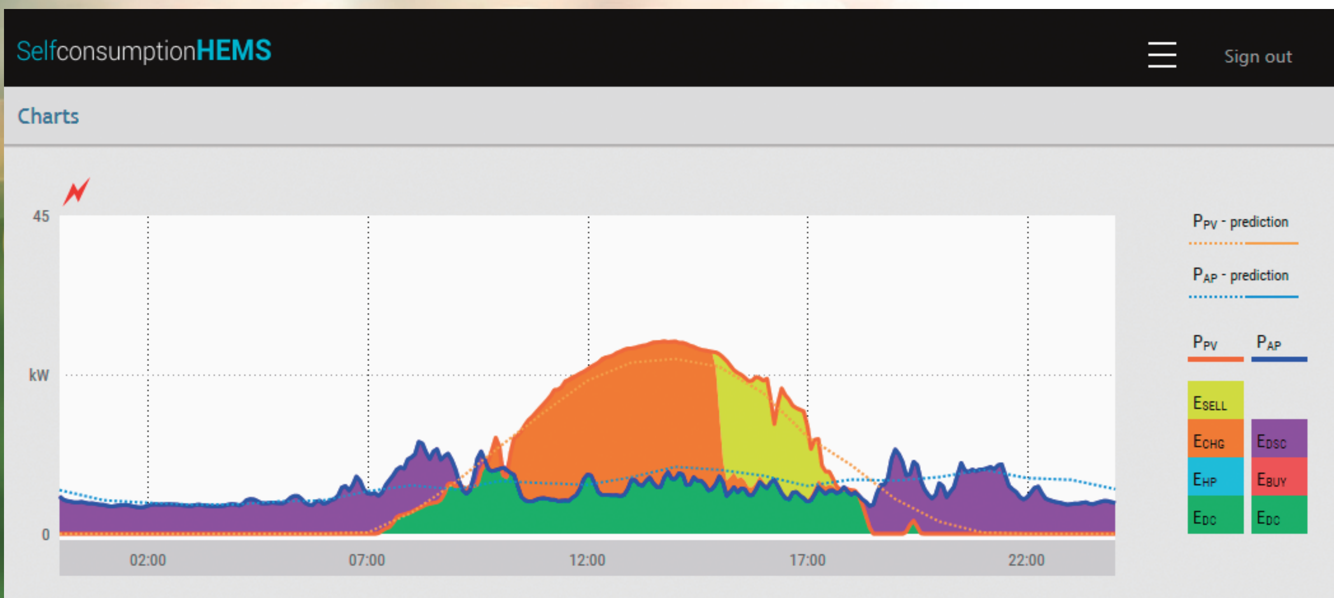
Hitachi Chemical
Working On Wonders

Hitachi Chemical Technical Report

No.60 ／ March 2018



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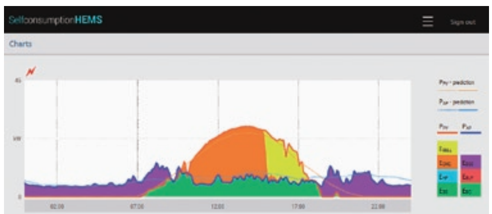

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COMMENTARY

Vice President and Executive Officer
General Manager
Energy Storage Business Headquaters

Misao Nakagawa

Global Expansion of Energy Business —Understanding the True Needs of Business Partners—

When Hitachi Chemical became independent of Hitachi, Ltd., in 1962, it took over four products as its original products: insulation varnishes, carbon brushes, industrial laminated plates, and porcelain insulators. Based on these, Hitachi Chemical has since produced many product groups based on material technology, process (synthesis and processing) technology, and evaluation technology. Currently our business focuses on four fields: information communications, environment and energy, life sciences, and automobiles.

This current special issue examines two applications in our energy storage business, for use in industries and automobiles. One is the use of power accumulation systems, which mainly include power storage devices, such as secondary batteries and capacitors. The second is the provision of services and solutions related to the monitoring and maintenance of batteries.

Core industries, such as telecommunications and automobiles, need power storage devices, and stable growth is expected in this business field in the future. In addition, because of the increased interest in global warming in recent years, the application of these devices is expanding to new fields, for example, to introduce renewable energy and to reduce CO_2 emissions by motorization.

To develop our energy business into a new core business of Hitachi Chemical, we are working toward non-continuous growth by expanding our business from the domestic market to the global market.

As the first step in this effort, in fiscal year (FY) 2014, we established a consolidated subsidiary, Hitachi Chemical Energy Technology Co. Ltd. (hereinafter "HCEN Co."), with the brand "CSB". Headquartered in Taiwan, HCEN Co. manufactures and sells small batteries for UPS (uninterruptible power supply) devices. Its customers include the three leading UPS companies in the world. In terms of their product lineups, HCEN Co. has a complementary relationship with Hitachi Chemical, which specializes in large industrial batteries and has a global sales network.

Next, in FY 2016, Hitachi Chemical established FIAMM Energy Technology S.p.A. (hereinafter "FET Co."), with the brand "FIAMM". A joint venture for which Hitachi Chemical owns the majority of the stock, FET Co. is headquartered in Italy, and

manufactures and sells automotive and industrial batteries. Through FET Co., which holds a large share of the market primarily in Europe, Hitachi Chemical was able to acquire its first manufacturing sites, sales channels, and brand in Europe. Consequently, for the Hitachi Chemical Group, FY 2017 can be thought of as its “first year in Europe”.

Then, in FY 2017, we proceeded to acquire stock of Thai Storage Battery Public Company Limited (hereinafter “TSB Co.”), ultimately making the company a consolidated subsidiary. With the brand “3K” and headquarters in Thailand, TSB Co. mainly manufactures and sells automotive batteries and has big brand power in ASEAN nations.

Through these activities, Hitachi Chemical has successfully expanded its energy business from the domestic market to the European and ASEAN markets, and aims to firmly establish its position in the global market by expanding its scale of business.

Crucial to the global expansion of our energy business is communication with our new Group companies. Through such communication, we can achieve synergy, particularly in the area of development, where it is important not only to integrate technologies but also to properly share information about our customers’ needs for cutting-edge technology and to create better products that address those needs. By leveraging our core technologies in the fields of materials, processes, and evaluation, Hitachi Chemical will respond to the needs of customers around the world. To become a battery manufacturer with a deep understanding of systems, Hitachi Chemical strives to learn about our customers’ systems and to propose the most suitable batteries to enable our customers to optimize the use of their systems.

This approach of correctly identifying a customer’s true needs and then creating new technology in collaboration with the customer applies not only to our energy business but also to the businesses of the Hitachi Chemical Group as a whole.

In January 2017, Hitachi Chemical opened the Innovation Center on the 29th floor of a building adjacent to our headquarters. With our energy storage business departments helping to promote the activities of the innovation center, the center provides a space where we can interact with customers and where visitors can view actual products, conceptual displays, and informational videos related to the various technologies owned by Hitachi Chemical. We hope you will come and visit this private gallery to learn about our technologies in the business fields of information communication, environment and energy, life science, and automobiles, as well as technologies tailored to specific customer requests. Through collaboration with our customers, Hitachi Chemical will create cutting-edge technology responding to our customers’ various needs.

With a pioneering spirit to explore uncharted areas, we will continue to develop innovative solutions beyond the boundaries of chemistry, delivering wonders that exceed the expectations of customers and society.

New Product Development to Support Global Growth of Energy Storage Business

Masatoshi Shiiki
Energy Storage Business Strategy Sector,
Energy Storage Business Headquarter

Satoshi Minoura
Advanced battery & System Development Center,
R&D Headquarters

With global warming becoming increasingly serious, the 21st Conference of the Parties (COP 21) to the United Nations Framework Convention on Climate Change (UNFCCC) was held in December 2015 and ended with the adoption of the Paris Agreement. So that all countries can vigorously promote measures against global warming, it is important to establish an energy innovation strategy leading towards an energy supply-demand outlook (energy mix) that minimizes the ratio of fossil fuel energy consumption in total energy use. It is essential to pursue rigorous energy-saving efforts; to make the maximum use of wind power, photovoltaic, and other renewable energy sources free from greenhouse gas (GHG) emissions; and to develop new energy systems in the power generation and transportation sectors. It is expected that the development and practical application of new energy systems using batteries will provide concrete solutions. An electrical energy storage device is an optimal device for achieving storage and spatiotemporal transfer of electrical energy. Our company has accumulated an extensive set of common core technologies and expertise through many years of product development related to batteries and electrical energy storage systems. We expect that the needs and demand for electrical energy storage devices will further increase as revolutionary advanced systems appear in key industries such as electric power and automotive. To prepare ourselves for the next big waves of electrical energy storage device revolutions, this issue organizes and outlines our proprietary technologies as global core technologies with focus on lead-acid and lithium-ion batteries.

1 Introduction

With global warming becoming increasingly serious, the 21st Conference of the Parties (COP 21) to the United Nations Framework Convention on Climate Change (UNFCCC) was held in December 2015 with the attendance of major emitter countries of greenhouse gases (such as CO_2). This Conference adopted the so-called Paris Agreement, an international framework that provides for, among other matters, setting a common long-term global target (2°C target) aiming at keeping the rise in global temperatures to less than 2°C.

This global warming prevention measure seeks to reduce GHG emissions from fossil energy consumption. After conversion losses occur in the power generation and petroleum refining processes that convert supplied primary energy into electricity, petroleum products, etc., secondary energy is supplied in various forms, such as electric power, heat, and petroleum products (gasoline, kerosene, etc.) to the ultimate consumers. This secondary energy is consumed as the end-user energy in the form of electric power energy and vehicle driving energy (such as gasoline) by households and in the industrial and transportation sectors. In Japan, assuming that the primary fossil energy supply for fiscal 2014 is 100%, electric power energy and vehicle drive energy accounted for approximately 65% of end-user energy consumption including conversion losses. These two forms of energy constitute the largest source of GHG emissions.

So that all countries can vigorously promote measures against global warming, it is important to establish an energy innovation strategy towards an energy supply-demand outlook (energy mix) that minimizes the ratio of fossil fuel energy consumption to total energy use. It is essential to pursue rigorous energy-saving efforts, to make the maximum use of wind power, photovoltaic, and other renewable energy sources free from GHG emissions, and to develop new energy systems in the power generation and transportation sectors.

Germany has advanced environmental measures and is also committed to its energy transition policy Energiewende. As such, Germany is rapidly replacing conventional power generation facilities, such as nuclear, fossil-fuel, or otherwise fired power plants, with renewable energy sources. On the other hand, renewable energy sources are unstable distributed power sources with large weather-induced fluctuations in the amount of supplied power. There are fears that increases in the use of such sources will lead

to unstable electric power grids, which poses a global common problem. The development and practical application of new energy systems using batteries is expected to resolve this problem. Our company has proposed the use of a hybrid electrical energy storage system consisting of a combination of lead-acid and lithium-ion batteries and other electrical energy sources. As a member of a Euro-Japan collaborative demonstration project on renewable energy implementation under the New Energy and Industrial Technology Development Organization (NEDO), we have been promoting the construction of new energy systems in Germany and Poland.

Another major source of GHG emissions is gasoline, kerosene, or other fuels used as vehicle driving energy in the transportation sector. The automotive sector has started to undergo a rapid shift from internal combustion engine vehicles, such as gasoline and diesel engine vehicles, to hybrid, plug-in hybrid, and electric vehicles (xEV vehicles). In the United States, California has enhanced its environmental measures through the enactment of the world's first Zero-Emission Vehicle (ZEV) regulations that require automotive manufacturers to produce eco-friendly vehicles free from CO_2 and other emissions. Additionally, China has established the New Energy Vehicle (NEV) regulations, which will come into effect in the administrative year 2018. Passenger vehicle manufacturing enterprises will have to meet the prescribed corporate average fuel economy (CAFC) value every year from 2018. To achieve this regulation value, it is necessary to continue increasing the production ratio of xEV vehicles. Hence, automotive manufacturers around the world have started vigorous promotion of electric motorization. In tandem with the start of the full-scale introduction of automated driving and IoT technologies, revolutionary changes in on-board batteries are also underway: for example, on-board power supplies with an enhanced capacity, increases in standby power, and transition from lead-acid to lithium-ion batteries. Europe and Japan are also moving to establish regulations aiming at the wider use of eco-friendly vehicles, and Europe in particular is geared toward boosting the use of micro-hybrid vehicles. We have set up FIAMM Energy Technology S.p.A. (hereafter "FET S.p.A."), a joint venture with a high market share of batteries for automotive and industrial applications mainly in Europe. Headquartered in Italy, FET S.p.A. works jointly with European automotive manufacturers to put new on-board batteries to practical use.

An electrical energy storage device is optimal for achieving storage and spatiotemporal transfer of electrical energy. Our company has accumulated extensive common core technologies and expertise through many years of product development related to batteries and electrical energy storage systems. We expect that needs and demand for electrical energy storage devices will further increase as revolutionary advanced systems appear in key industries such as electric power and automotive.

To prepare ourselves for the next big waves of electrical energy storage device revolutions, this issue organizes and outlines our proprietary technologies as global core technologies with a focus on lead-acid and lithium-ion batteries.

2 Active Material Technology for Lead-Acid Batteries

Active materials, on which lead-acid batteries depend for charge-discharge reactions, have been improved to meet the required characteristics. We have accumulated technologies related to negative active materials for vehicles equipped with an idling stop and start system, widely used in recent years as an automotive fuel economy improvement technology.[1,2,3] Here we will briefly summarize the battery characteristics required of lead-acid batteries for vehicles equipped with an idling stop and start system. **Figure 1** shows a typical Charge and Discharge model for such vehicles. After the engine starts, the lead-acid battery is in charge mode during traveling. While the vehicle is idling, the engine is stopped and required power is supplied from the lead-acid battery; hence, the lead-acid battery is in discharge mode.

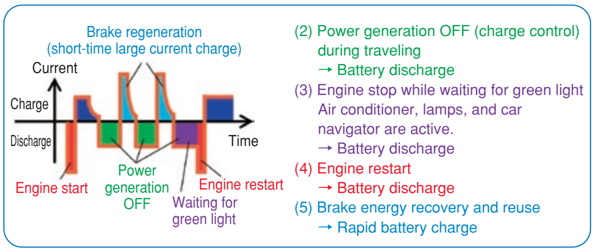

Figure 1 Charge and Discharge model of the battery for Idling stop and start system

Development technology	First generation	Second generation	Third generation
Positive active material		Development of high-durability active material	←
Negative active material	Development of new synthetic lignin	Development of new carbon material	←
Separator			Development of new separator

Figure 2 Techniques of the battery for Idling stop and start system

This model diagram shows that a lead-acid battery must be capable of rapidly restoring the electric power used during an engine stop and must be durable enough to withstand frequently repeated charge and discharge.

