VAPOR-GROWN CARBON FIBER AND NEW FORMS OF CARBONS FOR ELECTRIC ENERGY STORAGE APPLICATIONS AS A PIONEER IN THE 21ST CENTURY

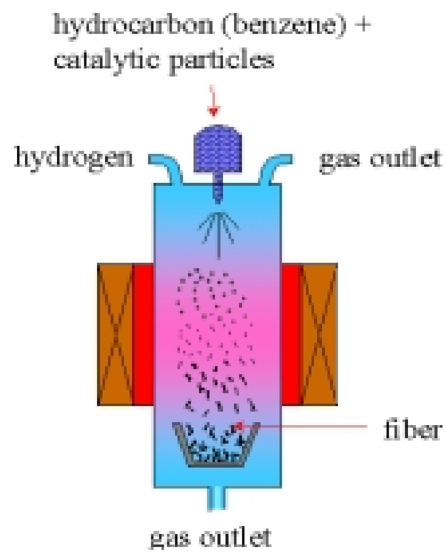
Morinobu Endo
Faculty of Engineering, Shinshu University, 4-17-1 Wakasato,
Nagano-shi 380-8553, Japan

Introduction

For many years, unique features of carbon materials such as excellent electrical and thermal conductivities, low density, high purity, low thermal expansion have made them applicable in various electric energy storage systems. Additionally, many types of carbon materials such as powders, fibers, solid and porous materials can be obtained at relatively low cost. In terms of microstructure, all carbon materials, except diamonds, contain the basic structural unit that is consisting of the hexagonal carbon layer. The extent and stacking arrangements of these layers induce the diversity of carbon materials. In this study, practical applications of carbon materials in electric energy storage systems will be described in relation with macro-morphology, microstructure and nano-structure. Firstly, vapor-grown carbon fibers (VGCFs) obtained by floating reactant method are characterized, and also evaluated as an additive to anode material in LIB and EDLC systems. Secondly, various carbon materials, in the range from highly graphitic carbons (mesophase pitch based graphite fiber) to highly disordered carbons (PPP-based carbon), as anode materials in Li-ion secondary battery (LIB) will be mentioned comparatively in relation with intercalation and de-intercalation of Li ions or doping and undoping mechanism. Thirdly, the variation of specific capacitance in electric double layer capacitor (EDLC) was evaluated as a function of starting materials and activation method based on surface structure of carbon materials. A new pore characterization method will be shown on the basis of TEM image analysis. Fourthly, substituted boron in the lattice observed by scanning tunneling microscopy will be mentioned, which could be future technology to tailor the hexagonal carbon system in order to control the basic properties in nano-scale. Finally, I will consider possible direction of carbon materials in energy storage systems in the near future.

Vapor-grown Carbon Fibers (VGCFs)

The development of the floating reactant method (Fig. 1) allows a three-dimensional dispersion of the hydrocarbon together with the catalytic particles, resulting in a high yield and a rather uniform diameter of the fibers (Fig. 2 (a) and (b)). Hydrocarbon decomposition takes place on the catalytic particle, leading to continuous carbon uptake



by the catalytic particle and continuous output by the particle of well-organized tubular filaments of the carbon honeycomb lattice (Fig. 3). As a result, the success of mass production by using floating reactant method has spurred research for the application of these fibers in various fields [1]. Combining effects in its excellent physical properties of these fibers and low production costs promise to enable production cost reductions for industrial applications. High degree of graphitizability, high surface to volume ratio, specific electric, mechanical and chemical properties caused by small

