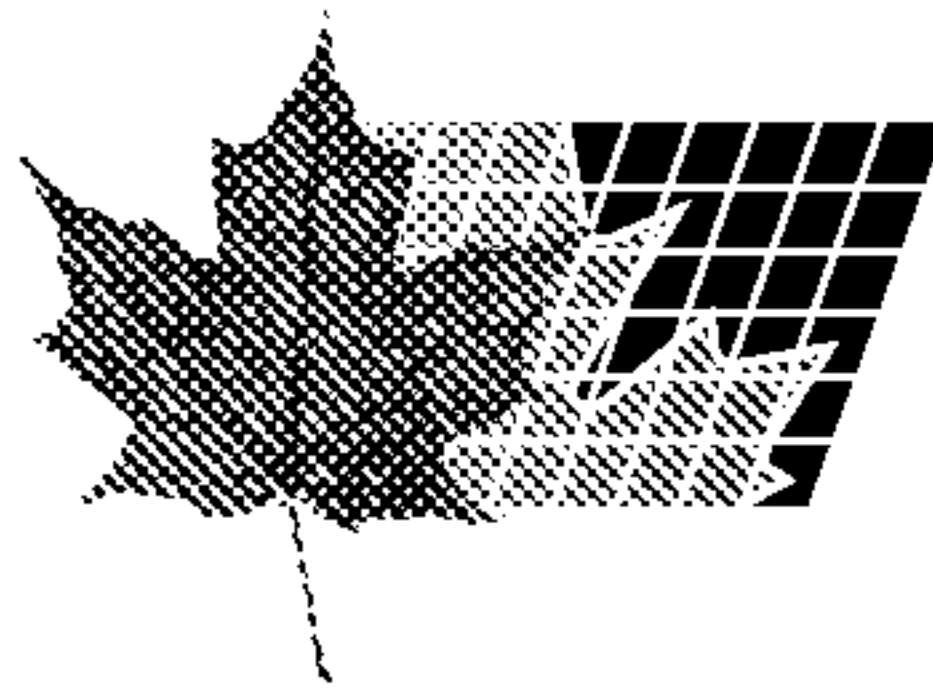




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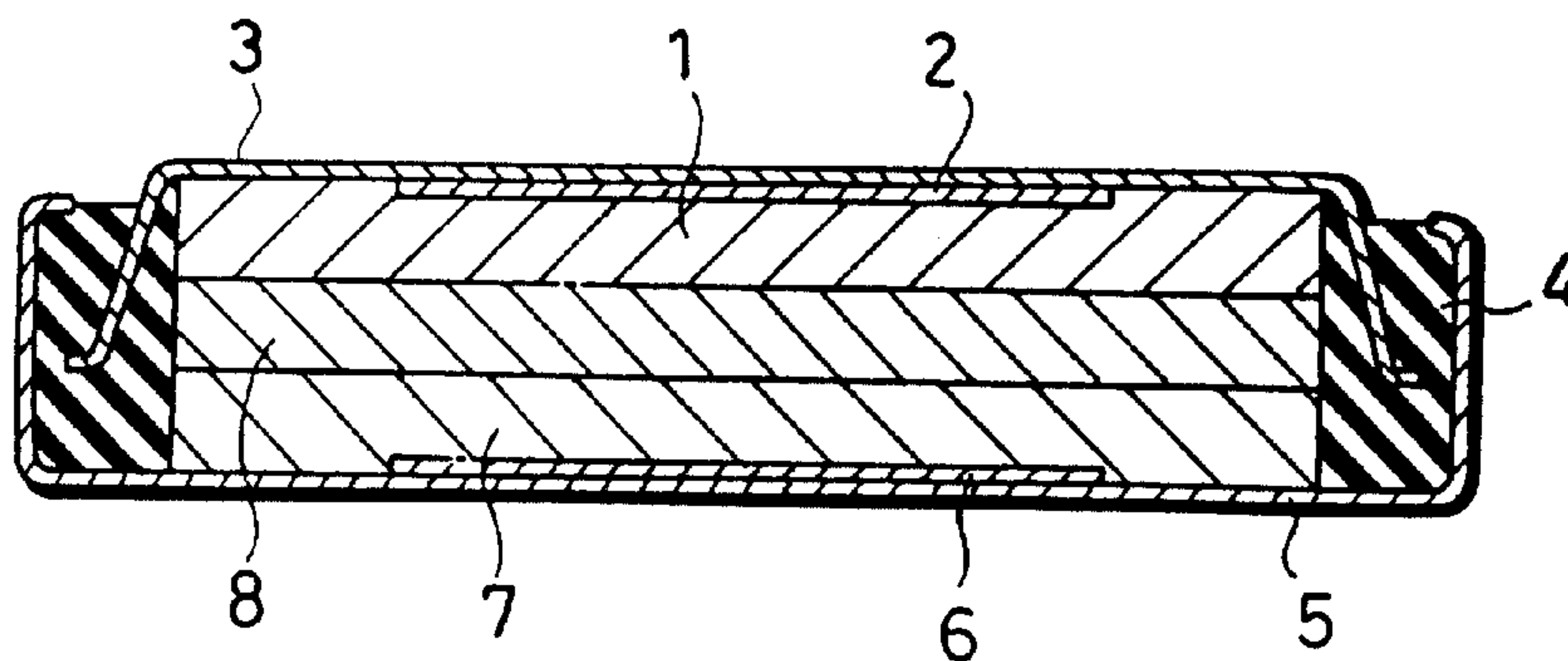
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(54) **ACCUMULATEUR A ELECTROLYTE NON AQUEUX**

(54) **NON-AQUEOUS ELECTROLYTE CELL**



(57) A non-aqueous electrolyte cell comprising a positive electrode, a negative electrode, and an electrolyte consisting of a solute and an organic solvent, characterized in that the solvent is a solvent mixture of a cyclic carbonate and a non-cyclic carbonate.

Abstract of the Disclosure

A non-aqueous electrolyte cell comprising a positive electrode, a negative electrode, and an electrolyte consisting of a solute and an organic solvent, characterized in that the solvent is a solvent mixture of a cyclic carbonate and a non-cyclic carbonate.

NON-AQUEOUS ELECTROLYTE CELL

BACKGROUND OF THE INVENTION

1) Field of the Invention

5 The present invention relates to a non-aqueous electrolyte cell comprising a positive electrode, a negative electrode and a non-aqueous electrolyte consisting of a solute and an organic solvent.

2) Description of the Prior Art

10 A non-aqueous electrolyte cell in which a negative electrode has lithium or a lithium alloy as an active material provides advantages of high energy density and low self-discharge rate.

15 In this type of cell, a low boiling point solvent such as dimethoxyethane or dioxolane has been conventionally used as a solvent of an electrolyte. However, this entails a problem that the solvent reacts on lithium, whereby a film, which is inactive and has a low conductivity, is formed on surfaces of the negative electrode. This causes internal
20 resistance of the cell to be increased, resulting in deterioration of a storage characteristic (especially, a high rate discharge characteristic after storage).

25 In order to solve the above problem, it has been proposed to employ a solvent mixture of a cyclic carbonate and a low boiling point solvent to form a

film of Li_2CO_3 having a high conductivity on surfaces of the negative electrode, thereby improving the storage characteristic. However, this do not realize a satisfactory storage characteristic yet.

5 SUMMARY OF THE INVENTION

An object of the present invention, therefore, is to provide a non-aqueous electrolyte cell capable of drastically improving a high rate discharge characteristic after storage as well as before
10 storage.

