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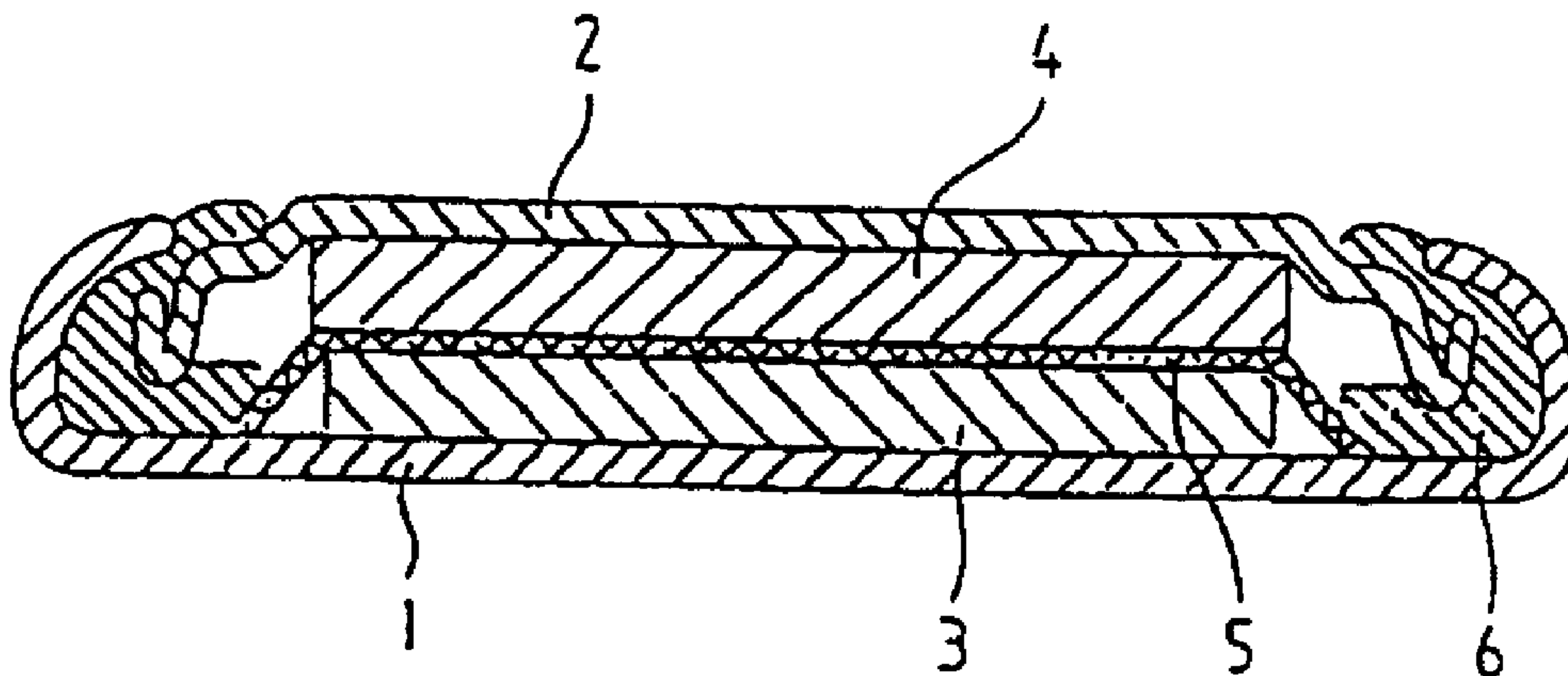
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(54) Titre : METHODE DE PRODUCTION D'OXYDE DE MANGANESE COMPLEXE ET DE LITHIUM DE TYPE SPINELLE

(54) Title: METHOD FOR PRODUCING SPINEL TYPE LITHIUM MANGANESE COMPLEX OXIDE



(57) Abrégé/Abstract:

A method for producing a spinet type lithium manganese complex oxide comprises the steps of: synthesizing a spinet type lithium manganese complex oxide represented by a general formula of $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$ (wherein x is defined by the relation of $0 < x \leq 0.08$) by a spray pyrolysis method; and subjecting the oxide to a heat treatment at a temperature of $T^\circ\text{C}$ (T is defined by the relation of $T < 865 - 2027x$, wherein x corresponds to that in the general formula $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$).