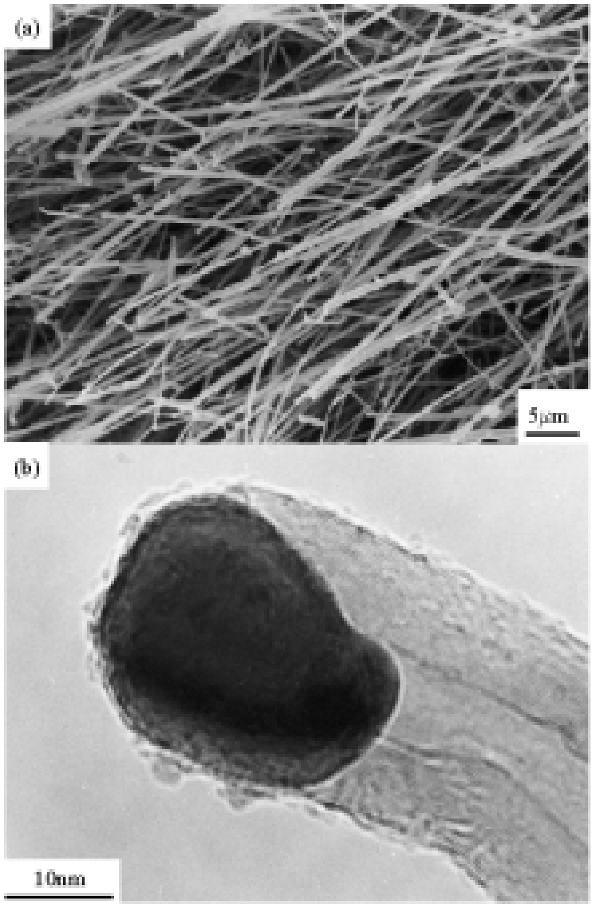


Figure 2. (a) FE-SEM of VGCFs and (b) TEM images showing early stage of growth in the floating reactant method.

diameter, and characteristic structure make these fibers potentially useful for various electrochemical fields. Electrochemical application such as the anode material itself or additive in lithium-ion battery system, and the electrode in double layer capacitor will be presented by exploiting their excellent properties of these fibers above

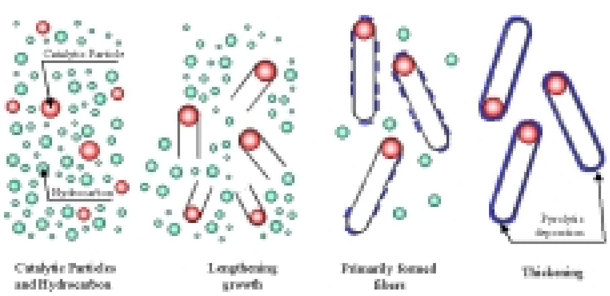


Figure 3. Suggested growth mechanism of thin VGCFs in floating reactant method

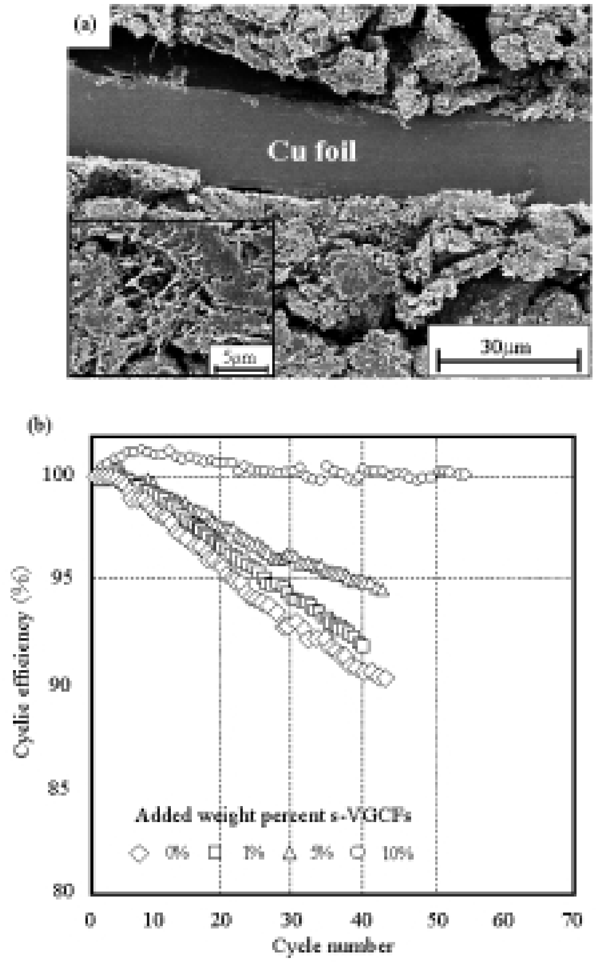
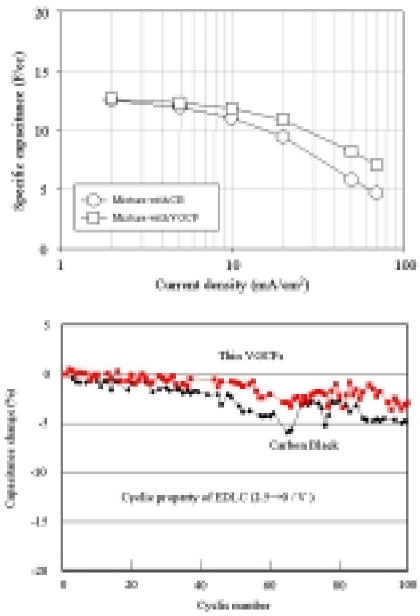


