UDC 621 . 3 . 035 . 2 : 621 . 355

# Development of Anode Materials for Lithium Secondary Battery

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## Abstract

***A new graphite material, Granode Type-H, having a high capacity and other excellent properties as the anode material of lithium secondary battery was developed through graphitization of a raw material, i.e. pitch coke carbon added with a boron compound. Fundamental studies leading to the material design of the new graphite product were carried out and the basic characteristics and performance with those of conventional graphite materials were compared. Superior properties of the new material were confirmed in the comparison, such as high anodic performance in an electrolyte containing propylene carbonate in the solvent, which markedly deteriorates performance of conventional materials, besides excellent discharge capacity, rate characteristics, press formability, etc.***

## 1. Introduction

With the rapid development of small portable equipment, like cellular phones and notebook personal computers (PCs), in recent years, the production of lithium secondary batteries (batteries that can be charged and used repeatedly) has dramatically grown as power supplies for the portable devices. This is because lithium secondary batteries are higher in electric capacity in mA per unit weight and volume than conventional secondary batteries like nickel-cadmium (Ni-Cd) and nickel-hydrogen batteries, and they feature a high operating voltage of 3.6 V. In addition to the power supplies for small portable equipment, lithium secondary batteries are expected to find applications in potential markets like larger power supplies for automobiles, for example. The operating principle of lithium secondary batteries is shown in **Fig. 1**, and its construction is schematically illustrated in **Fig. 2**. This report gives an overview of a new lithium secondary battery active anode material developed by Nippon Steel, and especially describes its material design considerations and basic properties.

**Cell reaction equation** $Li_1CoO_2 + C \rightleftarrows Li_{1-x}CoO_2 + Li_xC$

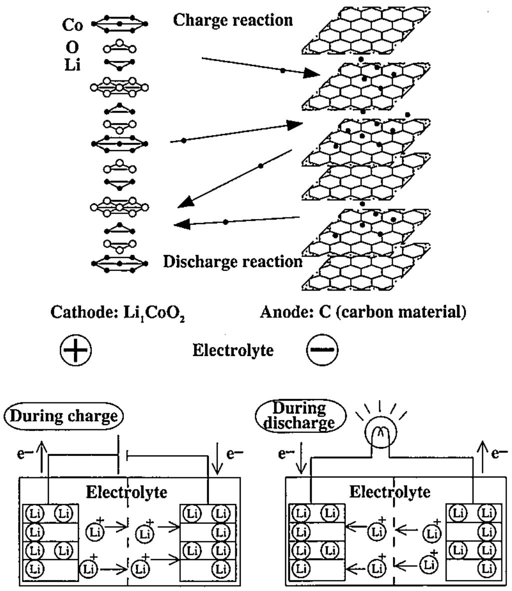

**Fig. 1 Operating principle of lithium secondary battery**

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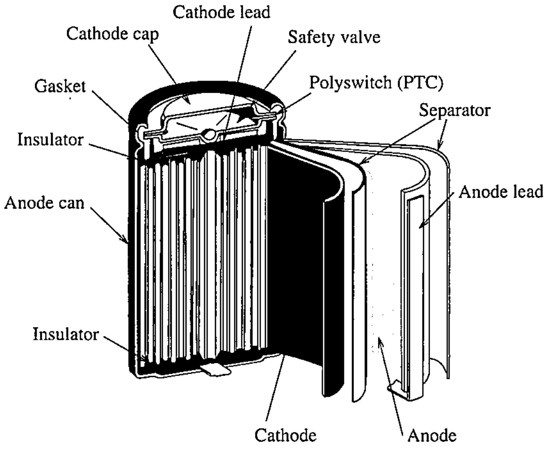

**Fig. 2 Construction of lithium secondary battery (cylindrical type)**

## 2. Present Situations of Lithium Secondary Batteries and Anode Materials

The lithium secondary batteries have a high electric capacity as already described. In the lithium secondary battery history of about 10 years, the battery capacity has increased about 1.7 times, mainly due to battery structure improvements and anode material capacity enhancements. In the reaction schematic diagram of Fig. 1, the reaction amount of reversible intercalated lithium ion into anode and cathode materials corresponds to the electric capacity. In terms of battery manufacturing technology, the battery capacity has been increased by improving the cell structure, or increasing the amount of the active anode material in the cell inner volume and decreasing the container wall thickness. These efforts seem to have come near their limits. To achieve an inherently higher battery capacity, it is essential to improve the capacity of active material itself.