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ABSTRACT OF THE DISCLOSURE

A method for producing a spinel type lithium manganese complex oxide comprises the steps of: synthesizing a spinel type lithium manganese complex oxide represented by a general formula of $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$ (wherein x is defined by the relation of $0 < x \leq 0.08$) by a spray pyrolysis method; and subjecting the oxide to a heat treatment at a temperature of $T^\circ\text{C}$ (T is defined by the relation of $T < 865 - 2027x$, wherein x corresponds to that in the general formula $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$).

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METHOD FOR PRODUCING SPINEL TYPE
LITHIUM MANGANESE COMPLEX OXIDE

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a method for producing a spinel type lithium manganese complex oxide used for an cathode active material of a lithium secondary battery.

2. Description of the Related Art

Various methods as described below have been proposed as methods for producing a spinel type lithium manganese complex oxide used for an cathode active material of a lithium secondary battery.

(a) A solid state method in which powders such as lithium carbonate and manganese dioxide are mixed together and sintered at a temperature of about 800°C.

(b) A melt-impregnation method in which porous manganese dioxide is impregnated with lithium nitrate or lithium hydroxide having a low melting point.

(c) A spray pyrolysis method in which lithium nitrate and manganese nitrate dissolved in water are sprayed and thermally decomposed.

(d) A method in which a solution of lithium nitrate and manganese nitrate dissolved in water is subjected to a spray pyrolysis followed by an additional heat treatment.

However, the methods described above involved the following problems.

In the solid state method (a), a relatively high sintering temperature was required since carbonates and oxides were used as starting materials. Accordingly, defective spinels such as an oxygen excess spinel is liable to be synthesized.

Since it is impossible to mix the respective powders uniformly on a molecular level with each other, Li_2MnO_3 and LiMnO_2 , for example, are sometimes adversely formed besides desired

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LiMn_2O_4 . Several repeated sinterings for a long period of time while adjusting the oxygen concentration was required for preventing the side reaction as described above.

Although uniform distribution of Li and Mn is improved as compared with the solid state method, a porous manganese as a starting material is required in the melt-impregnation method described in (b). However, a crushing treatment is required for obtaining this porous manganese material, forcing a special crushing machine to be installed for applying this crushing treatment. Moreover, impurities such as the crushing treatment medium or friction products of the inner wall of the machine are mixed with the starting material, causing problems in that the quality of the complex oxide obtained as an cathode active material is deteriorated; installation of a special crushing machine results in an increase of the production cost.

Crystallinity of the mixed oxide obtained becomes poor when the oxide has not been subjected to a long period of sintering at a low temperature in order to suppress evaporation of the low melting point lithium material. Therefore, the crystal structure is collapsed during repeated charge-discharge cycles of the secondary battery when this complex oxide is used for the active material of the secondary battery, causing a decrease of the capacity of the secondary battery.

Uniformity of the spinel type lithium manganese complex oxide can be markedly enhanced in the spray pyrolysis method described in (c) as compared with the melt-impregnation method, because the elements constituting the spinel type lithium manganese complex oxide can be uniformly mixed in an ion level with each other. Eliminating the need for a crushing step of the starting material as in the melt-impregnation method brings about an advantage that invasion of impurities originating from the crushing step can be avoided.

However, since a series of operations of dehydration, drying and thermal decomposition is performed within a time period of as short as several seconds in this spray pyrolysis method, heat

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hysteresis is quite short compared with conventional baking treatments so that crystallinity of the synthesized complex oxide tends to be poor. Accordingly, there was a problem that the crystal structure is collapsed to decrease the capacity of the secondary battery during repeated charge-discharge cycles of the battery when this complex oxide is used for these active material of the secondary battery.

In addition, since the specific surface area of the synthesized complex oxide is as large as several tens m^2/g , the electrolyte solution making a contact with this complex oxide is decomposed, causing a problem that charge-discharge cycle characteristics and preservation characteristics of the secondary battery are extremely deteriorated.

The method for applying a heat treatment in addition to the spray pyrolysis method as described in (d) was proposed for solving the foregoing problems, making it possible to obtain a superior characteristics to the conventional method.

Other phenomena were also observed, however, when the active material of the spinel type lithium manganese complex oxide obtained by the spray pyrolysis method was subjected to a heat treatment (annealing) at a temperature of 800°C or more in order to improve its crystallinity, particle size and specific surface area. The phenomena are: charge-discharge characteristic of the active material is markedly improved and the characteristics are hardly deteriorated during a long period of charge-discharge cycle test, and, although there are no remarkable characteristic changes during initial 100 cycles or so, the capacity is gradually decreased when the numbers of charge-discharge cycles are increased further.