Figure 2 shows the technical characteristics of each generation of our lead-acid batteries for vehicles equipped with an idling stop and start system. For the first generation batteries, a synthetic lignin was developed to optimize the functional groups in the organic material and was adopted to replace natural lignin, which was then the mainstream of additives for negative active material. As a result, the charge acceptance was increased by 1.9 times.[1] For second generation batteries, the carbon material added to the negative electrode active material was reviewed for higher durability.[2] It is said that carbon is absorbed into the active material to destabilize the produced lead sulfate and prevent its accumulation. We investigated how long acetylene black, the conventionally used carbon, maintains such an effect. **Figure 3**[2] compares the two carbon materials in terms of the duration of lead sulfate accumulation prevention effect. It turned out that flake graphite maintains the effect longer than conventional acetylene black. Through the development of the first two generations, we obtained technologies for manufacturing new batteries with 2.0 times higher charge acceptance and 3.5 times higher durability than conventional lead-acid batteries.

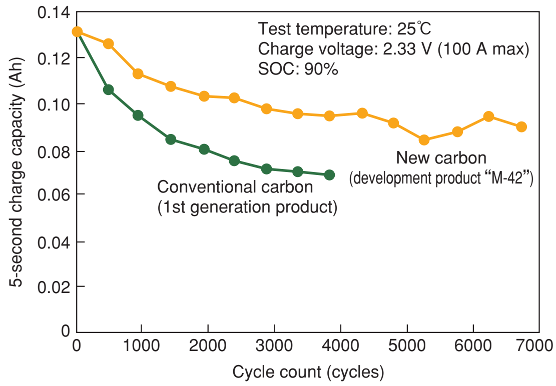

Figure 3 Change in charge capacity for 5 seconds

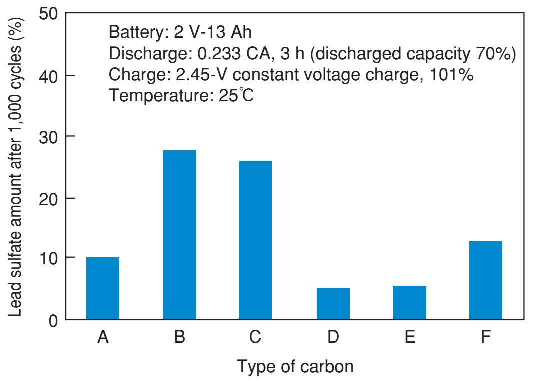

Figure 4 Comparison of amount of lead sulfate in negative active material using different carbon

We will now show a typical active material technology for industrial lead-acid batteries. We developed the LL Series as lead-acid batteries for wind power output stabilization.[4,5,6] The characteristics required of lead-acid batteries for wind power output stabilization are improved charge and durability characteristics in a long-period fluctuation absorbing region, in other words, a relatively long-time region. We studied the additives to the negative active material for both improved charge performance and durability. **Figure 4** shows the results of the study on typical additives. Based on these results, we successfully optimized the additive to the negative active material.

3 Lead-Acid Battery Design Technology

Current collectors in mainstream use for lead-acid batteries are cast grids obtained by die-casting molten lead alloy, punched grids obtained by punching out rolled lead alloy sheets, and expanded grids obtained by expansion processing. The function required of a current-collecting grid is the electrical current collection function for efficiently conducting the electricity generated by the electrochemical reaction of the active material to the current collecting part. Accordingly, an optimal grid design can be obtained by appropriately specifying the thickness and position of the grid to match the current density. **Figure 5** shows a simulated distribution of grid resistance.[1] This shows the results of a simulation used for designing a battery grid for idling stop and start systems (ISS). These results reveal that the conventional grid experienced a voltage drop of approximately 1.2 V in its lower part, whereas the development product showed a voltage drop of approximately 0.8 V in its lower part, thus achieving an approximately 25-percent resistance reduction compared with the conventional grid. On the other hand, a grid made of lead alloy becomes gradually corroded during use and consequently undergoes grid growth, which may lead to internal short-circuiting. Therefore, a grid design that minimizes grid growth caused by corrosion[7,8] is necessary. **Figure 6** shows the results of grid growth analysis of lead-acid batteries for power storage.[7] The existing product was significantly grown at 4,500 cycles; its failure mode was grid growth. However, the developed product is expected to show an approximately 35% decrease in grid growth compared with the existing product. These results also reveal the correlations with

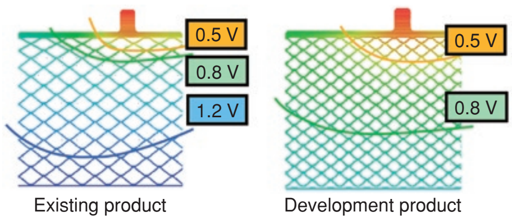

Figure 5 Results of grid resistance simulation

the amount of grid growth during actual use and show the validity of the simulation used for the grid design. Conventionally, grid designs were determined through a cyclic process consisting of design, trial manufacture, experiment, and review. Now created with the use of simulations, grid designs help not only to reduce development lead-time and development costs but also to improve product reliability.

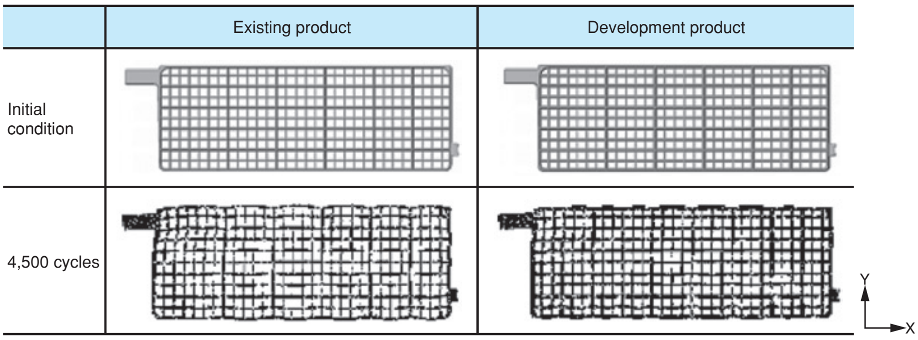

Figure 6 Typical simulation result of corrosion deformation in LL type VRLA batteries

4 State Monitoring Technology for Lead-Acid Batteries

Lead-acid batteries have flat voltage characteristics, which makes it difficult to determine the state of a battery, including its state of charge (SOC) and state of health (SOH). Determining the state of batteries is important for the optimal operation of lead-acid batteries and for managing the power supply in systems powered by lead-acid batteries. The parameters measurable from a battery in use are limited to voltage, current, and temperature. Hence, we have been committed to developing technologies for estimating battery states based on limited measurement data. This section outlines battery monitoring technologies for automotive applications[9-13] and industrial applications.[14,15]

In automotive applications, and vehicles equipped with an idling stop and start system in particular, it is important to determine whether the engine can be started while it is in an idling-stop state, whether the idling-stop state can continue, and how long the lead-acid battery will last. These operations are called idling-stop go/no-go decision, state-of-charge estimation, and replacement necessity determination, respectively. **Figure 7** shows the relationship between voltage and SOC at engine start.[9] Based on this relationship, an idling-stop go/no-go decision can be made given a predetermined minimum required voltage at engine start. As for state-of-charge estimation, the SOC value determined from the battery internal resistance and that determined from the circuit voltage were Kalman-filtered to determine the SOC value before traveling; and to determine that during traveling, the SOC value before traveling was added to the electricity amount determined by current integration. **Figure 8** shows the results of estimation of the SOC during travel of vehicles equipped with an idling stop and start system.[9] There was a four percent error between the measured SOC value after the test and the estimated SOC value. Lead-acid batteries show various states of health depending on their usage conditions. Hence, batteries with different SOH were used for error estimation. **Figure 9** shows the estimated errors,[9] which fell within ±10% regardless of the SOH and can be said to be very small as errors estimated under different usage conditions.

Next, we will show a typical degradation analysis method developed for industrial lead-acid batteries. **Figure 10** shows major degradation modes of industrial lead-acid batteries.[15] Their degradation takes the form of increases in the ohm resistance

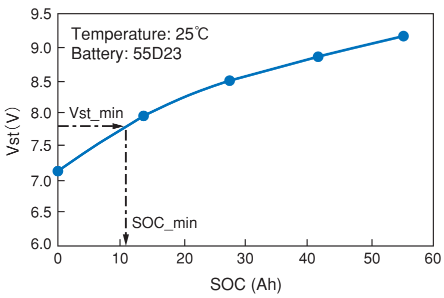

Figure 7 Relationship between SOC and voltage at engine start

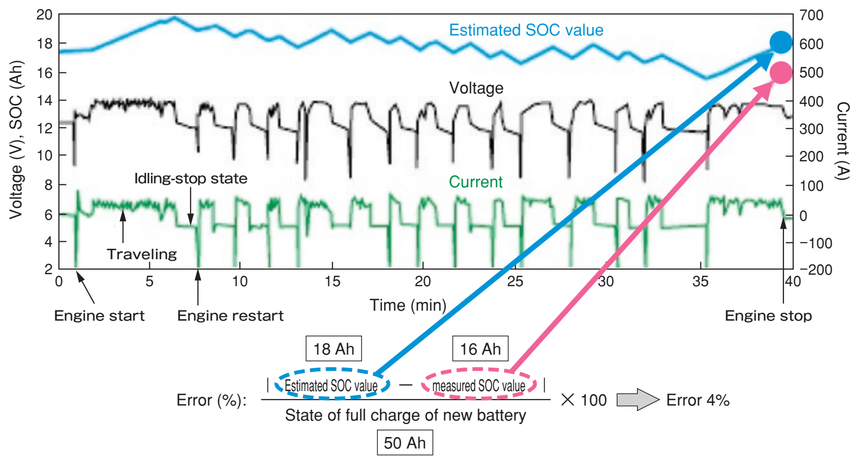

Figure 8 Results of SOC estimation in the idling stop and start system

component and reaction resistance component. In principle, the ohm resistance component affects the high frequency region in electrochemical impedance measurement, while the reaction resistance component affects the low frequency region. **Figure 11** shows the relationship between frequency and resistance in batteries with different SOH.[15] Based on the analysis of these batteries with different SOH, we developed a method of selecting a multiple number of frequencies for use for battery resistance measurement from the high, medium, and low frequency regions. These resistance values showed high correlations with the discharge behavior of the batteries, allowing us to perform a degradation analysis for lead-acid batteries.

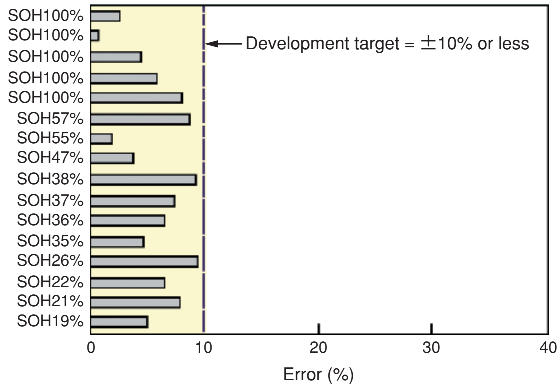

Figure 9 SOC errors of deteriorated batteries

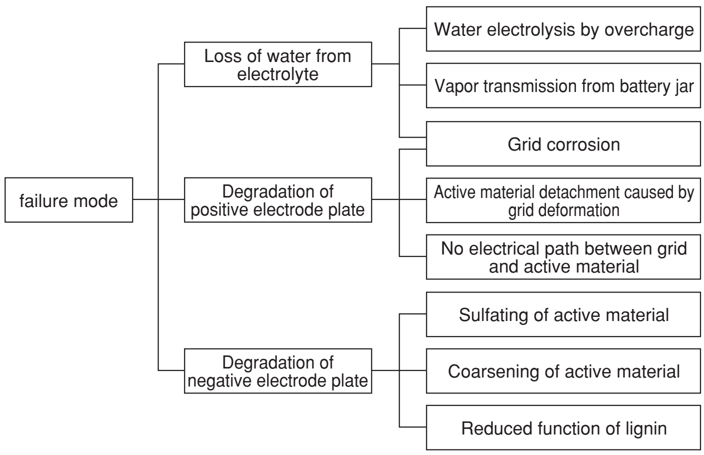

Figure 10 Lifetime factor of VRLA battery

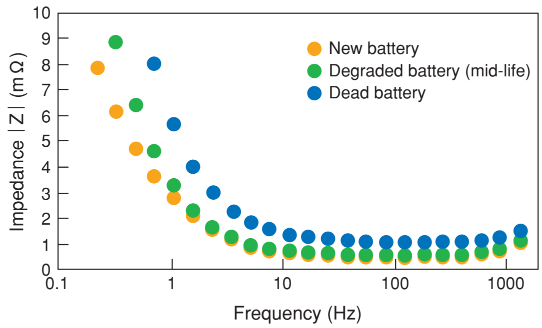

Figure 11 Frequency characteristics of different batteries

5 LIB Capacity Expansion Technology and Battery System Technology

Our lithium-ion batteries have been developed aiming at providing batteries that have a large capacity and are also very safe.[16-19] One of the merits of batteries with an increased capacity is that a large electrical energy storage system can be configured with a relatively small number of cells. Moreover, our lithium-ion batteries are capable of 3C continuous discharge and support 30-minute or shorter time discharge although they are large-capacity cells. **Figure 12** shows the outline of our CH75 battery.[19] This battery has three high-safety features. The first is a cylindrical structure with pressure uniformly applied to the electrodes. This reduces local degradation resulting from the expansion and shrinkage of the active material, allows the long-term maintenance of the active material structure, and provides the battery with improved reliability. The second is a stainless steel can, which

battery		CH75	External view photo
Nominal voltage		3.7 V	
Nominal capacity		75 Ah	
Conduction current	Discharge	Continuous: 225 A Maximum: 300 A	
	Charge	225 A	
Mass		Approximately 3 kg	
Dimensions		Φ 67×410 mm	
Expected usage life*1		10,000 cycles	

*1 Expected usage life: The usage life expected under our recommended operating conditions

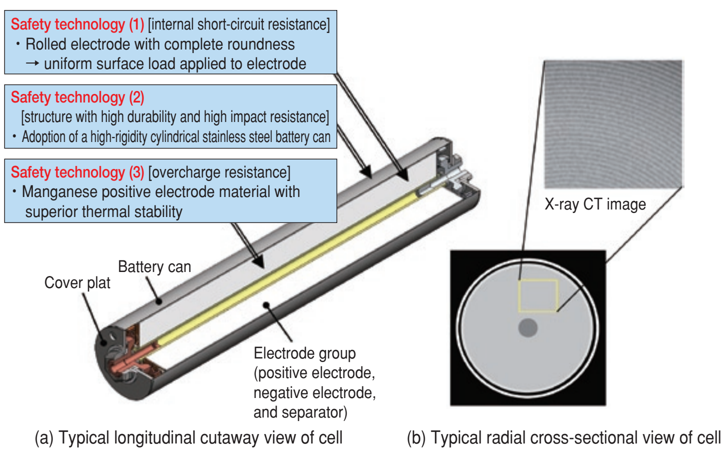

Figure 12 Specifications, appearance and safety technologies of lithium-ion battery “CH75” cell

is more resistant to external shock and vibration than laminated type and provides high structural reliability in non-stationary, mobile applications. The third is a manganese positive electrode with superior thermal stability, which reduces the risk of thermal runaway. These technologies are combined with temperature environment simulations for pack mounting configurations and/or with optimal cooling systems to provide batteries simultaneously featuring both a large capacity and high safety.

