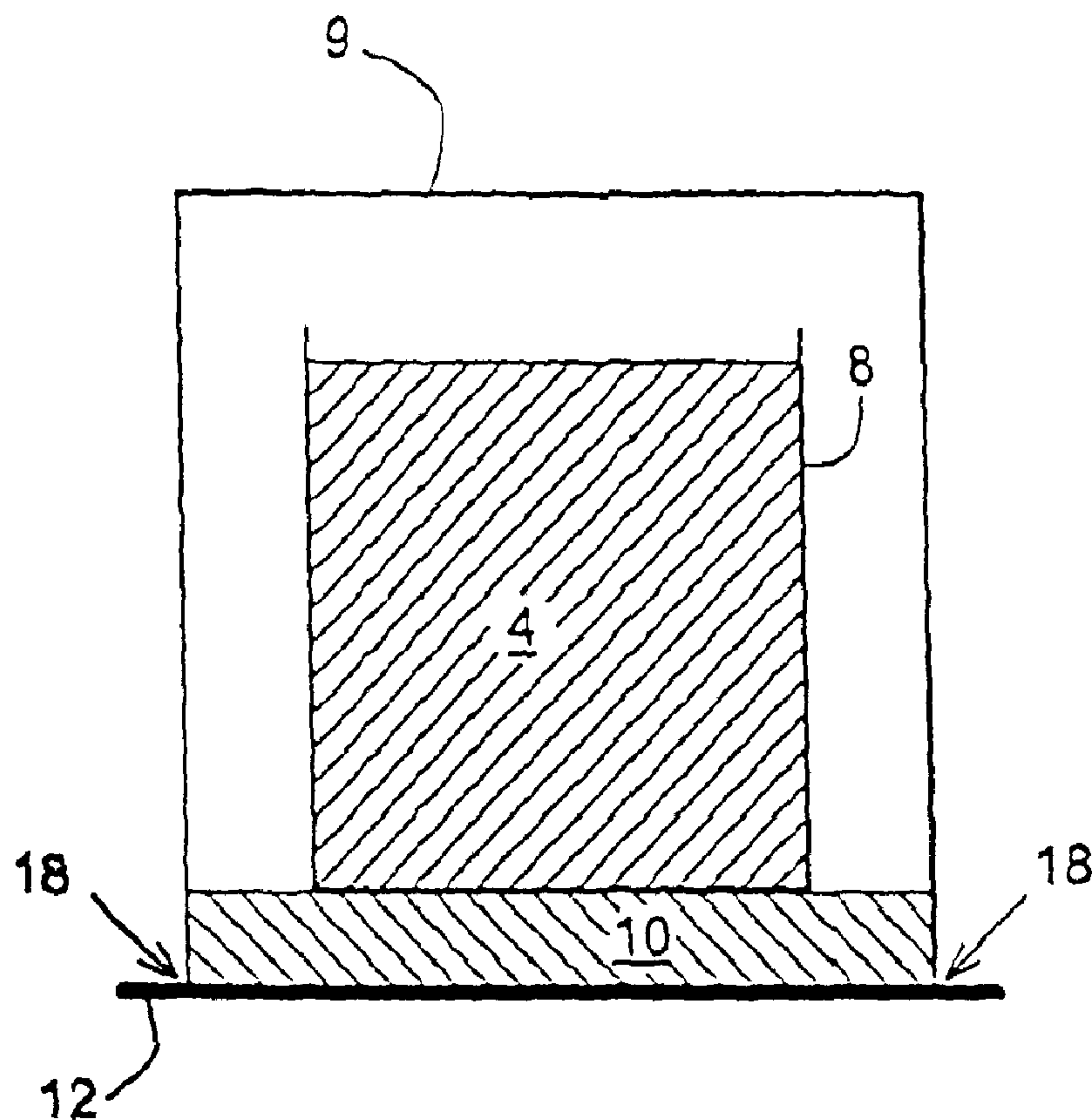




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(54) Titre : PROCEDE ET DISPOSITIFS DE PRODUCTION DE MATERIAUX D'ELECTRODE SENSIBLES A L'AIR POUR APPLICATIONS SUR BATTERIE A IONS LITHIUM
(54) Title: METHOD AND DEVICES FOR PRODUCING AIR SENSITIVE ELECTRODE MATERIALS FOR LITHIUM ION BATTERY APPLICATIONS



(57) Abrégé/Abstract:

A system for use in a synthesizing process for synthesizing precursors to form a synthesized product at elevated temperatures is disclosed. The system comprises materials of the synthesizing process, a furnace, a vessel and a solid reductive material. The



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

furnace is open to air of the atmosphere, with gases within the furnace chamber consisting essentially of gases resulting from heating the materials of the synthesizing process and air of the atmosphere entering the furnace. The vessel, having at least one opening, is for containing the materials of the synthesizing process. When the system is used, the materials of the synthesizing process are completely separated from the air of the atmosphere within the furnace by at least one of the vessel and the solid reductive material.

