

# **Firefly Technology**

## HISTORY OF OUR INNOVATION

Firefly's revolutionary battery technology was born in the Research and Development laboratories of Caterpillar, Inc., a world-renowned manufacturer of heavy equipment. Unlike many companies these days, Caterpillar spends a substantial amount of revenue (approximately \$900 million a year) researching for innovative ways to improve its products.

Caterpillar has long been a consumer of batteries for its many heavy equipment products. Earthmoving equipment, by its very nature, put a severe strain on batteries. Heat and cold extremes, severe vibration, and prolonged periods of disuse between jobs all pose strenuous challenges on heavy equipment batteries. CAT has always set tough standards for batteries supplied with their products, and several years ago decided to put its own brand name on these sourced products. After a time, Caterpillar began receiving a disturbing increase in battery related feed-back from customers. Further investigation revealed that although battery quality and performance hadn't eroded, the customers' expectations were heightened by the Caterpillar branding and expected ruggedness!

With a corporate focus on constant improvement and customer satisfaction, the CAT Electronics Group turned the issue over to their R&D arm. Kurt Kelley (now Firefly's Chief Technology Officer) assumed the task of addressing the two main failure modes of a lead acid battery: Reduced life caused by corrosion (of the battery's positive plate) and sulfation (of the battery's negative plate). In short, Kelley's task was, first of all, to find a corrosion-resistant material that could displace much of the lead within a traditional battery and



secondly, to take advantage of the material's properties to harness the battery's energyproducing chemistry in a more efficient and powerful manner. In Microcell<sup>TM</sup> foam, Kelley found a material that fulfilled both requirements. Through lengthy research, he optimized the material in such a way that it not only survived in the harsh lead acid chemistry, but actually thrived.

This begs the question as to why such an important discovery was made by Caterpillar and not by a company directly involved in the battery industry. It's interesting to note that the previous major advancement in the lead acid battery industry was the valveregulated lead acid (VRLA) battery. This invention was created, not by a battery manufacturing company, but by a rubber hose and belt company – Gates. The parallel is clear; smart materials scientists with the backing of major corporations, were unconstrained by traditional mental roadblocks and preconceptions of how to design and optimize a battery!

Becoming convinced of the potential of this new concept, Caterpillar executive management decided in 2003 to provide seed funding for a separate business solely dedicated to the new technology. Firefly Energy was born!

## BATTERY OBJECTIVES AND CHALLENGES

In the design of any high performance battery, there are always four major overriding objectives:

- 1) Maximize specific energy (energy storage per unit of weight, measured in watthours per kilogram) over designated discharge scenarios.
- 2) Maximize the specific power (power per unit of weight, measured in watts per kilogram) over designated high rate discharge scenarios.
- 3) Maximize battery life, not only in environmental durability but most importantly in cycle life (number of possible charges and discharges).
- 4) Do it all at extremely low costs.

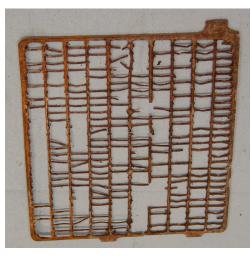
The final point has traditionally driven lead acid battery producers to the use of low cost lead materials, which of course has limited the first three criteria. Given the long-standing use of lead metal, improvements in battery current collector (i.e., grid) design and advances in lead-alloys appear to be reaching a plateau. The lead acid battery industry has been working in obscure corners of the Periodic Table to find alloying elements that would help stabilize current collector behavior. Improved manufacturing techniques have allowed mechanically more delicate and thinner lead based alloys to be employed in high speed production. But without the development and insertion of new materials and processes, the traditional lead-acid industry's gains appear to be approaching the limits for electrode thickness, alloy corrosion rates, and active material pellet structures.

## LEAD ACID BATTERY FAILURE MODES

To make an advance in battery technology that goes beyond evolutionary engineering improvements requires a paradigm shift to new materials and/or new processes. Like others before, Caterpillar's internal pursuit of higher performance in lead-acid batteries found the typical product limitations, namely:

• <u>Service Life:</u> Both *corrosion* (on the positive plate) and *sulfation* (on the negative plate) define two key failure modes of today's lead acid batteries. Although average industry battery life has been extended over the past 20 years these failure modes result in products that achieve only a fraction of the life associated with more advanced energy storage systems. Further, these life limiting factors become exacerbated by the varying temperature environments of many applications.

Regarding corrosion failures, this failure mode begins to accelerate either as temperatures rise about 70°F, and/or if the battery is left uncharged. To mitigate the effects of the corrosion process, most battery companies focus their research on developing more corrosion resistant leadalloys and grid manufacturing processes that reduce the mechanical stresses in the as-manufactured grids. Regardless of the alloy or grid fabrication process. essentially all battery manufacturers engineer battery service life based on lead alloy and grid wire cross-sectional area.