For the foregoing reasons, there is a need for a method for producing a spinel type lithium manganese complex oxide capable of obtaining an excellent charge-discharge cycle characteristic for a long period of time when the oxide is used for the active material of the lithium secondary battery.

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SUMMARY OF THE INVENTION

The present invention is directed to a method that satisfied this need. The method for producing a spinel type lithium manganese complex oxide comprises the steps of: synthesizing a spinel type lithium manganese complex oxide represented by a general formula of $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$ (wherein x is defined by the relation of $0 < x \leq 0.08$) by a spray pyrolysis method; and subjecting the oxide to a heat treatment at a temperature of $T^\circ\text{C}$ (T is defined by the relation of $T < 865 - 2027x$, wherein x corresponds to that in the general formula $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$).

In the method, it is preferable to use the spinel type lithium manganese complex oxide represented by a general formula of $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$ ($0 < x \leq 0.05$), and it is more preferable that x satisfies the relation $0 < x \leq 0.02$.

According to the present invention, an uniform and fine spinel type lithium manganese complex oxide having a good cycle characteristics can be obtained. Limiting the substitution ratio of Mn with Li in a specified range makes it possible to obtain a high initial capacity, besides obtaining a spinel type lithium manganese complex oxide having an excellent charge-discharge cycle characteristic of more than 500 cycles.

Accordingly, a lithium secondary battery excellent in the charge-discharge cycle characteristic can be produced by using this spinel type lithium manganese complex oxide for the cathode active material of the lithium secondary battery.

In accordance with another aspect of the present invention, there is provided a method for producing a spinel type lithium manganese complex oxide comprising the steps of: synthesizing a spinel type lithium manganese complex oxide

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represented by the general formula of $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$, by spray pyrolysis in which lithium compound and manganese compound dissolved in liquid are sprayed and thermally decomposed; and subjecting the oxide thus synthesized to a heat treatment at a temperature of $T^\circ\text{C}$ where T is $< 865 - 2027x$, wherein x is $0 < x \leq 0.08$.

In accordance with another aspect of the present invention, there is provided a method for producing a spinel type lithium manganese complex oxide comprising the steps of: synthesizing a spinel type lithium manganese complex oxide represented by the general formula of $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$ wherein x is $0 < x \leq 0.08$, by spray pyrolysis in which lithium compound and manganese compound dissolved in liquid are sprayed and thermally decomposed; and subjecting the oxide thus synthesized to a heat treatment at a temperature which does not exceed the oxygen dissociation temperature by more than 5°C .

For the purpose of illustrating the invention, there is shown in the drawings several forms which are presently preferred, it being understood, however, that the invention is not limited to the precise arrangements and instrumentalities shown.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a typical example of the TG diagram obtained by performing TG-DTA measurement on $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$.

FIG. 2 is a cross-section showing one example of the lithium secondary battery.

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FIG. 3 shows one example of the TG (thermo-gravimetry) diagrams of the compositions having different substitution ratios.

FIG. 4 shows one example of the graph indicating the relation between the compositions with different substitution ratios and the oxygen dissociation temperature.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The inventors of the present invention studied the spinel type lithium manganese complex oxide, whose characteristics had been markedly improved, and the spinel type lithium manganese complex oxide whose characteristics had not been so markedly improved, using a variety of analytical methods, observing that a large amount of weight loss had occurred in the spinel type lithium manganese complex oxide whose characteristics had not been so markedly improved, due to dissociation of oxygen by a heat treatment at a temperature of about 800°C.

With respect to this phenomenon, the inventors of the present invention found that the respective temperatures at which a large amount of weight loss due to dissociation of oxygen from the spinel type lithium manganese complex oxide starts (the oxygen dissociation temperature) are different depending on the composition of the spinel type lithium manganese complex oxide and found a relationship among the composition ratio of Li/Mn at which the characteristics are largely improved, the oxygen dissociation temperature and the heat treatment temperature, thereby completing the invention as will be described hereinafter.

The present invention provides a method for producing a spinel type lithium manganese complex oxide, wherein a spinel type lithium manganese complex oxide represented by a general formula of $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$ (wherein x is defined by the relation of $0 < x \leq 0.08$) is synthesized by the spray pyrolysis method followed by subjecting the oxide to a heat treatment at a temperature of $T^\circ\text{C}$ (T is defined by the relation of $T < 865 - 2027x$, wherein x corresponds to that in the general formula $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$).

