

Executive Summary

1

R&D Trends for High-Energy Automobile Capacitors to Hasten CO₂ Reductions

p. 7

Society is demanding storage systems that maintain higher and higher power output and energy capacity as policies encourage cuts in CO₂ emissions and greater energy conservation. Energy storage systems are rechargeable batteries such as lithium-ion batteries (LIBs) that undergo an electrochemical reaction when they store and release electrical energy, and capacitors that primarily obtain electrical energy from physical absorption and desorption of ions. Capacitors have mainly been electric double layer capacitors (EDLCs).

Capacitors are still not used much as primary power supplies for plug-in hybrid vehicles, electric vehicles and the like, which are the most demanding environments in which they are used. While capacitors enjoy advantages over rechargeable batteries such as high power density and rapid charging/discharging that allow them to respond well to load fluctuations, their long shelf-life allowing many charge/discharge cycles, good safety and high reliability, but their disadvantage of having lower energy density compared to rechargeable batteries is a major weak point. Accordingly, most research and development on capacitors is attempting to imbue them with high energy capacity. The approaches involved can be broadly categorized as giving electrode materials high capacitance and making cells with high operating voltage. The candidate receiving the most attention for the time being is a lithium-ion capacitor (LIC) with a cell structure: a hybrid capacitor employing a set of electrodes including an LIB as the anode. LICs have the same power density and charge/discharge cycle shelf-life as conventional EDLCs, along with having small self-discharge, being very safe and having excellent performance under high temperatures.

Furthermore, a fast way to raise capacitor energy density to the level of rechargeable batteries would be R&D to discover charge storage mechanisms by, for example, analyzing the structure of cells' constituent materials as well as electrochemical analysis and assessments based on compositional analysis. If a capacitor could be created with the same energy density or more as an LIB while maintaining the advantages of a regular capacitor, then it could be applied to primary power supplies or regenerative braking in automobiles, with the possibility of further applications in a wide range of storage systems for various other types of industrial machinery. We could expect the result to be a drastic reduction in CO₂ emissions.

(Original Japanese version: published in July/August 2012)

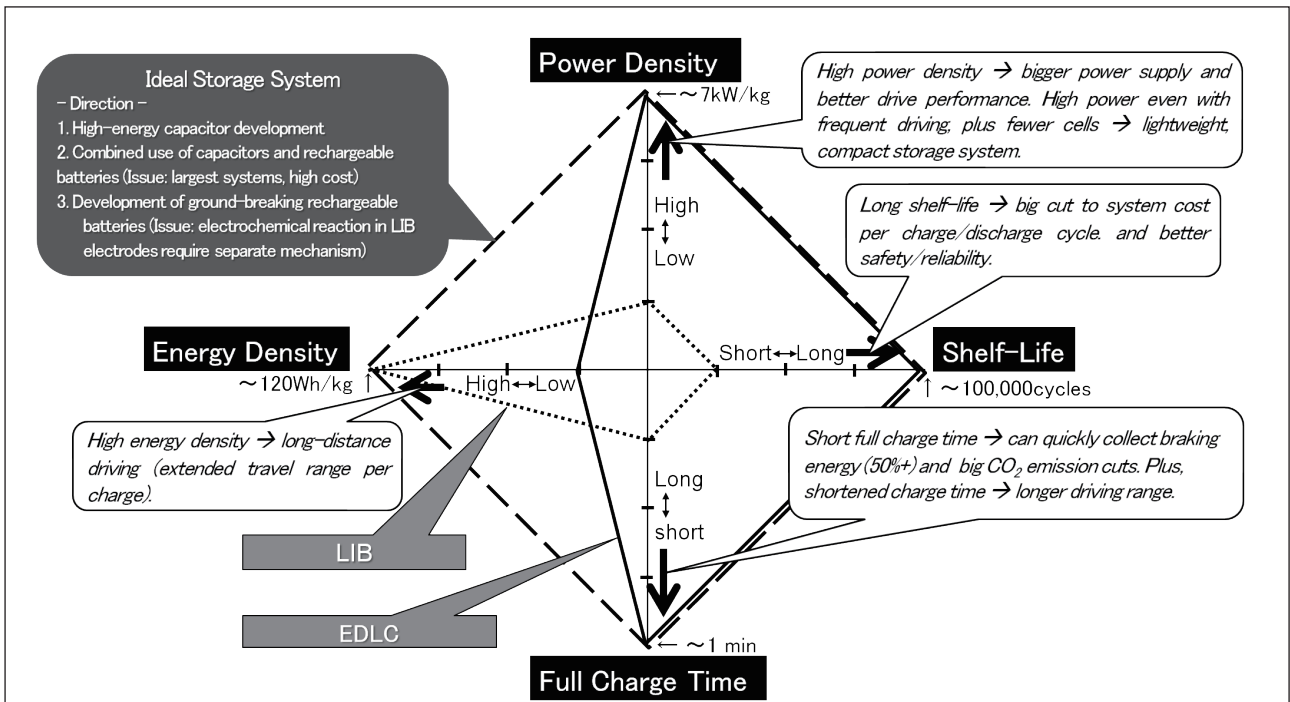


Figure : Comparison of EDLC and LIB Storage Performance--Direction of Ideal Automobile Storage System

Compiled by the Science and Technology Foresight Center

R&D Trends for High-Energy Automobile Capacitors to Hasten CO₂ Reductions

Hiroshi KAWAMOTO
Visiting Fellow

1 Introduction

Capacitors have become a subject of interest in research and development to build storage systems allowing, for example, exhaust energy recovery and the absorption of small to medium amounts of wasted electricity. These would make automobiles, industrial machinery, renewable energy systems and the like utilize energy more effectively. Japanese industry has proudly created technologies with small environmental impacts, some of which include capacitors, rechargeable batteries and other storage system technologies. These have secured a high degree of potential in global markets. In particular, energy-saving capacitors have become common backup power supplies in electronic devices and other products, and these storage systems are now becoming more widely adopted in devices to reduce CO₂ emissions and conserve energy. Furthermore, our society is demanding that storage systems have higher and higher output and energy capacity.^[1,2]

The automotive sector provides cases of adopting capacitors as backup power supplies in automobile equipment. The industry is examining techniques such as recovering the kinetic energy wasted during braking to provide auxiliary power for the engine.^[3] However, we cannot say that we have yet seen the full-scale introduction of capacitor storage system technologies.

Compared to rechargeable batteries such as nickel-hydrogen batteries or a lithium ion batteries (LIBs) employing electrochemical redox reactions, capacitors have high power density. Their short recharge times and ability to instantly discharge give them advantages that include high responsiveness to load fluctuation, a long shelf-life allowing many charge/discharge cycles, as well as good safety and reliability. On the other hand, a capacitor's disadvantage is that it has a lower energy density compared to a rechargeable battery. If a compact, low-cost capacitor could be

created with the same energy density or more as an LIB while maintaining the advantages of a regular capacitor, then it could be applied to primary power supplies or regenerative braking in automobiles, with the possibility of further applications in a wide range of storage systems for various other types of industrial machinery. We could expect the result to be a drastic reduction in CO₂ emissions.

This paper addresses the current state of R&D on and the need for high-energy capacitors in automobiles, as well as the direction the materials technology field is heading in to create these capacitors.

2 Strategies for Using High-Energy Capacitors

2-1 Reducing CO₂ Emissions by Popularizing Automobiles Running on Capacitors

Backed by green government policies, the use of hybrid vehicles (HVs), plug-in hybrid vehicles (PHVs) and electric vehicles (EVs) is rapidly expanding. Improving the performance of installed storage systems will be the key to a further policy push encouraging the spread of these technologies. LIBs are currently the most common rechargeable batteries installed in automobiles. Meanwhile, the ability of capacitors to quickly recharge is used for recovering energy, stop-and-go driving and auxiliary power supplies that instantly provide the high output required by automobiles, among other functions. In general, the term "capacitor" often refers to an electric double layer capacitor (EDLC).

