) capacity so that the negative would not go into overcharge and generate hydrogen gas
- re-formation of water at the negative electrode as a result of the chemical reactions between oxygen, the negative plate material, and the electrolyte.

Oxygen recombination and the development of nickel/cadmium technology

During and after World War II, nickel/cadmium (Ni/Cd) cells based upon oxygen-recombination principles were developed in Germany and elsewhere. In 1951, Neumann and Gottesmann [6 - 8] were issued a patent for 'Bureau Technique Gautrat' showing several methods for recombining oxygen in a fluid-tight alkaline cell. Most of the methods used were not practical on a commercial basis, but the following advances towards full elucidation of the oxygen cycle were put forth:

- presence of void spaces between the electrodes
- rudimentary exposition of an electrode thin-film condition
- de-activation of the recombining power of the cadmium negative electrode without electrochemical regeneration.
- stressing use of excess negative capacity to prevent hydrogen generation
- use of a safety valve or cell-wall rupture area.

At about the same time, SAFT came out with two patents addressing aspects of the gassing characteristics and recombination chemistry in Ni/Cd cells, the first [9] dealt with a rectifier circuit to kick out cells in a series string when they are driven into reversal on discharge and may generate explosive gas mixtures. The second patent, attributed to Jeannin [10], taught more fundamental design principles that tied gas management and oxygen recombination to the following cell-construction attributes:

- thin, high-surface-area plates, either sintered or pressed
- thin, gas-permeable separator, cotton or cellophane
- substantial compression within the separator/plate stack
- excess electrolyte with an appreciable portion held in the plate pores.

This approach did not entail the use of excess negative active material and was, instead, focussed upon a cell design that would minimize cell reversal upon deep discharge.

The problem of overdischarge was addressed in later patents using different approaches. Dassler [11] proposed the use of an antipolar mass in the positive electrode (*e.g.*, $\text{Cd}(\text{OH})_2$ or $\text{Fe}(\text{OH})_3$) combined with an overbuilt negative to reduce the amount of gassing when one or more cells in a series string would be driven into reverse during discharge. Thus, the positive, rather than generating hydrogen gas upon reversal, would experience reduction of the antipolar material. Smith [12] dealt with overdischarge of the positive by increasing its mass beyond that of the negative and adjusting the ratios of charged and uncharged active materials in the two plates at assembly. The focus was to prevent the build-up of hydrogen gas and it was conceded that some oxygen would accumulate due to reversal of the cadmium negative electrode, but that this would then be consumed at the beginning of recharge by reaction with electrogenerated cadmium metal. This patent was important because it contained several additional key elements in the recombination mechanism:

- reduction in electrolyte quantity to provide some void volume within the plate pores and between the plates
- a thin-film condition in the plate pores
- use of a microporous separator (here PVC) that would hold 'a substantial quantity of electrolyte'.

This patent clearly expounded the necessity for an unsaturated electrolyte condition in a Ni/Cd cell to facilitate direct oxygen transport from the positive to the negative plates within the bulk of the cell and not just in the head space above an electrolyte reservoir.

At about the same time, Peters [13] was issued a patent that taught the use of high-surface-area metal powders in the negative plate to enhance its ability to react with electrogenerated oxygen, but not plate-to-plate, rather in an adjacent gas space.

Through the 1950s and early 1960s, the recombination picture for sealed Ni/Cd was further augmented by studies [14] involving microscopic aspects of gas transport and oxygen reaction at the negative plate. It was estimated that negative-plate film thicknesses are typically in the range 10 - 30 μm and

that diffusion through this film, and not transport through the separator gas space, is rate limiting with respect to oxygen recombination.

Through these and other patents, as well as many literature articles not mentioned here, the proper functioning and manufacture of commercially-feasible Ni/Cd sealed cells were defined. Sealed operation was also achieved [15] for a variety of primary and secondary couples in this same time frame, but up to the early 1960s the known principles for the oxygen cycle had not been commercially applied to the lead/acid system.

Other approaches to gas recombination

Brief mention has been made above to several methods aimed at direct recombination or consumption of oxygen and/or hydrogen gases to keep internal cell pressures low and thus facilitate production of a truly-sealed lead/acid cell. In the 1950 - 1970 period, efforts were intensified to translate these concepts into commercially-viable products; the approaches used were the following:

- catalyst plugs
- auxiliary electrodes
- exposed negative electrode surfaces.

For various reasons, none of these provided the level of recombination efficiency necessary for widespread application at a reasonable cost and throughout a useful cycle lifetime.

Catalyst plugs

The gas-recombination work done on heated platinum wires by Edison [1] and Tichenor [2] are examples of catalytic recombination techniques, but later attempts at developing commercially-feasible products focussed on using catalyst plugs having high surface areas and enhanced chemical activity towards hydrogen and/or oxygen. Using a composite catalyst, Dyson and Sundberg [16] developed a lead/acid cell with limited, but substantial, recombination capability in a miner's cap lamp out to about 50 cycles. Voltage control was found to be critical and the life of the product was limited by build-up of excess hydrogen and residual carbon dioxide leading to deactivation of the catalyst. The two-stage catalyst limited the rate of recombination to levels that would not generate sufficient heat to create an explosive condition in the cell. Excellent recombination efficiencies were implied by the data until the cells failed due to excessive pressure build-up, particularly without tight charge-voltage control.