Figure 13 shows a typical battery system using CH75 batteries.[20] Each battery pack is equipped with a cell controller for monitoring the voltage of all cells to detect voltage variations occurring among the cells due to repeated charge and discharge and automatically bring the cells to the same voltage. There are 24 battery packs connected in series to each battery panel. This system has a battery management unit for monitoring the cell controller of each battery pack to detect various anomalies and failures and adjust variations among the battery packs. The battery management unit has a function that allows uninterrupted operation with any battery panels disconnected in case they fail.

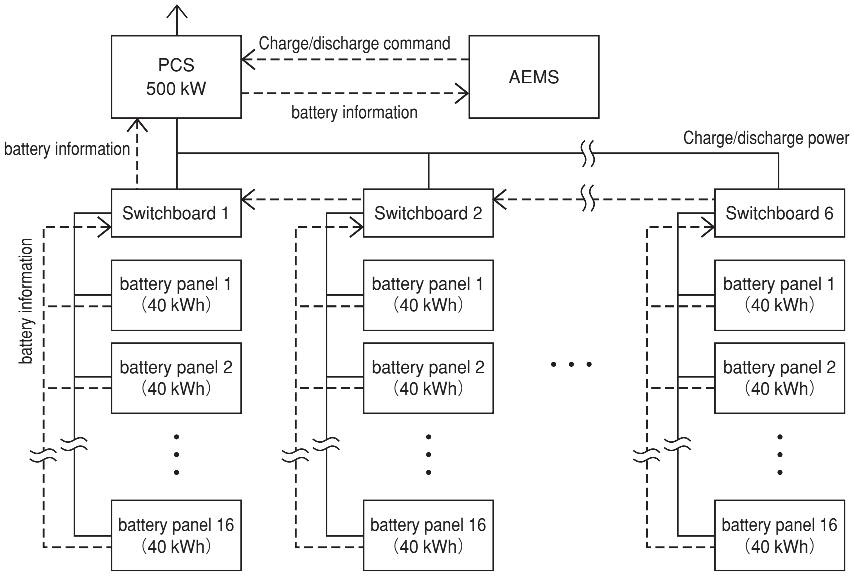

Figure 13 Block diagram of the lithium-ion battery system

6 Battery Analysis Technology

Most chemical reactions in a battery active material occur at the interface between a solid surface and electrolyte and depend on the properties of the solid surface. An active material contains a conductive material and a binder and has a complicated three-dimensional structure in which inorganic and organic materials are intermingled with each other. Visualization of these materials and estimation of their contributions to reactions provide very useful information for battery performance enhancement. The images in **Figure 14**, each taken using a latest Raman spectrometer, show differences in distribution between different binders and

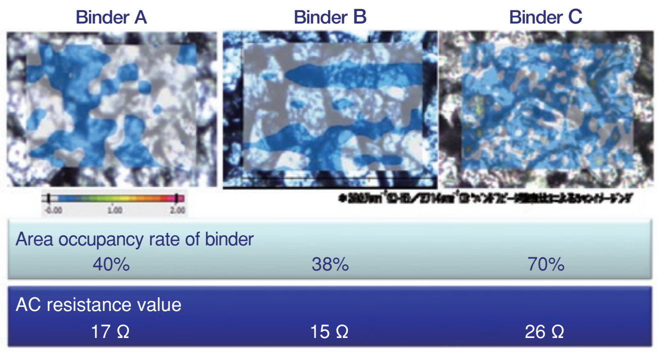

Figure 14 Relationship between binder distribution and AC resistance based on the difference among binders

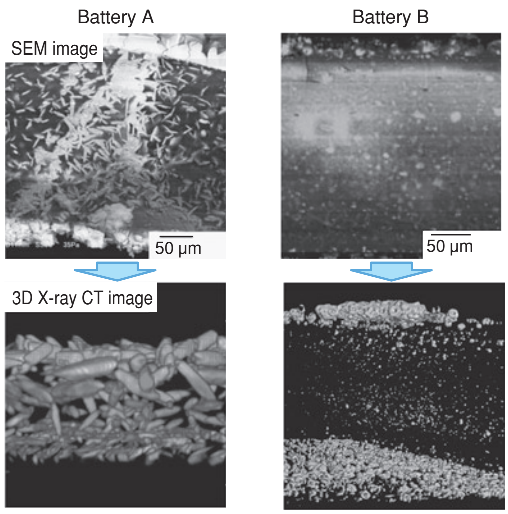

Figure 15 Cross-sectional SEM image and three dimensional structure analysis of separators after hydration short by X-ray CT

display visually how the electrode resistance value depends on the area occupancy rate of the binder.[21] These images allow visual observation of the distribution of the binder in the electrode active material, help to optimize binder dispersibility and electrode material composition, and contribute to improved battery characteristics.

The invention of lead-acid batteries dates back more than 150 years. Some aspects of them, however, still remain unclear: for example, the effects of carbon materials on the reactions of active materials and on the precipitate form of lead sulfate. With advancements in analysis technologies, we have applied such technologies to clarifying phenomena associated with lead-acid batteries, including analysis of additive-dependent charge reactions and structural analysis of corrosion products. Outlined here is the technology used for 3D visualization of penetration short-circuits in which lead sulfate continuously precipitates and causes internal short-circuiting. **Figure 15** shows 3D X-ray CT images of lead sulfate produced when penetration short-circuit occurs.[22] Conventionally, cross sections of separators were polished and observed using SEM; with this method, stereoscopic analysis was difficult. Three-dimensional X-ray CT analysis has revealed that lead sulfate is in the form of flakes and that fine precipitates exist that were impossible to observe conventionally. We expect that further research into these phenomena, which were difficult to clarify using conventional analysis technologies, will lead to improved battery characteristics.

7 Summary

This report described some of the battery technologies we have developed. Our Battery Business Division has been working to enhance its competitive edge in the global market through activities including the acquisition of Hitachi Chemical Energy Technology Co., Ltd., followed by the establishment of FIAMM Energy Technology S.p.A. and by the acquisition of Thai Storage Battery Public Company Limited. We are determined to promote new technology development while widely deploying the battery technologies presented above.

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Demonstration of a Renewable Energy Self-Consumption System for an Apartment in Germany

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1 Abstract

To prevent global warming, renewable energy sources, such as PV (photovoltaic) and wind power, are becoming increasingly popular throughout the world. In particular, Germany is focusing on installing renewable energy sources in their power systems so that 80% of generated power will be from renewable energy by 2050. However, the FIT (Feed-in-tariff) rate is decreasing with the increasing number of renewable-energy installations, and the FIT rate is now less than half the electricity rate. As a result, much attention is being paid to the “self-consumption model” in which PV power is consumed within a household, and the amount sold outside the household is decreasing. With this background, we developed a self-consumption system that enables more effective use of PV power. The system uses both rechargeable batteries and a heat pump, and has been operating since it was installed in June 2016.

2 Characteristics of the Energy Self-consumption System

・The system has storage batteries and a heat pump to maximize the consumption of PV-generated power and minimize the cost of energy of apartment homes.
・The Home Energy Management System (HEMS) generates optimal operation plans for the storage batteries and heat pump based on forecasts of the demand for electricity and hot water.
・The system consists of containers compliant with German and EU regulations and standards, and can be installed in existing homes.
・The system includes a remote monitoring function that enables the real-time observation, from locations such as Japan, of the system’s operating status.

3 Background of the Development

Germany leads the world in the field of renewable energies and the FIT rate in Germany is already cheaper than the electricity rate. To reduce the reverse energy flow in a household, it is important to achieve the self-consumption of PV power. Since July 2015, we have been working on a smart community technology demonstration project (hereinafter the “demonstration project”) commissioned by NEDO to establish a model for the self-consumption of PV power and for reducing energy costs, and have started operation according to the following schedule.

June 2016: Installed a system consisting of PV, storage batteries (LIBs), inverters, a heat pump, various sensors, and an HEMS and started operation of the system for demonstration purposes.

September 2016: Constructed a hybrid power storage system[2] equipped with lead-acid storage batteries (LABs) in addition to LIBs, and started the operation of the system.

April 2017: Started energy cost-minimizing operation through the optimization of the storage batteries and heat pump based on the HEMS’s forecasts of the demand for electricity and hot water.

This report describes the compliance of the project with German and EU regulations and standards, and the energy cost-minimizing operation achieved through the optimization of the storage batteries and heat pump. Out of consideration for the residents of the apartment building selected for this project, the hot water supply was left as it was to avoid the otherwise necessary indoor refurbishment. In other words, the hot water supply from the heat pump was used exclusively to heat the apartments.

Moreover, a remote monitoring system was introduced so that the operating status of the system installed in Germany could be monitored from Japan.

4 Technical Details

a) Compliance with German and EU regulations and standards

Obtaining a fire license was the largest challenge for this demonstration project, which required the installation of large-

capacity lithium ion batteries (LIBs) in a residential area. Experts and the relevant fire department assessed risks with respect to the installation of fire extinguishing equipment. Based on the assessment, our approach to fire protection included directly monitoring the temperature of the lithium ion batteries, in addition to using to general-use sensors to detect gas, heat, etc. Furthermore, to prevent false detection, fire extinguishing measures start only after multiple sensors are activated. Finally, as a measure against adverse impacts on the environment, such as soil contamination due to the discharge of untreated water, the demonstration system includes a tank for containing fire water (water that has been used to extinguish fire).

Figure 1 is a system configuration diagram, while **Figure 2** shows the external view of the final demonstration system. In Germany, in accordance with the Renewable Energy Sources Act (EEG* 2017), facilities with a PV output of 30 kW to 100 kW are required to have a remotely operable disconnection mechanism that stops the power supply to the utility grid upon request from the power company. To meet this requirement, this system, which has a PV output of 46.8 kW, is equipped with a function that turns the connection to the grid on and off in response to remote commands from the demonstration project counterpart, Stadtwerke Speyer GmbH (SWS).

* EEG: Erneuerbare-Energien-Gesetz

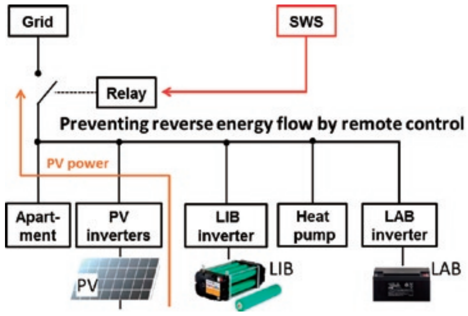


Figure 1 System configuration

Figure 2 External view of the demonstration system

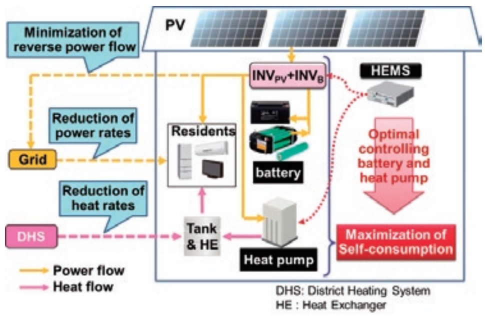
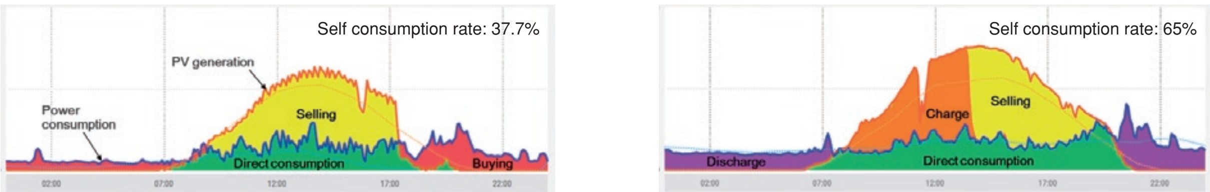


Figure 3 Control image

b) Energy cost-minimizing operation

Figure 3 shows the control concept for this system. This system uses PV power to recharge the storage batteries and to produce hot water by heat pump. The power accumulated in the storage batteries during the day is discharged at night, and the hot water produced by the heat pump is fed out to heat rooms, thus minimizing the reverse power flow and reducing the costs of heating and lighting. However, as PV power generation peaks in summer and the demand for heating peaks in winter, it is necessary to distribute PV power to the storage batteries and to the heat pump according to the demand for power and heating. To this end, the HEMS is capable of energy cost-minimizing operation via the following three steps: 1) it forecasts the PV power generation output and the demand for power and heating, 2) it uses linear programming to generate an operation plan for several days ahead based on the forecast results, and 3) it charges and discharges the storage batteries and controls the production of hot water by the heat pump according to the operation plan. In this way, the system achieves efficient and effective use of PV power in a way that accounts for changes in the weather. **Figure 4(a)** shows operation of the system with PV generation only, whereas **Figure 4(b)** shows energy cost-minimizing operation controlled by the HEMS. With PV generation only, the self-consumption ratio is 37.7% because all surplus power generated during the day is sold, and the power required at night must be purchased. On the other hand, under energy-cost minimizing operation, the storage batteries are recharged with just enough power as is needed at night, and the remaining surplus power generated during the day is sold. Because the power required at night is supplied from the storage batteries, no power needs to be purchased, resulting in an improved self-consumption ratio of 65% and lower energy cost.



(a) Operation with PV generation only (August 2016) (b) Energy cost-minimizing operation (July 2017)

Figure 4 Comparison of self-consumption rates and behavior when (a) only PV generation is applied and (b) operation to minimize energy costs is applied

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Hitachi Chemical
Working On Wonders

Next Generation Wireless Battery Monitoring System (Gen.2)

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1 Abstract

The lead acid battery used for backup use is adopted in communications equipment for the use of UPS, such as cell phone base station. The UPS needs are especially growing for the use in large scale sites requiring high reliability, as in data centers, which are increasing their size continuously. On the other hand, the lead acid battery of the staff and the maintenance of the automation to measure were expected very much. Therefore, we develop a monitoring system in the next generation called Gen.2 in substitution for the system which was developed before being called Gen.1. This paper takes a flow and next generation monitoring system called Gen.2.