Another object of the present invention is to provide a non-aqueous electrolyte cell capable of improving a charge and discharge cycle characteristic before and after storage when used as a secondary
15 cell.

The above objects are fulfilled by a non-aqueous electrolyte cell comprising a positive electrode, a negative electrode, and an electrolyte consisting of a solute and an organic solvent, the cell being
20 characterized in that the solvent is a solvent mixture of a cyclic carbonate and a non-cyclic carbonate.

The above objects are also fulfilled by a dischargeable non-aqueous electrolyte primary cell comprising a positive electrode; a negative electrode
25 including either one of lithium and a lithium alloy;

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and a non-aqueous electrolyte consisting of a solute and an organic solvent, wherein the organic solvent is a solvent mixture of a cyclic carbonate and a non-cyclic carbonate.

5 The above objects are also fulfilled by a rechargeable non-aqueous electrolyte secondary cell comprising a positive electrode having a rechargeable substance as an active material; a negative electrode having lithium or a lithium alloy as an active
10 material; and a non-aqueous electrolyte consisting of a solute and an organic solvent, wherein the organic solvent is a solvent mixture of a cyclic carbonate and a non-cyclic carbonate.

 In another aspect, the present invention provides
15 a non-aqueous electrolyte cell comprising a positive electrode, a negative electrode, and an electrolyte consisting of a solute and an organic solvent, said cell being characterized in that the solvent is a solvent mixture of a cyclic carbonate and a non-cyclic
20 carbonate, and that the solute is LiPF_6 .

 In a still further aspect, the present invention provides a non-aqueous electrolyte cell comprising: a positive electrode composed of manganese oxide or

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cobalt oxide; a negative electrode; and an electrolyte consisting of LiPF_6 as a solute and an organic solvent, said cell being characterized in that the solvent is a solvent mixture of a cyclic carbonate and a non-cyclic carbonate, the amount of the cyclic carbonate in the solvent being from 30vol% to 70vol%.

In a still further aspect, the present invention provides A rechargeable non-aqueous electrolyte secondary cell comprising: a positive electrode having a rechargeable substance as an active material and composed of manganese oxide or cobalt oxide; a negative electrode having either one of lithium and a lithium alloy as an active material; and a non-aqueous electrolyte consisting of a solute and an organic solvent, wherein the organic solvent is a solvent mixture of a cyclic carbonate and a non-cyclic carbonate, the amount of the cyclic carbonate being contained in a range of 30vol% to 70vol% against the whole solvent, and the solute is LiPF_6 .

The above objects are fulfilled for the following reasons:

A storage characteristic in a non-aqueous electrolyte cell is deteriorated since a film having a

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low conductivity is generated by reaction between lithium and a solvent during long-term storage. When the solvent comprises a cyclic carbonate such as propylene carbonate or ethylene carbonate, a film of
5 Li_2CO_3 , which does not increase the internal resistance of the cell, is formed on the negative electrode, whereby the storage characteristic can be improved.

However, if the solvent consists of a cyclic

carbonate only, the high rate discharge characteristic is deteriorated due to high viscosity of the electrolyte. Therefore, a solvent mixture of a cyclic carbonate and a low boiling point solvent having a low viscosity such as dimethoxyethane or dioxolane is generally used. However, such a solvent mixture also has a problem that reaction between lithium and the low boiling point solvent is inevitable after long term storage although the high rate discharge characteristic is improved. The reaction forms an inactive film of Li_2O , whereby the high rate discharge characteristic is deteriorated after long term storage.

In order to solve the above problems, the present invention employs a solvent mixture of a cyclic carbonate and a non-cyclic carbonate having a low viscosity. In this case, the viscosity of the electrolyte becomes lower than the case of the cyclic carbonate solvent, whereby the high rate discharge characteristic is improved. Moreover, since each carbonate forms a film of Li_2CO_3 , the post-storage high rate discharge characteristic is further improved.

When the present invention is applied to a secondary cell, thanks to the formation of the film having a high conductivity, not only the storage

characteristic but also the charge and discharge cycle characteristic are improved.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other objects, advantages and features
5 of the invention will become apparent from the following description thereof taken in conjunction with the accompanying drawings which illustrate specific embodiments of the invention. In the drawings:-

10 Fig. 1 is a sectional view of a flat type non-aqueous electrolyte cell according to an embodiment of the present invention,

Fig. 2 is a graph showing initial high rate discharge characteristic of Cell A according to the
15 present invention and Comparative Cells X_1 and X_2 ,

Fig. 3 is a graph showing post-storage high rate discharge characteristics of Cells A, X_1 and X_2 ,

Fig. 4 is a graph showing relationship between the mixing ratio of ethylene carbonate and dimethyl
20 carbonate and discharge capacity,

Fig. 5 is a graph showing initial high rate discharge characteristics of Cell B according to the present invention and Comparative Cells Y_1 and Y_2 ,

Fig. 6 is a graph showing post-storage high rate
25 discharge characteristics of Cells B, Y_1 and Y_2 ,

Fig. 7 is a graph showing initial high rate discharge characteristics of Cell C according to the present invention and Comparative Cells Z_1 and Z_2 ,

Fig. 8 is a graph showing post-storage high rate discharge characteristics of Cells C, Z_1 and Z_2 , and

Fig. 9 is a graph showing relationship between the mixing ratio of propylene carbonate and dimethyl carbonate and discharge capacity.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

10 Embodiment I

[Example 1]

Fig. 1 is a sectional view of a flat type non-aqueous electrolyte primary cell as an embodiment of the present invention.

15 The cell comprises a negative electrode 1 formed of lithium metal and pressed upon an inner surface of a negative collector 2. The negative collector 2 is secured to an inner bottom surface of a negative can 3 formed of ferritic stainless steel (SUS430). The
20 negative can 3 is peripherally secured in an insulating packing 4 formed of polypropylene, while a positive can 5 is secured peripherally of the insulating packing 4. A positive collector 6 is secured to an inner bottom surface of the positive can
25 5. A positive electrode 7 is secured to an inner

surface of the positive collector 6. A separator 8 impregnated with an electrolyte is disposed between the positive electrode 7 and the negative electrode 1.

The positive electrode 7 was produced as follows.
5 First, manganese dioxide heat-treated in a temperature range of 350-430°C acting as an active material, carbon powder acting as a conductive agent and fluoro-resin powder acting as a binder were mixed in a weight ratio of 85:10:5. Then, the mixture was molded
10 under pressure and heat-treated at 250-350°C.

The negative electrode 1 was produced by punching a piece having a predetermined size out of a rolled plate of lithium.

The electrolyte was prepared by dissolving
15 lithium phosphate hexafluoride in an equivalent volume solvent mixture of ethylene carbonate and dimethyl carbonate in 1mol/lit.

The cell has a diameter of 20.0mm, a height of 2.5mm and a capacity of 130mAh.

20 The cell manufactured as above is referred to as Cell A, hereinafter.

[Comparative Example 1]

A cell was manufactured in the same way as Example 1 except that a solvent of ethylene carbonate
25 was employed instead of the solvent mixture of ethylene carbonate and dimethyl carbonate.

The cell manufactured as above is referred to as Cell X₁, hereinafter.

[Comparative Example 2]

5 A cell was manufactured in the same way as Example 1 except that an equivalent volume solvent mixture of ethylene carbonate and dimethoxyethane was employed instead of the solvent mixture of ethylene carbonate and dimethyl carbonate.