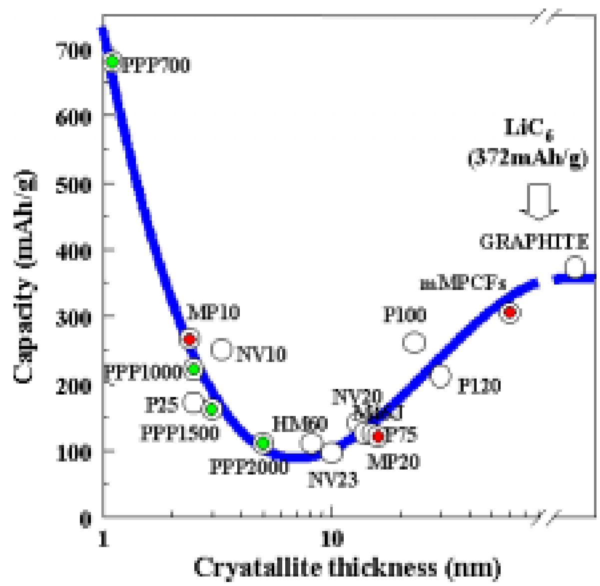
Figure 4. (a) Practical anode cell containing thin VGCFs, (b) cyclic characteristic of synthetic graphite as a function of added weight percent of thin VGCFs.

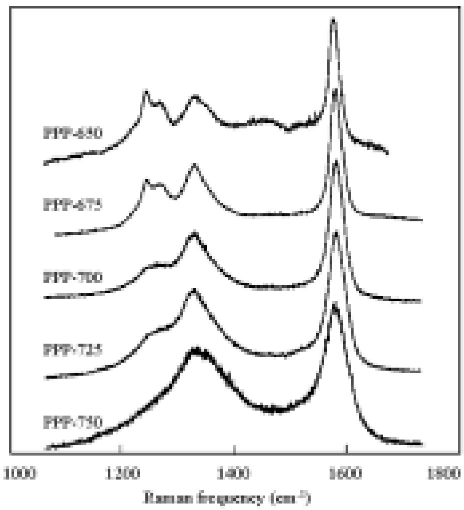
mentioned, to interconnect the performance with nano-structure including size effects. VGCFs showed prominent performance not only as anode material itself but also as the additive in the electrode of Li-ion battery system [2]. FE-SEM image of practical anode electrode containing 10wt.% of graphitized thin VGCFs by floating reactant method (diameter: 0.1-0.2μm) as additive shows homogeneous distribution of fibers in synthetic graphite (Fig 4 (a)). Figure 4 (b) shows the cyclic efficiency of a synthetic graphite (HTT=2900) anode as a function of weight percent of graphitized thin VGCFs added. By increasing weight percent of graphitized thin VGCFs, the cyclic efficiencies of the synthetic graphite anode increase continuously, and in particular when 10wt.% of the thin VGCFs was added, the cyclic efficiency was maintained at almost 100% up to 50 cycles. At higher concentrations, the thin VGCFs interconnect graphite