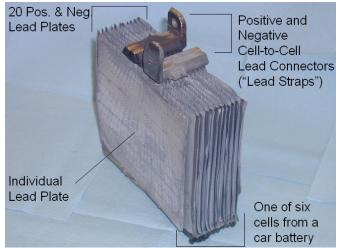
Normally this engineering translates as a change in grid thickness and corresponding plate thickness. Thicker grids provide longer life, but usually sacrifice power density, cost, weight, and volume.

Regarding sulfation failures, when a lead acid battery is left on open circuit stand, or kept in a partially or fully discharged state for a period of time, the lead sulfate formed in the discharge reaction recrystallizes to form larger, low surface area lead sulfate crystals which are often referred to as hard lead sulfate. This low surface area, non-conductive lead sulfate, blocks the conductive path needed for recharging. These crystals, especially those furthest removed from the electrode grid, are difficult to convert back into the charged lead and lead dioxide active materials. Even a well maintained battery will lose some capacity over time due to the continued growth of large lead sulfate crystals that are not entirely recharged during each recharge. These sulfate crystals, at 6.287 g/cc, are also larger in volume than the original paste, so they mechanically deform the plate Sulfation is the main problem in recreational and push material apart. applications during battery storage when the season ends. Boats, motorcycles, snowmobiles lie dormant in their off months and, left uncharged, discharge toward a 0% state-of-charge, leading to progressive sulfation of the battery. Thus, the battery can not be recharged anymore, is irreversibly damaged, and must be replaced.

- Cycle Life (# of discharges/charges) As users have come to know portable battery products in cell phones and laptop computers, they have correspondingly become comfortable with the process of bringing a battery down to almost "0" charge and then bringing it back to full, complete charge and power capabilities within hours. Traditional lead-acid batteries, because of their inherent design and active material utilization limitations, only provide relatively good cycle-life when less than about 80% of the rated capacity is removed during each discharge event in an application. A battery of this type suffers a significant decrease in the number of times it can be discharged and recharged when 100% of the rated capacity is consumed during a single discharge in an application. Many new products that historically used lead-acid batteries are requiring a significant jump in cycle life. The most notable examples are Hybrid Electric Vehicles, which operate in a High Rate Partial-State-of-Charge condition. This is a punishing application which dramatically shortens the cycle life of a typical lead acid battery, and has therefore left car companies with no choice but to go to much more expensive Nickel-Metal Hydride batteries, and experiment with Lithium Ion batteries.
- <u>Recharge Time</u> Typically, a lead-acid battery will require a recharge time significantly longer than competitive batteries containing advanced materials seen in portable products. A complete charging of a lead-acid battery, such as found in electric vehicles, can take from 8 to 16 hours. In the case of Uninterrupted Power Supplies (UPS), a rapid charge rate is essential to ensuring quality performance,

as well as reducing the related capital expenditures for back up equipment while charging takes place on initial batteries put into service.

 <u>Size and Weight</u> – Although lead-acid batteries are the cheapest rechargeable energy storage products in the world to manufacture, the extensive use of lead gives them an exceptionally large footprint



and weight. Again, like other performance aspects of this industry's products, this limits their form factors and overall utilization in new product designs. In addition, most lead battery plates (e.g., over 100 in a typical car starting battery) only utilize 20% to 40% of their surface area during each discharge over the life of the battery. This creates even more inefficiencies in power-to-weight ratios.

Primary users of lead-acid battery products from automotive companies to power utilities, military and motive power (e.g. lift trucks) have sought for decades, the ability to obtain

advanced performance beyond the current limitations of lead-acid batteries, yet ideally retain the comparative costs of the existing products.

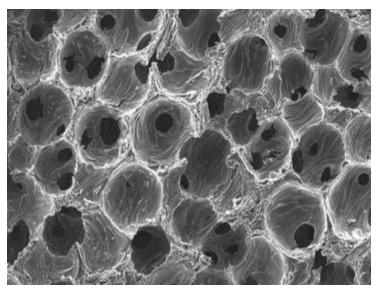
Many industries, such as transportation, have been forced to address new product designs with alternative battery systems employing expensive advanced materials, and leaving their traditional long-term lead-acid battery manufacturers behind. These conditions have led automotive manufacturers to embrace the new battery entrants such as those based in the Pacific Rim. Unfortunately the cost penalty for these more exotic batteries can still be as high as 5-10 times the cost of lead-acid batteries.

Lead acid batteries have always faced severe trade-offs with respect to power, capacity, weight, life, and cost. Firefly technology breaks through these constraints and creates a much higher set of trade-offs, enabling new levels of performance, reliability, and affordability.

