In recent years performance requirements with respect to lead-acid batteries for automotive applications are beginning to undergo major changes as the vehicles themselves change. In addition to the traditional “SLI functions” (starting, lighting and ignition), there is also a need to provide advances in technologies for environmental improvement, batteries for accessory applications (power steering, stabilizers, etc.), new functions such as alternator control for charging controls aimed at suppressing gaseous emissions and improving fuel economy, stopping of idling, and regenerative braking. Furukawa Battery is engaged not only in basic technology and product development for lead-acid batteries to meet these requirements but also in developing the “Ultrabattery”—a new type of lead-acid battery that will meet the sophisticated requirements of next-generation vehicles.

1. INTRODUCTION

More than 50 years have passed since the time when lead-acid automotive batteries changed from 6-V to the current 12-V system. During this period, car batteries were optimized for SLI duty, and because they were mounted in the engine compartment, they were required to withstand high temperatures. Furthermore, when left in the discharged condition, lead-acid batteries also undergo a process known as sulfation, in which lead sulfate crystals, the product of discharge, grow larger, so that the process becomes irreversible and service life is shortened. Thus the batteries have to be kept at full charge and need to have overcharge resistance. Progress has been made in reducing maintenance by suppressing electrolysis of the water in the electrolyte by using Pb–Ca grid alloy instead of Pb–Sb alloy, and in improving the corrosion-resistance of the positive grid. By these means the life of lead-acid batteries has been extended, and topping of water has been made virtually unnecessary.

In recent years however, there have been significant changes in the environment in which automotive lead-acid batteries are used. In addition to the traditional “SLI functions”, there is also a need to provide advances in technologies for environmental improvement, batteries for accessory applications (power steering, stabilizers, etc.)—the so-called “Micro-HEV” functions such as alternator control for charging controls aimed at suppressing gaseous emissions and improving fuel economy, idling-stop and regenerative braking for the next generation of automobiles.

Up until the present, what is known as charge control consisted of limiting the overcharging carried out to maintain a lead-acid battery at full charge, and by keeping the amount of charge low, to reduce fuel consumption to generate electricity. This means that there is a greater chance of the battery’s state of charge being less than 100 %.

In addition, regenerative braking, in which the energy previously dissipated by friction is converted to rotary motion of the alternator thereby generating power to charge the battery, is the function that has come to be seen as the panacea for cutting fuel consumption. In order for the electrical energy that has been generated to be stored efficiently, it is necessary that the battery be kept at a partial state of charge (PSOC) of from 60 % to 90 %. This means it must be operated under conditions which in the past presented difficulties owing to the occurrence of sulfation. It is also necessary to develop diagnostic equipment that not only maintains the state of charge under specified conditions but also, due to the need to guarantee starting performances after idling-stop shutdowns, is able to detect the battery’s failure status.

At Furukawa Battery, we are carrying out development of basic technology for lead-acid batteries suited to these needs, battery development, and development of status detection technology, as well as pursuing the development of the Ultrabattery—a capacitor hybrid lead-acid battery that provides for the sophisticated requirements of the next generation of automobiles. In this paper we will introduce some aspects of technologies addressing the need for lead-acid batteries of increasing sophistication.

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2. DEVELOPMENTAL ACTIVITIES

For a start, Figure 1 is a graph showing the relationship between typical failure modes of lead–acid storage batteries and life span in terms of number of cycles. These modes are identified as premature capacity loss modes: PCL-1, -2 and -3. In PCL-1, a non-conductive layer composed of lead sulfate and lead oxide forms at the interface between the positive grid and the active material, leading to capacity loss. In PCL-2, changes in the microstructure of the positive active material (PAM) cause softening and shedding, resulting in capacity loss. PCL-1 and -2 are failure modes that have been clarified by using Pb–Ca alloy to replace Pb–Sb alloy in the positive grid---the antimony-free effect, and understanding of the mechanism and measures to address it are progressing. PCL-3 is a failure mode that first became evident in PSOC applications. It has been found that a fine lead sulfate film is formed on the surface of the negative electrode, inhibiting ion movement and reducing capacity, and countermeasures are being developed worldwide.