In the method, it is preferable to use the spinel type

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lithium manganese complex oxide represented by a general formula of $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$ ($0 < x \leq 0.05$), and it is more preferable that x satisfies the relation $0 < x \leq 0.02$.

According to the present invention, dissociation of oxygen from $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$ can be prevented by heat-treating the spinel type lithium manganese complex oxide represented by a general formula of $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$ (wherein x is defined by the relation of $0 < x \leq 0.08$) at a temperature of $T^\circ\text{C}$ (T is defined by the relation of $T < 865 - 2027x$, wherein x corresponds to that in the general formula $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$) by the spray pyrolysis method according to the present invention. Therefore, the method prevents oxygen deficient $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_{4-z}$ from being synthesized, enabling a spinel type lithium manganese complex oxide with a high degree of cycle characteristics to be obtained.

The charge-discharge capacity can be prevented from being decreased by restricting the range of x in $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$ in the range of $0 < x \leq 0.05$.

A higher degree of charge-discharge capacity can be obtained by restricting the range of x in $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$ in the range of $0 < x \leq 0.02$.

Hereinafter, the preferred embodiments of the present invention are explained in detail with reference to the drawings.

Lithium nitrate and manganese formate as starting materials for constituting the spinel type lithium manganese complex oxides were prepared. The lithium nitrate and manganese formate were precisely weighed and placed in a vessel so that $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$ (wherein x is defined by the relation of $0.005 \leq x \leq 0.100$) as a spinel type lithium manganese oxides shown in TABLE 1 could be obtained. After adding 1000 ml of water to prepare mixed solutions, the concentrations of the solutions were adjusted to be 0.5 mol/litter as converted into $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$ (wherein $0.005 \leq x \leq 0.100$).

These mixed solutions were sprayed into a thermal decomposition furnace adjusted to 750°C from a nozzle at a spray

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speed of 1200 ml/hour for thermal decomposition, thereby obtaining individual powders of the spinel type lithium manganese complex oxide.

Then, the powders of the spinel type lithium manganese complex oxide were placed in a vessel made of alumina, and each powder was subjected to heat-treatment (annealing) at a prescribed temperature of 700 to 850°C for 2 hours, thereby obtaining the spinel type lithium manganese complex oxides having respective compositions shown in Sample Nos. 1 to 24 in TABLE 1.

TABLE 1			
Sample No.	$\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$ x=	Heat treatment temperature (°C)	Oxygen dissociation temperature (°C)
1	0.005	775	854
2	0.005	800	854
3	0.005	825	854
4	0.005	850	854
5	0.010	775	844
6	0.010	800	844
7	0.010	825	844
*8	0.010	850	844
9	0.018	775	828
10	0.018	800	828
11	0.018	825	828
*12	0.018	850	828
13	0.030	750	803
14	0.030	775	803
15	0.030	800	803
*16	0.030	825	803
17	0.050	700	763
18	0.050	725	763
19	0.050	750	763
*20	0.050	775	763
21	0.080	700	702
*22	0.080	725	702
*23	0.080	750	702
*24	0.100	700	661

The oxygen dissociation temperature of these spinel type lithium manganese complex oxides were measured by TG-TA (thermogravimetric - differential thermal assay) and the results are also shown in TABLE 1. The oxygen dissociation temperature refers to a temperature at which oxygen is dissociated to start a rapid weight decrease as shown by the temperature T in FIG. 1

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showing TG (thermogravimetry). The samples attached with a mark (*) in TABLE 1 correspond to those out of the range of the present invention.

A secondary battery was produced by using the active material of the spinel type lithium manganese complex oxide as an cathode. In other words, a powder of the active material described above was kneaded with polytetrafluoroethylene to form a sheet, which was used for the cathode by press-adhering it to a SUS mesh.

Metallic lithium as an cathode 3 and an anode 4 were stacked with each other via a separator 5 made of polypropylene so that the SUS mesh of the cathode 3 comes to outside. The assembled electrodes were accommodated in an cathode can by placing the cathode 3 downward, and an electrolyte solution was impregnated into the separator 5. A solution prepared by dissolving lithium perchlorate into a mixed solution of propylene carbonate and 1,1-dimethoxyethane was used for the electrolyte solution. The orifice of the cathode can 1 was sealed with a anode plate 2 made of a stainless steel, thereby completing the lithium secondary battery.

The lithium secondary battery thus obtained was subjected to a charge-discharge test under the condition of a charge-discharge current density of 0.5 mA/cm^2 with a charging stop voltage of 4.2 V and a discharge stop voltage of 3.0 V as one cycle.