## FIREFLY'S MICROCELL<sup>TM</sup> FOAM-BASED BATTERY TECHNOLOGY

Firefly's technology is an innovative material science that removes almost all limitations of current lead acid battery products. The materials also hold the promise of major simplification for manufacturing of lead-acid batteries and will potentially deliver more flexible form factors or configurations, which may be the catalyst to change the entire distribution and profitability models of the battery industry.

As he began his research into lead acid battery chemistry and structure. Kurt Kelley discovered that much of the lead in the grid structure of conventional batteries can be replaced by a totally new type of material. Of course, once the basic material was determined to have the requisite physical and chemical properties, much subsequent research and testing was determine required to the optimum configuration and "architecture" within the



battery itself. These results are confirmed in two U.S. Patents granted in December of 2005.

In the advanced battery architectures that Firefly has perfected, the composite foam "grids" are impregnated with a slurry of lead oxides which are then formed up to the sponge lead and lead dioxide in the normal fashion. Because of the foam structure, the resultant negative and positive plates have enormous energy generating capacity

advantages over conventional lead acid grid structures. This results in much-improved active material utilization levels (i.e., from 20-50% up into the range of 70 - 90%), as well as enhanced fast-recharge capability and greater high-rate / low-temperature discharge times.

The signal advantage of Firefly's Microcell<sup>™</sup> technology is that it fundamentally changes the distribution of active materials within the lead acid cell due to its unique architecture. Overall, the Firefly composite foam electrode structure results in a redistribution of electrolyte from the smaller separator reservoir to the pores of the foam plate(s), resulting in a 70/30 to 30/70% reversal, respectively, relative to conventional lead acid products. Each foam plate contains hundreds or thousands of spherical microcells (depending on the foam pore diameters). This leads to enhanced activematerial utilization levels, because each microcell has its full complement of sponge lead or lead dioxide and sulfuric acid electrolyte. Liquid diffusion distances are reduced from the traditional levels of millimeters over linear paths (the conventional "2D" diffusion mechanism found in the lead metal grid-based classic lead acid battery architecture) to the level of micron diffusion path lengths in the three-dimensional space within the discrete microcells that, collectively comprise a totally new type of electrode structure (what Firefly calls a "3D" electrode). Such a structure results in much higher power and energy delivery and rapid recharge capabilities relative to conventional lead acid products.

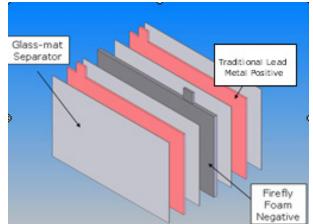
## Firefly Advanced Battery Technologies: Introduction

Firefly Energy has developed two significant technologies that will deliver advanced battery performance for an entire spectrum of uses served by lead acid, nickel, and lithium based chemistries.

The two technologies--"3D" & "3D<sup>2</sup>"--involve the use of a porous three dimensional composite material to replace the lead metal grids in either flooded or VRLA lead acid battery designs. Consequently the technology will obviate the use of corrodible lead metal grids found in a traditional lead acid battery design, and finally unleash the full power potential of lead acid chemistry for energy storage. This delivers a formidable jump in specific power, energy and cycle life. Firefly's Advanced Battery technology increases the cycle life of lead acid chemistry by a factor of four, delivering a performance very similar to advanced materials batteries (Lithium & Nickel), but can be built for a cost similar to today's lead acid batteries (1/5 the cost of advanced material batteries).

## **3D** Technology

As the initial implementation phase of its Microcell<sup>TM</sup> foam grid technology, Firefly's 3D cell architecture involves replacing the conventional negative lead metal-based plate with a



composite foam electrode. These products are configured in such a way as to be easily incorporated into the manufacturing processes possessed by all existing lead acid manufacturers.

Because of this relatively seamless integration into established manufacturing techniques, Firefly will manufacture the pasted foam negative electrodes and furnish them to existing manufacturing partners who will incorporate them into finished battery products. To all outward appearances, these batteries will be indistinguishable from currently available products. Hydrogen overvoltage levels on the composite negative plates are comparable or slightly superior to conventional lead negatives, which mean that gassing levels, and corresponding water loss rates, are low. Self-discharge rates are very low at approximately 0.3mV/cell-day, which equates to a shelf life of 2 years or more without recharge. Due to the use of an electrolyte compatible with conventional lead-acid cell designs the open-circuit voltages and recharge/float voltages correspond to those for conventional lead-acid batteries. This condition permits the use of conventional lead-acid chargers with Firefly Energy's 3D batteries.

