Capacitor devices for rapid charge/discharge storage

— R&D strategies of electrode materials for high performance capacitor devices —

Hiroaki Hatori [*], Osamu Tanaike, Yasushi Soneda and Masaya Kodama

[Translation from *Synthesiology*, Vol.6, No.4, p.228-237 (2013)]

Energy storage devices now require rapid charge/discharge performance, not only high storage capacity for convenient and energy efficient devices. Research and development of rapid charge/discharge storage devices are carried out in an interdisciplinary field of nanotechnology and device manufacturing, where the scope of research is very different in size and scale. This R&D is an interesting subject from the viewpoint of synthesiology, because the keys to device manufacturing are selection and combination of element technologies. In this paper, approaches and methods employed in the R&D of high performance capacitors are introduced from the discovery of innovative materials to device manufacturing, by citing examples carried out in research projects under industry-academia-government collaboration.

Keywords **:** Capacitors, energy storage device, electrode materials, quick charge/discharge, carbon materials

1 Background

The electric storage device that can be repeatedly charged and discharged include the secondary battery such as lead storage battery and lithium ion battery, and the electric double layer capacitor (EDLC) used specifically for rapid charge/discharge. We are surrounded by devices referred to as "batteries," and the application range of storage devices is extremely wide. In the recent years, there are active developments for the storage devices to fulfill the social demand for energy saving cars that can run as far as gasoline cars and for electric power leveling that enable the employment of natural energy. The performance requirement of a storage device is, first, the achievement of high energy density to improve the convenience of long hour use. Lithium ion batteries were created to meet such a requirement, and the rapid development and market expansion mainly for portable devices were astounding. On the other hand, even with the excellent performance of the lithium ion battery, it seemed to be difficult to commercialize the electric vehicle with the same running distance as the gasoline vehicle. However, the entry of the hybrid cars kicked off the active development of a storage device that allows high input/output and withstands repeated charge/discharge. Currently, the demand for plug-in hybrid and electric vehicles has increased along with the development for residential power storage in view of the diffusion and promotion of natural energy, and the development of low cost yet high energy density storage devices is in demand. Such changes in the development trend occurred in the past ten years, and the technological demand shifts continuously due to the social background. The demands for the performance requirement of storage devices are diverse.

The EDLC is a power storage device without chemical reaction, and in principle, it has rapid charge/discharge performance and excellent durability.[1][2] The market for small capacitors with electrostatic capacitance of 1 F or less has been established in the latter half of the 1970s. Later, large devices of 1,000 F class were developed for the power regeneration system of automobiles and construction machines. The devices specializing in rapid charge/discharge (power density) are expected to play important roles in attaining the outcome "to allow people to live comfortably" in various scenes. The application to copiers is a case study of practical application of large capacitors to reduce the standby power needed for preheating, and thereby allowing start-up without waiting time. This was made possible by rapid heating using the high output property of the capacitor. It is an excellent example of industrial technology where energy saving was accomplished while maintaining convenience in everyday use. There is a toy train that can run continuously on a circuit rail by instantly charging the capacitor when passing through a charging point. The basic concept of the modern electric vehicle is to charge the high energy density storage device at a time with energy needed for long distance drive. In the future, a new concept electric vehicle may emerge where the car runs along the road and is repeatedly charged without the passenger knowing, allowing long-distance travel by combining a rapid charge/discharge device and a noncontact charger.

The EDLC currently used has an extremely simple structure, where the activated carbon is used as the electrode material for both the anode and cathode, and other main parts are the electrolyte solution and the aluminum collector. As it can be said for storage devices in general, the energy density and

---

Energy Technology Research Institute, AIST　Tsukuba West, 16-1 Onogawa, Tsukuba 305-8569, Japan　* E-mail : h.hatori@aist.go.jp

Original manuscript received September 18, 2012, Revisions received July 9, 2013, Accepted July 11, 2013

power density are in a trade-off relationship. Currently, when an attempt is made to improve one, the other is sacrificed, and this cannot be avoided in creating a device. As the social demand for rapid charge/discharge storage device increases, we have conducted R&D of carbon electrode materials that may be used as the electrode active materials for capacitors. As already mentioned, the application range of the storage device is wide, and the performance requirements of the system directly linked to the social demand are diverse. Also, when an innovative potential appears and the performance limit (or projection of such) increases, new demands will appear and the development toward that goal will become activated. With this background, we conducted R&D on how to increase the energy density without losing the excellent rapid charge/discharge property of the capacitor. While this development strategy set the performance required by the current social demand as a goal to be achieved, it was the development of electrode materials that involved a wide range of stances, from the exploration of breakthrough that enabled breaking the existing principles (*Type 1 Basic Research*), the accurate understanding of the existing phenomenon (core research of *Type 2 Basic Research*), and the realization of the performance limit based on the existing principle (*Type 2 Basic Research*) (Fig. 1).

2 Categorization of the technology to achieve advanced performance of capacitors and the selection of technology

2.1 Principle of the EDLC and the electrochemical capacitor

The electric double layer capacitor (EDLC) is a storage device that stores electricity by using the ion adsorbing layer formed at the interface of the electrode surface and the contacting electrolyte solution (Fig. 2). Storage by electric double layer is based on the electrostatic adsorption and desorption. Since it does not involve chemical reaction as in a secondary battery, rapid charge and discharge are possible, and it has small deterioration despite repeated charge/discharge. Since the electric double layer capacitance related

