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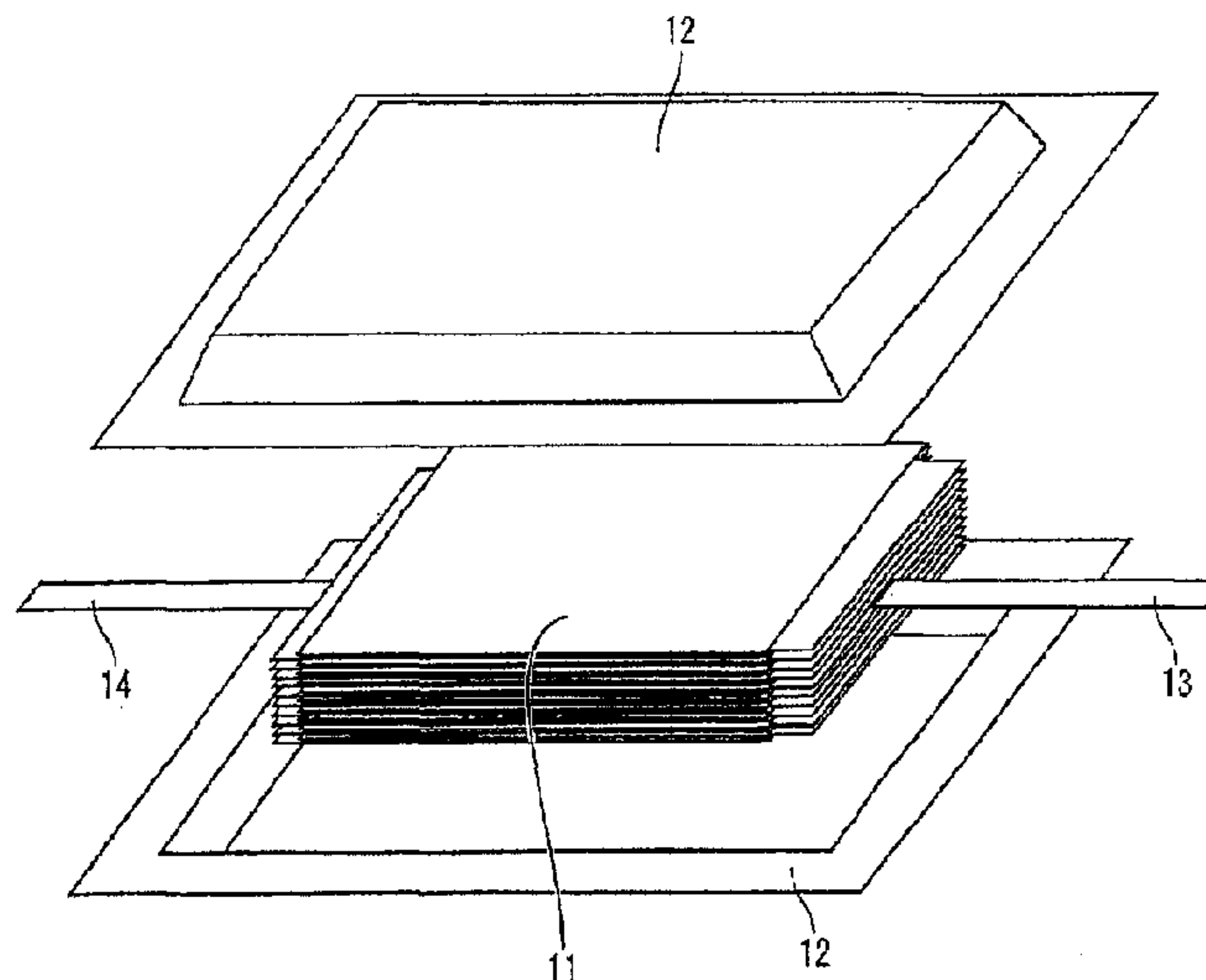
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(54) **Titre :** MATERIAU CATHODE ACTIF CONTENANT DU LITHIUM ET COMPORTANT UN OXYDE METALLIQUE DE TRANSITION, CATHODE CONTENANT DU LITHIUM ET COMPORTANT UN OXYDE METALLIQUE DE TRANSITION ET BATTERIE SECONDAIRE NON AQUEUSE CONTENANT DU LITHIUM ET COMPORTANT UN OXYDE METALLIQUE DE TRANSITION

(54) **Title:** CATHODE ACTIVE MATERIAL CONTAINING LITHIUM AND HAVING TRANSITION METAL OXIDE, CATHODE CONTAINING LITHIUM AND HAVING TRANSITION METAL OXIDE, AND NONAQUEOUS SECONDARY BATTERY CONTAINING LITHIUM AND HAVING TRANSITION METAL OXIDE



(57) **Abrégé/Abstract:**

A nonaqueous secondary battery of the present invention is a nonaqueous secondary battery, comprising: a cathode including: a cathode active material; a conductive material; and a binder, the cathode active material having a composition represented by

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(57) **Abrégé(suite)/Abstract(continued):**

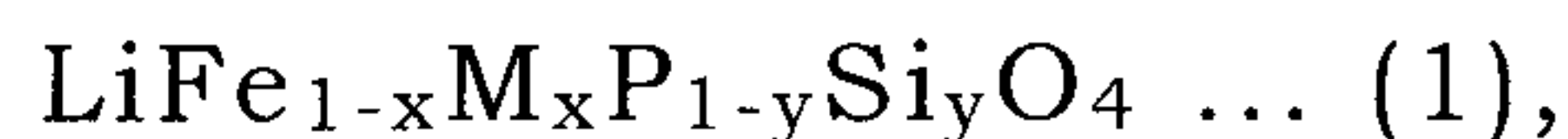
General Formula (1) below,

$\text{LiFe}_{1-x}\text{M}_x\text{P}_{1-y}\text{Si}_y\text{O}_4 \dots (1)$,

where: an average valence of Fe is +2 or more; M is an element having a valence of +2 or more and is at least one type of element selected from the group consisting of Zr, Sn, Y, and Al; the valence of M is different from the average valence of Fe; $0 < x \leq 0.5$; and $0 < y < 1.0$, the conductive material being a material selected from the group consisting of acetylene black, carbon, graphite, natural graphite, artificial graphite, and needle coke.

Abstract

A nonaqueous secondary battery of the present invention is a nonaqueous secondary battery, comprising: a cathode including: a cathode active material; a conductive material; and a binder, the cathode active material having a composition represented by General Formula (1) below,



where: an average valence of Fe is +2 or more; M is an element having a valence of +2 or more and is at least one type of element selected from the group consisting of Zr, Sn, Y, and Al; the valence of M is different from the average valence of Fe; $0 < x \leq 0.5$; and $0 < y < 1.0$, the conductive material being a material selected from the group consisting of acetylene black, carbon, graphite, natural graphite, artificial graphite, and needle coke.

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Description

CATHODE ACTIVE MATERIAL CONTAINING LITHIUM AND
HAVING TRANSITION METAL OXIDE, CATHODE CONTAINING
5 LITHIUM AND HAVING TRANSITION METAL OXIDE, AND
NONAQUEOUS SECONDARY BATTERY CONTAINING LITHIUM
AND HAVING TRANSITION METAL OXIDE

10 This application is a divisional of Canadian Patent
Application No. 2,835,832, filed on November 28, 2013
which is a divisional of Canadian Patent Application No.
2,762,142, filed on May 20, 2010.

Field of the Invention

15 The present invention relates to a cathode active
material, a cathode in which such a cathode active material
is used, and a nonaqueous secondary battery (lithium
secondary battery) in which such a cathode is used. More

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specifically, the present invention relates to a nonaqueous secondary battery excellent in cycling characteristics.

Background of the Invention

5 Lithium secondary batteries have been in practical and widespread use as secondary batteries for portable electronic devices. Furthermore, in recent years, lithium secondary batteries have drawn attention not only as small-sized secondary batteries for portable electronic devices but also
10 as high-capacity devices for use in vehicles, power storage, etc. Therefore, there has been a growing demand for higher safety standards, lower costs, longer lives, etc.

 A lithium secondary battery is composed mainly of a cathode, an anode, an electrolyte, a separator, and an
15 armoring material. Further, the cathode is constituted by a cathode active material, a conductive material, a current collector, and a binder (binding agent).

 In general, the cathode active material is realized by a layered transition metal oxide such as LiCoO_2 . However, in a
20 state of full charge, such layered transition metal oxides are prone to cause oxygen desorption at a comparatively low temperature of approximately 150°C , and such oxygen desorption may cause a thermal runaway reaction in the battery. Therefore, when a battery having such a cathode
25 active material is used for a portable electronic device, there

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is a risk of an accident such as heating, firing, etc. of the battery.

For this reason, in terms of safety, expectations have been placed on lithium manganate (LiMn_2O_4) having a spinel-type structure, lithium iron phosphate (LiFePO_4)
5 having an olivine-type structure, etc. that are stable in structure and do not emit oxygen in abnormal times.

Further, in terms of cost, cobalt (Co) is low in degree of existence in the earth's crust and high in price. For this
10 reason, expectations have been placed on lithium nickel oxide (LiNiO_2) or a solid solution thereof ($\text{Li}(\text{Co}_{1-x}\text{Ni}_x)\text{O}_2$), lithium manganate (LiMn_2O_4), lithium iron phosphate (LiFePO_4), etc.

Further, in terms of life, the insertion and desorption
15 of Li into and from a cathode active material along with charging and discharging cause structural destruction in the cathode active material. For this reason, more expectations have been placed on lithium manganate (LiMn_2O_4) having a spinel-type structure, lithium iron phosphate (LiFePO_4)
20 having an olivine-type structure, etc. than on layered transition metal oxides because of their structural stability.

Therefore, for example, such lithium iron phosphate having an olivine-type structure has drawn attention as a cathode active material for a battery in consideration of
25 safety, cost, and life. However, when lithium iron phosphate

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having an olivine-type structure is used as a cathode active material for a battery, there are such declines in charge-discharge behavior as insufficient electron conductivity and low average potential.

5 In order to improve charge-discharge behavior, there has been proposed an active material represented by general formula $A_aM_b(XY_4)_cZ_d$ (where A is an alkali metal, M is a transition metal, XY_4 is PO_4 or the like, and Z is OH or the like) (e.g., see Patent Literature 1).

10 Further, there have been also proposed an active material, represented by general formula $LiMP_{1-x}A_xO_4$ (where M is a transition metal, A is an element having an oxidation number of +4 or less, and $0 < X < 1$), whose P site has been replaced by the element A (e.g., see Patent Literature 2).

15 Further proposed as a cathode active material for a nonaqueous electrolyte secondary battery excellent in large-current charge-discharge behavior is a material represented by general formula $Li_{1-x}A_xFe_{1-y-z}M_yMe_zP_{1-m}X_mO_{4-n}Z_n$ (where A is Na or K; M is a metal element other than Fe, Li, and Al; X is Si, N, or As; Z is F, Cl, Br, I, S, or N) (e.g., see Patent Literature 3). Further proposed as an electrode active material that can be economically produced, is satisfactory in charging capacity, and is satisfactory in rechargeability over many cycles is a material represented by general
20 formula $A_{a+x}M_bP_{1-x}Si_xO_4$ (where A is Li or Na, or K; and M is
25

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a metal) (e.g., see Patent Literature 4).

There has also been disclosed lithium transition metal phosphorus, such as LiFePO_4 , which includes at least two coexisting phases including a lithium-rich transition metal phosphate phase and a lithium-poor transition metal phosphate phase, the coexisting phases being different from each other in molar volume by approximately 5.69 (e.g., see Table 2 of Patent Literature 5).

Citation list

10 Patent Literature 1

Japanese Patent Application Publication (Translation of PCT Application), Tokuhyou, No. 2005 -522009 (Publication Date: July 21, 2005)

Patent Literature 2

15 Japanese Patent Application Publication (Translation of PCT Application), Tokuhyou, No. 2008 -506243 (Publication Date: February 28, 2008)

Patent Literature 3

20 Japanese Patent Application Publication, Tokukai, No. 2002-198050 A (Publication Date: July 12, 2002)

Patent Literature 4

Japanese Patent Application Publication (Translation of PCT Application), Tokuhyou, No. 2005 -519451 (Publication Date: June 30, 2005)

25 Patent Literature 5

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PCT International Publication No. 2008/039170,
pamphlet (Publication Date: April 3, 2008)

Summary of the Invention

5 Technical Problem

Unfortunately, however, the active materials
structured as described in Patent Literatures 1 to 5 above
result in short-life batteries.

Specifically, according to the structures of the active
10 materials as described in Patent Literatures 1 to 5, the
insertion and desorption of Li into and from a cathode active
material along with charging and discharging cause great
expansion or contraction in the cathode active material;
therefore, an increase in the number of cycles may cause the
15 cathode active material to gradually detach from the current
collector and the conductive material physically and
therefore cause structural destruction in the cathode active
material. This is because a material that greatly expands or
contracts due to charging and discharging causes
20 destruction of secondary particles and destruction of the
conductive path between the cathode active material and the
conductive material and therefore causes an increase in
internal resistance of the battery. This results in an increase
in active materials that do not contribute to charging or
25 discharging, causes a decrease in capacity, and therefore

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makes the battery short lived.

As mentioned above, there has been a demand for cathode active materials excellent in terms of safety, cost, and life. However, the active materials structured as described in Patent Literatures 1 and 2 above are high in rate of expansion and contraction in volume (rate of change in volume) during charging and discharging and therefore result in short lives.

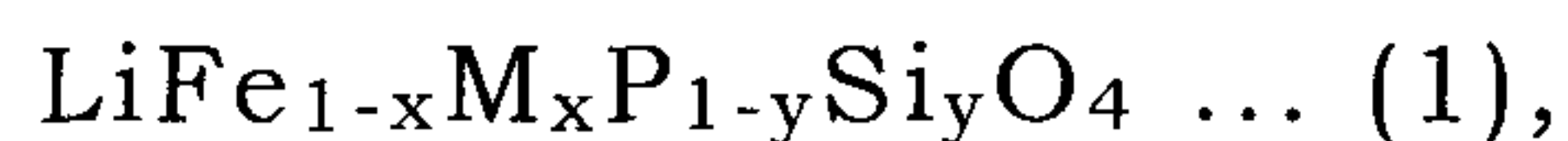
The present invention has been made in view of the foregoing problems, accordingly, the present invention provides a cathode active material that not only excels in terms of safety and cost but also can provide a long-life battery, a cathode in which such a cathode active material is used, and a nonaqueous secondary battery in which such a cathode is used.

Solution to Problem

The present invention extends the life of a battery through suppression of expansion and contraction by carrying out element substitution with use of lithium iron phosphate as a basic structure.

Specifically, in order to solve the above problems, a cathode active material of the present invention is a cathode active material having a composition represented by General Formula (1) below,

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where: an average valence of Fe is +2 or more; M is an element having a valence of +2 or more and is at least one type of element selected from the group consisting of Zr, Sn, Y, and Al; the valence of M is different from the average valence of Fe; $0 < x \leq 0.5$; and $y = x \times (\{\text{valence of M}\} - 2) + (1-x) \times (\{\text{average valence of Fe}\} - 2)$.

According to the foregoing structure, a change in volume during Li insertion and desorption can be suppressed by replacing at least part of P site with Si and replacing part of Fe site with an element capable of compensation for charges in the crystal structure. As a result, in the case of a battery made with use of such a cathode active material, the cathode can be prevented from expanding or contracting due to charging and discharging. This brings about an effect of providing a cathode active material that not only excels in terms of safety and cost but also can provide a long-life battery.

Furthermore, Zr, Sn, Y, and Al are easily combined because they do not change in valence, can be combined in a reducing atmosphere, and do not require control of the partial pressure of oxygen for controlling the valence of a substituting element.

In order to solve the foregoing problems, a cathode of the present invention includes: the cathode active material

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of the present invention; a conductive material; and a binder.

According to the foregoing structure, the inclusion of such a cathode active material according to the present invention brings about an effect of providing a cathode that not only excels in terms of safety and cost but also can provide a long-life battery.

In order to solve the foregoing problems, a nonaqueous secondary battery of the present invention includes: the cathode of the present invention; an anode; an electrolyte; and a separator.

According to the foregoing structure, the inclusion of such a cathode according to the present invention brings about an effect of providing a long-life battery excellent in terms of safety and cost.

A module of the present invention includes a combination of a plurality of the nonaqueous secondary battery of the present invention.

According to the foregoing structure, the inclusion of such a nonaqueous secondary battery according to the present invention brings about an effect of providing a long-life module excellent in terms of safety and cost.

A power storage system of the present invention includes the nonaqueous secondary battery of the present invention.

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According to the foregoing structure, the inclusion of such a nonaqueous secondary battery according to the present invention brings about an effect of providing a long-life power storage system excellent in terms of safety and cost.

Advantageous Effects of Invention

As described above, a cathode active material of the present invention has a composition represented by General Formula (1) above.

This brings about an effect of providing a cathode active material that not only excels in terms of safety and cost but also can provide a long-life battery.

As described above, a cathode of the present invention includes: the cathode active material of the present invention; a conductive material; and a binder.

This brings about an effect of providing a cathode that not only excels in terms of safety and cost but also can provide a long-life battery.

As described above, a nonaqueous secondary battery of the present invention includes: the cathode of the present invention; an anode; an electrolyte; and a separator.

This brings about an effect of providing a long-life battery excellent in terms of safety and cost.

A module of the present invention includes a combination of a plurality of the nonaqueous secondary

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battery of the present invention.

This brings about an effect of providing a long-life module excellent in terms of safety and cost.

5 A power storage system of the present invention includes the nonaqueous secondary battery of the present invention.

This brings about an effect of providing a long-life power storage system excellent in terms of safety and cost.

Accordingly, as an aspect of the present invention, there is provided a cathode active material having a composition represented by general formula (1) below,

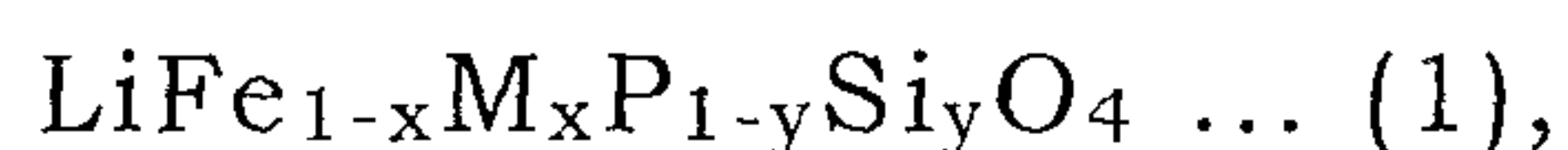
$\text{LiFe}_{1-x}\text{M}_x\text{P}_{1-y}\text{Si}_y\text{O}_4 \dots (1)$, where: an average valence of Fe is +2 or more; M is an element having a valence of +2 or more and is at least one type of element selected from the group consisting of Zr, Sn, Y and Al; the valence of M is different from the average valence of Fe; $0 < x \leq 0.5$ and $0 < y \leq 1.0$.