The results are shown in TABLE 2.

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TABLE 2			
Sample No.	Charge-discharge capacity (mAh/g)		
	Initial	After 100 cycles	After 500 cycles
1	135	131	124
2	135	133	128
3	134	132	128
4	130	128	123
5	132	129	126
6	133	131	127
7	131	129	123
*8	127	124	109
9	129	127	123
10	130	127	124
11	129	126	124
*12	126	123	111
13	124	122	118
14	126	124	121
15	126	123	117
*16	123	119	106
17	121	118	116
18	122	119	116
19	121	117	115
*20	120	117	107
21	115	113	111
*22	114	111	98
*23	114	110	93
*24	107	102	86

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As is evident from TABLE 1 and TABLE 2, performing a heat treatment (annealing) at a temperature of $T^{\circ}\text{C}$ (T is defined by the relation of $T < 865 - 2027x$, wherein x corresponds to that in the general formula $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$) after synthesizing the spinel type lithium manganese complex oxide represented by the general formula of $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$ (wherein x is defined by the relation of $0 < x \leq 0.08$) allows oxygen to be prevented from being released, making it possible to synthesize an active material of the spinel type lithium manganese complex oxide having a good cycle characteristic.

It is true that the charge-discharge capacity does not largely differ from the initial value after 100 cycles of charging and discharging when the heat treatment temperature is higher than the oxygen dissociation temperature as shown in sample Nos. 8, 12, 16 and 20, and from 22 through 24. However, the charge-discharge capacities of the oxides are largely decreased after 500 cycles of charging and discharging as compared with those subjected to a heat treatment at a temperature lower than the oxygen dissociation temperature. It is therefore preferable that the heat treatment temperature does not exceed the oxygen dissociation temperature.

As will be understood, the oxygen dissociation temperature is a temperature at which oxygen begins to dissociate, and it is not true that all of the oxygen dissociates at the temperature. Therefore, there exists a marginal temperature beyond the oxygen dissociation temperature and it is possible to perform a heat treatment at the marginal temperature within the scope of the present invention. According to the further study by the inventors, the heat treatment can be performed at a temperature higher than the temperature T by 5°C or less.

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As long as the heat treatment is performed at a temperature lower than the oxygen dissociation temperature, dissociation of the oxygen can be prevented. However, when the temperature of the heat treatment is too low, it takes a considerably long time to improve the crystallinity, particle size and specific surface area. In view of this reason, it is preferable that the heat treatment is performed at a temperature of about 650°C or higher regardless of the substitution ratio x , and it is more preferable that the heat treatment is performed at a temperature between the oxygen dissociation temperature and a temperature lower than the oxygen dissociation temperature by about 50°C. That is, it is more preferable that the heat treatment is performed at a temperature of $T^{\circ}\text{C}$ (T is defined by the relation of $835 - 2027x < T < 865 - 2027x$, wherein x corresponds to that in the general formula $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$) after synthesizing the spinel type lithium manganese complex oxide represented by the general formula of $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$ (wherein x is defined by the relation of $0 < x \leq 0.08$).

The substitution ratio x of the Mn site with Li is limited in the range of $0 < x \leq 0.05$ in the present invention because the cycle characteristic is deteriorated due to Jahn-Teller effect when the Mn site is not substituted with Li at all, while when the substitution ratio x exceeds 0.05, the initial capacity is decreased. If the substitution ratio x of the Mn site with Li is further limited in the range of $0 < x < 0.02$ in the present invention, a higher charge-discharge capacity is obtained as shown in the sample Nos. 1 to 7 and sample Nos. 9 to 11.

Accordingly, it is preferable that the substitution ratio x of the Mn site with Li in the general formula of $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$ is in the range of $0 < x \leq 0.05$, more preferably in the range of $0 < x < 0.02$.

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The equation $T < 865 - 2027x$ for determining the heat treatment temperature was derived as follows: The coefficient (2027) for the substitution ratio x of Mn with Li was calculated from the slope of the curve obtained by plotting the relation between the oxygen dissociation temperature and substitution ratio x , as shown in FIG. 3, based on the oxygen dissociation temperature ($T_A - T_D$) in respective compositions (C_A to C_D) with corresponding substitution ratio x .

While preferred embodiments of the invention have been disclosed, various modes of carrying out the principles disclosed herein are contemplated as being within the scope of the following claims. Therefore, it is understood that the scope of the invention is not to be limited except as otherwise set forth in the claims.

