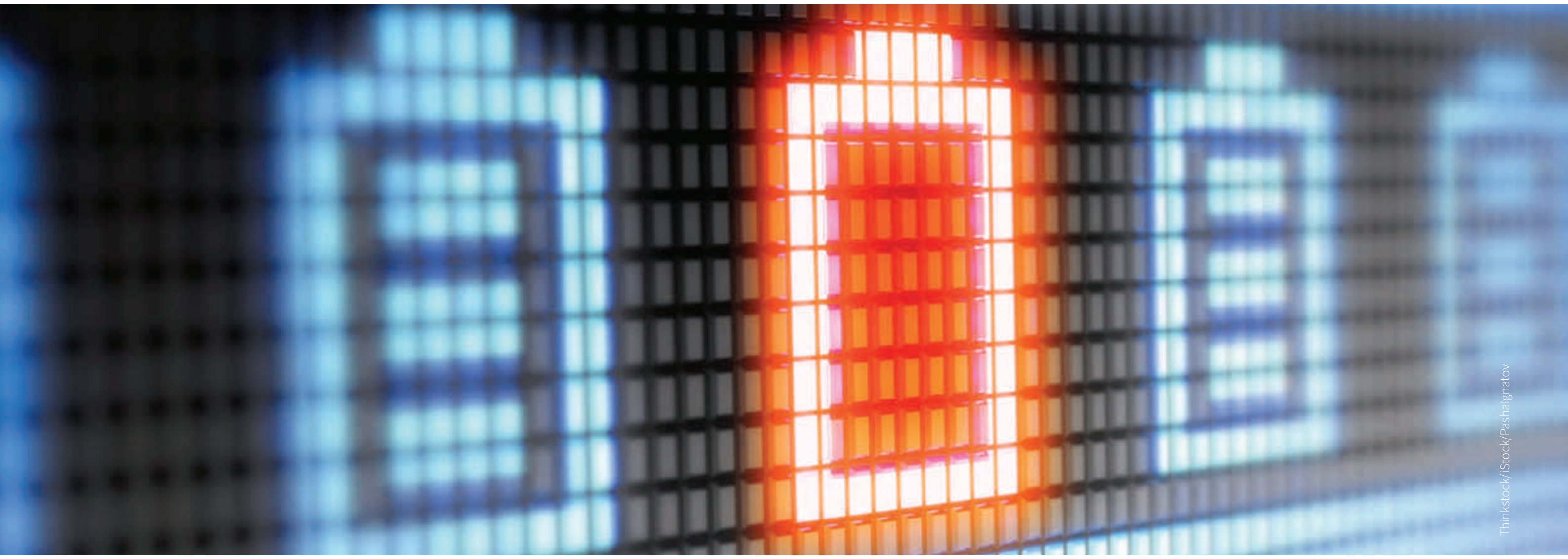

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Waseda University

Staying on top

Japan was the first country to commercialize the lithium-ion battery in the 1990s and is once again reasserting its market dominance with more efficient commercial lithium-ion batteries for automotive applications.

Japan pioneered many of the innovative technologies that we now take for granted. From wristwatches and CDs, to liquid-crystal displays, flash memory, digital cameras and lithium-ion batteries (LIBs). Yet a closer look at what's on offer reveals that currently most of these products are probably made in China or Korea. Wresting market share from the manufacturing powerhouses of its Asian neighbours is a perpetual challenge for Japan, but Tetsuya Osaka of Waseda University envisages a turnaround in Japan's fortunes in the global battle for supremacy in next-generation LIB technology.

"The painful lessons of the past have taught us that we need to protect Japan's state-of-the-art technology from quickly losing market share to followers such as South Korea and China," says Osaka. "So far, Japan is maintaining its leading market share in automotive LIBs, but we urgently need to strengthen our strategic research and development system in anticipation of commercialization and standardization."

For a technology in which the cost of materials typically represents more than two-thirds of the price of production, resource-challenged Japan starts with a significant handicap relative to its competitors in the LIB market. Osaka, through the Battery Research Platform of the Advanced Low Carbon Technology Research and Development Program funded by the Japan Science and Technology Agency (JST) and the New Energy and Industrial Technology Development Organization (NEDO) programmes, has developed a strategy for Japan to innovate its way to continued market dominance.

Deputy president of Waseda University, Tetsuya Osaka.

"Japan is currently leading the world in automotive LIBs, which use different technology to conventional compact portable LIBs due to more stringent safety requirements," says Osaka. "By serving as a joint industry–academic research platform, the Battery Research Platform will help Japan stay at the forefront of battery development utilizing next-generation battery materials."

The safety of LIBs has been under the spotlight since a series of fires originating from batteries in laptop computers and phones in the mid-2000s, which led to millions of batteries being recalled worldwide. While most of these fires were attributed to manufacturing defects or contamination leading to short-circuit failure, these incidents highlighted the fact that the flammable, pressurized liquid electrolyte used in conventional LIBs does not have the inherent safety required for automotive and aeronautical applications. "The next generation of lithium batteries will be solid state, using a safe solid material for the electrolyte instead of a liquid organic electrolyte with its risk of ignition," says Osaka.

The lithium electrode in next-generation LIBs will also be different. Automotive LIBs use a lithium–iron–phosphate electrode rather than lithium cobalt oxide of conventional LIBs. This replacement significantly lowers the risk of thermal runaway failure — a major cause of ignition.

"The next challenge will involve electrochemical device engineering at the atomic and molecular level to develop new two- and three-dimensional nanoparticle-based electrodes and solid-state electrolytes with a focus on improved safety, larger capacity, higher power density and wider range of potential applications."

Centre for battery innovation

The Battery Research Platform is a collaborative programme that brings together Japan's prestigious Waseda University and two of the country's flagship research institutes: the National Institute for Materials Science (NIMS) and the National Institute of Advanced Industrial Science and Technology (AIST). Waseda University was selected for the platform because it is one of the national leaders in battery technology and has a long track record of research excellence in physics, chemistry, materials and nanotechnology.

Related to smart energy systems, Takayuki Homma leads the development of novel processes for solar cells, funded by the Core Research for Evolutional Science and Technology (CREST) programme of the JST. The innovative research is being accelerated through collaboration with young researchers, including PhD students at Waseda's Leading Graduate Program in Science and Engineering tackling problems under the theme of Energy-Next, coordinated by Toru Asahi and Hiroyuki Nishide, and supported by the Ministry of Education, Culture, Sports, Science and Technology (MEXT).

