New Product Development to Support Global Growth of Energy Storage Business

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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.

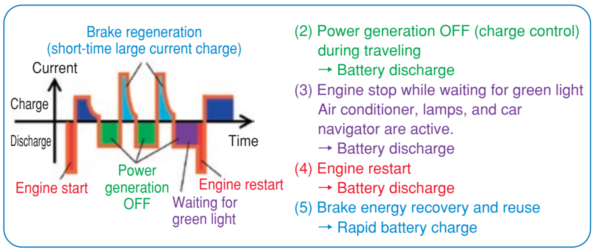


Figure 1 Charge and Discharge model of the battery for Idling stop and start system

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.

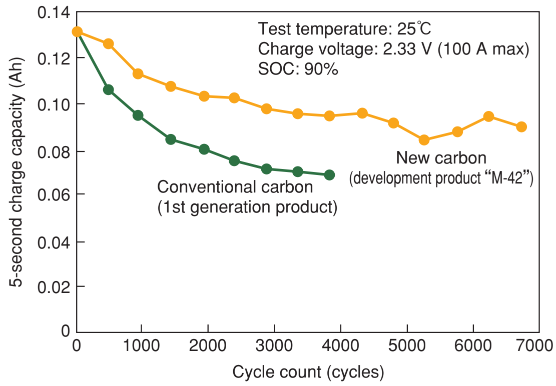


Figure 3 Change in charge capacity for 5 seconds

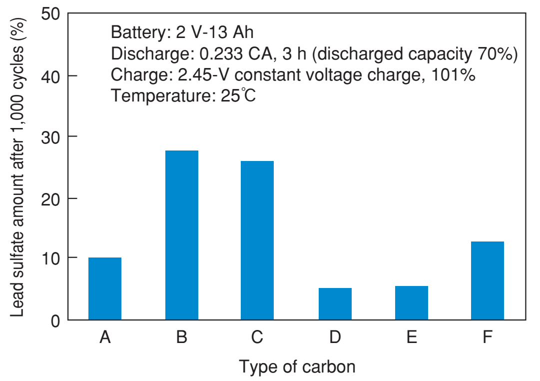


Figure 4 Comparison of amount of lead sulfate in negative active material using different carbon

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

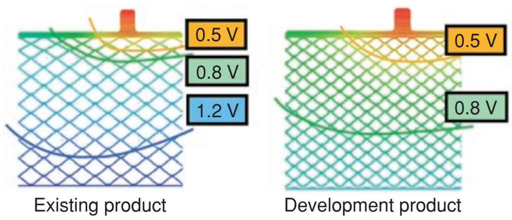


Figure 5 Results of grid resistance simulation

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.

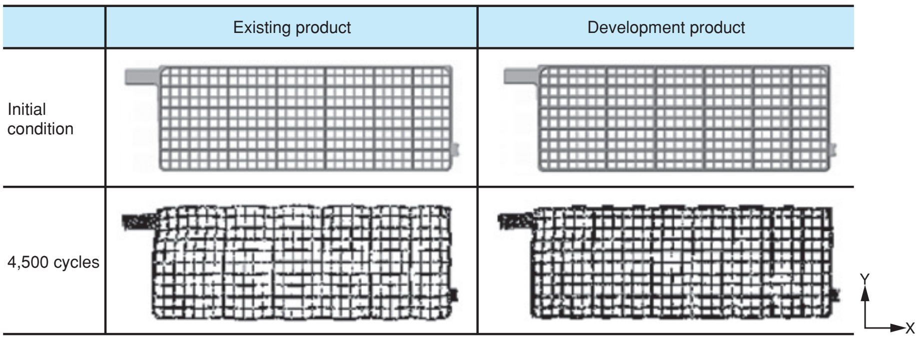


Figure 6 Typical simulation result of corrosion deformation in LL type VRLA batteries