2 Characteristics of the New Product (Gen.2)

- We adopted a configuration in which a slave monitoring device installed in the lead acid battery automatically measures the voltage, impedance, and temperature of (or near) the battery. The measurement data is then transmitted wirelessly to a master monitoring device. This configuration, in which the battery conditions can be monitored on a cloud server, is provided as a basic option. However, some customers might want to restrict communications with outside devices because of security concerns. To handle such a situation, we also provide an optional configuration that works in the same way as Gen.1, and enables operation by installing a higher-level PC.
- The master monitoring device incorporates a function that enables communication by switching between multiple antennas, and a function that changes frequencies if a communication abnormality occurs. These functions improve the reliability of wireless communications between the master and slave monitoring devices.
- This configuration enables measurements of impedance values at low frequencies in addition to measurements of regular internal resistance, and also enables improvements in the state-detection function, such as for capacity estimates of discharge characteristics.
- This configuration also enables a balancing function that can stabilize the battery state by equalizing the battery voltage.

3 Background of the Development

Industrial lead acid batteries for backup use are widely employed in various fields: such as for landline phones, cell phone base stations, communications infrastructures of backbone networks, DC power supply of power plants and buildings, and the power supply to data centers.[1), 2)] Higher reliability of lead acid batteries is desired as data centers increase in size because of various factors: in particular, the spread of e-shopping (web-based businesses), the computerization and globalization of transactions, and the spread of smartphones[3)]. In addition, requirements for equipment used for social infrastructure, such as communications and electric power, are that remote personnel must be able to verify whether a battery used for backup power is in a normal state and that, when a disaster occurs, the remote personnel must be able to check whether the battery is usable. As a method for detecting battery abnormalities, trend management by measuring the temperatures, voltages, and internal resistance values of the battery is often used. In addition, automation (the need to change from conventional manual measurements to status monitoring by automated measurements) is becoming increasingly important. Furthermore, upgrading lead acid battery equipment requires both money and time, and there is a need to precisely grasp the timings for such upgrades. Therefore, when we developed the Gen.1 wireless battery monitoring system, we applied automated measurements to large-scale lead acid battery equipment. This enabled safety-oriented automated measurements, which reduces installation work, simplifies harnesses, and avoids insulation breakdowns due to harness contact. In addition, automated measurements made it possible to provide a calendar function that indicates when it is time to upgrade a battery. Furthermore, IoT has become widespread in recent years. To handle

IoT and to enable remote monitoring of data at multiple installation sites, we decided to develop Gen.2. Gen.2 is designed on the premise of continuous remote monitoring by using cloud servers. In addition, we decided to support single-cell measurements (not supported by Gen.1), and to enhance communication reliability.

4 Details of the Technology

Figure 1 shows an example of the usage period of a backup battery, and the typical characteristics of the internal resistance and trickle current. As shown in the figure, the internal resistance and trickle current gradually decrease after use of the lead acid battery starts, and then gradually increase in the end-of-life period. Then, if a lead acid battery continues to be used beyond its end-of-life period, the internal resistance and trickle current increase sharply. Continued use of the battery under such conditions may result in heat generation and smoke.[4] Therefore, we need to have adequate controls that detect sharp rises and to report that a battery upgrade is required. Note that the relative ratio of the usage period is the relative value when 100% is set as the designed service life.

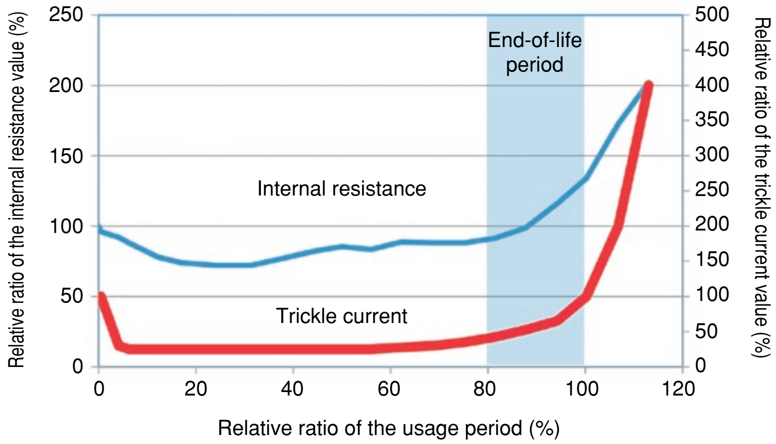
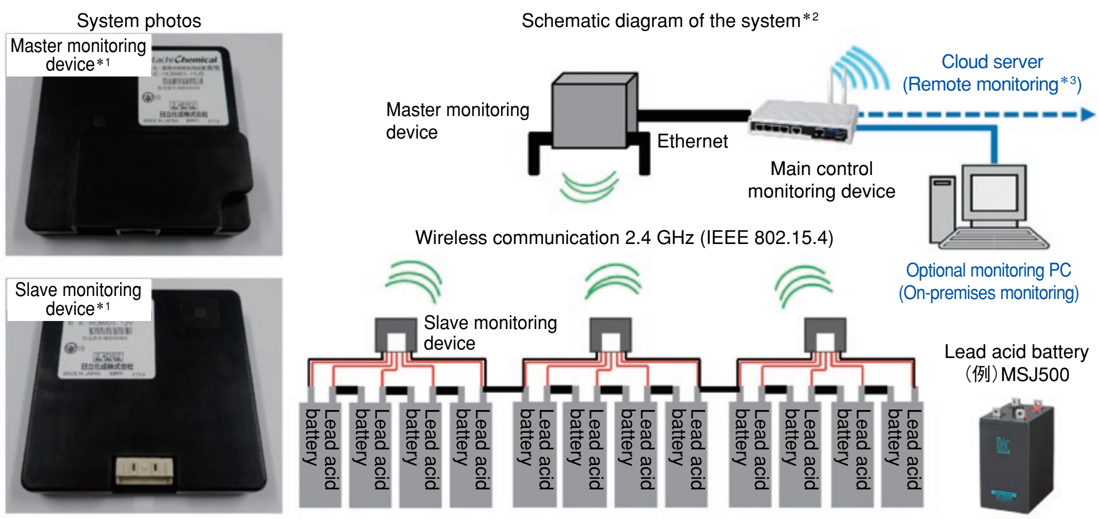


Figure 1 Typical characteristics diagram of impedance and trickle current

Gen. 1 and Gen. 2 wireless battery monitoring systems are designed to report the standard battery upgrade times based on the usage period, and to confirm the soundness of a lead acid battery by continuously monitoring trends in its voltages, temperatures, and internal resistance values.

Figure 2 shows the equipment configuration for a wireless monitoring system of storage battery states. **Table 1** shows the specifications of the developed system.



*1 Built-in antenna
*2 Installation with existing battery equipment is also possible.
*3 Proven IoT platform services are adopted, and high security is ensured.

Figure 2 Equipment configuration of wireless monitoring system of storage batteries states

Table 1 shows the specifications of the developed system.

Table 1 Specification of the developed system

Item	Description		
Component devices	Basic configuration	Master monitoring device, slave monitoring device, main control monitoring device	
	Optional	Cloud server, higher-level controller	
Wireless communication system	IEEE 802.15.4 (2.4 GHz)		
Supported battery	Mono-block type	12 V series	UP, HSE/MSE/MSJ
		6 V series	HSE/MSE/MSJ
	Unit cell type	2 V series	MSE/MSJ MU series
No. of batteries that can be monitored (per main control monitoring device)	Mono-block type (6 V or 12 V types)	2,160 (8 master monitoring devices x 270 slave monitoring devices x 1 battery/slave monitoring device)	
	Unit cell type (2 V type)	8,640 (8 master monitoring devices x 270 slave monitoring devices x 4 batteries/slave monitoring device)	
Monitored items	Voltage, temperature, internal resistance (impedance: multiple frequencies)		

The Gen.2 system includes a wireless slave monitoring device, wireless master monitoring device, main control monitoring device, and cloud server or higher-level controller. The wireless slave monitoring device is connected to the battery to measure temperatures of (or near) the battery, battery voltage, and internal impedance, and transmits the data to the master monitoring device wirelessly. The data is transmitted by an Ethernet connection to the main control monitoring device, where the data is stored. After that, the data is transferred to the cloud server or higher-level controller. The cloud server or higher-level controller manages the measurement data, and uses trend and threshold management to determine whether the battery is in a deteriorated or abnormal state. The system we developed for Gen.2 is based on a cloud server, and enables data to be shared between the customer and our service (administration) department. However, some customers might want to restrict communications with outside devices because of security concerns. To handle such a situation, we also provide an optional configuration that enables operation by installing a higher-level controller.

Table 2 compares the existing system (Gen.1) with the newly developed system (Gen.2).

Table 2 Comparison between Gen.1 and Gen.2

No.	Item			Existing system (Gen. 1)	Developed system (Gen. 2)
1	Equipment performance	Communication method		Wireless 2.4 GHz band IEEE 802.15.4	Wireless 2.4 GHz band IEEE 802.15.4
2		Battery to be measured		・12 V or 6 V mono-block battery ・2 V battery (to be measured with three or four batteries connected in series)*	・12 V or 6 V mono-block battery ・2 V battery
3		No. of data items for batteries to be measured		1,620 or below	2,160 or below (6 V or 12 V batteries) 8,640 or below (2 V batteries)
4		Voltage	Range (V)	4.0～15.5	1.5～15.5
			Accuracy (mV)	±200 or below	±50 or below
5		Temperature	Range (℃)	−10～60	−10～60
			Accuracy (%)	±1.5 or below	±1.5 or below
6		Internal resistance	Range (mΩ)	0.1～20	0.1～30
			Accuracy (%)	±3.0 (FSR)	±3.0 (FSR)
7		Current consumption (slave monitoring device: mA)		2 or below on average	2 or below on average
8	Extra features	Abnormality detection		Voltage, temperature Internal resistance, communication	Voltage, temperature Internal resistance, communication
9		Prediction of lifetime		Refer to the designed service life. (Without temperature compensation)	Refer to the designed service life. (With temperature compensation, under development) Predictive-indicator diagnosis (Under development)
10		Estimation of high ratio service capacity		Not supported	Under development
11		Voltage balancing		Not supported	Under development
12		Remote monitoring		Not supported	Supported
13		Communication stability	Antenna diversity	Not supported	Supported
14			Ch change, timing control	Not supported	Supported

* The 2V battery is monitored as a pseudo mono-block battery with three or four batteries connected in series.

Figure 3 shows an internal block diagram of the Gen.2 wireless slave monitoring device (for unit cells).

Gen.1 was able to measure the voltage and internal resistance of only one battery, by using one slave monitoring device.

To measure the voltages and impedances of a unit cell, the Gen.2 slave monitoring device carries out measurements with ADC by switching terminal voltages of multiple cells with the multiplexer (MUX). In addition, Gen.1 adopts a commercial wireless communication module equipped with a chip antenna. However, as shown in **Figure 4**, Gen.2 adopts an on-board wireless circuit unit to reduce costs, and the antennas are pattern antennas. Note that the wireless master monitoring device of Gen.2 has a configuration in which two pattern antennas use different half wavelengths, which enables communication by both antennas. This improves the reliability of communications.

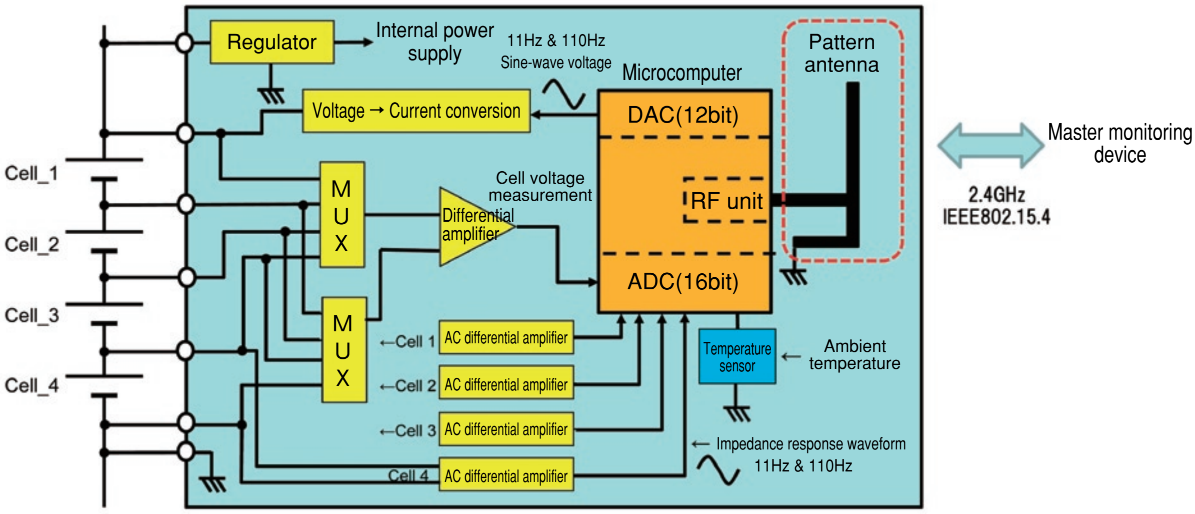


Figure 3 Block diagram of the Gen.2 wireless slave monitoring device

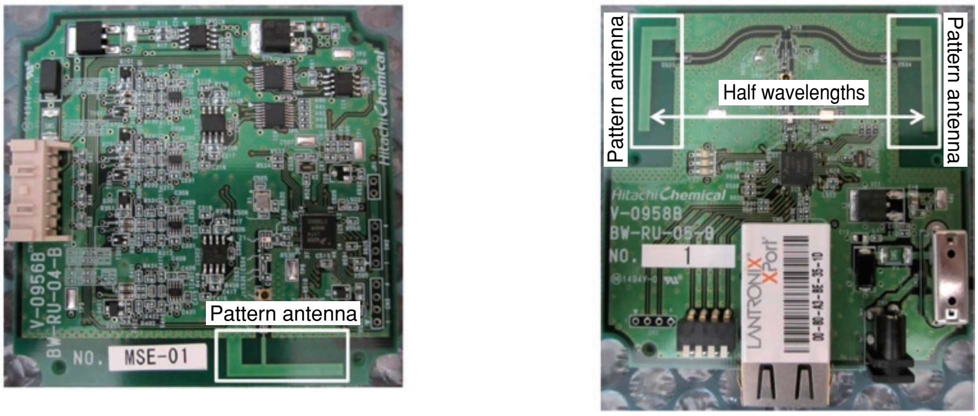


Figure 4 Photographs of wireless slave monitoring device (left) and master monitoring device (right)

Table 3 shows the specifications of the slave monitoring devices. Multiple types of slave monitoring devices are used this time. More specifically, there are types for unit cells and types for mono blocks. The types for unit cells assume an assembled battery in which multiple unit cell batteries are connected in a series as one item, and measurement is conducted for each unit cell. Although it is possible to install a slave monitoring device for each unit cell, such installation increases the number of slave monitoring devices, thereby increasing costs, congestion during wireless communication, and radio-wave interference. Therefore, we adopted the previously described configuration. Furthermore, taking radio-wave interference into account, we equipped the master monitoring device with a function to enable communication by switching between the two antennas, a frequency-switching function that varies the frequency during a communication abnormality, and a function to adjust communication timing in order to prevent redundancy of communications between the master monitoring device and multiple slave monitoring devices. **Table 4** shows the specifications of the wireless master monitoring device. One master monitoring device is capable of monitoring up to 270 slave monitoring devices. **Table 5** shows the specifications of the main control monitoring device. Up to eight master monitoring devices can be controlled.