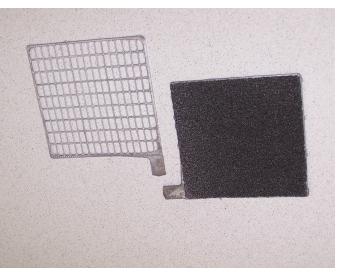
## **3D** Technology Performance Attributes

#### **Energy & Power Improvements**

#### Surface Area

The real quest for performance improvements in lead acid batteries is all about surface area. Of course, selective enhancements have been applied that have made incremental gains over the last several decades, but the overwhelming restriction to lead acid battery

efficiency has always been the lack of interface area between the active chemistry and the With chemistry electrodes. capable of delivering approximately 170 Watt Hours per Kilogram (Whr/kg), why are today's lead acid batteries only averaging around 30-50 Whr/kg? The answer to this question, and to those facing the quandary over how to achieve higher surface areas are embroiled in the same century's-old paradigm; that lead electrodes (shown in left side of



picture) are necessary in lead acid batteries. Unfortunately, lead electrodes corrode, so increasing surface area increases corrosion and decreases life.

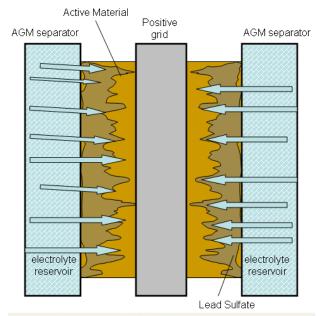
Firefly technology (shown in right side of picture) does increase surface area, enormously. High electrode surface-area has advantages, some beyond the obvious. It is

fairly obvious that increasing the interface area between active chemistry and the electrode allows better and faster utilization of the chemistry. Charge and discharge times decrease, and a higher percentage of active material is accessible so efficiency goes up. Utilization efficiencies can potentially rise over 90%. These benefits drive up both gravimetric and volumetric energy and power values.

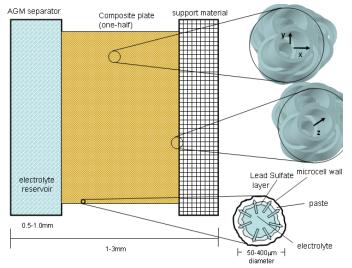
Not as immediately obvious is the effect on a battery's overpotential. As the electrode surface area increases, the real current density is reduced and this causes a corresponding reduction in the battery's overpotential. In a practical sense, lower overpotential leads to higher efficiency because losses to heat are reduced, lower charging voltage is required, and there is less voltage drop on discharge. Discharge voltage curves are also flatter. Curiously, low overpotential also results in a lower open-circuit-voltage (OCV) in Firefly batteries, which is closer to theoretical.

#### Utilization and Spatial Efficiency

Traditional lead flat-plate and spiralwound electrodes (depicted at left) can be thought of as <u>two-dimensional</u> in terms of pore structure/reactivity and <u>one-dimensional</u> in terms of electrolyte diffusion. Roughly only one-half of the active materials are available for reaction to produce energy, due to the plate structure where diffusion must take place through previously-discharged material in order to sustain the energyproducing electrochemical reactions.



Traditional pasted lead plates depend upon linear diffusion of electrolyte into the plate pores from the separator or inter-plate reservoir for delivery of electrical energy as a part



discharge process. of the Discharge begins at the plate surfaces and progresses into the interiors as long as electrolyte diffusion rates can support the load current being applied. In low-rate applications with present lead-acid technology, it is possible to achieve utilization levels (i.e., the ratio of the amount of active material actually discharged to the total present in the plates) of about 50-60%, but little more due to the long diffusion paths and the buildup of highly resistive lead sulfate in the plate pores. This effectively chokes off access of electrolyte to the deeper plate pores. The distances traveled by the electrolyte during a full discharge in SLI or thin-plate VRLA products is on the order of 1-3 mm to reach the interiors of the plates. In thick-plate deep-cycle batteries it can be as much as 4-6 mm. Obviously, as we go to higher rates of discharge, these relatively long diffusion path lengths become limiting in terms of total capacity output. Because of this, lead-acid batteries for high-rate applications usually have thin plates with small plate spacings. However, this design approach adds cost and weight (relatively more grid material), increases manufacturing scrap and shortens lifetimes due to corrosion.

The Firefly Energy architecture (shown above right) goes well beyond the traditional lead-acid construction by promising huge advances over traditional lead-acid pasted plate (or tubular plate) batteries. Firefly's <u>three-dimensional</u> composite plate will result in a significant increase in active material utilization levels.