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WHAT IS CLAIMED IS:

1. A method for producing a spinel type lithium manganese complex oxide comprising the steps of: synthesizing a spinel type lithium manganese complex oxide represented by the general formula of $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$, by spray pyrolysis in which lithium compound and manganese compound dissolved in liquid are sprayed and thermally decomposed; and subjecting the oxide thus synthesized to a heat treatment at a temperature of $T^\circ\text{C}$ where T is $< 865 - 2027x$, wherein x is $0 < x \leq 0.08$.

2. A method for producing a spinel type lithium manganese complex oxide according to Claim 1, wherein $0 < x \leq 0.05$.

3. A method for producing a spinel type lithium manganese complex oxide according to Claim 1, wherein $0 < x \leq 0.02$.

4. A method for producing a spinel type lithium manganese complex oxide according to Claim 3, wherein $835 - 2027x < T < 865 - 2027x$.

5. A method for producing a spinel type lithium manganese complex oxide according to Claim 2, wherein $835 - 2027x < T < 865 - 2027x$.

6. A method for producing a spinel type lithium manganese complex oxide according to Claim 1, wherein $835 - 2027x < T < 865 - 2027x$.

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7. A method for producing a spinel type lithium manganese complex oxide comprising the steps of: synthesizing a spinel type lithium manganese complex oxide represented by the general formula of $\text{Li}(\text{Mn}_{2-x}\text{Li}_x)\text{O}_4$ wherein x is $0 < x \leq 0.08$, by spray pyrolysis in which lithium compound and manganese compound dissolved in liquid are sprayed and thermally decomposed; and subjecting the oxide thus synthesized to a heat treatment at a temperature which does not exceed the oxygen dissociation temperature by more than 5°C .

8. A method for producing a spinel type lithium manganese complex oxide according to Claim 7, wherein the heat treatment temperature is not less than the oxygen dissociation temperature by more than about 50°C .

9. A method for producing a spinel type lithium manganese complex oxide according to Claim 8, wherein the heat treatment temperature does not exceed the oxygen dissociation temperature.