Employing storage systems with high output and energy as primary and auxiliary power sources for automobile engines could significantly reduce CO₂ emissions. The rapid popularization of HVs and other such vehicles in Japan has contributed to a declining trend in CO₂ emissions volume, while further incentives to use HVs, PHVs, EVs and the like could

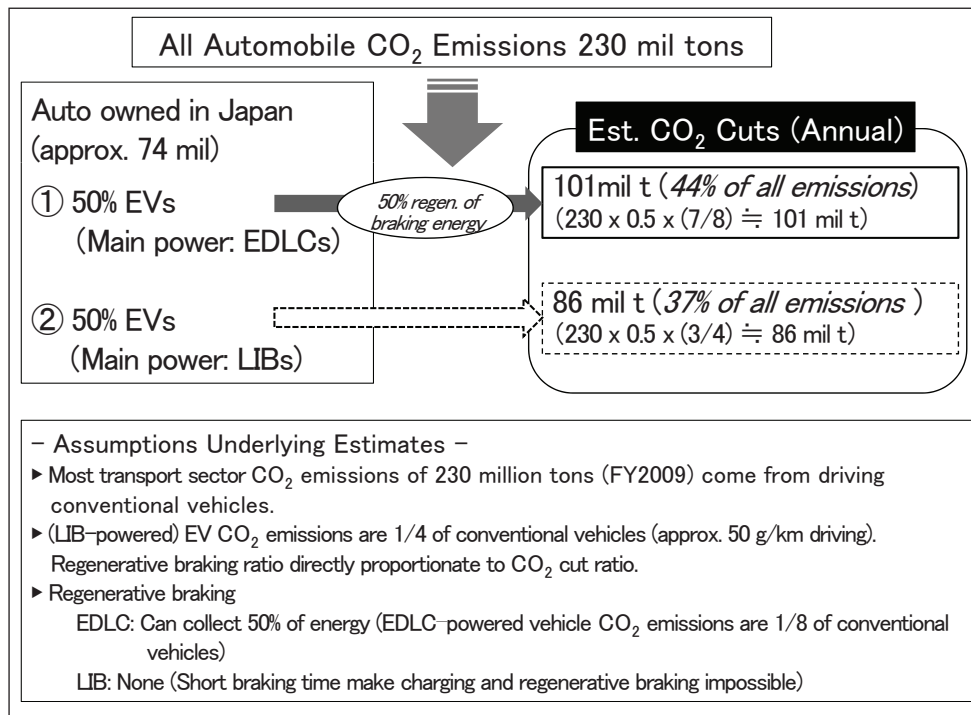


Figure 1 : Estimated CO₂ Cuts Resulting from Greater Use of EDLC-Powered Automobiles
Compiled by the Science and Technology Foresight Center

lead to much larger cuts. “Building a Low Carbon Society,” an action plan formulated by the Ministry of Environment, and “Next-Generation Vehicle Strategy 2010,” a report published by the Ministry of Economy, Trade and Industry (METI), set an ambitious target for vehicles equipped with rechargeable batteries such as HVs, PHVs and EVs to account for 50% to 70% of all new vehicle sales in Japan by 2030.^[4, 5]

Figure 1 shows a simplified estimate of the CO₂ reductions resulting from the popularization of vehicles running on EDLCs. The spread of vehicles such as EVs, which emit roughly a quarter the CO₂ emissions of conventional vehicles running on fossil fuels (around 50 g/km), would produce a drastic cut in total CO₂ emissions by automobiles. If 50% of all automobiles on the road in Japan (a fleet of approximately 74 million vehicles in FY 2009)^[6] were EVs and we assume that almost all CO₂ emissions are produced by the transportation sector (230 million tons in FY 2009), then this would cut total CO₂ emissions by about 37% (about 86 million tons).^[8] If we then suppose that the EVs primarily run on EDLCs capable of recovering braking energy, which accounts for roughly 50% of a vehicle's kinetic energy, then total CO₂ emissions would drop by around 44% (around 101 million tons). Even if 50% of all vehicles were HVs (with a conventional engine and an EDLC-powered engine) with EDLCs as their auxiliary power supply, collecting and reusing around 50% of a vehicle's kinetic energy

could still reduce total CO₂ emissions by about 25% (58 million tons). This is how estimates show that adopting EDLCs as primary or auxiliary drives for automobiles could result in a vast drop in total CO₂ emissions.

Recovering braking energy, or regenerative braking, is a process in which the main motor's function is converted to that of a power generator, converting kinetic energy (with the exclusion of mechanical/electrical loss, etc.) produced by energy conversion into electrical energy to be stored for later use. It has been postulated that, in theory, it is possible to recover 50% or more of a vehicle's kinetic energy as braking energy.^[9, 10] For the time being, a good strategy would be to make large cuts in automobile CO₂ emissions by using the advantageous traits of EDLCs and applying them to energy recovery systems for use as auxiliary drives, to be followed in the future with more powerful EDLC storage that can be used for the instantaneous high output that is impractical with today's LIBs and that can undergo numerous and frequent charge/discharge cycles.

2-2 Options for Capacitors to Run Automobiles

Figure 2 shows a comparison of EDLC and LIB storage performance^[3, 11, 12] and the steps to create an ideal storage system for automobiles. This figure simplifies the advantages of EDLCs and LIBs on a 0-100 scale. For example, this scale is applied to EDLC power density and LIB energy density

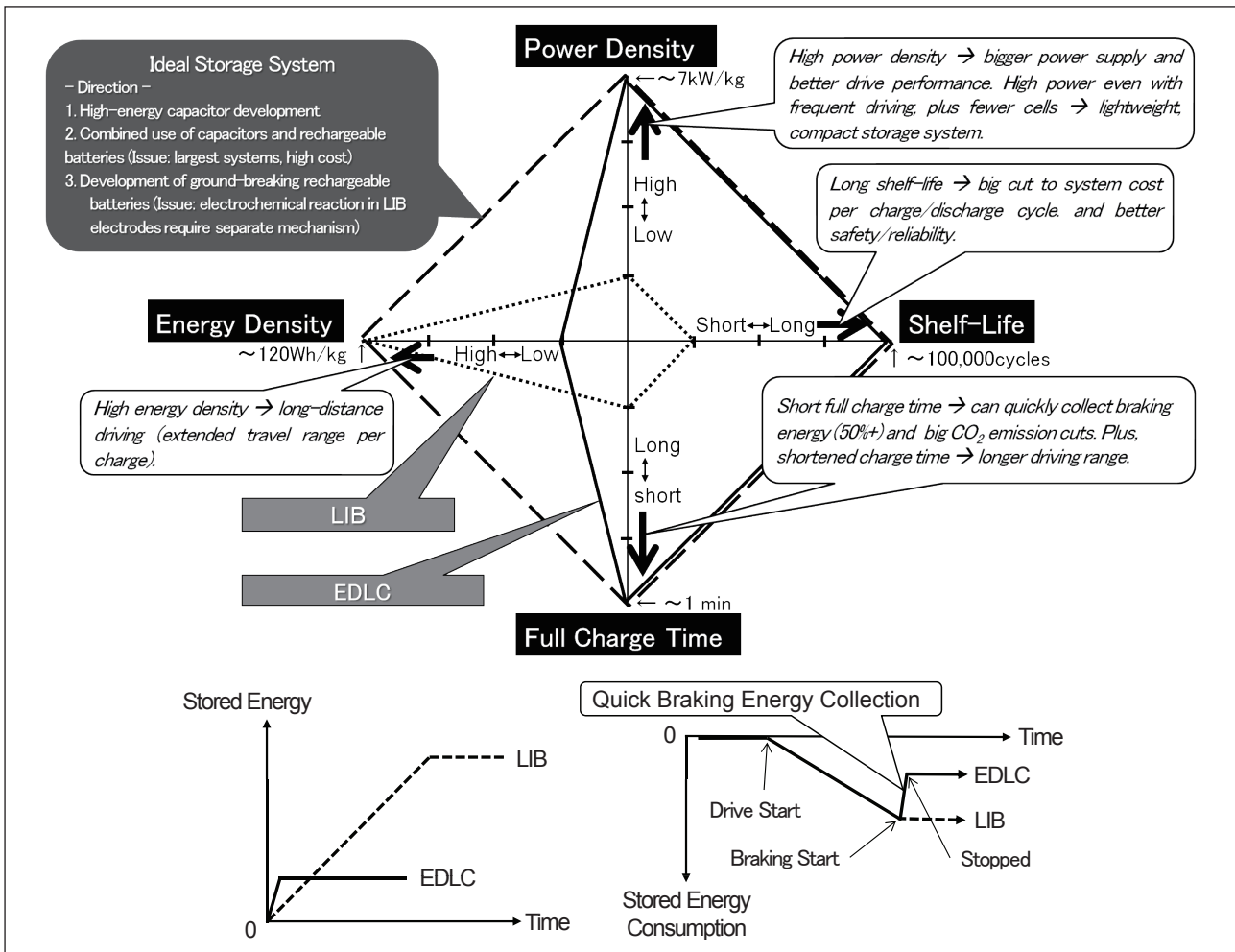


Figure 2 : Comparison of EDLC and LIB Storage Performance--Direction of Ideal Automobile Storage System

Compiled by the Science and Technology Foresight Center

along the horizontal axis. Each attribute's storage performance is assessed at four points along each line. Compared to LIBs, which are superior rechargeable batteries, EDLCs have much higher power density, shorter charge times and longer charge/discharge shelf-life. EDLCs also have advantages that LIBs do not: high energy efficiency (discharge/charge efficiency of 90% or better) due to low heat of reaction on the cathodes, among other reasons; they are very safe and have a low environmental impact because they do not use heavy metals, halides and the like as constituent materials. Supplying resources for constituent materials becomes a worry when carbon materials are used in electrodes. However, EDLCs suffer a serious disadvantage compared to LIBs due to their low energy density, so a major R&D issue is to improve this attribute.