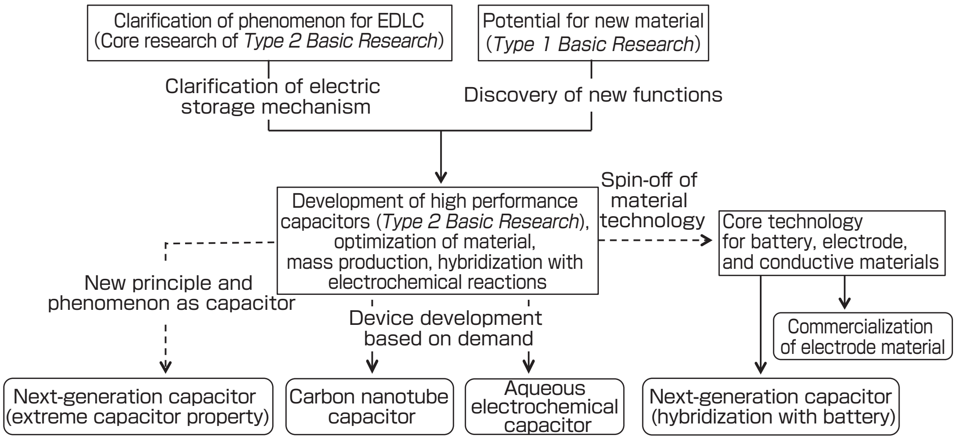


Fig. 1 R&D model of the electrode material for high-performance capacitor

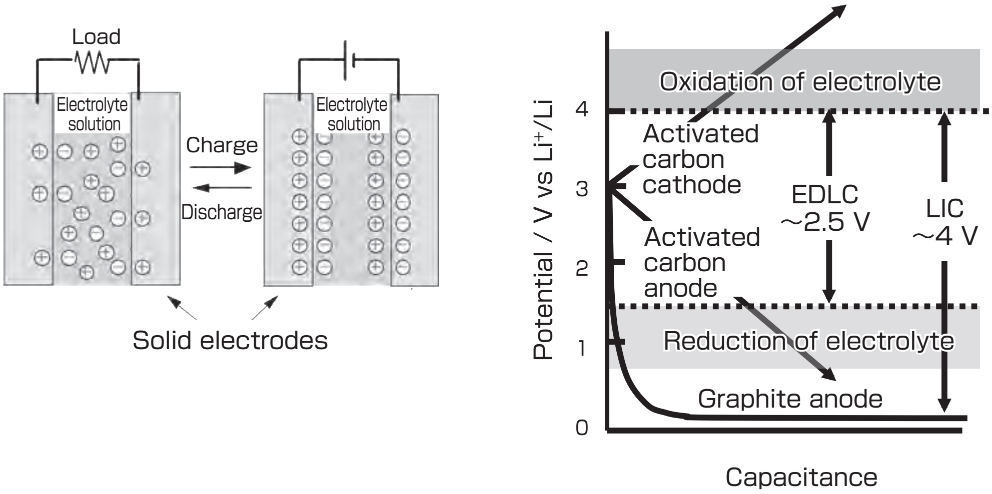


Fig. 2 Electric storage principle of the EDLC (left) and comparison with the LIC
As shown in the figure on the right, the operating voltage of the EDLC is limited by the oxidation-reduction voltage of the electrolyte solution, while the LIC can take large operating voltage since the reduction potential of the graphite anode is low.

Table 1. Categorization by capacitor and secondary battery types

		Cathode	Anode
Electric double layer capacitor		Electric double layer (activated carbon, porous carbon)	Electric double layer (activated carbon, porous carbon)
Electrochemical capacitor	Lithium ion capacitor	Electric double layer (activated carbon, porous carbon)	Redox reaction (graphite, hard carbon)
	Redox capacitor	Redox reaction (RuO_2, MnO_2, conductive polymer, etc.)	Redox reaction (RuO_2, MnO_2, conductive polymer, etc.)
	Third-generation capacitor	Redox reaction (phosphoric acid iron lithium in nanoparticle form, etc.)	Redox reaction (phosphoric acid iron lithium in nanoparticle form, etc.)
Lithium ion battery (secondary battery)		Redox reaction (oxides)	Redox reaction (graphite, hard carbon)

to energy density is proportional to the electrode surface area, activated carbon, a high surface area material, is used in the commercial EDLC.

On the other hand, the disadvantage of the capacitor is that the amount of energy that can be stored is limited compared to batteries. The electrochemical capacitor is a capacitor that employs the electrochemical reaction (oxidation-reduction or redox) to improve the energy density, and is categorized as “capacitor” in a wide sense, assuming it possesses rapid charge/discharge property. The categorization is shown in Table 1. Among the capacitors in the intermediary position where the electrochemical reaction is used in either the cathode or anode, the lithium ion capacitor (LIC), shown in Fig. 2, leads the way in terms of practical application. Recently, the so-called third-generation capacitor that incorporates electrochemical reaction in both the cathode and anode for higher energy density has been proposed. Figure 3 shows the relationships of the energy density and power density for the representative secondary batteries and capacitors discussed in this paper.

2.2 Reasons for technological selection

As indicated in the above technological categorization, the orthodox development for improving the energy density that is the disadvantage of capacitors is to add the capacitance gained by the electrochemical reaction at the electrode surface (this is called “pseudo-capacitance” in capacitors). However, introducing the chemical reaction means that a battery element must be added to the capacitor, and the disadvantage of the battery must be accepted in return for increased capacitance. This means that the capacitance and lifespan are traded off in many cases, and it is not easy to increase the capacitance without losing the superiority of capacitors against batteries. Amongst the potential nanocarbon manufacturing materials, we found nitrogen-doped carbon and exfoliated carbon fiber (ExCF) through the development of electrode materials to which electrochemical reaction could be introduced, while utilizing the characteristic of the capacitor. We aimed for the development of an aqueous electrochemical capacitor where the structural control of the carbon materials was conducted at nano level to achieve increased capacitance by introducing the electrochemical reaction. On the other hand, it was a challenge of how much performance of the carbon nanotube capacitor could be realized in an actual device, using only the original functional principle of a capacitor without electrochemical reaction. These two developments will be explained.