FIG. 1

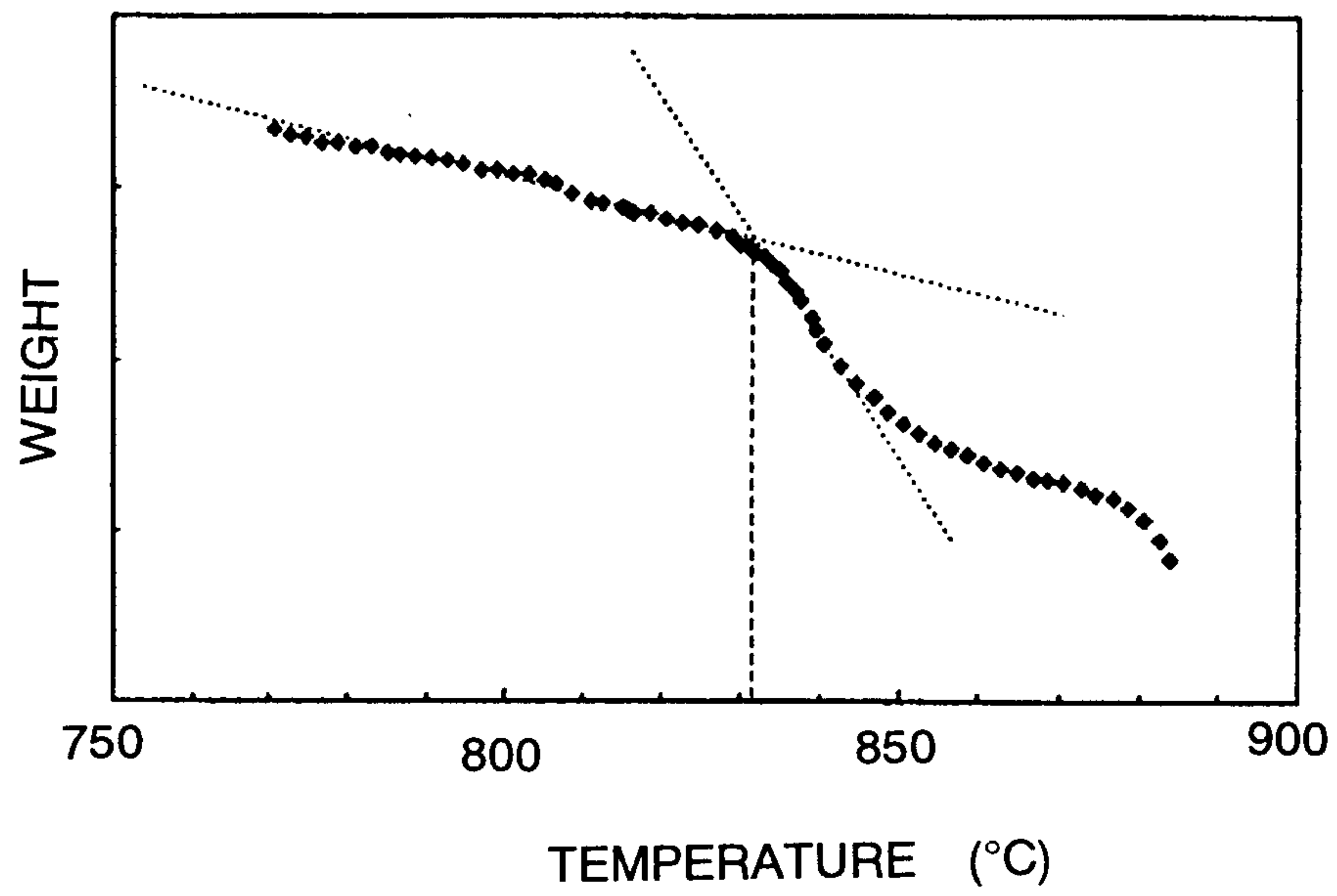


FIG. 2

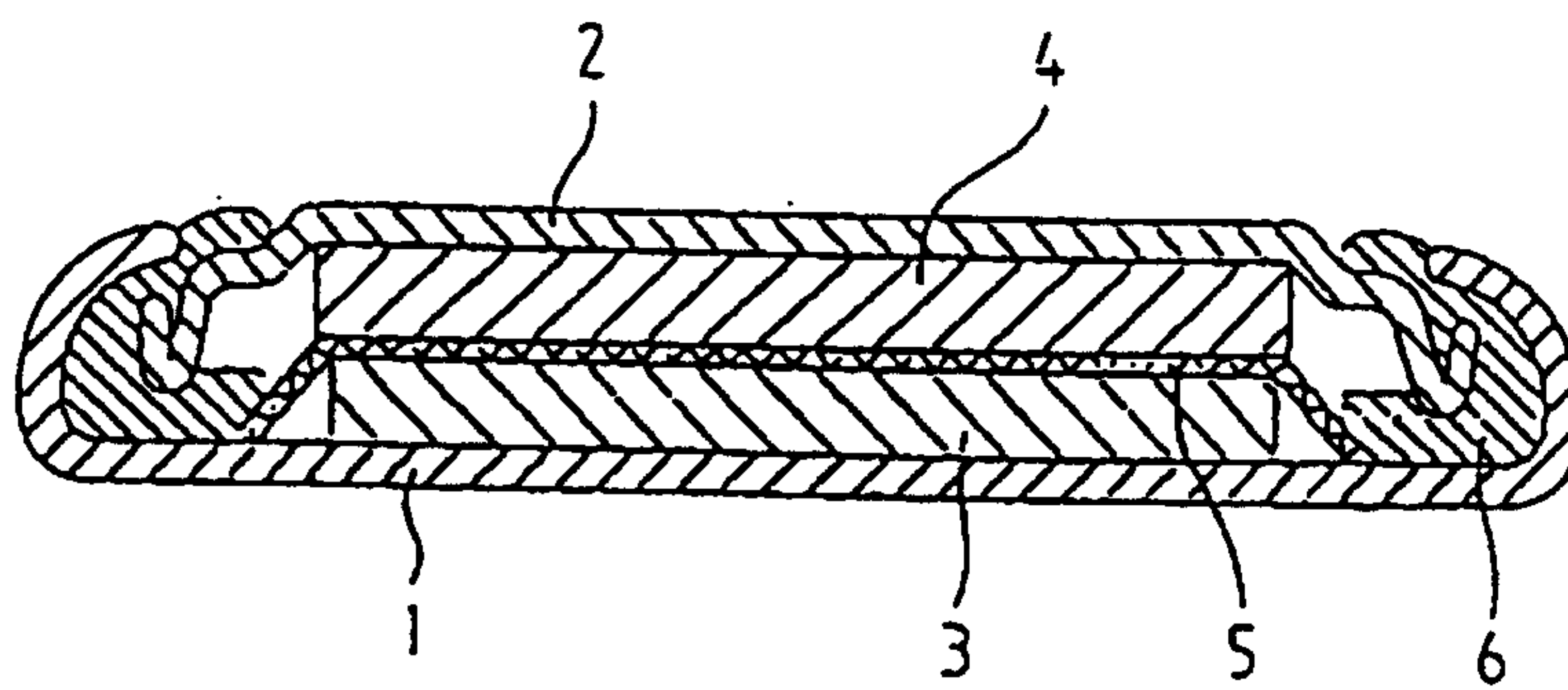