Firefly's three dimensional foam plate technology holds the promise of increasing lowrate utilization levels to some extent and high-rate utilizations by significant amounts (above the traditionally accepted 67% theoretical limit in some cases). The key lies in the basic construction of the Firefly composite plate. Lead plates have a linear structure that requires electrolyte diffusion over relatively large distances (typical diffusion rate coefficients are on the order of  $1 \times 10^{-6} \text{ cm}^2/\text{sec}$ , which means that in 1 second electrolyte will diffuse only a distance of ~0.01 mm). Put another way, it will take ~100 seconds to diffuse 1 mm. Firefly's diffusion path lengths are more on the order of ~100 microns or less – i.e., ~0.1 mm. Given these numbers, virtually all of the electrolyte within each Firefly plate could be completely depleted in ~5 seconds. This means that under very high current loads, the effect of electrolyte diffusion would not be significant unless a full discharge was carried out in ~5 seconds or less. In addition, if the proper balance of active materials and electrolyte is achieved in the Firefly design, utilization levels well in excess of the practical limit of ~67% should be achieved due to the dispersed nature of lead sulfate (PbSO<sub>4</sub>) buildup.

Thus, lead sulfate buildup is not as likely to "shut down" the discharge reaction by choking off electrolyte diffusion. Moreover, since electrolyte diffusion paths in the Firefly electrodes are on the order of microns rather than millimeters (a potential improvement of 2-3 orders of magnitude) this change in electrode design should result in large increases in active-material utilizations and high-rate discharge capacities, as well as sharp reductions in recharge times.

#### Low and High Temperature Advantages

#### Cold Temperature

Though economical in many applications, lead-acid batteries have a relatively low specific-energy and, similar to competitive batteries, are severely affected by cold temperatures. This effect, or increase in internal resistance, is due to the "slowing down"

Table 1 : Battery Power vs. Temperature

of the battery's chemicalreaction and ion-diffusion rates. As a "rule of thumb", reaction rates are cut in half for each 10°C drop in temperature. "Cold cranking" is a discharge which needs a high current, and reaction-rates are critical to

Available Power From Battery	Temperature Degree C	Power Required To Crank Engine
100 %	27°	100 %
65 %	0°	155 %
40 %	- 18°	210 %

Source: Bill Darder	, Car Battery FAQ	Jan 2001, bj	b_darden@yahoo	o.com)
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sizing a battery. A high current implies a lot of active material conversion in a short time, and this is related to the amount of electrode surface area covered with activematerial that is available for conversion. Therefore, a starter battery needs a lot of surface area (meaning a large number of lead plates).

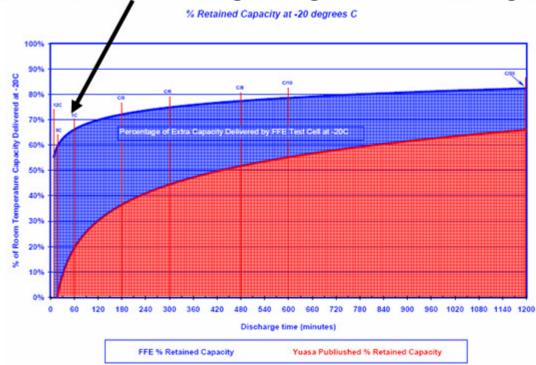
Sizing a lead-acid battery for starting applications at -18°F, for example, requires an approximate 200% size increase over room temperature operation. Because of an acknowledged corrosion rate for the positive lead grids in lead-acid batteries, attempts to increase cold temperature starting power by increasing electrode surface area without "sizing up" the overall battery, results in short warm temperature life.

Firefly's 3D (and  $3D^2$ ) products have outstanding discharge performance at low ambient temperatures relative to commercial flooded lead-acid and VRLA batteries. This is due to the extremely high electrochemically-available surface area of the composite foam coated with sponge lead. At high discharge rates and/or low temperatures, the discharge performance of a typical lead metal-based negative plate limits a cell's output, due in large part to the relatively low surface areas of conventional planar negative plates. The Firefly 3D negative, with hundreds or thousands of tiny microcells, each with its own complement of sponge lead and electrolyte, is ideal for discharge (and charge) conditions where electrolyte diffusion is limited by surface area, distance or temperature. The distances for electrolyte diffusion in the microcells are on the order of tens of microns while in a conventional lead-acid battery (either flooded or VRLA) path lengths are measured in millimeters. Diffusion rates at low temperatures are reduced in a 3D cell just as they are in conventional commercial products, but the distances traveled to react with the sponge lead are much smaller. This enhanced electrolyte supply also results in higher, flatter voltage-time curves on discharge, which means higher energy outputs when combined with the lower current densities that accrue from the high foam electrochemical surface area.

As the temperature is lowered, it takes more power to start the engine at the same time that the available power from the battery drops, here to only 40% of what can be provided at ambient when the car is started at  $-18^{\circ}$ C. By comparison, a Firefly 3D battery will provide 69% of its ambient-temperature power at  $-18^{\circ}$ C. This means that Firefly's 3D engine-start battery could be smaller to have the same cold-crank amps or it would be more powerful and last longer if its size were comparable to a commercial product.