Catalyst plugs were used extensively in Japan in large cells up to about 2000 A h capacities [17]. The catalyst materials were in a high-surface-area pelletized form, typically being palladium or another platinum-group metal dispersed in an alumina or activated carbon body. The pellets were treated with either a silicone or fluorocarbon resin to impart hydrophobic properties to the catalyst. Watering frequencies were reportedly reduced to about 5-year

intervals and recombination efficiencies in excess of 95% up to overcharge levels of about $C/10$ were reported [17]. Apparently, performance was adequate and cost was not a prohibitive factor in these large stationary cells.

Catalyst plugs never gained wide acceptance due, in part, to the following factors:

- cost and materials requirements
- complexity of manufacturing, especially in small cells
- re-formed water freezing at low temperatures
- formation of electrolyte concentration gradients and possibly localized 'concentration cells' due to water being condensed and returned to the cell, leading to excessive top lead and/or upper grid corrosion
- early failure due to wetting, contamination, and/or sintering of the catalyst surface, leading to inactivation.

Auxiliary electrodes

The concept of the use of auxiliary electrodes to deal with non-stoichiometric gassing conditions was established early by Dassler [3] in his landmark patent. He proposed the use of single- or dual-electrode configurations to deal with hydrogen and/or oxygen generation on overcharge or over-discharge. Platinum-group metals were used for the auxiliary electrode materials and these were electrically connected to the two working electrodes. Recombination or gas consumption could be either chemical or electrochemical and would occur exclusively in the cell head-space. Some degree of voltage control was later developed using diode arrangements [18], and functioning lead/acid cells were constructed using graphite/silver [19] and mercury-type [20] single auxiliary electrodes for oxygen removal. Hydrogen generation was prevented by the use of excess negative active material.

The history, basic principles and functioning of auxiliary electrodes in lead/acid batteries have been clearly and effectively elucidated by Rüetschi [15]; approaches and applications in the Japanese market have also been reviewed [21]. Recombination efficiencies were reportedly excellent, particularly at low overcharge rates [21] but, again, commercial feasibility was limited by the following shortcomings:

- cost and complexity of manufacture
- loss of auxiliary electrode activity upon prolonged use
- sulphation of the negative plate adjacent to the auxiliary electrode, leading to unequal charge distribution on the negative
- long-term build-up of hydrogen and carbon dioxide gases
- decrease in energy density to accommodate the auxiliary electrode(s)
- limited effectiveness at high overcharge rates.

Exposed negatives/top lead

All lead/acid batteries will recombine oxygen to some extent on the surfaces of the top lead in the head space of the battery. Due to the low surface areas involved, this is usually very inefficient in flooded cells and, over the years, attempts were made to utilize portions of the negative plates

for recombination, starting with early patents employing a number of novel means to either replenish negative active material surfaces in the cell head-space [5 - 8], or provide auxiliary chambers [4]. All this work was developed for alkaline cells, but would also apply to lead/acid systems. Later studies [22, 23] were specifically targeted towards development of a sealed lead/acid product using exposed negative plates. It is interesting to note that the 'Noyper' battery line developed by Yuasa [23], which used exposed negative plate surfaces to recombine oxygen, also used a coarse glass-fibre-mat in conjunction with a microporous envelope layer as separator materials. Excellent recombination efficiency was quoted at overcharge rates up to about C/33, but it was not clear how this varied with battery ageing and different usage conditions.

Other approaches [24] to the use of exposed negatives for recombination involved the outside portions of the negative plates. While the cell was flooded, these outer plate surfaces had only thin films of electrolyte and could thus recombine oxygen fairly effectively.

These types of systems did not flourish for at least the following reasons:

- de-activation of the exposed negative area(s)
- reduced volumetric and gravimetric energy densities
- cost of additional paste, grid, and plastic
- limited ability to recombine oxygen at moderate-to-high overcharge rates.

Other systems, chemistries

Other approaches to developing a functional recombinant cell dealt with the use of gas, voltage, or pressure sensors to limit the amount of overcharge applied to the battery, the principal goal being to limit water loss by restricting the time a cell would be exposed to overcharge conditions, when most gassing occurs. Again, cost, manufacturing complexity and poor electrical properties prohibited a wide-scale application of these devices.

One product that was apparently on the market for a short time in 1963 was the 'Vesta' cell put out by the Yagashita Electric Company of Japan. It was purported to be a completely sealed cell with excellent cycle-life and rechargeability properties. Very little information is available on this product, but it apparently recombined oxygen with carbon auxiliary electrodes near the backside of the negative plates. It was rated at only 1 A h for a D-size cell.

Two patents issued to Abramson in 1965 [25, 26] disclosed a novel electrochemical couple that could operate on the oxygen cycle, namely, $\text{PbO}_2/\text{Sb}/\text{H}_2\text{SO}_4$. It was pointed out that the technology could be extended to traditional lead/acid or Ni/Cd systems. These patents dealt primarily with means for equalizing capacities of unbalanced cells in a battery, and it is not clear how recombination was achieved and with what efficiency. This chemistry was further elucidated by Rüetschi [27], purportedly in a sealed recombinant cell, but no details were provided for a commercially-feasible product.