Table 3 Specification of slave monitoring device

Item	Unit cell		Mono-block	
	3 cells	4 cells	6 V type	12 V type
Voltage range monitored (V)	1.400～3.000	1.400～3.000	4.20～9.00	8.40～18.0
Temperature range monitored (℃)	−10.0～60.0	−10.0～60.0	−10.0～60.0	−10.0～60.0
Monitored internal resistance range (mΩ)	0.100～10.000	0.100～10.000	1.00～30.00	1.00～30.00
Input voltage (V)(DC)	4.2～12.0 (To be supplied from a battery)	4.2～12.0 (To be supplied from a battery)	4.2～18.0 (To be supplied from a battery)	4.2～18.0 (To be supplied from a battery)
Current consumption (mA)	≦2.0	≦2.0	≦2.0	≦2.0
Outside dimensions (mm)	W:86.0×H:86.0×D:13.0	W:86.0×H:86.0×D:13.0	W:86.0×H:86.0×D:13.0	W:86.0×H:86.0×D:13.0

Table 4 Specification of master monitoring device

Item	Common to each type
Max. number of slave monitoring devices connected (units)	270
Input voltage (V)	DC:4.5-5.5
	100 V AC (compact UPS) Power is from an AC adapter.
Current consumption (A)	0.5
Outside dimensions (mm)	W:86.0×H:86.0×D:13.0 (excluding protrusions)

Table 5 Specification of main control monitoring device

Item	Common to each type
Max. number of master monitoring devices connected (units)	8
Input voltage (V)	DC:12.0～20.0
	100 V AC (compact UPS) Power is from an AC adapter.
Current consumption (A)	3/12V
Outside dimensions (mm)	W:117.0 ×H:92.0×D:35.0
Ethernet port	RJ45 (10BASE-T, 100BASE-TX)

The features of the software are described next:

(i) To ensure the reliability of communications of the master and slave monitoring devices, we implemented a system in which the master monitoring device communicates with the slave monitoring device by continuously switching between two antennas, and can switch communication frequencies during communication abnormalities.[5), 6)] In addition, to enable communication with multiple slave monitoring devices, we used a method in which the master monitoring device controls the communication timing.

(ii) To equalize cell voltages, for the software for unit cells, we provided a function to control the balancing circuit for each unit cell; for the software for mono-blocks, we provided a function to control balancing by using a function to measure internal resistance.

(iii) To shorten the hours needed to develop the software, we adopted a general-purpose Linux gateway for the main control monitoring device.

(iv) By using the general-purpose IoT platform, connections to the cloud server can be established with security ensured, while using (public) mobile communications.

(v) The main control monitoring device adopts the Modbus TCP specifications for communication, which enables the main control monitoring device to communicate data as a slave device. By developing software that runs as the master for the Modbus TCP, it is also possible to use an existing monitoring system.

(vi) We provided a function to report the replacement timings of lead acid batteries. The function measures the temperature of the battery or of the surrounding area, and converts the temperatures to the usage period of the battery, based on Arrhenius's rule.

(vii) We enhanced the resistance of impedance measurements to noise.

Feature (vii) of the software is explained next. In practical use, ripple voltage may affect the measurement values of internal impedance. This depends on the types of UPS and DC power supplies used, and the size and frequency components differ according to the type of power supply.[4), 7)] With Gen.2, we decided to measure the impedance at frequencies of 110 Hz and 11 Hz, taking into account the noise[7), 8)] from commercial power sources. Note that we plan to provide a function to obtain the value at 1 kHz, for compatibility with past measurement data.

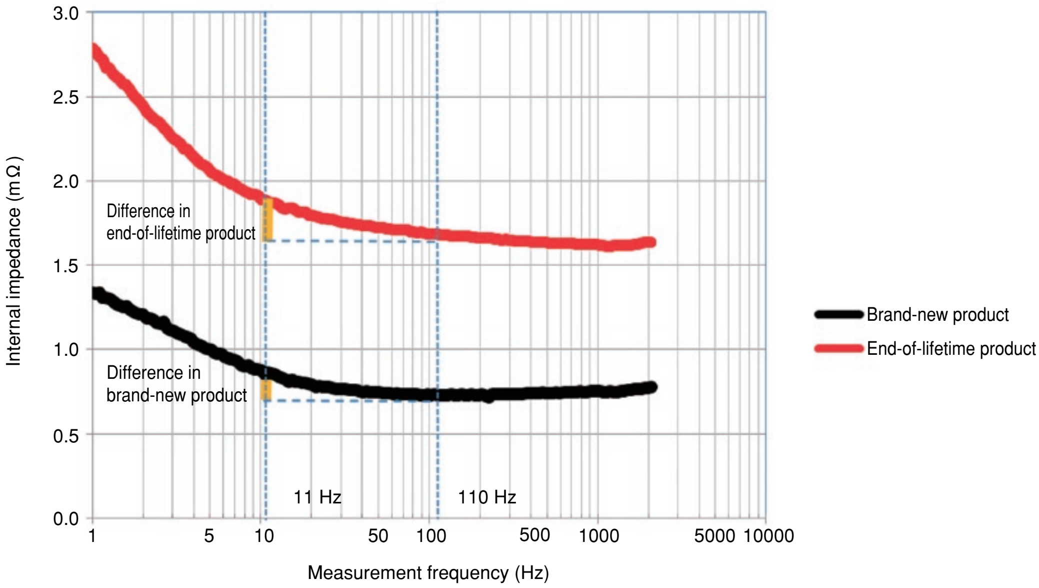


Figure 5 Typical characteristics diagram of impedance and measurement frequency

The impedance at lower frequencies from 5 Hz to 100 Hz is explained next. It is known that the high-rate discharge characteristics of a lead acid battery are dependent on the effective reaction surface area of the negative electrode,[9), 10)] and the indices for this include the electrical double-layer capacity and the charge-transfer resistance. The difference between the impedance of low frequencies in the range from 5 Hz to 100 Hz to be measured with Gen.2 (11 Hz at this time) and the impedance of high frequencies is equivalent to the charge-transfer resistance of the previously mentioned negative electrode; therefore, discharge characteristics at a higher rate than the value can be expected.

As described above, for Gen.2, we adopted specifications that enable measurements of impedance values at low frequencies, which is effective for the assumption that there is high-rate discharge. In addition, the specifications take into account compatibility and continuity with Gen.1 and with the impedance value of 1 kHz, which is the standard in the lead acid battery industry.

5 Future Business Development

- Commercialize the products.
- Further improve reliability.
- Increase the precision of predictions of the lifetime of, and predictive-indicator diagnosis for, lead acid batteries
- Take action to handle overseas requirements (wireless authentication and conformance to laws and regulations).

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New Technology for Industrial Lead Acid Battery

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1 Abstract

Today, the demand for lead acid battery have constantly grown in use, such as vehicle, industrial backup, and industrial starter, and the improving performance of lead acid battery can afford no further delay. In addition, as the interest to the environmental aspect increases, resources saving batteries are required.

It is an ultimate challenge to improve the four elements of the lead acid battery, including battery capacity, high rate discharge performance, service life, and environmental applicability.

For this solution, this article will introduce our latest technology, Pure lead, Punching, Carbon technology (hereinafter referred to as PPC). This technology has combined the cutting edge of the carbon material compounding techniques with innovative structure design, greatly enhancing the battery performance. Moreover, we have developed an automation system for the PPC technology, achieving product quality stabilization and high yield rate. The technology will also reduce water and energy usage, resulting to reduce carbon footprint, and achieving to produce an environmental friendly product.

2 Characteristics of the Developed Technology

- Alloy material with no grain boundary corrosion applied to grid improves the corrosion resistance and battery life.
- Integration of terminal with copper core embedded and strap by automatic welding reduces welding defects. Shorter electrically conductive path and larger area of piercing welding section decreases heat generation and improves performance in high-rate discharge.
- The alteration of manufacturing methods of a grid results in a lightweight thin grid with a smaller mesh opening, which improves electrical conductivity and the active material utilization.
- Adding electrically conductive carbon to negative active material leads to larger the specific surface area, better conductivity and charge acceptability.

3 Background of the Development

With technology evolving rapidly and demand in energy market increasing continuously, related technology advances ceaselessly for wider application of industrial lead acid battery.

Table 1 shows the challenges we face currently and strategy. The PPC technology was developed by changing the design structure and introducing new materials aiming at longer life and superior performance during high-rate discharge. **Figure 1** shows the main factors technology.

Table 1 Issues and their measures of a lead acid battery

Challenges of lead acid batteries	Characteristics of related component materials	Strategies
Short battery life	Corrosion resistance of the grid	Improving corrosion resistance by alloy materials modification
Temperature increase by high-rate discharge	Conductivity of terminals and strap zone	Decreasing heat generation by changing the design of the conductive part structure
Satisfaction of high output	Energy stored in the electrode plate group (high rate discharge performance and charge acceptability)	Modifying the grid manufacturing method and increasing the electrode plates
Low utilization of active materials		Improving the surface area and porosity of the electrode plates
Energy consumption due to excessive charge time		Improving charge acceptability by adding a carbon material with electrical conductivity

4 Technical Details

The large crystals in existing Pb-Ca-Sn alloy prone to degrades from grain boundary corrosion. The Pb-Sn alloy adopted by PPC technology with smaller crystals is corroded by general corrosion (**Figure 1 (a)**).[1] The amount of corrosion of a grid made of Pb-Ca-Sn alloy is 132.1% of that of a pure lead grid, and the amount of Pb-Sn alloy is 71.9%. The adoption of Pb-Sn alloy reduces corrosion rate of the grid and extends the battery life.

To enable higher output during high rate discharge, the PPC battery structure was improved (**Figure 1 (b)**). By changing to integration of COS electrode with electrode and copper core pre-embedded and strap using the COS (cast-on strap) construction method shortened the conductive paths. Furthermore, enlarging the contact area of the piercing welding section between the cells reduced internal resistance. Introducing an automated facility improved the production speed and suppressed the generation of defective welding, lead flow, and fusing caused by manual welding, which resulted in great improvements in the yield rate. As a result of changing the structure, the amount of heat generation at discharge in the strap is reduced by 60% and that in the terminal section between the cells by 58%. Consequently, these reductions improve performance in high-rate discharge.

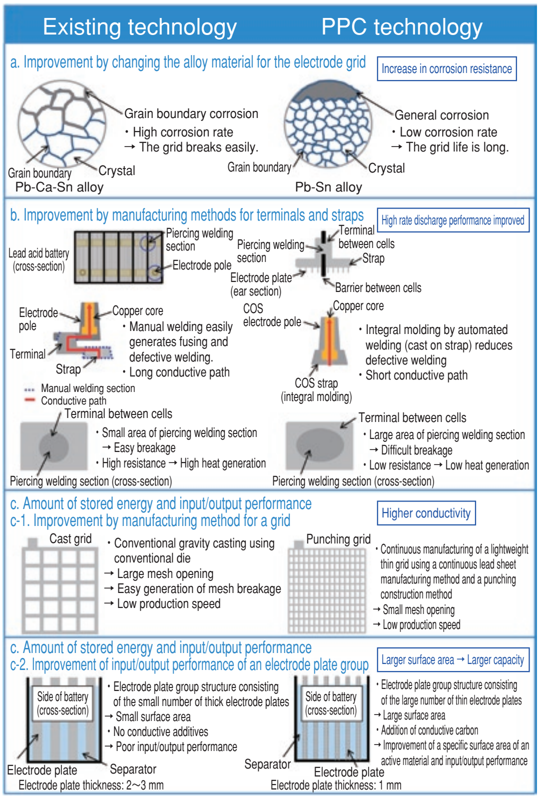

Figure 1 Developed new technologies for industrial lead acid battery

PPC technology enabled the creation of a thinner grid (**Figure 1 (c-1)**) with a smaller mesh opening using a continuous lead sheet manufacturing and punching methods in order to the reduction in weight and thickness. This improved conductivity and enabled an increase in the number of electrode plates to be installed even in the same battery size, which led to an increase in energy storage (**Figure 1 (c-2)**).

Furthermore, the addition of electrically conductive carbon to the negative active material improved the charge acceptability and suppressed[2] the sulfation of the negative electrode, which is the main degradation factor in lead acid batteries. In addition, the charge-discharge acceptability of the electrode plate is also improved.

Besides, the increase in battery capacity due to the increase in the amount of an active material per electrode plate contributed to the fact that the discharge capacity of the PPC battery improved by 25% in a 15-minute rate discharge and by 43% in a 5-minute rate discharge, in comparison with current batteries. In addition, the use of an alloy with a small change in the composition at re-melting achieves 100% of the reuse rate of punched lead. **Table 2** shows a comparison between the PPC battery and current batteries.

Furthermore, in PPC technology, the adoption of a battery jar forming system, in which electrification is performed after the battery is assembled, allowed the forming and charge processes to be integrated, in comparison with the tank forming used in the conventional charge system. This system not only eliminated the water washing and drying process but saved energy and reduced CO_2, as well as providing an environment friendly manufacturing process.

Table 2 Performance comparison between the current battery and PPC battery

Indices for reference	Current battery	PPC battery	Expected effects
Amount of corrosion of a positive grid (%)	100	54	The usable life (years) increases, and battery exchange expenses are reduced.
Amount of heat generation due to discharge (%)	100	40	High-rate discharge is possible, and energy savings are achieved for air conditioning at the place of installation.
Increase rate of 15-minute rate discharge capacity (%)	100	125	The following are all reduced: the number of batteries, the number of battery racks, the space occupied, and battery inspection expenses.
Increase rate of 5-minute rate discharge capacity (%)	100	143	

5 Future Business Development

・Increase the battery models adopting this technology.

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Development of Automotive Lead Acid Battery for Global Expansion

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FIAMM Energy Technology S.p.A R&D Product Innovation Dept.

1 Abstract

Eco-friendly automobiles with idling stop system (ISS) are increasingly attracting attention recently and the market of ISS-equipped automobiles is expanding worldwide. ISS-equipped automobile frequently stops and starts engine supplying electric power from the battery to electrical components while the engine is shut off, and enables regenerative charging through alternator during traveling. Therefore, high charge acceptance performance and high durability are required to the battery for ISS-equipped automobiles. Hitachi Chemical (HC) has developed several new technologies for these requirements[1) and FIAMM Energy Technology S.p.A (FET) has also developed. Both companies became the group company to expand global market share. A battery characterized by the advanced technologies of Enhanced Flooded Battery (EFB), as usually referred a battery for ISS-equipped automobile in European market, was developed by merging specific technologies of HC and FET.