While EDLCs have the perfect power density and charge/discharge cycle shelf-life as main power sources for HVs, PHVs, EVs and so on, their energy density is low compared to rechargeable batteries such as LIBs, meaning that the EDLC would have to be recharged

frequently during a long trip. Capacitors' high power density is already used in, for example, automobile idle reduction systems. These capacitors provide the high current needed to frequently switch the engine on and off.^[3, 13] Accordingly, the use of capacitors in HVs, PHVs and EVs that run on rechargeable batteries could lead to smaller rechargeable batteries that move the vehicle and allow the vehicle to very efficiently and instantaneously recover power from the energy wasted during braking. Converting this recovered energy into electrical energy, which is instantly stored in a capacitor for later use in moving the vehicle, could further reduce CO₂ emissions. To expand the use of capacitors as auxiliary power sources, for the time being we should first promote applications that utilize capacitors' high power by using them in conjunction with rechargeable batteries. Then, further on in the future, if the energy density of capacitors reaches or exceeds that of LIBs, these high-energy capacitors could potentially perform as primary power sources for automobiles and replace LIBs.

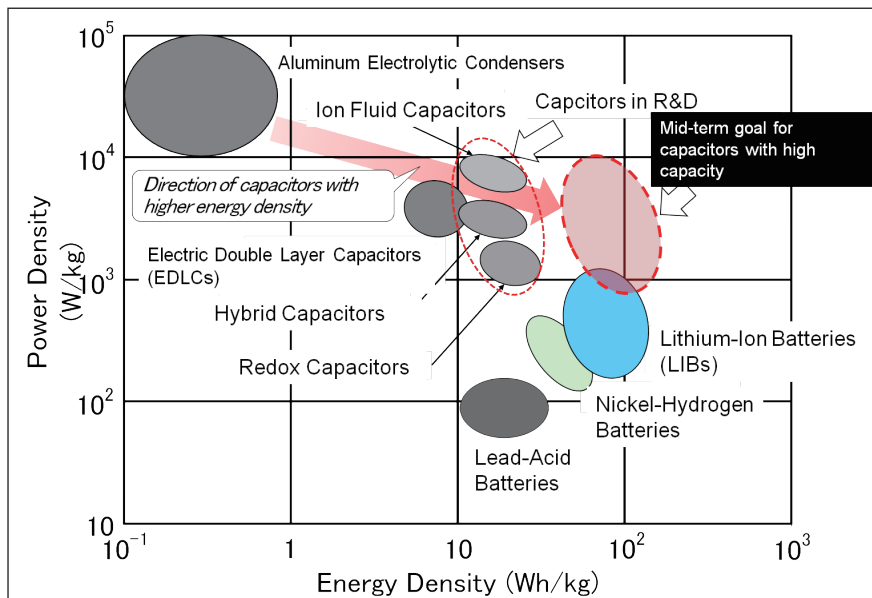


Figure 3 : Storage System Power/Energy Density Relationships and Mid-Term High-Energy Capacitor Goal

Compiled by the Science and Technology Foresight Center

2-3 Target Attributes for High-Energy Capacitors

Figure 3 shows the relationship between power density and energy density over weight for various storage systems.^[3, 8, 9, 13-15] The storage systems are capacitors that mainly gain electrical energy from the physical absorption and desorption of ions and rechargeable batteries that gain electrical energy via electrochemical reactions on the cathodes during the storage and discharge of electrical energy. EDLCs operate in volts (V). Their attributes, which allow them to store a large amount of electrical charge with low voltage and their usability over many charge/discharge cycles, have led to the use of ultra-small and small EDLCs in many electrical circuits with low operating voltage. Some examples of systems that use EDLCs in this manner are backup memory power sources in audio-visual and mobile devices, solar-powered watches and emergency gas valves. These EDLCs were first commercialized and mass produced in Japan during the 1970s.

Capacitors developed thus far with relatively high energy density include: redox capacitors that use intercalation reactions (the insertion of ions between the crystal structures of electrode materials) or redox reactions in the cathode/anode or both; hybrid capacitors that use charge transfer reactions in a rechargeable battery's electrode (either the cathode or anode); ionic fluid capacitors that use ionic fluid as an electrolyte for creating high voltage. For example, a lithium-ion capacitor (LIC), which is a hybrid capacitor that uses activated carbon on the cathode

and graphite pre-doped with lithium ions on the anode, is a leading candidate for becoming a High-Energy capacitor.^[1, 3, 11, 13] It should be noted that redox capacitors, LICs and the like are also collectively called electrochemical capacitors. However, these capacitors that are still in the R&D phase and have an energy density that is an order of magnitude less than those of LIBs.

Figure 3 shows the range of medium-term targets for the power density and energy density that high-energy capacitors should aim for. For the medium-term, we should set a target of reaching an energy density level equivalent to today's LIBs. To do this, R&D should devote efforts focused on electrodes and electrolytes. In its long-term roadmap, the New Energy and Industrial Technology Development Organization (NEDO) has set a target of vastly increasing the energy density of rechargeable batteries that employ electrochemical reactions on electrodes to 500 Wh/kg or better. However, considering how capacitors compete against LIBs so well in terms of their other attributes, the first R&D step should be to try and create capacitors with an energy density equivalent to today's LIBs.

Capacitors are also applied to fields outside of automobiles such as laser printers and copy machines, for which capacitors negate the need for standby power and make the equipment for use in a short time by quickly discharging a high current; as large-scale emergency power supplies for factories manufacturing industrial goods; and as uninterruptible power

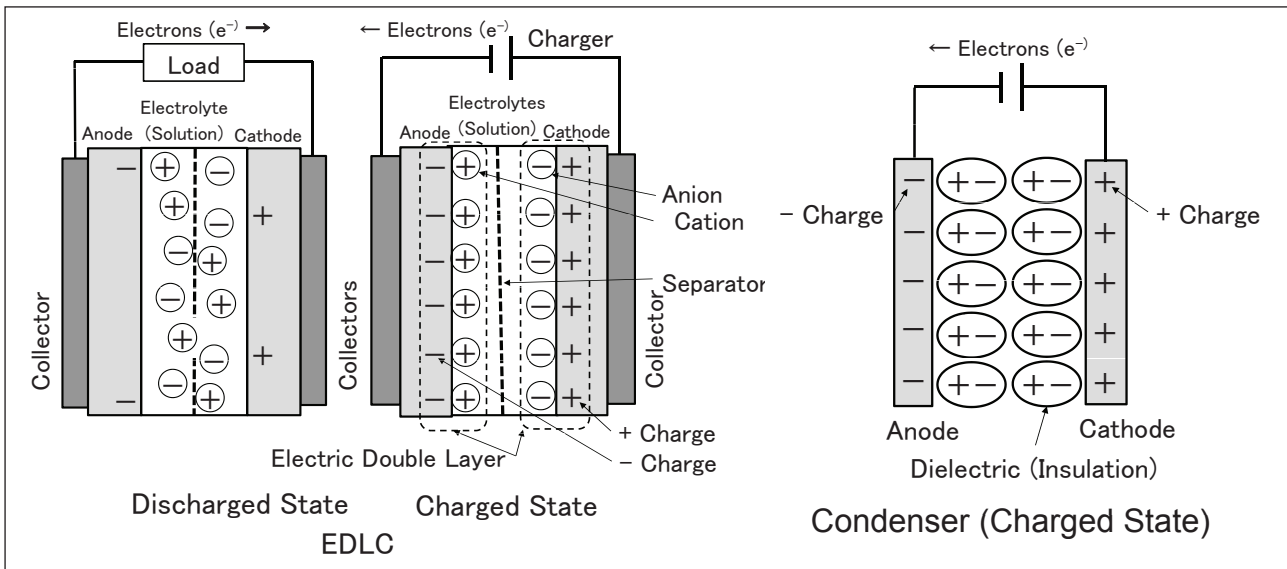


Figure 4 : Basic Storage Mechanisms of EDLCs and Condensers

Compiled by the Science and Technology Foresight Center

supplies that quickly discharge a high current. As for current market demand for these systems in terms of the attributes of capacitors versus today's LIBs, it is around three to ten times higher for power density, but around one-tenth lower for energy density.^[16] These attribute levels are somewhat far from the mid-term targets proposed in Figure 3, but capacitors continue to be used for the abovementioned purposes. However, it goes without saying that using capacitors with an even higher energy density would make these applications even more beneficial, such as by lengthening power supply lifespan for these systems.