"In Japan, it is very rare to do what we are doing: working in vertical collaboration with companies from various industries including battery manufacturers, automotive manufacturers and materials manufacturers, and continuing research and development until prototypes are ready for practical use," Osaka remarks.

Osaka's battery group has worked on joint industry projects with multiple companies from different sectors, including Toshiba and Toyota, to create a research and development ecosystem for battery technology that encompasses the entire development chain, from materials to fabrication, diagnosis and performance evaluation.

To support their battery research, Waseda University established the Smart Life Support Innovation R&D Center in 2014. The centre was adopted by MEXT as an example of an industry–university cooperation project that seeks to improve international scientific innovation by making use of regional resources. This new five-storey complex houses all of the facilities required to develop the most advanced LIB technologies, including two super-dry and clean rooms with automated fabrication lines, and a range of non-destructive evaluations systems such as electrochemical impedance spectroscopy.

"To support innovation, we are also key partners in the Advanced Battery Systems Research and Development Project funded by the Saitama prefectural government, north of Tokyo, where we are collaborating locally with companies like Mitsubishi Electric and other small- to medium-sized companies with the aim of identifying concepts for battery systems that can be used in every conceivable situation, including residential, commercial and industrial sites," says Osaka.

LIBs remain a rich playground for innovation, with many potential and unexplored routes to improved safety and stability as well as increased power density and charge–discharge performance. Through the development of new electrode materials, the power density per kilogram has already been increased from less than 100 watt-hours per kilogram to over 250 watt-hours per kilogram. Future advances will require the integration of new materials, physics, electrochemistry and structures with a level of engineering sophistication unprecedented in the battery technology sector.

Here, Japan has a distinct edge over its competitors. "The Japanese concept of *suriawase*, namely the precise inter-refinement and integration of individual high-precision components, is particularly important for the development of next-generation LIB technologies because of the emphasis on safety and reliability," says Osaka. *Suriawase* applies not just to fabrication but also to research and development. It is an integrative development strategy that will allow Japan to create advanced LIB technologies that are not easily replicated.

"As energy consumption grows with the increasing global population, batteries as a device for storing electricity will become increasingly important, not just in the mass consumer market, but also in optimizing the efficiency of electricity generation and minimizing carbon emissions," says Osaka. "Over the next few years, we expect the energy density per kilogram of LIBs to more than double, and the price per stored watt-hour to halve. If the safety aspects can be dealt with, this will open up many new applications, from vehicles and aircraft, to home energy management systems, decentralized 'smart grid' electricity storage to compliment solar and wind power, and even factory energy management systems. The opportunities for innovation are almost endless."

Toyota Motor Corporation

Beyond lithium: Toyota's foray into next-generation batteries

As the need to be eco-friendly is becoming increasingly important, Toyota Motor Corporation is working hard to develop next-generation batteries that will supersede lithium batteries. All-solid-state and metal–air batteries are two cutting-edge technologies that the car manufacturer is actively developing.

In 1997, Toyota Motor Corporation launched its first mass-produced hybrid vehicle, Prius. The model car dramatically changed the attitudes of car owners and helped make society more eco-conscious. As a leader in eco-friendly car technologies, the Japanese automaker is now striving to develop batteries for its vehicles that will have practically unlimited shelf-lives and that will far exceed drivers' expectations.

Lithium-ion batteries are in increasing demand for electric and hybrid cars because they are lightweight and fully rechargeable. But they are also relatively expensive and prone to thermal runaway when overheated.

Looking far ahead, Toyota is working hard to make groundbreaking batteries that are significantly smaller, lighter, safer and cheaper than lithium-ion batteries. The company is also working on developing recyclable batteries made from Earth-abundant materials, while pursuing its ultimate goal of making batteries that do not require recharging.

Two promising batteries are now under development: an all-solid-state battery and a metal–air battery. The all-solid-state battery uses a solid electrolyte rather than a liquid-based electrolyte, allowing for high-density packaging. And since it does not contain any volatile organic materials, it will be much less flammable. The solid electrolyte will also make batteries more compact and stable, and will enable higher power levels to be achieved for the same or lower battery weight.

Full charge ahead

Toyota started its research on the all-solid-state battery in 2006, when scientists at Japan's National Institute for Materials Science succeeded in reducing the resistance of an all-solid-state battery to one hundredth that of earlier solid-electrode batteries — a resistance close to that of conventional lithium-ion batteries with liquid electrolytes.

Convinced of the potential of this all-solid-state battery, Toyota established its Battery Research Division in 2008 to develop innovative batteries. The research centre at the foot of Mount Fuji, 225 kilometres from the hubbub of the company's headquarters, houses a team of about 50 experts, including battery engineers and researchers from academia, who are developing new materials with a view to creating an entirely new concept of batteries.

In 2010, Toyota opened a Battery Production Engineering Development Division on the same floor of the laboratory building and assigned some 50 staff members to work closely with the Battery Research Division to develop Toyota's dream batteries.

Toyota is a company synonymous with technical excellence, and its Battery Research Division has maintained a high reputation among industry experts, academics and the Japanese government. Top scientists and researchers at universities and other institutions across Japan eagerly collaborate with the team.

Solid electrolytes

In 2011, the team, together with external experts, including Ryoji Kanno at the Tokyo Institute of Technology, published a seminal paper in *Nature Materials* that described a battery with the new solid electrolyte $Li_{10}GeP_2S_{12}$ (LGPS). This electrolyte had a comparable or higher lithium-ion conductivity (a measure of the ease with which lithium ions flow) than other electrolytes, including liquid electrolytes used in commercial batteries.

"The discovery of LGPS changed the received wisdom that lithium ions cannot travel quickly in a solid-state electrolyte," explains Hideki Iba, general manager of Toyota's Battery Research Division.

The faster ions can travel in a solid electrolyte, the higher the power of a battery will be. Consequently, this was a landmark moment and resulted in all-solid-state batteries becoming the front-runner of next-generation rechargeable batteries. A coin-sized prototype is still in the development phase, but in 2014 this battery achieved a power output that was five times higher than an earlier version developed in 2012.

Now that the feasibility of the technology has been demonstrated, the next challenges are to improve its component materials, to extend its range and to reduce its cost. It will also be important to strike a balance between the capacity and power density of the battery and find more efficient and effective ways to manufacture the battery.