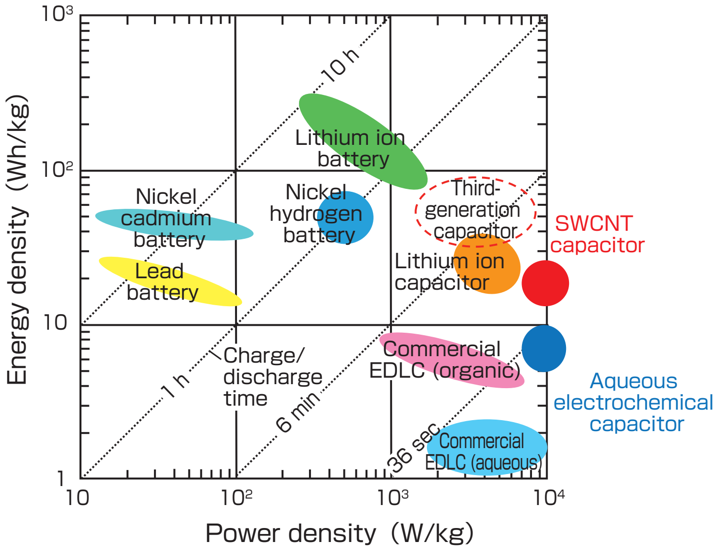


Fig. 3 Energy density and power density of various storage devices

3 Development of the aqueous electrochemical capacitor by hybrid nanocarbon electrode

3.1 R&D for potential technologies: ExCF and nitrogen-doped carbon

Carbon materials such as the activated carbon used for capacitor electrodes are low crystalline carbon materials that have undergone heat treatment at low temperature. The high crystalline carbon material (graphite material) that was high-temperature treated is expected to have superior conductivity and withstand voltage, but it is hard to obtain a wide surface area necessary for capacitor electrodes. Soneda *et al.* found that the exfoliated carbon fiber (ExCF) obtained by rapid pyrolysis after electrolyzing the graphitized carbon fiber possessed high crystallinity and a relatively large surface area, and showed characteristic behavior as a capacitor electrode material.[3][4] The capacitance of ExCF in the sulfuric acid electrolyte solution was twice the capacitance compared to activated carbon in diluted sulfuric acid, but increased rapidly with increased sulfuric acid concentration, and reached dozen times more in concentrated sulfuric acid (Fig. 4). Such large capacitance is considered to be a pseudo-capacitance effect due to the charge transfer interaction between the ExCF and sulfuric acid molecules.

On the other hand, Kodama *et al.* studied the template method to control the pore structure using the template to design porous electrodes for capacitors. In this process, they discovered that template carbon that contained nitrogen in the carbon structure showed high electric capacitance in the sulfuric acid electrolyte solution.[5][6] Particularly, the capacitance per surface area reached 1.2~2.2 F/m^2, and this was over 10 times that of activated carbon (Fig. 5). Such a high figure was not from storage by an ordinary electric double layer, but was considered to be the pseudocapacitance by the action of nitrogen atoms in the carbon skeleton. After this report, many studies were conducted on the capacitor property of the nitrogen-containing carbon prepared from various raw materials, and recently, there were new findings that the nitrogen doping of carbon electrode material increased the voltage withstand property of the capacitor using an organic electrolyte.[7]

3.2 Research strategy for the aqueous electrochemical capacitor development and the results

The capacitors can be categorized according to the type of electrolyte solution used: aqueous (operating voltage: ~1.2 V) and organic (operating voltage: ~2.7 V). For use in large electric storage, the organic capacitor is considered

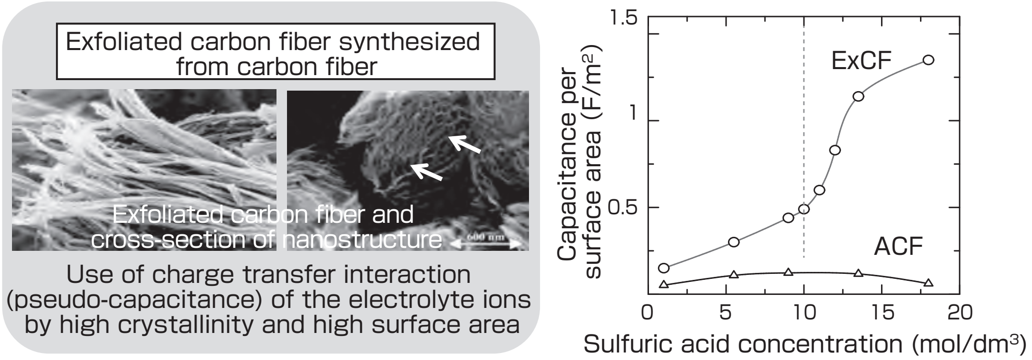
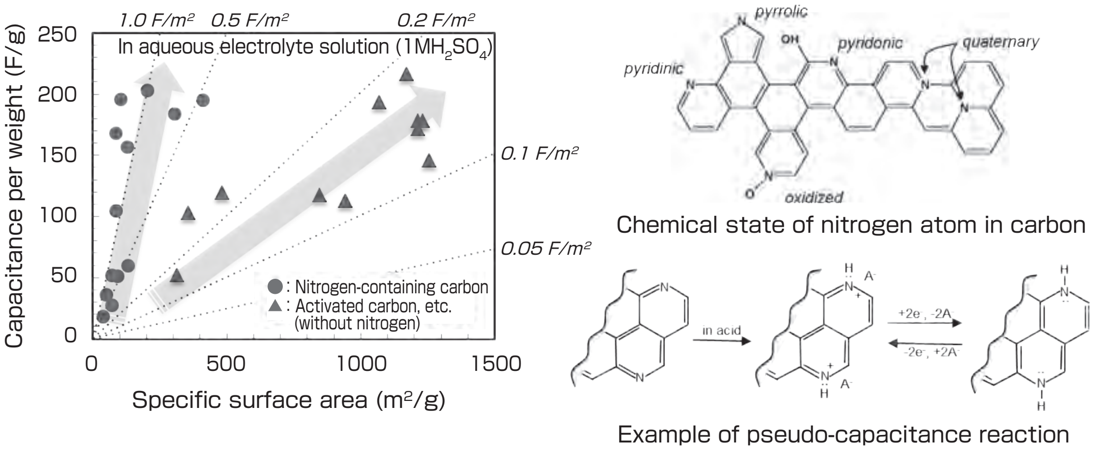