As another aspect of the present invention, there is provided a nonaqueous secondary battery, comprising: a cathode including the cathode active material; a conductive material; and a binder; an anode; an electrolyte; and a separator, when the battery reached a voltage of not less than 3.9V, cathode active material have a composition represented by general formula (2) below,

$\text{Li}_x\text{Fe}_{1-x}\text{M}_x\text{P}_{1-y}\text{Si}_y\text{O}_4 \dots (2)$.

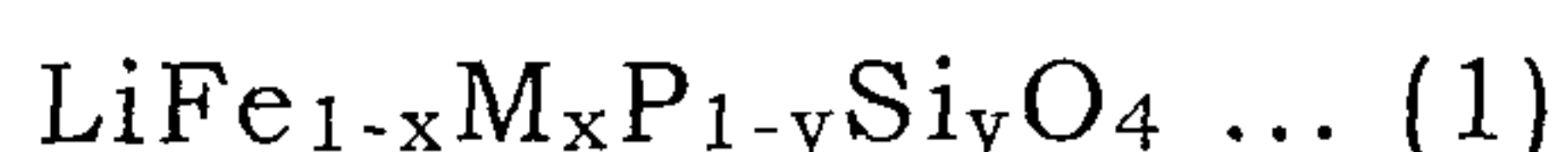
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As another aspect of the present invention, there is provided a nonaqueous secondary battery, comprising: a cathode including: a cathode active material; a conductive material; and a binder, the cathode active material having a composition represented by General Formula (1) below,



Fe^{2+} is contained at a proportion of not less than 95% as calculated from a Mössbauer spectrum; M is an element having a valence of +2 or more and is at least one type of element selected from the group consisting of Zr, Sn, Y, and Al; the valence of M is different from the average valence of Fe; $0 < x \leq 0.5$; and $0 < y \leq 0.5$, the conductive material being a material selected from the group consisting of acetylene black, carbon, graphite, natural graphite, artificial graphite, and needle coke.

As another aspect of the present invention, there is provided a nonaqueous secondary battery, comprising: a cathode including a cathode active material; and an anode including an anodic active material and a binder, the cathode active material having a composition represented by General Formula (1) below,

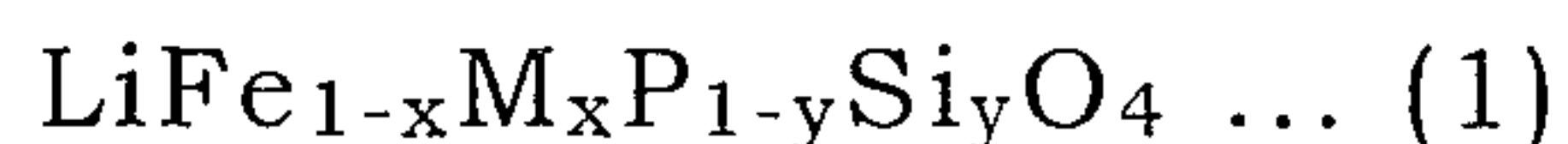


Fe^{2+} is contained at a proportion of not less than 95% as calculated from a Mössbauer spectrum; M is an element having a valence of +2 or more and is at least one type of

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element selected from the group consisting of Zr, Sn, Y, and Al; the valence of M is different from the average valence of Fe; $0 < x \leq 0.5$; and $0 < y \leq 0.5$, the anodic active material being either artificial graphite or natural graphite.

5 As another aspect of the present invention, there is provided a nonaqueous secondary battery, comprising: a cathode including a cathode active material; and an anode including an anodic active material and a binder, the cathode active material having a composition represented by
10 General Formula (1) below,



Fe^{2+} is contained at a proportion of not less than 95% as calculated from a Mössbauer spectrum; M is an element having a valence of +2 or more and is at least one type of
15 element selected from the group consisting of Zr, Sn, Y, and Al; the valence of M is different from the average valence of Fe; $0 < x \leq 0.5$; and $0 < y \leq 0.5$, the anodic active material being $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

20 Brief Description of the Drawings

Fig. 1 is a graph illustrating an X-ray diffraction pattern for a cathode active material prepared in Example 2.

Fig. 2 is a graph illustrating an X-ray diffraction pattern for a cathode active material prepared in Example 3.

25 Fig. 3 is a graph illustrating an X-ray diffraction

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pattern for a cathode active material prepared in Example 4.

Fig. 4 is a graph illustrating an X-ray diffraction

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pattern for a cathode active material prepared in Example 5.

Fig. 5 is a graph illustrating an X-ray diffraction pattern for a cathode active material prepared in Example 6.

Fig. 6 is a graph illustrating an X-ray diffraction pattern for a cathode active material prepared in Example 7.

Fig. 7 is a graph illustrating an X-ray diffraction pattern for a cathode active material prepared in Comparative Example 1.

Fig. 8 is a graph illustrating an absorption spectrum measured by Mössbauer spectrometry of the cathode active material prepared in Example 2.

Fig. 9 is a graph illustrating an absorption spectrum measured by Mössbauer spectrometry of the cathode active material prepared in Example 3.

Fig. 10 is a cross-sectional view schematically illustrating a configuration of a battery used for evaluation of a capacity retention rate in Examples.

Fig. 11 is a perspective view schematically illustrating a configuration of a flat-plate laminate battery prepared in Example 9.

Fig. 12 is a perspective view schematically illustrating a configuration of a layered cuboidal battery prepared in Example 10.

Fig. 13 is a perspective view schematically illustrating a configuration of a wound cylindrical battery prepared in

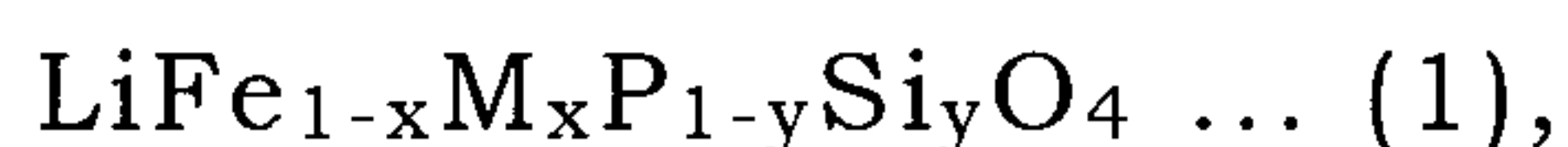
Example 11.

Detailed Description of the Preferred Embodiments

The present invention is described below in detail. It should be noted, in this specification, that the range "A to B" means "A or more to B or less". Further, the various properties enumerated in this specification mean values measured by methods described later in Examples, unless otherwise noted.

(I) Cathode Active Material

A cathode active material of the present embodiment is a cathode active material having a composition represented by General Formula (1) below,



where: an average valence of Fe is +2 or more; M is an element having a valence of +2 or more and is at least one type of element selected from the group consisting of Zr, Sn, Y, and Al; the valence of M is different from the average valence of Fe; $0 < x \leq 0.5$; and $y = x \times (\{\text{valence of M}\} - 2) + (1-x) \times (\{\text{average valence of Fe}\} - 2)$.

The term "average valence of Fe" here means the average of the valences of all the Fe atoms constituting the cathode active material.

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In general, in the case of olivine-type lithium iron phosphate, there is a contraction in volume during desorption of Li from the initial structure due to charging. During this structural change, there are contractions along the a axis and the b axis, and there is an expansion along the c axis. For this reason, the inventors found it possible to suppress a change in volume by reducing the rates of contraction along the a axis and the b axis and increasing the rate of expansion along the c axis through any sort of substitution.

Then, the inventors found that by replacing part of P site with Si and replacing part of Fe site with another atom, compensation for charges in the crystal structure is made and a change in volume during Li desorption is suppressed, whereby expansion and contraction due to charging and discharging are also suppressed.

It should be noted that although most of the materials that have compositions represented by general formula (1) have olivine-type structures, the scope of the present invention is not limited to those materials which have olivine-type structures. Those materials which do not have olivine-type structures are also encompassed in the scope of the present invention.

In the cathode active material according to the present embodiment, P site has been replaced by Si, and P and Si

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are different in valence from each other. Therefore, it is necessary to make compensation for charges in the crystal structure. For this reason, Fe site has been replaced by M.

5 That is, because the valences of P and Si in general formula (1) are +5 and +4, respectively, the substitution amount y of Si comes to satisfy $y = x \times (\{\text{valence of M}\} - 2) + (1 - x) \times (\{\text{average valence of Fe}\} - 2)$ according to the principle that the total of charges in the structure is 0.

10 In General Formula (1), y preferably falls within the range $(x \times (\{\text{valence of M}\} - 2)) \leq y < (x \times (\{\text{valence of M}\} - 2) + 0.05)$.

15 Fe in general formula (1) can generally take on a valence of +2 or +3. Fe^{2+} is preferably contained at a proportion of not less than 95% as calculated from a Mössbauer spectrum. More preferably, the average valence of Fe is +2, and particularly preferably, every Fe has a valence of +2.

20 In the present embodiment, the rate of change in volume of a unit cell in $\text{Li}_x\text{Fe}_{1-x}\text{M}_x\text{P}_{1-y}\text{Si}_y\text{O}_4$ is preferably 5% or less, or more preferably 4% or less, relative to the volume of a unit cell in General Formula (1).

25 The reason why the rate of change in volume is preferably 4% or less is that the cathode active material according to the present embodiment has a change in slope of the volume maintenance ratio relative to the rate of

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change in volume at a point where the rate of change in volume (rate of expansion and contraction due to charging and discharging) of the volume of a unit cell reaches approximately 4%. That is, when the rate of change in volume becomes higher than approximately 4%, the volume maintenance ratio comes to decrease to a greater extent than the rate of change in volume increases. Therefore, if the rate of change in volume is approximately 4% or less, it is possible to better suppress a decrease in volume maintenance ratio.

The element M, which replaces Fe site, is an element capable of taking on a valence of +2 or more and at least one type of element selected from the group consisting of Zr, Sn, Y, and Al. Further, it is preferable that the element M, which replaces Fe site, be an element having a valence of +3 or +4. For a greater effect of suppressing the rate of change in volume, it is more preferable that Fe site be replaced by an element having a valence of +4.

It is preferable that the trivalent element M, which replaces Fe site, be Y, because Y does not change in valence during synthesis. Since there occurs no change in valence during synthesis, the cathode active material can be synthesized stably.

It is preferable that the tetravalent element M, which replaces Fe site, be Zr or Sn, because Zr and Sn do not

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change in valence during synthesis. Since there occurs no change in valence during synthesis, the cathode active material can be synthesized stably.

5 It is preferable that M in general formula (1) have a valence of +3 or +4, and it is more preferable that every M have a valence of +3 or that every M have a valence of +4.

10 The substitution amount x on Fe site falls within a range of larger than 0 to 0.5 or smaller. If the substitution amount x on Fe site falls within the above range, it is possible to prevent (i) a significant reduction in the discharging capacity of a battery in which the cathode active material is used and (ii) a volume change occurring during Li insertion and desorption.

15 The larger the amount of substitution on Fe site is, the better the rate of change in volume can be suppressed. In other words, the larger the amount of substitution on Fe site is, the better the volume maintenance ratio is at 500 cycles. If the rate of change in volume is 4% or less, the volume maintenance ratio can be 90% or more.

20 On the other hand, the larger the amount of substitution on Fe site, the smaller the initial capacity is. In the case where Fe is replaced by Zr, the substitution amount x on Fe site is (i) preferably 0.35 or less to obtain an initial capacity of 100 mAh/g or greater, (ii) more preferably 0.3 or less to obtain an initial capacity of 110 mAh/g or greater, or
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(iii) even more preferably 0.25 or less to obtain an initial capacity of 120 mAh/g or greater.

In the case where Fe is replaced by Sn, the substitution amount x on Fe site is (i) preferably 0.3 or less to obtain an initial capacity of 100 mAh/g or greater, (ii) more preferably 0.25 or less to obtain an initial capacity of 110 mAh/g or greater, or (iii) even more preferably 0.2 or less to obtain an initial capacity of 120 mAh/g or greater.

In the case where Fe is replaced by Y, the substitution amount x on Fe site is (i) preferably 0.35 or less to obtain an initial capacity of 100 mAh/g or greater, (ii) more preferably 0.3 or less to obtain an initial capacity of 110 mAh/g or greater, or (iii) even more preferably 0.25 or less to obtain an initial capacity of 120 mAh/g or greater.

In the case where Fe is replaced by Al, the substitution amount x on Fe site is (i) preferably 0.45 or less to obtain an initial capacity of 100 mAh/g or greater, (ii) more preferably 0.4 or less to obtain an initial capacity of 110 mAh/g or greater, or (iii) even more preferably 0.3 or less to obtain an initial capacity of 120 mAh/g or greater.

When Fe site is replaced by metal atoms having a valence of +3 and every Fe has a valence of +2, the same amount of Si as the amount of substitution of Fe site is required for the maintenance of electroneutrality. In this case, the amount of substitution is preferably 0.25 or

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greater for Al and 0.15 or greater for Y to keep the rate of change in volume to 5% or less. Further, the amount of substitution is preferably 0.35 or greater for Al and 0.2 or greater for Y to keep the rate of change in volume to 4% or less.

When Fe site is replaced by metal atoms having a valence of +4 and every Fe has a valence of +2, the amount of Si twice as large as the amount of substitution of Fe site is required for the maintenance of electroneutrality. In this case, the amount of substitution is preferably 0.05 or greater for Zr and 0.15 or greater for Sn to keep the rate of change in volume to 5% or less. The amount of substitution is preferably 0.15 or greater for Zr and 0.25 or greater for Sn to keep the rate of change in volume to 4% or less. The amount of substitution is preferably 0.2 or greater for Zr and 0.3 or greater for Sn to keep the rate of change in volume to 3% or less. Further, the amount of substitution is preferably 0.25 or greater for Zr to keep the rate of change in volume to 2% or less.

The present invention encompasses the following embodiment: When Fe site is replaced by Zr atoms having a valence of +4 and every Fe has a valence of +2, the substitution amount x of Zr may be within the range $0.05 \leq x \leq 0.15$.

The aforementioned cathode active material according

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to the present embodiment can be produced by using any combination of a carbonate of each element, a hydroxide of each element, a chloride salt of each element, a sulfate salt of each element, an acetate salt of each element, an oxide of each element, an oxalate of each element, a nitrate salt of each element, etc. as raw materials. Examples of production methods include methods such as a solid-phase method, a sol-gel process, melt extraction, a mechanochemical method, a coprecipitation method, a hydrothermal method, evaporative decomposition, etc. Further, as has been commonly done in olivine-type lithium iron phosphate, electrical conductivity may be improved by covering the cathode active material with a carbon film.

As described above, the cathode active material of the present invention may preferably be arranged such that a rate of change in volume of a unit cell in $\text{Li}_x\text{Fe}_{1-x}\text{M}_x\text{P}_{1-y}\text{Si}_y\text{O}_4$ is 5% or less with respect to a volume of a unit cell in General Formula (1).

According to the foregoing structure, the rate of change in volume is 5% or less. This makes it possible to better prevent a cathode from expanding or contracting due to charging and discharging, thus making it possible to provide a cathode active material capable of providing a long-life battery.

The cathode active material of the present invention

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may preferably be arranged such that a rate of change in volume of a unit cell in $\text{Li}_x\text{Fe}_{1-x}\text{M}_x\text{P}_{1-y}\text{Si}_y\text{O}_4$ is 4% or less with respect to a volume of a unit cell in General Formula (1).

According to the foregoing structure, the rate of change in volume is 4% or less. This makes it possible to better prevent a cathode from expanding or contracting due to charging and discharging, thus making it possible to provide a cathode active material capable of providing a long-life battery.

The cathode active material of the present invention may preferably be arranged such that the valence of M is +4.

The foregoing structure, which is highly effective in suppressing the rate of change in volume, it possible to better prevent the cathode from expanding or contracting due to charging and discharging, thus making it possible to provide a cathode active material capable of providing a long-life battery.

The cathode active material of the present invention may preferably be arranged such that M in General Formula (1) is Zr; and $0.05 \leq x \leq 0.5$.

According to the foregoing structure, the rate of change in volume is approximately 5% or less. This makes it possible to better prevent a cathode from expanding or contracting due to charging and discharging, thus making it possible to provide a cathode active material capable of

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providing a long-life battery.

The cathode active material of the present invention may preferably be arranged such that M in General Formula (1) is Zr; and $0.15 \leq x \leq 0.5$.

5 According to the foregoing structure, the rate of change in volume is approximately 4% or less. This makes it possible to better prevent a cathode from expanding or contracting due to charging and discharging, thus making it possible to provide a cathode active material capable of
10 providing a long-life battery.

The cathode active material of the present invention may preferably be arranged such that M in General Formula (1) is Zr; and $0.25 \leq x \leq 0.5$.

15 According to the foregoing structure, the rate of change in volume is approximately 2% or less. This makes it possible to even better prevent a cathode from expanding or contracting due to charging and discharging, thus making it possible to provide a cathode active material capable of providing a battery with an even long life.

20 The cathode active material of the present invention may preferably be arranged such that M in General Formula (1) is Sn; and $0.25 \leq x \leq 0.5$.

25 According to the foregoing structure, the rate of change in volume is approximately 4% or less. This makes it possible to better prevent a cathode from expanding or

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contracting due to charging and discharging, thus making it possible to provide a cathode active material capable of providing a long-life battery.

5 The cathode active material of the present invention may preferably be arranged such that the valence of M in General Formula (1) is +3.

The cathode active material of the present invention may preferably be arranged such that M in General Formula (1) is Y; and $0.2 \leq x \leq 0.5$.

10 According to the foregoing structure, the rate of change in volume is approximately 4% or less. This makes it possible to better prevent a cathode from expanding or contracting due to charging and discharging, thus making it possible to provide a cathode active material capable of
15 providing a long-life battery. Further, because Y does not change in valence during synthesis of a cathode active material, the cathode active material can be synthesized stably.

20 The cathode active material of the present invention may preferably be arranged such that M in General Formula (1) is Al; and $0.35 \leq x \leq 0.5$.