Early immobilized electrolyte systems/gel technology

All of the abovementioned approaches to gas recombination to allow a sealed construction for lead/acid batteries were basically flooded systems and the physical and electrical restrictions on their general usage were fairly stringent. Auxiliary materials added to the cells to effect recombination were generally costly, bulky, and did not function extremely well for the expected lifetime of the battery. It was felt strongly by lead/acid technologists that excess electrolyte would be necessary to maintain the expected high capacity of the lead/acid cell, and that if one went down to electrolyte levels comparable with Ni/Cd cells (roughly 4 cm^3 per ampere-hour of capacity), discharge capacities would be severely compromised. In a Ni-Cd cell, the primary function of the electrolyte is to maintain conductivity and only incidentally to function in the cell reaction, as shown in Fig. 1, where the lead/acid and Ni/Cd chemistries are compared. For the lead/acid system, the bisulphate ion in the electrolyte is an integral component of the basic cell reactions and the discharge capacity is a direct function of its quantity. It was felt that reduction of the electrolyte amount to a point where substantial void volume would exist in the separator area directly between the plates, thus allowing plate-to-plate recombination, was not feasible. Several approaches were initiated in the 1960s to use immobilized electrolyte in sealed recombinant lead/acid products, but in all cases the electrolyte volume was at least as great as the total pore volumes of the plates and separator, *i.e.*, the cells were either saturated or flooded.

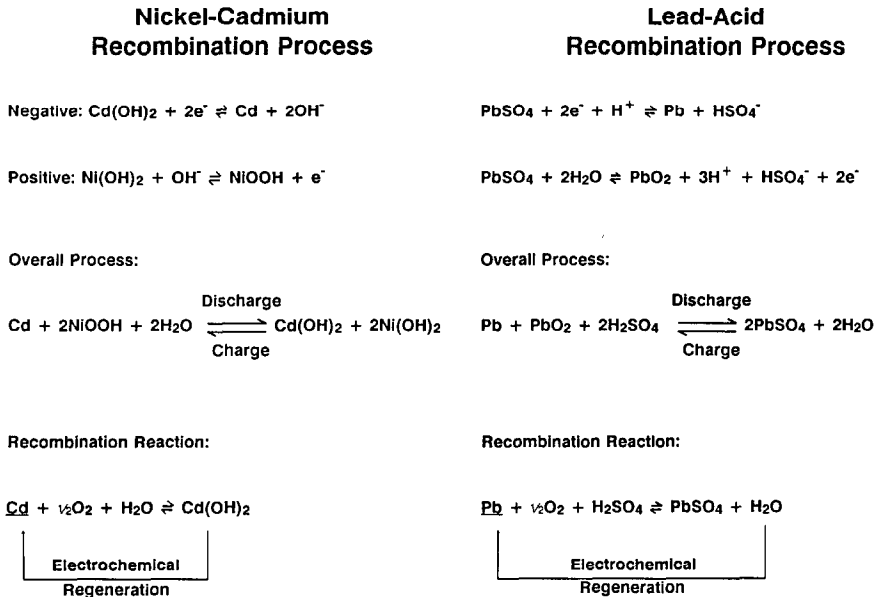


Fig. 1. Comparison of nickel/cadmium and lead/acid chemistries.

Varley technology

An early, but largely undocumented, approach to a semi-recombinant lead/acid battery was the so-called 'supported active material' approach developed by Szper [28] at Varley in the United Kingdom and used by the British Ministry of Defence up until 1987 in virtually all aircraft batteries. These batteries were nominally spillproof and had measurable recombination levels and electrical performance due to the following design features:

- thin plates (1 mm or less) with high cell-surface-areas
- tight plate stacks with very little mud space or head room
- a separator using a paper carrier impregnated with a mix of diatomaceous earth and latex.

The separator, which had high porosity and a strong affinity for sulphuric acid, may have allowed for some plate-to-plate recombination, especially as the batteries aged. While they were spillproof and aerobic in operation, they could not be charged in an inverted position and contained excess electrolyte.

Gel technology

The process of making a gelled electrolyte by combining dilute sulphuric acid with fumed silica, diatomaceous earth, or the like, is an old process, described by Vinal in his classic text [29]. This technology was translated into practice in an absorbed electrolyte system by Eberts and Jache [30 - 32] in the mid-1960s for Sonnenschein G.m.b.H. under the product line named 'Dryfit'. These batteries were developed with lead/calcium grids, to reduce gassing, standard automotive-type pastes, and a separator of coarse glass fibres impregnated with electrolyte immobilized by combination with a thixotropic gelling agent comprised of very fine silica or alumina (mean particle diameters of less than $0.1 \mu\text{m}$) particles at about a 6% loading level [30]. The original intent was apparently to gel the electrolyte to allow use in any position and control gassing by the use of sophisticated charging methods [31], but later work reported that reasonably good recombination levels could be achieved by oxygen reacting with exposed lead and/or diffusion through microcracks that developed in the gel as the battery aged.

In these first developments, the possibility of plate-to-plate recombination was expressly ruled out [30], and excessive water loss was prevented by careful charging with relatively complex circuitry [31] and novel 'spillproof' venting systems [33]. It has been reported [33], however, that with ageing, water loss in overcharge is dramatically reduced and at overcharge levels up to the C/6 rate good recombination efficiency can be attained for long periods of overcharge. Tophorn [34] has also claimed that under controlled charging conditions recombination efficiency (presumably early in life) increases with cell size.

Recent work by both Sonnenschein and Johnson Controls has extended the development of the technology to solar [35], large stationary [36], and electric vehicle [37, 38] applications. The conventional gel cell technology has recently been extended to the use of polymerized polysilicate to retain

the performance advantages of gel technology and overcome some of its drawbacks related to relatively low levels of ion mobility [39]. A claim is also made for extended life compared with conventional gel cells.