Fig. 4 Clarification of high capacitance occurrence mechanism in the sulfuric acid electrolyte solution by exfoliated carbon fiber



Chemical state of nitrogen atom in carbon

Example of pseudo-capacitance reaction

Fig. 5 Capacitor electrode property of the nitrogen-containing carbon and the occurrence mechanism of pseudo-capacitance

advantageous since it has high operating voltage and high capacitance. On the other hand, the aqueous capacitor, although it has low operating voltage, is known to be superior to the organic capacitor in almost all electric properties including internal resistance and frequency property, as well as the physical properties such as the operating temperature range.[8] Moreover, strict dehydration and sealing are required for the organic capacitor, since the electrolyte is highly water prohibitive, and as a result, the cost of the electrolyte solution dominates 40 % of the raw material cost. In contrast, in the aqueous capacitor, diluted sulfuric acid is used as the electrolyte solution, just as in the widely available lead batteries, and this is advantageous in terms of quality control, cost, as well as environmental control when considering the toxicity and flammability seen in many organic solvents. The aqueous capacitors with such excellent properties are expected to be used in small, high-output devices for the control systems of automobiles and energy management of mobile devices.

Although still in the basic research stage, it was found that the aforementioned nitrogen-doped carbon and ExCF did not loose the cycle property despite the pseudo-capacitance.[3][9] The NEDO R&D for the Practical Utilization of Nanotechnology and Advanced Materials "Development of the aqueous electrochemical supercapacitor by hybrid nanocarbon electrode" was started as joint research with carbon manufacturers and capacitor manufacturers.[10] As a result, by selecting the carbon fiber material, the capacitance of 500 F/g, which was unseen in conventional activated carbon (commercially available activated carbon for capacitors shows 100-200 F/g), was observed in the 40 % sulfuric acid electrolyte solution for ExCF. For the pseudo-capacitance by nitrogen doping, polymers that reacted similarly were developed to effectively cause the redox reaction as shown in Fig. 4. By coating the aforementioned ExCF with sufficient thickness, an extremely high energy density could be achieved for the aqueous capacitor. It was necessary to obtain a film at nanometer order considering the capacitance, diffusion resistance, and time constant of charge/discharge when using the polymers as the active material for pseudo-capacitance, and in principle, this was because ExCF had an appropriate structure as a supporting material, and ExCF itself possessed high capacitance that could not be attained earlier. Also, the fact that ExCF had high conductivity and polymer coating had high binding property, and therefore did not need a binder and an auxiliary conducting agent that were components that did not contribute to capacitance and were components of electrodes made of conventional activated carbon powder, helped increase the electrode capacitance. Further advances are expected in the future for hybrid carbon materials with such properties, and for the creation of practical devices and verification of their performance.

3.3 Commercialization of new porous carbon

In this project, the achievement of higher surface area of nitrogen-containing carbon was studied using magnesium oxide (MgO) as the template. The MgO method is a new method for synthesizing porous carbon materials by using low cost organic acid magnesium salts and polymers that are carbon precursors.[11] The aforementioned nitrogen-containing carbon was found to have extremely high capacitance per surface area, but the issue was how to increase the surface area. In this investigation, detailed knowledge and know-how were accumulated for the synthesis condition of porous carbon with abundant mesopores of 2 nm or more using magnesium citrate as the raw material. Toyo Tanso Co., Ltd., one of the companies that participated in the project, commercialized the "CNovel R" that is characterized by abundant fine pores categorized as mesopores (diameter 2~50 nm), as well as a large surface area equivalent to that of activated carbon.[12][13] Ordinary activated carbon has micropores, where the fine pore diameter is 2 nm or less, and mass transfer resistance inhibits the rapid charge/discharge of the capacitor. With CNovel R, it was found that mass transfer resistance was small, and it had an extremely excellent property as a capacitor for rapid charge/discharge. Until now, carbon materials with mesopores were synthesized by grams in a laboratory setting, but with the development of this method, the supply could be obtained by kilograms, and it is now being applied to wider use such as secondary batteries and fuel cell electrodes, other than capacitor electrodes. This is an excellent case where the material that could be used for various purposes was commercialized in an extremely short period as a spin-off from the core technology of *Type 2 Basic Research* for the capacitor electrode material development.

4 Development of the SWCNT

4.1 Development strategy of the carbon nanotube capacitor and the initial goal

Carbon nanotube is a fibrous material made by rolling and closing the hexagonal mesh sheet of carbon called the graphene into a hollow cylindrical shape without seams. As mentioned earlier, the electric quantity that can be stored in the electrode interface is, in principle, proportional to the surface area of the electrode surface. Since the theoretical surface area of one sheet of graphene is 2,630 m^2/g, the theoretical surface area of single-walled carbon nanotubes (SWCNT) that is made by rolling the sheet should be the same as the graphene, combining the exterior and interior walls of the tube. However, in multilayered carbon nanotubes where the cylindrical graphene is rolled concentrically, there will be planes where parts of graphene are in contact with each other, and the surface area will become smaller than the theoretical value because the electrolyte cannot reach such areas. Therefore, to achieve high energy density, it is important to obtain a nanostructure that maximizes the surface of the carbon nanotubes for charge storage.

On the other hand, power density is determined by the transfer resistance of the electron and ion in parts that comprise the cell. Since activated carbon is an aggregation of minute graphene layers and has nano-scale fine pores in its structure, it has a high surface area, but the transfer routes of the electron and ion in the particles are complex and the resistance is great. However, if the transfer route of the electron and ion can be controlled precisely by the nanostructure design where the individual SWCNTs are arranged in line, an electrode with ideally small charge transfer resistance of the electron and ion, or a capacitor with extremely small internal resistance can be achieved (Fig. 6).