10 The cell manufactured as above is referred to as Cell X₂, hereinafter.

[Experiment 1]

15 With respect to Cells A, X₁ and X₂, initial high rate discharge characteristics immediately after cell assembly and post-storage high rate discharge characteristics after the cells were stored for 3 months at 60°C were checked. Figs. 2 and 3 respectively show the results. The experiment was conducted under the condition that the cells were discharged with a constant resistance of 300Ω at
20 25°C.

As apparent from Figs. 2 and 3, Cell A according to the present invention is superior in both initial and post-storage high rate discharge characteristics. In contrast, Cell X₁ is excellent in the post-storage
25 high rate discharge characteristic but is poor in the initial high rate discharge, whereas Cell X₂ is

excellent in the initial high rate discharge characteristic but is poor in the post-storage high rate discharge characteristic.

This is considered due to the following reasons.

5 1) Comparative Cell X_1

Cell X_1 employs the solvent consisting of one cyclic carbonate (ethylene carbonate). Therefore, a film of Li_2CO_3 is formed by reaction between lithium of the negative electrode and the solvent as in Cell A
10 of the present invention. This restricts deterioration of the post-storage high rate discharge characteristic. However, due to high viscosity of the electrolyte, the initial high rate discharge characteristic is lowered.

15 2) Comparative Cell X_2

In Cell X_2 , the solvent contains a low boiling point solvent (dimethoxyethane). This prevents the viscosity of the electrolyte from being heightened, thereby improving the initial high rate discharge
20 characteristic. However, after long-term storage at a high temperature, the low boiling point solvent reacts on lithium, whereby an inactive film of Li_2O is formed on surfaces of the negative electrode. As a result, the post-storage high rate discharge characteristic is
25 lowered.

3) Cell A of the present invention

Since the solvent contains a non-cyclic carbonate (dimethyl carbonate), the viscosity of the electrolyte is prevented from being heightened, resulting in improvement in the initial high rate discharge characteristic. Further, since a film of Li_2CO_3 , which does not increase the internal resistance of the cell, is formed, deterioration of the high rate discharge characteristic after long-term storage is restricted.

10 [Experiment 2]

An optimum ratio range of ethylene carbonate and dimethyl carbonate was found by checking the relationship between the mixing ratio and discharge capacity. The experiment was conducted under the condition that the cell manufactured in the same way as Cell A was discharged with a constant resistance of 300Ω at 25°C after storage for 3 months at 60°C .

As apparent from Fig. 4, it is preferable that ethylene carbonate is contained in a range of 30-70vol%.

Embodiment II

[Example 1]

A cell was manufactured in the same way as Example 1 of Embodiment I except that lithium trifluoromethane sulfonate was employed as the solute and that an equivalent volume solvent mixture of

propylene carbonate and dimethyl carbonate was employed as the solvent.

The cell manufactured as above is referred to as Cell B, hereinafter.

5 [Comparative Cell 1]

A cell was manufactured in the same way as the above Example 1 except that a solvent of propylene carbonate was employed.

The cell manufactured as above is referred to as
10 Cell Y₁, hereinafter.

[Comparative Cell 2]

A cell was manufactured in the same way as the above Example 1 except that an equivalent volume solvent mixture of propylene carbonate and dioxolane
15 was employed.

The cell manufactured as above is referred to as Cell Y₂, hereinafter.

[Experiment]

With respect to Cells B, Y₁ and Y₂, initial high
20 rate discharge characteristics and post-storage high rate discharge characteristics were checked. Figs. 5 and 6 show the results. The experiment condition was the same as Experiment 1 of Embodiment I.

As apparent from Figs. 5 and 6, Cell B according
25 to the present invention is superior in both initial and post-storage high rate characteristics. In

contrast, Comparative Cell Y_2 is excellent in the initial high rate discharge characteristic but is poor in the post-storage high rate discharge characteristic. Comparative Cell Y_1 is excellent in the post-storage high rate discharge characteristic but is poor in the initial high rate discharge characteristic.

Embodiment III

[Example 1]

10 In this embodiment, the present invention is applied to a secondary cell.

The secondary cell in this embodiment has substantially the same construction as the cell of Fig. 1 except the kinds of an active material for the positive electrode and an electrolyte.

15 More specifically, rechargeable cobalt oxide is used as the active material for the positive electrode and the electrolyte is prepared by dissolving lithium phosphate hexafluoride in an equivalent volume solvent mixture of propylene carbonate and dimethyl carbonate in 1mol/lit.

The cell manufactured as above is referred to as Cell C, hereinafter.

[Comparative Example 1]

25 A cell was manufactured in the same way as the above Example 1 except that a solvent of propylene

carbonate was employed.

The cell manufactured as above is referred to as Cell Z₁, hereinafter.

[Comparative Example 2]

5 A cell was manufactured in the same way as the above Example 1 except that an equivalent volume solvent mixture of propylene carbonate and dimethoxyethane was employed.

10 The cell manufactured as above is referred to as Cell Z₂, hereinafter.

[Experiment 1]

15 With respect to Cells C, Z₁ and Z₂, initial cycle characteristics immediately after cell assembly and post-storage cycle characteristics after storage for 3 months at 60°C were checked. Figs. 7 and 8 respectively show the results. The experiment was conducted under the condition that the cells were repeatedly charged with a charge current of 2mA for 3 hours and discharged with a discharge current of 2mA for 3 hours until the cell voltages drop to 2.5V.

20 As apparent from Figs. 7 and 8, Cell C according to the present invention is superior to Comparative Cells Z₁ and Z₂ in both initial and post-storage cycle characteristics.

25 [Experiment 2]

An optimum mixing ratio range of propylene

carbonate and dimethyl carbonate was found by checking the relationship between the mixing ratio and the post-storage cycle number. Fig. 9 shows the result.

As apparent from Fig. 9, it is preferable that
5 propylene carbonate is contained in a range of 30-70vol%.

Other Points

In the above three embodiments, ethylene carbonate or propylene carbonate is employed as the
10 cyclic carbonate. Other cyclic carbonates such as butylene carbonate, vinylene carbonate may also be employed.

In the above embodiments, dimethyl carbonate or diethyl carbonate is employed as the non-cyclic
15 carbonate. Other non-cyclic carbonates such as methyl ethyl carbonate may also be employed.

The negative electrode is not limited to lithium metal but may be formed of a lithium alloy such as a lithium-aluminum alloy.

20 Although the present invention has been fully described by way of embodiments with reference to the accompanying drawings, it is to be noted that various changes and modifications will be apparent to those skilled in the art. Therefore, unless otherwise such
25 changes and modifications depart from the scope of the present invention, they should be construed as being

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included therein.

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

- 5 1. A non-aqueous electrolyte cell comprising:
 a positive electrode composed of manganese oxide
 or cobalt oxide;
 a negative electrode; and
 an electrolyte consisting of LiPF_6 as a solute
10 and an organic solvent, said cell being characterized
 in that the solvent is a solvent mixture of a cyclic
 carbonate and a non-cyclic carbonate, the amount of
 the cyclic carbonate in the solvent being from 30vol%
 to 70vol%.
- 15 2. A non-aqueous electrolyte cell as claimed in
 Claim 1, wherein the cyclic carbonate is selected from
 a group consisting of ethylene carbonate, propylene
 carbonate, butylene carbonate and vinylene carbonate.
- 20 3. A non-aqueous electrolyte cell as claimed in
 Claim 1 or 2, wherein the non-cyclic carbonate is
 selected from a group consisting of dimethyl

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carbonate, diethyl carbonate and methyl ethyl carbonate.