25 According to the foregoing structure, the rate of change in volume is approximately 4% or less. This makes it possible to better prevent a cathode from expanding or contracting due to charging and discharging, thus making it

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possible to provide a cathode active material capable of providing a long-life battery.

5 The cathode active material of the present invention may preferably be arranged such that the average valence of Fe in General Formula (1) is +2.

10 The foregoing structure makes it possible to better prevent the cathode from expanding or contracting due to charging and discharging, thus making it possible to provide a cathode active material capable of providing a long-life battery.

The cathode active material of the present invention may preferably be arranged such that M in General Formula (1) is Zr; and $0.05 \leq x \leq 0.15$.

15 The foregoing structure makes it possible to better prevent the cathode from expanding or contracting due to charging and discharging, thus making it possible to provide a cathode active material capable of providing a long-life battery.

(II) Nonaqueous Secondary Battery

20 A nonaqueous secondary battery according to the present embodiment has a cathode, an anode, an electrolyte, and a separator. Each of the components is described below. It should be noted that it is preferable that the nonaqueous secondary battery according to the present embodiment be a
25 laminate battery, a layered cuboidal battery, a wound

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cuboidal battery, or a wound cylindrical battery.

(a) Cathode

The cathode, composed of such a cathode active material according to the present embodiment, a conductive material, and a binder, can be made, for example, by a publicly-known method such as application to a current collector of a slurry obtained by mixing the active material, the conductive material, and the binder with an organic solvent.

Usable examples of the binder (binding agent) include polytetrafluoroethylene, polyvinylidene fluoride, polyvinylchloride, ethylene-propylene diene polymer, styrene-butadiene rubber, acrylonitrile-butadiene rubber, fluorocarbon rubber, polyvinyl acetate, polymethyl methacrylate, polyethylene, nitrocellulose, etc.

Usable examples of the conductive material include acetylene black, carbon, graphite, natural graphite, artificial graphite, needle coke, etc.

Usable examples of the current collector include a foam (porous) metal having continuous holes, a metal shaped in a honeycomb pattern, a sintered metal, an expanded metal, nonwoven cloth, a plate, foil, a perforated plate, perforated foil, etc.

Usable examples of the organic solvent include N-methylpyrrolidone, toluene, cyclohexane,

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dimethylformamide, dimethylacetoamide, methyl ethyl ketone, methyl acetate, methyl acrylate, diethyltriamine, N-N-dimethylaminopropylamine, ethylene oxide, tetrahydrofuran, etc.

5 It is preferable that the cathode have a thickness of approximately 0.01 to 20 mm. Too great a thickness undesirably causes a decrease in electrical conductivity, and too small a thickness undesirably causes a decrease in capacity per unit area. It should be noted that the cathode,
10 obtained by application and drying, may be consolidated by a roller press, etc. so that the active material has a higher filling density.

(b) Anode

 The anode can be made by a publicly-known method.
15 Specifically, the anode can be made by the same method as described in the method for making the cathode, i.e., by mixing such a publicly-known binding agent and such a publicly-known conductive material as named in the method for making the cathode with an anodic active material,
20 molding the mixed powder into a sheet, and then pressure-bonding the molded product to a net (current collector) made of a conducting material such as stainless steel or copper. Alternatively, the anodic can also be made by applying, onto a substrate made of metal such as copper, a slurry obtained
25 by mixing the mixed powder with such a publicly-known

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organic solvent as named in the method for making the cathode.

5 The anodic active material may be a publicly-known material. In order to constitute a high-energy density battery, it is preferable that the potential of insertion/desorption of lithium be close to the deposition/dissolution potential of metal lithium. Typical examples of such an anodic active material include carbon materials such as natural or artificial graphite in the form of particles (scales, clumps, fibers, whisker, spheres, crushed particles, etc.).

10 Examples of the artificial graphite include graphite obtainable by graphitizing mesocarbon microbeads, mesophase pitch powder, isotropic pitch powder, etc. Alternatively, it is possible to use graphite particles having amorphous carbon adhering to their surfaces. Among these, natural graphite is more preferable because it is inexpensive, close in oxidation-reduction potential to lithium, and can constitute a high-energy density battery.

20 Alternatively, it is possible to use a lithium transition metal oxide, a transition metal oxide, oxide silicon, etc. as the anodic active material. Among these, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is more preferable because it is high in potential flatness and small in volume change due to charging and discharging.

25 (c) Electrolyte

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Usable examples of the electrolyte include an organic electrolyte, a gel electrolyte, a polymer solid electrolyte, an inorganic solid electrolyte, a molten salt, etc. After injection of the electrolyte, an opening in the battery is sealed. It is possible to turn on electricity before the sealing and remove gas generated.

Examples of an organic solvent that constitutes the organic electrolyte include: cyclic carbonates such as propylene carbonate (PC), ethylene carbonate (EC), and butylene carbonate; chain carbonates such as dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate, and dipropyl carbonate; lactones such as γ -butyrolactone (GBL), γ -Valerolactone; furans such as tetrahydrofuran and 2-methyl tetrahydrofuran; ethers such as diethyl ether, 1,2-dimethoxy ethane, 1,2-diethoxy ethane, ethoxy methoxy ethane, dioxane; dimethyl sulfoxide; sulforan; methyl sulforan; acetonitrile; methyl formate; methyl acetate; etc. These organic solvents can be used alone or in combination of two or more of them.

Further, the cyclic carbonates such as PC, EC, and butylene carbonate are high boiling point solvents and, as such, are suitable as a solvent to be mixed with GBL.

Examples of an electrolyte salt that constitutes the organic electrolyte include lithium salts such as fluoroboric lithium (LiBF_4), lithium hexafluorophosphate (LiPF_6),

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trifluoromethanesulfonic lithium (LiCF_3SO_3), trifluoroacetic
lithium (LiCF_3COO), lithium-
bis(trifluoromethanesulfone)imide ($\text{LiN}(\text{CF}_3\text{SO}_2)_2$), etc. These
electrolyte salts can be used alone or in combination of two
5 or more of them. A suitable salt concentration of the
electrolyte is 0.5 to 3 mol/l.

(d) Separator

Examples of the separator include a porous material,
nonwoven cloth, etc. It is preferable that the separator be
10 made of such a material as mentioned above that neither
dissolves not swells in response to the organic solvent
contained in the electrolyte. Specific examples are polyester
polymers, polyolefin polymers (e.g., polyethylene,
polypropylene), ether polymers, and inorganic materials such
15 glass, etc.

The components, such as the separator, a battery
case, and other structural materials, of the battery
according to the present embodiment may be, but are not
particularly limited to, various materials that are used in a
20 conventional publicly-known nonaqueous secondary battery.

(e) Method for Producing a Nonaqueous Secondary Battery

The nonaqueous secondary battery according to the
present embodiment can be made, for example, by layering
25 the cathode and the anodic in such a way that the separator

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is sandwiched between them. The layered electrode may have a rectangular planar shape. Further, when a cylindrical or flat battery is made, the layered electrode may be wound.

Such a single layered electrode or a plurality of such layered electrodes is/are inserted into a battery container. Usually, the cathode(s) and the anodic(s) are each connected to an external conductive terminal of the battery. After that, the battery container is sealed so that the electrode(s) and the separator(s) are shielded from outside air.

In the case of a cylindrical battery, the battery container is usually sealed by fitting a resin gasket in the opening of the battery container and then caulking the battery container. In the case of a cuboidal battery, the battery container can be sealed by mounting a metal lid (called a sealing plate) on the opening and then joining them by welding. Other than these methods, the battery container can be sealed by a binding agent or by fastening it with a bolt through a gasket. Furthermore, the battery container can be sealed by a laminate film obtained by joining a thermoplastic resin on top of metal foil. When sealed, the battery container may be provided with an opening through which the electrolyte is injected.

As described above, the cathode active material according to the present invention undergoes only a small change in volume during charging/discharging, and is thus

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less likely to cause destruction of secondary particles or destruction of the conductive path between the cathode active material and the conductive material. Therefore, the cathode active material itself has a long life.

5 An electrode prepared by applying a conventional cathode active material onto a metal foil made of, for example, aluminum is, since the cathode active material has a large change in volume during charging/discharging, problematic in that the thickness of the electrode itself
10 changes during charging/discharging.

 If the thickness of the electrode itself changes, a battery armor containing a collection of such electrodes is repeatedly subjected to stress. In the case where the battery armor is made of a metal, such repeated stress may cause a
15 crack in the battery armor itself or a sealing part. In the case where the battery armor is made of, for example, a laminated material, repeated stress causes only a little fatigue, but changes the thickness of the battery itself, which in turn causes stress to a module containing such
20 batteries stacked on one another. This may decrease reliability of the module.

 In contrast, an electrode prepared by applying the cathode active material of the present invention onto a metal foil made of, for example, aluminum, since the cathode
25 active material has only a small change in volume during

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charging/discharging, has a small change in thickness during charging/discharging. This reduces a change in the thickness of the battery during charging/discharging, and thus reduces stress on the armor of the battery in the case where the armor is made of a metal. As a result, it is possible to provide a highly reliable battery.

A battery including the cathode of the present invention, as described above, excels in long-term reliability, and is thus suitably used to store power over an extended period of time, the power including solar power, late-night power, and power from a natural energy such as wind power, geothermal power, and wave power.

The present invention is not limited to the description of the embodiments above, but may be altered by a skilled person within the scope of the claims. An embodiment based on a proper combination of technical means disclosed in different embodiments is encompassed in the technical scope of the present invention.

[Examples]

The present invention is described below in more detail with reference to Examples; however, the present invention is not limited to Examples below. It should be noted that reagents etc. used in Examples are highest quality reagents manufactured by Kishida Chemical Co., Ltd.

(I) Calculation of Rate of Change in Volume and

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Theoretical Discharging Capacity and Evaluation of Calculation Results

[References 1 to 4]

For each of the compounds listed in Table 1, the rate of change in volume of the compound (the rate of change in volume of a unit cell in $\text{Li}_x\text{Fe}_{1-x}\text{M}_x\text{P}_{1-y}\text{Si}_y\text{O}_4$ relative to the volume of a unit cell in general formula (1)) was calculated according to the VASP, which is a general program for first principle calculation.

Specifically, the volume of a unit cell having four Li atoms, four Fe atoms, four P atoms, and sixteen O atoms was calculated under the following conditions: ENCUT = 400, IBRION = 1, ISIF = 3, EDIFF = $1.0\text{e-}05$, EDIFFG = -0.02, ISPIN = 2. Further, the value U of Fe was 3.71.

The rate of change in volume was calculated according to the following formula:

$$\text{Rate of change in volume (\%)} = (V_0 - V_1) / V_0 \times 100,$$

where V_0 is the volume as calculated in the presence of Li; and V_1 is the volume as calculated in the absence of Li.

For consideration of the amounts of substitution, calculations were performed on structures twice and four times as large as a unit cell, with half and a quarter the amount of substitution of each element. The calculations confirmed that the amount of substitution was directly proportional to a lattice constant. The rate of change in

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volume for each amount of substitution was calculated in a similar manner.

Further, from (i) the amount of change in valence of Fe from +2 to +3 during discharging and (ii) the molecular weight of the compound, a theoretical discharging capacity of the compound was calculated. Specifically, the theoretical discharging capacity was calculated according to the following formula:

$$\text{Theoretical discharging capacity (mAh/g)} = F / 3600 / \text{Mw} \times 1000 \times (1-x),$$

where F is a Faraday constant; Mw is the molecular weight of the compound; and x, which is equivalent to x in General Formula (1), is the amount of substitution by M of Fe site.

Table 1 shows the results of the above calculation.

It should be noted that among values that are calculated according to first principle calculation, such a rate of change in volume is calculated with high reproducibility because the lattice constant is a value that contains few errors in calculation. These calculation results coincide highly accurately with values obtained by actually preparing cathode active materials and measuring their rates of change in volume.

The above calculation of the theoretical discharging capacity uses a general formula for calculating a theoretical capacity, and thus uses a change in valence of a transition

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metal element from +2 to +3. The calculation gives a maximum value of the capacity of an actually synthesized material. As will be described in Reference 5 below, lithium iron phosphate with no substitution achieved a capacity substantially equivalent to the theoretical capacity. These calculation results should coincide highly accurately with values obtained by actually preparing batteries with use of cathode active materials and measuring their discharging capacities.

Table 1

Ref			Value of x											
			0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50		
		Rate of change in volume (%)	5.84	4.65	3.46	2.26	1.05	-0.17	-1.39					
1	$\text{Li}(\text{Fe}_{1-x}\text{Zr}_x)(\text{P}_{1-2x}\text{Si}_{2x})\text{O}_4$	Theoretical discharging capacity (mAh/g)	159.8	149.8	140.1	130.6	121.2	112.0	103.0					
		Rate of change in volume (%)	6.35	5.68	5.00	4.33	3.65	2.98	2.30					
2	$\text{Li}(\text{Fe}_{1-x}\text{Sn}_x)(\text{P}_{1-2x}\text{Si}_{2x})\text{O}_4$	Theoretical discharging capacity (mAh/g)	158.4	147.3	136.6	126.3	116.4	106.8	97.5					
		Rate of change in volume (%)	6.16	5.31	4.46	3.61	2.76	1.92	1.08	0.24				
3	$\text{Li}(\text{Fe}_{1-x}\text{Y}_x)(\text{P}_{1-x}\text{Si}_x)\text{O}_4$	Theoretical discharging capacity (mAh/g)	159.9	150.1	140.4	130.9	121.6	112.5	103.5	94.7				
		Rate of change in volume (%)	6.59	6.16	5.73	5.29	4.85	4.41	3.97	3.52	3.08	2.63		
4	$\text{Li}(\text{Fe}_{1-x}\text{Al}_x)(\text{P}_{1-x}\text{Si}_x)\text{O}_4$	Theoretical discharging capacity (mAh/g)	163.1	156.1	148.9	141.6	134.2	126.6	118.8	110.9	102.8	94.5		

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As shown in Table 1, each of the compounds of References 1 to 4 exhibited a low rate of change in volume without significantly reducing its theoretical discharging capacity. This low rate of change in volume means that each of the compounds of References 1 to 4 had a low rate of change in volume during charging and discharging, and was therefore a cathode active material with which a long-life battery can be produced.

[Reference 5]

The accuracy of the calculation results was confirmed by actually preparing cathode active materials from LiFePO_4 and FePO_4 , respectively, and calculating their rates of change in volume. Table 2 shows the results.

<Synthesis of LiFePO_4 >

A lithium source LiOH , an iron source $\text{Fe}(\text{CH}_3\text{COO})_2$, and a phosphate source H_3PO_4 were used as starting materials, and these starting materials were measured out so that the molar ratio was $\text{Li:Fe:P} = 1:1:1$. Next, the Fe source and the P source were put into a small amount of water, and the Li source was put after the Fe source had been completely dissolved. Into this aqueous solution, sucrose containing 20 percent by mass of LiFePO_4 , which would be a final product, was added. This aqueous solution was dried overnight at 60°C in a drying furnace under a nitrogen flow, and then sintered for twelve hours at 600°C .

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Thus synthesized was LiFePO_4 single-phase powder, which is an olivine-type cathode active material.

<Measurement of the Rate of Change in Volume>

5 The LiFePO_4 cathode active material thus synthesized was crushed in a mortar into fine powder, and the lattice constant was calculated by X-ray measurement at 10° to 90° at room temperature with use of a Cu tube.

10 Further, the lattice constant of an active material after desorption of Li was calculated by using, as a cathode active material after Li desorption, a cathode active material whose charging capacity had been confirmed and which had the same composition as in a state of Li desorption and performing X-ray measurement on the cathode active material at room temperature. Specifically, XRD
15 measurement of the cathode active material after Li desorption was performed after preparing a battery according to the after-mentioned method for preparing a battery, taking out the cathode with the battery fully charged, and then washing the cathode with ethanol.

20 After calculating the volume of a structure during charging and the volume of the structure during discharging according to the lattice constant of the structure during charging and the lattice constant of the structure during discharging, the rate of change in volume (%) due to
25 charging and discharging was calculated according to the

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following formula:

Rate of change in volume (%) = (1 - volume of structure during charging/volume of structure during discharging) × 100.

5 It should be noted here that the structure during charging is a structure during Li desorption and the structure during discharging is an initial structure during synthesis.

<Method for Preparing a Battery>

10 After the cathode active material, acetylene black (marketed as "Denka Black"; manufactured by Denki Kagaku Kogyo Kabushiki Kaisha), and PVdF (polyvinylidene fluoride) (marketed as "KF Polymer"; manufactured by Kureha Corporation) were mixed with a mass ratio of 70:30:10, the
15 mixture was mixed with N-methylpyrrolidone (manufactured by Kishida Chemical Co., Ltd.) to form slurry. A cathode was obtained by applying the slurry onto a 20-μm-thick aluminum foil so that the cathode had a thickness of 50 μm to 100 μm. It should be noted that the cathode had an
20 electrode size of 2 cm × 2 cm.

 After the cathode had been dried, the cathode was used as an electrode and Li metal was used as a counter electrode, with 50 ml of an electrolyte contained in a 100-ml glass container. The electrolyte (manufactured by Kishida
25 Chemical Co., Ltd.) used was obtained by dissolving LiPF₆ in

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a solvent so that the concentration was 1.4 mol/l, and the solvent used was obtained by mixing ethylene carbonate and diethyl carbonate with a volume ratio of 7:3.

5 The battery prepared as above was charged and discharged at a rate of 0.1 C, which showed that the battery had a capacity of 163 mAh/g.

Table 2

Composition	Item	Experimental value	Calculated value
LiFePO ₄	a axis (angstrom)	10.33	10.207
	b axis (angstrom)	6.01	5.978
	c axis (angstrom)	4.69	4.666
	Volume (angstrom ³)	291.17	284.71
FePO ₄	a axis (angstrom)	9.82	9.753
	b axis (angstrom)	5.79	5.73
	c axis (angstrom)	4.79	4.737
	Volume (angstrom ³)	272.35	264.73
	Expansion/Contraction (%)	6.5	7.0

10 As shown in Table 2, each of the actually prepared cathode active materials exhibited a rate of change in volume of 6.5%, which is almost the same as the calculated value of 7.0%.