3 Capacitor Storage Mechanisms

Figure 4 shows a comparison between the basic storage mechanisms of an EDLC and a condenser. An

EDLC cell generally comprises a pair of electrodes (a cathode and anode) with activated carbon and other materials with a large specific surface area and electrolytes (an electrolyte solution), along with a separator and a current collector. Like a capacitor, a condenser is generally an electrode region where charge is collected and comprises two dielectric materials (oxides such as tin, aluminum or tantalum) between two electrodes. Meanwhile, an EDLC essentially does the same by accumulating positive charge (i.e. electron holes) in the cathode and negative charge (electrons) in the anode by recharging. The two charges and ions of opposite charges line up against and are attracted to each other near the surface of the electrodes in the electrolytes. The ions act equally upon electrodes of the opposite charge, and an electric double layer comprising charge and ions forms in

[NOTE 1] In Japan, a condenser usually refers to an electrical circuit component. Outside Japan, both condensers and capacitors are called capacitors. Recently, capacitors with advanced functions have been called supercapacitors.

[NOTE 2] Farad (F) is a unit of capacitance. 1 F is defined as "the potential between two conductors created by 1 V of direct voltage during the release of electrical charge carried by 1 A (ampere) of current over 1s (second)." The potential (C) is represented by the equation $C = \epsilon S/d$, in which ϵ is the permittivity of the dielectric between the electrodes, S is the surface area of the electrodes and d is the distance between electrodes.

[NOTE 3] In a condenser, electric polarization occurs within the electrical field that enters the insulation between the electrodes, and the electrodes accumulate positive and negative charge. The event that creates electric polarization is called a dielectric phenomenon. The material that causes this phenomenon is called a dielectric (if the insulation is focused on the dielectric phenomenon). A typical condenser is an aluminum electrolytic condenser (a cell structure wrapped in a sheet impregnated with an electrolyte solution within an aluminum oxide coating), but the energy density of an aluminum electrolytic condenser, which is the highest among all condensers, is extremely low compared to an EDLC at only around one-hundredth (see Figure 3).^[17]

the interface region between the electrolytes and the cathode/anode. In an EDLC as well, the region where ions and charge are separated from each other at a nanoscale distance is equivalent to a dielectric. The capacitance is proportionate to the surface area (S) of the electrodes and the distance (d) between the electrodes (charge and ions) is inversely proportionate. However, an EDLC can achieve greater capacitance than a condenser with an electric double layer.

As with a condenser, the capacitance accumulated in the electric double layer is represented as C (measured in farads [F]). The stored energy (E) is calculated with C and operating voltage (V) as in the equation below.

$$E=0.5CV^2$$

Here, C, is calculated according to the equation below, with the permittivity of the dielectric between the electrodes represented as ϵ .

$$C=\epsilon S/d$$

Large capacitance and high operating voltage are needed to condense high amounts of energy per unit weight/volume.

During charging, ions are absorbed by the electrode surfaces. During discharge, the charge within the electrodes is released while the ions break free from the electrode surfaces. As a rechargeable battery does, there is no accompanying electrochemical reaction (the release/capture of electrons when oxides break down/form due to redox reactions). Thus, rapid charging and discharging are made possible by physical charging and discharging performed merely through the absorption and desorption of ions. Because a capacitor's charging and discharging is performed only via the movement of the ions gathered on the electrode surfaces, it can quickly switch from charging/discharging to large power output via a high current. There are few side reactions during charge/discharge. This gives a capacitor the advantages of no degradation of electrode materials or electrolyte solutions, long shelf-life and superior safety and reliability. On the other hand, because the application of a certain amount of voltage causes electrolysis if the electrolyte is a solution, the rated voltage of current EDLCs is between 2.5V and 3V.^[3, 13]

4 Policies and Issues for Development of High-Energy Capacitors

4-1 Creating Electrode Materials with High Capacitance and Cells with High Operating Voltage

Figure 5 is a structured depiction of the main approaches for creating a capacitor with high energy density. These approaches are broadly divided between the creation of electrode materials with high capacitance and cells with high operating voltage.^[3,11-13,18,19] Experiments are currently underway to create electrode materials with high capacitance by substituting activated carbon with carbon materials, metal oxides, conductive polymers and the like with structures that are regulated on the nanoscale, which then increase capacity through charge transfer. Because there is a limit to the capacitance an electric double layer can have on the surface of a carbon material, further increasing the number of pores in accordance to the ions absorbed, in order to increase the capacitance per unit weight of the electrode material, will not necessarily raise the material's per-volume capacitance. Inorganic materials, polymers and various other materials are known as electrode materials, but ruthenium oxide can reportedly be used to create materials with a capacitance of over 1,000 F/g. An example of research to increase the utilization rate of charge and ions in electrodes and improve stability over numerous charge/discharge cycles is that done on oxide electrode materials, which has used the material three-dimensionally to increase their surface area (S), accomplished by cellular and layered material structures.^[11, 12]

The energy (E) accumulated by a capacitor increases in proportion to the square of operating voltage (V), so a high-energy capacitor would result in high operating voltage. The approaches to creating cells with high operating voltage are divided into creating those with high withstand voltage in their electrolytes and those with a hybrid electrode composition. One known approach for creating cells with high operating voltage is to increase voltage from the breakdown of the electrolyte solution by using electrolyte materials such as ionic fluid with a wide potential window (the potential range in which the electrolyte solution will not undergo a redox reaction). Electrolyte solutions are

classified as aqueous and non-aqueous. Because the potential window of non-aqueous electrolyte solutions (around 2.5 V) is relatively wide compared to aqueous electrolyte solutions (around 0.8 V), currently, non-aqueous electrolyte solutions employing, for example, propylene carbonate as a solvent and ammonium salt as a supporting electrolyte, are primarily in use.^[3, 11, 12]

At present, the approach for developing high-energy capacitors thought to be the most effective is to create cells with high operating voltage with a hybrid structure combining a capacitor with a rechargeable battery, using the rechargeable battery electrode as either the cathode or anode. A prototype high-performance capacitor that nearly reaches the energy density of an LIB has been created. It is an LIC with a cell comprising a rechargeable battery anode and a capacitor cathode (see Figure 6).^[20, 21] For the time being, R&D will continue in order to achieve the creation of high-energy capacitors by using this cell structure with LICs or combined cells that blend the superior attributes of both LICs and LIBs (see Figure 7).

4-2 Hybrid Capacitors

The abovementioned LIC made from a combined cell with a hybrid structure is a storage system that incorporates the advantages of an EDLC and LIB. Figure 6 shows the discharge mechanism in an example of an LIC cell using activated carbon on the cathode and graphite pre-doped with lithium ions on the anode. In an LIC, the cathode forms an electric double layer and charges and discharges with a physical mechanism, while the charge/discharge mechanism of the anode works through a lithium electrochemical reaction. That is to say, it is a storage mechanism combining the functions of an LIB anode and an EDLC cathode. An LIC has a higher energy density than an EDLC because the anode's capacitance is increased by doping the anode with lithium ions, thus allowing the cell voltage to rise from 2.5 - 3 V to around 4 V. The LIC's power density, charge/discharge cycle shelf-life and other attributes are equal to an EDLC's. It is also very safe because self-discharge is small and it performs well at high temperatures. In the anode, lithium ions undergo intercalation. During charge and discharge, the electric potential is fixed near the redox potential of lithium. Meanwhile, the potential in the cathode, an activated carbon electrode, changes. During discharge, the lithium ions face the

cathode and the negative ions face the anode, while the reverse happens when charging.^[3, 13]

LICs that utilize the high power, long shelf-life and good safety of EDLCs while increasing energy density to the level of a lead-acid battery could potentially be used as primary power sources for HVs, PHVs and EVs. LICs employing lithium salt in an electrolyte solution are already in practical use in disc capacitors,^[22] but they are not yet fully practical in layered, rolled up and other types of large capacitors due to the difficulty of lithium ion pre-doping, among other reasons. Issues concerning LICs include increasing the cell's overall electromotive force, increasing overall cell capacitance by using electrode materials with low voltage dependence for the electrical charge, and creating high energy by employing electrode materials that balance electric potential for the electrical charge.