The development of gel technology was a significant step forward in the mid- and late-1960s in that it provided batteries with the following characteristics:

- limited maintenance-free operation
- usable in any position for discharge and moderate levels of recharge
- operable at low float voltages for direct replacement of flooded batteries
- relatively little electrolyte stratification
- good deep-discharge recovery
- good charge efficiency and low levels of grid corrosion with controlled charging
- good energy densities (25 - 30 W h kg⁻¹) [36], large electrolyte quantities relative to starved-electrolyte systems [39]
- use of pure materials and low- or non-antimonial grids to enhance shelf life.

The introduction of gel cells did not provide answers to all the questions posed by users looking for highly versatile, truly sealed lead/acid batteries, due to the following initial and still-existing (to some extent) product shortcomings:

- high internal impedances due to reduced levels of ion transport rates in the gelled phase
- limited ability for high-rate discharging and fast recharging
- sensitivity to overcharge, thus requiring the use of relatively expensive, sophisticated chargers for enhanced voltage control [31, 32]
- active material loosening with gassing
- high initial weight losses [33], heavy gassing levels, and poor initial recombination efficiency
- large top-of-charge voltage variations [35] (100 - 150 mV) relative to flooded cells early in life.

At the time the technology was introduced (late 1960s), probably its biggest advantage was its enhancement of maintenance-free operation, but its rapid and widespread dissemination was limited by the charging requirements and susceptibility to heavy gassing and acid leakage under abusive usage conditions.

Early absorbed electrolyte products

In the early- and mid-1960s, several companies worked on, and published results for, so-called 'maintenance-free' lead/acid cells and batteries, namely, the 'CP' batteries from Electromite/C & D [40], the 'MF' or 'EMF' products from ESB [41 - 44] and the 'Noyper' series made by Yuasa [45], previously mentioned.

The ESB MF batteries employed lead-calcium grids and a polyolefin or PVC separator. The latter was saturated with electrolyte and ribbed to allow

gas escape. While these were touted as being maintenance-free and having long cycle and float lives, they could only be used in an upright position and they required a specialized charger to rigidly control the amount of overcharge. A cylindrical 'D' cell called the MFR20 and having an energy density of about 32 Wh kg^{-1} was shown to compare favorably with Leclanché and Ni/Cd products [44]. Because of their limited recombination capabilities and the customized chargers required, these products saw limited use in portable TVs and heart defibrillators; they apparently did not enjoy wide application. Volumetric energy densities were in the range $0.6\text{--}0.8 \text{ Wh in}^{-3}$ for the EMF-1 and EMF-2 models [41].

The CP battery had a number of interesting design features, but apparently it was never widely marketed. It had a 'Unisep' separator made of a polyolefin blend with other thermoplastics and it was made to surround and encase the plates completely. It had a complex combination of an acid-neutralizing pad, a series of valves and channels and, apparently, a catalyst to effect gas recombination and prevent leakage or acid spray. One important aspect was to stress the use of pure materials for all battery components to minimize the self-discharge and gassing levels. Water addition was possible and, again, strict charger design and voltage control were emphasized.

The Okada and Ono (Yuasa) patent disclosed several principles necessary for the proper functioning of a recombinant lead/acid system [45], but the batteries were not usable in any position and depended upon exposed negative plate surfaces for recombination. They did use a coarse glass separator, but it was saturated with electrolyte and the batteries contained acid-spray filters below the vent valves.

In general, these batteries, developed in the 1960s, both of the gelled and immobilized-electrolyte types, offered more or less the same advantages and suffered from the same shortcomings. They were a step forward in that they were reasonably maintenance-free and had fairly long, useful lives. Due to the use of lead-calcium grids and pure materials, their gassing and self-discharge levels were reduced relative to flooded open systems. Gassing also diminished with product life and recombination efficiencies correspondingly improved, but usually with a concomitant reduction in discharge capacity. To a limited extent, they could be used in portable electronic equipment in proximity to sensitive electrical components and personnel.

Applications were limited, however, by their inability to be used in any position due to their sensitivity to overcharge, particularly early in life. They often required expensive, sophisticated chargers to keep end-of-charge voltages below the gassing level. Manufacturing designs were relatively complex in order to accommodate the possibility of acid leakage or spraying (thus reducing volumetric energy densities by requiring more head space), and the batteries were still not highly resistant to abusive use. Grid corrosion appears to have been a dominant failure mode. In retrospect, it appears that many of these shortcomings were linked to the products' inability to

effect substantial levels of direct plate-to-plate gas recombination throughout life and still maintain competitive discharge capacities; it was not at all clear at the time how that could be accomplished.

Maturation of recombinant lead/acid technology

In the late 1960s/early 1970s, development work was going on at a number of traditional battery companies such as Ray-O-Vac [46] and Chloride [47], as well as within new battery venture groups such as the one in the Gates Rubber Company. No doubt work continued at a frantic pace at the firms mentioned in the previous section and at other lead/acid companies not enumerated here.