Positive grid corrosion and growth are also failure modes that are typical of lead–acid batteries, and by developing new alloys, we have achieved improvements in life span not equaled elsewhere.

In Section 2.1, therefore, we introduce technology for improving positive grid durability that has attracted notice worldwide, and in Section 2.2 we describe a unique approach to status detection. In Sections 2.3 and 2.4 we introduce lead–acid batteries for next-generation automobiles, incorporating advanced PCL-3 solutions. Then in Section 2.5 we outline the developmental status of the "Ultrabattery" a capacity hybrid lead–acid battery that is the focus of world attention.

2.1 Highly Corrosion–Resistant Alloy for Positive Grid

The primary failure mode in conventional lead–acid automotive batteries has been positive grid corrosion, and this corrosion was particularly rapid in vehicles whose engine compartments reached high temperatures and in regions of high temperature. Corrosion also gave rise to growth—creep caused by the tensile strain of its products. The grid plays a role as current collector, and a role as supporter for the active material, so if grid corrosion proceeds it will lead to an increase in electrical resistance due to a reduction in the current-carrying area and to a drop in discharge performance resulting from poorer contact between the grid and the active material caused by grid growth, and this will reach the service life limit. Higher temperatures in the operating environment result in synergistic acceleration of corrosion and growth, and this will have an important impact on battery service life.

As a means of countering high temperatures, alloys with 0.01 to 0.03 wt % of Ag added to Pb, Ca and Sn have come into wide use in other industrial countries since the 1990s, and it is reported that as a result the concentration of Ag impurities in lead for recycling has risen rapidly from about 15 ppm to around 50 ppm. Since not only JIS but the industrial standards of many other countries have set 50 ppm as the upper limit of Ag concentration, there are fears for the effect on battery performance. As an alternative, attention has been given to alloys with added Ba, but these have not come into general use.

We have taken another look at Ba as an additive element that does not build up through recycling, and by performing a large number of experiments and evaluations of alloys combining it and other additives, we have developed a new alloy that in terms of corrosion-resistance and creep-resistance is far superior to what has come before. In the belief that this alloy will achieve customer satisfaction in the 21st century, we have named it the "C-21 alloy".

We compared other representative positive grid alloys and the C-21 alloy. Table 1 shows the composition of the alloy samples used in the comparison. Figure 2 shows the result of constant-potential corrosion tests using these alloys, and Figure 3 shows the result of high-temperature creep-time-to–rupture tests (100°C, 16. 5 MPa, constant load). It can be seen that the C-21 alloy exhibited clear superiority to the other positive grid alloys in

![Figure 1](image1.png) Failure modes of lead–acid batteries.

![Figure 2](image2.png) Corrosion weight loss for selected alloys at constant potential (720 hr, 1350 mV vs. Hg/HgSO₄, 4.9M H₂SO₄, 60°C).

Table 1 Composition of test alloys (wt %).

<table>
<thead>
<tr>
<th>Base alloy</th>
<th>Additive element</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional (a)</td>
<td>High Sn conc. Pb-Ca alloy</td>
</tr>
<tr>
<td>C-21 (b)</td>
<td>Pb-Ca-Sn</td>
</tr>
<tr>
<td>Ag added (c)</td>
<td>Pb-0.04Ca-0.60Sn</td>
</tr>
<tr>
<td>Ba added (d)</td>
<td>Pb-0.06Ca-1.60Sn</td>
</tr>
</tbody>
</table>

We then made a prototype battery using the C-21 alloy and carried out the JIS shallow cycle life test at 75°C. Figure 4 shows the result, and Figure 5 shows the appearance of the positive grids after the test. These results demonstrate that the C-21 alloy is superior in terms of corrosion- and growth-resistance, and significantly extends service life over batteries using the conventional alloy. Batteries using the C-21 alloy were brought to aftermarket in October 2002, and since then have been widely adopted by automobile manufacturers and overseas recipients of technical assistance.