(II) Preparation of a Cathode Active Material

[Example 1]

15 A lithium source Li(OC₂H₅), an iron source Fe(CH₃COO)₂, a zirconium source Zr(OC₂H₅)₄, a phosphate source (NH₄)₂HPO₄, and a silicon source Si(OC₂H₅)₄ were

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used as starting materials, and these starting materials were measured out so that the molar ratio was Li:Fe:Zr:P:Si = 1:0.875:0.125:0.75:0.25. Next, the Li source, the Zr source, and the Si source were dissolved in 20g of butanol. Further, the Fe source and the P source were dissolved in water whose number of moles was four times as large as that total number of moles of metal alcoxide (the Fe source, the Si source, and the Li source). After one hour of stirring of a mixture of the butanol, in which the metal alcoxide had been dissolved, and the water, in which the Fe source and the P source had been dissolved, the resulting mixture was dried at 60°C in a dryer into a powdery precursor.

The resultant amorphous precursor was sintered for twelve hours at 600°C in a nitrogen atmosphere. Thus synthesized was $\text{LiFe}_{0.875} \text{Zr}_{0.125} \text{P}_{0.75} \text{Si}_{0.25} \text{O}_4$ single-phase powder, which is an olivine-type cathode active material. The lattice constants of the resultant cathode active material along the a axis, the b axis, and the c axis were 10.344, 6.003, and 4.712, respectively.

[Example 2]

<Preparation of a Cathode Active Material>

A lithium source LiCH_3COO , an iron source $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, a zirconium source ZrCl_4 , a phosphate source H_3PO_4 (85%), and a silicon source $\text{Si}(\text{OC}_2\text{H}_5)_4$ were used as starting materials. These starting materials were measured out so

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that the molar ratio is $\text{Li:Fe:Zr:P:Si} = 1:0.75:0.25:0.5:0.5$,
with the lithium source LiCH_3COO used in an amount of
1.3196 g. These starting materials were dissolved in 30 ml of
 $\text{C}_2\text{H}_5\text{OH}$ and stirred by a stirrer for 48 hours at room
5 temperature. After that, the solvent was removed at 40°C in
a constant-temperature bath, with the result that a
brownish-red powder was obtained.

After addition of 15 percent by weight of sucrose
relative to the resultant powder, they were mixed well in an
10 agate mortar, and the resulting mixture was pressure-
molded into pellets. The pellets were sintered for twelve
hours at 600°C in a nitrogen atmosphere. Thus synthesized
was $\text{LiFe}_{0.75} \text{Zr}_{0.25} \text{P}_{0.5} \text{Si}_{0.5} \text{O}_4$ single-phase powder. The
resultant cathode active material is referred to as "A1".

15 <Preparation of a Cathode Electrode>

Approximately 1 gram of the cathode active material
A2 obtained as above was weighed out, crushed in an agate
mortar, and then mixed with approximately 10 percent by
weight of a conductive agent, acetylene black (marketed as
20 "Denka Black"; manufactured by Denki Kagaku Kogyo
Kabushiki Kaisha), relative of the cathode active material
and approximately 10 percent by weight of a binding agent,
polyvinylidene fluoride resin powder, relative to the cathode
active material.

25 This mixture was dissolved in a solvent such as N-

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5 methyl-2-pyrrolidone to form slurry, and the slurry was applied onto both surfaces of a 20- μ m-thick aluminum foil by a doctor blade method so that the amount of application was approximately 5 mg/cm². This electrode was dried, and then cut so that the applied electrode surface was 2 cm $\times$ 2 cm. The electrode was then pressed to provide a cathode electrode.

[Example 3]

10 A lithium source LiCH₃COO, an iron source Fe(NO₃)₃·9H₂O, a zirconium source ZrCl₄, a phosphate source H₃PO₄ (85%), and a silicon source Si(OC₂H₅)₄ were used as starting materials. These starting materials were measured out so that the molar ratio is Li:Fe:Zr:P:Si = 1:0.85:0.15:0.7:0.3, with the lithium source LiCH₃COO used in an amount of 15 1.3196 g. These starting materials were dissolved in 30 ml of C₂H₅OH and stirred by a stirrer for 48 hours at room temperature. After that, the solvent was removed at 40°C in a constant-temperature bath, with the result that a brownish-red powder was obtained.

20 After addition of 15 percent by weight of sucrose relative to the resultant powder, they were mixed well in an agate mortar, and the resulting mixture was pressure-molded into pellets. The pellets were sintered for twelve hours at 600°C in a nitrogen atmosphere. Thus synthesized 25 was LiFe_{0.85} Zr_{0.15} P_{0.7} Si_{0.3} O₄ single-phase powder. The

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resultant cathode active material is referred to as "A2".

The operation performed in Example 2 was performed also on the cathode active material A2 to prepare a cathode electrode.

5 [Example 4]

A lithium source LiCH_3COO , an iron source $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, a zirconium source ZrCl_4 , a phosphate source H_3PO_4 (85%), and a silicon source $\text{Si}(\text{OC}_2\text{H}_5)_4$ were used as starting materials. These starting materials were measured out so
10 that the molar ratio is $\text{Li:Fe:Zr:P:Si} = 1:0.875:0.125:0.75:0.25$, with the lithium source LiCH_3COO used in an amount of 1.3196 g. These starting materials were dissolved in 30 ml of $\text{C}_2\text{H}_5\text{OH}$ and stirred by a stirrer for 48 hours at room temperature. After that, the solvent
15 was removed at 40°C in a constant-temperature bath, with the result that a brownish-red powder was obtained.

After addition of 15 percent by weight of sucrose relative to the resultant powder, they were mixed well in an agate mortar, and the resulting mixture was pressure-
20 molded into pellets. The pellets were sintered for twelve hours at 600°C in a nitrogen atmosphere. Thus synthesized was $\text{LiFe}_{0.875} \text{Zr}_{0.125} \text{P}_{0.75} \text{Si}_{0.25} \text{O}_4$ single-phase powder. The resultant cathode active material is referred to as "A3".

The operation performed in Example 2 was performed
25 also on the cathode active material A3 to prepare a cathode

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electrode.

[Example 5]

5 A lithium source LiCH_3COO , an iron source $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and ZrCl_4 , a phosphate source H_3PO_4 (85%), and a silicon source $\text{Si}(\text{OC}_2\text{H}_5)_4$ were used as starting materials. These starting materials were measured out so that the molar ratio is $\text{Li}:\text{Fe}:\text{Zr}:\text{P}:\text{Si} = 1:0.9:0.1:0.8:0.2$, with the lithium source LiCH_3COO used in an amount of 1.3196 g. These starting materials were dissolved in 30 ml of $\text{C}_2\text{H}_5\text{OH}$ and stirred by a stirrer for 48 hours at room temperature. After that, the solvent was removed at 40°C in a constant-temperature bath, with the result that a brownish-red powder was obtained.

15 After addition of 15 percent by weight of sucrose relative to the resultant powder, they were mixed well in an agate mortar, and the resulting mixture was pressure-molded into pellets. The pellets were sintered for twelve hours at 600°C in a nitrogen atmosphere. Thus synthesized was $\text{LiFe}_{0.9} \text{Zr}_{0.1} \text{P}_{0.8} \text{Si}_{0.2} \text{O}_4$ single-phase powder. The resultant cathode active material is referred to as "A4".

20 The operation performed in Example 2 was performed also on the cathode active material A4 to prepare a cathode electrode.

[Example 6]

25 A lithium source LiCH_3COO , an iron source $\text{Fe}(\text{NO}_3)_3 \cdot$

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9H₂O, a zirconium source ZrCl₄, a phosphate source H₃PO₄ (85%), and a silicon source Si(OC₂H₅)₄ were used as starting materials. These starting materials were measured out so that the molar ratio is Li:Fe:Zr:P:Si = 1:0.93:0.07:0.86:0.14, with the lithium source LiCH₃COO used in an amount of 1.3196 g. These starting materials were dissolved in 30 ml of C₂H₅OH and stirred by a stirrer for 48 hours at room temperature. After that, the solvent was removed at 40°C in a constant-temperature bath, with the result that a brownish-red powder was obtained.

After addition of 15 percent by weight of sucrose relative to the resultant powder, they were mixed well in an agate mortar, and the resulting mixture was pressure-molded into pellets. The pellets were sintered for twelve hours at 600°C in a nitrogen atmosphere. Thus synthesized was LiFe_{0.93} Zr_{0.07} P_{0.86} Si_{0.14} O₄ single-phase powder. The resultant cathode active material is referred to as "A5".

The operation performed in Example 2 was performed also on the cathode active material A5 to prepare a cathode electrode.

[Example 7]

A lithium source LiCH₃COO, an iron source Fe(NO₃)₃·9H₂O, a zirconium source ZrCl₄, a phosphate source H₃PO₄ (85%), and a silicon source Si(OC₂H₅)₄ were used as starting materials. These starting materials were measured out so

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that the molar ratio is $\text{Li:Fe:Zr:P:Si} = 1:0.95:0.05:0.9:0.1$,
with the lithium source LiCH_3COO used in an amount of
1.3196 g. These starting materials were dissolved in 30 ml of
 $\text{C}_2\text{H}_5\text{OH}$ and stirred by a stirrer for 48 hours at room
5 temperature. After that, the solvent was removed at 40°C in
a constant-temperature bath, with the result that a
brownish-red powder was obtained.

After addition of 15 percent by weight of sucrose
relative to the resultant powder, they were mixed well in an
10 agate mortar, and the resulting mixture was pressure-
molded into pellets. The pellets were sintered for twelve
hours at 600°C in a nitrogen atmosphere. Thus synthesized
was $\text{LiFe}_{0.95}\text{Zr}_{0.05}\text{P}_{0.9}\text{Si}_{0.1}\text{O}_4$ single-phase powder. The
resultant cathode active material is referred to as "A6".

15 The operation performed in Example 2 was performed
also on the cathode active material A6 to prepare a cathode
electrode.

[Comparative Example 1]

A lithium source LiCH_3COO , an iron source $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and a phosphate source H_3PO_4 (85%) were used as
20 starting materials. These starting materials were measured
out so that the molar ratio is $\text{Li:Fe:P} = 1:1:1$, with the
lithium source LiCH_3COO used in an amount of 1.3196 g.
These starting materials were dissolved in 30 ml of $\text{C}_2\text{H}_5\text{OH}$
25 and stirred by a stirrer for 48 hours at room temperature.

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After that, the solvent was removed at 40°C in a constant-temperature bath, with the result that a brownish-red powder was obtained.

5 After addition of 15 percent by weight of sucrose relative to the resultant powder, they were mixed well in an agate mortar, and the resulting mixture was pressure-molded into pellets. The pellets were sintered for twelve hours at 600°C in a nitrogen atmosphere. Thus synthesized was a cathode active material. The resultant cathode active
10 material is referred to as "B1".

The operation performed in Example 2 was performed also on the cathode active material B1 to prepare a cathode electrode.

(III) Evaluation of Cathode Active Material

15 (III-I) X-Ray Analysis

The cathode active materials A1 to A6 and B1 thus obtained were each crushed in an agate mortar and subjected to a X-ray analysis apparatus (marketed as MiniFlexII; manufactured by Rigaku Co., Ltd.) to give a
20 powder X-ray diffraction pattern. Figs. 1 through 7 show X-ray diffraction patterns for the cathode active materials A1 to A6 and B1, respectively, as the results of the X-ray analysis.

(III-II) Evaluation of Valence of Fe

25 The respective cathode active materials prepared in

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the Examples and Comparative Example were each crushed in an agate mortar and subjected to a Mössbauer spectrometry with use of a Mössbauer spectroscopy device.

5 A Mössbauer absorption spectrum was measured under the following conditions: A gamma ray source was ^{57}Co , which is an isotope of cobalt. A sample targeted for the measurement was placed in an amount of 200 mg between the gamma ray source and a gamma ray detector. The sample was vibrated at an amplitude of $5\text{ cm} \pm 6\text{ mm/s}$ with
10 respect to the detector. A Mössbauer spectrum was measured by measuring absorption of gamma rays.

Assuming that four absorption peaks centered at the respective velocity regions of -0.1 mm/s , 0 mm/s , 1 mm/s , and 2.7 mm/s were Lorentz functions, fitting was performed
15 by a least-squares method on the data obtained as above. The respective peaks at the velocity regions of -0.1 mm/s and 2.7 mm/s were presumed to be due to absorption by Fe^{2+} , and the respective peaks at the velocity regions of 0 mm/s and 1 mm/s were presumed to be due to absorption
20 by Fe^{3+} . A ratio between Fe^{2+} and Fe^{3+} was calculated from an area ratio of the respective peaks for Fe^{2+} and Fe^{3+} .

Fig. 8 shows an absorption spectrum, measured by the above method, of the cathode active material A1. This spectrum measurement result shows that (i) two large
25 absorption peaks were observed, that (ii) a value of an

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isomer shift, that is, a medium value between the two peaks, was approximately 1.25, and that (iii) a quadropole split, corresponding to a distance between the peaks, was approximately 2.8. The above absorption peaks coincide well with typical absorption peaks of Fe^{2+} . The spectrum of the cathode active material A1 showed, other than the peaks attributed to Fe^{2+} , peaks attributed to Fe^{3+} , the peaks having an isomer shift value of approximately 0.5 and a quadropole split of approximately 0.6 to 1.0. These results showed that the cathode active material A1 was made up of Fe^{2+} and Fe^{3+} . An area ratio between Fe^{2+} and Fe^{3+} in the above spectrum showed that $\text{Fe}^{2+}:\text{Fe}^{3+} = 95:5$.

Fig. 9 shows an absorption spectrum obtained by a Mössbauer spectrometry for the cathode active material A2. This spectrometry result shows that (i) two large absorption peaks were observed, and as a result of fitting the peaks by double Lorentzian, that (ii) a value of an isomer shift, that is, a medium value between the two peaks, was approximately 1.25, and that (iii) a quadropole split, corresponding to a distance between the peaks, was approximately 2.8. The above absorption peaks coincide well with typical absorption peaks of Fe^{2+} . This showed that the cathode active material A2 was made up of Fe^{2+} . It should be noted that no peak attributed to Fe^{3+} was observed, unlike in the cathode active material A1.

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A measurement similar to the above was performed on each of the other cathode active materials A3 to A6, with a result similar to the above. This confirmed that the iron in each of the cathode active materials A2 to A6 had a valence of 2+.

(IV) Evaluation of Battery

(IV-I) Capacity Ratio

Put into a 50-ml beaker a 30 ml electrolyte. The electrolyte was mixed 50% by volume of diethyl carbonate with 50% by volume of ethylene carbonate. 1 mol/L of LiPF_6 was dissolved in the electrolyte. With use of (i) the cathode electrode prepared in each of the Examples and the Comparative Example and (ii) metal lithium as an anodic active material serving as a counter electrode, a battery was prepared.

Each of the batteries thus prepared was first charged in an environment of 25°C. The charging current was 0.1 mA, and the charging was finished at a point in time where the battery reached a potential of 4V. After the charging was finished, the battery was discharged at 0.1 mA, and the discharging was finished at a point in time where the battery reached a potential of 2.0 V, with the result that the actually measured capacity of the battery was obtained. These results are shown in Table 3.

Table 3

	Cathode active material	Theoretical capacity (mAh/g)	Actually measured capacity (mAh/g)	Capacity ratio (%)
Example 2	A1	121.7	110.4	90.6%
Example 3	A2	140.5	128.4	91.4%
Example 4	A3	145.3	130.3	89.7%
Example 5	A4	150.1	127.9	85.2%
Example 6	A5	156.0	138.0	88.5%
Example 7	A6	159.9	140.3	87.7%
Comparative Example 1	B1	169.9	147.5	86.8%

(IV-II) Rate of Change in Volume

Furthermore, each battery prepared in "(IV-I) Capacity Ratio" was charged at a constant current of 0.1 mA until 4 V so that lithium was desorbed. After that, the lattice constant after lithium desorption was calculated by taking out the electrode and performing powder X-ray diffractometry on the electrode.

Table 4 shows lattice constants before charging. Table 5 shows lattice constants after charging. Table 6 shows rates of change in volume.

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Table 4

	Cathode active material	Lattice constant			Lattice volume
		a axis (angstrom)	b axis (angstrom)	c axis (angstrom)	(angstrom ³)
Example 2	A1	10.413	6.031	4.750	298.3
Example 3	A2	10.366	6.022	4.715	294.3
Example 4	A3	10.355	6.020	4.712	293.7
Example 5	A4	10.343	6.010	4.706	292.5
Example 6	A5	10.335	6.005	4.701	291.8
Example 7	A6	10.332	6.005	4.699	291.6
Comparative Example 1	B1	10.328	6.007	4.696	291.3

Table 5

	Cathode active material	Lattice constant			Lattice volume
		a axis (angstrom)	b axis (angstrom)	c axis (angstrom)	(angstrom ³)
Example 2	A1	10.190	6.015	4.877	298.9
Example 3	A2	10.077	5.934	4.819	288.2
Example 4	A3	9.997	5.884	4.808	282.8
Example 5	A4	9.972	5.862	4.796	280.4
Example 6	A5	9.948	5.852	4.792	279.0
Example 7	A6	9.912	5.840	4.790	277.3
Comparative Example 1	B1	9.830	5.802	4.785	272.9

Table 6

	Cathode active material	Rate of change in volume (%)
Example 2	A1	-0.2
Example 3	A2	2.1
Example 4	A3	3.7
Example 5	A4	4.2
Example 6	A5	4.4
Example 7	A6	4.9
Comparative Example 1	B1	6.3

(IV-III) Evaluation of Capacity Retention Rate

<Preparation of Battery>

5 Used as an anodic active material were natural
graphite powder and lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$). The anodic
active material was mixed with approximately 10% by weight
of polyvinylidene fluoride resin powder serving as a binding
agent. Further, in the case where lithium titanate was used
10 as an anodic active material, 10% by weight of acetylene
black was mixed as a conductive agent. This mixture was
dissolved in N-methyl-2-pyrrolidone to form slurry, and the
slurry was applied onto both surfaces of a 20- μm -thick
copper foil. The applied slurry was dried and then pressed to
15 provide an anode.

The cathode prepared in each of the Examples and the
Comparative Example and the above anode were each cut out

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in a size of 30 mm × 30 mm. As a current introducing terminal for a battery, an aluminum tab having a width of 3 mm and a length of 50 mm was welded to the cathode, whereas a copper tab having a width of 3 mm and a length of 50 mm was welded to the anode. Thus prepared were a cathode electrode and an anode electrode.

A separator made of porous polyethylene was placed between the cathode electrode and the anode electrode. The layered product thus prepared was placed between laminate films including two metal foils to each of which a thermoplastic resin was attached. The metal foils were thermally welded to each other along the periphery to be sealed, which provided the battery with an armor. This laminate had an opening for injecting an electrolyte.

