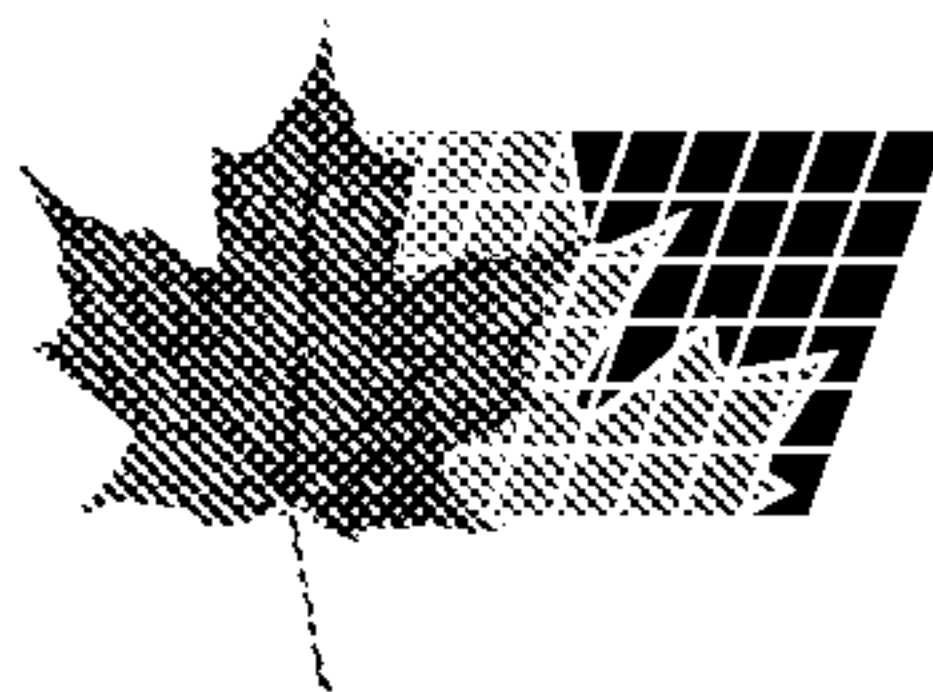




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(72) Honbo, Hidetoshi, JP

(72) Takeuchi, Seiji, JP

(72) Momose, Hideto, JP

(72) Horiba, Tatsuo, JP

(72) Muranaka, Yasushi, JP

(72) Ishii, Yoshito, JP

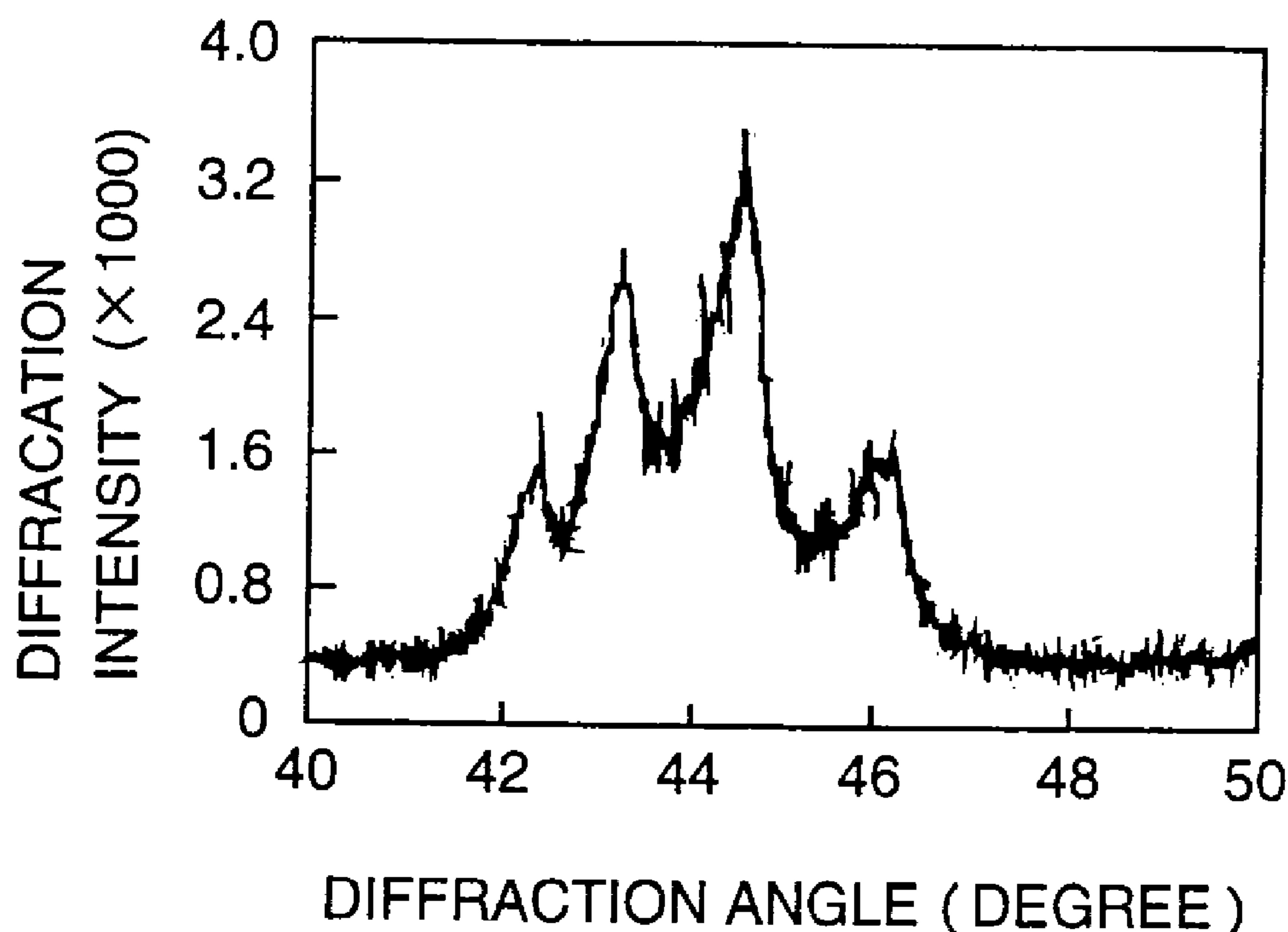
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(54) **BATTERIE SECONDAIRE NON AQUEUSE ET METHODE DE
FABRICATION DE POUDRE DE GRAPHITE**

(54) **NON-AQUEOUS SECONDARY BATTERY AND A
MANUFACTURING METHOD OF GRAPHITE POWDER**



(57) A carbon material having a superior reversibility in the lithium intercalation-deintercalation reaction is used in a non-aqueous secondary battery as the active material for the negative electrode. The result is a high energy density and excellent rapid charging and discharging characteristics. Graphite powder having a maximum particle diameter of less than 100 μm and a fraction of rhombohedral structure in the crystalline structure of less than 20% is used as the active material for the negative electrode of the battery. This graphite powder can be obtained by pulverizing raw graphite with a jet mill, and subsequently treating the powder at a temperature equal to or higher than 900° C.



Abstract

5 A carbon material having a superior reversibility in the lithium intercalation-deintercalation reaction is used in a non-aqueous secondary battery as the active material for the negative electrode. The result is a high energy density and excellent rapid charging and discharging characteristics. Graphite powder having a maximum particle diameter of less than 100 μm and a fraction of rhombohedral structure in the crystalline structure of less than 20% is used as the active
10 material for the negative electrode of the battery. This graphite powder can be obtained by pulverizing raw graphite with a jet mill, and subsequently treating the powder at a temperature equal to or higher than 900°C.

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NON-AQUEOUS SECONDARY BATTERY AND
A MANUFACTURING METHOD OF GRAPHITE POWDER

The present invention relates to a carbon material that intercalates into or deintercalates from lithium, and to a method for manufacturing the same. In particular, the present invention relates to a lithium secondary battery, that uses the carbon material as a negative electrode active material, having a high energy density and a long life. The lithium battery is suitable for using in portable apparatus, electric automobiles, power storage, etc.

A secondary battery using lithium metal for the negative electrode has some problems in safety. For example, lithium easily deposits like dendrite on the lithium metal negative electrode during repeated charging and discharging of the battery, and if the dendritic lithium grows to a positive electrode, an internal short circuit is produced between the positive electrode and the negative electrode.

Therefore, a carbon material has been disclosed as the negative electrode active material replacing lithium metal. Charge and discharge reactions are lithium ions intercalation into the carbon material and deintercalation from the carbon material, and lithium is hardly deposited like dendrite. As for the carbon material, graphite is disclosed in JP-B-62-23433 (1987).

The graphite disclosed in JP-B-62-23433 (1987) forms an intercalation compound with lithium, because of the intercalation or deintercalation of lithium. The graphite is used as a material for the negative electrode of a lithium secondary battery. In order to use this graphite as the negative active material, it is necessary to pulverize the graphite to increase the surface area of the active material to enable the charging and discharging reactions to proceed smoothly. Desirably, it is necessary to pulverize the graphite to a powder having a particle diameter equal to or less than 100 μm . However, as is apparent from the fact that the graphite is used as a lubricating material, the graphite easily transfers its layers. Its crystal structure is changed

by the pulverizing process, and the formation of the lithium intercalated compound might be influenced by undesirable effects. Accordingly, after the pulverizing process the graphite has a great deal of crystalline structural defects.

5 In a case where this graphite is used as an active material for the negative electrode of a lithium secondary battery, there is a disadvantage that a large capacity cannot be obtained. Furthermore, the preferable performances of rapid charge and discharge are not obtained, because the lithium
10 intercalation-deintercalation reaction is disturbed by the above defects.

An object of the present invention is to solve the above problems of the prior art, to disclose a carbon material having a large lithium intercalation-deintercalation capacity
15 and a method for manufacturing the same; and also to provide a non-aqueous secondary battery that has a large capacity and is superior in its rapid charging and discharging characteristics using the above disclosed materials.