2.2 Status Detection Technology

2.2.1 Methodology
Status detection for lead-acid batteries has two objectives: 1) diagnosis of failure status to determine the time of battery replacement; and 2) determination of state of charge (SOC), state of health (SOH) and state of function (SOF) in Micro-HEVs and other next-generation vehicles.

In 2) is incorporated the measurement of battery temperature, open-circuit voltage, charge and discharge current, voltage, AC impedance, etc., and methods of diagnosis through simultaneous logging and correlation of these values. Since lead-acid batteries used in Micro-HEVs provide charging through regeneration while assuring engine restarting performance, they need to be regulated to a specific PSOC. They also need to provide precise sensing, based on information on current, voltage, temperature etc., of the frequent changes in battery status while running. From the standpoint of the problem of electrolyte stratification that is inherent to lead-acid batteries, the world’s manufacturers of automobiles, electrical accessories and batteries are in the process of developing status detection algorithms and sensors, and some of these have appeared in commercial form.

2.2.2 Lead-acid Batteries with Built-in Tester Functions
The diagnosis as to when to replace a car battery has generally been made using testers installed in service stations, but more recently batteries have appeared that themselves incorporate a diagnostic function. Here we present the world’s first practical car storage battery having a tester function built in.

In the past the main type used was the load tester, which determines the drop in voltage when subjected to intentional discharge, but that had the disadvantage that diagnosis was not possible in the discharged state. It was also necessary to visit a service station equipped with such a tester. To eliminate these failings, the “FGUARD®” lead-acid storage battery with built-in tester function, capable of diagnosing the failure status any time, any where, was introduced to the aftermarket in October of 2003. The FGUARD incorporates in its lid diagnostic circuitry based on the conductance method, which was developed by America’s MIDTRONICS. Both SOC and SOH are determined by pressing the tester button, which then measures open circuit voltage, battery temperature and conductance under application of pulse current, and checks against a control algorithm. The result is shown by LED display. Figure 6 shows the appearance of the FGUARD battery. Even now, three years after it went on sale, the FGUARD is well regarded by customers.

2.3 Lead–Acid Battery for Idling–Stop Vehicles (Micro–HEVs)
Idling-stop, the shutting down of an internal combustion engine instead of idling, is a measure to counteract global warming that has begun to find favor by some taxis and
transit buses. It has been reported that in a transit bus idling-stop test done by the Tokyo Metropolitan authorities, fuel economy was increased by 14%. Idling-stop was also proposed in 2002 by the Outline for Promotion Effects to Prevent Global Warming as one of the measures in its transportation sector, and they have been working to extend its implementation among Japan’s automobile manufacturers. Against this background methods for testing the cycle life of lead-acid batteries from vehicles offering the idling-stop feature were investigated jointly by the Society of Automotive Engineers of Japan (JSAE) and the Battery Association of Japan (BAJ), and in 2006 was established as a Standard of the BAJ. (SBA S0101 Idling-Stop Life Cycle Testing).

In conventional lead-acid car batteries, however, the main factor affecting the service life cycle was positive electrode failure, while in the idling-stop cycle life test, reduction in the specific gravity of the electrolyte and sulfation of the negative electrode proceeded preferentially and, when they become far advanced, the phenomenon of thinning of the lugs that serve as current collectors at the negative electrode appeared. We at Furukawa Battery have been able to clarify the reasons for the thinning of negative lugs, and by controlling negative electrode sulfation and further improving the positive electrode, have developed a battery with greatly extended idling-stop cycle life.

Figure 7 shows the cycle life test profile for idling-stop by SBA S0101. This charge/discharge profile is repeated for 3,600 cycles, after each of which it is left 40 to 48 hours, after which the cycle is repeated. Since the testing environment is a 25°C air chamber that limits the impinging of wind on the battery, battery temperature rises due to Joule heating. The target cycle life with this test is 30,000 cycles or more.