This point is reinforced in the graph below, which compares the discharge performance of a 3D battery with that of a typical commercial VRLA product at  $-20^{\circ}$ C. It can be seen

that at slow discharge rates there is a small but real advantage for 3D and this becomes significantly greater as the rate of discharge is increased, to the point where the advantage is three-fold at high (but realistic) discharge rates. Although it isn't shown, it is also the case that the Firefly 3D battery will continue to operate at lower temperatures on both charge and discharge, possibly even down to  $-40^{\circ}$ C or lower where other lead-acid products cease to function. The Firefly composite plate technology is distinctly different from traditional batteries, and the net result is Firefly's battery does not need to be "sized up" for cold weather performance.



# Greater than 3x advantage at High Rates of Discharge!

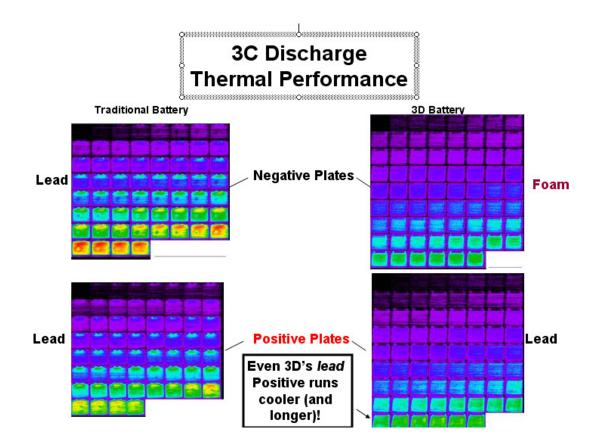
#### Hot Temperature

The optimum operating temperature for a lead-acid battery is  $25^{\circ}$ C (77°F). As a rule of thumb, every 8-10°C (14-18°F) rise in temperature will cut the battery life in half. This is a simple calculation based on field observations and on the increased chemical activity at higher temperatures. Lead grids corrode in the acidic electrolyte in the presence of lead dioxide, the positive plate active material.

Firefly batteries have superior performance in terms of thermal management. The heattransfer characteristics of the composite foam are better than metals such as aluminum and copper and approach that of diamond.

The pictures below show thermal images taken of a Firefly 3D cell and a comparable commercial VRLA cell to illustrate further the heat-transfer superiority of the composite foam. Both cells were subjected to a 3C-rate discharge, with thermal images being taken

every 15 seconds. The colors correspond to temperatures above ambient, with the green near or at ambient and the white some 10 degrees Centigrade above ambient.



Even though the Firefly 3D design utilizes a standard lead grid positive plate, the Firefly negative foam plate operates much cooler, and generates a "calming" influence to reduce the temperature of the lead grid positive. It can be seen that the Firefly cell runs cooler overall and the temperature gradient down the negative foam plate is more uniform than for the conventional VRLA cell – this in spite of the fact that the Firefly cell's discharge lasted about 2.5 minutes longer! More interesting, this temperature scan shows that the conventional positive plate used in the Firefly 3D cell has a cooler, more uniform heat signature throughout the discharge relative to the other VRLA cell's positive plate, again illustrating the outstanding heat-transfer performance of the foam negative. It not only dissipates the heat generated on it but also absorbs heat away from the positive plate and out of the cell. While not shown, the same will be true during recharge and on float, thus suggesting that lifetimes where positive grid corrosion is the failure mode will be longer in Firefly's 3D product. It will also make ultra-fast recharging more feasible for 3D batteries.

The thermal response patterns for these materials mean that graphite's heat-transfer performance is outstanding. Thus, batteries made with composite foam electrodes will

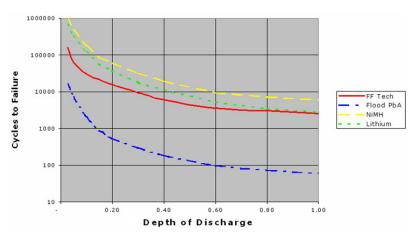
transfer heat out of the battery rapidly as it is generated by the electrochemical reactions taking place, thus making thermal runaway less likely and overall "cool" operation compared to conventional lead-acid batteries. The fact that heat is generated more uniformly and dissipated rapidly translates to longer life in many applications.

#### Dramatic Cycle Life Improvements

A full discharge of today's lead acid battery causes extra strain, and each cycle robs the battery of a small amount of capacity. In lead-acid batteries, deeper discharges convert larger amounts of charged active-material into lead sulfate. Lead sulfate has a significantly larger volume (about 37% more) than the charged material, and this volume change stresses the electrode structures. This expansion induces mechanical forces that deform the grid, and ultimately result in the lead grid "disappearing" into the paste.