2 Key Features

・By merging technologies of HC and FET, a new EFB was developed, characterized by charge acceptance performances 1.5 times higher than that of European competitor.

3 Development Background

ISS-equipped automobiles are expanding worldwide because ISS can improve fuel efficiency and economy more than the conventional systems with gasoline, by simple redesign of automotive system. Higher charge acceptance performance and higher durability are required to the batteries intended for ISS-equipped automobile in comparison with the conventional one because of the frequent discharging during idling stop and regenerative charging. HC has introduced 1st generation[2) and 2nd generation[3) of EFB products into Japanese market and has expanded their sales. On the other hand, HC has made efforts for enhancing product capabilities and expansion of manufacturing locations for the expansion of global market share, and FET became a group company on February 2017. By merging technologies of HC and FET, HC accelerate the development of EFB for the European market. Therefore, we tried to develop this by merging technologies of HC and FET.

4 Technical Content

HC's technology of the additive for Negative Active Material (NAM) and FET's technology of the pasting layer for positive plates were integrated to develop a new generation of EFB characterized by improved charge acceptance and durability performances. Each specific technology is described below.

1. HC's technologies of the additive for NAM

HC has developed the technology of lignin material which has the function to reduce particle size of lead sulfate ($PbSO_4$) generated by discharging. **Figure 1** shows in-situ AFM (Atomic Force Microscope) images related to the changes in NAM morphology during charge-discharge cycles through a comparison between conventional and developed battery. These observations were conducted by potential-step method to analyze transient current response corresponding to electrode potential-step. AFM images after charging show that larger size of $PbSO_4$ crystals still remain in the conventional active material, on the other hand, only Pb crystals were observed in the developed active material. These results imply that miniaturization of active material may make dissolution rate of $PbSO_4$ faster and lead to improve the efficiency of charge reaction.

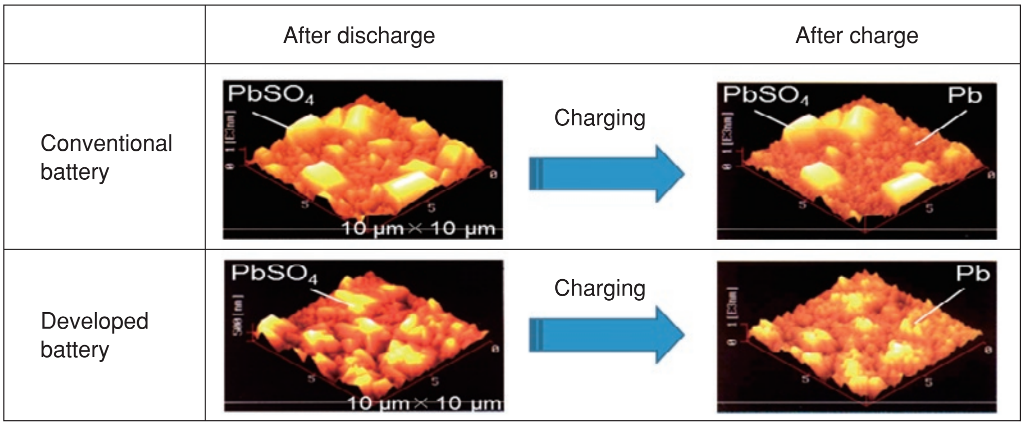

Figure 1 Images of *in-situ* AFM observations which visualize changes in morphology of active materials during charge-discharge cycles

2. FET's technologies of the positive pasting layer

FET developed the technology of pasting layer for positive plates in order to increase durability performances. By analysis and testing of several materials (glass-fiber or totally organic based ones) alternative to the standard pasting paper, FET selected the best one in terms of overall performances and processability. The new pasting layer replaces the standard paper during pasting process and improve the adhesion of the positive active mass, especially during cycling. By using pasting layer, the loss of the active material is significantly reduced and its functionality is maintained. Therefore the durability of the battery, especially at higher Depth of Discharge (DoD) where the functionality of the positive active mass is more stressed, is improved

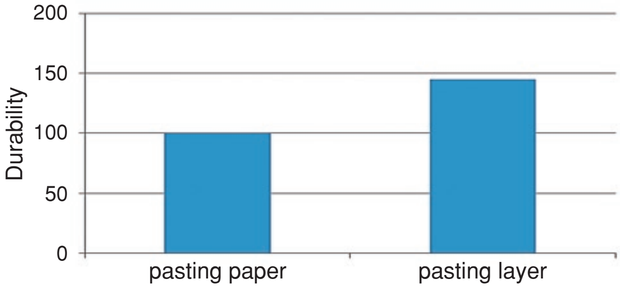

Figure 2 Relative comparison in durability performances between pasting paper and pasting layer on positive plates

3. Performance of Developed Product

Trial products of European Standard (EN) sized EFB including above technologies were manufactured at the plant of FET and some battery performances were evaluated. **Table 1** shows performance comparison between developed product and that of competitor. Developed product has same or higher level of battery performance, like capacity, charge acceptance and cold cranking performance in comparison with that of competitor. Especially, developed product has 1.5 times higher charge acceptance performance. Durability tests are still ongoing, we think that the use of positive pasting layer will improve them.

Table 1 Relative comparison of developed battery performances with competitor's battery performances

Item	Competitor	Developed
Capacity test	100	105
Charge acceptance	100	150
Cold cranking	100	100
Durability*	100	135 (estimated)

*under evaluation

5 Future Business Development

・Sales expansion of developed EFB for European market.

【Reference】

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2) Keiichi Wada, et al.: Battery for ISS (Idling-Stop System) Vehicle, Shin-Kobe Technical Report, No.20, pp.17-21 (2010)

3) Koji Otsu, et al.: ISS Lead-Acid Battery 'M-42' for Light Cars, Shin-Kobe Technical Report, No.22, pp.15-18 (2012)

【Reference Patents】

Patent Number 4396527, Patent Number 5445655

Hitachi Chemical
Working On Wonders

Ultra-Low Loss Build-up Film for Fine Pitch Applications, "AS-500HS"

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1 Abstract

With the recent expansion of globalization and cloud services, devices used for server and wireless communications need to transmit large amounts of data at high speed. Thus the semiconductor components of such devices must be able to handle high-speed and wide-band signal transfers. To satisfy these requirements, we have developed a new ultra-low loss, build-up film (AS-500HS).

"AS-500HS" is processable for semi-additive processes, shows only small surface roughness after chemical roughening (Ra:220nm), and has a high peel strength with plated copper (0.7kN/m). Moreover AS-500HS shows a low dissipation factor (0.0034), low CTE, high heat resistance, and excellent reliability.

2 Characteristics of the Product

- It has an excellent dielectric dissipation factor (0.0034) and a low coefficient of thermal expansion (17 ppm/°C).
- It allows fine-pitch wiring formation with a line and space (L/S) ratio of 2/2 μm.
- It provides high insulation reliability to L/S=2/2 μm fine-pitch pattern circuit (no insulation deterioration for 200 hours or more under test conditions of 130°C/85% RH and applied voltage of 3.3 V).

3 Background of the Development

Following the full-scale opening of the IoT Age, needs are mounting for high-speed, large-capacity data exchange.[1] Accordingly, the mainstream method of fabricating semiconductor mounting substrates (semiconductor packages) is now the semi-additive process (SAP), which allows wiring pitch reduction, density enhancement, and thickness reduction.[2] Wiring pitch reduction, however, causes an increased transmission loss, which can easily lead to signal quality deterioration. It is known that the transmission loss is proportional to the dielectric constant (Dk) or the dielectric dissipation factor (Df), and the roughness (Ra).[3] Therefore, it is important to reduce Dk, Df and Ra. Moreover, semiconductor package thickness reduction leads to a lower rigidity of the chip mounting substrate. Hence, it is also important to reduce the warpage caused by the difference in the coefficient of thermal expansion (CTE) between the chip and the substrate. Accordingly, there is a need for a SAP-compatible, build-up film that features excellent dielectric properties (Dk $\leq$ 3.3 and Df $\leq$ 0.0040), a low CTE (20 ppm/°C or less), and a small Ra (250 nm or less).[4]

Then, we embarked on the development of a build-up film incorporating our proprietary primer resin technology, low dielectric resin technology, and low CTE resin technology.

4 Technical Details

1. Development Concept of "AS-500HS"

In SAP, build-up film first undergoes chemical roughening by desmear and then electroless copper plating. Therefore, the adhesion to the electroless copper plating layer is critically important from the perspective of stable multilayer substrate manufacturing. On the other hand, the resin approach to transmission loss reduction or CTE reduction requires the use of a low-polarity material or an increased amount of filler and hence is disadvantageous to achieve high adhesion strength. Accordingly, we applied, to "AS-500HS", a bifunctional structure (bilayer film structure) that consisted of a primer layer having a low-roughness roughened surface morphology and high adhesion properties advantageous for fine-pitch wiring formation, and a base resin layer for developing low dielectric properties and a low CTE.

2. General Properties of “AS-500HS”

Table 1 shows the general properties of “AS-500HS”, which shows good dielectric properties including a Dk of 3.3 and a Df of 0.0034 at 5 GHz. Its CTE is reduced by approximately 60% (17 ppm/°C) compared with our existing proprietary product.[4] Moreover, when it has small surface roughness after desmear treatment (Ra: 220 nm), it exhibits strong adhesion to the copper plating layer (0.7 kN/m). This characteristic is advantageous for fine-pitch wiring formation and enables line formation with an L/S of 2/2 μm (**Figure 1**). At the same time, this wiring region shows high insulation reliability. Furthermore, the via bottom resin residue left after laser via formation is completely removed by desmear, thereby providing SAP processability.

3. Transmission Characteristics of “AS-500HS”

Figure 2 shows the evaluation results of the transmission characteristics (transmission loss) of “AS-500HS” micro-strip line. “AS-500HS” has lower transmission characteristics, in each temperature range, than our existing build-up films.[5]

Table 1 Properties of “AS-500HS”

Item		Unit	***AS-500HS***	AS-11G*3
Dk (5 GHz)*1	—	—	3.3	3.4*3
Df (5 GHz)*1	—	—	0.0034	0.0140*3
CTE	TMA (30-120℃)	ppm/℃	17	45*3
	TMA (250-300℃)		44	—
Tg	DMA	℃	233	165*3
Elastic Modulus	DMA (30℃)	GPa	12	2.4-2.6*3
Roughness*2	Ra	nm	220	300-400*3
Resin residue after desmear at via bottom*2	—	—	No residue	—
Peel strength*2	Cu plating	kN/m	0.7	0.7*3
Reflow cycle Resistance*2	260℃ reflow	cycle	20	—
Reliability at fine line space (L/S=2/2 μm)*2	130℃ / 85%RH, 3.3 V DC	h	200	—

*1) Cavity resonator perturbation method
*2) Treatment condition : Swelling 60℃ 10 min, Etching 80℃ 15 min
*3) Catalog value

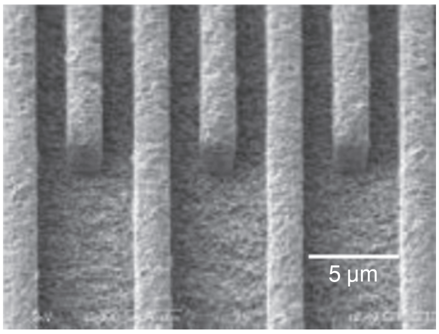

Figure 1 SEM image of L/S=2/2 μm on “AS-500HS” by SAP

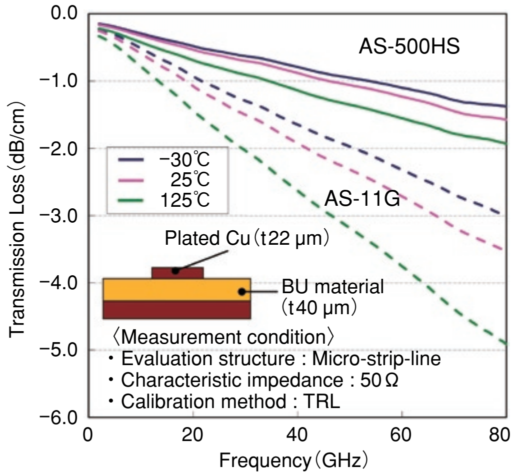

Figure 2 Transmission loss of “AS-500HS”

5 Future Business Development

・Development of build-up film with a further lower transmission loss and lower coefficient of thermal expansion.

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2) Kiyoshi Takagi, Everything from Start to Finish on the Making of Build-Up Multi-Layer Printed Circuit Boards (2006)
3) Y. Mizuno,“Low Transmission Loss Multilayer PWB Materials for High-Speed and High-Frequency Applications”, ECTC, 2013.
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5) Shin Takanezawa, “Build-Up Material AS-11G for Next Generation Packaging Substrates,” Hitachi Chemical Technical Report No. 41 (2003))

New Evaluation Technology of EMC to Improve Electrical Reliability of High-Voltage Package

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1 Abstract

Energy policy is an important issue in the world, and power semiconductors are expected to achieve high efficiency by (1) increasing the voltage, (2) increasing the power density, and (3) reducing the energy loss. Therefore, the EMC (encapsulation molding compound) for power semiconductors is required to have further higher heat resistance and higher break-down voltage reliability. In this report, we discuss the mechanism and degree of EMC's impact to leakage current. As a result, it was found that the polarization of EMC contributes to the leakage current after applying high bias at high temperature for a long time, and the dielectric constant including space charge polarization has high correlation with leakage current as a polarization evaluation method.

2 Characteristics of the New Technology

Correlations were obtained between general electrical properties (volume resistivity and dielectric constant at 1 MHz) and leakage current by applying a new concept of dielectric constant. The correlations included space-charge polarization to leakage current, for which no correlation could be obtained by the general electrical properties.

3 Background of the Development

In recent years, power electronics-driven energy policies and associated technology developments have been vigorously promoted in different countries. Next-generation SiC power semiconductors in particular are expected to reduce power loss by band gap expansion, and hence have started to go into mass production for use in some electric railways or vehicles. Challenges, however, remain with the wafer fabrication cost at a high level. Though advantageous in terms of cost, Si power semiconductors have the drawback of a large power loss. Accordingly, the author decided to establish a leakage current reduction technology related to power losses in order to propose an encapsulation molding compound (EMC) for SiC and Si power semiconductor packages capable of further power loss reduction.

It has been expected that the electrical properties of an EMC contribute to leakage current. Because of its low correlation with general physical properties, such as volume resistance or dielectric constant (1 MHz), there has been no well-defined method for reducing leakage current. Then, assuming that leakage current increases because of the polarization of the EMC applied on chips, the author turned her attention to the polarization under high temperature bias for a long time. In this study, as reported below, the author established a technique for determining a new physical property value (dielectric constant including space-charge polarization) correlated with leakage current, which is the indicator of breakdown voltage reliability.