In 1974, a patent was issued to Desai (filed in 1968) describing a sealed lead/acid cell designed to be gas tight [48], and assigned to Globe-Union, Inc. This cylindrical cell had a central positive electrode pin surrounded by a microporous separator (at least 70% porosity) and a cylindrical, negative outer electrode. A wide range of separator materials, from rubber/silica gel, to thermoplastics, to microfibre glass mats was proposed. Reasonably good recombination levels were quoted in spite of the active material pores, and possibly the separator, being saturated with electrolyte; oxygen uptake appears to have been effected by diffusion into an upper gas space and then reaction with the outer negative electrode surface. The cell had a relatively low energy density and does not appear to have been translated into a practical, manufacturable product.

At about the same publication time (1974), Mahato and coworkers, [49, 50], also at Globe-Union, presented data on a sealed recombinant cell that was efficient at recombining both hydrogen *and* oxygen gases generated on overcharge. The oxygen recombination current density at the negative electrode was calculated [49] to be about 15 mA cm^{-2} of geometric surface area (corresponding to a rate of about $3 \text{ cm}^3 \text{ h}^{-1} \text{ cm}^{-2}$), and the hydrogen recombination rate at the PbO_2 electrode was measured at $1.74 \times 10^{-2} \text{ cm}^3 \text{ h}^{-1} \text{ cm}^{-2}$ of geometric area. Again, a microporous glass separator, made by Gelman for filtration applications, was used, and it is significant to note that in their design the separator was only 85 - 90% saturated, *i.e.*, there was substantial void volume in the separator for plate-to-plate gas transport. The cells had cycle lives comparable with Ni/Cd products, and internal cell pressures remained low during overcharge levels up to the $C/20$ rate, indicating essentially complete recombination, but the products were not commercialized. This was an excellent exposition of the cell design features necessary to achieve high levels of recombination, but it was academic at this point, in the light of a cell previously developed by Gates.

In the mid-1960s, a research effort began in the R&D section of the Gates Rubber Company aimed towards the development of a recombinant lead/acid cell. The approach involved the spiral winding of two plates using soft, pure lead for the grids and a microfibre glass separator material only

partially filled with electrolyte, thus allowing effective plate-to-plate oxygen recombination *over all the plate interfaces*, not just at top or backside exposed lead. This approach was patented [51] and, most important, was translated into an easily manufacturable, commercially successful line of products beginning in 1971 under the name Gates Energy Products, Inc.

Since then, a host of companies has had patents issued and articles published describing flat-plate and spiral-wound analogs of the Gates products. Among these were, but not restricted to, Chloride [52-55], SAFT [56, 57], Yuasa [58, 59], GNB [60, 61], Sanyo [62] and Matsushita [63]; in addition, General Electric took a licence from Gates to make spiral-wound cells in 1976, and since then a number of U.S., Japanese, and European companies have also been licensed to utilize the Gates recombination technology in their products. It is beyond the scope of this work to discuss all the activities published and under study in the last several years, as the interest and growth in this technology have increased exponentially.

Gas recombination — principles and practice

From inspection of the references given in this paper, a clearer picture of the oxygen cycle and how it is translated into practice emerges.

The principles of the oxygen cycle and gas recombination in a lead/acid cell are demonstrated macroscopically by the chemical reactions given in Fig. 1. The generation of oxygen at the positive plate is conceded and, in fact, the provision of an excess of negative active material ensures this. For the lead/acid system to function like its Ni/Cd analogue, the oxygen generated at the positive must easily diffuse through the void space in the separator, then through the electrolyte film in the negative pore surfaces; chemical reaction with the sponge lead then readily follows. As mentioned previously, the Ni/Cd-system chemistry is ideally suited to this situation, since only small amounts of water are involved in the cell chemistry and, thus, electrolyte volumes in the range of 4 cm³ per A h of capacity are needed for adequate chemical reactivity and conductivity. This ensures a substantial void volume in the separator and relatively small film thicknesses on the two plates, calculated as being about 10 - 30 μm on the cadmium electrode [14]. The pore filling for the Ni/Cd cell as a whole is typically about 70 - 85% and, because of the nature of the (usually nylon) separator, only about 10% of the electrolyte is held there, with the remaining 90% being distributed roughly equally between the two plates [65]. As long as the separator is permeable to oxygen, the rate-limiting step to recombination in the Ni/Cd system is diffusion through the electrolyte film in the negative pores. The same will hold true for the lead/acid system, as liquid and gas diffusion rates vary by several orders of magnitude [15].

The lead/acid system typically requires about 8 cm³ of electrolyte per A h of capacity, and the electrolyte distribution between the separator and the plates is quite different. The large amounts of electrolyte required,

relative to Ni/Cd, is probably the major factor that drove researchers in sealed-lead development down the path towards systems with flooded separators to get optimal capacity, and then to attempt recombination in ways other than plate-to-plate. In the Gates cell, roughly 25% of the electrolyte is more or less evenly divided between the plates, and the remaining 75% is in the separator; no electrolyte is unabsorbed and the total pore filling for the cell is of the order of 70 - 90%. From surface area measurements and determinations of electrolyte volumes, it can be calculated that approximately 50% of the pore volume of the negative plate is filled and this results in an average film thickness of about $0.1 \mu\text{m}$ [66]. Rotating-disc studies have shown that, taking into account the differences in electrolyte distribution, the functioning of the two systems with regard to the oxygen cycle is very similar [55, 67].