The resulting expansion and deformation of the plates also causes active material to separate from the electrodes with a commensurate loss of performance.

Additionally, over time, sulfate crystals can grow together, resulting in large lead sulfate crystals that are difficult or impossible to convert



back into the charged state. This wear-down characteristic also applies to other battery chemistries in varying degrees. To prevent the battery from being stressed through repetitive deep discharge, a larger lead acid battery and shallower discharge is typically recommended. Depending on the depth of discharge and operating temperature, the sealed lead-acid battery provides 200 to 300 discharge/charge cycles. Short cycle life also results from grid corrosion of the positive electrode, which undergoes extensive oxidative stress during extended recharge conditions. These changes are exacerbated at higher operating temperatures.

In contrast, Firefly's Microcell<sup>TM</sup> composite plate technology provides a design which fully accommodates the volume changes of the active material during charge and recharge. Within each Firefly plate is contained a full compliment of active materials, electrolyte, and volume which will allow complete discharge without causing physical stress on the plate itself. This results in an electrode plate which does not undergo volume change during deep discharges. Firefly's



New Foam

Used Firefly Electrode

electrode material is not reactive in the chemistry and so does not corrode. This is in part due to a natural stability of the base material, but is also due to the formation process used which maximizes exposure of the most chemically resistive surfaces and minimizes exposure of chemically less-stable surfaces.

The growth of large sulfate crystals is also restricted, resulting in a low incidence of crystals which are too large to recharge. The strong resistance of Firefly's electrode material to corrosion also severely reduces the deleterious effects of long recharges. Because of the removal of grid corrosion as a life-limiting factor, the Firefly approach offers significant improvements over conventional lead-acid technologies in both float and deep-cycle applications.

Cycling in irregular applications such as partial-state-of-charge (PSoC) regimes used in hybrid vehicles and photovoltaic energy storage are also well suited to 3D technology. This is because the conditions of partial or heavy sulfation of the negative plate – a process that can render present-generation lead acid products unrecoverable – are easily reversed in 3D products, even after long periods of storage. Sulfation reversal is achieved because the nature of the lead sulfate deposits in 3D cells is fundamentally different from those in traditional lead acid cells. In the latter, lead sulfate is deposited on the surfaces of the plates in dense layers of relatively large crystals, somewhat remote from the lead grid members. Because the sponge lead active material in a 3D cell is deposited on the walls of the foam's many small pores in thin layers, and the surface characteristics of the foam result in relatively low current densities, the lead sulfate deposits are comprised of small, porous crystal structures (on the order of 3-10 microns, much smaller than in commercial products) that are easily dissolved on the subsequent recharge. Moreover, these very small crystal sizes grow only slowly over time. A final factor that facilitates recharge is the proximity of the carbon-graphite foam (as well as residual sponge lead) that can act as efficient current-carrying paths during recharge for the small, local deposits of lead sulfate crystals. This resistance to the effects of sulfation make Firefly 3D batteries ideal for seasonal applications where devices and their associated batteries (electric lawn mowers, boats, RVs, motorcycles, etc.) may go unused for months on end, often in a partially or fully discharged state. Conventional batteries are difficult or impossible to recover from these conditions, and are often replaced far short of their potential life span. With 3D products this problem is greatly reduced.

The low self-discharge rate and easy recovery from sulfation also mean that 3D batteries are not subject to the distribution chain and inventory time constraints of conventional lead acid products. 3D batteries can be subjected to much longer periods of inactivity without damaging effects. Conventional lead acid batteries are limited to storage times of 3 - 6 months at most before requiring a recharge – often with great logistical difficulty and expense.

Float and cycle lifetimes for 3D batteries have yet to be fully determined, but it is anticipated that they will be superior to those of comparable lead acid products due largely to the superior thermal conductivity levels of the composite foam relative to conventional lead electrodes, in combination with lower cell impedances and negative plate current densities.

A final life characteristic of the 3D cells is that, because of its use of light weight composite foam, their low mass makes them highly resistant to vibration. 3D cells subjected to vibration testing at Caterpillar's Technology Center have exceeded Caterpillar's stringent specifications by a wide margin, at which point they still had not failed. Clearly, foam robustness under the abusive conditions found in commercial, offroad, military, and many other applications will not be an issue for Firefly products.