4. A non-aqueous electrolyte cell as claimed in
5 Claim 1, wherein the negative electrode is formed of either one of lithium and a lithium alloy.

5. A dischargeable non-aqueous electrolyte primary cell comprising:

10 a positive electrode composed of manganese oxide or cobalt oxide;

a negative electrode including either one of lithium and a lithium alloy; and

15 a non-aqueous electrolyte consisting of a solute and an organic solvent,

wherein the organic solvent is a solvent mixture of a cyclic carbonate and a non-cyclic carbonate, wherein the cyclic carbonate being contained in a range of 30vol% to 70vol% against the whole solvent,
20 and the solute is LiPF_6 .

6. A non-aqueous electrolyte primary cell as claimed in Claim 5, wherein the cyclic carbonate is selected

from a group consisting of ethylene carbonate, propylene carbonate, butylene carbonate and vinylene carbonate.

- 5 7. A non-aqueous electrolyte primary cell as claimed in Claim 5 or 6, wherein the non-cyclic carbonate is selected from a group consisting of dimethyl carbonate, diethyl carbonate and methyl ethyl carbonate.

10

8. A non-aqueous electrolyte primary cell as claimed in Claim 5, wherein the positive electrode includes manganese dioxide.

- 15 9. A rechargeable non-aqueous electrolyte secondary cell comprising:

 a positive electrode having a rechargeable substance as an active material and composed of manganese oxide or cobalt oxide;

20 a negative electrode having either one of lithium and a lithium alloy as an active material; and

 a non-aqueous electrolyte consisting of a solute and an organic solvent,

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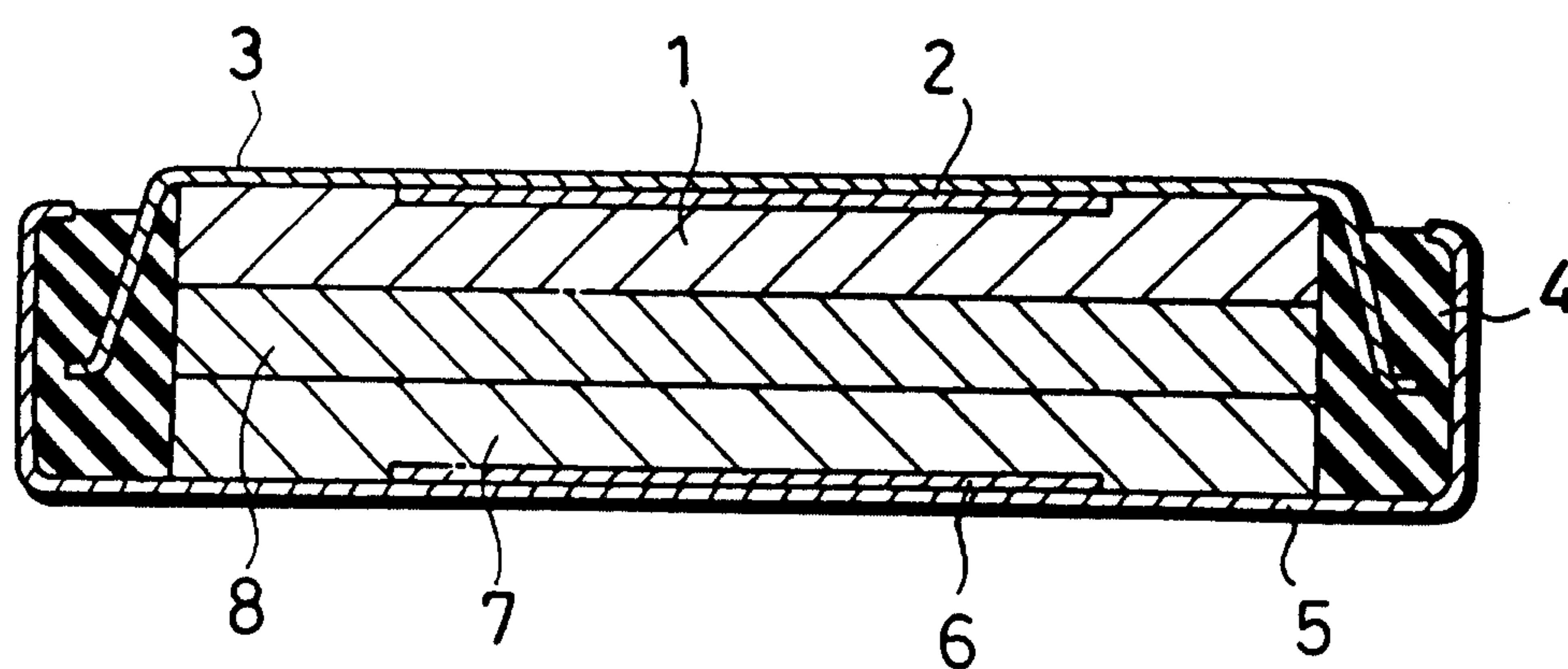
wherein the organic solvent is a solvent mixture of a cyclic carbonate and a non-cyclic carbonate, the amount of the cyclic carbonate being contained in a range of 30vol% to 70vol% against the whole solvent,
5 and the solute is LiPF_6 .

10. A rechargeable non-aqueous electrolyte secondary cell as claimed in Claim 9, wherein the cyclic carbonate is selected from a group consisting of
10 ethylene carbonate, propylene carbonate, butylene carbonate and vinylene carbonate.

11. A rechargeable non-aqueous electrolyte secondary cell as claimed in Claim 9 or 10, wherein the non-
15 cyclic carbonate is selected from a group consisting of dimethyl carbonate, diethyl carbonate and methyl ethyl carbonate.

12. A rechargeable non-aqueous electrolyte secondary
20 cell as claimed in any one of Claims 9, 10 or 11, wherein the positive electrode includes cobalt oxide.