Looking back, the basic recombination principles appear to be quite simple, and on paper may be easily understood. The translation of theory to practice in getting electrogenerated oxygen from the positive to the negative plate was, however, very difficult. The lead/acid system is thermodynamically unstable and it is fortunate indeed that the oxygen and hydrogen gas evolution reactions are kinetically hindered. Still, these gases are generated in overcharge and on stand, and one key aspect of an effective recombinant cell is to have cell materials of optimal purity, with low levels of contaminants that would lower the overvoltages, particularly at the negative electrode. Gas transport must be facilitated, both by a thin-film condition in the negative plate and by having substantial void volume in the separator. Microfibre glass mats are ideal in that they are highly porous, have large surface areas, and have a strong affinity for sulphuric acid. Thus, via wetting and capillary effects, the separator holds the bulk of the electrolyte in a quantity sufficient to give acceptable discharge capacities and, at the same time, there is still sufficient void volume to accommodate oxygen transport. In the Gates spiral-wound system, this allows heavy overcharge levels, up to about the $C/3$ rate, without excessively fast drying out or acid/vapor spraying. This single performance factor demonstrates quite dramatically the effectiveness of the glass separator/starved electrolyte approach to recombination.

Direct plate-to-plate recombination is a key factor in the success of this technology, but other factors are also significant, and it is the overall system design that affords a high-performance, easily-marketable, readily-manufactured product; a list of major attributes that pertain to the Gates approach would include the following (different manufacturers would no doubt have other design parameters, but many of these would find common application):

- the use of pure materials for all cell components, and high hydrogen-overvoltage/corrosion-resistant grid alloys (pure lead for the Gates approach), at least for the negative electrode
- use of a separator material having a high surface area, a high porosity (85 - 95%), and a strong affinity for sulphuric acid, but a low acid solubility

- a separator that is compressible, and the plate stack, when formed, has substantial stacking pressure such that there is intimate contact between the separator and the plates

- a carefully measured amount of electrolyte added such that good cell capacities are achieved, yet substantial void volumes exist in the plate pores and separator to accommodate efficient oxygen transport

- distribution of electrolyte such that the bulk is contained within the separator stack and there is a portion uniformly distributed throughout the plate pores, creating a thin-film condition

- thin plates with high surface areas, closely spaced, affording optimal gas-recombination capabilities and low internal cell impedances.

In looking back on the previous literature, it is clear that many of these principles had been expounded and, with the exception of the glass separator, the materials used were not unique. The success of this approach was clearly in understanding what was needed conceptually, taking various elements of the prior art from here and there, coming up with a relatively new key material, and converting this into a manufacturable, functional product.

These new recombinant products are superior to earlier 'maintenance-free' batteries in the following ways:

- volumetric energy densities are greater due to reduced head-space and mid-space requirements

- because recombination is so efficient, rigorous charge voltage control is not necessary and less expensive chargers can be used; charging times may also be shorter

- direct plate-to-plate recombination simplifies cell design and manufacture and leads to reduced cost (though the glass separator is a relatively expensive component)

- with no free electrolyte and a valve-regulated construction, the products can be discharged and overcharged in any position, even upside down in many cases, and the absence of heavy gassing and acid spray allows them to be used in sensitive electronics and populated environments

- they are more tolerant of abuse in field applications, particularly with regard to overcharge.

This brings us up to the 1980s. In the past several years, virtually every existing lead/acid battery company has been developing and/or manufacturing either a starved-electrolyte glass separator or an advanced gel-cell line of products. The level of activity is high and the technology, while maturing, is far from fully understood.

Drawbacks and limitations of recombinant technology

Recombinant batteries are a new technology and as such limitations exist on the manufacture and application of these valve-regulated lead/acid products. Manufacturing processes are not documented and widely published and thus manufacturers each have their own respective set of unique

problems. Processing areas such as plate pasting, separator handling/plate stacking, drying, filling and formation are particularly sensitive areas, at least in Gates' experience.

In applications situations, the major limitation is the variation of top-of-charge voltages and currents due to the variability in the negative electrode polarization behaviour attributable to different levels of oxygen recombination cell-to-cell [39, 68]. In large (and small) strings and series/parallel arrays small cell-to-cell imbalances can result in premature system failure due to some cells being undercharged and then deep discharged; as this process is repeated weak cells become progressively weaker. One method that has been used to address this is the use of a common gas space for multicell batteries [69]. Testing has shown that use of a common gas space has a beneficial result in drawing top-of-charge voltages closer together [70]. Float currents also tend to be higher for recombinant cells, due again to differences in negative plate polarization behaviour relative to flooded cells [68].

Thermal management and the potential for overheating and, possibly, thermal runaway in the extreme, is more of a consideration for valve-regulated cells because of the following factors:

- more heat is generated due to the recombination process
- recombinant batteries tend to be smaller and lighter than flooded analogs; thus, heat buildup and dissipation are more of a problem
- reduced gassing levels hinder heat dissipation
- because of their perceived versatility, they are put into more abusive environments
- in general, battery applications are becoming tougher and more demanding (*e.g.*, automotive batteries).

Finally, a general comment from personal experience is that there is very little in the way of published data on recombinant systems design, analysis, performance, and applications, not only because of the newness of the technology but also due to the need for secrecy tied into patent positions and business strategies. As time goes on, this factor will, hopefully, become less important, but on a day-to-day basis this, at present, is a real limitation.

Cycle and float lives are less than for some flooded battery designs, but this is largely offset by the maintenance-free service, portability, and ease of installation of recombinant batteries, and also by the rapid rate of change in electronics and instrument technologies; as systems designs change, new batteries are needed, and thus long battery life is not the dominant factor it once was.