In the laminate, 50% by volume of ethylene carbonate, in which 1 mol/L of LiPF_6 was dissolved, and 50% by volume of diethyl carbonate were impregnated as an electrolyte.

After the electrolyte was injected in the battery, the opening of the battery container was sealed, to complete the preparation of a secondary battery.

Fig. 10 is a cross-sectional view illustrating the battery prepared as above. Fig. 10 illustrates a cathode electrode 1, an anode electrode 2, a separator 3, cathode and anode tabs 4, and a laminate 5.

<Evaluation of Capacity Retention Rate>

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Each of the batteries thus prepared was first charged in an environment of 25°C. The charging current was 0.2 mA, and the charging was finished at a point in time where the battery reached a potential of 4V. After the charging was finished, the battery was discharged at 0.2 mA, and the discharging was finished at a point in time where the battery reached a potential of 2.0 V, with the result that the initial capacity of the battery was obtained. Further, the battery was repeatedly charged and discharged at a current of 0.2 mA. A discharging capacity of the battery at a hundredth cycle was then measured, and a capacity retention rate was calculated according to the following formula:

Capacity retention rate = discharging capacity at hundredth cycle / initial discharging capacity.

Table 7 shows the results for the case where the anode is made of carbon. Table 8 shows the results for the case where the anode is made of lithium titanate.

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Table 7

	Cathode active material	Initial discharging capacity (mAh/g)	Discharging capacity at hundredth cycle (mAh/g)	Capacity retention rate (%)
Example 2	A1	102.1	100.9	98.8
Example 3	A2	118.9	117.8	99.1
Example 4	A3	118.6	115.6	97.5
Example 5	A4	122.1	120.9	99.0
Example 6	A5	128.4	123.5	96.2
Example 7	A6	131.5	125.8	95.7
Comparative Example 1	B1	136.4	110.5	81.0

Table 8

	Cathode active material	Initial discharging capacity (mAh/g)	Discharging capacity at hundredth cycle (mAh/g)	Capacity retention rate (%)
Example 2	A1	108.0	105.9	98.0
Example 3	A2	125.2	123.3	98.4
Example 4	A3	126.1	123.5	97.9
Example 5	A4	127.8	125.7	98.3
Example 6	A5	136.5	129.8	95.1
Example 7	A6	138.3	130.8	94.6
Comparative Example 1	B1	145.6	130.8	89.8

5 Tables 7 and 8 show the following: The batteries including the respective cathode active materials A1 to A6 are superior in capacity itself and capacity retention rate to the battery including the cathode active material B1 of Comparative Example 1. Among the batteries including the

10 respective cathode active materials A1 to A6, the batteries

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including the respective cathode active materials A2 to A6, in each of which every Fe has a valence of +2, are superior in property to the battery including the cathode active material A1, which includes Fe atoms having a valence of 3.

5 Further, the batteries including the respective cathode active materials A1 to A3 each have a capacity retention rate of approximately 99%, and are thus extremely excellent in cycling characteristics.

10 The batteries including the respective cathode active materials A4 to A6 are, on the other hand, lower in capacity retention rate than the batteries including the respective cathode active materials A1 to A3, but are better in cycling characteristics than the cathode active material of Comparative Example 1 and also larger in capacity itself
15 than the batteries including the respective cathode active materials A1 to A3. Thus, an application that requires a long life preferably involves as a cathode active material a composition, such as the cathode active materials A1 to A3, in which the amount of substitution is $0.1 \leq x \leq 0.5$, whereas
20 an application that requires a long life and a higher capacity preferably involves as a cathode active material a composition, such as the cathode active materials A4 to A6, in which the amount of substitution is $0.05 \leq x \leq 0.1$.

25 (IV-IV) Evaluation of Changes in Thickness during Charging and Discharging

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[Example 8]

Ten grams of the cathode active material A1 obtained in Example 1 were weighed out, crushed in an agate mortar, and then mixed with approximately 10 percent by weight of a
5 conductive agent, acetylene black (marketed as "Denka Black"; manufactured by Denki Kagaku Kogyo Kabushiki Kaisha), relative of the cathode active material and approximately 10 percent by weight of a binding agent, polyvinylidene fluoride resin powder, relative to the cathode
10 active material.

This mixture was dissolved in a solvent such as N-methyl-2-pyrrolidone to form slurry, and the slurry was applied onto both surfaces of a 20- μ m-thick aluminum foil by a doctor blade method so that the amount of application
15 was approximately 20 mg/cm². This electrode was dried, and then oil-pressed so that its thickness was approximately 100 μ m, including the thickness of the aluminum foil. Thus prepared was an electrode having an electrode size of 2 cm $\times$ 2 cm.

20 After the electrode had been dried, a battery was prepared by using the electrode as a cathode, using Li metal as a counter electrode, and pouring 50 ml of an electrolyte into a 100-ml glass container. The electrolyte (manufactured by Kishida Chemical Co., Ltd.) used was obtained by
25 dissolving LiPF₆ in a solvent so that the concentration was

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1.4 mol/l, and the solvent used was obtained by mixing ethylene carbonate and diethyl carbonate with a volume ratio of 7:3.

As a result of charging of the resultant battery at 0.1 mA, a charging capacity of 140 mAh/g was obtained. As a result of measurement of the thickness of the cathode taken out after completion of charging, the cathode had a thickness of 97 μm , while it had had a thickness of 101 μm before the charging.

[Comparative Example 2]

An electrode was prepared through the same procedure as in Example 8 except that the cathode active material B1 prepared in Comparative Example 1 was used instead of the cathode active material A1. A battery prepared by using the electrode as cathode was charged and discharged, and the thickness of the cathode was measured. As a result, the cathode had a thickness of 93 μm , while it had had a thickness of 102 μm before the charging.

Comparison between Example 8 and Comparative Example 2 shows that a cathode according to the present invention has a smaller amount of change in thickness during charging and discharging than a conventional cathode.

[Example 9: Flat-plate Laminate Battery]

A lithium source LiCH_3COO , an iron source $\text{Fe}(\text{NO}_3)_3 \cdot$

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9H₂O, a zirconium source ZrCl₄, a phosphate source H₃PO₄(85%), and a silicon source Si(OC₂H₅)₄ were used as starting materials. These starting materials were measured out so that the molar ratio is Li:Fe:Zr:P:Si = 1:0.75:0.25:0.5:0.5, with the lithium source LiCH₃COO used in an amount of 131.96 g. These starting materials were dissolved in 3000 ml of C₂H₅OH and stirred by a stirring motor for 48 hours at room temperature. After that, the solvent was removed at 40°C in a constant-temperature bath, with the result that a brownish-red powder was obtained.

Two hundred grams of the resultant brownish-red powder were weighed out, crushed in steps of 10 g in an automatic mortar, and then mixed with approximately 10 percent by weight of a conductive agent, acetylene black (marketed as "Denka Black"; manufactured by Denki Kagaku Kogyo Kabushiki Kaisha), relative of the cathode active material and approximately 10 percent by weight of a binding agent, polyvinylidene fluoride resin powder, relative to the cathode active material.

This mixture was dissolved in a solvent such as N-methyl-2-pyrrolidone to form slurry, and the slurry was applied onto both surfaces of a 20-μm-thick aluminum foil by a doctor blade method. After the slurry had been applied onto one surface, the same slurry was applied onto the other

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surface, whereby an electrode as formed on both surfaces of the metal foil. It should be noted that the slurry was applied so that the amount of application per surface was approximately 15 mg/cm².

5 After the electrode had been dried, a cathode electrode was prepared by pressing the electrode by passing it through a space between two metal rollers placed at a distance of approximately 130 μm, in order that its thickness was approximately 150 μm, including the thickness of the
10 aluminum foil.

 Next, approximately 500 g of natural graphite powder having an average particle diameter of approximately 5 μm were weight out as an anodic active material, and this anodic active material was mixed with approximately 10
15 percent by weight of a binding agent, polyvinylidene fluoride resin powder, relative to the anodic active material.

 This mixture was dissolved in a solvent such as N-methyl-2-pyrrolidone to form slurry, and the slurry was applied onto both surfaces of a 12-μm-thick copper foil by a
20 doctor blade method. After the slurry had been applied onto one surface, the same slurry was applied onto the other surface, whereby an electrode as formed on both surfaces of the metal foil. It should be noted that the amount of application per surface was approximately 7 mg/cm².

25 After the electrode had been dried, an anodic electrode

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was prepared by pressing the electrode by passing it through a space between two metal rollers placed at a distance of approximately 120 μm , in order that its thickness was approximately 140 μm , including the thickness of the copper foil.

The cathode electrode thus obtained was cut into ten cathode electrodes each having a width of 10 cm and a height of 15 cm. Similarly, the anodic electrode was cut into eleven anodic electrodes each having a width of 10.6 cm and a height of 15.6 cm. It should be noted that the cathodes and the anodes had their shorter sides provided with unpainted parts each having a width of 10 mm and a length of 25 mm, and these unpainted parts served as collector tabs.

As separators, twenty polypropylene porous films each having a thickness of 25 μm , a width of 11 cm, and a height of 16 cm were used. Such a layered product 11 as shown in Fig. 11 was obtained by: layering the cathodes, the anodes, and the separators in such a way that the separators are disposed on both surfaces of the cathodes so that the anodes and the cathodes do not have direct contact with each other; and fixing them with an adhesive tape made of Kapton resin. Welded ultrasonically to each of the cathode tabs of the layered product 11 was a cathode collector lead 13, made of aluminum, which had a width of 10 mm, a length of 30 mm,

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and a thickness of 100 μm . Similarly welded ultrasonically to each of the anode tabs was an anode collector lead 14, made of nickel, which had a width of 10 mm, a length of 30 mm, and a thickness of 100 μm .

5 The layered product 11 thus prepared was placed between two aluminum laminates 12, three of whose sides were heat-sealed. In this state, the layered product 11 was dehydrated by heating it for twelve hours at a temperature of approximately 80°C in a chamber decompressed by a rotary
10 pump.

 The layered product 11 thus dried was placed in a dry box in an Ar atmosphere, and a flat-plate laminate battery was prepared by injecting approximately 50 cc of an electrolyte (manufactured by Kishida Chemical Co., Ltd.) and
15 sealing the opening under reduced pressure. The electrolyte used was obtained by dissolving LiPF_6 in a solvent so that the concentration was 1.4 mol/l, and the solvent used was obtained by mixing ethylene carbonate and diethyl carbonate with a volume ratio of 7:3.

20 The prepared battery had a thickness of 4.1 mm. A current of 100 mA was applied to this battery, and the charging was finished at a point in time where the battery reached a voltage of 3.9 V. After the charging, the battery had a measured thickness of 4.2 mm. This shows that there
25 was almost no change in thickness during the charging.

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[Comparative Example 3]

A flat-plate laminate battery was prepared through exactly the same procedure as in Example 8 except that a lithium source LiCH_3COO , an iron source $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$,
5 and a phosphate source $\text{H}_3\text{PO}_4(85\%)$ were used as starting materials and that these starting materials were measured out so that the molar ratio is $\text{Li:Fe:P} = 1:1:1$, with the lithium source LiCH_3COO used in an amount of 131.96 g.

The prepared battery had a thickness of 4.1 mm. A
10 current of 100 mA was applied to this battery, and the charging was finished at a point in time where the battery reached a voltage of 3.9 V. After the charging, the battery had a measured thickness of 4.7 mm.

The results of Example 9 and Comparative Example 3
15 show that a battery in which a cathode according to the present invention is used changes less in thickness than a battery in which a conventional cathode is used.

[Example 10: Layered Cuboidal Battery]

A lithium source LiCH_3COO , an iron source $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, a zirconium source ZrCl_4 , a phosphate source $\text{H}_3\text{PO}_4(85\%)$, and a silicon source $\text{Si}(\text{OC}_2\text{H}_5)_4$ were used as
20 starting materials. These starting materials were measured out so that the molar ratio is $\text{Li:Fe:Zr:P:Si} = 1:0.75:0.25:0.5:0.5$, with the lithium source LiCH_3COO used
25 in an amount of 1319.6 g. These starting materials were

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dissolved in 30 L of C₂H₅OH and stirred by a stirring motor for 48 hours at room temperature. After that, the solvent was removed at 40°C in a constant-temperature bath, with the result that a brownish-red powder was obtained.

5 One thousand grams of the resultant brownish-red powder were weighed out, crushed in steps of 10 g in an automatic mortar, and then mixed with approximately 10 percent by weight of a conductive agent, acetylene black (marketed as "Denka Black"; manufactured by Denki Kagaku
10 Kogyo Kabushiki Kaisha), relative of the cathode active material and approximately 10 percent by weight of a binding agent, polyvinylidene fluoride resin powder, relative to the cathode active material.

 This mixture was dissolved in a solvent such as N-
15 methyl-2-pyrrolidone to form slurry, and the slurry was applied onto both surfaces of a 20-μm-thick aluminum foil by a doctor blade method. After the slurry had been applied onto one surface, the same slurry was applied onto the other surface, whereby an electrode as formed on both surfaces of
20 the metal foil. It should be noted that that the amount of application per surface was approximately 15 mg/cm².

 After the electrode had been dried, a cathode electrode was prepared by pressing the electrode by passing it through a space between two metal rollers placed at a distance of
25 approximately 130 μm, in order that its thickness was

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approximately 150 μm , including the thickness of the aluminum foil.

Next, approximately 500 g of natural graphite powder having an average particle diameter of approximately 5 μm were weight out as an anodic active material, and this anodic active material was mixed with approximately 10 percent by weight of a binding agent, polyvinylidene fluoride resin powder, relative to the anodic active material.

This mixture was dissolved in a solvent such as N-methyl-2-pyrrolidone to form slurry, and the slurry was applied onto both surfaces of a 12- μm -thick copper foil by a doctor blade method. After the slurry had been applied onto one surface, the same slurry was applied onto the other surface, whereby an electrode as formed on both surfaces of the metal foil. It should be noted that the amount of application per surface was approximately 7 mg/cm^2 .

After the electrode had been dried, an anodic electrode was prepared by pressing the electrode by passing it through a space between two metal rollers placed at a distance of approximately 120 μm , in order that its thickness was approximately 140 μm , including the thickness of the copper foil.

The cathode electrode thus obtained was cut into ten cathode electrodes each having a width of 10 cm and a height of 15 cm. Similarly, the anodic electrode was cut into

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eleven anodic electrodes each having a width of 10.6 cm and a height of 15.6 cm. It should be noted that the cathodes and the anodes had their shorter sides provided with unpainted parts each having a width of 10 mm and a length of 25 mm, and these unpainted parts served as collector tabs.

As separators, twenty polypropylene porous films each processed to have a thickness of 25 μm , a width of 11 cm, and a height of 16 cm were used.

Such a layered product 15 as shown in Fig. 12 was obtained by: layering the cathodes, the anodes, and the separators in such a way that the separators are disposed on both surfaces of the cathodes so that the anodes and the cathodes do not have direct contact with each other; and fixing them with an adhesive tape made of Kapton resin.

Welded ultrasonically to each of the cathode tabs of the layered product 15 was a cathode collector lead 16, made of aluminum, which had a width of 10 mm, a length of 30 mm, and a thickness of 100 μm . Similarly welded ultrasonically to each of the anode tabs was an anode collector lead 17, made of nickel, which had a width of 10 mm, a length of 30 mm, and a thickness of 100 μm .

The layered product 15 was dehydrated by heating it for twelve hours at a temperature of approximately 80°C in a chamber decompressed by a rotary pump.

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The layered product 15 thus dried was inserted into a battery can 18 in a dry box in an Ar atmosphere, and the collector leads 16 and 17 of the layered product 15 were welded ultrasonically to the ends of collector terminals (cathode terminals, anode terminals 21) of a battery lid 19 provided with two piercing terminals and made of an aluminum metal plate. It should be noted that the battery can 18 used was a 1-mm-thick aluminum can shaped into cuboid with the dimensions 12 cm × 18 cm × 2 cm and provided with a safety valve 20.

Then, the battery lid 19 was fitted in the opening of the battery can 18, and the battery was sealed by laser-welding the joint.

A cuboidal battery was prepared by injecting approximately 300 cc of an electrolyte (manufactured by Kishida Chemical Co., Ltd.) through a hole of 1 mm diameter made in the battery lid 19 and then sealing the injection hole by laser welding. The electrolyte used was obtained by dissolving LiPF_6 in a solvent so that the concentration was 1.4 mol/l, and the solvent used was obtained by mixing ethylene carbonate and diethyl carbonate with a volume ratio of 7:3.

The prepared battery had a thickness of 20.0 mm in its central part. A current of 100 mA was applied to this battery, and the charging was finished at a point in time

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where the battery reached a voltage of 3.9 V. After the charging, the battery had a measured thickness of 20.0 mm in its central part. This shows that there was almost no change in thickness during the charging.

5 [Comparative Example 4]

A layered cuboidal battery was prepared through exactly the same procedure as in Example 10 except that a lithium source LiCH_3COO , an iron source $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and a phosphate source $\text{H}_3\text{PO}_4(85\%)$ were used as starting materials and that these starting materials were measured out so that the molar ratio is $\text{Li:Fe:P} = 1:1:1$, with the lithium source LiCH_3COO used in an amount of 131.96 g.

10 The prepared battery had a thickness of 20.0 mm in its central part. A current of 100 mA was applied to this battery, and the charging was finished at a point in time where the battery reached a voltage of 3.9 V. After the charging, the battery had a measured thickness of 21.5 mm in its central part.

15 The results of Example 10 and Comparative Example 4 show that a battery in which a cathode according to the present invention is used changes less in thickness than a battery in which a conventional cathode is used.

(IV-V) Evaluation of the Capacity Retention Rate of Wound Cylindrical Battery

25 [Example 11: Wound Cylindrical Battery]

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A lithium source LiCH_3COO , an iron source $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, a zirconium source ZrCl_4 , a phosphate source $\text{H}_3\text{PO}_4(85\%)$, and a silicon source $\text{Si}(\text{OC}_2\text{H}_5)_4$ were used as starting materials. These starting materials were measured
5 out so that the molar ratio is $\text{Li:Fe:Zr:P:Si} = 1:0.75:0.25:0.5:0.5$, with the lithium source LiCH_3COO used in an amount of 1319.6 g. These starting materials were dissolved in 30 L of $\text{C}_2\text{H}_5\text{OH}$ and stirred by a stirring motor for 48 hours at room temperature. After that, the solvent
10 was removed at 40°C in a constant-temperature bath, with the result that a brownish-red powder was obtained.