Although SWCNT was expected to be good as a capacitor electrode material because it possessed high conductivity and high surface area, there were over 10 % of impurities such as catalyst metals and noncrystalline carbons in the synthesis stage, and it was not easy to make highly pure SWCNT in large volume. Coincidentally, a technology called the super growth method[14] that enabled the manufacture of extremely highly pure SWCNT at impurity concentration of several hundred ppm or less by weight was developed at the Nanocarbon Research Center, AIST. To create a high performance capacitor using the innovative materials and to aim for a synergetic effect of inducing mass production and low cost of SWCNTs, the Carbon Nanotube Capacitor Technology Development Project was started with the cooperation of two companies and AIST, and with Dr. Sumio Iijima of the Nanocarbon Research Center as the project leader. The main topics of this project were the mass production of the commercial level SWCNTs and the establishment of a manufacturing technology for a practical capacitor device that used the mass-produced SWCNTs as electrodes.

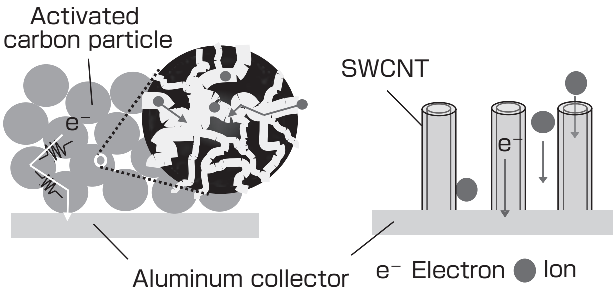


Fig. 6 Model structure of the SWCNT electrode that is vertically aligned with activated carbon electrode and the passageway of electrons and ions

4.2 Results achieved in the development of a practical capacitor device

In this project, the characteristic electrochemical property of SWCNT was clarified (Fig. 7).[15]-[17] Originally the electric capacitance arising from the electric double layer does not depend on voltage and is constant, while the SWCNT electrode increases in capacitance approximately proportional to the voltage. It is known that in SWCNTs, the electron structure becomes metallic or semiconductive depending on the chirality or the way graphene is rolled. The voltage dependency observed in SWCNTs arises from this unique electron structure, and can be explained as a phenomenon similar to the electrochemical doping of conductive polymers. It has been experimentally confirmed that the electroconductivity of the electrode sheet increased to 10 times or more since potential polarization occurs in the electrolyte through the injection of electrons and holes in the SWCNTs.[16] Moreover, with ordinary activated carbon electrodes, the upper limit of single cell voltage is 2.5~2.7 V, while with the electrode consisting only of highly pure SWCNTs, it has been found that sufficient durability is maintained even when operated at high voltage of over 3 V. This is thought to be because there is only an extremely small amount of contaminants such as functional groups or metal elements on the graphene surface that may promote the breakdown of the electrolyte solution. Since the energy density of the capacitor is proportional to the square of the charge voltage, this property is extremely important to increase the energy density.

The SWCNTs have the potential for high voltage operation when used as capacitor electrodes due to the structure where there are very few graphene terminals that may cause the breakdown of the electrolyte. The currently commercially available activated carbon electrode is made by kneading the powdered activated carbon particles with polymers called the binders and carbon black, an auxiliary conducting agent

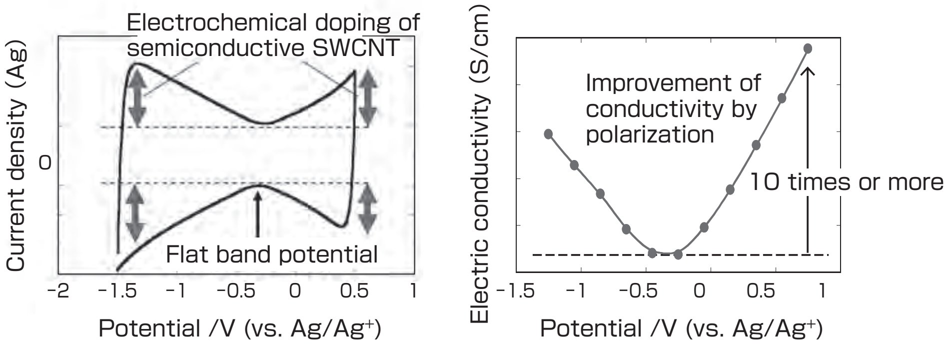


Fig. 7 Characteristic electrochemical property of the SWCNT

to reduce the contact resistance between the particles. These additives induce the breakdown of the electrolytes in high voltage conditions and inhibit increasing the energy density. In contrast, since SWCNT is fibrous, it requires no binder and can be made into a sheet in the manner of papermaking. Also, SWCNT made by the super growth method can be made into a flexible electrode sheet simply by pressing. The SWCNT itself is highly pure, and the SWCNT, itself an electrode active material, can gain 100 % electrode property on its own. Moreover, the project was successful in achieving the adhesive-free bonding of the SWCNT electrode sheet and the aluminum collector (Fig. 8).

In addition to the high voltage withstand property originally possessed by SWCNT and by avoiding the mixing and inclusion of the impurities that induce the breakdown of electrolytes under high voltage conditions, the SWCNT capacitor showed two to three times higher performance compared to the current activated carbon electrode in both energy density and power density. Moreover, the durability was over 15 years, and thereby the goal of the project was achieved.[18]

The SWCNT electrode that showed a vertical alignment as shown in Fig. 6 had an ideal structure to reduce the diffusion resistance of the ion and to maximize the power density, and the potential for the forming technology that can achieve such an electrode structure was found.[19] However, it was also found in this project that sufficient power density could be achieved by selecting the papermaking method or a simple pressing method, and it can be said that the success of device manufacturing was the selection of an electrode manufacturing method with high productivity from the perspective of practicality rather than an ideal structure.