Fig. 1



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Fig. 2

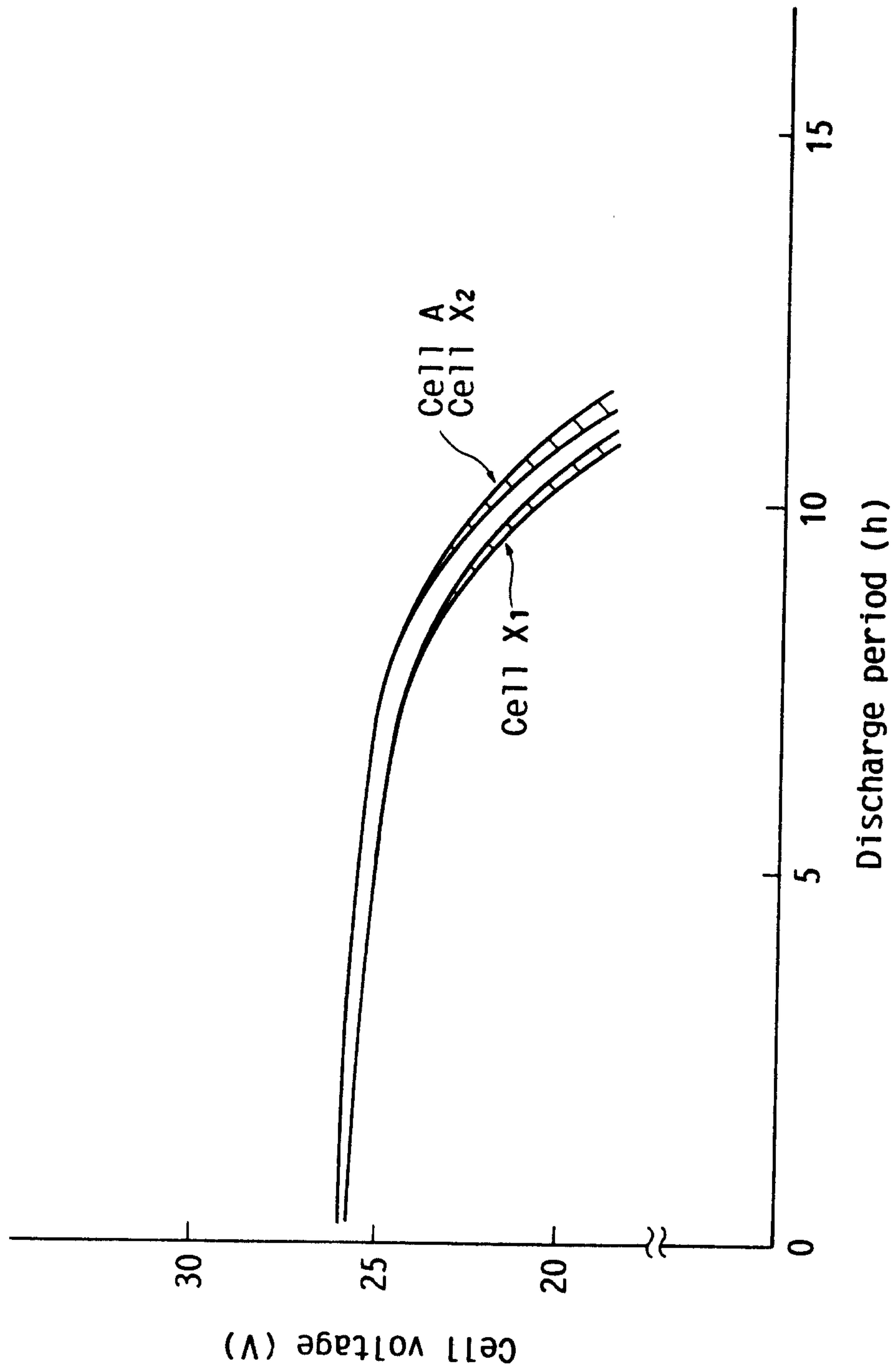
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Fig. 3