When the test was carried out on a conventional lead-acid battery of JIS D23 size, the life was 15,000 cycles or less. The failure mode was negative electrode sulfation, but negative lug thinning was also observed. Methods of suppressing negative electrode sulfation have included increasing the amount of carbon additive to the negative electrode to form a conductive network around the lead sulfates, allowing the lead sulfates to be more readily reduced. In this idling-stop cycle life test, however, the effect obtained was inadequate, so we attempted to achieve further suppression of negative electrode sulfation by the use of a new additive. When the test was carried out on a D23 size lead-acid battery using the new additive, negative electrode sulfation was significantly suppressed and negative lug thinning was not observed. The life span was 75% greater than with the conventional battery, but did not reach the 30,000 cycle target.

The significant factor in the life of this battery with suppressed negative electrode sulfation, however, changes to softening of the active material of the positive electrode, so for further extension of cycle life, improvement of the positive electrode was required. Accordingly in order to suppress this softening, we proceeded to optimize active material density and develop a new additive, as well as to develop a new type of separator. The improvement obtained by these means was confirmed by a JIS heavy-load test that reflects the influence of softening, and life was extended by 35%.

We therefore manufactured prototypes of D23 size lead-acid batteries for idling-stop that implemented these improvements. In terms of 5-hour rate capacity factor, high-rate discharge characteristics at -15°C, and the like, performance equivalent to conventional lead-acid batteries was maintained. Figure 8 shows the results of idling-stop cycle life tests. In the product under development, the drop in electrolyte specific gravity was reduced, and it was possible to extend the service life significantly beyond the target of 30,000 cycles. Even in a tear-down examination after testing, virtually no negative electrode sulfation or negative lug thinning was observed. Currently this battery is undergoing in-service testing in taxis and owner-driven cars, and as we accumulate practical data we are preparing for commercial introduction.

2.4 Lead-Acid Batteries for High-Voltage Hybrid Vehicles (Medium-HEVs)

Valve-regulated lead-acid (VRLA) batteries use a separator in the form of a mat made of fine glass fibers, and

![Figure 7 Cycle life test profile for idling-stop by SBA S0101.](image_url)

![Figure 8 Improvements in idling-stop cycle life and electrolyte specific gravity for the product under development.](image_url)
since the electrode plates are kept under high compression while the electrolyte is limited to the amount impregnated in the electrode plates and separator, they are light in weight and have superior charge/discharge characteristics. For this reason they are better suited than wet-type batteries to vehicles with idling-stop (Micro-HEVs) and mild hybrid vehicles (Mild-HEVs). Furukawa Battery is also proceeding with the development of long-life 12- and 36-V VRLA batteries for this type of application. Here we will present an outline of the development of the FT7C–HEV VRLA battery that is installed in the Suzuki “Twin”, a high-voltage type hybrid sub-compact vehicle that went on sale in January 2003. Figure 9 shows the appearance of the battery. It is a 12-V battery having a 6.3-Ah (3 HR) capacity, featuring compact size, high-density structure, excellent input-output performance, extended PSOC cycle life, and so on. A battery pack, consisting of 16 of these connected in series, is installed in the Twin.

To allow this battery to be mounted on a narrow base, a design was adopted that minimized the space inside the battery, achieving a 10% reduction in volume compared to a VRLA battery of the same capacity for motor cycles. The terminals used a high clamping strength structure to provide reliability when connected.

For the positive electrode plates, an alloy of high corrosion resistance was used for the grid, and active material density was maximized with respect to charge/discharge profile and depth of discharge (DOD) for the Twin.

Further, since in high-voltage type hybrid vehicles the battery generally undergoes frequent repetition of large-current charge and discharge, lead-acid batteries suffer a drop in charge/discharge performance and regenerative charging performance due to sulfation of the negative electrode. Accordingly we revisited the question of additives for the negative electrode active material, and by maximizing the amounts of added carbon, lignin, and barium sulfate, we managed to reduce sulfation. Also in battery packs, each individual battery needs high reliability, so that the role of the separator is important. Thus reliability was enhanced by adopting a separator having a level of resistance to short-circuiting that was greatly improved by the optimization of fine glass fiber and additives.

Figure 10 compares input power characteristics for the battery under development here and a VRLA battery for motor cycles. At a DOD of 50%, the battery developed here showed more than double the input power of the battery for motor cycles. Figure 11, for its part, shows the results of the PSOC cycle life test. Compared to the lead-acid battery for motor cycles, the battery developed here had a life span about four times longer.