One thousand grams of the resultant brownish-red powder were weighed out, crushed in steps of 10 g in an automatic mortar, and then mixed with approximately 10
15 percent by weight of a conductive agent, acetylene black (marketed as "Denka Black"; manufactured by Denki Kagaku Kogyo Kabushiki Kaisha), relative of the cathode active material and approximately 10 percent by weight of a binding agent, polyvinylidene fluoride resin powder, relative
20 to the cathode active material.

This mixture was dissolved in a solvent such as N-methyl-2-pyrrolidone to form slurry, and the slurry was applied onto both surfaces of a 20- μm -thick aluminum foil by a doctor blade method. After the slurry had been applied
25 onto one surface, the same slurry was applied onto the other

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surface, whereby an electrode as formed on both surfaces of the metal foil. It should be noted that that the amount of application per surface was approximately 15 mg/cm².

After the electrode had been dried, a cathode electrode was prepared by pressing the electrode by passing it through a space between two metal rollers placed at a distance of approximately 130 μm, in order that its thickness was approximately 150 μm, including the thickness of the aluminum foil.

Next, approximately 500 g of natural graphite powder having an average particle diameter of approximately 5 μm were weight out as an anodic active material, and this anodic active material was mixed with approximately 10 percent by weight of a binding agent, polyvinylidene fluoride resin powder, relative to the anodic active material.

This mixture was dissolved in a solvent such as N-methyl-2-pyrrolidone to form slurry, and the slurry was applied onto both surfaces of a 12-μm-thick copper foil by a doctor blade method. After the slurry had been applied onto one surface, the same slurry was applied onto the other surface, whereby an electrode as formed on both surfaces of the metal foil. It should be noted that the amount of application per surface was approximately 7 mg/cm².

After the electrode had been dried, an anodic electrode was prepared by pressing the electrode by passing it through

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a space between two metal rollers placed at a distance of approximately 120 μm , in order that its thickness was approximately 140 μm , including the thickness of the copper foil.

5 The cathode electrode thus obtained was cut so as to have a width of 5 cm and a length of 150 cm. Similarly, the anodic electrode was cut so as to have a width of 5.2 cm and a height of 160 cm.

10 The cathodes and the anodes had their shorter sides provided with unpainted parts to which collector tabs were welded. Welded ultrasonically to each of the unpainted parts was a metal lead having a width of 4 mm, a thickness of 100 μm , and a length of 10 cm. Further, as those metal leads for the cathodes were made of aluminum, and those for the
15 anodes were made of nickel.

 As a separator, a 25- μm -thick polypropylene porous film processed to have a width of 6 cm and a length of 350 cm was used. The separator was folded in half so as to have a width of 6 cm and a length of 175 cm, and the cathode was
20 sandwiched between the halves. Such a cylindrical wound product 22 as shown in Fig. 13 was obtained by putting the anode on top of the intermediate product and winding it around a polyethylene spindle having a diameter of 5 mm and a length of 6.5 cm. The final wound product 22 was
25 bound tightly with a Kapton tape so as not to be unwound.

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The wound product 22 thus prepared was dehydrated by heating it for twelve hours at a temperature of approximately 80°C in a chamber decompressed by a rotary pump. It should be noted that after this operation, following
5 operations were carried out in an argon dry box at a dew point of -40°C or lower.

An aluminum pipe, having a diameter of 30 mm and a length of 70 mm, one end of which had been closed by welding an aluminum disc having a diameter of 30 cm was
10 used as a battery can 24. It should be noted that a bottom lid was joined by laser welding.

The wound product 22 was inserted into the battery can 24 and, as shown in Fig. 13, a cathode collector lead 23 was spot-welded to a cathode terminal 25 of a battery lid 26,
15 and an anode lead (not shown) was spot-welded to the bottom surface of the battery can 24. Then, the battery was sealed by laser-welding the battery lid 26 to the opening of the cylinder.

Then, a cylindrical battery was prepared by injecting
20 approximately 5 cc of an electrolyte (manufactured by Kishida Chemical Co., Ltd.) through a hole of 1 mm diameter made in the battery lid 26 and then sealing the injection hole by laser welding. The electrolyte used was obtained by dissolving LiPF_6 in a solvent so that the concentration was
25 1.4 mol/l, and the solvent used was obtained by mixing

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ethylene carbonate and diethyl carbonate with a volume ratio of 7:3.

Five such batteries were prepared. A current of 100 mA was applied to each of the batteries, and the charging was finished at a point in time where the battery reached a voltage of 3.9V and, furthermore, the battery was discharged until 2.2V. This cycle was repeated a hundred times. Table 9 shows the result of an evaluation.

[Comparative Example 5]

A cylindrical battery was prepared through exactly the same procedure as in Example 11 except that a lithium source LiCH_3COO , an iron source $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and a phosphate source $\text{H}_3\text{PO}_4(85\%)$ were used as starting materials and that these starting materials were measured out so that the molar ratio is $\text{Li:Fe:P} = 1:1:1$, with the lithium source LiCH_3COO used in an amount of 131.96 g.

Table 9 shows the result of a charge-discharge evaluation carried out through exactly the same procedure as in Example 11. As shown in Table 9, it was confirmed that the battery of the present invention has a higher capacity retention ratio and a longer life than the comparative example.

Table 9

	n	Initial discharging capacity (mAh/g)	Discharging capacity at hundredth cycle (mAh/g)	Capacity retention rate (%)
Example 11	1	2.61	2.58	98.7
	2	2.62	2.60	99.2
	3	2.60	2.59	99.5
	4	2.66	2.66	100
	5	2.64	2.61	98.9
Comparative Example 5	1	3.02	2.88	95.2
	2	3.11	3.00	96.5
	3	3.03	2.94	97.2
	4	3.04	2.83	93.2
	5	3.00	2.83	94.5

Industrial Applicability

A cathode active material of the present invention not only excels in terms of safety and cost but also can provide a long-life battery, and as such, can be suitably used as a cathode active material in a nonaqueous secondary battery such as a lithium ion battery.

10 Description of Reference Characters

11, 15 layered product

12 aluminum laminate

13, 16, 23 cathode collector lead

14, 17 anode collector lead

15 18, 24 battery can

19, 26 battery lid

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- 20 safety valve
- 21 anode terminal
- 22 wound product
- 25 cathode terminal

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The embodiments of the present invention in which an exclusive property or privilege is claimed are defined as follows:

1. A nonaqueous secondary battery, comprising:

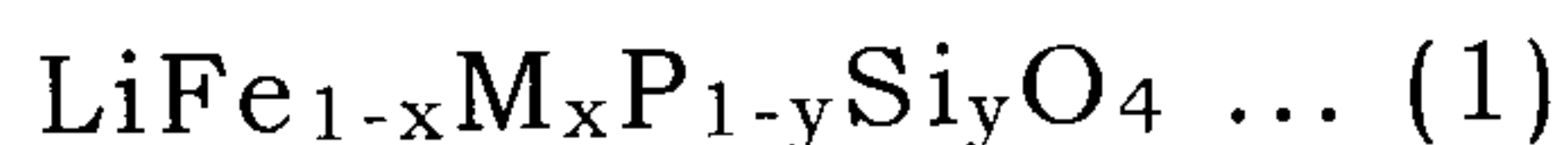
a cathode including:

a cathode active material;

a conductive material; and

a binder,

the cathode active material consisting of a composition represented by General Formula (1) below,



where:

Fe^{2+} is contained at a proportion of not less than 95% and less than 100% relative to Fe which is a mixture of Fe^{2+} and Fe^{3+} , as calculated from a Mössbauer spectrum;

M is an element having a valence of +2 or more and is at least one type of element selected from the group consisting of Zr, Sn, Y, and Al;

the valence of M is different from the average valence of Fe;

$$0 < x \leq 0.5;$$

$$0 < y \leq 0.5;$$

$y \neq x \times (\text{valence of M} - 2) + (1 - x) \times (\text{average valence of Fe} - 2)$; and

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the conductive material being a material selected from the group consisting of acetylene black, carbon, graphite, natural graphite, artificial graphite, and needle coke.

2. The nonaqueous secondary battery according to claim 1,

wherein:

the binder is a material selected from the group consisting of polytetrafluoroethylene, polyvinylidene fluoride, polyvinylchloride, ethylene-propylene diene polymer, styrene-butadiene rubber, acrylonitrile-butadiene rubber, fluorocarbon rubber, polyvinyl acetate, polymethyl methacrylate, polyethylene, and nitrocellulose.

3. The nonaqueous secondary battery according to claim 2,

wherein:

the conductive material is acetylene black;

the binder is polyvinylidene fluoride;

the acetylene black is contained at 10% to 42% by weight with respect to the cathode active material; and

the polyvinylidene fluoride is contained at 10% to 14% by weight with respect to the cathode active material.

4. The nonaqueous secondary battery according to

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claim 1, further comprising:

a current collector to which a slurry has been applied that is obtained by mixing the cathode active material, the conductive material, and the binder,

the slurry including an organic solvent made of a material selected from the group consisting of N-methylpyrrolidone, toluene, cyclohexane, dimethylformamide, dimethylacetoamide, methyl ethyl ketone, methyl acetate, methyl acrylate, diethyltriamine, N-N-dimethylaminopropylamine, ethylene oxide, and tetrahydrofuran.

5. The nonaqueous secondary battery according to claim 1, further comprising:

a current collector to which a slurry has been applied that is obtained by mixing the cathode active material, the conductive material, and the binder,

the slurry having been applied in an amount of a dry weight of 5 to 20 mg/cm² with respect to the current collector.

6. The nonaqueous secondary battery according to claim 1, further comprising:

a current collector to which a slurry has been applied that is obtained by mixing the cathode active material, the

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conductive material, and the binder,

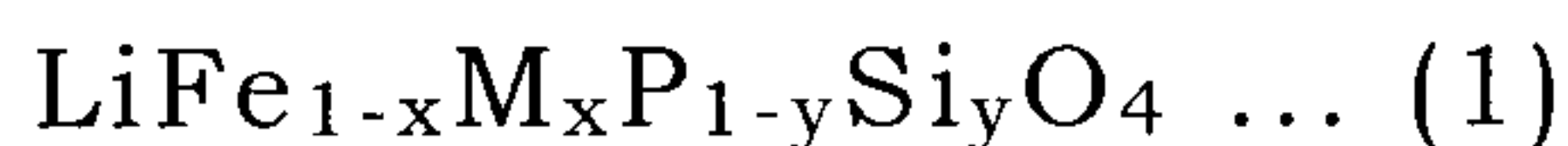
the current collector being made of a metal selected from the group consisting of a porous metal having continuous holes, a metal shaped in a honeycomb pattern, a sintered metal, and an expanded metal.

7. A nonaqueous secondary battery, comprising:

a cathode including a cathode active material; and

an anode including an anodic active material and a binder,

the cathode active material consisting of a composition represented by General Formula (1) below,



where:

Fe^{2+} is contained at a proportion of not less than 95% and less than 100% relative to Fe which is a mixture of Fe^{2+} and Fe^{3+} , as calculated from a Mössbauer spectrum;

M is an element having a valence of +2 or more and is at least one type of element selected from the group consisting of Zr, Sn, Y, and Al;

the valence of M is different from the average valence of Fe;

$$0 < x \leq 0.5;$$

$$0 < y \leq 0.5;$$

$$y \neq x \times (\text{valence of M} - 2) + (1 - x) \times (\text{average valence of Fe} -$$

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2); and

the anodic active material being either artificial graphite or natural graphite.

8. The nonaqueous secondary battery according to claim 7,

wherein:

the anodic active material is a graphite particle having amorphous carbon adhering to a surface thereof.

9. The nonaqueous secondary battery according to claim 7,

wherein:

the anode includes a conductive material; and

the conductive material is a material selected from the group consisting of acetylene black, carbon, graphite, natural graphite, artificial graphite, and needle coke.

10. The nonaqueous secondary battery according to claim 9,

wherein:

the conductive material is acetylene black.

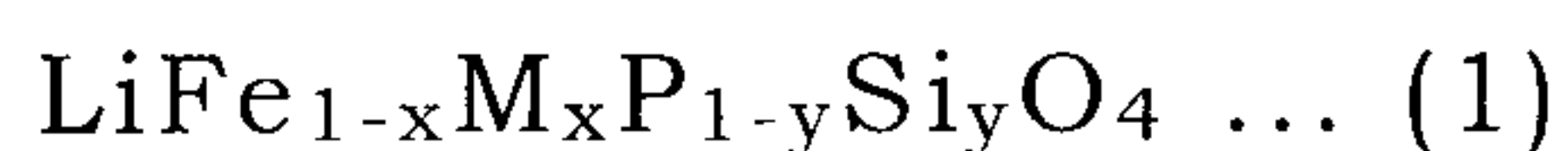
11. A nonaqueous secondary battery, comprising:

a cathode including a cathode active material; and

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an anode including an anodic active material and a binder,

the cathode active material consisting of a composition represented by General Formula (1) below,



where:

Fe^{2+} is contained at a proportion of not less than 95% and less than 100% relative to Fe which is a mixture of Fe^{2+} and Fe^{3+} , as calculated from a Mössbauer spectrum;

M is an element having a valence of +2 or more and is at least one type of element selected from the group consisting of Zr, Sn, Y, and Al;

the valence of M is different from the average valence of Fe;

$$0 < x \leq 0.5;$$

$$0 < y \leq 0.5;$$

$y \neq x \times (\text{valence of M} - 2) + (1 - x) \times (\text{average valence of Fe} - 2)$; and

the anodic active material being $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

12. The nonaqueous secondary battery according to claim 11,

wherein:

the anode includes a conductive material; and

the conductive material is a material selected from the

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group consisting of acetylene black, carbon, graphite, natural graphite, artificial graphite, and needle coke.

13. The nonaqueous secondary battery according to claim 12,

wherein:

the conductive material is acetylene black.