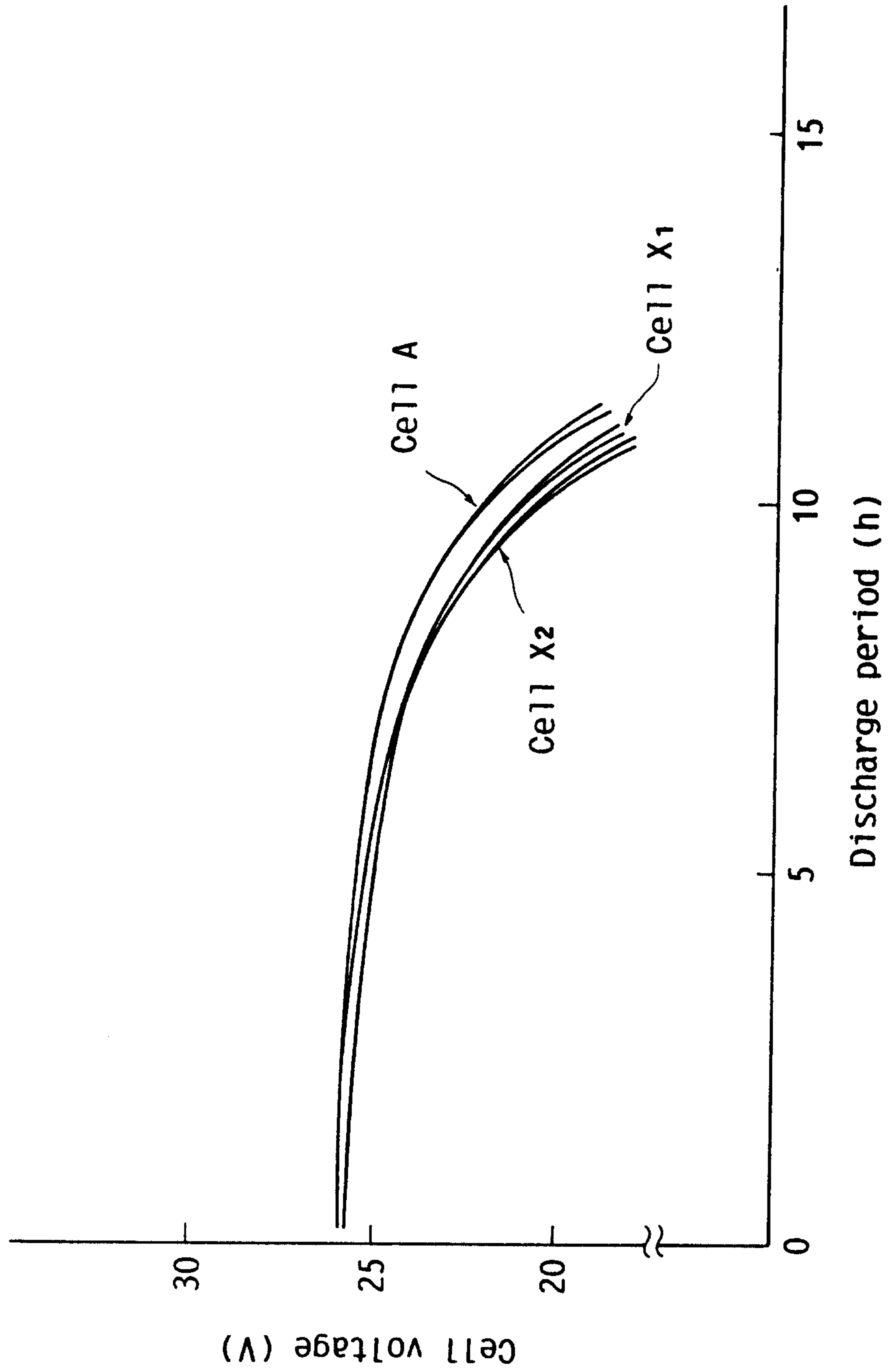
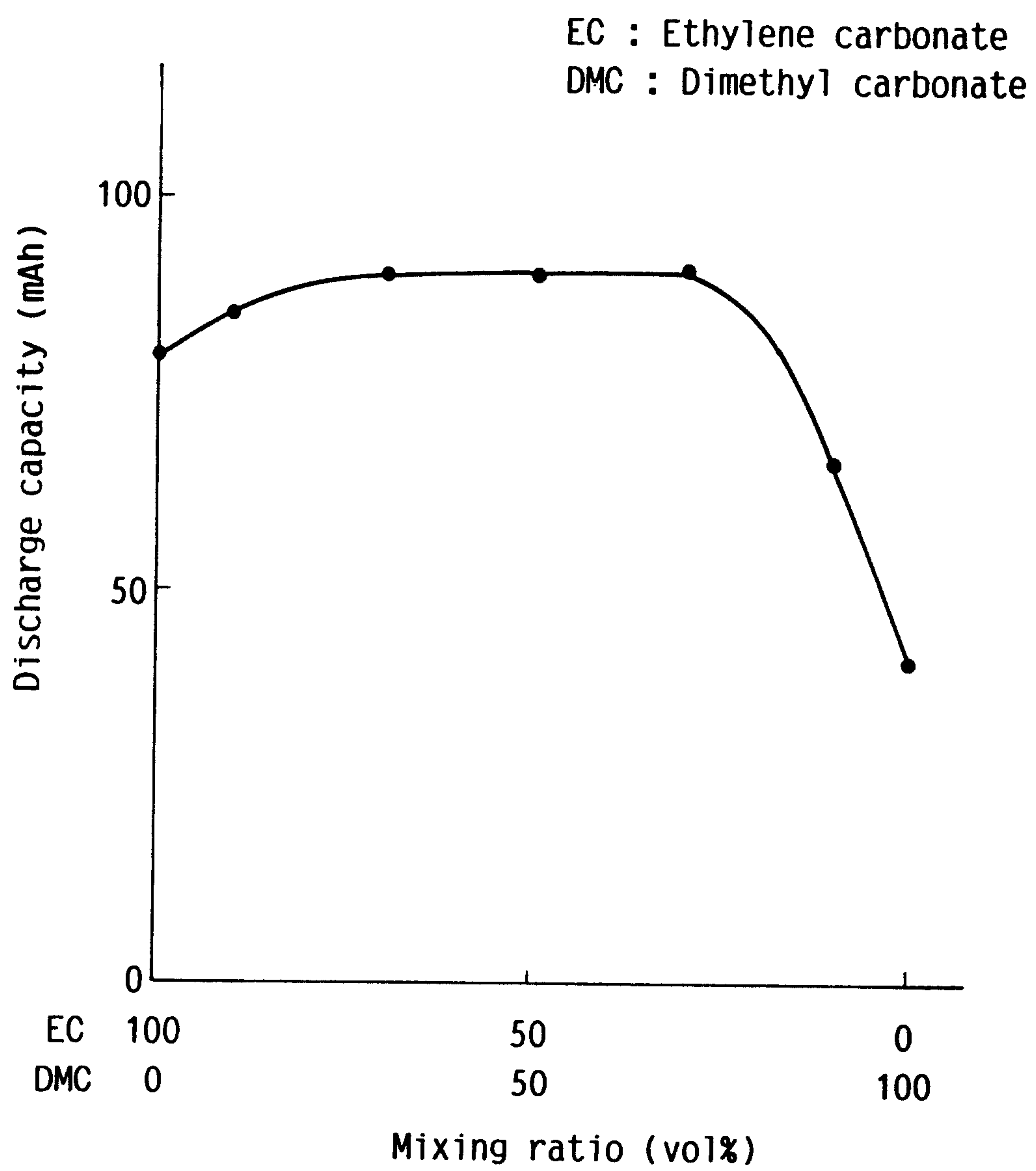
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Fig. 4