Failure modes

In general, failure modes in recombinant lead/acid batteries are not the same as those of flooded types. Grid and top-lead corrosion are not as significant (in the absence of manufacturing deficiencies) and stratification is

much reduced, although it is still a potential factor. Recombinant batteries are, however, more susceptible to failure modes such as excessive sulphation/overdischarge and deep discharge, drying out/thermal runaway and cell imbalance/battery failure. Probably due to their newness, recombinant batteries suffer more variability and more potential for defects in manufacture. The 'desired' failure mode, if that can be said, is gradual loss of capacity due to porosity changes in the positive active material. The following is a brief list of recombinant battery failure modes, in approximate order of frequency, primarily from a personal perspective of products now on the market.

- excessive sulphation/deep discharge
- cell imbalance/battery failure
- loss of positive active material structure
- drying out/thermal runaway
- grid and/or top lead corrosion, growth
- plate-to-plate or plate-to-top-lead shorting; dendrites
- manufacturing defects
- applications abuse
- electrolyte stratification

The last factor has not been experienced in small batteries but it is a potential failure mode, particularly in large products.

Ongoing development work

The following is a list of development areas of active interest to those in the lead/acid field; this list is by no means exhaustive and probably reflects some personal bias:

Cell/battery design

- large (>300 A h) stationary recombinant batteries
- UPS systems design
- purpose-built, small 'designer' batteries (VCRs, radios, etc.)
- bipolar lead/acid batteries
- automotive and motive power recombinant batteries
- thin-plate, high energy density, small cells/batteries
- development of mathematical models, CAD/CAE.

Improved float and cycle life

- materials balance
- plate morphology studies
- oxides, pastes, active materials characterization
- additives, electrolyte studies
- low-antimony, lead-calcium-tin alloys, composite grids
- failure analysis
- process effects (filling, formation, etc.)

- reliability assessments in large UPS systems
- state-of-health, remote monitoring
- valid accelerated-life test methods

Recombination chemistry/electrochemistry

- thermal management
- calorimetry
- plate mapping/reference-electrode studies
- microscopic studies of the oxygen cycle

Disposal and recycling

- materials recovery
- lobbying/legislation
- definitions of reusability

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References

- 1 T. A. Edison, *U.S. Pat 1,016,874* (1912).
- 2 R. L. Tichenor, *U.S. Pat. 2,578,027* (1951).
- 3 A. Dassler, *U.S. Pat. 2,104,973* (1938).
- 4 A. E. Lange, E. Langguth, E. Breuning and A. Dassler, *U.S. Pat. 2,131,592* (1938).
- 5 G. F. Rublee, *U.S. Pat. 2,269,040* (1942).
- 6 G. Neumann and U. Gottesmann, *U.S. Pat. 2,571,927* (1951).
- 7 Bureau Technique Gautrat, *U.K. Pat. 677,724* (1952).
- 8 Bureau Technique Gautrat, *U.K. Pat. 677,770* (1952).
- 9 M. C. J. Jacquier, *U.S. Pat. 2,624,033* (1952).
- 10 R. A. A. Jeannin, *U.S. Pat. 2,646,455* (1953).
- 11 A. Dassler, *U.S. Pat. 2,934,581* (1960).
- 12 W. W. Smith and H. J. Strauss, *U.S. Pat. 3,057,942* (1962); *Can. Pat. 595,665* (1960).
- 13 F. Peters, *U.S. Pat 2,988,585* (1961).
- 14 U. B. Thomas, Jr., in D. H. Collins (ed.), *Batteries*, Pergamon, Oxford, 1963, pp. 117 - 128, and references therein.
- 15 P. Rüetschi and J. B. Ockerman, *Electrochem. Technol.*, 4 (1966) 383.
- 16 J. I. Dyson and E. Sundberg, in D. H. Collins (ed.), *Power Sources 4*, Oriel Press, Newcastle upon Tyne, 1973, pp. 505 - 523.
- 17 K. Shimizu and A. Tsubuki, in *Rechargeable Batteries in Japan*, JEC Press, Cleveland, OH, 1977, Ch. 7.
- 18 P. Rüetschi, *U.S. Pat. 3,080,440* (1963).
- 19 P. Rüetschi, *U.S. Pat. 2,951,106* (1960).
- 20 E. Voss and K. Dehmelt, *U.S. Pat. 3,170,816* (1965).
- 21 K. Shimizu and Y. Ohkawa, in *Rechargeable Batteries in Japan*, JEC Press, Cleveland, OH, 1977, Ch. 8.
- 22 S. Hills and D. L. K. Chu, *J. Electrochem. Soc.*, 116 (1969) 115.
- 23 K. Okada, in *Rechargeable Batteries in Japan*, JEC Press, Cleveland, OH, 1977, Ch. 10.