Extensive studies have been made to replace lithium cobalt oxide, the most widely used anode material now, with lithium nickel oxide and lithium manganese oxide (spinel-type). Since the amount of lithium insertion is practically determined by the cathode compound used, it is considered that improvement of electrical capacity in battery owes much to the properties of anode materials.

Various graphite materials are now used as anode. When the lithium secondary battery is charged, lithium ions are intercalated to graphite and they form a graphite intercalation compound as illustrated in **Fig. 3**. When a lithium secondary battery is discharged, lithium ions come out from the graphite layers. It is known that the geometry of the intercalated lithium ions between graphite layers is commensurate with graphite carbon atoms and that one lithium ion corresponds to six carbon atoms in graphite crystals[1]. Namely, the intercalation and de-intercalation of lithium ions proceed in the following proportions:

$$6\cdot\mathrm{C} + \mathrm{Li}^+ + e^- \rightarrow \mathrm{C_6Li}\ \text{(charge)}$$
$$\leftarrow\ \text{(discharge)}$$

Based on the above reaction equations, the theoretical capacity of graphite is put at 372 mAh/g. This theoretical value is the final target for the capacity of graphite anode materials (unless another insertion mechanism is considered).

Anode materials in current use are mainly made of artificial graphite and have capacities of about 300 to 320 mAh/g. It is necessary to apply graphite materials with higher crystallinity (degree of graphitization) toward higher battery capacity.

High degree of graphitization is essential requirement for improving capacity of anode. Materials with high degree of graphitization, such as natural graphite, have a high irreversible capacity during the first charge, and degradation proceeds in accordance with charge-discharge cycles probably due to the anisotropy of crystals within particles. These problems make it difficult to use such highly graphitized materials for anodes.

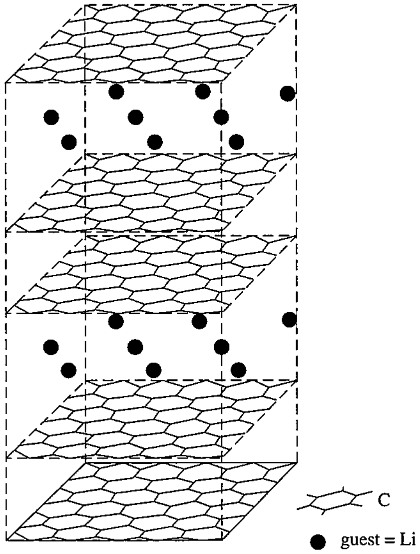

**Fig. 3 Graphite intercalation compound (2nd stage, commensurate)**

**Table 1 Structure and performance factors of graphite-based anode materials**

| | Natural graphite (scale-shaped) | Artificial graphite (fine carbon) |
|---|---|---|
| Degree of graphitization | High | Low |
| Structure (orientation) | Large | Small |
| Specific surface area | Large | Small |
| Surface structure | (Graphite) | (Turbostratic layer) |
| Discharge capacity | ◎ | △ |
| Irreversible capacity | △ | ◎ |
| Rate characteristic | △ | ○ |
| Bulk density dependence | △ | ○ |
| (Handling ability) | △ | ◎ |

As described above, improving the anode material calls for optimizing the balance of performance factors, such as high discharge capacity and low irreversible capacity as shown in **Table 1**. It was made clear that a new anode material with excellent properties could be obtained by optimizing the structure of raw carbon material from this standpoint and graphitizing the carbon by adding a boron compound. The new anode material is described in the following sections.