FIG. 1

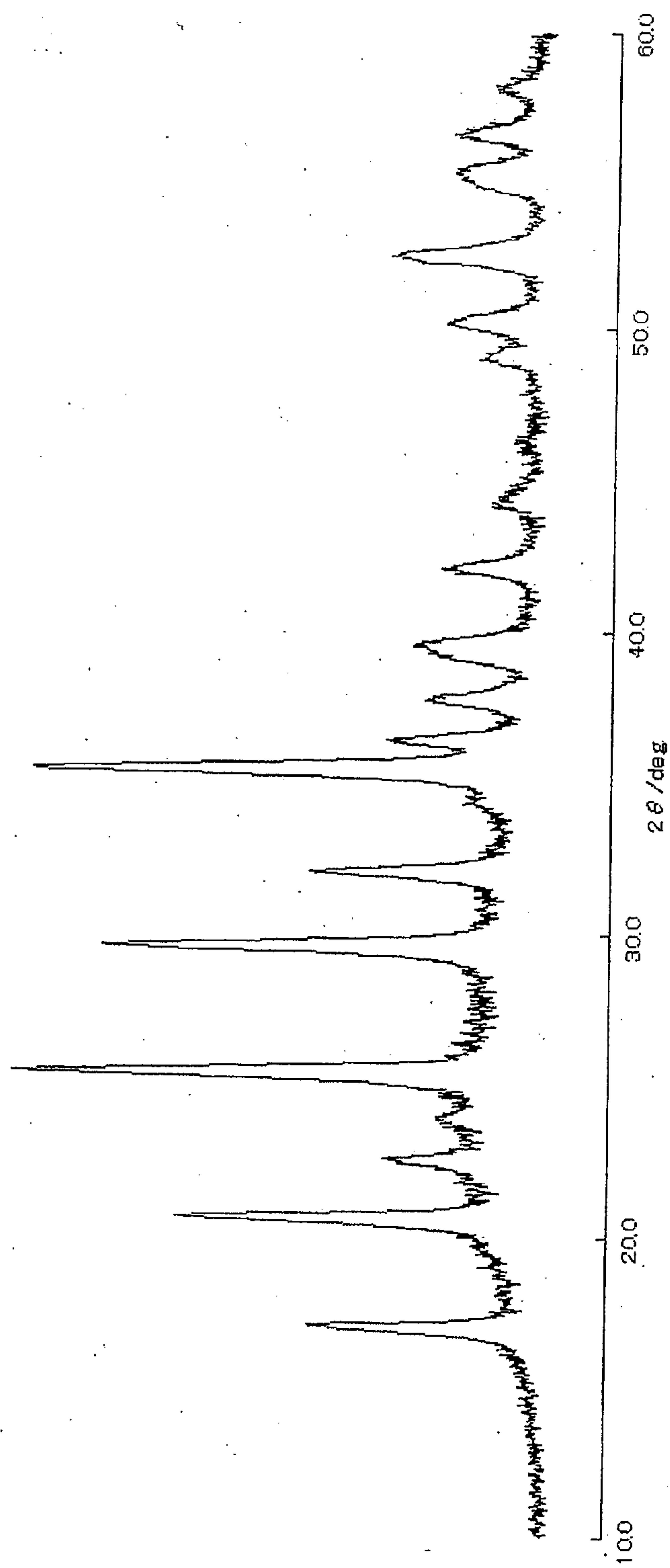


FIG. 2

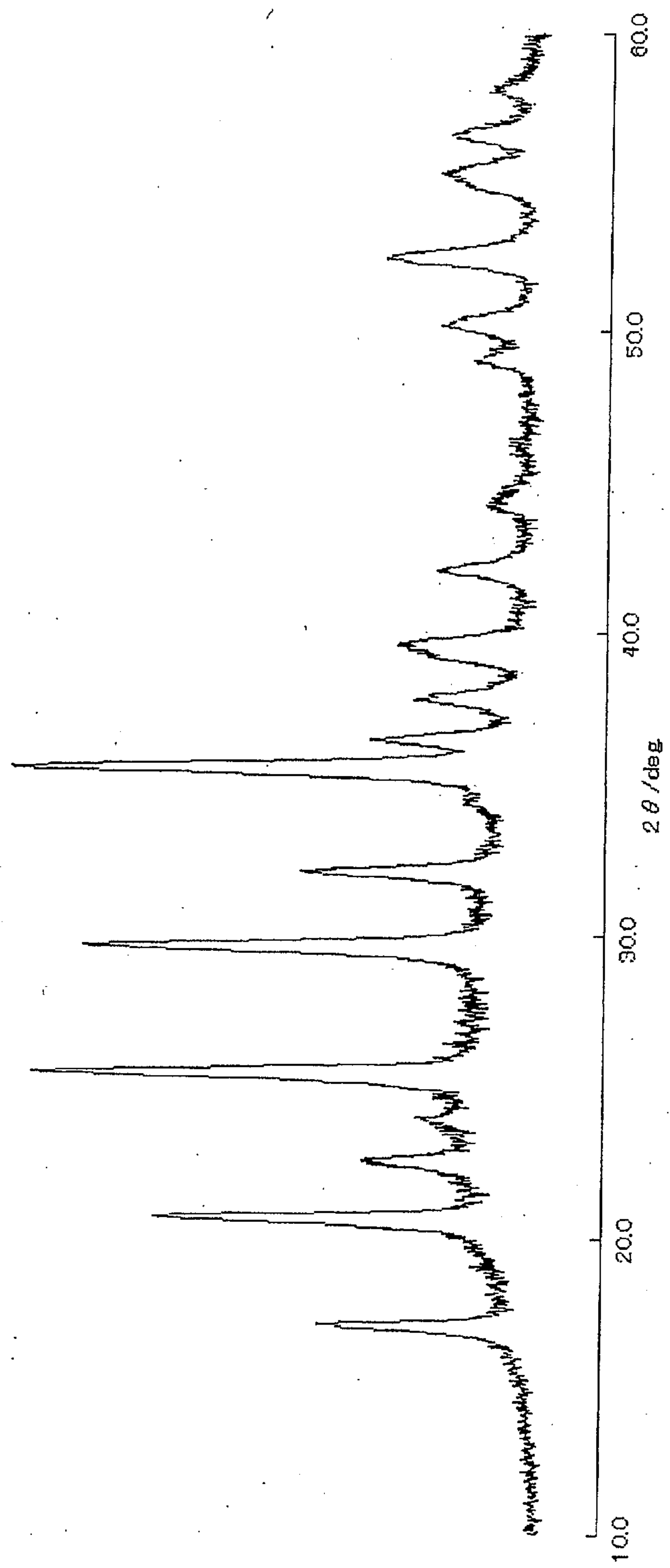


FIG. 3

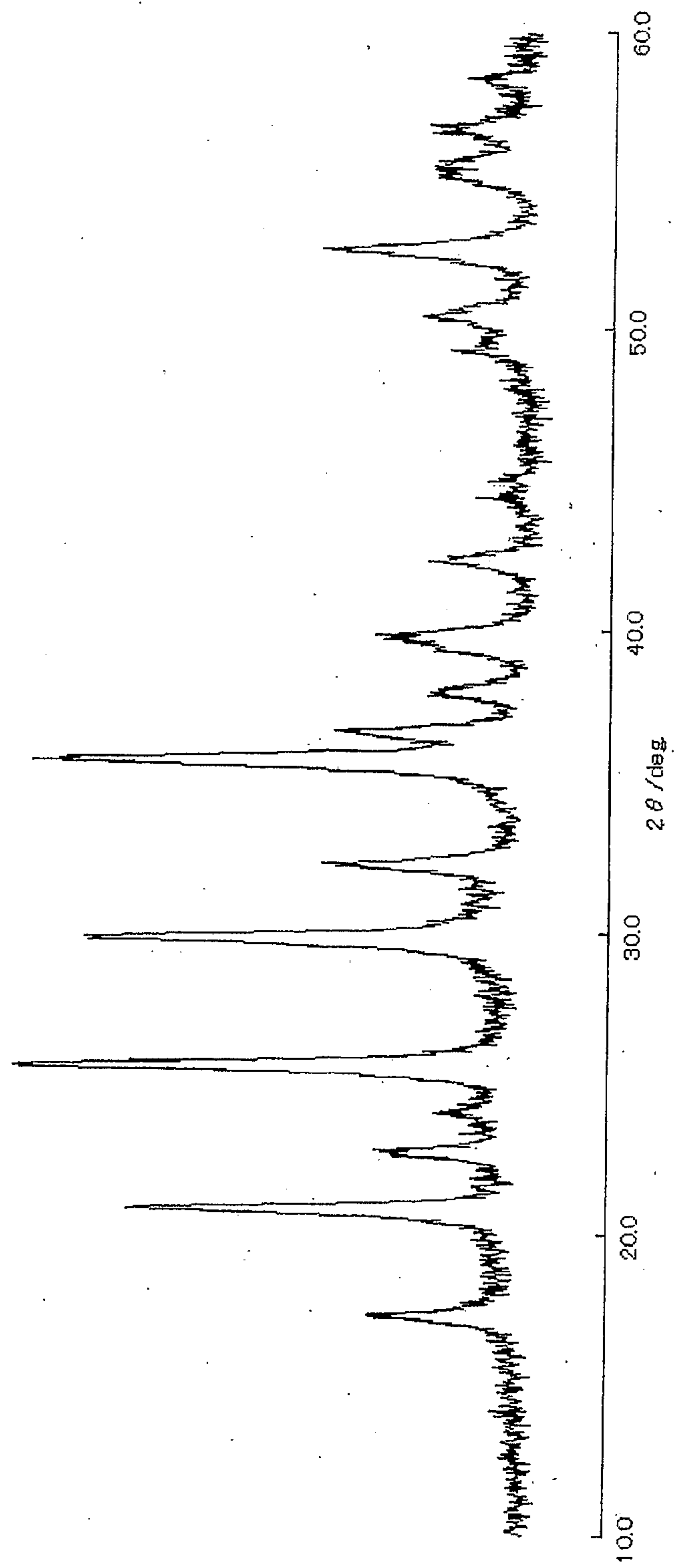


FIG. 4

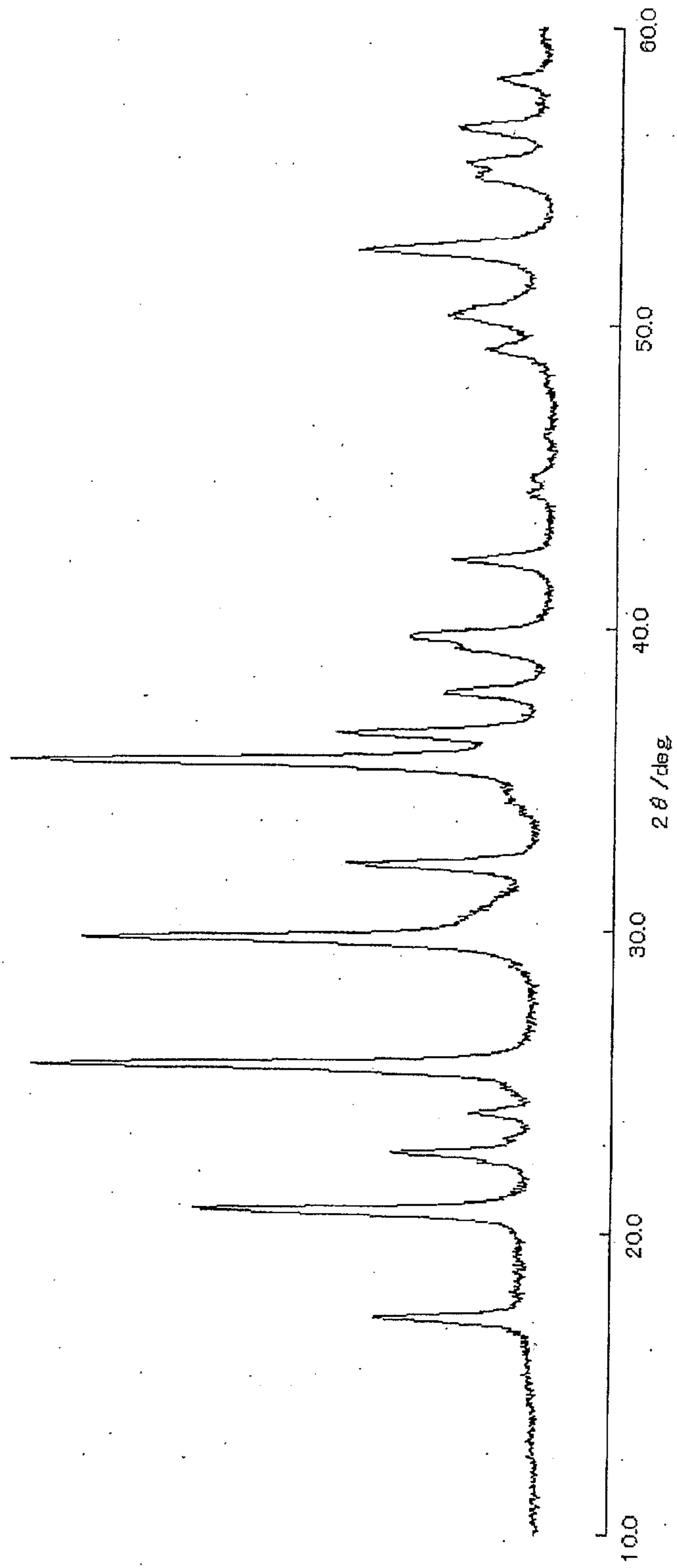


FIG. 5

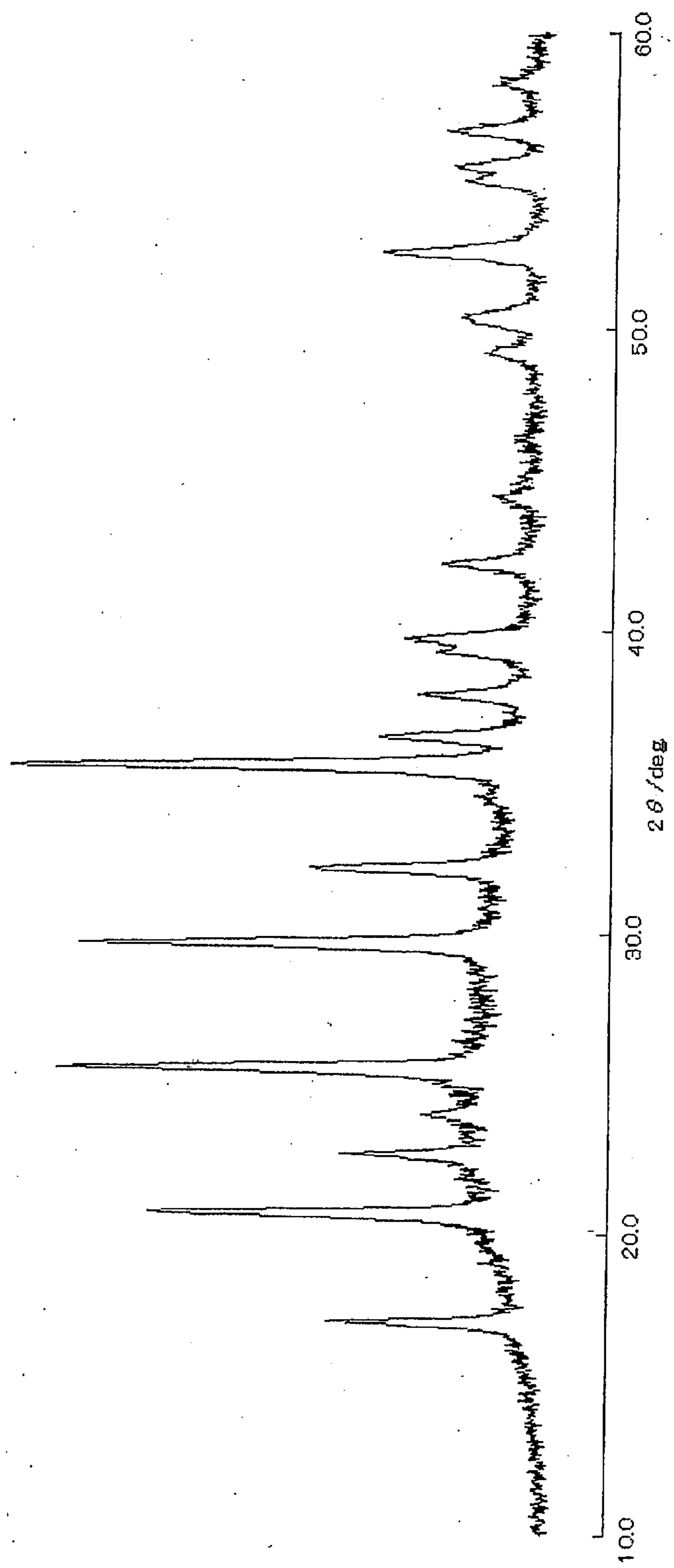


FIG. 6

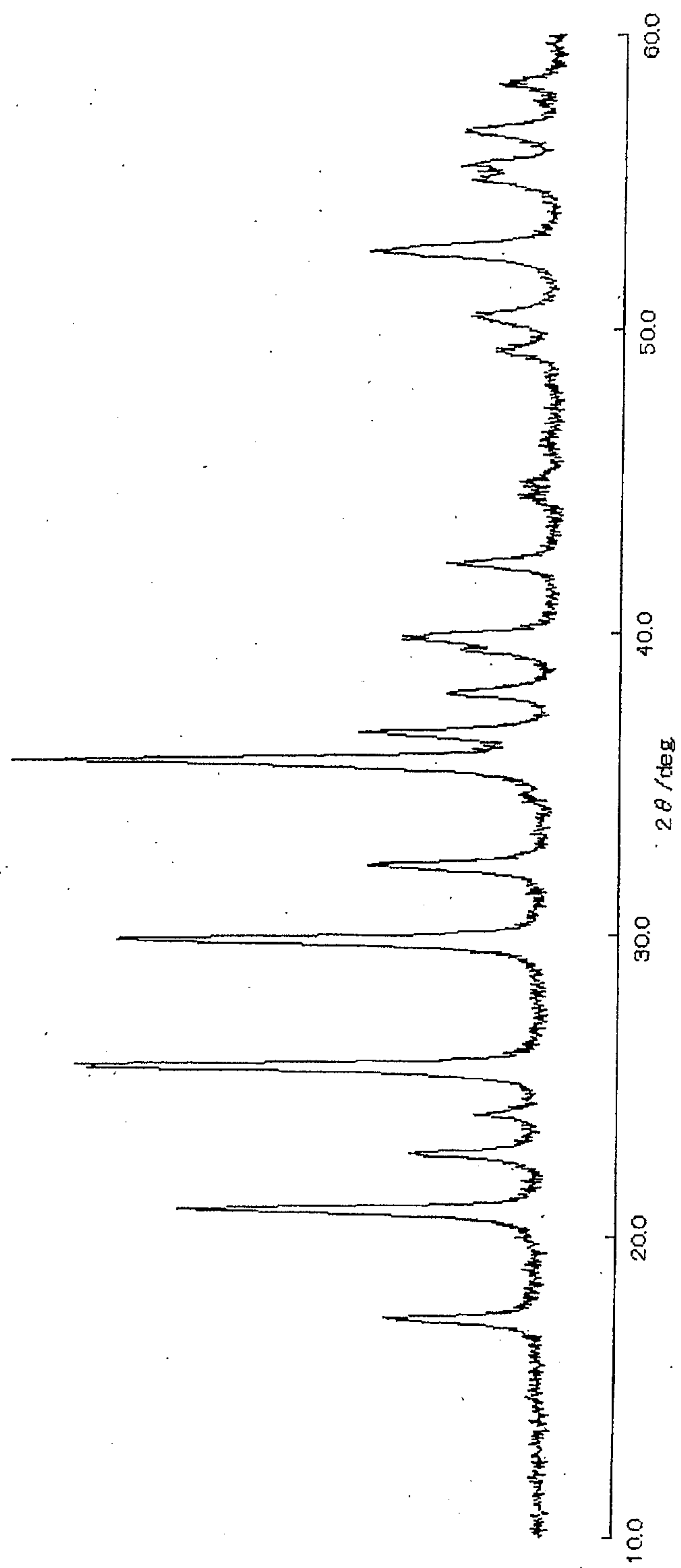


FIG. 7