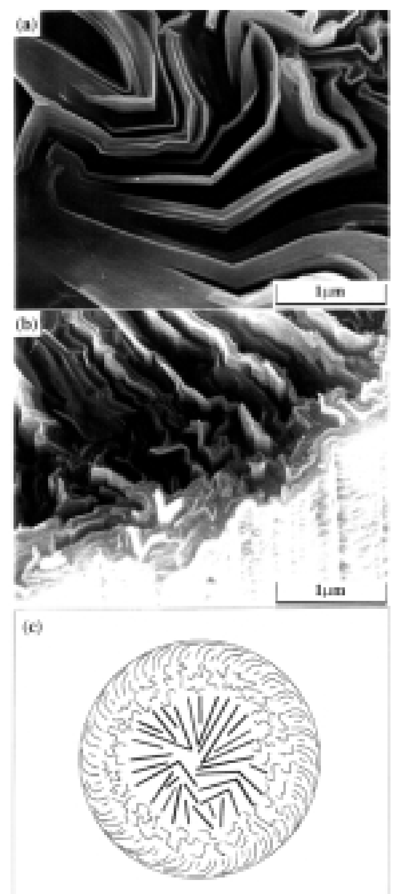
powder particles together to form a continuous conductive network. When applied this fiber as an additive in the electrode of double layer capacitor (EDLC), improved capacity, especially, at higher current density (Fig. 5 (a)), enhanced cycle characteristics (Fig. 5 (b)) indicate that resistance property of electrode has improved through network formation as compared with those of carbon black. This system will be very promising for EV (electric vehicle) and also for fuel cell EV. We can summarize the desirable characteristics of this fiber for use as the additive, especially in the electrode of Li-ion batteries as follows: (a) the small diameter of the fiber makes it possible to distribute the fibers homogeneously in the thin electrode material and to introduce a larger surface area to react with the electrolyte. (b) The improved electrical conductivity of the electrode is related to the high electrical conductivity of the fiber itself, and the network formation of the fibers with the graphite particles in the anode to form a fiber-mat. (c) In contrast to conventional whiskers, the relatively high intercalation ability of this fiber doesn't deteriorate the capacity of anode material itself upon cycling. (d) High flexibility of the electrode is achieved due to the network formation of the fiber in a fiber-mat structure with high mechanical properties. (e) High endurance of the electrode because this fiber absorb the stress caused by intercalation of Li-ions. (f) Improved penetrability of the electrolyte due to the homogeneous distribution of the fibers surrounding the anode material. (g) As compared with that of carbon black, the cycle efficiency of the Li-ion battery was improved for a relatively long cycle time. In the near future, the application of this fiber as a filler material in various electrochemical systems is expected to become widespread due to the excellent properties of the VGCFs, especially, for applications where improved conductivity is needed.

Lithium storage of carbon materials





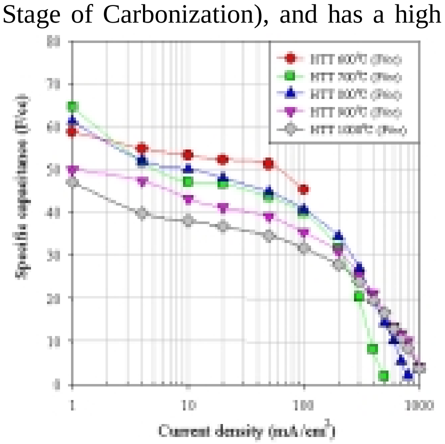
Various types of carbonaceous materials have been investigated experimentally and theoretically as the potential anode materials ranging from highly ordered graphite to disordered carbons. Researches have been focused to improve the specific capacity, cyclic efficiency and the cyclic lifetime as the secondary energy storage devices. For anode material of lithium ion batteries the microstructure and morphologies must be controlled for used in practical devices. It has been well known that the performances of lithium ion batteries depend strongly on the thermal history and morphology of carbon and graphite materials used for the anode. And much effort has been paid to identify the key parameters of carbon and graphite for the battery [3-5]. Because carbon and graphite materials have large variety in their microstructure, texture, crystallinity and morphology, it has been important to design and choose the anode material from wide variety in order to get better battery performances. Typical two types of carbon materials, highly ordered graphite heat-treated at high temperature as 3000^{o}C and non-graphitizable carbon heat-treated at low temperatures as 1000^{o}C, have been used in anode for present commercial batteries. Figure 6 shows the second cycle charge capacity as a function of crystal thickness, L_c, on various kinds of carbon fiber, and heat-treated polyparaphenylene (PPP)-based carbon electrodes. PPP is one of the conductive polymer and produced by Kovacic method. Well-ordered graphites (L_c>20nm) and low crystalline materials (L_c<3nm) have a larger capacity. However, intermediate crystallite sizes (~10nm) possess minimum capacity. The extremely enhanced charge capacity in PPP-700 can be explained by unique microstructure [6]. Raman spectra were taken for samples heat-treated from 650 to 750^{o}C in increment of T_{HT} = 25^{o}C. Figure 7 displays the results of these scans, revealing a detailed peak profile which quickly evolves over the given temperature range. The lines at 1240cm^{-1} and 1330cm^{-1} imply the presence of regions in the sample with a quinoid-like structure produced by the introduction of defects states through heat-treatment. And also the lines near 1218cm^{-1} and 1270 cm^{-1} could be due to benzenoid PPP peak remnants, which appears slightly downshifted. As a result, Raman analysis suggests that, at a THT of 700^{o}C, the PPP samples are only partially carbonized and show the signature of a highly disordered quinoid-like PPP structure. And also, relatively high capacity and low polarization of milled mesophase pitch graphite fiber is attributed to specific morphology of fibers, that is, bamboo shoot structure (Fig. 8) [7]. In terms of scientific view, the insertion behaviors and