## 3. Development of Boron-doped Graphite Anode Material (Granode Type H)

It is reported that the graphitization of carbon material in the presence of a boron compound yields a lithium ion secondary battery anode material with high discharge capacity[2]. The present study evaluated the properties of the anode material produced by the graphitization of a structure-controlled pitch coke-based carbon material with a boron compound, and investigated it as compared with vari-

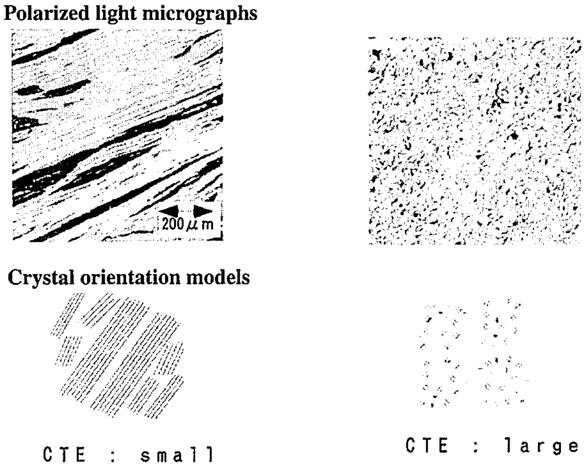

**Fig. 4 Carbon structure (polarized light microscopy) and coefficient of thermal expansion (CTE)**

ous conventional graphite-based materials.

To derive a material with a high degree of graphitization from the heat treatment (graphitization) of pitch-coke, the large structure and unidirectional crystal alignment of raw carbon material are preferred for achieving a higher degree of graphite crystals. The coefficient of thermal expansion (CTE) in the major axis direction of cylindrical test pieces obtained by graphitizarion of the raw material was used as structure parameter of carbon material. The CTE of graphite from room temperature to 500°C is as large as $2 \times 10^{-5}$/T (where T is temperature) in the direction perpendicular to graphite plain (c-axis direction), and is practically zero along in-plane. Since the test pieces were prepared by mixing pitch coke with a binder and extruding the mixture, graphite layer plane was mainly oriented along major axis. That is, carbon materials with the higher structural orientation show the lower CTE. **Fig. 4** shows the relationship between structure and CTE of carbon.

The CTE of the new anode material and its electrode properties after graphitization were then evaluated[3,4]. Coal pitch-based coke was used as raw material, and graphitization was done under argon atmosphere at 2,800°C. For electrode manufacture, graphite as active anode material was kneaded with 10 wt% of polytetrafluoroethylene (PTFE) and a few drops of iso-propanol in an agate mortar and formed into a sheet of about 100 μm thickness. The sheet was then cut into sizes of 10 × 10 mm. Electrode performance evaluation used a three-electrode glass cell with counter and reference electrodes of lithium metal, and the electrolyte was prepared by dissolving 1 mol of lithium perchlorate ($LiClO_4$) in a solvent composed of one part ethylene carbonate (EC) and one part diethyl carbonate (DEC). The charge capacity and discharge capacity were measured in the voltage range of 1.5 to 0 V at constant current with a current density of 0.1 or 0.5 mm/cm$^2$.