Furthermore, an example of developing a combined storage system is one that blends an LIC and LIB inside a cell.^[23] As Figure 7 shows, this is a storage system that blends an LIC cell with an LIB cell by sharing the anode via the collector. The LIC section performs rapid charging and discharging, while the LIB section performs long-term charging and discharging, thus allowing the storage system to produce instantaneous as well as sustained power. The prototype cell (a flat, rolled up, 10 Wh cell) has a power density of 3 kW/kg and an energy density of 60 Wh/kg, nearly that of an LIB. This is how combining an LIC and LIB within a cell can improve on the LIB's weakness with the quick charging and discharging of an LIC, while making up for the LIC's weakness with the LIB's long-term electrical power storage. This approach to creating a combined storage system could be one way to create a high-energy capacitor.

5 | Materials Technology to Create High-Energy Capacitors

R&D into new electrode materials will need to surmount various issues such as those concerning effective operation at low and high temperatures, tolerance to damage due to overcharging and long-term retention of charged energy in order to create the high-power and high-energy capacitors of the future. This R&D will likely be conducted on carbon materials, inorganic materials, polymers and other materials. Meanwhile, even higher withstand voltage,

greater electric double layer capacitance, a wider range of operating temperatures and other improvements will be demanded of electrolytes. R&D is now underway on ionic fluids, solid electrolytes and other materials with better properties than combustible electrolytes. The following sections discuss R&D trends in materials technology that will be essential for creating high-energy capacitors.

5-1 Electrode Materials R&D

As Figure 5 shows, the main approaches to giving capacitors high energy density through R&D into materials technology include carbon materials with structures regulated on the nanoscale, metal oxides to exceed the capacitance of carbon materials and polymers capable of storing large amounts of charge.

(1) Carbon Materials with Nanoscale Structures

Carbon materials have long attracted attention as electrode materials. The reason is that regulating their structures on the nanoscale can ensure a wide surface area and achieve high capacitance. Electrodes that employ activated carbon are formed with porous structures with large electric double layer capacitance that is maximized relative to weight or volume. Activated carbon pores are pathways for absorbing and desorbing ions that help diffuse the ions, thus playing a role in improving ionic conductivity. Because carbon formed by activated carbon has low self-discharge, it has the optimal weight of oxygen-bearing compounds such as hydroxyls and carbonyls. The electron conductivity of activated carbon is inferior to that of graphite, so the resistance at the edges of its constituent particles reduces charge/discharge speed.^[3,13] Thus, activated carbon needs better electron conductivity as an electrode material. Combining activated carbon with graphite particles possessing good electron conductivity as well as with graphite particles and carbon nanotubes (CNTs) is being investigated.

Furthermore, the CNTs under consideration as capacitor electrode materials are mainly single wall CNTs (SWCNTs) with a wide surface area per unit weight, thus giving them a large electric double layer capacitance per unit weight (100-200 F/g). Because SWCNTs have surfaces that absorb ions well and high electron conductivity, they can handle rapid charging and discharging with high current. This allows them to act as an electrode material for high-

power capacitors. However, when a CNT aggregate, called a bundle, forms, the surface area available for forming electric double layers and the electric double layer capacitance per unit volume are reduced, thus lowering electron conductivity. In addition, there are problems such as amorphous carbon byproducts in CNTs and the insertion of catalytic particles to grow CNTs. R&D on capacitors that employ SWCNTs is still ongoing. Other than SWCNTs, research is also being conducted on carbon nanofibers (CNFs).

Researchers at the Brookhaven National Laboratory in the United States have discovered the nanoscale graphene structure of graphene with a wide specific surface area (2,630 m²/g) that absorbs charge. They are trying to develop capacitors with an energy density equivalent to lead-acid batteries and that can charge and discharge quickly.^[24] This graphene has a three-dimensional network structure possessing numerous holes (void space 0.6-5.0 nm) formed by a curved wall as thick as a single carbon atom. Reportedly, the researchers are conducting computer simulations concerning the process of three-dimensional network formation in graphene, and are investigating the nanoscale structure of the holes with high-resolution electron microscopes, in order to make it possible to lay out the holes' dimensions and structure. Figure 8 shows a reported case in which electrodes were made by inserting CNTs between layers of graphene.^[25] This electrode structure absorbed large amounts of ions in the electrolyte solution on the graphene's surface. Furthermore, it used the ionic fluid within the electrolyte solution to succeed in achieving an energy density equivalent to a nickel-metal hydride battery. However, it may be possible to improve energy density in the same manner by dispersing and blending graphite fragments and single-layered CNTs rather than through a combination of graphene and SWCNTs.

(2) Metal Oxides

Using metal oxides as electrode materials in capacitors should have the benefit of allowing the capacitor to achieve high capacitance compared to carbon materials. Compared to activated carbon, the capacitance accumulated with a metal oxide has been reported to be approximately 10 times greater. Hydrus ruthenium oxide (RuO₂ · nH₂O) is a typical electrode material that collects and releases charge through redox reactions and can be used to build capacitors with large charge/discharge capacity. Until

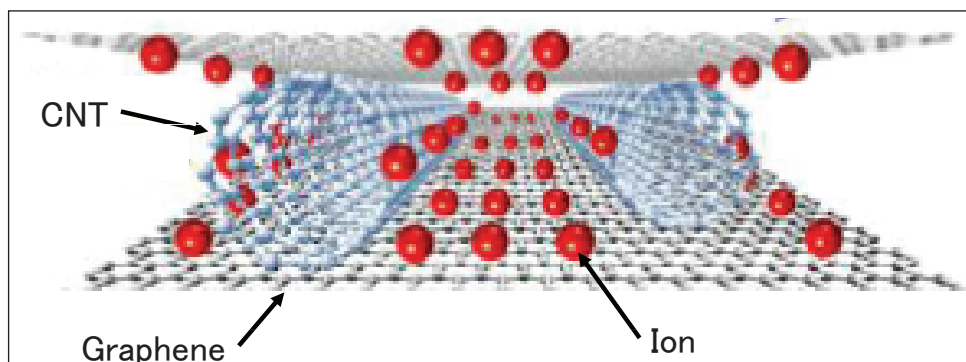


Figure 8 : Schematic of Electrode with CNT Distributed between Graphene Layers for Greater Ion Absorption

Figure in Reference #25 recreated by the Science and Technology Foresight Center

now, blending this material's nanoparticles and thinned forms of it with dissimilar metals, carbon materials and conductive polymers has been investigated. High capacitance densities of 600 to 1,200 F/g have been reported in all of them.^[11, 12] While ruthenium is not considered a rare metal, reserves are not plentiful and supplies are not steady. It would be preferable to use cheap metal oxides with a steady supply in order to provide a large volume of capacitors. Metal oxides such as manganese dioxide (MnO_2 , capacitance 480 F/g) and nickel oxide (NiO , capacitance 300 F/g) also reportedly have a comparatively high capacitance density, but none have yet been found that exceed ruthenium oxide's. Issues common to all capacitors that employ metal oxide electrodes include inadequate electrode durability and fluctuations in charge due to charge/discharge speed.

One reported technique to combine metal oxides with carbon materials is to highly disperse nanocrystal grains (5-20 nm) of lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) and combine them with nanocarbons (CNF, CNT) in an anode that is then used to create an LIC with an energy density approximately three times greater than an EDLC's. Figure 9 shows the properties of an LIC comprising an anode of nanocarbons with dispersed $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanocrystal grains and a cathode of activated carbon, as well as a high-resolution transmission electron microscope image of the anode's material.^[26] Improving electron conductivity in the anode with nanocarbons and expanding capacitance by employing an anode with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanocrystal grains makes it possible to achieve higher energy density with a flat anode potential of around 1.6 V. Using $\text{Li}_4\text{Ti}_5\text{O}_{12}$ eliminates the need to pre-dope with lithium ions and ensures that the LIC is safe by operating within a potential range with no electrolyte breakdown.

(3) Polymers

Using polymers as electrode materials in capacitors should be able to achieve high capacitance by storing and releasing large amounts of charge through reversible redox over a wide potential range. Such polymers include polyaniline, diaminoanthraquinone and cyclic indole trimmers, which power hydrogen ions within a solvent, and polyfluorophenylthiophene and polymethylthiophene, which provide power within a non-aqueous electrolyte solution. Using these polymers as electrode materials can achieve capacitance density of 200-300 F/g, several times greater than an activated carbon electrode.^[11] However, these polymers' capacitance is relatively low compared to metal oxides. Additionally, an issue with these polymers is the deterioration due to excessive oxidation and hydrolysis accompanying numerous charge/discharge cycles, resulting in lowered capacitance density.