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

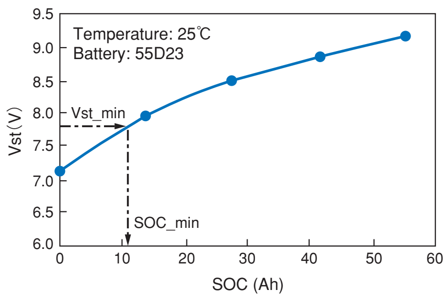


Figure 7 Relationship between SOC and voltage at engine start

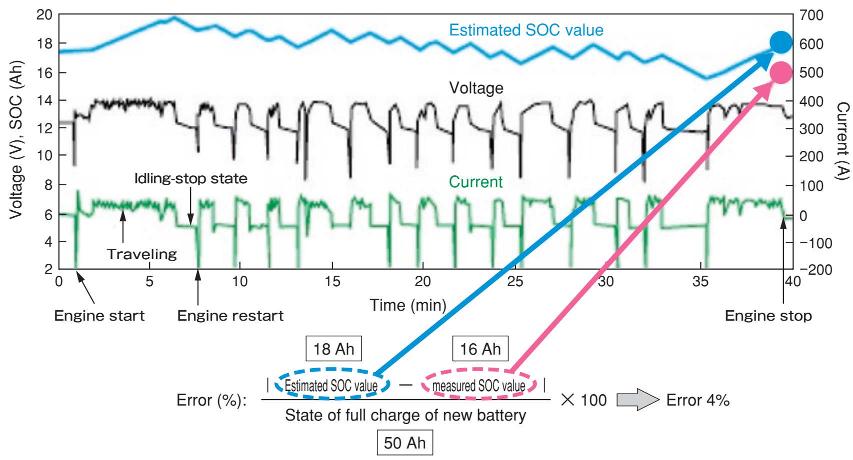


Figure 8 Results of SOC estimation in the idling stop and start system

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.