Fundamental research

In addition to working on specific projects like the all-solid-state battery, Toyota's Battery Research Division also conducts fundamental studies, such as the fabrication of thin-film batteries by vapour-phase synthesis (see image). In 2010, the team, together with researchers from the Japan Fine Ceramics Center, the University of Tokyo and Tohoku University, developed a high-resolution electron microscopy technique that can be used to visualize light elements in a material. This technique enabled lithium atoms in the crystal of a positive electrode material to be imaged for the first time — a vital breakthrough in the pursuit of better materials for batteries, as it can be used to reveal the mechanisms of ion conduction and battery deterioration.

> "Our ultimate goal is to make batteries that will power electric vehicles without the need to be recharged."

The team is also investigating sodium compounds, which are abundant in sea water. "People focus on their abundance, but we focus more on the larger variety and higher potentials of sodium compounds," says Iba. Over 8,000 sodium compounds are currently known, compared with about 5,000 lithium compounds. "If we can identify an appropriate sodium compound, we could create a battery whose performance far exceeds those of lithium-ion batteries."

In 2012, the team discovered new positive electrode materials suitable for high-voltage sodium-ion batteries, adding the sodium-ion battery to the list of potential next-generation batteries.

Dream battery

After the all-solid-state battery, the most promising battery that Toyota is now working on is a metal–air battery. It uses a metal such as lithium or zinc for the anode, and air drawn from the environment as the cathode. The use of oxygen as the cathode active material is very appealing as it is abundant, free and does not require a heavy casing to keep it within the battery cell. Theoretically, a metal–air battery for electric vehicles could be extremely lightweight and have a long-lasting regenerative cathode.

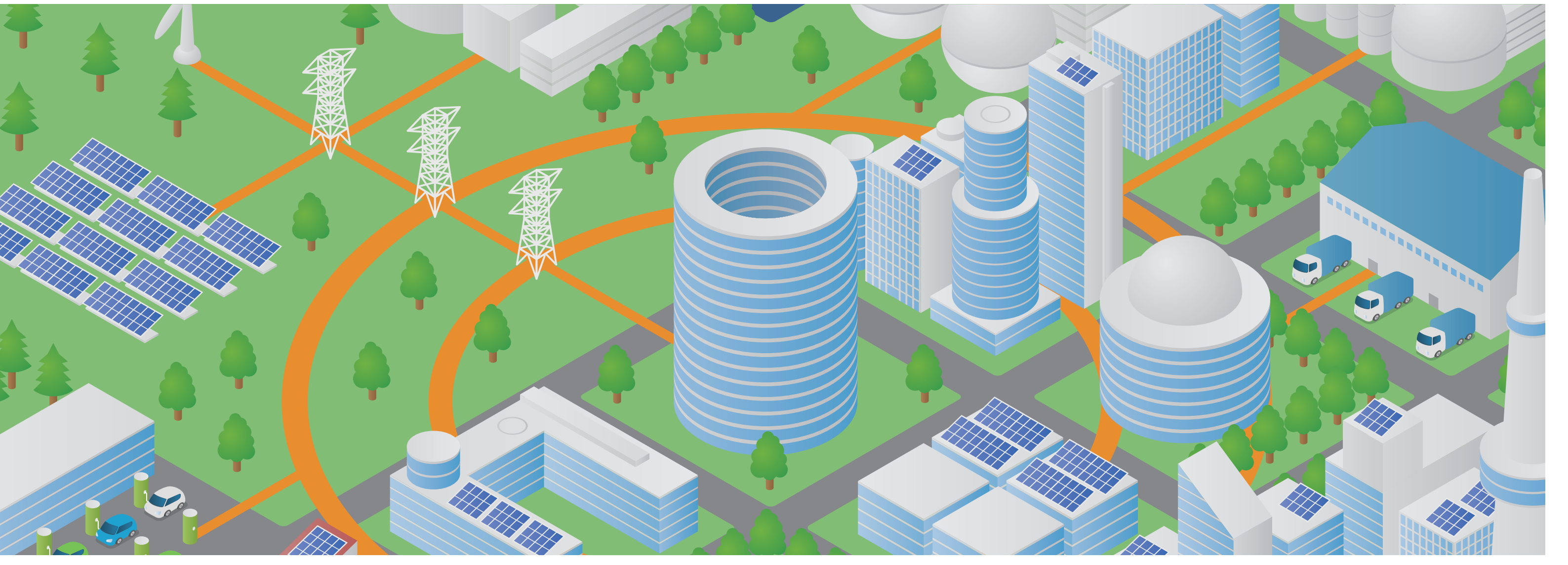
Currently, metal–air batteries such as zinc–air batteries are used only as primary batteries, since they cannot be recharged.

While the use of metal–air batteries as secondary batteries is still in the early stages of research, these batteries are expected to have energy densities per mass that are over five times greater than those of the latest lithium-ion batteries. "If we manage to put it to practical use, it will certainly be a dream battery," Iba notes.

Toyota is one step closer to achieving a revolutionary development in battery performance and thus the team has shifted its focus to studying the reaction mechanisms of metal–air batteries by analysing liquid electrolytes and their influences, especially during charging.

For Iba and his team, the ultimate goal is to create a battery that would require just a single charge to keep an electric vehicle on the road for its entire life.

"We are not simply seeking to develop batteries for electric vehicles that will replace conventional gasoline-powered cars. Our ultimate goal is to make batteries that will power electric vehicles without the need to be recharged," Iba concludes.



Toshiba Corporation Social Infrastructure Systems Company

A pioneer of mass-produced lithium-ion batteries based on lithium titanium oxide

A battery that combines lithium titanium oxide technology and state-of-the-art production techniques is Toshiba's solution to the growing demand for energy storage.

In 2007, Toshiba commercialized an attractive lithium-ion battery (LIB) using lithium titanium oxide (LTO) as the anode material under the brand name SCiB™. The technology has since been used to produce a range of batteries with excellent characteristics, including long life, quick charging, low-temperature operation and a high level of safety.

LTO has many benefits. Titanium oxide is an insulator, but transforms into a conductor when lithium ions are absorbed during the charging process. The LTO material maintains a low conductance even when a short circuit occurs, thus preventing the drastic flow of short-circuit current and rapid heat generation. Unlike carbon-based batteries, which exhibit changes in volume with repeated charging and discharging cycles, LTO batteries are characterized by low changes in volume. The minimal swelling contributes to their long lifetimes of more than 15,000 charge–discharge cycles.