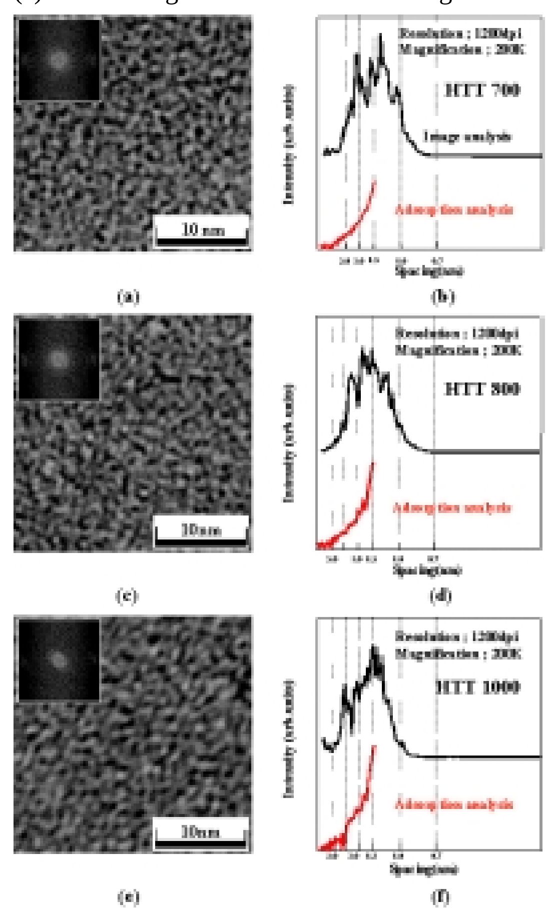
mechanism of lithium ions into various kinds of carbon and graphite hosts have been extensively studied both experimentally and theoretically based on GIC science. In particular, the lithium insertion mechanism and electrochemical properties in low temperature carbons unlike the case of well-ordered graphite are not yet fully understood as described before, and the perfect analysis is indispensable for the practical uses. The low temperature forms of carbon might be very promising for next following stage of Li ion battery because of their superior capacity for electric vehicles. And also the low temperature forms of carbons are expected from electric energy saving view point for anode production, since graphite materials for anode application heat-treated at around 3000^{o}C has become already as big as about 2500 ton/year. And also, scientific as well as technical accumulation have developed an advanced Li ion battery such as polymer type thin card battery, already started on the market and also for future full electric vehicle (EV) applications.

Carbon electrode for EDLC electrode

Recently, extensive studies of various carbon materials such as activated carbon, activated carbon fiber and other types of carbons, for high energy density EDLC for use in electric vehicles or hybrid vehicles drivelines have been performed eagerly. Generally, activated carbon materials have been prepared by activating process. On the other hand, PVDC-derived carbon materials showed a well-defined pore size distribution without activating process [8]. This material was named as VESC (Very Early Stage of Carbonization), and has a high potential



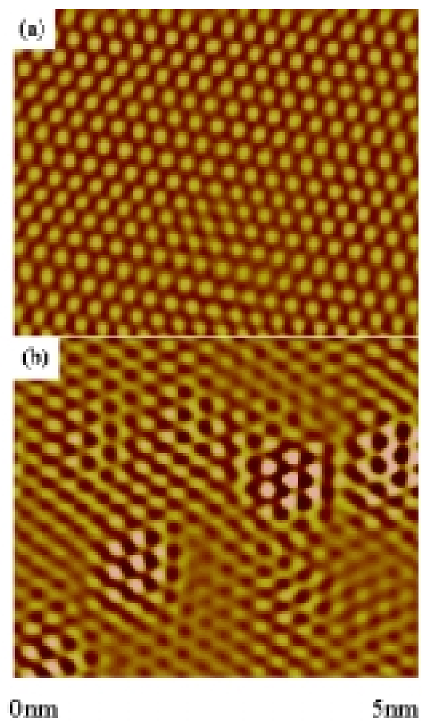
for aqueous EDLC. They showed a high specific capacitance as compared with those of conventional activated carbons such as carbon char. Figure 9 shows the specific capacitance per unit volume (F/cc) as a function of the output current density for various VESC bulk electrodes. The specific capacitance for each sample is observed to decrease with increasing current density. The higher the heat treatment temperature, the better is the maintenance of the specific capacitance with increasing current density. The present performance is very much promising as a high power capacitor applicable for HEV or EV and electricity load conditions. In order to investigate the relation between the pore size distribution (PSD) and the specific capacitance, novel method by image analysis for TEM image was used. Figure 10 (a), (c), (e) shows high-resolution TEM image and the