The crystalline structure of the graphite powder relating
20 to the present invention has a feature that the existing fraction of the rhombohedral structure in the crystalline structure of the graphite is small (equal to or less than 20%). Another feature is that an existing fraction of the hexagonal structure is great (at least 80%). These existing
25 fractions of the rhombohedral structure and the hexagonal structure can be determined by analyzing the intensity ratio of the peaks in X-ray diffraction.

A graphite powder relating to the present invention can be manufactured by a method comprising the steps of a
30 graphitizing treatment (heating to at least 2,000°C) of a raw material, such as an oil coke or coal coke, pulverizing the graphitized raw material to a powder, sieving the powder to obtain a maximum particle diameter equal to or less than 100 μ m, heating the powder to at least 900°C as a heat
35 treatment, and further heating the powder to at least 2,700°C for eliminating impurities such as Si. For instance, when the powder is heated to at least 2,700°C, Si, which is a main

component of impurities, can be reduced to less than 10 ppm. The heat treatment of the powder for eliminating impurities can be omitted depending on the content of impurities in the raw material. In the pulverizing process, various
5 conventional pulverizers can be used. However, a jet mill is preferable, because pulverization with a jet mill produces a minimum destruction of the graphite crystalline structure in the raw material.

Furthermore, the graphite powder can be obtained by
10 immersing it into an acidic solution containing at least one compound selected from the group consisting of sulfuric acid, nitric acid, perchloric acid, phosphoric acid, and fluoric acid as an immersing treatment, after pulverising the raw graphite to obtain a graphite powder having a particle
15 diameter equal to or less than 100 μm ; subsequently washing with water, neutralizing, and drying.

A non-aqueous secondary battery for achieving the object of the present invention can be manufactured by using such graphite powder as the negative electrode active material.
20 The positive electrode is desirably composed of a material comprising a compound expressed by the chemical formula Li_xMO_2 (where X is in the range from zero to 1, and M is at least any one of the chemical elements selected from the group of Co, Ni, Mn and Fe), or LiMn_2O_4 , that is a lithium transient metal
25 complex oxide.

The active materials for the battery are preferably used in the form of a powder in order to obtain the charging and discharging reaction by increasing the surface area of the active material, which is the field of the charging and
30 discharging reaction. Therefore, the smaller the particle size of the powder, the more will the performance of the battery be improved. Furthermore, when an electrode is manufactured by applying an agent mixed with the active material and a binding agent to a current collector, the
35 particle diameter of the active material is desirably equal to or less than 100 μm in view of its applicability and the

maintenance of the preciseness of the thickness of the electrode.

As to the negative electrode active material for the lithium secondary battery, natural graphite, artificial graphite, and others are disclosed. However, for the above described reason, it is necessary to pulverize these materials. Therefore, in the pulverizing process, various graphite powders having a diameter equal to or less than 100 μm were prepared with various pulverizing methods using a ball mill, a jet mill, a colloidal mill and other apparatus, at various times. The lithium intercalation-deintercalation capacity of the various graphite powders were determined by searching a superior material for the negative electrode material of the lithium secondary battery.

However, the graphite powder obtained by the above method had lithium intercalation-deintercalation amounts per weight in a range of 200-250 mAh/g, and their capacities as the material for the negative electrode of a lithium secondary battery were not enough.

In order to investigate the reason for the small capacity, crystalline structures of the above, various graphites were examined by an X-ray diffraction method. Fig. 1 indicates an example of the results. Four peaks can be observed in the range of the diffraction angle (2θ , θ : Bragg angle) from 40 degrees to 50 degrees in the X-ray diffraction pattern. The peaks at approximately 42.3 degrees and 44.4 degrees are diffraction patterns of the (100) plane and the (101) plane of the hexagonal structure of the graphite, respectively. The peaks at approximately 43.3 degrees and 46.0 degrees are diffraction patterns of the (101) plane and the (102) plane of the rhombohedral structure of the graphite, respectively. As explained above, it was apparent that there were two kinds of crystalline structure in the pulverized graphite.

Further, the existing fraction (X) of the rhombohedral structure in the graphite powder was calculated by the following equation (Equation 1) based on the data of the

observed peak intensity (P_1) of the (100) plane of the hexagonal structure, the observed peak intensity (P_2) of the (101) plane of the rhombohedral structure, and a theoretical relationship of the intensity ratio in the X-ray pattern of graphite. As a result, it was revealed that the graphite having the rhombohedral structure was contained by approximately 30% in all the graphite pulverized equal to or less than 100 μm in particle diameter.

$$X = 3P_2 / (11P_1 + 3P_2) \quad \dots \quad (\text{Equation 1})$$

Similarly, the existing fraction (X) of the rhombohedral structure of the graphite powder was verified by the relationship of the observed peak intensity (P_1) of the (100) plane of the hexagonal structure, the observed peak intensity (P_3) of the (102) plane of the rhombohedral structure, and the theoretical relationship of the intensity ratio in the X-ray pattern of graphite. In this case, the following equation 2 was used instead of equation 1. As the result, it was confirmed that the graphite having the rhombohedral structure was contained by approximately 30% in all the graphite pulverized equal to or less than 100 μm in particle diameter.

$$X = P_3 / (3P_1 + P_3) \quad \dots \quad (\text{Equation 2})$$

The reason for the existence of the two kinds of crystalline structure is assumed to be that the graphite itself has a lubricating property, and the original graphite having the hexagonal structure transforms to graphite having the rhombohedral structure by the pulverizing process with strong shocks. The graphite powder having a few microns in particle diameter obtained by further continued pulverization had a significantly broadened X-ray diffraction peak (P_4) at the (101) plane of the hexagonal structure, and it was revealed that the content of amorphous carbon in the graphite was increased because the half band width of the peak was increased. Accordingly, the reason for the small lithium

intercalation-deintercalation capacity of conventional graphite powder can be assumed to be that the crystalline structure of the graphite has been transformed to the rhombohedral structure and generated amorphous carbon, proceeding of the lithium intercalation-deintercalation reaction being disturbed by the rhombohedral structure and the amorphous carbon.

Analysis on the impurities of the graphite powder revealed that impurities such as Si, Fe, and others were present in more than 1,000 ppm. Naturally, in addition to the impurities contained in the raw material, impurities from the processing apparatus, such as a ball mill, a jet mill, or the like can be mixed into the graphite at the pulverizing process. Therefore, the influence of the above impurities can be assumed to be another reason for the small capacity, in addition to the above formation of the rhombohedral structure and amorphous carbon.

For the present invention, a graphite powder having a particle diameter equal to or less than 100 μm , wherein the content of the above-described rhombohedral structure is less than 30% and the content of the amorphous carbon is small, has been developed. Additionally, the content of Si, in particular, which is the main component of the impurities in the graphite powder, has been decreased to be equal to or less than 10 ppm. Therefore, extremely high purity is one of the features of the graphite for use in the present invention. The particle diameter equal to or less than 100 μm is determined with the invention of using the graphite for a battery, as described previously. Therefore, when the graphite is used for other purposes, its particle diameter is not necessarily restricted to being equal to or less than 100 μm .

Details of graphite powder relating to the present invention, and the method for manufacturing the same will now be explained.

Two preferred methods (manufacturing method 1 and manufacturing method 2) for obtaining graphite having a small fraction of the rhombohedral structure are disclosed.

(Manufacturing method 1)

5 As for the raw material for the graphite powder both natural graphite and artificial graphite can be used. In particular, flaky natural graphite is preferable. Among the above raw graphites, the one for which the maximum diffraction peak in the X-ray diffraction pattern by the $\text{CuK}\alpha$ line appears
10 at a diffraction angle (2θ , θ : Bragg angle) in a range from 26.2 degrees to 26.5 degrees, that is, the interval between two graphite layers is equal to or less than 0.34 nm, is desirable, because, a graphite powder containing a small amount of the rhombohedral structure can be obtained from the
15 highly crystalline raw material.

 As for the pulverizing apparatus for crushing the raw graphite to a particle diameter equal to or less than 100 μm , a jet mill is desirable. The reason is that amorphous carbon is generated less with a jet mill than when other pulverizing
20 apparatus is used.

 The pulverized raw graphite (raw powder) contains graphite having a rhombohedral structure at approximately 30%, as previously described. Then, in accordance with the present manufacturing method 1, the existing fraction of the
25 rhombohedral structure is decreased by the following heat treatment.

 The heat treatment is performed at at least 900°C under an inert gas atmosphere. As for the inert gas, nitrogen gas, argon gas, or the like is used. The inert gas atmosphere can
30 also be maintained by covering the raw powder with coke to seal it from the atmosphere.

 The heat treatment is important for transforming the rhombohedral structure to the hexagonal structure. It is necessary to perform the heat treatment after pulverization of
35 the raw graphite (more preferably, as the last stage of the manufacturing process).

If the heat treatment is performed before the pulverization of the graphite and subsequently the graphite is pulverized, a graphite powder containing a rhombohedral structure as small as possible, which is desirable, cannot be obtained. A graphite powder containing a rhombohedral structure as small as possible can be obtained only by performing the heat treatment after the pulverizing process (more preferably, as the last stage of the manufacturing process).

The raw graphite powder contains Al, Ca, Fe, and particularly much Si, as impurities. The impurities can be eliminated by heating and sublimating the materials at at least 2,700°C. Therefore, the heating temperature in the heat treatment is preferably at least 2,700°C in order to perform a purification treatment concurrently.

(Manufacturing method 2)

The raw graphite and the pulverizing process is the same as in manufacturing method 1.

The needed graphite powder can be obtained by treating the graphite powder obtained by the pulverizing process with an acidic solution containing at least one compound selected from the group consisting of sulfuric acid, nitric acid, perchloric acid, phosphoric acid, and fluoric acid, and subsequently washing with water; neutralizing and drying.