In addition, the electrochemical potential of LTO compared to lithium metal is 1.55 volts, which means that lithium deposition on the anode surface can be prevented during low-temperature charging and rapid charging. This eliminates the risk of short circuits and improves safety.

SCiB™ combines the interesting properties of LTO with Toshiba's manufacturing technology. The lithium-ion battery technology has been incorporated into several products, from a 20-ampere-hour cell to a 2.9-ampere-hour cell, which have been used in a wide range of applications described below.

Japan's largest LIB energy storage system

Toshiba supplied a large-scale battery energy storage system (BESS) to Tohoku Electric Power Company's Nishi-Sendai Substation in February 2015. With a power rating of 40 megawatts and a storage capacity of 20 megawatt-hours, it is currently one of the world's largest lithium-ion BESSs. The system consists of an array of energy-type SCiB™ cells. These are used to improve frequency stabilization and balance electrical supply with demand. At the Nishi-Sendai Substation, frequency variations over a few minutes are stabilized through repeated charging and discharging of the battery. In addition, Toshiba is constructing another 40-megawatt-hour-class BESS for the Minami-soma Substation, which will commence operation in 2016.

An energy-saving solution for railway systems

When a train brakes, it generates energy that can be harnessed by nearby accelerating trains. In conventional systems, this regenerated energy is not efficiently utilized by the next train and is wasted as heat in the onboard or wayside resistors. Toshiba's Traction Energy Storage System has been installed at stations to efficiently store surplus regenerated energy from decelerating trains in SCiB™ batteries and then discharge it to accelerating trains, thus facilitating a stable supply of electricity. This system is installed with Toshiba's patented advance control system, which controls the charge–discharge in accordance with the state-of-charge of the battery.

Advanced recuperating Start & Stop vehicles

In 2012, Suzuki Motor Corporation, the leading seller of compact cars in Japan, launched its new generation of compact cars with an advanced Start & Stop system named ENE-CHARGE. The system consists of dual batteries connected in parallel — a conventional lead–acid battery and an additional battery — to absorb and recuperate the energy produced during braking. The additional battery consists of power-type 2.9-ampere-hour SCiB™ cells connected in series, which have high power during charging and discharging. The cell offers power densities as high as 6,000 watts per litre at 25 degrees Celsius, which surpasses other batteries in its ability to charge from the high output of the regenerative braking system. The dual-battery system can be used without a voltage transformer, reducing both the number of parts and the costs. These cars have been very popular in Japan, with more than 1.3 million units sold so far.

Toshiba has supplied Japan's Tohoku Electric Power Company with one of the world's largest lithium-ion battery energy storage systems.

Battery monitoring technology for long-term use of LIBs

Toshiba and Waseda University are developing the ultimate battery evaluation technology for estimating the performance degradation of LIBs installed in electric vehicles, plug-in hybrid vehicles and stationary BESSs. This technology allows the health of batteries in these products to be easily monitored, and it can be used to improve the long-term reliability of batteries. It is expected to accelerate the use of long-term batteries in electric vehicles, plug-in hybrid vehicles and stationary BESSs. The technology is also anticipated to create a market for used electric vehicles and plug-in hybrid vehicles and spawn the development of rental and reuse businesses for lithium-ion batteries.

Electric vehicles will soon be a common sight and many BESSs will be connected to the grid. By 2020, electric vehicles and plug-in hybrid vehicles are predicted to be powered by 60 gigawatt-hour batteries, while BESSs are expected to make a big contribution to society. However, deterioration during operation is unavoidable for chemically rechargeable batteries such as LIBs. If a battery that has been used for a long time cannot perform according to its rated capacity and input and output powers, it might not be socially beneficial. Therefore, monitoring capacity degradation via the input and output powers of the battery will be essential. Moreover, it is practically important that monitoring can be performed during operation, without the need to remove the battery.

Through these efforts and activities, Toshiba continues to create high-quality batteries for the sustainable development of society.

TOSHIBA

www.scib.jp/en

Waseda University and Saitama Prefecture

Saitama leading the way

Saitama Prefecture's innovative projects to improve its economy, environment and the health of its people could be expanded across Japan.

In Japan, solar power systems have been incorporated into approximately 3 per cent of households in an effort to generate energy from renewable sources. These systems generate electricity at home without polluting the environment. Excess electricity is sold to power companies to reduce electricity costs. Storage batteries can be installed to further utilize the electricity generated in this manner. They enable power demand and supply to be controlled highly efficiently since excess electricity generated by the home's solar power system can be stored and used later when needed. Furthermore, power can be stored for emergencies, making it important for disaster management.

A research partnership between Saitama Prefecture and Waseda University is leading the way in the development of next-generation storage battery systems for 'smart communities'.

Saitama Eco-Town project

In 2012, Saitama Prefecture launched the Saitama Eco-Town Project, a great example of a local initiative that could be expanded across Japan. The project promotes strict energy conservation along with the local production of energy for local consumption through renewable-energy-based power generation from existing city blocks.

Two years later, in 2014, Saitama launched the Leading-Edge Industry Design Project. It aims to create new and growing industries that can support the Eco-Town project. This project has been working on the research and development of a next-generation operative system for stationary storage batteries to support the Eco-Town. The research base is located at the Honjo campus of Waseda University.

One of the aims of the smart community is to produce electricity locally for local consumption. By transferring excess

Greetings from the governor

Governor of Saitama Prefecture, Kiyoshi Ueda.

Saitama Prefecture has a population of seven million people, similar to those of Serbia, Bulgaria and Paraguay. The prefecture generates more than 20 trillion yen a year — the fifth-highest gross production of municipalities in Japan. Most of the population of Saitama Prefecture is concentrated in its large cities, but it also has small to medium cities scattered in the suburbs and mountainous regions where the population is declining. The industries in Saitama are diverse, ranging from agriculture and engineering to services.

Saitama can be considered a small-scale representation of Japan since it is dealing with similar issues to those that face the rest of the country, such as an ageing population. Consequently, strategies shown to generated electricity into storage batteries, electricity is pooled for the region, and through effective use, the cost of electricity decreases for the entire region. To create a smart community from an existing city without large-scale redevelopment, it is necessary to combine the management of various storage batteries and power-generation facilities.