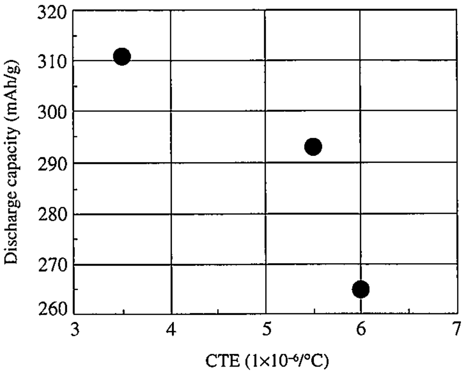

**Fig. 5 Relationship between coefficient of thermal expansion (CTE) and discharge capacity**

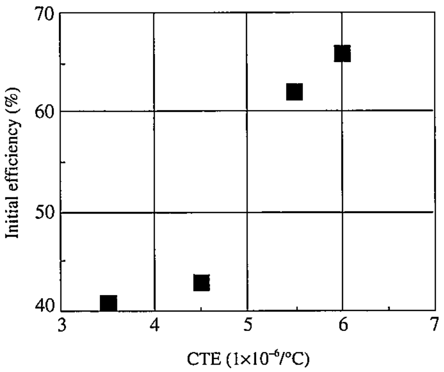

**Fig. 6 Relationship between coefficient of thermal expansion (CTE) and initial efficiency**

The effects of the CTE on the discharge capacity and initial efficiency are shown in **Figs. 5 and 6**, respectively. The smaller the CTE or the higher the structural orientation, the higher the discharge capacity. This indicates that the graphitization treatment favors the development of crystallinity. The larger the CTE, the higher the initial efficiency or the lower the irreversible capacity. A lower structural orientation is preferred for reduction in the side reaction attendant on the insertion of lithium ions. It was also found that a structure with a high CTE or with a smaller structural size and lower structural orientation is desirable in terms of load characteristic (or ability of the battery to maintain its performance when charged and discharged at a high current density).

In this way, the structural size and orientation of the raw carbon materials have strong effects on properties of anode materials after graphitization. It is evident that CTE has contradictory effects on capacity and initial efficiency (irreversible capacity) in the same way as on capacity and rate performance. Furthermore, even if these contradictory parameters such as discharge capacity and initial efficiency are balanced by using the CTE as parameter in this way, it is indispensable to improve discharge capacity and initial efficiency in view of absolute performance. Then the graphitization was conducted in the presence of boron compounds for the purposes of promoting the development of the graphite structure to increase the discharge capacity and of reducing side reaction to improve the initial efficiency.

Pitch-coke (with its CTE changed by its structure control) was used as raw material, doped with 2 wt% of metal boron, and treated for graphitization under an argon atmosphere at 2,800°C. **Fig. 7** shows the ideas of material design and the properties of the developed material. When no boron was added, the discharge capacity and initial efficiency were not high as already described. The boron-doped anode material had a discharge capacity of 340 mAh/g and an initial efficiency of 90%, which are good initial characteristics. Nippon Steel has already prototyped the developed material on a mass-production basis and supplied its samples under the tradename "Granode Type H". The basic properties of Granode Type H are described below in comparison with those of other anode materials.

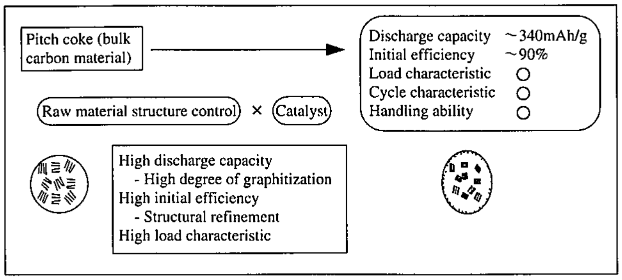

**Fig. 7 Ideas of material design and properties of developed material**

A SEM micrograph of a Granode Type H powder is shown in **Photo 1**. Granode Type H is amorphous carbon in morphology and is different from the scale form of natural graphite. This is because while natural graphite has graphite crystals grown in one direction, the developed anode materials consists of particles in which graphite crystals are oriented in other directions.

**Fig. 8** shows the first charge and discharge curves. The characteristics to be noted here are that the charge and discharge capacities are large and that an irreversible capacity component is recognized in the early stage (> 1 V) of the charge curve. When the material was doped with boron and heat treated for graphitization, some of the boron atoms are replaced by the carbon atoms in graphite. This irreversible capacity component is presumably due to the insertion of helium ions in vicinity of such boron atoms.