During the treatment, a compound is formed with anions in the above acidic solution and the graphite, and the rhombohedral structure graphite is largely eliminated by the formation of the compound. The anions from the acidic solution in the compound are eliminated from the compound during the washing, the neutralizing, and the drying.

The crystalline structure of the graphite powder obtained by manufacturing methods 1 and 2 was analyzed by an X-ray diffraction. The ratio of the P_1 and P_2 , (P_2/P_1), was less than 0.92, and the half band width of the P_4 was less 0.45 degrees. The ratio of the P_1 and P_3 , (P_3/P_1), was less than 0.75.

By substituting the above observed data for equations 1 and 2, the fact that the existing fraction of the rhombohedral structure has been decreased to less than 20% and the existing fraction of the hexagonal structure has been increased to at least 80% was confirmed. Simultaneously, the content of Si was confirmed to be less than 10 ppm from the result of the impurity analysis.

An electrode was then prepared using graphite powder so produced as the active material, and its lithium intercalation-deintercalation capacity was studied. The lithium intercalation-deintercalation capacity of the graphite powder was 320-360 mAh/g per unit weight of the active material, and the capacity was significantly improved in comparison with the capacity of conventional graphite material (200 - 250 mAh/g). Furthermore, it was found that the fraction of the rhombohedral structure was equal to or less than 10%, because the less the fraction of the rhombohedral structure in the powder, the more the capacity will be increased.

The rhombohedral structure is evidently a crystalline structure that hardly intercalates or deintercalates lithium. Therefore, it is assumed that the high lithium intercalation-deintercalation capacity of the present graphite powder is achieved by decreasing the existing fraction of the rhombohedral structure and increasing the existing fraction of the hexagonal structure.

The feature of a lithium secondary battery of the present invention is using the new graphite powder as the negative active material. A lithium secondary battery according to the present invention has a large load capacity, so that a high energy density can be realized.

As the result of an evaluation on the characteristics of a lithium secondary battery of the present invention, it was confirmed that the battery had a superior performance in rapid charging and discharging characteristics, and the capacity was improved at least 30% in comparison with a conventional lithium battery under the same rapid charging and discharging

conditions. The reason for the improvement can be assumed to be that the reversibility for the lithium intercalation-deintercalation reaction of the new graphite is improved in comparison with conventional carbon material by decreasing the existing fraction of the rhombohedral structure and eliminating the influence of the impurities such as Si.

As the positive active material for a lithium secondary battery, materials such as Li_xCoO_2 , Li_xNiO_2 , $\text{Li}_x\text{Mn}_2\text{O}_4$, (where, X is in a range 0-1) and the like are desirable, because a high discharge voltage of at least 3.5 V can be obtained, and the reversibility of the charge and discharge of the positive electrode itself is superior.

As for the electrolytic solution, a mixed solvent composed of ethylene carbonate mixed with any one selected from the group consisting of dimethoxyethane, diethylcarbonate, dimethylcarbonate, methylethylcarbonate, γ -butyrolactone, methyl propionate, and ethyl propionate, and at least one of the electrolytes selected from the group consisting of salts containing lithium such as LiClO_4 , LiPF_6 , LiBF_4 , LiCF_3SO_3 , or the like are used. It is desirable to adjust the lithium concentration in a range 0.5 - 2 mol/l, because the electric conductivity of the electrolytic solution is favourably large.

In the drawings:

Figure 1 indicates an X-ray diffraction pattern of conventional graphite,

Figure 2 indicates an X-ray diffraction pattern of graphite powder relating to embodiment 1 of the present invention (heat treatment temperature: 900°C),

Figure 3 indicates an X-ray diffraction pattern of graphite powder relating to embodiment 1 of the present invention (heat treatment temperature: 2,850°C),

Figure 4 indicates an X-ray diffraction pattern of graphite powder prepared in comparative example 1,

Figure 5 indicates an X-ray diffraction pattern of graphite powder relating to embodiment 2 of the present invention,

Figure 6 indicates a schematic cross section of a battery used in embodiment 3 and comparative example 2,

Figure 7 is a graph indicating the relationship between the electrode potential and the lithium intercalation-deintercalation capacity,

Figure 8 is a partial cross section of a lithium secondary battery in embodiment 5 of the present invention,

Figure 9 is a graph indicating the relationship between the discharge capacity and the number of repeated the charge and the discharge cycles, and

Figure 10 is a graph indicating the relationship between the discharge capacity and the charging and discharging current.

Referring to drawings, embodiments of the present invention are now explained.

Embodiment 1

Flaky natural graphite was produced from Madagascar was used as the raw material, and the raw material was pulverized to a powder, of which the particle diameter was equal to or less than $46\text{ }\mu\text{m}$, by a jet mill. The powder was sieved to obtain raw material powder. The average diameter of the raw material powder was $8.0\text{ }\mu\text{m}$. Subsequently, the raw material powder was processed with a heat treatment by heating at 900°C or $2,850^{\circ}\text{C}$ for ten days under a nitrogen atmosphere, and a graphite powder was obtained.

The crystalline structures of this graphite powder and the raw material powder were analyzed by an X-ray diffraction method using an apparatus RU-200 made by Rigaku Denki, and the impurity content was analyzed by an inductively coupled plasma spectrometry (ICP) using an apparatus P-5200 made by Hitachi.

The X-ray diffraction patterns of this graphite powder, which were observed under a condition of X-ray tube voltage; 40 kV, X-ray tube current; 150 mA, and X-ray source; $\text{CuK}\alpha$ line, are shown in FIGs. 2 and 3. FIG. 2 is the pattern obtained by the heat treatment at 900°C , and FIG. 3 is the pattern obtained by the heat treatment at $2,850^{\circ}\text{C}$. The X-ray

diffraction patterns of the graphite powder in both FIG. 2 and FIG. 3 indicate that the peaks at diffraction angles of 43.3 degrees and 46.0 degrees, both of which belong with the rhombohedral structure, are decreased by either of the above heat treatments.

The amount of Si contained in the graphite powder as an impurity was 1,140 ppm when the heating temperature was 900°C, and 27 ppm when the heating temperature was 2,850°C. Therefore, it is found that a highly purified graphite powder, in which Si is virtually eliminated, can be obtained by heat treatment at a high temperature of at least 2,700°C.

Comparative example 1

In order to compare with the embodiment of the present invention, the non-pulverized raw graphite was heated at 2,850°C, and subsequently pulverized to obtain the graphite powder. The X-ray pattern of the graphite powder obtained by the above process is shown in FIG. 4. It is apparent from FIG. 4 that the peaks at diffraction angles of 43.3 degrees and 46.0 degrees, both of which belong with the rhombohedral structure, are not decreased. That means, the rhombohedral structure cannot be eliminated by the above process.

Embodiment 2

In accordance with embodiment 2, the raw graphite was pulverized by a jet mill to less than 100 μm in particle diameter. The graphite powder was then immersed in a mixed acid of sulfuric acid and nitric acid for a whole day. Subsequently, washing with distilled water and neutralization with a dilute aqueous solution of sodium hydroxide were performed. The powder obtained by the above process was dried at 120°C to obtain the desired graphite powder. The X-ray pattern of the powder obtained by this process is shown in FIG. 5. The peaks at diffraction angles of 43.3 degrees and 46.0 degrees, both of which belong with the rhombohedral structure, are decreased. Accordingly it was found that the

rhombohedral structure was substantially eliminated by this process.

Embodiment 3

In accordance with embodiment 3, a carbon electrode was prepared using a graphite powder of the present invention as an electrode active material and the lithium intercalation-deintercalation capacity, in other words the load capacity of the negative electrode in a lithium secondary battery was studied.

A mixed agents slurry was prepared by mixing 90% by weight in total solid of the graphite powder prepared in embodiment 1, 10% by weight of polyvinylidene fluoride (PVDF) as a binder, and N-methyl-2-pyrrolidone, of which the heating temperatures were 900°C and 2,850°C, respectively. The mixed agents slurry was applied onto a sheet of copper foil of 10 μm thick, and dried in a vacuum at 120°C for one hour. After the vacuum drying, an electrode was fabricated by roller pressing, the thickness of which was in the range 85 - 90 μm . The average amount of the applied mixed agents per unit area was 10 mg/cm². The electrode was prepared by cutting the copper foil with the mixed agents applied into a sheet of 10 mm x 10 mm.

FIG. 6 is a schematic cross section of a battery used for studying the lithium intercalation-deintercalation capacity of the present electrode. The battery has a structure comprising a working electrode current collector 30, an electrode of the present invention 31, which is a working electrode, a separator 32, a piece of lithium metal 33, which is a counter electrode, and a counter electrode current collector 34, piled and inserted into a batter vessel 35. A lid 36 is screwed on. A reference electrode 37 made of lithium metal is attached to the battery. As for the electrolytic solution, a mixed solvent of ethylene carbonate and diethylcarbonate by 1:1 in volume and lithium hexafluorophosphate were used with a lithium concentration of 1 mol/l.

The intercalation-deintercalation of lithium was repeated by applying a constant current between the working electrode and the counter electrode, and the capacity was determined. The terminated potentials of the intercalation and the deintercalation of the working electrode were set at 0 V and 0.5 V, respectively.

Comparative example 2

In order to compare with the embodiment of the present invention, a carbon electrode was prepared with the graphite powder obtained in the comparative example 1 by the same method as in embodiment 3, and the load capacity (the amount of lithium intercalation-deintercalation) was determined. The same study was performed on an electrode prepared with conventional graphite powder (the same powder as the raw powder in embodiment 1).