With SWCNTs, generally, the tubes aggregate together to form a bundle structure, but when they are used as capacitor electrodes, the surface where the tubes are in contact with each other cannot be used for charge storage because the electrolyte ions cannot approach the outer surface of the SWCNT inside the bundle structure. We were aware of this point, and studied the method for releasing the bundles electrochemically, and verified this method in the commercially available SWCNTs that formed the bundle structure.[20] The SWCNTs manufactured by the super growth method were idiosyncratic products where most of the surface area could adsorb the materials. Similar to the aforementioned electrode formation technology by the papermaking method, it is important to have versatile manufacturing technology options in preparation of diverse SWCNT products, and this bundle releasing technology is considered to be one such option.

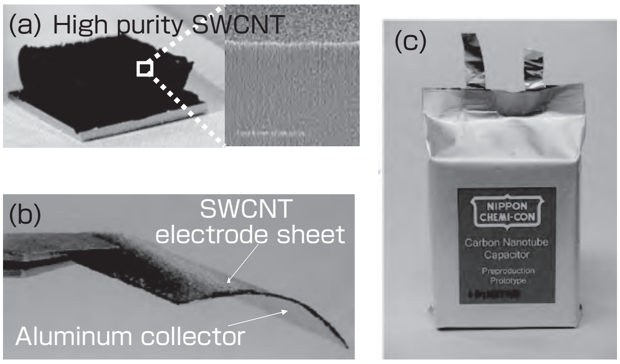


Fig. 8 Carbon nanotube capacitor
a) SWCNT that grows vertically on the substrate, b) SWCNT electrode sheet, and c) 1000 F class SWCNT capacitor.

The Carbon Nanotube Capacitor Technology Development Project ended in FY 2011 and was successful in manufacturing the SWCNT capacitor of 1,000 F level (Fig. 8). Moreover, the excellent conductivity and electrode forming properties were discovered for the SWCNT material, and direction of using the SWCNT for conductive and binding materials, not just as an electrode active material, was indicated. As a result, the development of an electrochemical capacitor in which the energy density was increased to 30 Wh/kg or more by compositing with nano-crystalline lithium titanate was successfully done.[18] At this point, the use of the expensive SWCNT could be decreased to about 15 %, and the device is expected to be adopted earlier for practical use.

4.3 Understanding the electrochemical property of the SWCNT and possibility of further increased capacitance

We propose that it is possible to increase the energy density of the carbon nanotube capacitor by utilizing the semiconductivity of the SWCNTs and by conducting the diameter and chirality control, based on the evaluation of the capacitor property by the metal semiconductor separation of the SWCNTs.[21] Comparing the storage behavior of EDLC where the charge storage at the electrode is proportional to the charge potential, and the storage behavior of the secondary battery where the charge storage occurs at constant voltage, the latter will have twice the energy density of the former in the electrode that can ultimately store the same charge capacitance. This means that the energy density of the device will double if we can optimally control the charge-discharge potential by conducting the electronic property control of the semiconductive SWCNT. However, since the diameter and chirality control of SWCNTs are technologies that add cost hurdles to the mass production technology, we must first see that SWCNTs can be mass produced and commercialized as metal-semiconductor mixtures, and hope that the SWCNT manufacturing technology will advance further in the next step.

5 Summary and future prospect

While new potentials are found for improving product performance through ever-evolving materials technology, recent development of electric storage technology progresses by mutual linkage from *Type 1 Basic Research* to *Product Realization Research*, as the devices and systems are constructed through the selection of fast moving technologies to meet the current social demand for practical application. Since there are diverse usages for storage devices, one way is to conduct development of a system that can handle lower performance or to compromise the usage due to cost concerns, instead of aiming for a high goal. Through the linkage of innovative materials such as carbon nanotubes and the practical outlet of developing an energy device, the researchers of wide ranging fields conducting *Type 1 Basic Research* engaged in the research of electrode materials with renewed desire for development. Also, from the *Type 2 Basic Research* that headed for the outlet of developing a capacitor, a material with wide application and versatility was discovered. As seen in the commercialization of the porous carbon made by the MgO template method, there is expectation for the birth of products other than capacitors from the spin-off of material technology.

With carbon nanotube capacitors, the excellent capability of SWCNTs was verified at the actual device level, and the various technological options needed for its manufacture is being accumulated. However, in the world of practical electrode materials, several thousand yen per kg is even considered expensive, and it cannot be denied that SWCNT is still expensive, and the expansion of the market including other uses and time are necessary. Carbon fiber, which is the same fibrous carbon and for which an industrial manufacturing method was invented by a Japanese, grew into an industry in which the Japanese company dominates about 70 % of the world share.[22] Currently, it is used as structural material of aircrafts and strengthening material for buildings. Now the price of general-purpose products has decreased to the level of several thousand yen per kg, but it was about 100,000 yen/kg at the beginning of its commercialization. Looking at the history of carbon fiber that proved that a truly excellent material could overcome the economic valley of death, we hope that the nanocarbon material with excellent characteristics will be commercialized for a wide range of fields starting with the capacitor electrode material.

Acknowledgements

The development of the aqueous electrochemical capacitor was conducted in the NEDO (New Energy and Industrial Technology Development Organization) R&D for the Practical Utilization of Nanotechnology and Advanced Materials “Development of the aqueous electrochemical supercapacitor by hybrid nanocarbon electrode” (FY 2008~2011). We are grateful to the people who engaged in the joint research at Oita University, Toyo Tanso Co., Ltd., and NEC Tokin Corporation. The development of the carbon nanotube capacitor was conducted in the NEDO Energy Innovation Program “Development of the carbon nanotube capacitor” (FY 2006~2010). We are grateful to all the people of the companies, universities, and AIST that participated in the joint research, particularly to the people of Nippon Chemi-Con Corporation.

References

[1] Y. Matsuda, T. Osaka and Y. Sato (eds.): *Kyapashita Benran* (Capacitor Handbook), Maruzen (2009) (in Japanese).