## 3D Performance Summary

In summary, then, the 3D cell architecture results in numerous attributes:

- Instantaneous Power (2 hours and faster run-time rates)
- Fast recharge capability
- Continuous power through discharge process
- Recovery to full capacity after off-season storage
- Excellent cold temperature capacity utilization
- High temperature resiliency
- Recovery to full capacity after discharge

The remarkable attributes of the composite foam negative electrode noted above make certain applications possible or more favorable, as well as improving many lead acid "weak points" such as sulfation recovery and active-material utilization limitations. At slow discharge rates, modest weight and volume improvements over existing lead-acid products (typically 15-20%) are achievable as well. For faster discharge rate applications (like HEV, Starting or UPS applications), the weight and volume saving can approach 50-75% or more.

## **3D<sup>2</sup> Technology**

With the second implementation phase of Firefly's composite foam grid technology, dubbed  $3D^2$ , this new battery architecture achieves its fullest potential. While the 3D technology significant is a evolutionary improvement over existing lead-acid technology, the true potential of the Microcell<sup>TM</sup> technology is limited bv the conventional positive plate, which acts as a "brake" on the cell



performance in fast charging and during high-rate/low-temperature discharges. In addition, the cell lifetime is still limited by the failure modes associated with the positive

plate – PCL1, PCL2, grid growth and/or grid corrosion. Building on the 3D product design, the  $3D^2$  product continues to take advantage of the composite foam material for both the negative and positive plates alongside other components, replacing up to 70% of the lead utilized in traditional lead-acid batteries. This delivers a formidable jump in power, energy and cycle life beyond the 3D and approximates the performance of fully packaged lithium and nickel metal hydride batteries without the cost or safety factors.

Conversion of the conventional positive plate to a composite foam electrode eliminates positive grid growth and corrosion, but it also introduces a different set of challenges. Various foams used in the positive plate are affected to varying degrees when exposed to extreme overcharge conditions. As a matter of thermodynamics, composite foams can corrode (oxidize) in the positive potential region similar to the way lead grids corrode; however, electrochemical data show that foams of certain grades react differently in the upper potential ranges commonly experienced during recharge of the positive plate. Firefly is actively refining and stabilizing foam chemistry as well as increasing the robustness of the foams used in positive plates through manipulation of combinations of both foam chemistry and processing, as well as methods of plate preparation. At present, these chemistries and methods are trade-secret intellectual property, for which Firefly is actively pursuing additional patent protection.

It should be noted that the Firefly foam positive "grid" and pasted plate are fundamentally different from conventional lead-acid positives. Conventional positive plates contain lead alloy grids that are over-pasted and subsequently formed. These conventional positives can fail in a variety of ways that are not likely to occur with a foam-based positive plate. Lead alloy grids can fail due to grid growth and/or grid corrosion. Growth can cause failure due to plate-to-top-lead shorting or battery container rupture; grid corrosion, when extreme, results in mechanical degradation of the plate structure and severe, fatal reduction in current-carrying capabilities during discharge and charge. Extended life in both float and cyclic applications should be possible with foam technology due to elimination of these failure modes. In addition, failures due to PCL1 (grid/paste interface passivation) and PCL2 (positive active material (PAM) loss of connectivity) should not occur in the  $3D^2$  design due to the fact that the conventional corrosion-layer structure is not present (thus eliminating PCL1) and the PAM is in proximity to the foam walls and is not as dependent upon plate-stack compression as in conventional lead-acid batteries. In fact, 25,000x high-magnification scanning electron microscope (SEM) images show that PAM crystals are mechanically bonded to the carbon foam walls.

Thus, Firefly's  $3D^2$  technology involves having foam-based "grids" for both plates. Positive plates are pasted in the same way as foam negatives in the 3D product. With both electrodes having foam structures,  $3D^2$  batteries will have the following packaging and performance characteristics:

• Significantly lower volumes and weights (by up to ~50%) relative to comparable lead-acid products in terms of energy output; greater differences may accrue in high-power applications such as engine start, UPS and HEV

- Lower plate mass results in a high level of vibration resistance.
- Can be constructed in either flooded or VRLA configurations
- Extremely rapid recharge capability
- Superior discharge performance
- Longer cycle life compared to existing lead-acid products, particularly in PSoC-type applications
- Longer float lifetimes, particularly in high-temperature usage

In summary,  $3D^2$  will be a "breakthrough" technology in that it offers the promise of allowing the use of lead-acid chemistry in new applications, some of which are currently being served by NiCad, NiMH and/or Li-Ion, as well as improving performance and life in existing lead-acid duty cycles.

## **Recycling of 3D and 3D<sup>2</sup> Products**

An added feature of both 3D and  $3D^2$  is that not only are they recyclable in the existing smelter operations, but the carbon/graphite acts as a fuel, thus lowering existing smelting costs. Batteries utilizing the composite foam technology pioneered by Firefly can be recycled within the industry's well-established infrastructure and require no modifications whatsoever to the process. Please follow this link www.fireflyenergy.com/environmental to read more about Firefly's Environmental advantages.