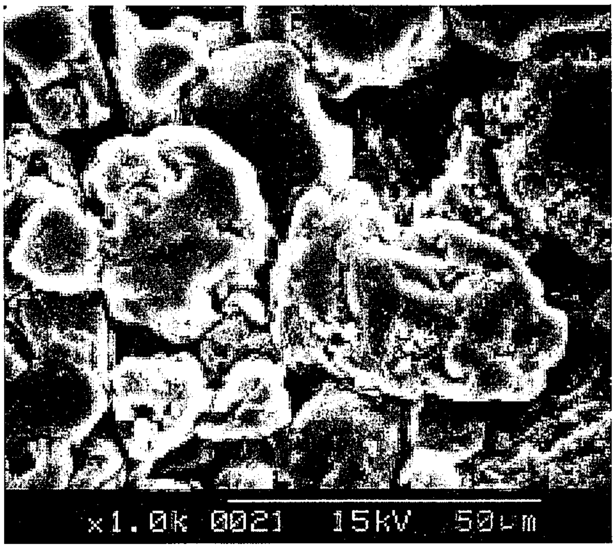

**Photo 1 Granode Type H**

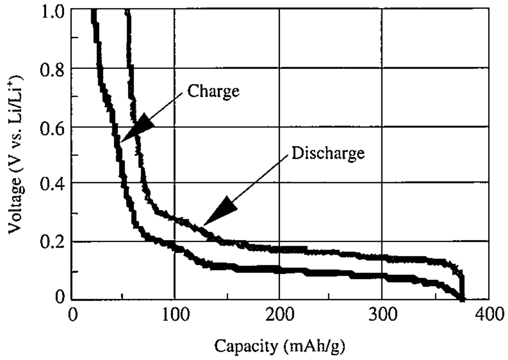

**Fig. 8 First charge and discharge curves**

**Table 2** gives the basic properties of Granode Type H. The graphite layer plane spacing ($d_{002}$) determined by x-ray diffraction is 0.3349 nm and is smaller than the theoretical value of 0.3354 nm for graphite. This is attributable to the presence of boron atoms in the solid solution condition, some of which are replaced by carbon atoms as noted above. The crystal size $L_c$ in the direction normal to the layer plane and the crystal size $L_a$ in the layer plane direction each exceed 100 nm. Since the graphite crystal structure developed by boron doping is obtained, the effect of increased discharge capacity is obtained. Furthermore, the true density is equivalent to the theoretical value of 2.26 g/cm$^3$ for graphite. That is, Granode Type H increases in the discharge capacity with the evolution of graphite crystals.

Next, Granode Type H was comparatively studied with various graphite materials conventionally used as anode materials. **Fig. 9** compares the discharge rate characteristics of the graphite anode materials. The discharge capacities obtained at discharge current densities of 0.5 to 4 mA/cm$^2$ are compared. The control materials used in the comparative study are mesophase spheres (MCMB, Osaka Gas Chemical, average particle size of 8 μm), artificial graphite (KS15, Lonza), and natural graphite (NG7, Kansai Netsu Kagaku). Granode Type H and MCMB have a smaller decrease in the discharge capacity at a high current density and exhibit practically flat, good load characteristics. In contract, artificial graphite and natural graphite exhibit the discharge capacity that markedly decreases with increasing current density. This is probably because the artificial graphite and natural graphite are greatly anisotropic in crystal orientations in particles and are low in effective current paths.

These highly oriented particles are sale-shaped or plate-shaped. When they are applied to the anode electrode copper foil, their graphite layer planes are aligned with the coated surface direction and

**Table 2 Basic properties of product**

| | |
|---|---|
| $d_{002}$ (XRD[*1]) | 0.3349nm |
| $L_c$ | ~ 100nm |
| $L_a$ | ~ 100nm |
| Average particle size | 30μm |
| Specific surface area ($N_2$-BET[*2]) | ~ 2.5m$^2$/g |
| True density | 2.25g/cm$^3$ |

[*1] : X-ray diffraction

[*2] : $N_2$ is nitrogen used as adsorption gas and BET is Brunauer-Emmett-Teller method for measuring specific surface area.