Until now, systems to manage smart communities have generally been introduced at the same time as construction, and, in many cases, the same manufacturer built both the storage batteries and the housing. While this helps reduce costs and ensures stable performance, it is difficult to apply this type of system to existing urban areas. In this project, we are developing a system that will be able to control the power supply to each household, even if the storage batteries and housing are built by different manufacturers. In the future, with the cooperation of municipalities and residents, we will tackle practical development. Given the large number of existing urban areas in Japan, highly versatile systems will be required.

A regional control system

As part of the Eco-Town initiative, Saitama Prefecture and Waseda University are working on developing a regional energy management system that incorporates technology that links and controls regional storage batteries. Concurrently, they are conducting a demonstration experiment in Honjo, with the goal of making it a working system. As part of this project, Mitsubishi Electric Corp. and Shin-Kobe Electric Machinery Co. Ltd (as well as Hitachi Chemical from January 2016) have been working with the Waseda Energy Management System Honjo Research Centre on the Honjo Campus (WERCH) at Waseda University (central base). This group has been conducting research with the aim of promoting Eco-Towns by designing a community energy management system that incorporates a highly reliable and safe power storage system.

Waseda University has focused on implementing technology that analyses the condition of storage batteries without destroying them. Since the condition of storage batteries can vary with the number of charges and usage style, it is important to understand the internal conditions of storage batteries in order to use them properly. However, this usually requires destroying the battery.

Tetsuya Osaka, who leads this project, hopes technology that can evaluate the condition of the storage batteries will permit the level of deterioration and exchange time to be determined for the expensive storage batteries used in regional infrastructure. This would improve the cost benefit of using storage batteries. This non-destructive examination technology will lead to a substantial increase in the capacity of storage batteries, which is somewhat limited because storage batteries prevent overcharging and excessive discharging. Although the range of the storage batteries depends on the manufacturer, operating batteries according to their current condition could allow their use to be optimized within a safe range.

Furthermore, a smart community that combines energy management based on the latest research with technology that extends the life of storage batteries will create businesses that use storage battery recycling technology. A stationary storage battery energy management system that creates Eco-Towns from existing regions will be launched in Saitama Prefecture.

Saitama Prefecture

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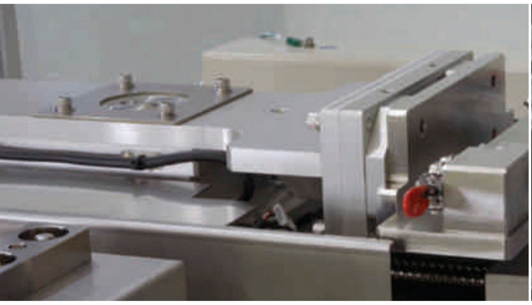
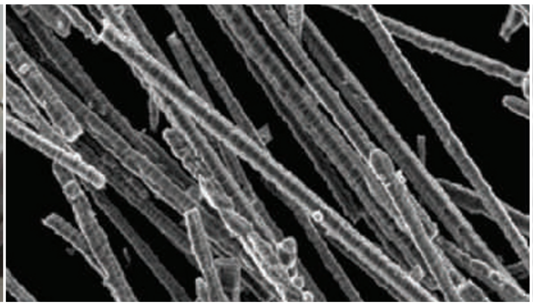
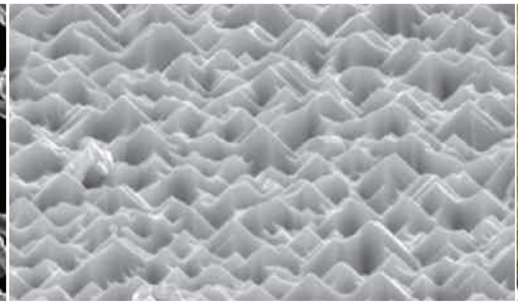
be successful in Saitama could point Japan in the right direction as well.

In the wake of the great Tohoku earthquake and Fukushima nuclear accident, Japan is reconsidering its energy policies. Saitama Prefecture is developing its own solution, called the Saitama Eco-Town Project. It is based on a local sustainability model and seeks to generate solar power locally as well as lower the overall energy consumption. Rather than develop new towns, the project aims to transform pre-existing residential areas — a highly adaptable approach that is expected to be applicable anywhere.

Saitama Prefecture's Leading-Edge Industry Design Project, which commenced in 2014, aims to create new growth industries by strongly supporting the development of services and products that combine leading-edge technologies used by companies and research conducted at universities and other research institutions. This cooperative endeavour is centred at the Honjo campus of Waseda University, which is located in Saitama. The project seeks to develop next-generation stationary battery systems for eco-towns, with the aim of creating smart communities that use new battery-based energy storage systems. By determining how different manufacturers' batteries operate, the project seeks to develop a new system for managing energy in all homes in the region. This system will be well suited for constructing smart grids in pre-existing localities, and will thus advance the Saitama Prefecture Eco-Town Project. Furthermore, the transformation into a battery-based eco-town will invigorate the storage battery industry, leading to the promotion of related local industries. This new energy management system, which has the potential to advance the development of both local eco-towns and industry, could ultimately benefit the whole of Japan.







Shinshu University

Crystalline battery materials

Shinshu University has emerged as a world leader in crystal growth research, with an emphasis on solution-based single-crystal growth for cutting-edge battery design.

Katsuya Teshima, Nobuyuki Zettsu and co-workers at Shinshu University in Japan's Nagano Prefecture have been refining the growth of single-crystal battery materials for over 8 years now. They use an approach called the flux method, which is based on the flow of source materials to the growing crystals. The main challenge of this method is selecting suitable fluxes to achieve shape-controlled crystal growth. Teshima, Zettsu and the Shinshu University team have published a series of reports detailing how to select fluxes so that high-quality crystalline battery materials, and hence optimal device performance, may be achieved.

Some highlights of their work include:

- **Growth of shape-controlled single-crystal battery materials from molten fluxes**
  The team used a strategic flux growth method involving one-dimensional cobalt oxide whiskers as starting templates and a high-temperature lithium-chloride–potassium-chloride solution to produce hexagonal cylindrical lithium cobalt oxide crystals via the lithiation reaction. Subsequent measurements confirmed that the lithium cobalt oxide crystals exhibited an excellent rate performance with more than 65 per cent capacity maintained under a current density of approximately 370 coulombs.