[2] K. Tamamitsu, S. Suematsu and S. Ishimoto: Daiyoryo kyapashita no kaihatsu (Development of large capacitors), *Tanso Sogenryo Kagaku To Zairyo Sekkei X* (Carbon Raw Material Science and Material Design No. X), CPC Society, 64-73 (2008) (in Japanese).

[3] Y. Soneda, M. Toyoda, K. Hashiya, J. Yamashita, M. Kodama, H. Hatori and M. Inagaki: Huge electrochemical capacitance of exfoliated carbon fibers, *Carbon*, 41, 2680-2682 (2003).

[4] Y. Soneda, J. Yamashita, M. Kodama, H. Hatori, M. Toyoda and M. Inagaki: Pseudo-capacitance on exfoliated carbon fiber in sulfuric acid electrolyte, *Appl. Phys. A*, 82 (4), 575-578 (2006).

[5] M. Kodama, J. Yamashita, Y. Soneda, H. Hatori, S. Nishimura and K. Kamegawa: Structural characterization and electric double layer capacitance of template carbons, *Mat. Sci. Engineer. B*, 108, 156-161 (2004).

[6] D. Hulicova, J. Yamashita, Y. Soneda, H. Hatori and M. Kodama: Supercapacitors prepared from melamine-based carbon, *Chem. Mater.*, 17 (5), 1241-1247 (2005).

[7] S. Shiraishi: Heat-treatment and nitrogen-doping of activated carbons for high voltage operation of electric double layer capacitor, *Key Eng. Mat.*, 497, 80-86 (2012).

[8] M. Ue: Denkaishitsu zairyo (Electrolyte material), *Daiyoryo Kyapashita Gijutsu To Zairyo: Denki Nijuso Kyapashita To Urutora kyapashita No Saishin Doko* (Technology and Material of Large Supercapacitors: Latest Trend in EDLC and Ultracapacitor) [A. Nishino and K. Naoi (eds.)], Ch. 9, CMC Publishing (1998) (in Japanese).

[9] D. Hulicova-Jurcakova, M. Kodama, S. Shiraishi, H. Hatori, Z.H. Zhu and G.Q. Lu: Nitrogen-Enriched Nonporous Carbon Electrodes with Extraordinary Supercapacitance, *Adv. Funct. Mat.*,19 (11), 1800-1809 (2009).

[10] FY 2008~2011 Research Report: R&D for the Practical Utilization of Nanotechnology and Advanced Materials “Development of the aqueous electrochemical supercapacitor by hybrid nanocarbon electrode,” NEDO Research Report Database No. 20120000000874 (in Japanese)

[11] T. Morishita, Y. Soneda, T. Tsumura and M. Inagaki: Preparation of porous carbons from thermoplastic precursors and their performance for electric double layer capacitors, *Carbon*, 44 (12), 2360-2367 (2006).

[12] T. Morishita: Fabrication of porous carbon using the carbon coating process and its performance, *Tanso Zairyo No Kenkyu Kaihatsu Doko 2012* (R&D Trend in Carbon Materials), CPC Society, 90-99 (2012) (in Japanese).

[13] http://www.toyotanso.co.jp/Products/Newly_developed_Porous_carbon.html

[14] K. Hata, D. Futaba, K. Mizuno, T. Namai, M. Yumura and S. Iijima: Water-assisted highly efficient synthesis of impurity-free single-walled carbon nanotubes, *Science*, 306, 1362-1364 (2004).

[15] S. Suematsu, K. Machida, K. Tamamitsu and H. Hatori: Development of super growth carbon nanotube (SG-SWCNT) capacitor, *Electrochemistry*, 75 (4), 374-379 (2007)

(in Japanese).
[16] O. Kimizuka, O. Tanaike, J. Yamashita, T. Hiraoka, D. N. Futaba, K. Hata, K. Machida, S. Suematsu, K. Tamamitsu, S. Saeki, Y. Yamada and H. Hatori: Electrochemical doping of pure single-walled carbon nanotubes used as supercapacitor electrodes, *Carbon*, 46 (14), 1999-2001 (2008).
[17] Y. Yamada, O. Kimizuka, K. Machida, S. Suematsu, K. Tamamitsu, S. Saeki, Y. Yamada, N. Yoshizawa, O. Tanaike, J. Yamashita, D. N. Futaba, K. Hata and H. Hatori: Hole opening of carbon nanotubes and their capacitor performance, *Energy Fuels*, 24, 3373-3377 (2010).
[18] NEDO: "Carbon Nanotube Capacitor Development Project" Post Project Evaluation Material (2012) (in Japanese). http://www.nedo.go.jp/introducing/iinkai/kenkyuu_bunkakai_23h_jigo_10_1_index.html
[19] D. N. Futaba, K. Hata, T. Yamada, T. Hiraoka, Y. Hayamizu, Y. Kakudate, O. Tanaike, H. Hatori, M. Yumura and S. Iijima: Shape-engineerable and highly densely packed single-walled carbon nanotubes and their application as super-capacitor electrodes, *Nat. Mater.*, 5 (12), 987-994 (2006).
[20] O. Tanaike, O. Kimizuka, N. Yoshizawa, K. Yamada, X. Wang, H. Hatori and M. Toyoda: Debundling of SWCNTs through a simple intercalation technique, *Electrochem. Commun.*, 11 (7), 1441-1444 (2009).
[21] Y. Yamada, T. Tanaka, K. Machida, S. Suematsu, K. Tamamitsu, H. Kataura and H. Hatori: Electrochemical behavior of metallic and semiconducting single-wall carbon nanotubes for electric double-layer capacitor, *Carbon*, 50 (3), 1422-1424 (2012).
[22] O. Nakamura, T. Ohana, M. Tazawa, S. Yokota, W. Shinoda, O. Nakamura and J. Itoh: Study on the PAN carbon-fiber-innovation for modeling a successful R&D management: An excited-oscillation management model, *Synthesiology*, 2 (2), 159-169 (2009) (in Japanese) [*Synthesiology English edition*, 2 (2), 154-164 (2009)].