The results of comparison on the lithium intercalation-deintercalation behavior of the electrode in embodiment 3 (the present invention) with the electrode in comparative example 2 (prior art) and the electrode prepared with conventional graphite powder are explained hereinafter. FIG. 7 is a graph indicating the relationship between the lithium intercalation-deintercalation capacity and the electrode potential at the fifth cycle, wherein the capacity becomes stable, after repeating the intercalation-deintercalation of lithium. In FIG. 7, the curve 40 indicates the potential variation of the electrode prepared with the graphite powder, of which the temperature at the heat treatment was 900°C, in embodiment 3. The curve 41 indicates the potential variation of the electrode prepared with the graphite powder, of which the temperature at the heat treatment was 2,850°C, in embodiment 3. The curve 42 indicates the potential variation of the electrode prepared with conventional graphite powder, and the curve 43 indicates the potential variation of the electrode prepared with the graphite powder that had been prepared in the comparative example 1 by the reversely ordered processes. The intercalation capacity and the deintercalation capacity

for lithium in both the cases of using the conventional graphite in comparative example 2 (the curve 42) and the graphite in comparative example 1 (the curve 43) were less than 250 mAh/g per unit weight of the active materials. On the contrary, in the case of embodiment 3 (the curves 40, 41), wherein the graphite powder prepared in the embodiment 1 was used as the active material, both the intercalation capacity and the deintercalation capacity for lithium were more than 300 mAh/g per unit weight of the active materials. That means, a large load capacity was obtained by using graphite powder having a small existing fraction of the rhombohedral structure. Furthermore, the case (the curve 41) using graphite powder highly purified by heating up to 2,850°C indicates the largest values in both the intercalation capacity and the deintercalation capacity for lithium in FIG. 7.

Embodiment 4

Embodiment 4 was performed in order to confirm the influence of treating time on the heat treatment. In embodiment 4, the graphite powder was obtained substantially in the same manner as in embodiment 1 (under a nitrogen atmosphere, the raw powder was heated at 2,850°C). However, the treating time of the heat treatment was varied in a range from 0 hours to 30 days.

The existing fraction of the rhombohedral structure was determined from the peak intensity in X-ray diffraction patterns. Furthermore, the same as embodiment 3, the electrodes were prepared with the obtained graphite powders, and the intercalation-deintercalation reactions of lithium were repeatedly performed. The result on the lithium intercalation-deintercalation capacity at the fifth cycle is shown in Table 1.

Table 1

Heating time	The existing fraction of the rhombohedral structure (%)	Lithium intercalation capacity (mAh/g)	Lithium deintercalation capacity (mAh/g)
0 hours	27.3	249	235
4 hours	18.2	332	320
10 hours	14.6	345	325
1 day	13.8	343	334
3 days	11.3	355	338
5 days	9.7	368	351
10 days	7.1	365	360
30 days	3.9	366	361

In accordance with the above result, it is apparent that the smaller the fraction of the rhombohedral structure, the more the lithium intercalation-deintercalation capacity will be increased. In particular, a fraction equal to or less than 10% is desirable.

Embodiment 5

This embodiment uses a cylindrical lithium secondary battery. The fundamental structure of the battery is shown in FIG. 8. In FIG. 8, the member designated 50 is a positive electrode. Similarly, a negative electrode 51, a separator 52, a positive electrode tab 53, a negative electrode tab 54, a positive electrode lid 55, a battery vessel 56, and a gasket 57 are shown.

The battery shown in FIG. 8 was prepared by the following steps. A mixed positive electrode agents slurry was prepared by mixing 88% by weight in total solid of LiCoO_2 as an active material for the positive electrode, 7% by weight of acetylene black as a conductive agent, 5% by weight of polyvinylidene fluoride (PVDF) as a binder, and N-methyl-2-pyrrolidone.

Similarly, a mixed negative electrode agents slurry was prepared by mixing 90% by weight in total solid of the graphite powder as an active material for the negative

electrode, 10% by weight of polyvinylidene fluoride (PVDF) as a binder, and N-methyl-2-pyrrolidone.

5 The mixed positive electrode agents slurry was applied onto both sides of a sheet of aluminum foil of 25 μm thick, and dried in vacuum at 120°C for one hour. After the vacuum drying, an electrode of 195 μm thick was fabricated by roller pressing. The average amount of the applied mixed agents per unit area was 55 mg/cm². The positive electrode was prepared by cutting the aluminium foil carrying the mixed agents into a
10 sheet of 40 mm in width and 285 mm in length. However, portions of 10 mm in length from both ends of the positive electrode did not have the mixed agents applied for the positive electrode. The aluminum foil was bared, and one of the bared portions was welded to the positive electrode tab by
15 ultrasonic bonding.

The mixed negative electrode agents slurry was applied onto both sides of a sheet of copper foil of 10 μm thick, and dried in vacuum at 120°C for one hour. After the vacuum drying, an electrode of 175 μm thick was fabricated by roller
20 pressing. The average amount of the applied mixed agents per unit area was 25 mg/cm². The negative electrode was prepared by cutting the copper foil carrying the mixed agents into a sheet of 40 mm in width and 290 mm in length. However, as with the positive electrode, portions of 10 mm in length from
25 both ends of the negative electrode did not have the mixed agents applied for the negative electrode. The copper foil was bared, and one of the bared portions was welded to the negative electrode tab by ultrasonic bonding.

A fine pored film made of polypropylene of 25 μm thick
30 and 44 mm in width was used as a separator. The positive electrode, the separator, the negative, and the separator were piled up in the order described above, and the pile was rolled to form a bundle of the electrodes. The bundle was contained in a battery vessel, the negative electrode tab was welded to
35 the bottom of the battery vessel, and a drawn portion for caulking the positive electrode lid was fabricated. An electrolytic solution prepared by adding lithium

hexafluorophosphate by 1 mol/l into a mixed solvent containing ethylene carbonate and diethylcarbonate by 1:1 in volume filled the battery vessel. The positive electrode tab was welded to the positive electrode lid, and the positive electrode lid was caulked to the battery vessel to form the battery.

Using this battery, charge and discharge were repeated under the conditions that the charging and discharging current was 300 mA, and the respective terminated potentials of the charge and the discharge was 4.2 V and 2.8 V. The charging and the discharging current was varied in a range from 300 mA to 900 mA, and a rapid charge and rapid discharge were obtained.

Comparative example 3

In order to compare with the present invention, a lithium secondary battery was manufactured by a method the same as embodiment 5 but using conventional graphite powder (the raw powder for the graphite powder of the present invention). The battery characteristics were determined in the same manner as in embodiment 5.

The result of the comparison of the characteristics of the lithium secondary battery of embodiment 5 (the present invention) and comparative example 3 (prior art) is now explained.

FIG. 9 indicates the variation in discharge capacity of the lithium secondary battery when the charge and discharge of the battery were repeated. The curve 60 indicates the discharge capacity of embodiment 5. The curve 61 indicates the discharge capacity of comparative example 3. In embodiment 5, the maximum discharge capacity was 683 mAh, and the ratio in the discharge capacity after 200 cycles to the maximum capacity was 86%. In comparative example 3, the maximum discharge capacity was 492 mAh, and the ratio in the discharge capacity after 200 cycles to the maximum capacity was 63%.

FIG. 10 indicates the relationship between the charging and discharging current and the discharge capacity when rapid charge and rapid discharge were performed. The curve 70 indicates the discharge capacity of embodiment 5. The curve 71 indicates the discharge capacity of comparative example 3. With a charging and discharging current of 900 mA, the discharge capacity of embodiment 5 was 573 mAh, while the discharge capacity of comparative example 3 was 256 mAh. The decreasing ratio of the discharge capacity in the present cases relative to the discharge capacity in the case of a charging and discharging current of 300 mAh/g were 16% and 48%, respectively. Therefore, by using a graphite powder of the present invention as the active material for the negative electrode, the decreasing ratio of the capacity was improved by at least 30%, and it became apparent that a lithium secondary battery in accordance with the present invention had excellent characteristics in rapid charge and discharge.

Embodiment 6

A mixed positive electrode agents slurry was prepared using LiMn_2O_4 as the positive electrode active material, and the positive electrode was prepared by applying the mixed positive electrode agents slurry onto both sides of a sheet of aluminum foil by the same method as in embodiment 5. The average amount of the applied mixed agents per unit area was 65 mg/cm^2 , and the electrode thickness after fabrication by roller pressing was $230 \text{ }\mu\text{m}$. The positive electrode was prepared by cutting the aluminum foil carrying the mixed agents into a sheet of 40 mm in width and 240 mm in length. However, portions of 10 mm in length from both ends of the positive electrode did not have the mixed agents applied for the positive electrode. The negative electrode was the same as the negative electrode prepared in embodiment 5. Then, a lithium secondary battery was prepared by the same method as in embodiment 5, such as forming an electrodes bundle, inserting the electrodes bundle into a vessel, welding the

bottom of the vessel, adding an electrolytic solution, caulking a positive electrode lid, and the other steps.

Using this battery, charge and discharge were repeated under the conditions of a charging and discharging current of 300 mA, and terminated potentials of the charge and discharge of 4.2 V and 2.8 V, respectively. As a result, the maximum discharge capacity was 581 mAh, and the ratio in discharge capacity after repeating the charging and discharging reactions for 200 cycles to the maximum discharge capacity was 84%. The above result indicates that the charging and discharging characteristics of the present embodiment is superior to comparative example 3.

A lithium secondary battery that has a high energy density and excellent charging and discharging characteristics can be obtained by using the new graphite powder. Such a battery is superior in the reversibility of the intercalation-deintercalation reaction of lithium, when the maximum particle size is less than 100 μm , wherein the fraction of the rhombohedral structure in the crystalline structure is less than 20%, using this as the active material for the negative electrode of the battery.

Claims:

1. A non-aqueous lithium secondary battery comprising:
a positive electrode,
a negative electrode, and

5 an electrolytic solution that is charged or discharged by repeating a reaction of intercalating and deintercalating ions at said positive electrode and said negative electrode, respectively, wherein

10 said negative electrode comprises graphite powder having a particle size equal to or less than 100 μm and a fraction of a hexagonal structure of at least 80% by weight,

15 said electrolyte solution is composed of ethylene carbonate at least one electrolyte being a salt containing lithium and any one from the group containing dimethoxyethane, diethylcarbonate, dimethylcarbonate, methylethylcarbonate, γ -butyrolactone, methyl propionate and ethyl propionate.