2.5 Development of the Ultrabattery

In Micro-HEVs having the idling-stop and discharge regulation features, and in mild hybrid vehicles and high-voltage type hybrid vehicles, which also have regenerative braking and power-assisted functions, the state of charge of the battery is constantly kept in the partial state. They are also subjected to large-current pulse charge and discharge, and other extreme conditions of use that were not previously encountered.

In these applications, lead-acid batteries are beset by the inherent problem that lead sulfate recrystallization cannot be avoided, but charge/discharge power characteristics must also be improved. As a means of improving such performance, proposals have been made for battery capacitor modules in which lead-acid batteries and high-capacitance electric double-layer capacitors are connected in parallel. However there are a number of problems with respect to configuring practical battery capacitor modules, including the high cost of electric double layer capacitors, their low volume energy density, and the further cost imposed by the need for control circuitry for hybridization with the batteries.

In order to achieve a complete solution to the PSOC issue, Furukawa Battery, working together with Australia’s CSIRO, has developed the Ultrabattery—a hybrid lead-acid battery in which battery and supercapacitor are integrated at the electrode plate level.

![Figure 9 Appearance of the FT7C–HEV battery.](image1)

![Figure 10 Input power characteristics.](image2)

![Figure 11 Cycle life test results.](image3)
2.5.1 Ultrabattery Structure
Figure 12 shows the structure of the Ultrabattery, which comprises a lead-acid battery and asymmetrical capacitor combined in a single cell. The lead-acid battery has a positive electrode of lead dioxide and a negative electrode of spongy lead. The asymmetrical capacitor, for its part, has the same positive electrode as the battery—lead dioxide, and a negative electrode of porous carbon. Since both have a common positive electrode, the lead negative electrode and the capacitor negative electrode can be connected in parallel and housed in the same cell with the positive electrode. This results in the capacitor electrode bearing a portion of the load of the lead storage electrode. This holds promise that it can be used in applications involving PSOC characteristics and large-current charge/discharge, which could not heretofore be adequately addressed by lead-acid batteries. What is more, since the Ultrabattery requires no special electronic control circuitry it has advantages in terms of cost.

2.5.2 Capacitor Electrodes
Since the capacitor electrodes are made of porous carbon, there is a need to suppress evolution of hydrogen gas during charging, and additives for this purpose were developed. Figure 13 shows the results of measurements of the amount of hydrogen evolved as potential was varied. In contrast to the capacitor electrode without additives, the amount of hydrogen evolved at the capacitor electrode with additives was substantially the same as at the lead electrode.

2.5.3 Ultrabattery Performance
We constructed a prototype 2-V valve-regulated Ultrabattery, and compared it with a conventional VRLA battery in terms of input and output performance and of cycle life characteristics.

Figure 14 shows the input and output characteristics. In mild hybrid vehicles the batteries are used at DOD ranging from 30 % to 70 %, but the Ultrabattery shows outstanding input and output characteristics over a wide DOD range, demonstrating its suitability for PSOC applications.

We carried out cycle life tests at a PSOC based on a reliable, highly optimized lead-acid battery (RHOLAB) profile that simulated a combination of high-speed and hill-climbing running conditions for a mild hybrid vehicle. Figure 15 shows the results. It can be seen that the life span achieved was outstanding—about four times longer than a lead-acid battery.
As has been confirmed above, the Ultrabattery is clearly superior to lead-acid batteries at PSOC, and has gained worldwide notice for the promise it holds for use in sophisticated next-generation vehicles, for which lead-acid batteries have heretofore been considered inapplicable.

3. CONCLUSION

At a time when measures to counter global warming have taken on new urgency, automobiles are beginning to face emission controls of unprecedented severity. We are indebted to the automobile industry for allowing us to attain a leading position for quality and technology as a supplier of automotive lead-acid batteries. In addition to the advanced technology for lead-acid batteries described in this paper, we are committed to further technological development, and by curtailing the emission of greenhouse gases from next-generation vehicles, we will contribute to the continued development of society.

REFERENCES