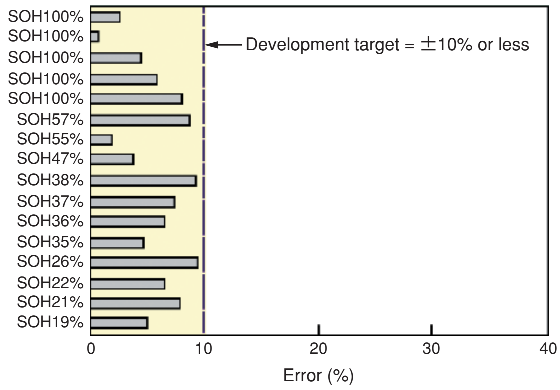


Figure 9 SOC errors of deteriorated batteries

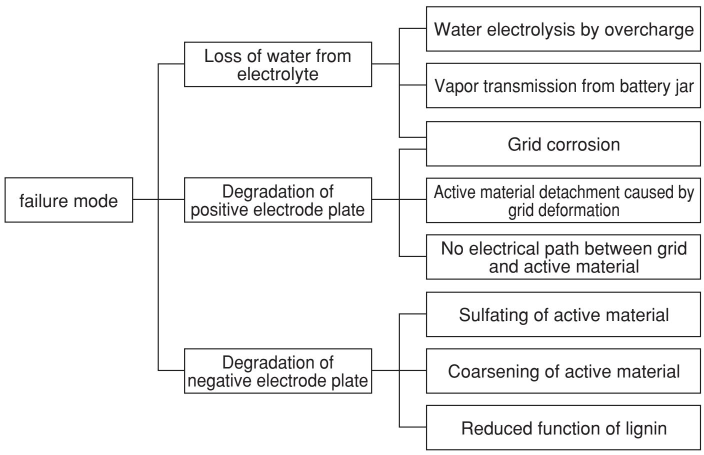


Figure 10 Lifetime factor of VRLA battery

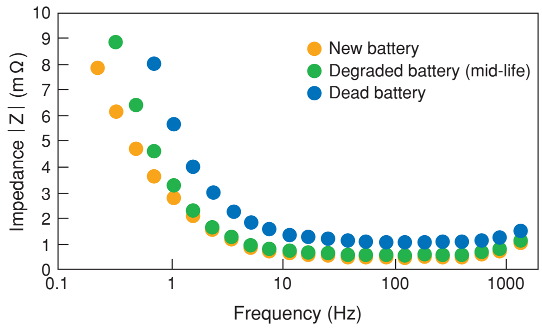


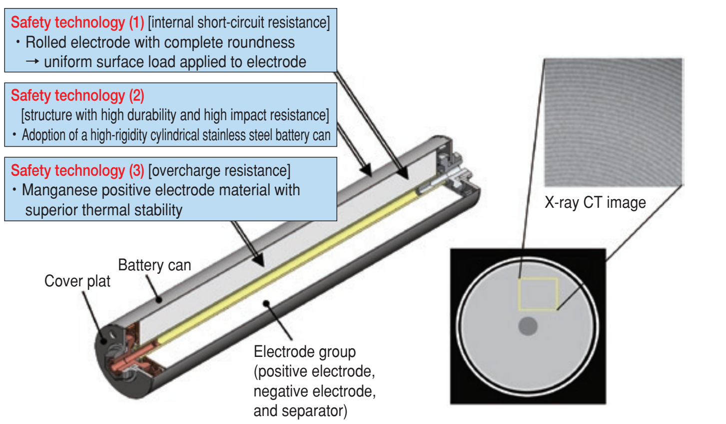
Figure 11 Frequency characteristics of different batteries

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



(a) Typical longitudinal cutaway view of cell (b) Typical radial cross-sectional view of cell

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.

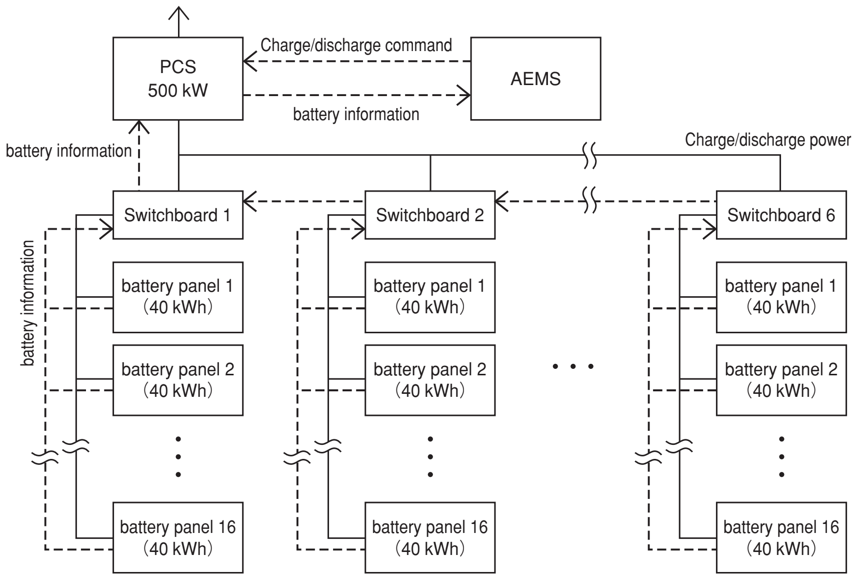


Figure 13 Block diagram of the lithium-ion battery system

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

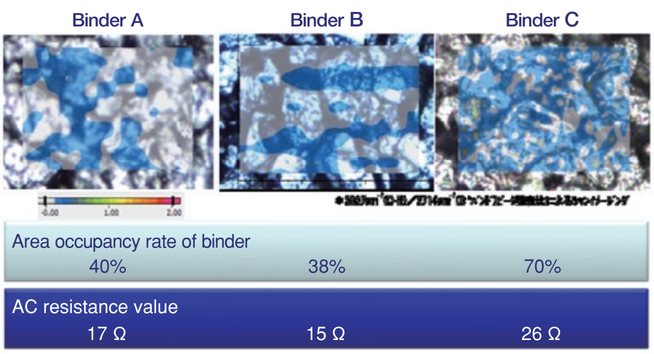


Figure 14 Relationship between binder distribution and AC resistance based on the difference among binders

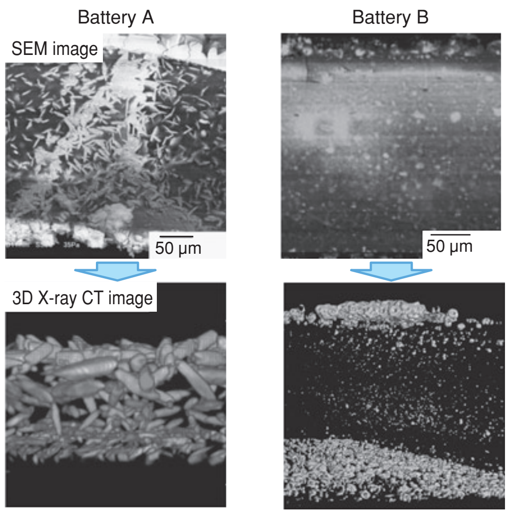


Figure 15 Cross-sectional SEM image and three dimensional structure analysis of separators after hydration short by X-ray CT

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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