- **Direct growth of highly oriented polycrystalline films from current collectors**
  The group demonstrated the growth of a polycrystalline film directly from a current collector through flux coating. The dense crystal layer with a thickness of 30 micrometres exhibited a capacity close to the theoretical value under a current density of approximately 0.2 coulombs without any additives. This material is promising as a component of additive-free electrodes, regarded as a way to achieve enhanced energy density per volume. Replacement of all additives with active materials increases the energy density to about two times that of conventional composite electrodes.

- **A new route to the fabrication of composite electrodes for all-solid-state lithium-ion batteries through the growth of single crystals of the active material from molten lithium-ion conducting glass (glass flux)**
  Crystallization from homogeneous molten glass resulted in the formation of atomic-scale single crystals of the active material coated with a glassy layer of lithium-ion conductive material. This reduced the interfacial resistance in the lithium-ion conduction. A composite electrode composed of barrel-shaped lithium cobalt oxide crystals with carbon-doped lithium borate glass, formed using this method, demonstrated excellent conductivity for both lithium ions and electrons.

Perhaps most exciting is the team's recent work on the concept of all-crystal-state lithium-ion secondary batteries as an important advancement of all-solid-state batteries. A slit-nozzle coater and heating devices manufactured by Toray Engineering were used to directly and sequentially grow lithium titanate crystal layers on a ceramic separator below 700 degrees Celsius through liquid-phase crystal growth methods. Orienting the crystals in a direction suitable for lithium-ion transfer at the interface could lead to superionic, conducting all-solid-state batteries, which will enable the theoretical energy density to be attained.

The team looks forward to continuing this promising line of research and passing on their knowledge to the next generation of researchers.

SHINSHU UNIVERSITY

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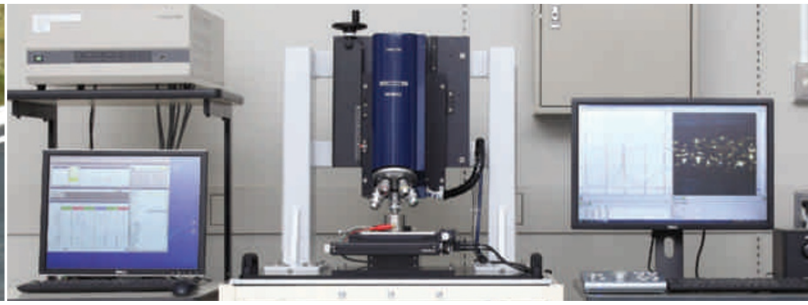


Hitachi Maxell

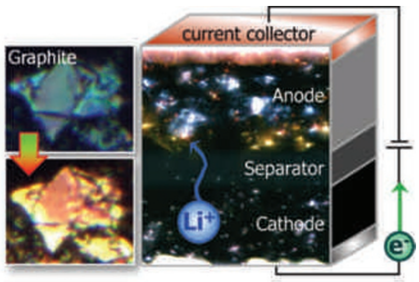
Uncovering the true colours of lithium-ion batteries

Maxell and Lasertec Corporation visualize the electrochemical reactions in a lithium-ion battery electrode during charging and discharging.

Maxell was founded in the early 1960s as a manufacturer of magnetic tapes and dry batteries. The company produced the first alkaline dry battery made in Japan in 1963. Its commitment over the past half century to the Japanese approach to integrated manufacturing known as *monozukuri* has led to the creation of new technologies and products in the areas of energy, industrial materials and electronic appliances.

Lithium-ion batteries contain many different materials. Their performance depends on the complex interactions between these materials, sometimes with surprising results. For example, enhancing the performance of a lithium-ion battery by replacing its cathode with a more effective one, initially results in a higher power output, but this improved performance is short-lived. Maxell partnered with Lasertec Corporation, a company with a unique real-colour confocal optics technology, to investigate such phenomena occurring inside a battery during charging and discharging.

The anode of a lithium-ion battery is typically made from graphite. During charging and discharging, the colour of a graphite anode changes dramatically: it is dark grey when the battery is fully discharged, but as the battery charges, it turns blue and then red, finally becoming yellow when the battery is fully charged (see image, left).



Researchers at Maxell took a closer look at these dynamic changes in colour during charging and discharging using a Lasertec confocal system specially designed to visualize electrochemical reactions in electrode cross-sections. This unique system allows the visualized reaction distributions to be compared with the battery's charge–discharge curves. It can also measure the expansion and contraction of component materials and be used to observe and measure the problematic formation of thin conductive fibres known as dendrites in real time.

This system permitted the researchers to investigate the stages of lithium-ion reactions inside batteries with high-performance cathodes while they were charging. The researchers observed that the anode surface turned yellow, whereas deeper locations remained grey and blue (see image, right). This indicated that there were plenty of lithium ions on the surface, allowing graphite to charge, but insufficient lithium ions in deeper areas. In other words, a lithium-ion 'jam' occurs on the anode surface, preventing lithium ions from flowing smoothly to deeper regions inside the anode. As the battery continues to be charged, the graphite on the surface becomes fully charged, but the lithium ions in the jam have nowhere to go and are eventually deposited as lithium dendrites.

The researchers believe that understanding and solving lithium-ion jams is essential to avoiding the deposition of lithium dendrites and the associated degradation in battery performance.

The study further demonstrates that using just one component material of the highest grade does not always improve the overall battery performance. What is most crucial for lithium-ion battery performance and safety is the interaction between all the component materials and the smooth flow of lithium ions inside the battery.

Maxell's innovative lithium-ion batteries will soon be used to power next-generation devices.

Shimadzu Corporation

R&D solutions for the next generation of batteries

Shimadzu's state-of-the-art analytical and measuring instruments are helping manufacturers improve fuel cells and lithium-ion batteries.

Japanese manufacturers lead the world in developing fuel cells and lithium-ion batteries, but several technical challenges still need to be overcome to enhance their performance and extend their application range while simultaneously ensuring their safety. Shimadzu assists in the research and development of these batteries by offering cutting-edge imaging and measuring instruments, which enable their internal structures to be analysed at high resolution.

Real-time imaging of oxygen consumption in fuel cells

As one of the most eagerly awaited, eco-friendly energy sources, fuel cell technologies have advanced greatly over the past few years to the extent that they are already used in various applications, including vehicles. Fuel cells use the reverse reaction of electrolysis of water to generate hydrogen ions at the cathode. These ions then travel through the electrolyte to the anode, where they react with oxygen to generate electricity, producing water as a by-product.