2. A non-aqueous lithium secondary battery comprising:
a positive electrode,
a negative electrode, and

20 an electrolytic solution that is charged or discharged by repeating a reaction of intercalating and deintercalating ions at said positive electrode and said negative electrode, respectively, wherein

25 said negative electrode is composed of graphite powder; said graphite powder comprises a fraction having a hexagonal structure of at least 80% by weight and a fraction having a rhombohedral structure of at most 20% by weight and having a maximum particle size of 100 μm ;

30 said electrolyte solution is composed of ethylene carbonate at least one electrolyte being a salt containing lithium and any one from the group containing dimethoxyethane, diethylcarbonate, dimethylcarbonate, methylethylcarbonate, γ -butyrolactone, methyl propionate and ethyl propionate.

3. A non-aqueous secondary battery as claimed in claim 2, wherein

5 a half band width of a diffraction peak (P_4), which appears in a range of the diffraction angle from 43.7 degrees to 45.0 degrees in an X-ray diffraction pattern of the graphite powder, is equal to or less than 0.45 degrees.

4. A non-aqueous secondary battery as claimed in claim 2, wherein

10 an angle of the diffraction (2θ , θ : Bragg angle) at the maximum diffraction peak is in a range from 26.2 degrees to 26.5 degrees in an X-ray diffraction pattern of the graphite powder.

5. A non-aqueous secondary battery as claimed in any one of claims 1-4, wherein

15 said graphite powder comprises Si in a range from nil to 30 ppm.

6. A non-aqueous secondary battery as claimed in any one of claims 1-5, wherein

20 said positive electrode comprises a compound defined by a chemical formula of Li_xMO_2 (where; $0 < X \leq 1$, and M is at least any one of chemical elements selected from the group of Co, Ni, Mn, and Fe) as a positive electrode active material.

7. A non-aqueous secondary battery as claimed in any one of claims 1-5, wherein

25 said positive electrode comprises a compound defined by a chemical formula of LiMn_2O_4 as a positive electrode active material.

8. A method for manufacturing non-aqueous lithium secondary batteries comprising the steps of;

30 laminating a graphite electrode with a lithium group oxide electrode via a separator, and

inserting the laminated electrodes into a cell container with an electrolytic solution: wherein

said electrolyte solution is composed of ethylene carbonate at least one electrolyte being a salt containing lithium and any one from the group containing dimethoxyethane, diethylcarbonate, dimethylcarbonate, methylethylcarbonate, 5 γ -butyrolactone, methyl propionate and ethyl propionate.

said graphite electrode is manufactured by the steps of; pulverizing graphite to graphite powder having a particle size equal to or less than 100 μm and a hexagonal structure of at least 80% by weight,

10 treating said graphite powder with heating at least 900°C, and

forming said negative electrode with said heat-treated graphite powder by pressing.

9. A method for manufacturing non-aqueous secondary 15 batteries as claimed in claim 8, wherein the manufacture of the graphite electrode further includes the step of:

removing impurities from the graphite powder by heating the graphite powder to at least 2,700°C prior to forming the negative electrode such that the amount of Si in the graphite 20 powder will be reduced to 30 ppm to 0 ppm.

10. A method for manufacturing graphite powder, comprising the steps of;

graphitizing raw graphite by heating raw graphite to at least 2,000°C,

25 pulverizing said graphitized raw graphite, sieving said pulverized graphite to obtain graphite powder having a maximum particle diameter of 100 μm ,

heating said graphite powder as a heat treatment to transform the crystalline structure to a hexagonal structure, 30 and

further heating said graphite powder at a higher temperature than said heat treatment to transform the crystalline structure for reducing impurities.

11. A method for manufacturing graphite powder as claimed in claim 10, wherein

the temperature of said heat treatment for transforming the crystalline structure to a hexagonal structure is in a range from 900°C to 1,100°C.

12. A method for manufacturing graphite powder as claimed in claim 10, wherein

the temperature of the heat treatment for eliminating impurities is in a range from 2,700°C to 2,900°C.

13. A method for manufacturing graphite powder as claimed in claim 10, wherein

the heat treatments are processed after the pulverizing process.

14. A method for manufacturing graphite powder, comprising the steps of;

graphitizing raw graphite by heating raw graphite to at least 2,000°C,

pulverizing said graphitized raw graphite,

sieving said pulverized graphite for obtaining graphite powder having a maximum particle diameter of 100 μm,

immersing said graphite powder in an acidic solution as an immersing treatment,

washing with water,

neutralizing, and

drying.

15. A method for manufacturing graphite powder as claimed in claim 14, wherein

said acidic solution contains at least one compound selected from a group consisting of sulfuric acid, nitric acid, perchloric acid, phosphoric acid, and fluoric acid.

16. A method for manufacturing graphite powder as claimed in any one of claims 10-14, wherein

said pulverizing is performed by a jet-mill.

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17. A method for manufacturing graphite powder as claimed in any one of claims 10-16, wherein

said raw graphite has a diffraction angle for the maximum diffraction peak in a range from 26.2 degrees to 26.5 degrees

5 in said X-ray diffraction pattern with the $\text{CuK}\alpha$ line.