Authors

Hiroaki HATORI

Completed the courses at the Graduate School of Science and Engineering, Tsukuba University in 1989. Joined the National Research Institute for Pollution and Resources, Agency for Industrial Science and Technology, Ministry of International Trade and Industry in 1989. After working as the Leader of the Energy Storage Material Group, Energy Technology Research Institute, AIST, became Principal Research Manager from 2012. In this paper, reviewed the technological development of creating a device from the SWCNT capacitor from a synthesiological perspective, and supervised the entire investigation.

Osamu TANAIKE

Completed the doctor's course at the Graduate School of Engineering, Hokkaido University in 1998. Doctor (Engineering). After working as post-doc researcher and NEDO Fellowship Training Program engineer, joined AIST in 2005. Currently, Senior Researcher, Energy Storage Material Group, Energy Technology Research Institute, AIST. In this R&D, was mainly in charge of the clarification of electrochemical property of carbon nanotube and its advancement as electrode material.

Yasushi SONEDA

Completed the doctor's course at the Graduate School of Engineering, Hokkaido University in 1993. Doctor (Engineering). Joined the National Research Institute for Resources and Environment, Agency for Industrial Science and Technology, Ministry of International Trade and Industry in 1993. Currently, Senior Researcher, Energy Storage Material Group, Energy Technology Research Institute, AIST. In this R&D, was mainly in charge of the development of the aqueous electrochemical capacitor using the exfoliated carbon fiber and MgO template carbon.

Masaya KODAMA

Completed the doctor's course at the Graduate School of Science, Tokyo University of Science in 1990. Joined the Government Industrial Research Institute, Kyushu, Agency for Industrial Science and Technology, Ministry of International Trade and Industry in 1990. Worked at the Energy Storage Material Group, Energy Technology Research Institute, AIST; and currently, Senior Planning Manager, Planning Division, Research and Innovation Promotion Headquarters, AIST. In this R&D, was mainly in charge of the development of aqueous electrochemical capacitor using nitrogen-doped carbon.

Discussions with Reviewers

1 Carbon nanotube capacitor

Question (Shuji Abe, Evaluation Department, AIST)

When creating a fine nanostructure like carbon nanotubes, it is obvious from the beginning that it will be more expensive compared to activated carbon, and the situation has not changed now even though we have advanced the mass production technology. I think the significance of the carbon nanotube development project is to actually present the potential of the carbon nanotube property, and to lead and induce mass production. How do you view such a research strategy?

Answer (Hiroaki Hatori)

Of the material cost, as you indicated, there was a concern from the beginning of the development. The R&D was conducted by assuming how much competitiveness can be gained against the current material by cost reduction due to the mass production of carbon nanotubes and by material cost reduction due to the improvement of the capacitor performance, and several options were kept at all times to attain realistic specs. As explained in the final paragraph of subchapter 4.2, through the design that is equivalent to the redox capacitor of Table 1, the development of device that required less amount of carbon nanotubes was conducted in the same R&D project, and a high performance was verified for the energy density.

In view of cost reduction of carbon nanotubes, unless the demand rises dramatically and the production technology improves, it is not possible to achieve. Therefore, it is explained at the end of subchapter 4.1 that one of the objectives of the R&D was the induction of mass production and commercialization of the SWCNTs through performance verification of the high-performance capacitor. For material cost and a path to commercialization, the example of carbon fiber is given at the end of "5 Summary and future prospect." Although carbon fiber is currently gaining attention as a structural material that may replace iron, it took 20 years from patent to use in niche products such as sporting goods, and 20 more years were necessary before it was used as a structural material that has the prospect of heavy demand. When considering SWCNTs as storage parts that demand prices at the level of general-purpose products, the history of the commercialization of carbon fiber is instructive. Since the carbon fiber R&D strategy has been analyzed in *Synthesiology*, I added this article as a reference.

2 R&D model (Fig. 1)

Question (Shuji Abe)

In "Fig. 1 R&D model," the "potential for new material (*Type 1 Basic Research*)" on the top right seems to indicate the SWCNT research. What specifically do you mean by the "discovery of new functions" on the arrow that leads from there?

Answer (Hiroaki Hatori)

Seen from the perspective of capacitor electrode material, the mass synthesis method of carbon nanotubes by the super growth method can be positioned as *Type 1 Basic Research*. The discovered "new functions" are the electrochemical properties that were found in the initial experiments: 1) high surface area due to the unique aggregate structure obtained in manufacturing, 2) potential dependency (as a result, more electricity can be stored in the limited potential window), and 3) capability of charge/discharge at high voltage. At the point when this R&D was started, 1) was written in the patent as a property expected of SWCNT as capacitor electrode but was not experimentally verified, and there were no scientific evidences for 2) or 3) in the academic papers or patents.

3 Aqueous capacitor

Question (Yasuo Hasegawa, AIST)

Compared with the conventional organic capacitor, what kind of characteristic does the newly developed aqueous capacitor have, and what are the expected fields of application?

Answer (Yasushi Soneda)

Although the electrochemical capacitor is a high-output, low-capacitance storage device compared to the conventional secondary battery, the device is designed according to actual usage such as high-output, high-capacitance, or somewhere-in-between capacitors. When pursuing the extreme limit of performance in the high-output type, the aqueous capacitor with a highly conductive electrolyte is more appropriate than the organic capacitor. Also, for the temperature property that is important in automobiles, the aqueous type is superior in both high and low temperatures than the general organic electrolyte. In terms of environmental load, the diluted sulfuric acid used in aqueous electrolyte solution is widely accepted, as seen in the diffusion of the lead battery, but some of the organic electrolytes may be toxic or dangerous when burnt, and there are different attitudes for their use in Japan and overseas.

There is a strong demand that small, substrate-implemented capacitors used in mobile devices have small environmental load and low cost, because the individual device cannot be recovered. The aqueous capacitor is also advantageous in these points.