An example of a combination used to create a prototype LIC is one comprising a conductive polymer membrane of polypyrrole, polythiophene and polyaniline for the cathode, activated carbon pre-doped with lithium ions as the anode, and, as in existing EDLCs, an organic solvent containing boron tetrafluoride ions (BF_4^-) for the electrolyte solution. This LIC achieves an energy density of 60-80 kWh/kg, nearly that of an LIB's, and a high power density of 7 kW/kg.^[20, 21] Figure 10 shows a schematic of the mechanism for absorbing negative ions in a cathode employing a conductive polymer membrane. The cell's capacitance is expressed as the reciprocal of the sum of the reciprocal of each electrode's (the cathode and anode) capacitance, thus increasing the energy density of each as their capacitance rises. In addition to increasing anode capacitance with lithium ion pre-doping, using conductive polymers also

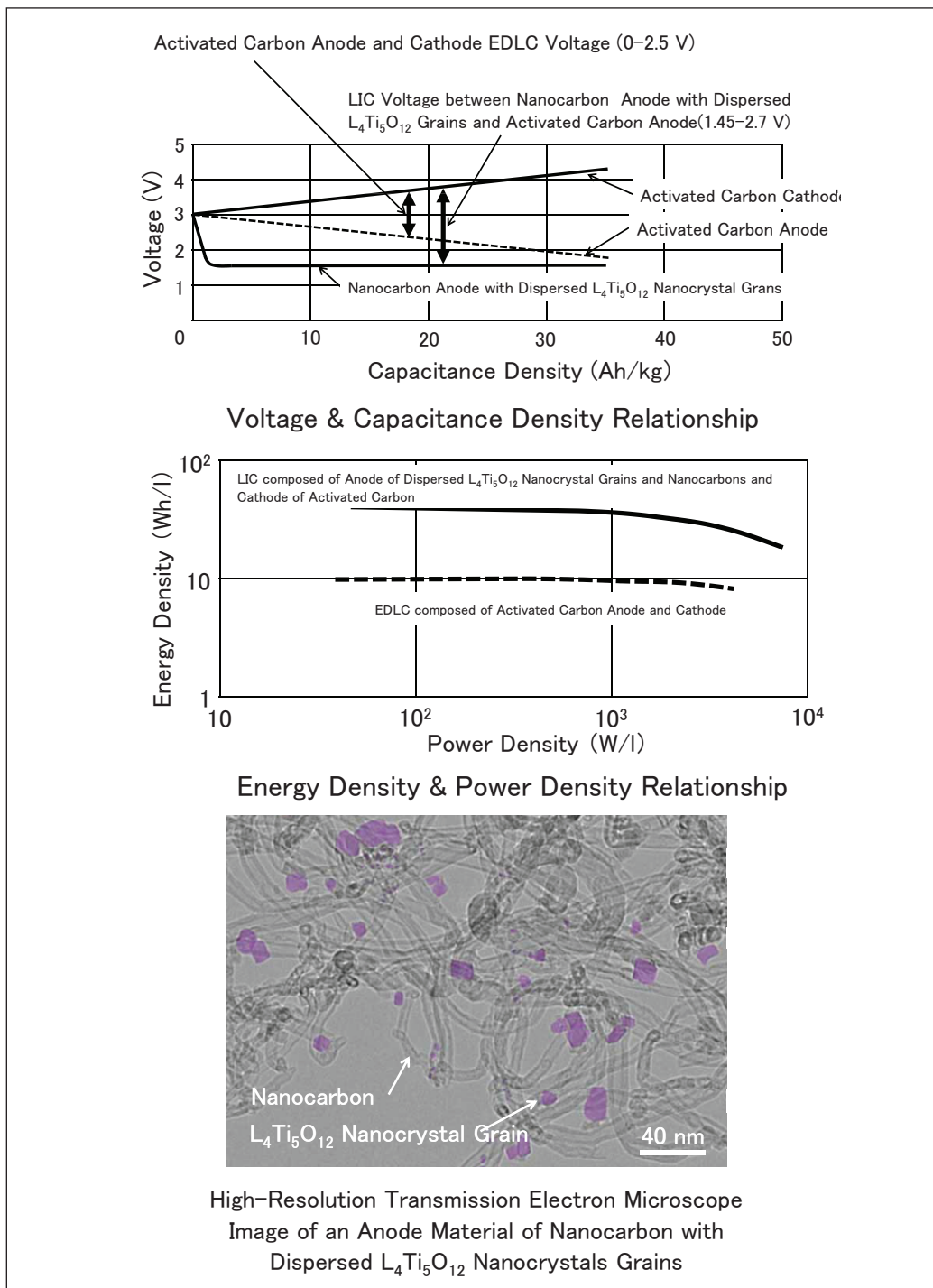


Figure 9 : Properties of an LIC composed of Nanocrystal with an Anode of Dispersed $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Nanocrystal Grains Nanocarbons and a Cathode of Activated Carbon, and High-Resolution Transmission Electron Microscope Image of the Anode Material

Figure in Reference #26 recreated by the Science and Technology Foresight Center

raises cathode capacitance. In the cathode, the fine conductive polymer membrane (thickness approx. $50 \mu\text{m}$, polymer radius approx. 0.5 nm) forms on the surface of the collector's aluminum foil (width approx. $30 \mu\text{m}$) through electrolytic polymerization. Since many BF_4^- ions are three-dimensionally inserted into the membrane, a high capacitance is achieved. Even with the use of conductive polymers in the electrodes, it could be possible to use this type of LIC as the

primary power source for automobiles if resistance to electron conduction in the electrodes can be reduced and the deterioration caused by numerous charge/discharge cycles over a long period of time and rapid charge/discharge can be lessened.

5-2 Electrolyte Materials R&D

As Figure 5 shows, R&D is being conducted on electrolyte materials to achieve high withstand

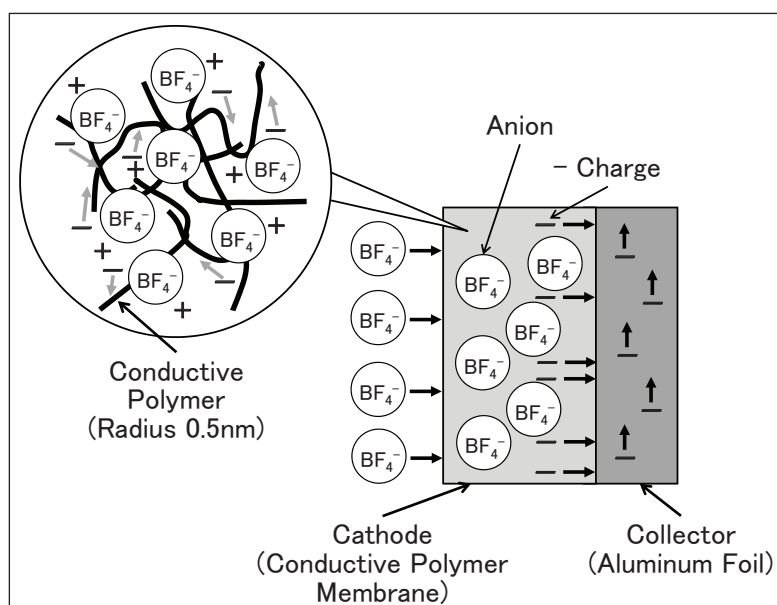


Figure 10 : Negative Ion Absorption Mechanism in a Cathode Employing a Conductive Polymer Membrane (Charged State)

Figure in Reference #20 recreated by the Science and Technology Foresight Center

voltage and give a cell a high operating voltage while maintaining high-speed charging and discharging inside a capacitor with a high energy density.