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FIG .1

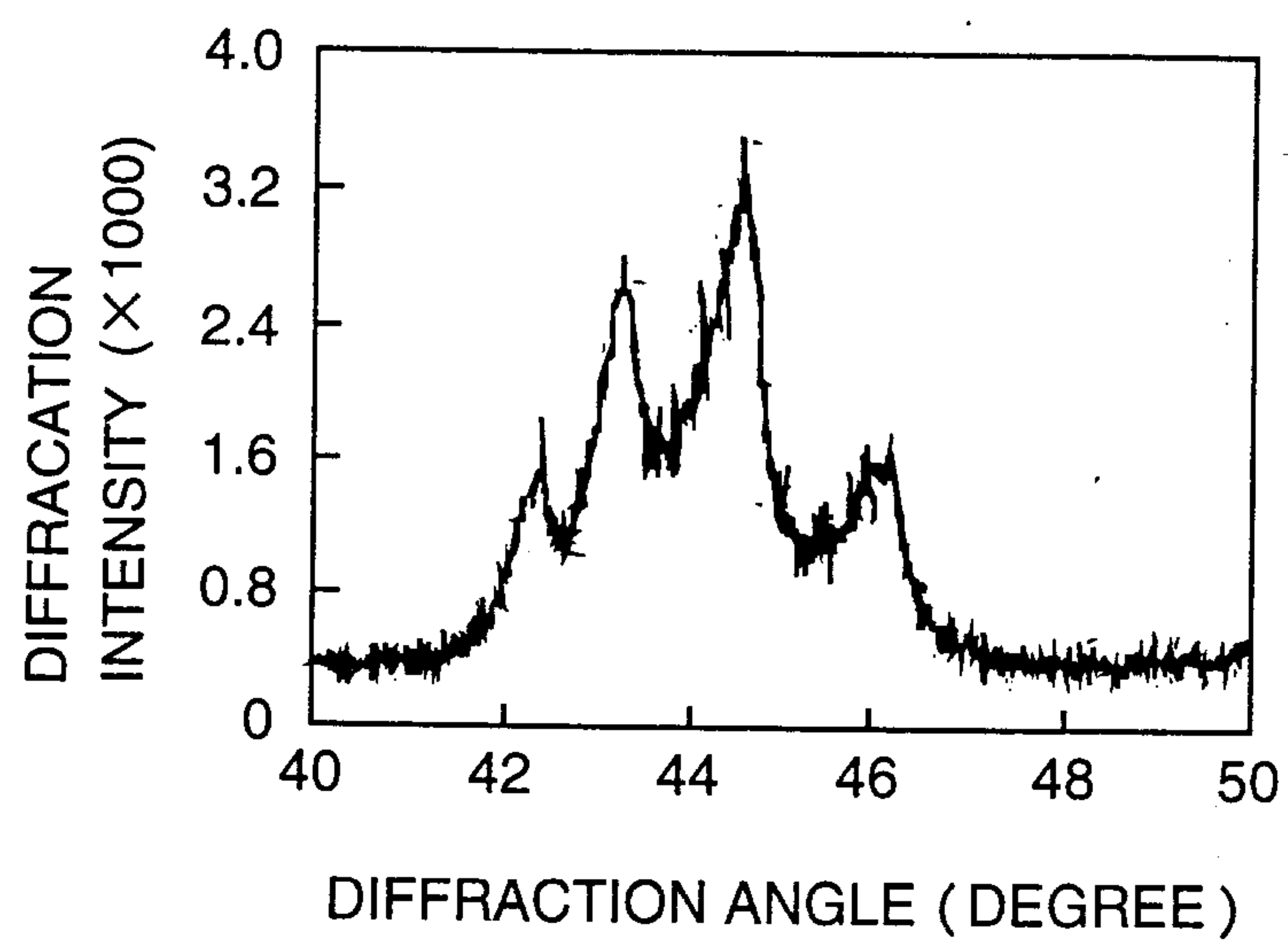


FIG .2

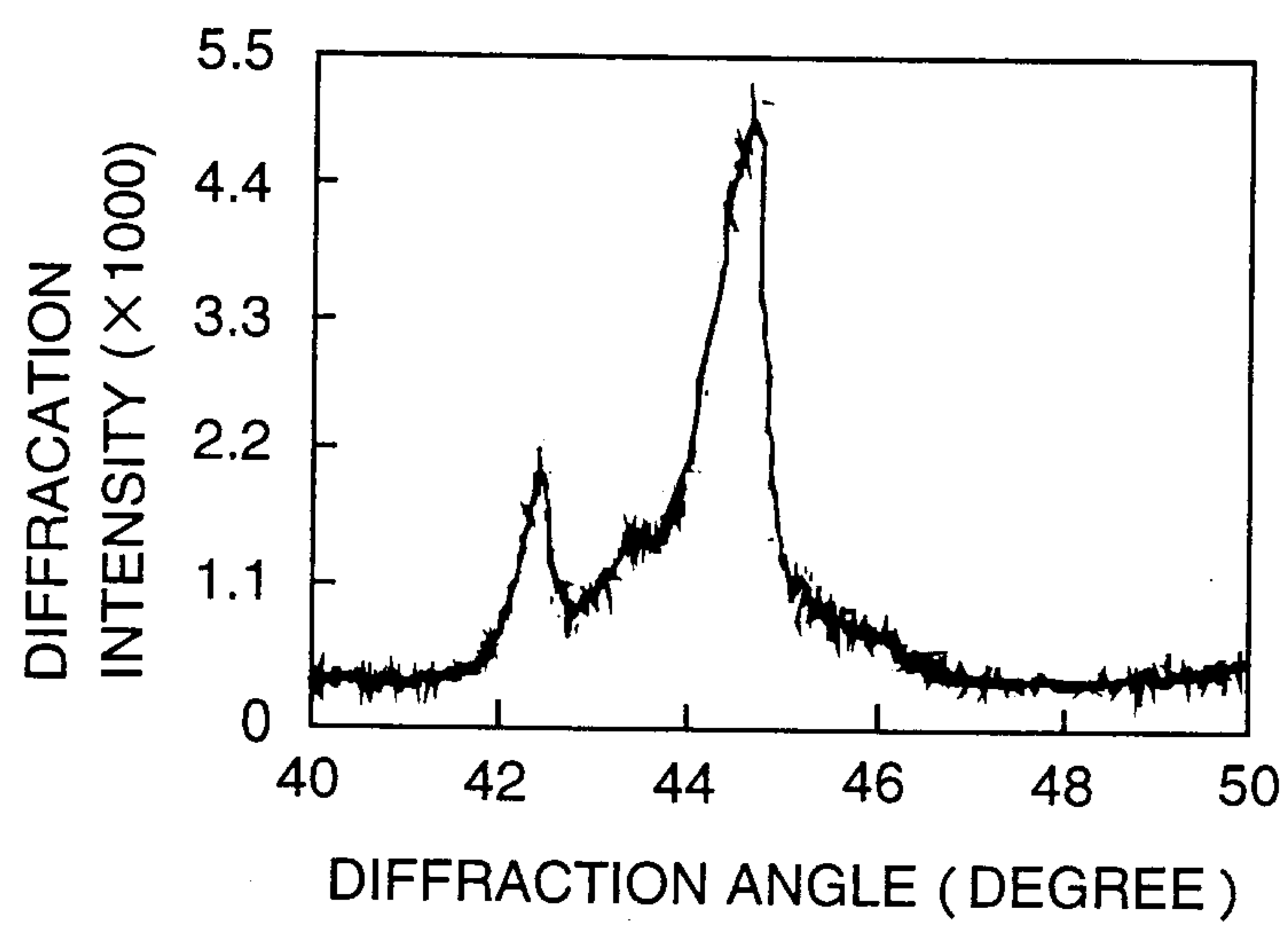


FIG .3