- 24 Ger. Gebrauchsmuster Pat. 1,782,752 (1959).
- 25 J. J. Abramson, U.S. Pat. 3,170,819 (1965).
- 26 J. J. Abramson, Can. Pat. 720,123 (1965).
- 27 P. Rüetschi, U.S. Pat. 3,265,534 (1966).
- 28 A. J. Szper, Proc. Int. Symp. on Batteries, 1958, Signals Research and Development Establishment, Ministry of Supply, Christchurch, Hants., U.K., Paper X, p. 10.
- 29 G. W. Vinal, Storage Batteries, Wiley NY, 4th Edn., 1955.
- 30 O. Jache, U.S. Pat. 3,257,237 (1966).
- 31 K. Eberts and O. Jache, Lead 65, Proc. 2nd Int. Conf. on Lead, Pergamon, Oxford, 1967, pp. 199 - 210.
- 32 K. Eberts, in D. H. Collins (ed.), Power Sources 2, Pergamon, Oxford, 1970, pp. 69 - 92.
- 33 A. Wantanabe, in Rechargeable Batteries in Japan, JEC Press, Cleveland, OH, 1977, Ch. 9.
- 34 H. Tophorn, in K. R. Bullock and D. Pavlov (eds.), Proc. Symp. on Advances in Lead-Acid Batteries, Electrochemical Society Ext. Abstr., 1984, pp. 441 - 450.
- 35 H. Tophorn, Prog. Batt. Solar Cells, 6 (1987) 145.
- 36 B. K. Mahato and K. R. Bullock, Prog. Batt. Solar Cells, 6 (1987) 136.
- 37 K. R. Bullock, B. K. Mahato, G. H. Brilmyer and G. L. Wierschem, in K. R. Bullock and D. Pavlov (eds.), Proc. Symp. on Advances in Lead-Acid Batteries, Electrochem. Soc. Ext. Abstr., 1984, pp. 451 - 465.
- 38 B. L. McKinney, B. K. Mahato and K. R. Bullock, in K. R. Bullock and D. Pavlov (eds.), Proc. Symp. on Advances in Lead/Acid Batteries, Electrochem. Soc. Ext. Abstr., 1984, pp. 426 - 440.
- 39 W. B. Brecht and N. F. O'Leary, in INTELEC '88 Conf. Proc., IEEE, 1988, pp. 35 - 42.
- 40 J. A. Orsino and H. E. Jensen, 21st Annu. Power Sources Conf., 1967, pp. 60 - 64.
- 41 J. R. Smyth, J. P. Malloy and D. T. Ferrell, Lead 65, Proc. 2nd Int. Conf. on Lead, Pergamon, Oxford, 1967, pp. 193 - 196.
- 42 Electric Storage Battery Co., U.K. Pat. 1,032,852 (1966).
- 43 J. P. Malloy, 21st Annu. Power Sources Conf., 1967, pp. 68 - 70.
- 44 A. I. Harrison and K. Peters, in D. H. Collins (ed.), Power Sources 3, Oriol Press, Newcastle upon Tyne, 1971, pp. 211 - 225.
- 45 K. Okada and M. Kono, Aust. Pat. 407,845 (1968).
- 46 J. Szymborski, personal communication.
- 47 K. Peters, personal communication.
- 48 R. R. Desai, U.S. Pat. 3,846,175 (1974).
- 49 B. K. Mahato, E. Y. Weissman and E. C. Laird, J. Electrochem. Soc., 121 (1974) 13 - 16.
- 50 B. K. Mahato and E. C. Laird, in D. H. Collins (ed.), Power Sources 5, Academic Press, London, 1975, pp. 23 - 41.
- 51 D. H. McClelland and J. L. Deavitt, U.S. Pat. 3,862,861 (1975).
- 52 K. Peters, S. Fewster, F. Wilson and K. D. N. Kearney, U.S. Pat. 4,119,772 (1978).
- 53 K. Peters, U.K. Pat. 2,048,556A (1980).
- 54 B. Culpin, K. Peters and N. R. Young, in J. Thompson (ed.), Power Sources 9, Academic Press, London, 1983, pp. 129 - 141.
- 55 J. Thompson and S. Warrell, in J. Thompson (ed.), Power Sources 9, Academic Press, London, 1983, pp. 97 - 112.
- 56 J. Atkin, French Pat. 77 01435 (1978).
- 57 J. Atkin and J. P. Sinet, Prog. Batt. Solar Cells, 2 (1979) 167.
- 58 M. Kono, H. Igarashi and K. Kishimoto, U.S. Pat. 4,262,068 (1981).
- 59 K. Okada, Y. Matsumura, J. Yamashita and K. Kishimoto, Eur. Pat. 0 141 568 A1 (1985).
- 60 J. Szymborski and B. Burrows, in J. Thompson (ed.), Power Sources 9, Academic Press, London, 1983, pp. 113 - 127.
- 61 J. Szymborski, S. S. Misra, M. L. Eggers and B. W. Burrows, U.S. Pat. 4,401,730 (1983).
- 62 Y. Morioka, U.S. Pat. 4,572,879 (1986).
- 63 K. Takahashi, H. Yasuda and T. Hasegawa, Prog. Batt. Solar Cells, 6 (1987) 126 - 129.
- 64 Y. Kobayashi, Y. Sakata and S. Fukuda, Prog. Batt. Solar Cells, 6 (1987) 133.
- 65 V. Puglisi, personal communication.

- 66 A. J. Salkind, unpublished data.
- 67 J. Atkin, R. Bonnaterre and Jean-François Laurent, in D. H. Collins (ed.), *Power Sources 6*, Academic Press, London, 1977, pp. 91 - 101.
- 68 D. Berndt, in *INTELEC '88 Conf. Proc.*, IEEE, NY, 1988, pp. 89 - 96.
- 69 D. McClelland, T. Uba and L. K. W. Ching, *U.S. Pat. 4,383,011* (1983).
- 70 P. R. Everatt and R. F. Nelson, unpublished data.