FIG. 3

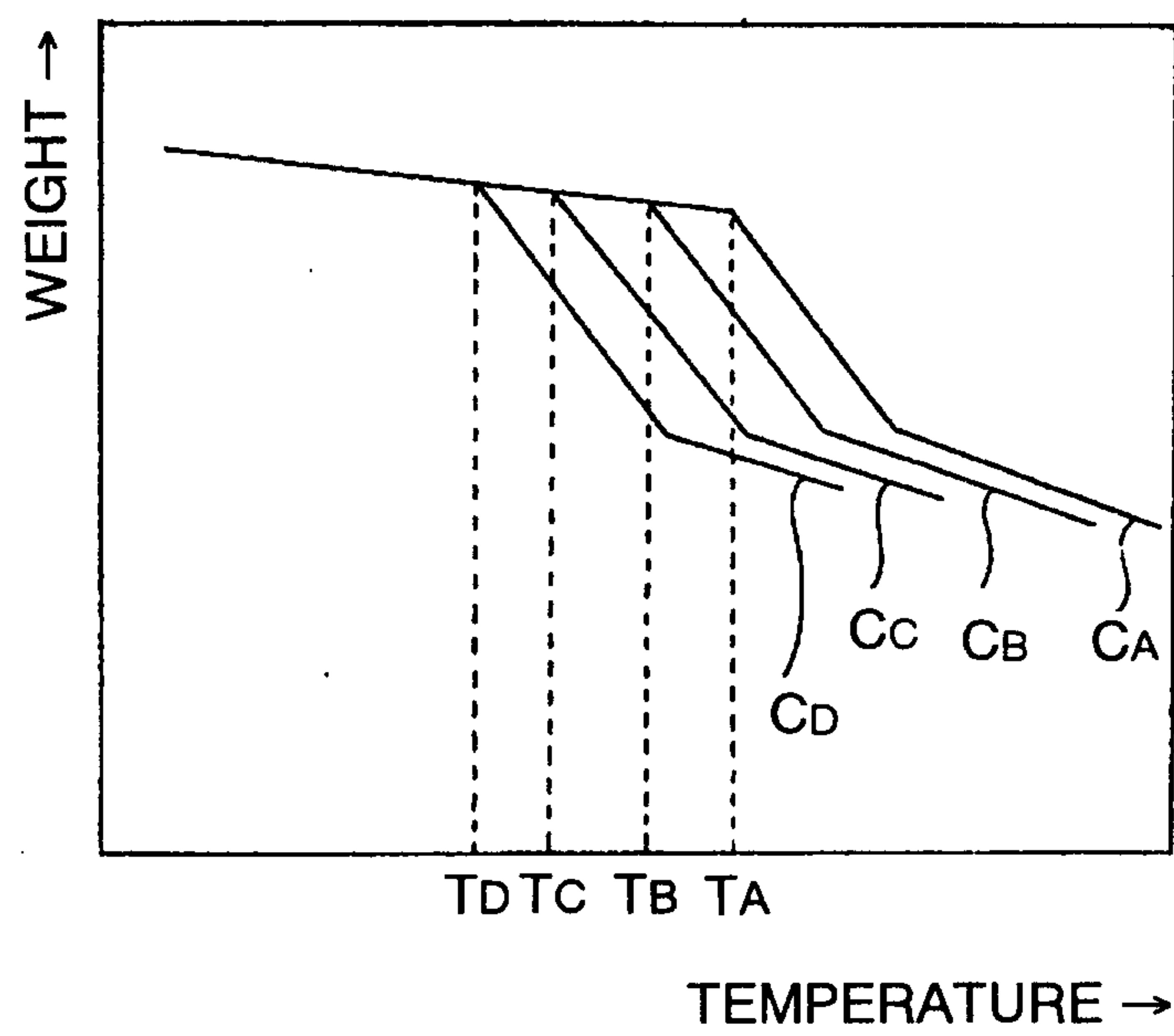


FIG. 4