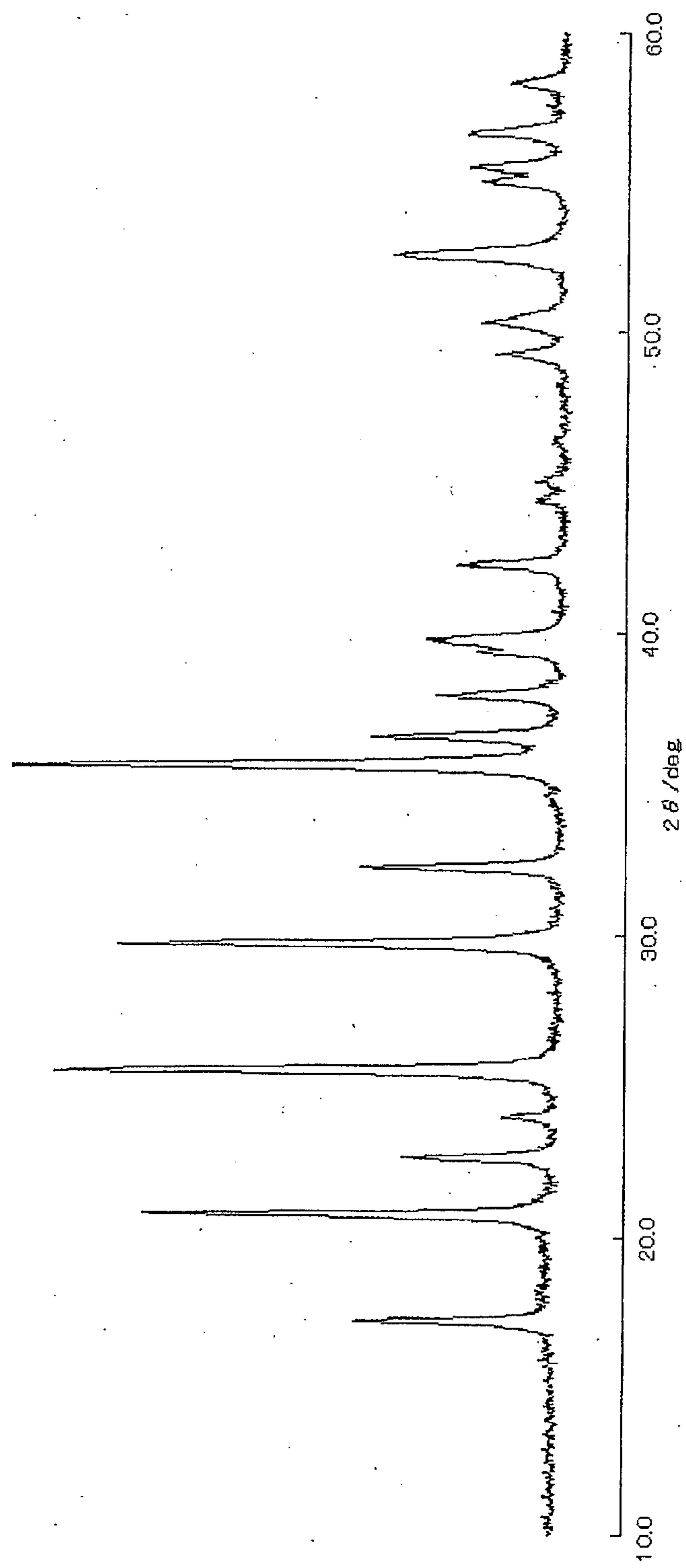


FIG. 8

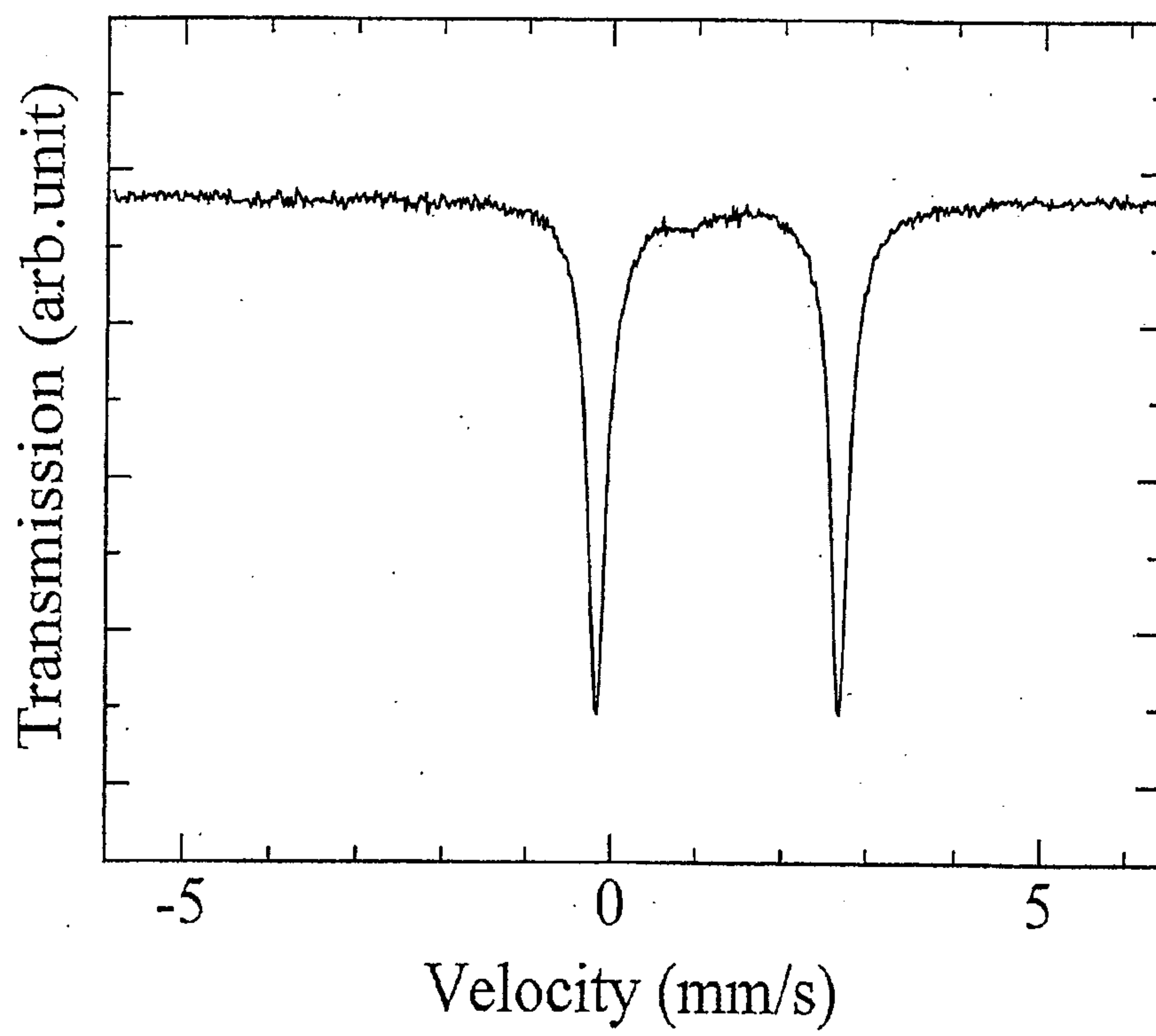


FIG. 9

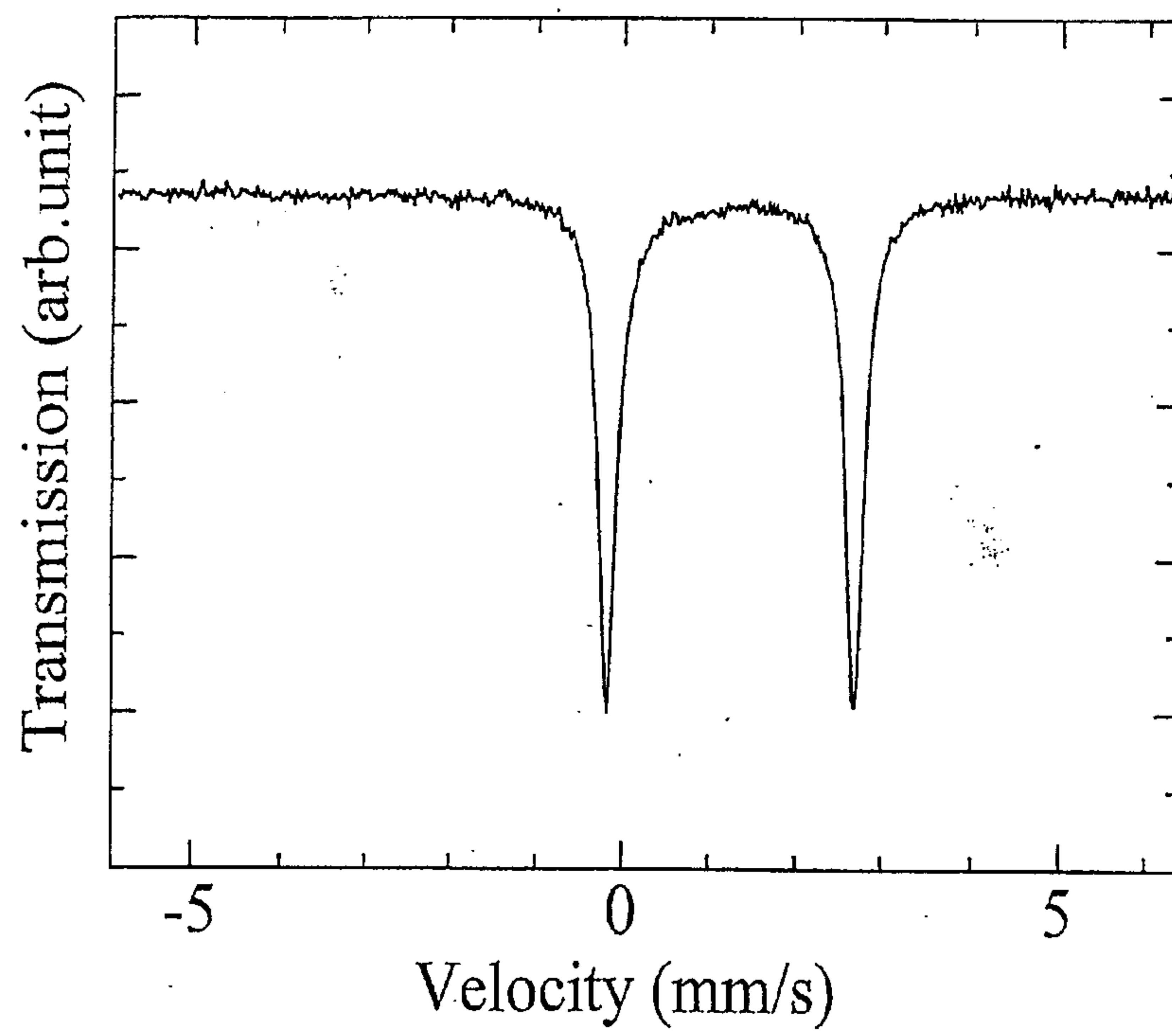


FIG. 10

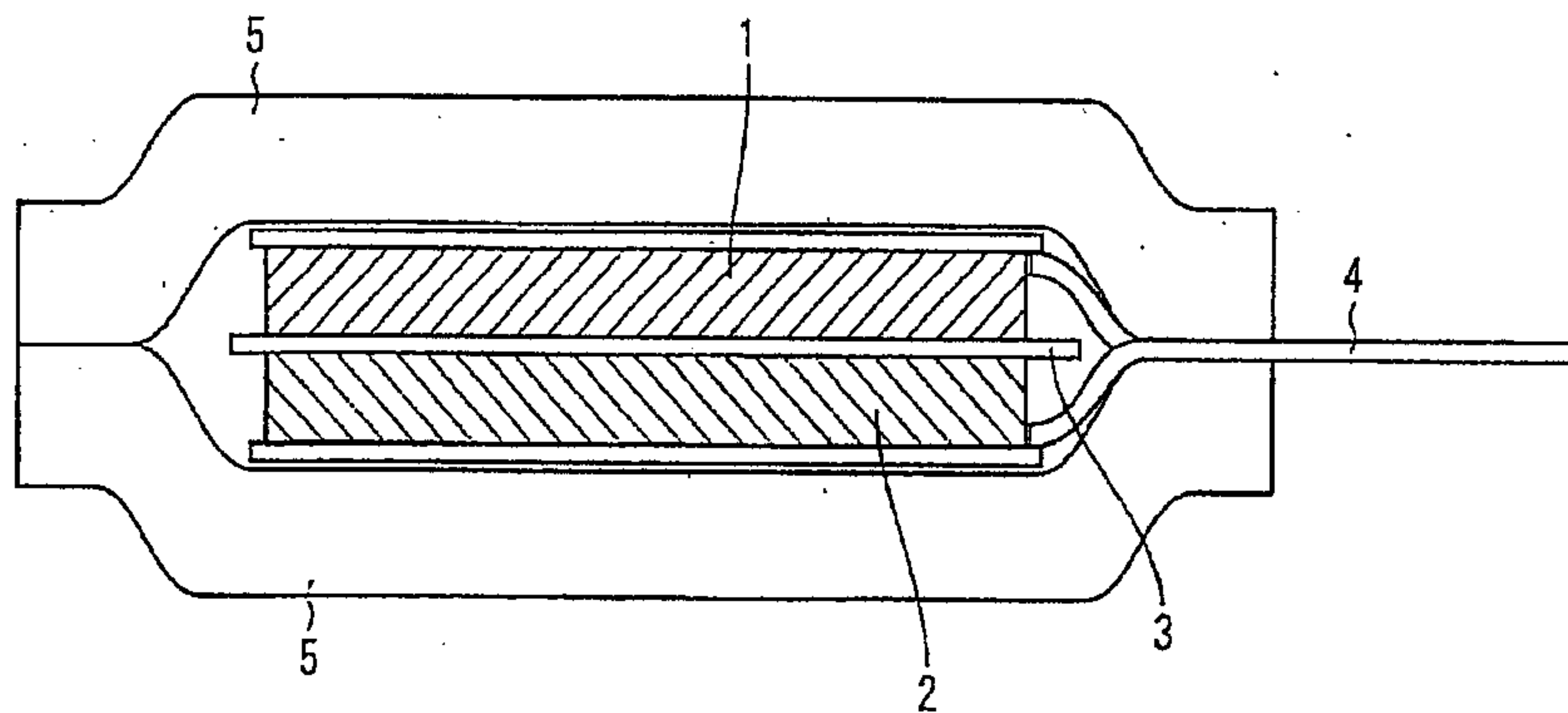


FIG. 11

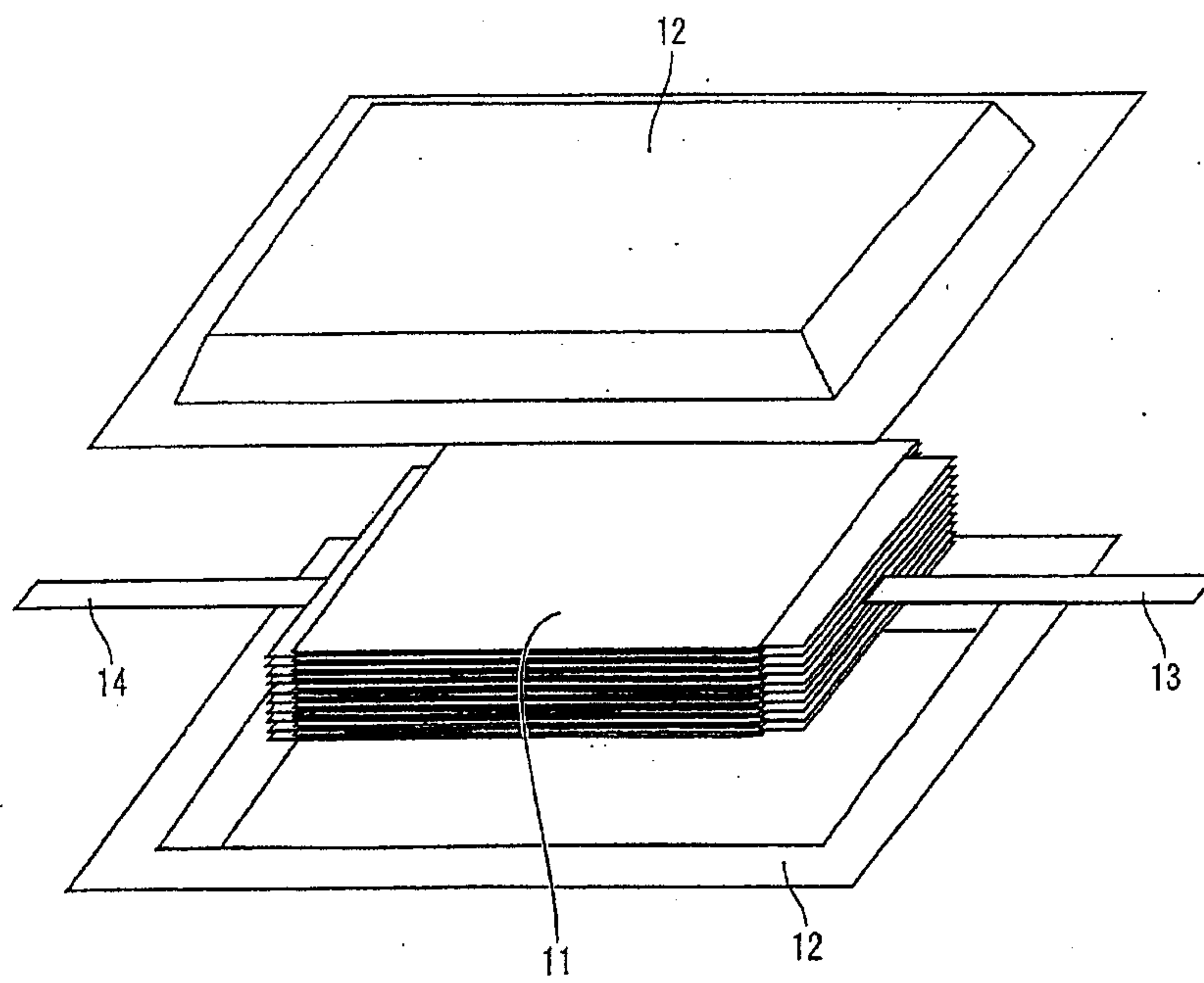


FIG. 12

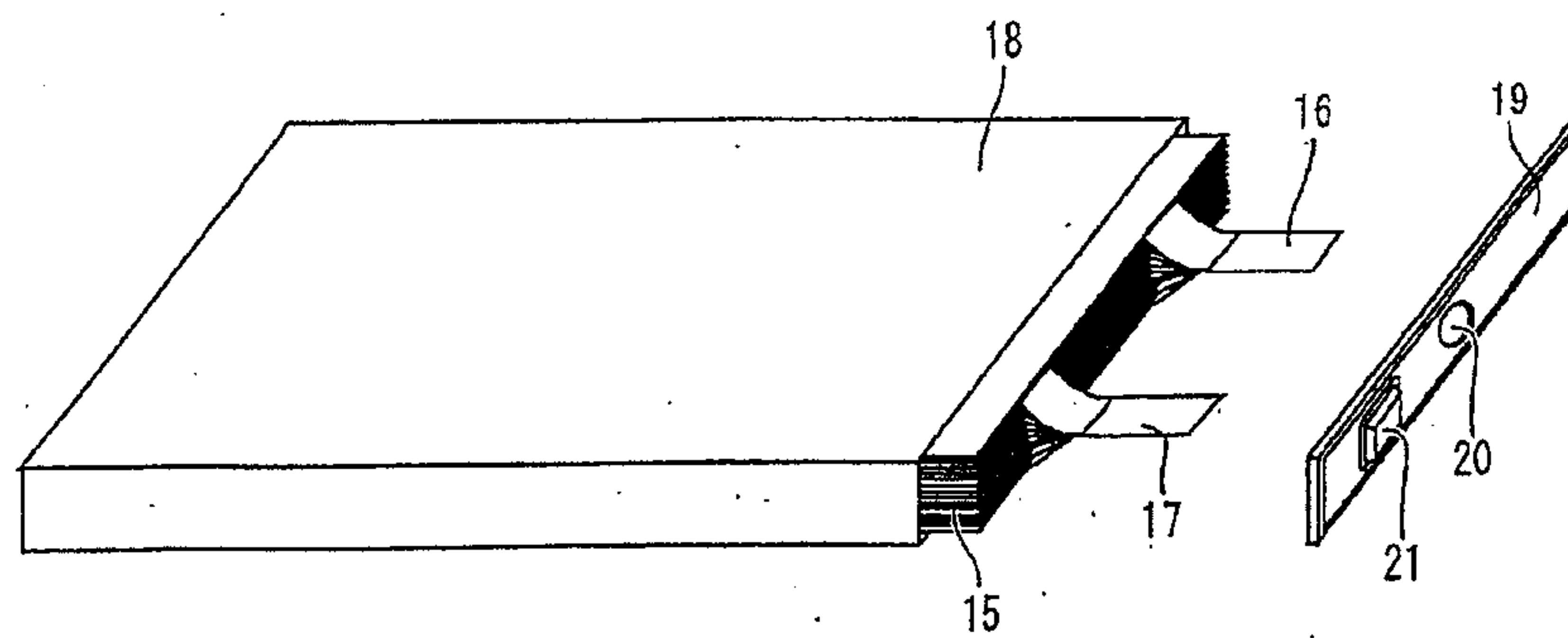


FIG. 13