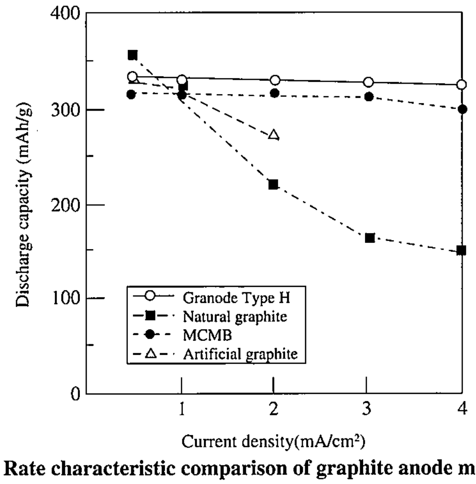

**Fig. 9 Rate characteristic comparison of graphite anode materials**

oriented in parallel with the electrode foil. In other words, the anisotropy that the electric conductivity in the direction normal to the electrode foil diminishes is probably responsible for anode deterioration. Conversely, Granode Type H and MCMB are small in this anisotropy and good in load characteristics. **Fig. 10** shows the relationship between the operating temperature and discharge capacity of the anode materials. As compared with Granode Type H and MCMB, natural graphite and artificial graphite undergo a conspicuous capacity reduction at low temperatures. This is also understood to be due to the anisotropy within the particles and the orientation of the scale-shaped particles.

**Figs. 11 and 12** show the effects of press pressure on discharge capacity and initial efficiency, respectively, when the coated film was pressed on a uniaxial press. The application of pressure increases the density of the anode material, but the different anode materials differ in ease of collapse under the same load. Natural graphite and artificial graphite, both composed of scale-shaped particles, are low in density when no pressure is applied and greatly change in density when pressure is applied. The pressing operation intensifies the orientation of scale-shaped and plate-shaped particles and badly degrades the properties of the particles. Granode Type H and MCMB are free from the degradation of properties with the application of pressure, and their density can be increased to about 1.5 g/cm$^3$ under a load of 5 tons/cm$^2$. These results indicate that the shape and structural orientation of powder particles are as important property factors as the degree of development of graphite crystals expressed by the degree of graphitization.

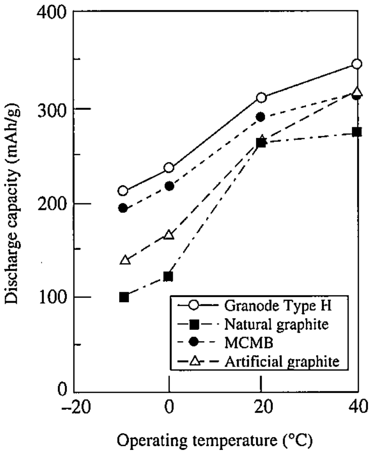

Fig. 10 Operating temperature vs. discharge capacity

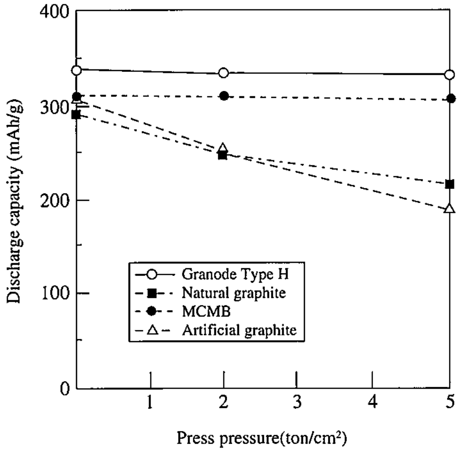

Fig. 11 Press pressure vs. discharge capacity

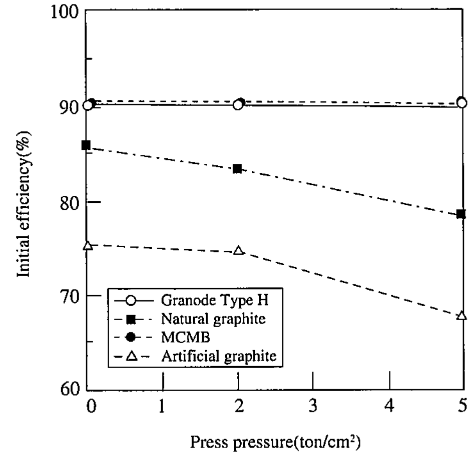

Fig. 12 Press pressure vs. initial efficiency

**Fig. 13** compares the electric resistance of powders for Granode Type H, MCMB, and natural graphite. Each powder was placed in a cylinder and pressed. The effect of the applied pressure on the electric resistance of the pressed powder is shown in Fig. 13. Unlike the above-mentioned pressing of coated films, these measurements are considered to have been taken under conditions to make the initial orientation of powder particles and their reorientation after the pressing more difficult. Although it is difficult to make a simple comparison because the macroscopic electric resistivity of powders is influenced by their average particle size and particle size distribution, Granode Type H is interpreted as keeping the powder particles in good contact, and MCMB has a high electric resistivity because its powder particles are spherical and narrow in size distribution.