4 Technical Details

The leakage current must be below a specified value after the environmental test processing (for example, high temperature reverse bias or high temperature high humidity reverse bias). On the other hand, it was inferred from the test time, and the occurrence tendency or the semiconductor chip structure, that the polarization of the EMC applied on chips contributes to increases in leakage current. For EMCs, the dielectric constant is often used as the indicator of polarization. In such cases, the dielectric constant is conventionally expressed as a measurement value obtained at ordinary temperature and 1 MHz (on the order of microseconds); these test conditions, however, differ widely from those of the relevant environmental test, which is performed at high temperature over a long time. Accordingly, with the focus on the dielectric constant, including space-charge polarization under high temperature, the author studied the evaluation method and performed measurements. Additionally, measurements were taken of leakage current using our HTRB evaluation system. Use was made of the result obtained after 336 hours under specific environmental test conditions (175°C and 1,200 V reverse bias). The results of the two tests revealed the correlation between dielectric constant and leakage current including space-charge polarization (**Figure 1**).

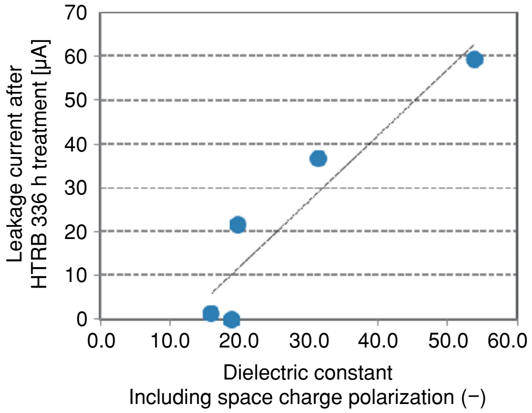
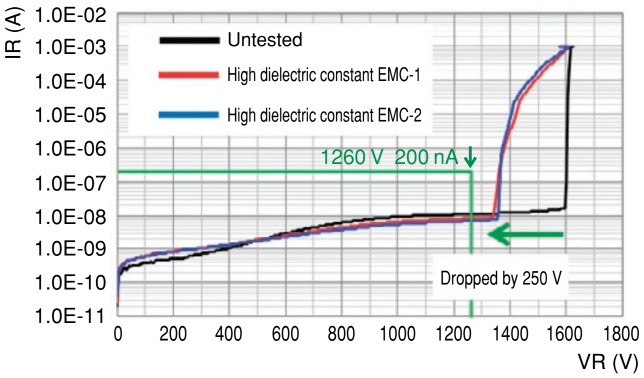
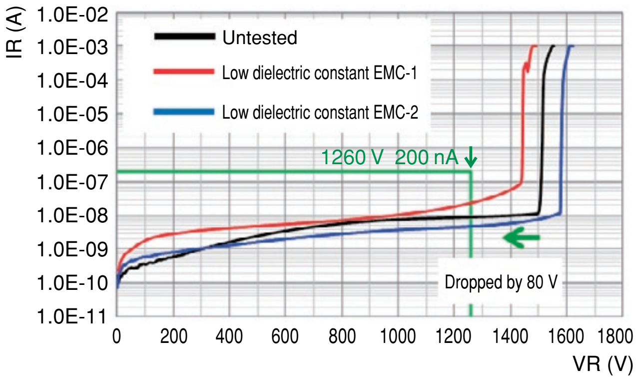


Figure 1 Relationship between leakage current after HTRB 336 h treatment and dielectric constant including space charge polarization

As for failure analysis, the packages were evaluated for I-V characteristic variations after the 336-hour HTRB test. As shown in **Figure 2**, the high dielectric constant EMC exhibited a decrease in I-V curve threshold voltage by 250 V as compared with the untested one, while the low dielectric constant EMC showed a decrease in I-V curve threshold voltage by 80 V. Thus, the results of the I-V curves also revealed the effects of the dielectric constants, including space-charge polarization on the electrical properties. In addition, an emission analysis also revealed that a high dielectric constant product easily undergoes changes in its depletion layer, which is the breakdown voltage control portion of the device, and therefore that the dielectric constant including space-charge polarization is useful for leakage current control.



(a) I−V characteristics with high dielectric constant EMC



(b) I−V characteristics with low dielectric constant EMC

Figure 2 Evaluation result of I-V characteristics with high or low dielectric constant EMC

5 Future Business Development

・Improve EMCs for high breakdown voltage power semiconductors based on this technology.

[References]

Latest Trend Study of Semiconductors Related Players 2015, Fuji Chimera Research Institute, Inc. (May 2015)

Thermal Conductive Sheet Containing Vertically Oriented Graphite Fillers "TC-BWP01" for FCBGA TIM1 Applications

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1 Abstract

As the performance of semi-conductor packages becomes higher and their size becomes smaller, the need to control heat through a thermal interface material (TIM) has become increasingly important. To meet the demand for a thermally conductive, flexible material, Hitachi Chemical has worked to develop and commercialize a high performance solution. By orienting graphite fillers vertically within an acrylic rubber based matrix, Hitachi Chemical's TIM provides both high thermal conductivity and flexibility.

Part of a TIM application depends on the cooling design of the electrical device. In TIM1 applications, where the TIM is applied directly to IC chips, the TIM must not only provide high thermal conductivity, the TIM must also be able to handle warpage of IC chips under lower pressure assembly, with high reliability.

In this report, we will discuss our developed TIM, which can handle the warpage of IC chips and provides high reliability in TIM1 applications.

2 Characteristics of the Developed Product

・Adoption of soft and highly adhesive resin for the sheet enables the handling of the warpage of IC chips.
・Adoption of thermally stability and moisture resistant resin ensures adhesion after a severe reliability test.

3 Background of the Development

Hitachi Chemical has developed and commercialized "TC-001", a vertically oriented graphite thermal conductive sheet in which graphite fillers are vertically oriented by creating a composite material consisting of graphite fillers and soft acryl rubber and by controlling the structure based on our unique technology. **Figure 1** shows a cross-sectional image of "TC-001". On "TC-001", graphite fillers with a large grain size are vertically oriented to penetrate through the sheet. Thermal conductivity of 90 W/m·K was achieved in the vertical direction.

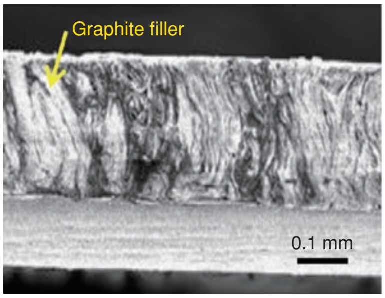


Figure 1 Cross sectional image of "TC-001"

TIM (thermal interface material) caught between the heat source and the heat dissipation material is used to improve heat transfer efficiency. In the TIM1 application in which TIM is used between IC chips as the heat source and the heat spreader, TIM must be able to handle the warpage of IC chips and to have high reliability capable of securing adhesion after reliability test.

In addition, market trends promote the use of IoT (Internet of Things) and require servers with high performance. A problem related to these trends is that general-use grease may have insufficient thermal conductivity.

With this as background, we attempted to develop a technology that provides warpage handling and high reliability while securing the high thermal conductivity of vertically oriented graphite sheets.

4 Technical Details

(1) Design concept for providing warpage handling ability and high durability

Figure 2 shows an outline of a TIM1 application, and **Table 1** shows the general properties of the "TC-BWP01", which has a conventional vertically graphite oriented structure and achieves (i) high thermal conductivity, (ii) flexibility and adhesion capable of handling the large warpage of IC chips, and (iii) reliability capable of maintaining adhesion with IC chips and a heat spreader after an reliability test by using soft, highly adhesive, thermally stability and moisture-resistant resin.

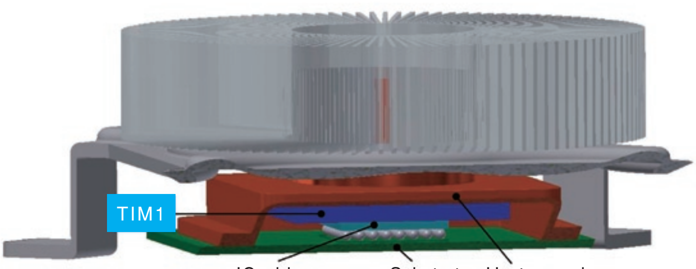


Figure 2 Outline of a TIM1 application

Table 1 General properties of "TC-BWP01"

Item	Unit	TC-001 thickness 0.3 mm	TC-BWP01 thickness 0.3 mm
Thermal resistance	K・cm²/W	0.14	0.15
Adhesive force	N・mm	4.0	7.6
Stiffness	N/mm	1050	966
Tensile strength	MPa	0.3	0.4

(2) Evaluation of warpage handling

Figure 3 shows the warpage in the IC chip area of a test package. **Figure 4** shows the adhesion performance of "TC-BWP01". When assembling a test package with a substrate size of 45 × 45 mm and an IC chip size of 20 × 20 mm, the warpage at the IC chip area was approximately 70 μm. In addition, it was confirmed that "TC-BWP01" adheres to the IC chip and the heat spreader without de-lamination after the assembly.

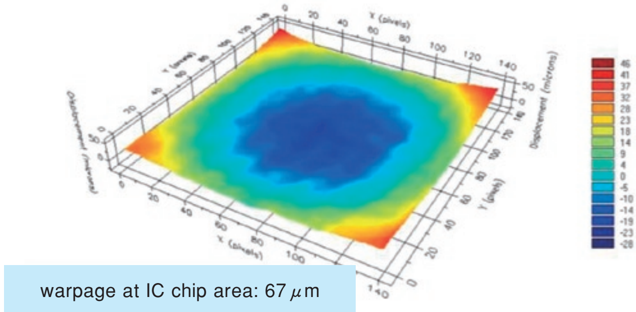


Figure 3 Warpage of an IC chip area

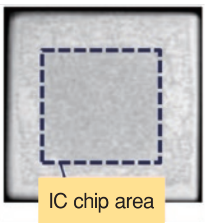
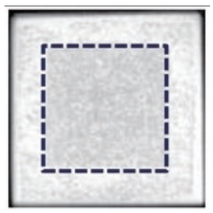
Item	"TC-BWP01" thickness 0.3 mm			
	After assembly	Reliability test		
		(a) HTSL (150℃ 1000 h)	(b) Heat cycle (−55⇔125℃ 1000 cycles)	(c) HAST (130℃ 85%RH 192 h)
Image of Scanning Acoustic Tomograph				
Coverage (%)	99	99	99	99

Figure 4 Coverage of a "TC-BWP01"

(3) Evaluation of durability

The endurance test for a test package was performed under three conditions: (a) HTSL (High Temperature Storage Test) 150°C 1000 h, (b) Heat cycle −55°C ⇔ 125°C 1000 cycles, and (c) HAST (High Accelerated Stress Test) 130°C 85% RH 192 h to recognize that adhesion similar to that after the assembly was secured.

"TC-BWP01" is capable of handling the large warpage of IC chips and has high reliability. Therefore, we expect FCBGA TIM1 to be applied to semiconductors, including applications to servers.

5 Future Business Development

・Expand the application of FCBGA TIM1 in Japan and overseas.
・Continuously improve adhesion by taking into consideration the increase of warpage associated with enlarged IC chip size.

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Net Shape Reactor Core Using Newly Developed Insulating-Lubricant

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1 Abstract

Recent years have seen a world-wide increase in the demand for energy savings, not only in the commercialization of new power generation systems (such as photovoltaic generation), but also in the commercialization of electric vehicles (EV) and hybrid electric vehicles (HEV).

Soft Magnetic Composite (SMC) effectively suppresses eddy currents by using insulating film for electrical isolation between metal magnetic powders, resulting in superior magnetic characteristics in the high frequency range. Recently, pure iron SMC cores have begun to be applied, and show great promise for miniaturization and for handling large capacities.

However, pure iron SMC has high ductility, which tends to cause problems in plastic flows. As a result of the high ductility, insulating film may be destroyed in the compaction process, and the desired original characteristics become unavailable because of increasing eddy current loss. To avoid such problems, we started development of a specialized lubricant for SMC cores.

This paper describes the effectiveness of the newly developed lubricant.

2 Characteristics of the New Product

- Insulation breakdown in the surface layer of a reactor core is suppressed, based on core-loss suppression technology that is based on Hitachi Chemical's independently developed new lubricant.
- Mass production of high-capacity small reactor cores based on a pure iron pressed powder magnetic core material was achieved by using net shape forming.

3 Background of the Development

Our company has developed pressed powder magnetic core materials for many years. Currently, magnetic characteristics equivalent to ingot steel are obtained through the development of high-compression forming technology, high purification of powder, and fine powder manufacturing methods. In addition, insulation processing technology for magnetic powder has evolved, and its application to motor cores[1,2] and reactor cores[3] has increased.

In recent years, inverters have been installed in photovoltaic power generation systems, HEVs, etc., which represents significant technical progress, and the reactor cores contribute to voltage boosting and rectification. Although silicon steel sheets have generally been used as conventional core materials, the pure iron pressed powder magnetic cores with high inductance values are attracting attention because of the requirement for lower iron loss associated with higher frequencies, and the need for miniaturization and larger capacities.

In pure iron materials with high ductility, however, plastic flow is generated during forming, and the insulating film is easily destroyed. The resulting increase in eddy currents was a problem, because such eddy currents made it impossible to obtain the original magnetic characteristics. Although there are various methods for removing plastic flow, such as etching, it has been impossible to use the advantage of pure iron materials because additional processing is required regardless of the method. Consequently, we focused on shaped lubricants and started the development of multi-functional lubricants capable of improving lubrication performance and protecting the insulation properties of film with the goal of achieving net-shaped reactor cores.

4 Technical Details

Figure 1 shows the concepts related to the developed lubricant.

(1) A lubricant with high cleavability is selected. The lubrication-component filling between metal particles prevents plastic flow.

(2) A special insulator, prioritized for adherence and maintenance on an insulation film during sliding, is selected to improve electrical resistivity on a surface layer.

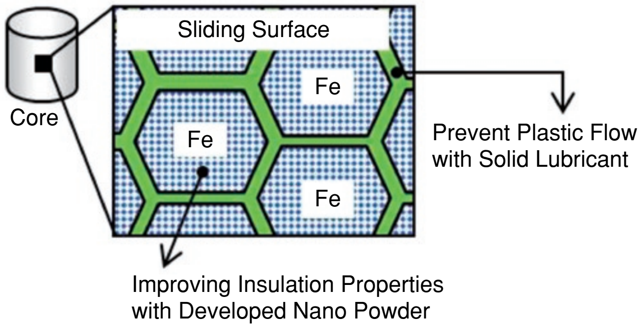

Figure 1 Concept of developed lubricant

Figure 2 shows the influence of electrical resistivity due to the use of the developed lubricant. The use of the developed lubricant provides the electrical resistivity of a sliding surface equivalent to that of a compaction surface.