corresponding pore size distributions of PVDC-base carbon samples, VESC, in comparison to the PSD obtained from the adsorption isotherms. The results show the existence of large numbers of nano-pores with diameters less than 1nm. Figure 10 (b), (d), (f) show the PSD obtained by image analysis of the TEM pictures, using the corresponding FFT patterns for each photographs. In this figure, it is shown that the pore size is shifted toward larger sizes with increasing HTT, and that the dominant pore sizes are less than 1.5 nm for all three cases. The pore size distributions obtained by image analysis are quite consistent with those of the N_2 adsorption isotherms. PVDC-based carbon has a porous structure with a proper pore-size distribution, which could be more suitable for EDLC applications. The results for capacitance measurements as a function of SSA for various AC/ACF and carbonized PVDC indicate that the PVDC-based electrodes show a higher capacitance than those of commercial AC/ACF materials. These PVDC-based carbon electrode samples, having a much smaller specific surface area than those of typical ACF/AC (~2000m^2/g), but nevertheless show a two times higher specific capacitance. A carbonized PVDC electrode dominated by ultra micro-pores less than 10 Å in size without using any activation process. The present PVDC-based carbons exhibit an especially suitable pore size and pore size distribution with a higher bulk density that induces a high specific capacitance. It is further possible to develop large-scale capacitor production using present PVDC-based polarizable carbons, and the homogeneous structure and properties attainable in these electrodes configuration could contribute to large-scale series and parallel connections of such as unit cells, for not only aqueous cell but also for organic EDLC.

Substitution of boron atoms in the lattice of graphite

During the heat treatment of highly oriented pyrolytic graphite (HOPG) in the presence of B_4C in the graphitization temperature range, boron atoms can be substituted for carbon atoms in the basal hexagonal plane of HOPG. Scanning tunneling microscope (STM) images clarify the substitution of boron atoms into the basal plane of HOPG. It is possible to observe that boron is substituted for carbon atoms in the boron-doped HOPG through the bright areas (ca. 1 nm diameter) of high electron density revealed in the STM image of the basal plane of boron-doped HOPG (Fig. 11). The closest distance between carbon atoms in the STM image of graphite is 0.246 nm. In comparison, the corresponding STM distance between boron and carbon atoms is 0.276 nm. Therefore, this result indicates that the substituted boron might be located at a slightly higher position than the surrounding carbon atoms in the basal plane of HOPG. It is clear from STM that the substitution of boron atoms enlarges some interlayer defects or introduces disorder into the graphene layers on the surface of HOPG. Molecular orbital calculations reveal that the boron-doped site in a graphene sheet has a high electron density, in agreement with STM results. These results can contribute to emphasize the performances of the Li ion battery as well as to control the hexagonal carbon nature in order to modify the electronic properties in sense of tailoring the carbon networks.



Future prospect of carbon materials for energy storage applications

It is not the overstatement that the success of the Li ion batteries is contributed from GIC as well as carbon sciences achieved up to the beginning of 1990's. They had been able to provide the designed anode materials for the battery. Enhancement of the battery performances and cost reduction have been also achieved in past 8 years since commercialization, and now further improvements in performances of the battery is demanding for future development. On the low temperature forms of carbons with high excess capacity than Li_6, elucidation of the storage mechanism of Li and improvement on the irreversible capacity are important keys. And further researches on carbonization and graphitization conditions of new starting materials as well as some additives such as B, N and P involving mechanical treatment will be required. A remarkable improvement in Li ion battery will be progressed in the future to approach the Li metal itself, but carbon and graphite such as low crystalline carbons can expect the higher capacity. The expectation for carbon and graphite as anode materials should be strengthened more and more from now on. For the above, the carbon and graphite will be greatly able to contribute to further development of Li ion batteries for soon coming the second generation of the Li ion battery, and also on surged EDLC system. High performance electric energy storage device will be requested more strongly in the coming 21 century of IT, energy and environmental ages.

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