Another property required of anode materials and expected to assume increasing importance is their ability to perform well in a solvent containing propylene carbonate (PC). Propylene carbonate solvates and holds lithium ions without decomposing itself, and has a wide practical temperature region (especially it can maintain low viscosity at low temperatures). Despite these excellent properties as electrolyte component, however, propylene carbonate has the problem of irreversible lithium consumption on the first charge for graphite

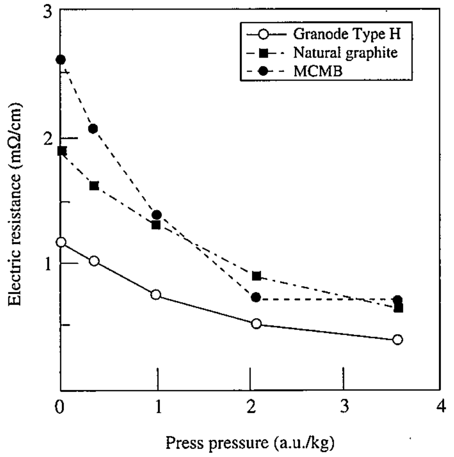

Fig. 13 Press pressure vs. electric resistance of powder

anode materials or drop in initial efficiency due to side reaction, so that it cannot be used as electrolyte component although we wand to do so.

**Fig. 14** shows the relationship between the propylene carbonate concentration of the solvent and the initial efficiency of Granode Type H and MCMB. Granode Type H exhibits almost the same initial efficiency up to a propylene carbonate concentration of 25%, while MCMB starts to decrease in the initial efficiency due to the increase in the side reaction from a propylene carbonate concentration of about 10%. The side reaction that increases with the use of propylene carbonate is said to be solvent co-intercalation into the lithium ions and graphite layer planes, resulting in electrolyte decomposition. For Granode Type H, it is estimated that the side reaction is inhibited by the boron atoms replaced as carbon atoms after graphitization and present in the graphite layers.

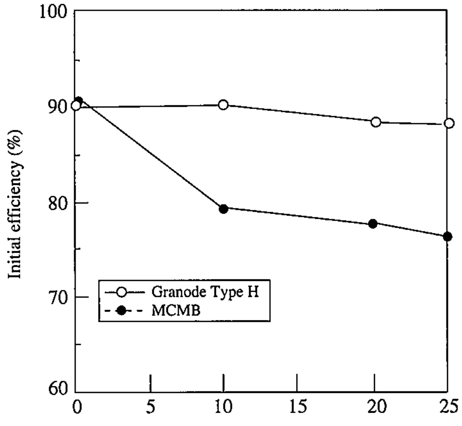

**Fig. 14 Propylene carbonate (PC) concentration and initial efficiency**

As discussed above, Granode Type H is found to have discharge capacity, rate characteristics, pressing characteristics, and other properties superior to those of conventional anode materials and also to perform well in the electrolyte that contains propylene carbonate in the solvent.

## 4. Conclusions

The excellent properties of a new anode material produced by adding a boron compound to pitch coke whose structure is controlled optimally and by heat treating the resultant powder for graphitization have been discussed above. Thinking that there is still room for improving the discharge capacity and initial efficiency, we are implementing various improvements by changing the manufacturing process, among other things. Recent years have seen widespread attempts to produce graphite-based anode materials with excellent properties by adding boron to various materials5,6). Granode Type H is considered to have high potential as Nippon Steel's original anode material in that it has been scaled up to production on commercial equipment.

As the portable equipment market grows and as the portable equipment decreases in size and increases in functionality, the capacity and other performance improvements of lithium ion batteries will assume ever increasing importance. We intended to contribute to the advancement of lithium secondary batteries in terms of anode material technology.

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