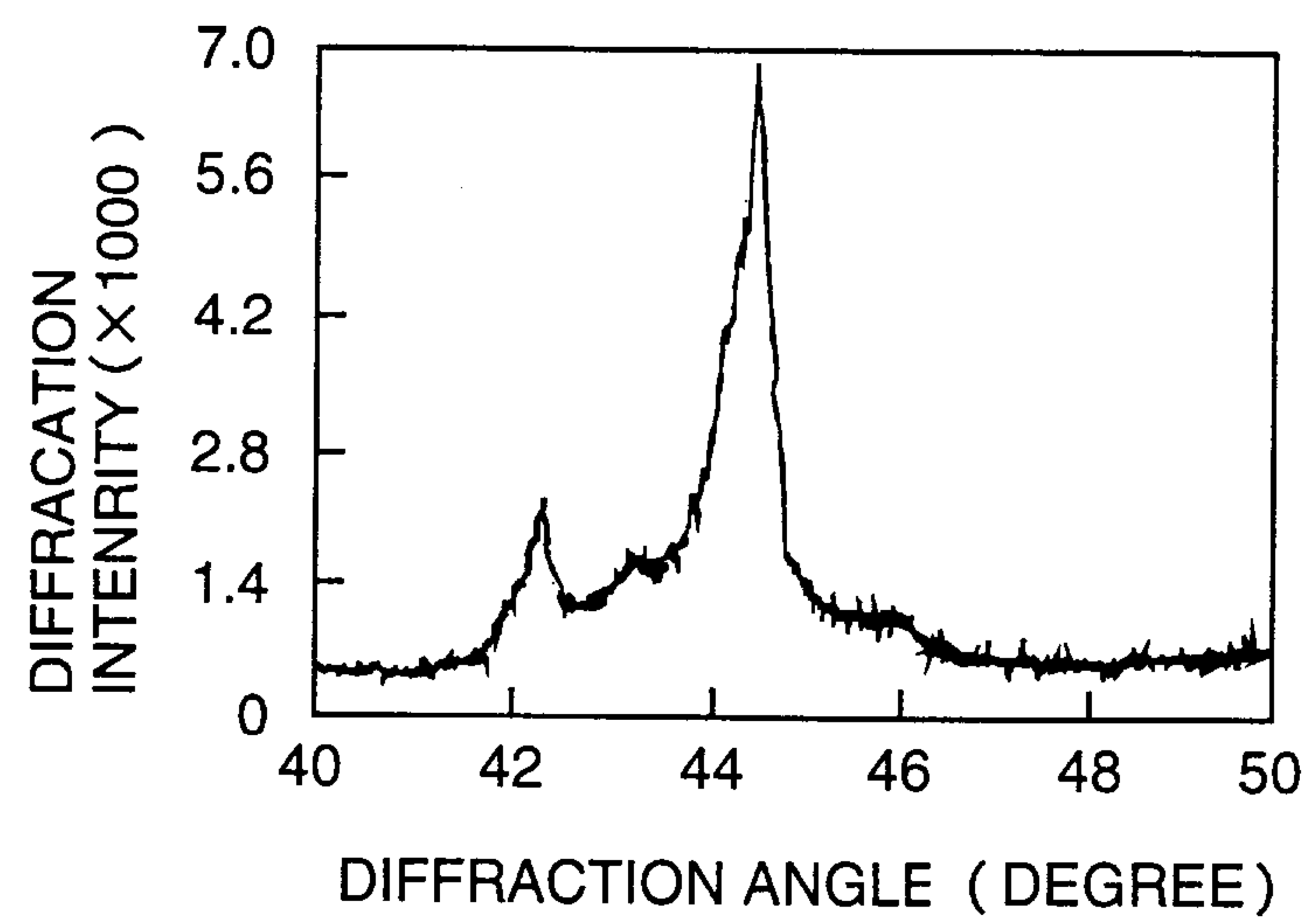


FIG .4

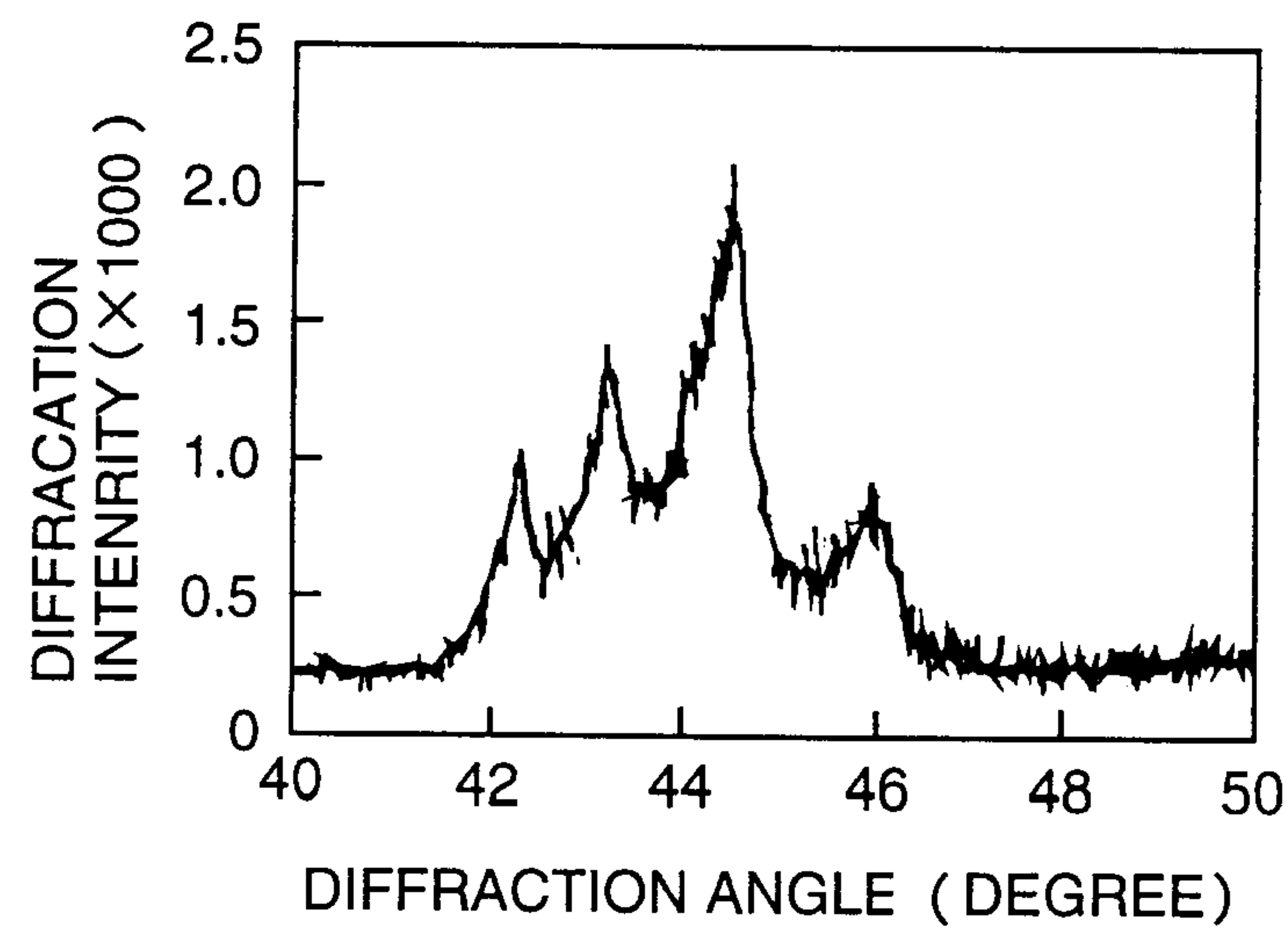


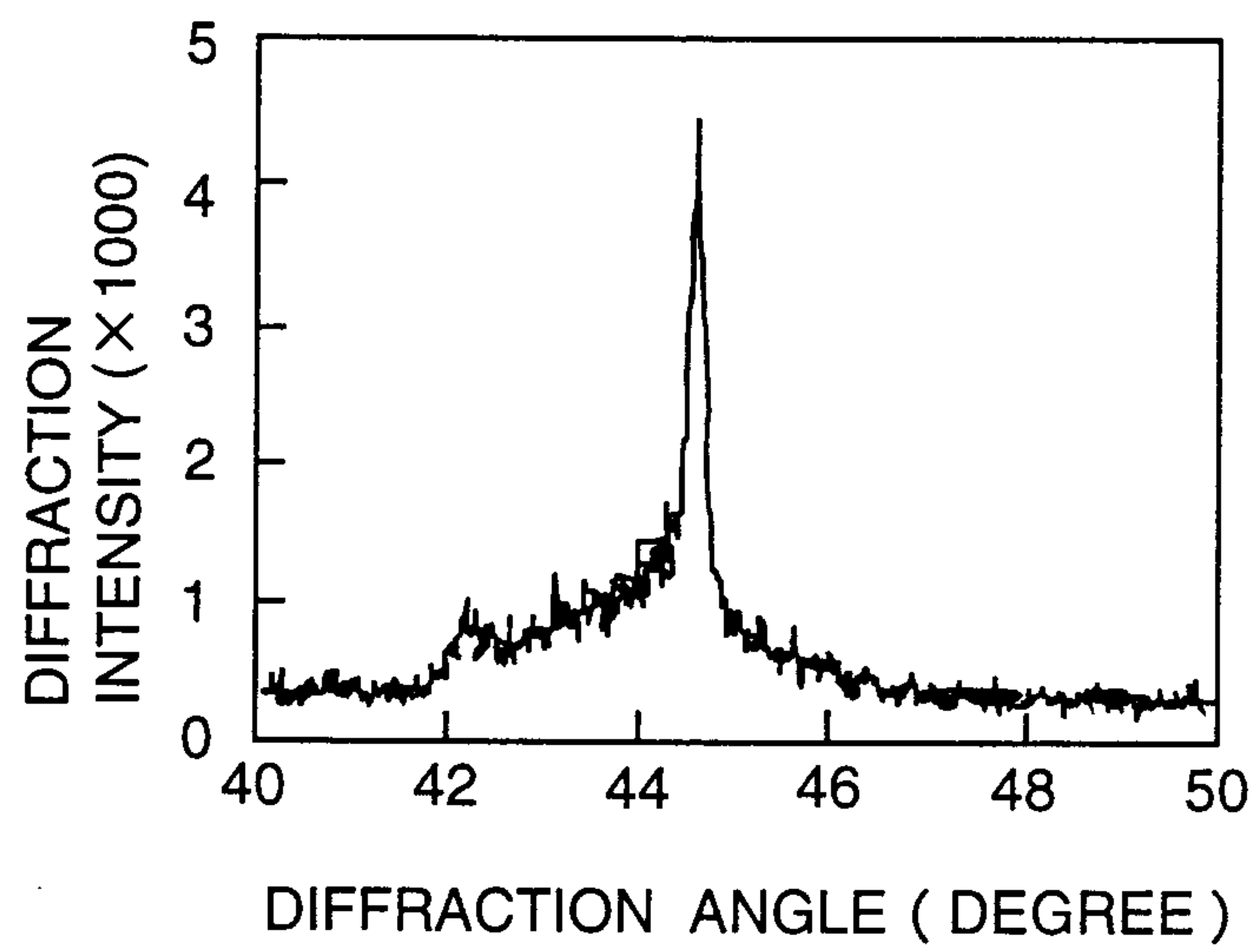
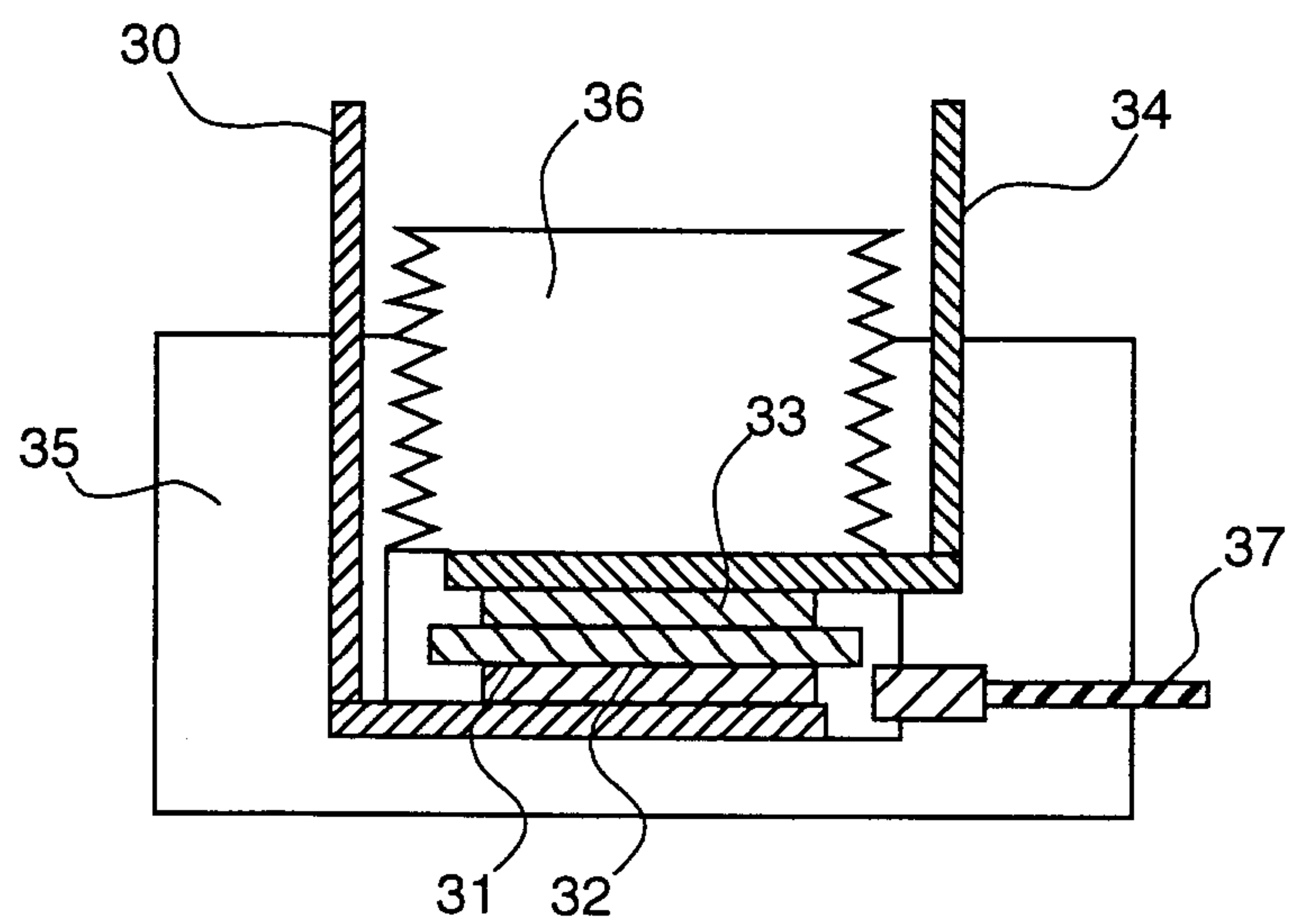
FIG .5*FIG .6*