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Fig. 5

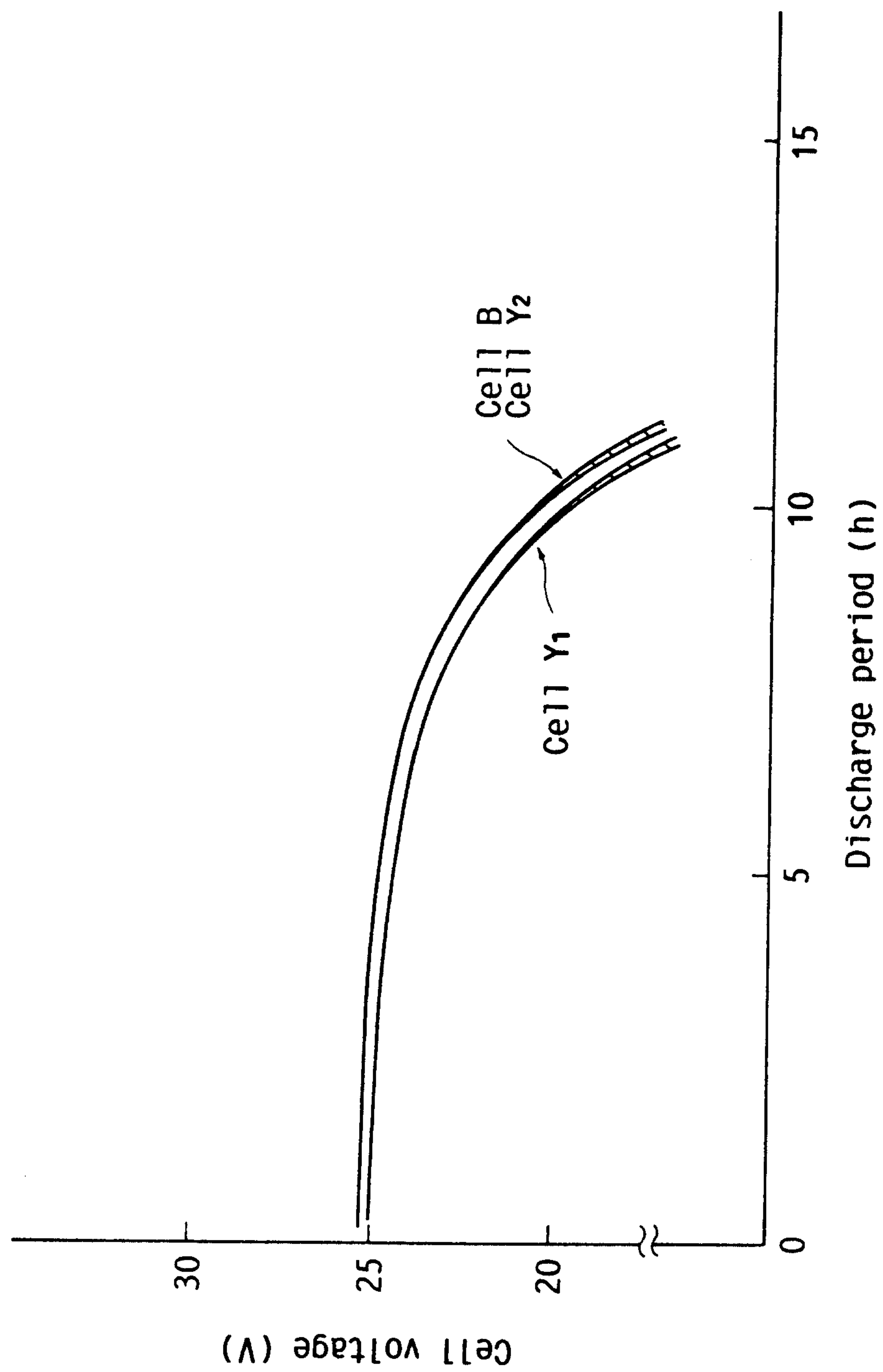
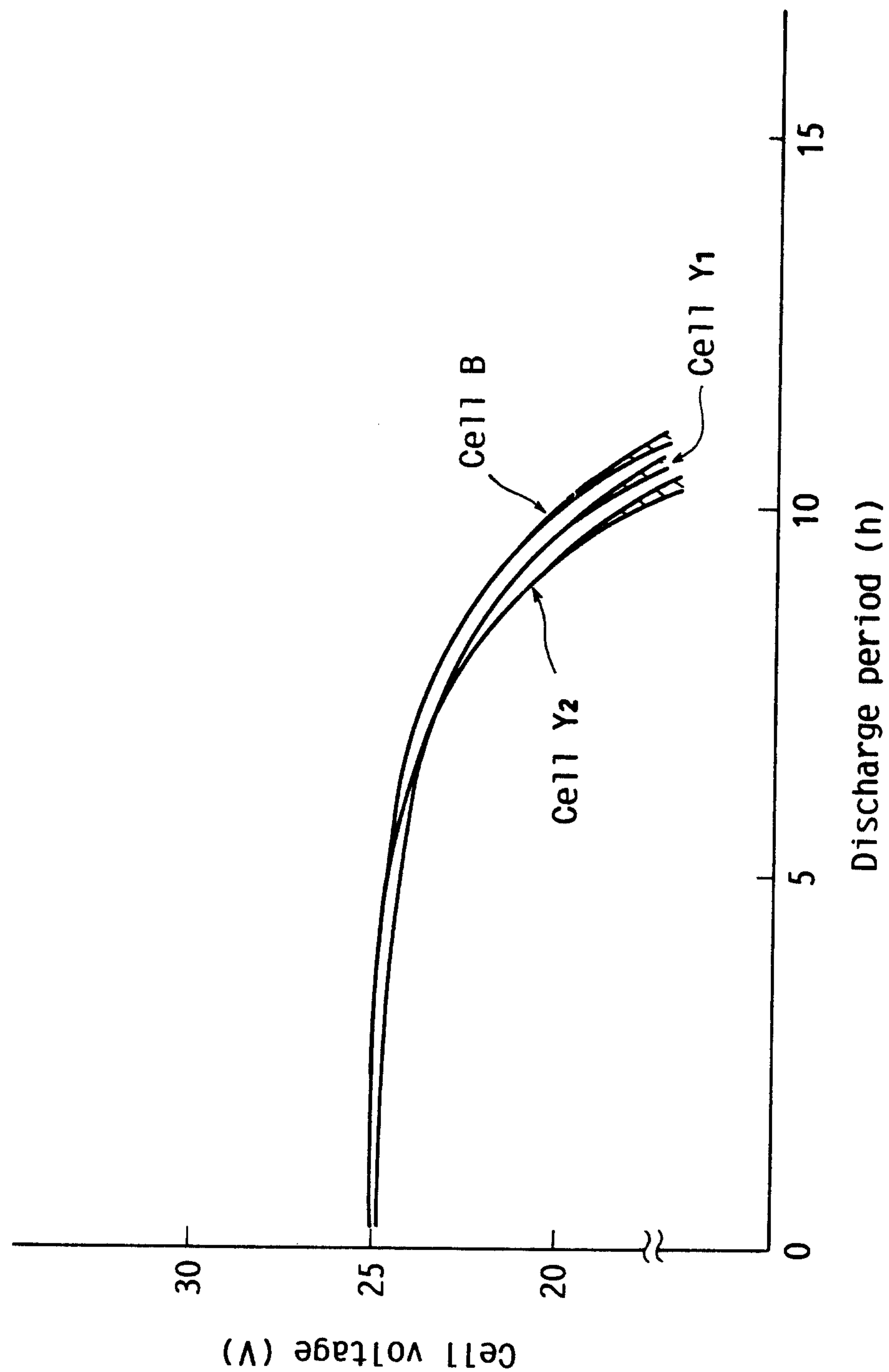
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Fig. 6