However, the commercialization of fuel cells is hindered by their high cost. "One of the most important tasks is to understand the consumption of oxygen — the energy source of fuel cells — with a view to increasing it in order to achieve higher efficiencies," says Takashi Ohno, manager of the Component Development Group, Sensor Device Business Unit, Device Department.

Shimadzu's FO-O2 Monitor creates high-quality, two-dimensional images that enable the oxygen distribution to be visualized in real time. "It is very important for researchers to be able to ascertain whether the electrochemical reaction is uniform in fuel cells," Ohno says.

In this monitor, a newly developed reagent is excited by light from light-emitting diodes, which causes it to fluoresce at a particular wavelength. The fluorescence intensity decreases with increasing oxygen concentration. This fluorescence is detected by a high-sensitivity charge-coupled device (CCD) camera, which has a maximum frame rate of 30 frames per second, allowing researchers to observe how oxygen consumption varies with time. The monitor can image polymer electrolyte fuel cells, the most common fuel cell systems, which are used in automobiles and home power generators.

This monitor will assist researchers in improving power-generation simulations during research and development. Its fast response is also suitable for developing accelerators that can rapidly turn on and off in automobile fuel cells.

Since its release in 2009, the monitor has remained as the only instrument capable of visualizing the oxygen distribution in fuel cells in real time. Ohno and his colleagues are now developing a more advanced version that can measure depth and thereby create three-dimensional images. "Our users want depth data as an additional function," Ohno says.

Looking inside lithium-ion batteries

Since their launch in 1991, lithium-ion batteries have quickly replaced nickel–cadmium batteries for use in portable high-tech devices, thanks to their light weight and high capacities. Lithium-ion batteries are used to power devices ranging from mobile phones to laptop computers and electric cars. During charging and discharging, lithium ions travel back and forth through the electrolyte between the lithium metal oxide cathode and the graphite anode.

But lithium requires careful handling since it can ignite if it comes into contact with air. "This means that we cannot easily open lithium-ion batteries," says Masahito Natsuhara, general manager of the Non-Destructive Inspection Business Unit, Analytical & Measuring Instruments Division. "Consequently, lithium-ion batteries need non-destructive imaging instruments similar to X-ray computed tomography scanners used at hospitals."

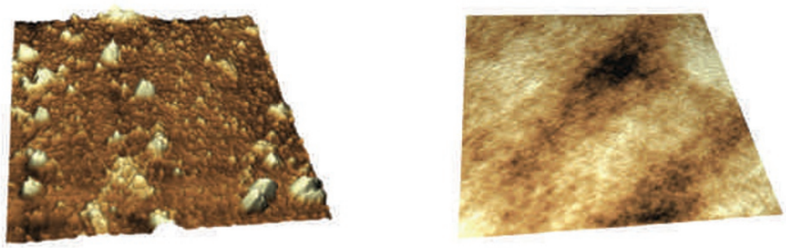
Shimadzu has developed several industrial X-ray computed tomography systems of which the highest-end model, the inspeXio SMX-225CT, is the most suitable for researching lithium-ion batteries. It provides a high performance with computational processing that is 80–170 times faster than conventional models, while creating sharp, high-contrast images with reduced artefacts.

As one example of its application, inspeXio SMX-225CT can be used to detect internal distortion in world-standard 18650 lithium-ion cells, a defect often caused by swelling produced by gas generated as a result of mixing various chemicals.

The inspeXio SMX-225CT can also be used to image larger lithium-ion batteries, such as those used in hybrid or electric cars. For example, researchers can image how the internal structure of a battery changes as it is repeatedly charged and discharged. It can also be used to image during heat-load tests. "Researchers can test how gas generated in the electrolyte deteriorates the battery when it is stored at 60 degrees Celsius for two weeks without anti-swelling agents," says Natsuhara. "They can then test whether the gas is harmful to human health using our gas chromatography systems."

In electrolyte

In nitrogen gas



Scanning probe microscopy images of the surface morphology of lithium-ion battery binders when placed in an electrolyte (left) and in nitrogen gas (right).

Natsuhara and colleagues are now developing an advanced model that can perform temporal observations, allowing researchers to observe structural changes in real time during recharging. "No such system has ever been developed previously," he says.

Observing key components with a nanotip

With a cantilever 1,000 times narrower than a human hair, scanning probe microscopes (SPMs) are typically used to image the surfaces of solid nanotech samples, such as semiconductors and polymers, in a wide range of environments including air, other gases and liquids. Shimadzu has now developed an SPM microscope (SPM-9700) for observing the key components of lithium-ion batteries, including separators and binders, whose conditions determine the cell's performance. "These components often look different when they are taken out of liquid electrolytes," says Ryohei Kokawa, a manager at the Global Application Development Center, Analytical & Measuring Instruments Division. "We are developing SPMs that can measure components within a cell."

A separator is made from a nanoporous polyolefin film, which effectively separates the anode and cathode. As lithium is prone to heating and ignition, the quality of the separator is critical to preventing short circuits. Shimadzu researchers and collaborators have observed how the fibres in a separator swell and how the pores close, preventing ion transfer, as the temperature is raised from room temperature to 140 degrees Celsius.

Another important research area is binders, which firmly hold the active materials in both electrodes. Battery researchers are investigating silicon as a next-generation anode material. They claim silicon has a larger capacity than graphite. But silicon is unstable and could lead to breakage and shorter life spans.

"The role of the binder is important," says Kokawa. "We need to understand how it behaves." In one experiment, Kokawa and his colleagues observed three polyacrylic binders both in and outside a liquid electrolyte. "One sample looked flat while another sample appeared rough with a protuberance in gas; but the opposite was true when the samples were placed in an electrolyte," Kokawa explains (see image).

As the next step, Kokawa is looking to use Shimadzu's high-end microscope, the SPM-8000FM, to observe thin liquid layers on solid surfaces in the electrolyte. "The electrode surfaces are in contact with the liquid electrolyte and give rise to both positive and negative reactions," he says. "Only Shimadzu instruments can image the liquid structure."

Waseda University — Battery research supported by NEDO

Integrated battery research at Waseda University

While active electrode materials have attracted much attention, it is also critical to consider battery designs that are safe and compatible with manufacturing processes — two aspects that researchers at Waseda University have been concentrating their efforts on.