(1) Ionic Fluid Electrolyte Materials

An ionic fluid is a liquid salt with both positive and negative ions that retains liquid form even though it does not contain a solvent. These fluids can be organic or inorganic. Their properties include flame-retardance, non-volatility and high ionic conductivity (10^{-3} - 10^{-4} s/cm). EDLCs that employ ionic fluids are very safe because they can prevent fires caused by leaking electrolyte solution. Typical organic salts in ionic fluids include imidazolium salts, pyridinium salts and aliphatic quaternary ammonium salts as positive ion ingredients. Known negative ion ingredients are inorganic materials such as BF_4^- and hydrogen hexafluoride ions (PF_6^-) and fluoride-containing organic positive ions such as CF_3SO_3^- and $(\text{CF}_3\text{SO}_2)_2\text{N}^-$. Ionic fluids retain their liquid form at room temperature because their structure makes it difficult for them to crystallize and they have little stabilization energy. Ionic fluids have a wide potential window (around 6.0 V) and are electrochemically stable, so they can be used in EDLCs to broaden their operating voltage range. Ionic fluids have been successfully used to broaden a cell's operating voltage range to 3.0 V while also suppressing internal resistance.^[3, 17]

A disadvantage of ionic fluids is that while their

melting point is lower than normal salt, their viscosity is higher than an organic solvent electrolyte, even at room temperature. They are also inconvenient for high-speed charging and discharging. In addition, other problems that have been cited include low ionic conductivity and susceptibility to transformations due to redox reactions at low temperatures. They are also difficult to crystallize, making it easy for them to become a salt with high bulk density. While a certain amount of ionic radius maintains ions' dissociation degree, if they are too big then they cannot enter the electrode pores and form an electric double layer. Thus, electrodes with pores must be combined with ionic fluid containing ions of the appropriate size. At present, organic solvent electrolytes with organic solvents added to ionic fluid are used. However, using a combustible solvent will take away from the ionic fluid's incombustibility. Materials that do not require the addition of solvents and the like and which can charge and discharge at high speed are needed.^[3, 17]

(2) Solid Electrolyte Materials

By not using liquids as electrolyte materials, one can create a storage system that will not leak and that has good durability and safety. However, capacitors have to maintain high ionic conductivity and sustain rapid charging and discharging. With this in mind, gel combining polymers, electrolytic salt and a plasticizing agent can be a solid electrolyte material. Studies are underway for LIB applications by using

solid electrolyte polymers blending a polyethylene oxide polymer with electrolytic salt in capacitors, as well as a polymer gel of disulfonate that has been the subject of recent research. If the gel can be kept at the right hardness, then this electrolyte can also play the role of the separator between the electrodes. The result is that making the electrolyte region thin and arranging many cells within a series can create a compact, powerful capacitor, even at high voltage. Moreover, lithium-ions travel quickly through inorganic solid electrolytes.⁸ However, a difficult hurdle for inorganic solid electrolytes to overcome in capacitors is that they must allow both positive and negative ions to move through the electrolyte.^[11,27]

5-3 Mechanism Identification Research

Looking at the long term, R&D into LICs with high energy density is ongoing and electrode and electrolyte material techniques that would be effective with regards to LIBs with rapid, high power output and high-energy are being investigated. Electrode materials garnering attention include layered oxides, olivine fluoride, silicates and sulfur for a cathode with high electric potential and high capacitance; and sulphides, silicon and lithium metals for an anode with low electric potential and high capacitance.^[8] It would probably be effective to use these electrode materials by analyzing intercalation reactions that the ions cause inside electrode materials, which would then be referenced for governing structures on the nanoscale. Meanwhile, electrolytes need to contain many ions, conduct quickly and be as dense as possible on the side of concentration to reduce the ions' dissociation degree. Furthermore, things that solvents which break down electrolytes need to do well include dissociating ions and being electrochemically affected by redox reactions.

Structural analysis of the constituent materials of cells, along with electrochemical analysis and assessment based on compositional analysis, could be faster ways of discovering charge storage mechanisms that can bring the energy density of capacitors up to LIBs'.^[8] An effective approach could be for universities and other institutions to implement these sorts of projects related to the constituent materials of capacitors and to use the results for continued R&D in the private sector.

6 International Trends in the R&D and Commercialization of Capacitors

6-1 R&D and Commercialization of Capacitors in the U.S., China and South Korea

In the U.S., four of the Department of Energy's national laboratories and thirteen companies were actively engaged in the Ultracapacitor Program starting in 1992, which shut down in 1998 before achieving its goals. Although thereafter the federal government and other entities were unable to put together large budgets for capacitor technology-related projects, the Department of Energy has supported small-scale R&D. However, the number of papers written by university and national laboratory researchers on subjects like capacitor electrode materials is increasing. Companies are devoting their attention to capacitors with even greater energy storage. There is great interest in important technologies outside of automobiles, such as uses in medicine, a field that demands top-level reliability, and for auxiliary power sources that supplement compact, high-output power sources. LICs are using lithium manganese oxide (LiMn₂O₄) are mass-produced.^[22, 28]

In China, buses equipped with capacitors (around 100 kWh) have been used in Shanghai's public transportation network since 2006. Charging stations are set up at every bus stop so they can recharge as passengers get on and off and the buses do not require recharging at other times (range of around 4 km per charge; recharge time of around 30 sec). Capacitor buses also ran through the venue for the 2010 Shanghai World Expo. These two examples are large-scale experiments on the use of capacitors. Although the capacitors are made by Chinese companies, they incorporate technologies from companies such as those from the U.S. that manufacture automobile capacitors.^[28, 29] A joint project between Japan and China installed 100-kWh EDLCs to absorb power and help deal with output fluctuations from solar power.^[30]

In South Korea, R&D on storage systems is mainly conducted by industry, with government backing. A national project developed high-capacity LIBs and EDLCs from 2004 to 2009. The government enacted the Low-Carbon, Green Growth Basic Law and formulated its Green New Deal policy in 2009. It also formulated the Science and Technology Basic

Plan (the 577 Initiative) at the end of 2008. The government listed “Next-generation Batteries and Energy Storage/Conversion Technology” as one of the key technologies to teach the country’s youth in its policies prioritizing the “Promotion of Research and Development on Global Issues.”^[31] Meanwhile, for a five-year period beginning in 2005, industrial, government and academic research institutes promoted R&D projects on high-energy capacitors for HVs worth around 400 million yen annually. South Korea has a smooth arrangement for projects to receive government subsidies and assistance from venture capital. There are companies in the country already manufacturing high-capacity LICs.^[22, 28] We can surmise from this that the pace of R&D in countries like the U.S. and South Korea has slowed somewhat in the 2000s.

6-2 R&D and Commercialization of Capacitors in Japan

Japanese industry has led the market ever since a Japanese company commercialized the first disc EDLC in 1978. Currently, Japanese, American, South Korean and Taiwanese firms account for approximately 70% of global EDLC production. Demand for LED disaster lights and other equipment using EDLCs rose after the Great East Japan Earthquake and imports of EDLCs from South Korea and China to Japan skyrocketed. In recent years, the use of advanced mobile equipment with ultra-small EDLCs has spread. Meanwhile, combined LICs were commercialized, mainly in Japan, in 2009. Capacitors with all manner of capacity rates have since been used in mobile equipment, household appliances, delivery robots and more. Supplies of EDLCs and LICs have been low for the past few years and all companies in the market are ramping up production. However, some of their customers have announced plans to produce their own capacitors. Furthermore, new companies continue to enter the business alongside the more established condenser makers.^[22]

The Demonstration Study of New Power Load Equalization Methods, which was conducted from 1997 to 2000 and performed R&D on storage systems to equalize solar power generation output, was the first effort to use capacitors in an energy system. Since 2000, development, mainly with the goal of HV applications, has continued under the framework of “Strategic Development of Energy Use

Rationalization” and the like. This development has produced prototype storage systems for HV passenger vehicles and buses.¹ Since then, various projects to promote research on industrial technology have also continued with capacitor-related R&D.

One of the important green innovation issues specifically mentioned in the 4th Science and Technology Basic Plan is the promotion of highly efficient energy use with the goal of developing and popularizing electricity control systems through, for example, rechargeable batteries in next-generation automobiles. This includes R&D on subjects such as rechargeable batteries and charging infrastructure and corresponds with the aim of building a new distributed system of supplying energy.^[32] Among the proposals compiled by the Industrial Technology Subcommittee of the Industrial Structure Council at METI, it espoused a distributed energy society through a “battery revolution,” comprising technological innovations that are more than simply an extension of current growth trends, in order to build a first-of-its-kind society that enjoys growth and harmony with the environment.^[33] We should also promote the use of capacitors to carry out a part of this battery revolution.

7 Conclusion

The most promising high-energy capacitors are LICs with a hybrid structure combining an EDLC and rechargeable battery. However, nothing has yet been developed to thoroughly demonstrate LICs’ attributes. Most prototype cells need to try and further improve their energy density.

If capacitors come into widespread use as automobile power sources—the most demanding conditions in which they would be used—they would have a large ripple effect in other fields such as energy storage, power load equalization and energy regeneration, as well as being an effective way of using energy and helping to further reduce CO₂ emissions. The Japanese people’s experience with rolling blackouts due to power shortages in the wake of the Great East Japan Earthquake has made power consumers feel that they need to reduce power consumption during peak hours and to use storage systems that ensure an emergency power supply. The number of storage system applications is increasing with regards to building smart grids as well as managing fluctuating output from renewable energy systems and the

balance between supply and demand. Capacitor R&D could gain momentum as one option for these storage systems.