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Fig. 7

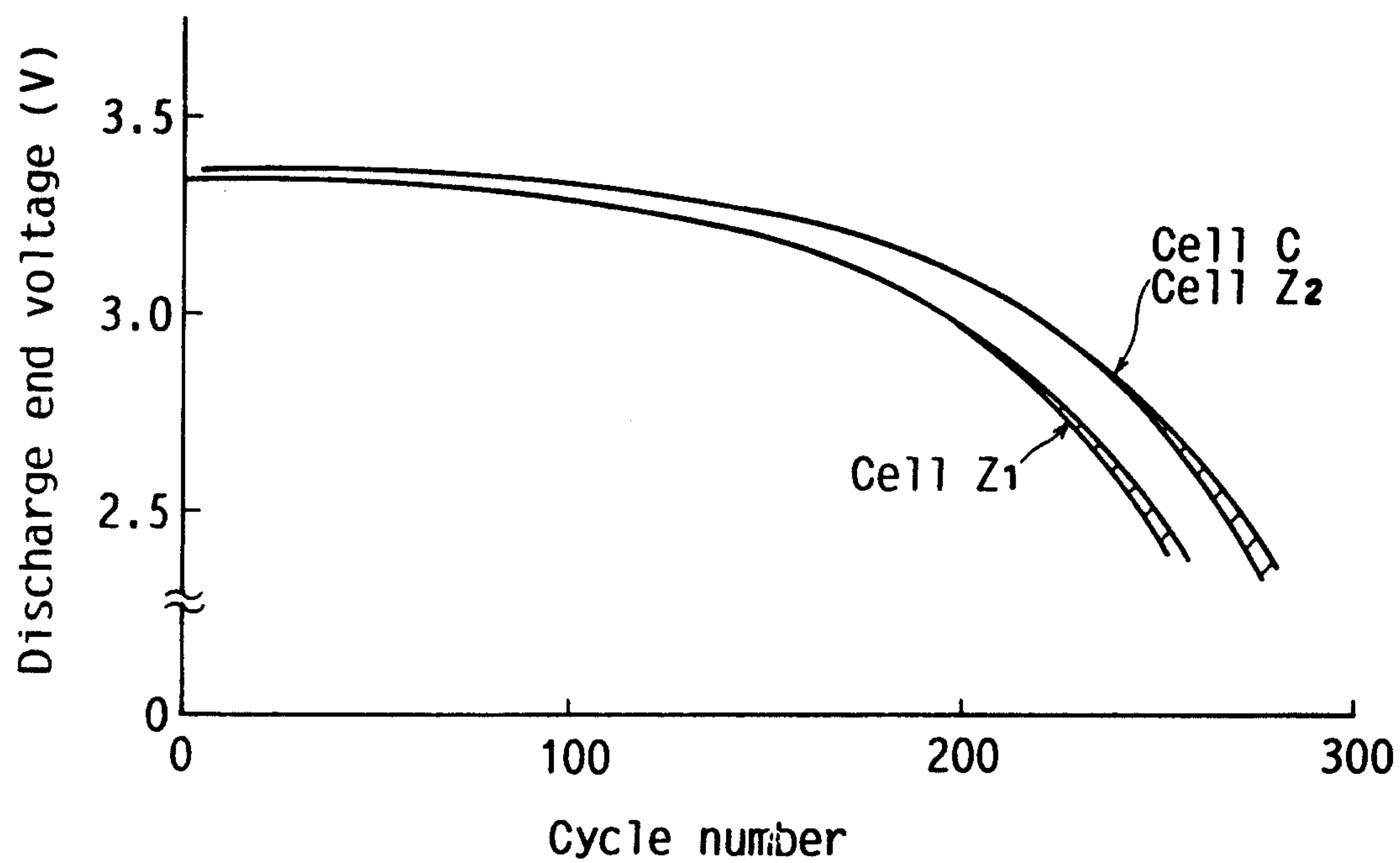
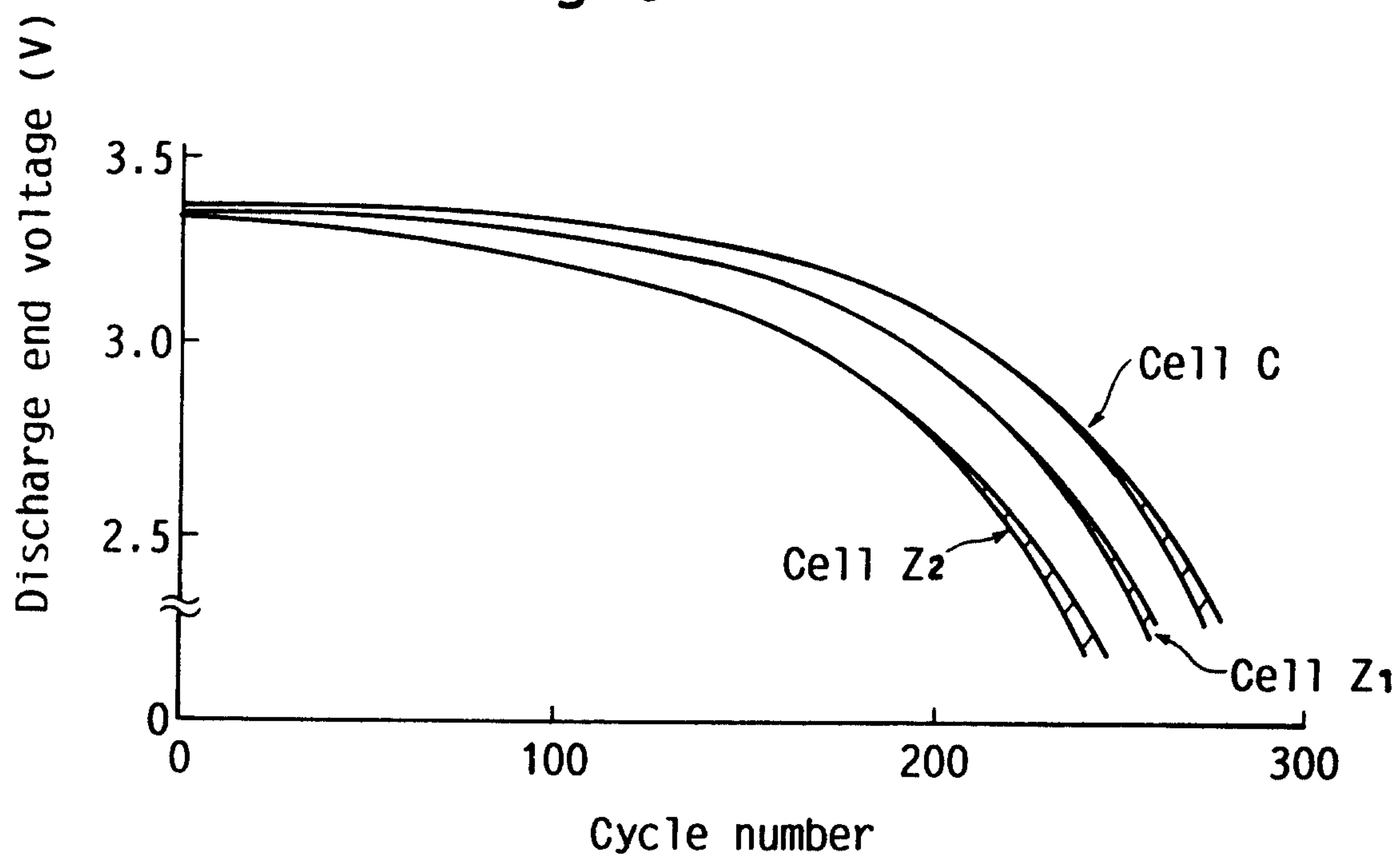
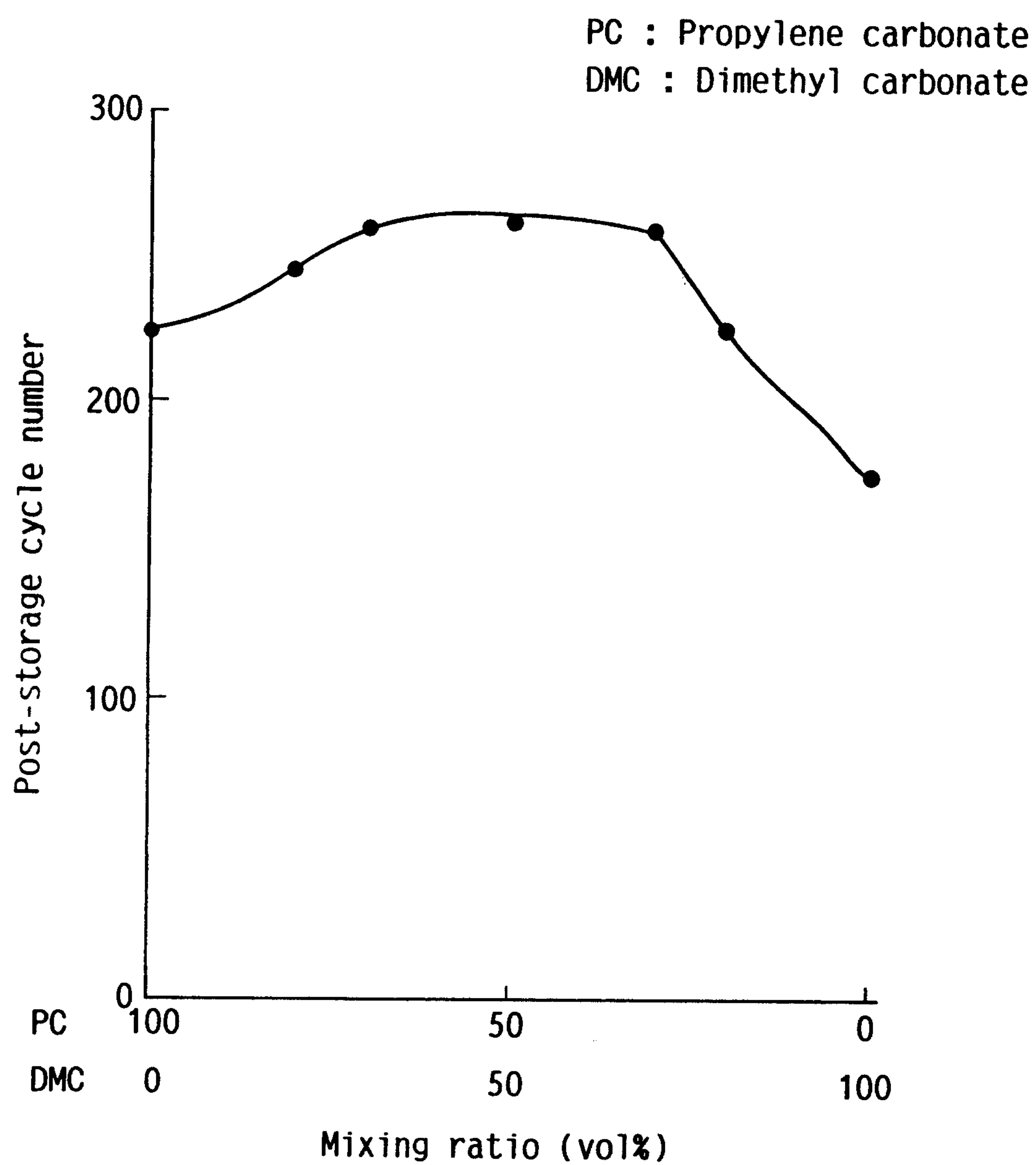


Fig. 8



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Fig. 9



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