This technology enabled the realization of a net-shaped pure iron pressed powder magnetic core and achieved mass production of reactor cores for photovoltaic power generation (**Figure 3**). Die lubrication molding is essential as the technology for the pressed powder magnetic cores requiring high pressure forming. This technology is also effective for motor cores exposed to higher frequencies and we believe it will be able to contribute to business expansion of soft magnetic parts hereafter.

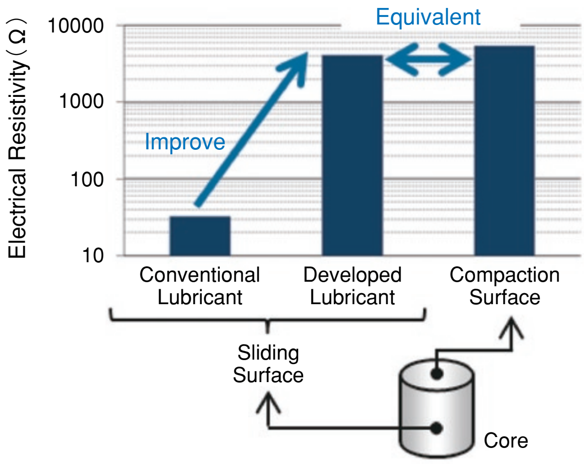

Figure 2 Electrical resistivity of sliding surface

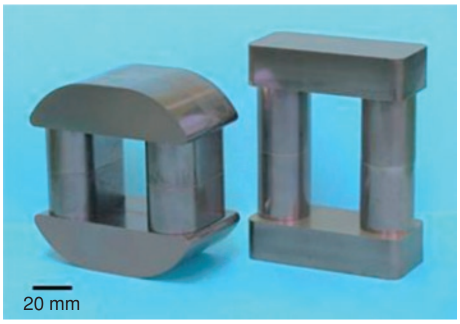

Figure 3 Appearance of reactor core for photovoltaic system

5 Future Business Development

・Apply the new technology to reactors used for on-board inverters, such as in HEVs or EVs.

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[Related patent]

Patent application 2015-508695, Patent application 2015-539285 and Unexamined patent application 2016-189441

Hitachi Chemical
Working On Wonders

Transient Liquid Phase Sintering Paste

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1 Abstract

Due to the miniaturization of chip sizes and higher temperatures in the use environments, recent years have seen increasing demands for new bonding materials to replace lead-free solder. Solder is very useful for conductive bonding, but has limitations such as being unsuitable for repeated bonding reflow processes and for precise control of bonding positions. The “HT Series” is a die bonding paste that uses the transitional liquid phase sintering method of copper and tin. Features of the “HT Series” are that it can be bonded under the same temperature conditions as solder and it does not re-melt after bonding. Utilizing these features, we are developing the “HT Series” for use in automobile engines and headlights.

2 Characteristics of the Product

- After bonding, the product does not re-melt at the reflow temperature and can be used for repeated bonding (re-melting temperature > 400°C).
- There is no self alignment and no shape change even after bonding.
- The bonding material has low elasticity.

3 Background of the Development

In recent years, the demand for repeated bonding has increased because of the integration of the bonded substrate. Although a method for using lead-free solder with a different melting temperature is available as a method of repeated bonding, this method is not practical because the usable temperature range is small when considering the heat resistance of the peripheral component materials. Therefore, we are developing a bonding paste that uses transient liquid phase sintering (TLPS) of copper and tin alloy. Because the reaction of the molten tin alloy with copper particles at the sintering temperature forms an intermetallic compound with a high melting temperature, this paste does not melt even when bonding is repeated.

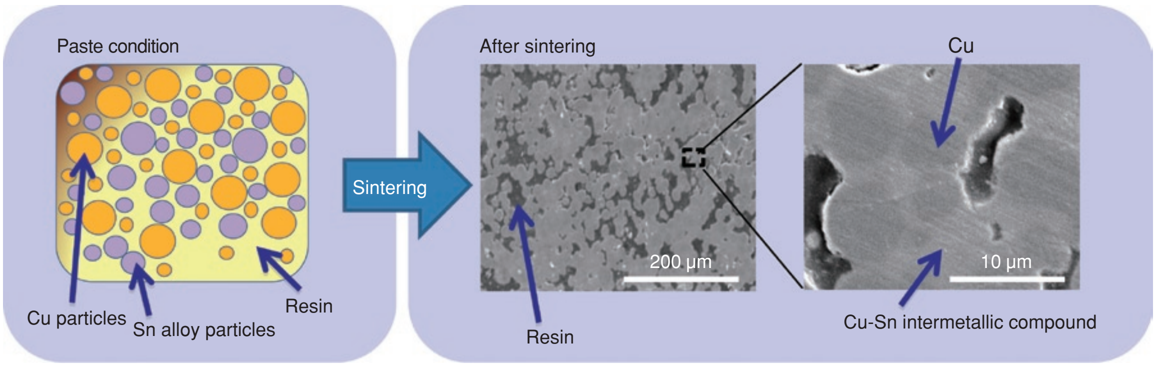


Figure 1　Structure of HT Series

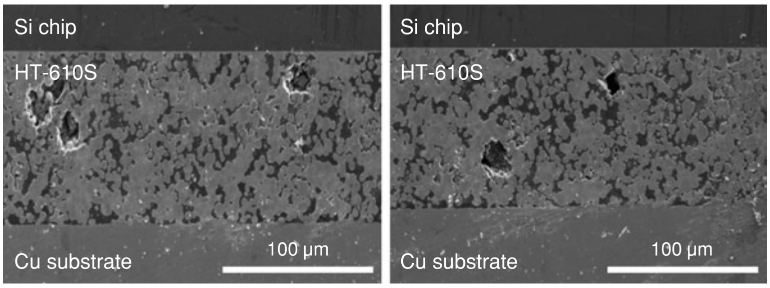
4 Technical Details

“HT-610S” is a bonding paste that combines the afore-mentioned metal composition and our unique thermoplastic resin to achieve the following at levels equivalent to lead-free solder: bonding processes, low elasticity, high heat resistance, shape-keeping performance, and the possibility of repeated bonding. **Table 1** shows the general characteristics of “HT-610S”. “HT-610S” suppresses cracks even close to voids because the deformation of thermoplastic resin relieves stress and demonstrates high temperature cycle reliability (**Figure 2**). In addition, the shape does not change before and after sintering, and does not re-melt during repeated bonding (**Figure 3**). Because this paste is capable of bonding in temperature conditions equivalent to

those for lead-free solder, does not re-melt after bonding, and has high temperature cycle reliability, we are planning to apply it to automobile component materials.

Table 1 Properties of "HT-610S"

Item	Unit	HT-610S	Pb-free solder SAC305	Sintered silver paste
Application	—	Die bonding material	Mounting material	Die bonding material
Conductor	—	Cu, Sn, etc.	Sn 96.5-Ag 3.0-Cu 0.5	Ag
Resin	—	Thermoplastic PI	—	—
Bonding condition	—	260℃ / N_2 Reflow	260℃ / N_2 Reflow	250℃ / Hot Press
Re-melting temp.	℃	> 400	220	960
Coefficient of thermal expansion	ppm/℃	19	19	20
Elastic modulus	GPa	3.5	31	30
Electrical resistivity	Ω·m	5.0×10^{-7}	1.1×10^{-7}	2.0×10^{-8}
Thermal conductivity	W/(m·K)	43	55	400
Reliability test	cycle	3000	2000	3000
	condition	−65℃ to 175℃	−40℃ to 125℃	−65℃ to 175℃
Whisker generation	—	No generation	Generation	No generation
Self-alignment	—	No self-alignment	Self-alignment	No self-alignment



Before temperature cycling test   After temperature cycling test

Figure 2 Cross-sectional images before and after temperature cycling tests (From –65°C to 175°C, 3000 cycles)

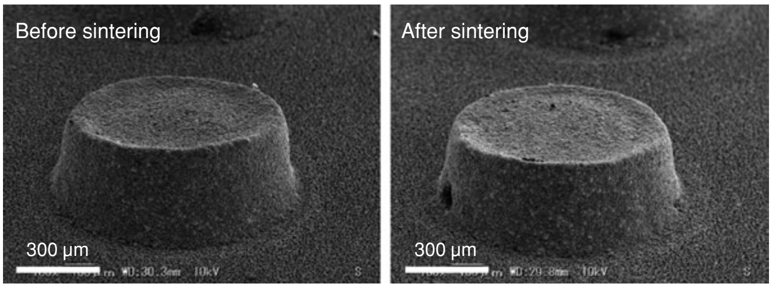


Figure 3 Shape change before and after sintering

5 Future Business Development

・Development of bonding materials for heat dissipation

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Sintering Cu Bonding Paste that can be Sintered without Pressure

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1 Abstract

We developed a sintering Cu bonding paste that can be cured without pressure at 225°C in an H_2 atmosphere. The die-shear adhesive strength with an adherend of Cu, Ni, Au, or Ag is at least 40 MPa. After sintering, the thermal conductivity of the sintered Cu bonding layer is 180 $W \cdot m^{-1} \cdot K^{-1}$. The sintered Cu bonding after a thermal cycle test (TCT) of 2000 cycles in the temperature range from −40 to 200°C showed a bonding reliability that is the same as, or better than, sintered Ag bonding or high lead solder. With its high thermal conductivity, high bonding reliability, good productivity, and reasonable cost, this sintering Cu bonding paste is likely to be an ideal bonding material for application in power electronics.

2 Characteristics of the New Product

- The product is sintered without any pressure (225°C, in hydrogen) to produce a highly heat-resistant, highly reliable metal bonding.
- The product produces a low-porosity sintered body of Cu with a high level of thermal conductivity (> 180 $W \cdot m^{-1} \cdot K^{-1}$).
- The sintered body consists entirely of Cu, and contains no environmental hazardous substances.

3 Background of the Development

Enhancing the operating temperature of a power device simplifies the cooling device and reduces the required number of device chips. This leads to smaller, lighter, and cheaper power modules. Accordingly, power device manufacturers are promoting development according to roadmaps that show the targets for improvements in the operating temperature of power devices.[1] The highest operating temperature of power device elements (junction temperature, $T_{j, max}$) was 125°C in 1990 and 150°C in 2005. In 2016, power device elements for which the highest operating temperature was 175°C were released. Moreover, studies have begun concerning the operation of compound semiconductor (SiC and GaN) devices in the temperature range from 200 to 250°C.

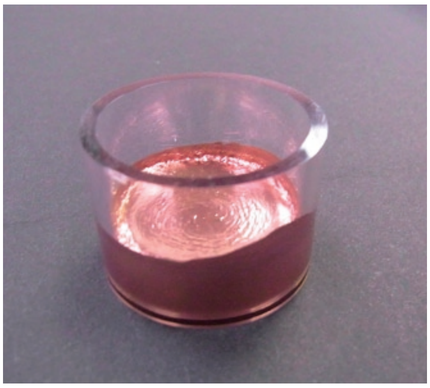
High-lead solder shows high levels of bonding reliability among conventional solder materials, and has therefore been widely used for power devices. Despite its high lead content, this material is exempted from the RoHS Regulations.[2] High-lead solder, however, poses the problem of insufficient power cycle reliability during operation at $T_{j, max} \geq 175$°C.[3] Another problem is that it forms a thermal bottleneck due to its lower thermal conductivity compared to other components.

4 Technical Details

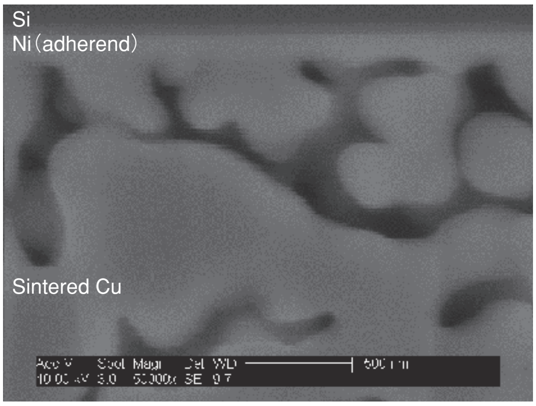
We developed a sintering Cu bonding paste that allows pressure-less bonding. This material can be sintered at 225°C or higher without any pressure in a hydrogen atmosphere. Although it needs hydrogen for the sintering, hydrogen reduces and removes oxide film from the adherend surface, thereby allowing bonding to Cu, Ni, and Pd in addition to Au and Ag. The thermal conductivity of this paste is 180 $W \cdot m^{-1} \cdot K^{-1}$, which is sufficiently high relative to 35 $W \cdot m^{-1} \cdot K^{-1}$ of high-lead solder, and therefore allows heat from power device chips to rapidly dissipate. In a thermal cycle test in the temperature range from −40°C to 200°C, in terms of bonding reliability, this paste performed better or equal to sintering Ag bonding paste and high-lead solder. In a power cycle test at $T_{j, max} = 175$°C, this paste showed better power cycle reliability than that of high-lead solder. Furthermore, the raw materials of this paste are available at more reasonable prices than those of the sintering Ag bonding paste, and this paste contains no environmentally hazardous substances (unlike high-lead solder). This sintering Cu bonding paste provides high levels of productivity, high levels of heat conductivity, and high levels of bonding reliability, all at a reasonable price. Sintering Cu bonding paste is expected to provide an ideal bonding material for power electronics.

Table 1 Comparison of die-bonding properties among sintering Cu bonding paste, sintering Ag bonding paste, and high-lead solder

Items		Sintering Cu bonding paste	Sintering Ag bonding paste	High-lead solder
Bonding conditions	Environment	H_2	Air	H_2 or HCOOH
	Bonding pressure	No pressure	Press (20 MPa)	No pressure
	Temperature	225–300 ℃	300–350 ℃	350 ℃
Adherent materials		Cu, Ni, Au, Ag, Pd	Ag, Au	Cu, Ni, Au, Ag
Properties of bonding layer	Thermal conductivity	180 $W \cdot m^{-1} \cdot K^{-1}$	280 $W \cdot m^{-1} \cdot K^{-1}$	35 $W \cdot m^{-1} \cdot K^{-1}$
	Power cycle reliability	> 40000	—	38000
	Thermal cycle reliability	> 2000	> 2000	> 2000
Material cost		Reasonable	Expensive	Cheap
Environmental friendliness		OK	OK	Pb



Appearance of the sintering Cu bonding paste



Cross sectional SEM of the bonding interface

Figure 1 Appearance of the sintering Cu bonding paste and an SEM image of the bonding interface

5 Future Business Development

- Application to large-area chips equivalent to or exceeding 10 mm × 10 mm (currently 7 mm × 7 mm)
- Development of materials curable in non-combustible gases (existing materials can be sintered only in 100% hydrogen)

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