Most companies that make capacitors are in Asia and many are Japanese. There are increasingly more small companies manufacturing and selling capacitors. Lowering costs, increasing energy density and improving reliability will be essential to maintaining the superiority of Japanese companies and popularizing the use of capacitors.

Another issue faced by EDLCs and LICs is their higher system costs compared to rechargeable

batteries.^[34] However, an assessment of a capacitor's system cost relative to capacitance that includes their long charge/discharge cycle shelf-life shows that they cost significantly less than rechargeable batteries. We also need to consider not using any expensive rare metals in electrodes. We also have to conduct R&D to vastly reduce the costs of cells' constituent materials. In the future, we can expect capacitors to cost less as they become more compact and lightweight, and their use may quickly become more widespread alongside the further popularization of rechargeable batteries. This could result in large reductions in CO₂ emissions.

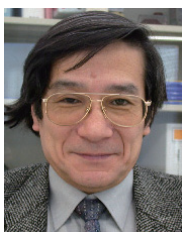
References

- [1] "Survey Concerning the Drafting of Technology Maps for Lithium-Ion Batteries, etc.," NEDO FY 2006 Results Report, (2009)
- [2] "Basic Research Needs for Electrical Energy Storage," Report of the Basic Energy Sciences Workshop on Electrical Energy Storage (2007), Office of Basic Energy Sciences, /U.S. Department of Energy: <http://science.energy.gov/bes/news-and-resources/reports/basic-research-needs/>
- [3] Masashi Ishikawa, "Capacitors Opening Up the Energy Society of the Future," KD Neobook, (2007)
- [4] Hiroshi Kawamoto and Wakana Tamaki, "Trends in Supply of Lithium Resources and Demand of the Resources for Automobiles," Science & Technology Trends, Dec. 2010, No. 117, p. 17-29
- [5] "Next-Generation Vehicle Strategy 2010," Ministry of Economy, Trade and Industry, (Apr. 12, 2010 announcement)
- [6] "Vehicle Ownership by Region/Country," Ministry of Land, Infrastructure, Transport and Tourism materials: www.mlit.go.jp/k-toukei/search/pdf/23/23000000x02401.pdf
- [7] "Japan's National Greenhouse Gas Emissions (Preliminary Figures)," Ministry of the Environment materials: <http://www.env.go.jp/earth/ondanka/ghg/index.html>
- [8] Hiroshi Kawamoto, "Trends of R&D on Materials for High-Power and Large-Capacity Lithium-Ion Batteries for Vehicles Applications," Science & Technology Trends, Jan. 2010, No.106, p.19-33
- [9] Shogo Nishikawa, "Chapter 3: Development of Capacitor Hybrid Trucks and Buses," Development of Large-Capacity Rechargeable Batteries for Automobiles, CMC Publishing, p. 209-221, (2008)
- [10] "Chapter 3: Considerations Concerning Regenerative Braking in Electric Vehicles and Improved Functionality": http://dSPACE.wul.waseda.ac.jp/dSPACE/bitstream/2065/2929/7/Honbun-4026_05.pdf
- [11] Katsuhiko Naoi, "Current State of Capacitors and their Prospects,": http://www4.fed.or.jp/tansaku/yuki/02_naoi.pdf
- [12] Wataru Sugimoto, Development of Supercapacitors Using Pseudocapacitance and Double Layers, NEDO FY 2006 Grant Industrial Technology Research Program Research Results Report (Final), (2008)
- [13] Michio Okamura, "Electric Double Layer Capacitors and Storage Systems (Ver. 3)," Nikkan Kogyo Shimbun, (2009)
- [14] Takashi Chiba, "Development of New Ultimo Lithium-Ion Capacitors," OHM, Aug. 2011, p.34-37
- [15] "ESA Technology Comparison": http://www.electricitystorage.org/technology/storage_technologies/technology_comparison
- [16] "High-Performance Capacitors Using Single-Layered Carbon Nanotubes (Carbon Nanotube Capacitor Development)," NEDO materials
- [17] "Technological Trends and Needs Study Concerning Ionic Fluids," NEDO FY 2007 Study Report (2008)
- [18] A. Burke, "Ultracapacitor Technologies and Application in Hybrid and Electric Vehicles," Institute of Transportation Studies, University of California, Davis, (2009)
- [19] "Redox Capacitors," Waki Group, Department of Energy Sciences, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology: http://www.es.titech.ac.jp/waki/research/r_cap-j.html
- [20] "Capacitor Batteries and Conductive Polymer Cathodes," Eamex materials: <http://www.eamex.co.jp/capa2>.

html

- [21] Capacitors Utilizing Conductive Polymers: Achieving Both Fast Charge/Discharge and High Capacity, NIKKEI MONOZUKURI November 2011, p.28-29
- [22] Atsushi Nishino, “Introduction: Expanding Fields of Application for Next-Generation Electric Double Layer Capacitors,” OHM, Aug. 2011, p. 17-23
- [23] “MHI Lithium-Ion Capacitor and Lithium-Ion Battery Combined Storage Device Development,.” Mitsubishi Heavy Industries PR materials (Feb. 16, 2010): <http://www.mitsubishielectric.co.jp/news-data/2010/pdf/0216-d.pdf>
- [24] “Activated Graphene Makes Superior Supercapacitors for Energy Storage”: http://www.bnl.gov/bnlweb/pubaf/pr/PR_display.asp?prID=1275&template=Today
<http://capacitors-forum.org/jp/files/CapFmag06.pdf>
- [25] Q. Cheng, et al., “Graphene and carbon nanotube composite electrodes for supercapacitors with ultra-high energy density,” Physical Chemistry Chemical Physics, DOI:10.1039/c1cp21910c:www.rsc.org/pccp
- [26] Katsuhiko Naoi and Kenji Tamamitsu, “New Nano-Hybrid Capacitors”: <http://www.tuat.ac.jp/~koukai/gakuho/2008/482/news15-2.pdf>, (2009)
- [27] Katsuhiko Naoi, “Next-Generation Nano-Hybrid Capacitors,” Capacitors Forum Newsletter, 2011, Vol. 6, p.15-18: <http://capacitors-forum.org/jp/files/CapFmag06.pdf>
- [28] “Electrochemical Supercapacitor Basic Research, Study on Trends and Joint Research on Application Development,” FY 2006 International Joint Research Program, Report on results of International Joint Research Program sending researchers abroad, NEDO, p.151-181, (2007)
- [29] Shuhei Monma, “Active Shanghai Capacitor Buses,” Capacitors Forum Newsletter, 2001, Vol. 6, p. 15-18: <http://capacitors-forum.org/jp/files/CapFmag06.pdf>
- [30] “International Joint Demonstration and Development Program for Advanced, Integrated and Stable Solar Generation Systems, etc. - Advanced, Integrated and Stable Microgrids (High-Quality Power Supply),” NEDO FY 2007-2009 Results Report, (2010)
- [31] “Next-Generation Rechargeable Battery and Storage Devices Technologies” strategic initiative, Japan Science and Technology Agency, Center for Research and Development Strategy, JST-CRDS-FY2011-SP-04, (2011)
- [32] “4th Science and Technology Basic Plan”: http://www.mext.go.jp/a_menu/kagaku/kihon/main5_a4.htm
- [33] “Founding a New National Project System – Proposals by the Research and Development Subcommittee,” Ministry of Economy, Trade and Industry: <http://www.meti.go.jp/press/2011/08/20110815001/20110815001-2.pdf>
- [34] “Wasting Capacitors,” Nikkei Monozukuri, March 2010, p.61-67

Profiles



Hhiroshi KAWAMOTO

Science and Technology Foresight Center, Visiting Fellow

<http://www.nistep.go.jp/index-j.html>

A doctor of engineering and a fellow of the Japan Society of Mechanical Engineers, at Toyota, Dr. Kawamoto took charge of the mechanical design and evaluation of automobile components at the design stage. After leaving Toyota, he was engaged in METI-related projects (R&D on fine ceramics, etc.) at Japan Fine Ceramics Center. He was a fellow at the Science & Technology Foresight Center for three years, starting in 2006, and has been a visiting fellow since 2009. Now, he is a visiting professor at Osaka University Graduate School of Engineering and is a part-time professor at Meijo University. He specializes in strength-design and reliability-evaluation for structural materials and components.

(Original Japanese version: published in July/August 2012)