When designing new batteries it is vital to consider combining separators and electrolytes with other components, optimizing electrode structure and cell modularization, and developing systems for assessing battery health. The battery research group at Waseda University headed by Tetsuya Osaka explores new electrode materials, designs battery cells that rival commercial ones, and develops nondestructive evaluation technology. Toshiyuki Momma, Tokihiko Yokoshima, Daikichi Mukoyama, and Hiroki Nara contribute to this group as key members. The group adopts an integrated strategy to their research. "To commercialize innovative products, battery research requires a more integrated research approach," says Osaka. This has enabled the group to secure competitive funding from various sources, including the Research and Development Initiative for Scientific Innovation of New Generation Batteries as well as Development of Large-scale Energy Storage System with High Safety and Cost Competitiveness — both projects under the umbrella of the New Energy and Industrial Technology Development Organization (NEDO).

Nanoelectrochemistry and its implications for battery research

Battery technology is founded on electrochemistry. The electrochemical properties that govern battery performance are controllable by the interface. To date, most research into the electrochemical reactions in batteries has focused on two-dimensional interfaces between a solid electrode and a liquid electrolyte. But it is becoming increasingly important to consider nanoelectrochemistry, which deals with three-dimensional structured interfaces and functional interfaces. When trying to optimize the interface to realize higher-efficiency electrochemical devices, in addition to considering the movement of the substances involved, it is essential to slightly expand the reaction field to a region with a certain thickness. Furthermore, to realize future devices, it is vital to consider systems in which the solid and ion-conduction phases are entwined as well as three-phase reaction fields.

One example of the success of the Waseda group's approach is its development of a Si–O–C composite anode for lithium-ion batteries (LIBs). This anode is prepared by electrodeposition and consists of amorphous SiO_x and decomposed product from an organic solution, both of which are dispersed on the nanoscale. This results in a three-dimensional structured material, which imparts the anode with an outstanding cycle durability — a discharge capacity of about 800 milliampere hours per gram of silicon after 7,000 cycles.

Analysing batteries

LIBs are widely used in everyday life, but their energy density, durability and safety still need to be enhanced. Electrochemical impedance spectroscopy (EIS) is essential for achieving this, as reflected by its listing as one of the national critical technologies of Japan. EIS provides insights that can be used to improve LIBs and their operation because it is applicable from the development stage to the practical application stage. In particular, it can ascertain the rate-determining step for battery operation, which is important for guiding LIB development. EIS analysis evaluates the rate-determining step of a complex LIB process by separating it into elemental steps, namely electron migration, ion migration and charge transfer for the chemical reactions at the anode and cathode. It is thus possible to estimate which elemental steps will become rate-determining during operation, which will clarify understanding of LIB degradation.

The team at Waseda University has designed equivalent circuits for EIS analysis of commercial LIBs with the aim of developing a method for monitoring LIB deterioration during actual use. Equivalent circuits consist of inductances relating to the current collector, wires and instruments and resistances relating to charge transfer, ionic diffusion, solid electrolyte interphase and particle size distribution. The equivalent circuit enables the impedance response to be analysed over a wide frequency range of 10 kilohertz to 1 millihertz. For example, EIS analysis using an equivalent circuit revealed the characteristics of power and capacity from the component variation of resistance and capacitance of a LIB after charge–discharge cycles. Furthermore, it shows the resistance variation of the electrolyte, solid electrolyte interphase, and diffusion with increasing number of charge–discharge cycles. EIS is also promising for LIB diagnosis.

Storage battery systems

Storage battery systems are effective for dealing with the levelling effects of the high peak powers generated by solar and wind power as well as other forms of renewable energy. A team at Waseda University is developing storage battery systems for stabilizing power grid applications with the aim of achieving significant cost savings, long service life and high stability.

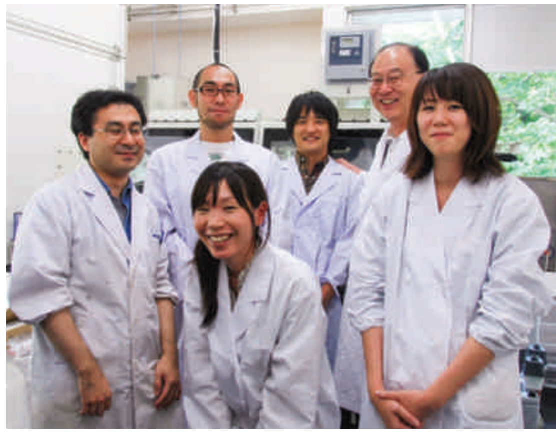
The team is also developing core technologies for diagnosing the degradation of battery systems used for stabilizing power grid setups. In addition to offering long-term stability and affordability, a large-scale storage battery system should be able to use both new and used batteries and permit long-term operation. Furthermore, it should have parts that can be replaced should a malfunction occur. The key to maintaining large-scale storage battery systems is the ability to diagnose when and where degradation is occurring.

The impedance of a storage battery system is measured by monitoring the electric signal response of the battery. By using a simple electrical signal for measurement, the impedance of large and other format batteries can be measured conveniently and inexpensively without the use of specialized equipment. The alternating-current impedance method allows the battery state and degree of degradation to be analysed, making it useful in contexts where storage batteries in power grid systems need to have stability and long service lives. The conventional method for measuring impedance response is extremely costly to add to battery systems after they have been installed.

The team determined that a simple and low-cost battery check system could be constructed if the power controllers installed in battery management systems could yield an impedance response with an easily controllable waveform. The researchers have developed a system that varies by less than 1 per cent from measurements by conventional high-precision impedance measurement systems. They are now developing a prototype that can be deployed in commercial storage battery systems.

Battery analysis facilities at Waseda

Internal battery analysis through a.c. impedance measurements, largely based on model batteries, has revealed the need



for examinations involving repeated trial-and-error of various LIB measurements that account for the form, manufacturing processes and environmental temperature of a model battery. For example, if the indicated performance range of a particular commercial LIB is improved, yet it is still sold under the same specifications, its impedance response will change greatly over several years. Consequently, equipment capable of stable manufacturing of LIBs in the laboratory is needed to interpret impedance response data and to obtain fundamental knowledge for proposing design criteria for next-generation electrode materials and structures that support long-lasting, fast-charging electrical discharges.

Since the materials in LIBs are greatly affected by their environment, Waseda University has installed a world-class dry room, which generates a low-humidity environment and permits semi-automatic manufacture of coin, laminated, and cylindrical cells. Waseda University is the only education and research-focused university in the world possessing a battery plant of this scale.