FIG. 7

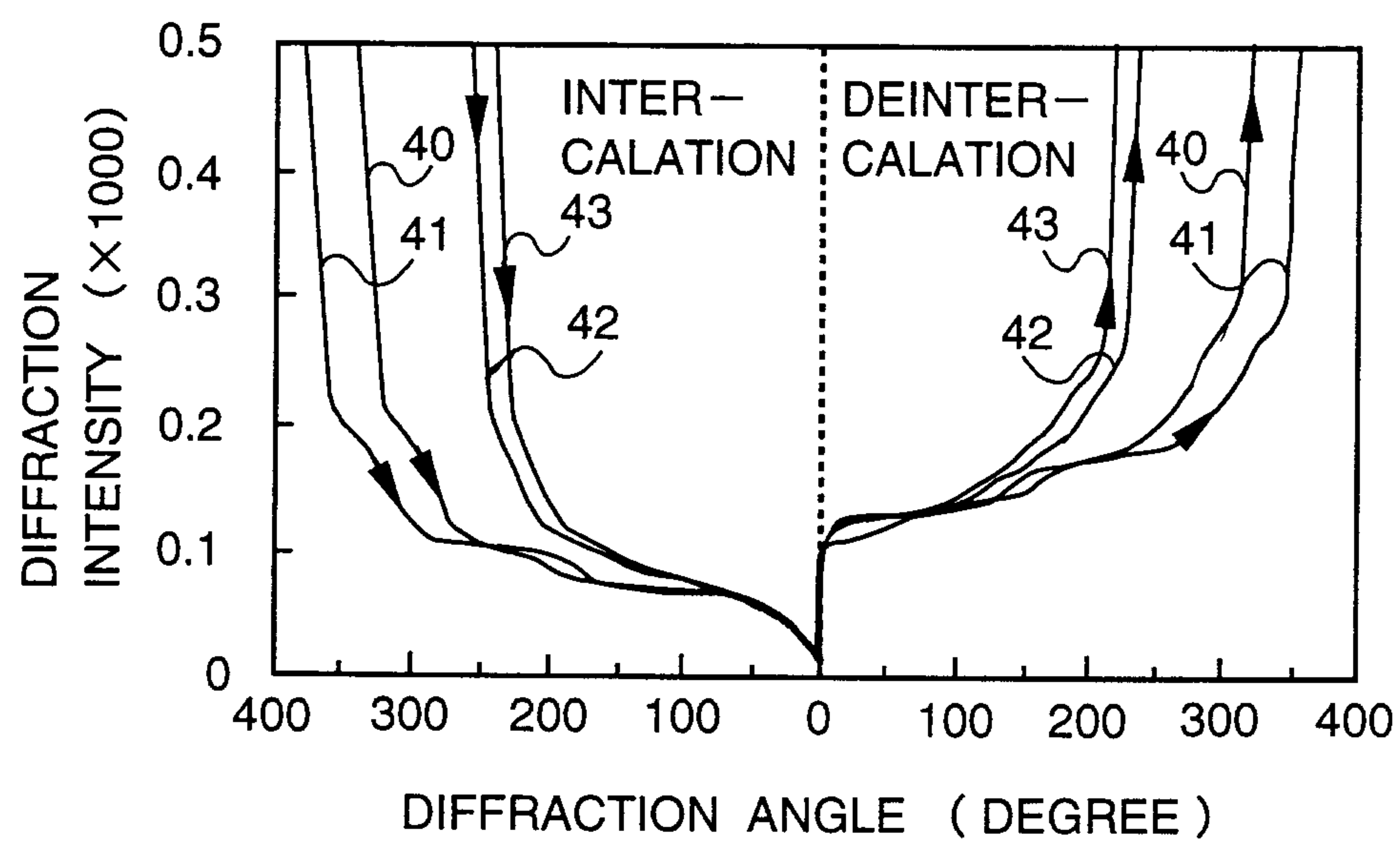


FIG. 8

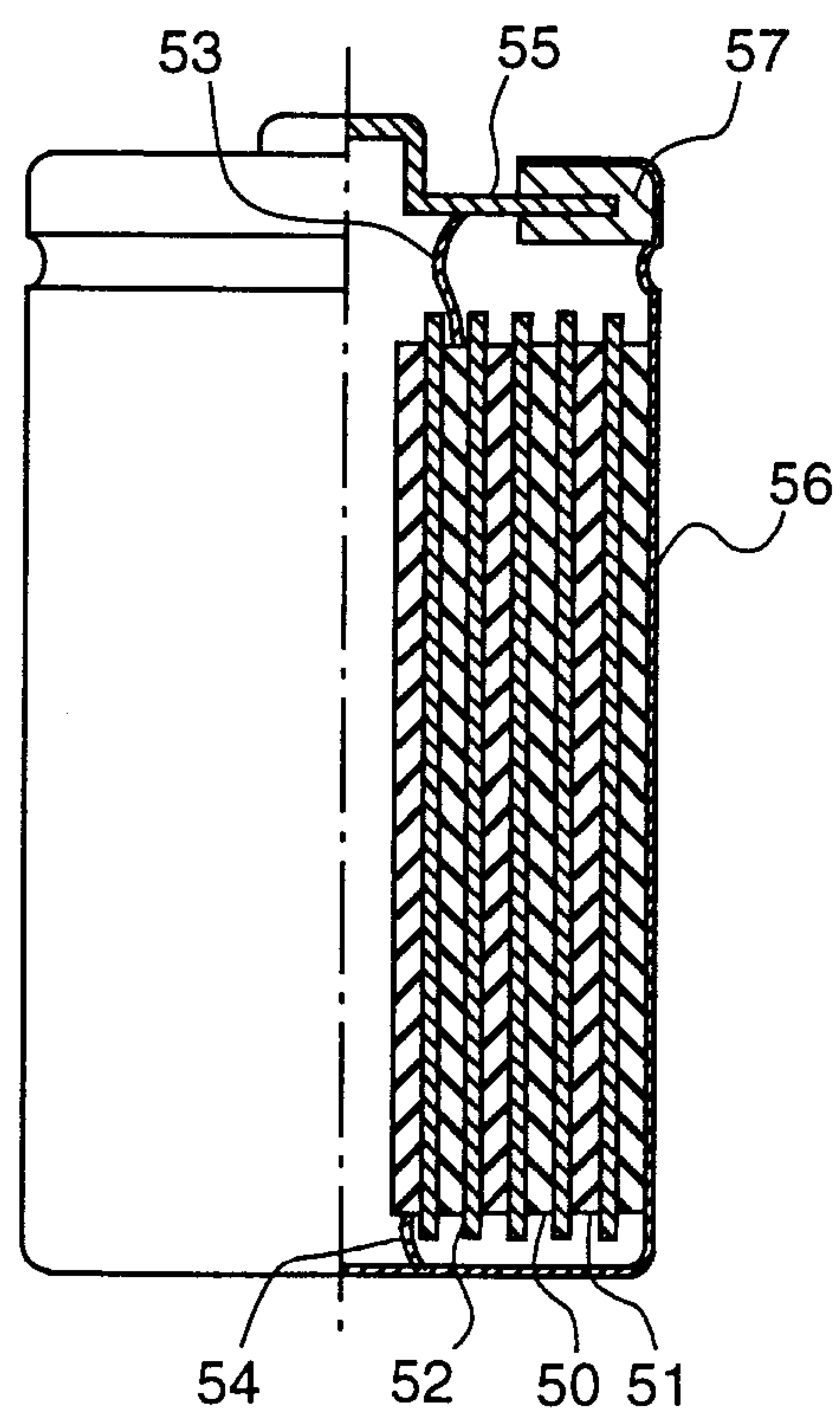


FIG. 9

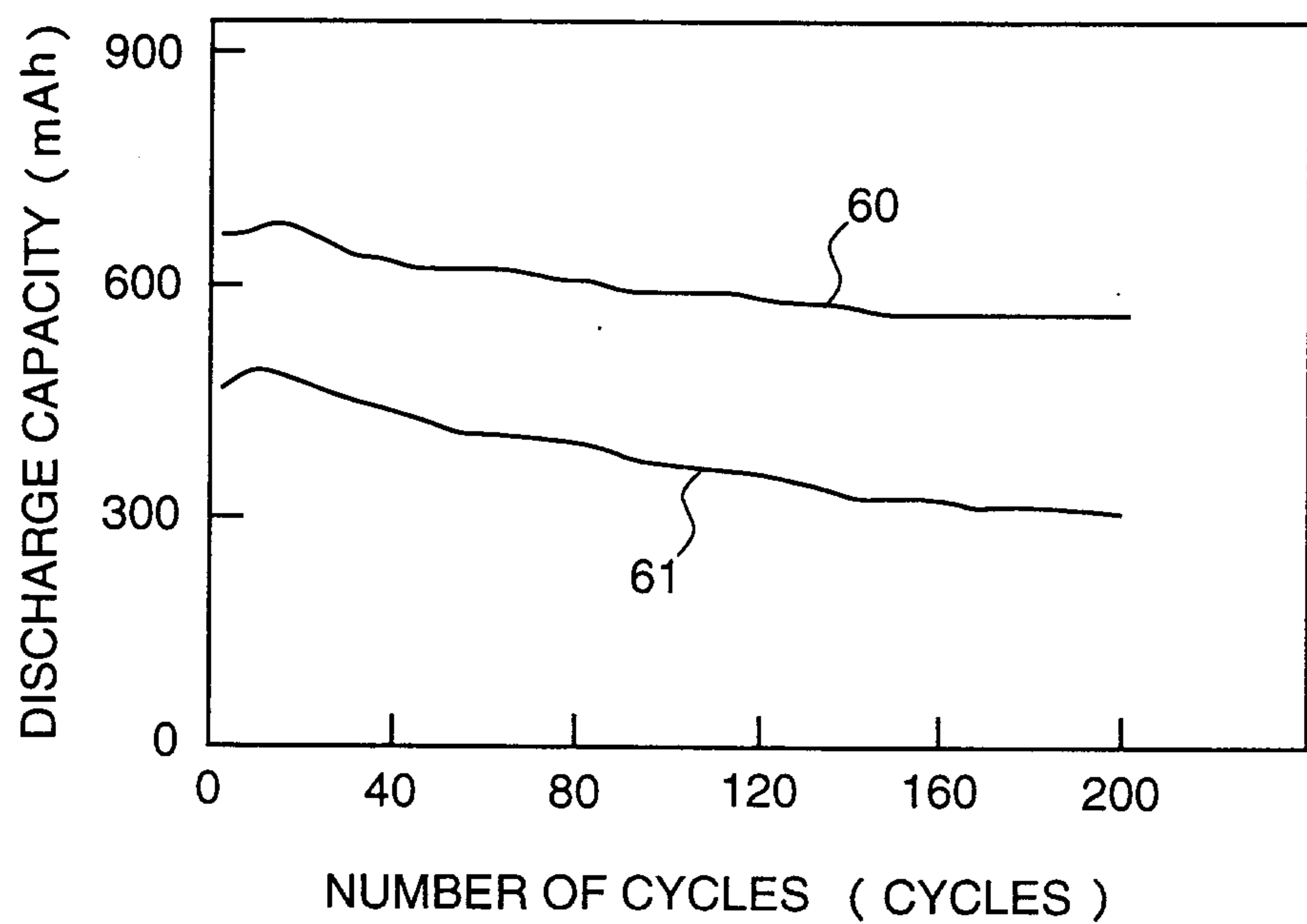


FIG. 10