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Abstract

A system for use in a synthesizing process for synthesizing precursors to form a synthesized product at elevated temperatures is disclosed. The system comprises materials of the synthesizing process, a furnace, a vessel and a solid
5 reductive material. The furnace is open to air of the atmosphere, with gases within the furnace chamber consisting essentially of gases resulting from heating the materials of the synthesizing process and air of the atmosphere entering the furnace. The vessel, having at least one opening, is for containing the materials of the synthesizing process. When the system is used, the materials of the synthesizing
10 process are completely separated from the air of the atmosphere within the furnace by at least one of the vessel and the solid reductive material.

METHOD AND DEVICES FOR PRODUCING AIR SENSITIVE ELECTRODE MATERIALS FOR LITHIUM ION BATTERY APPLICATIONS

FIELD OF THE INVENTION

The present invention is concerned with reaction chambers to be utilized for the mass production of air sensitive materials, especially for the synthesis of electrode materials for lithium batteries.

BACKGROUND OF THE INVENTION

Oxidation and reduction reactions are commonly utilized for the synthesis of inorganic crystalline materials. This is especially true for the synthesis of electrode materials for Li-ion batteries including cathode and anode materials. Conventionally, cathode materials such as lithium cobalt oxide, lithium nickel oxide, lithium manganese oxide and the mixed oxides are synthesized under oxidative environments. These materials are more readily obtainable since control of an oxidative heat treatment environment (e.g. heat treatment in open air environment) is not difficult. In contrast, a reductive environment is less feasible since control of a reductive heat treatment atmosphere is difficult. The difficulty stems from the fact that during the heat treatment steps of the synthesis, especially at elevated temperatures (e.g. $>500^{\circ}\text{C}$), a slight leakage of air during the heat treatment would be detrimental for the reaction and therefore degrade the quality of the synthesized materials. The difficulties in controlling a reductive atmosphere make mass production unlikely or very expensive. One example is the synthesis of lithium iron phosphate that is conventionally synthesized in a reducing or inert atmosphere. A LiFePO_4 type cathode material has been discussed for replacing LiCoO_2 for lithium ion battery applications because of the potentially lower cost (Fe replacing Co) and the safer operating characteristics of the material (no decomposition of the material during charging). However, processing issues such as high temperature heat treatment ($>600^{\circ}\text{C}$) under an inert or reducing atmosphere makes the material expensive and

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it is not widely accepted. Until the present, the maintenance of a reducing or an inert atmosphere at a high temperature was still a key factor limiting good control of the quality of the synthesized materials. To ensure a complete seal of the furnace, especially when heat treated at high temperatures, is very difficult.

5 Prior arts such as U.S. Patent Nos. 5,910,382, 6,723,470, 6,730,281, 6,815,122, 6,884,544, and 6,913,855, in general, teach methods and precursors utilized for the formation of stoichiometric LiFePO_4 , or the substitution of cations for iron. The above mentioned patents only show how the materials are synthesized. None of the prior art teaches how to control the heat treatment environment efficiently and cost effectively.

10 SUMMARY OF THE INVENTION

 Some embodiments of the present invention may provide methods and devices for controlling a heat treatment environment that can be widely applicable to the synthesis of materials to form electrode materials. Some embodiments of the invention may also provide methods and devices that are cost effective and insure good quality of the synthesized
15 material.

 According to one aspect of the present invention, there is provided a system for use in a synthesizing process for synthesizing precursors to form a synthesized product at elevated temperatures, comprising materials of the synthesizing process, a furnace that is open to air of the atmosphere, with gases within the furnace chamber consisting essentially of gases
20 resulting from heating the materials of the synthesizing process and air of the atmosphere entering the furnace, a vessel, having at least one opening, for containing the materials of the synthesizing process, and a solid reductive material, wherein said materials of the synthesizing process are completely separated from the air of the atmosphere within the furnace by at least one of the vessel and the solid reductive material.

25 According to another aspect of the present invention, there is provided a process for use in a synthesizing process for synthesizing precursors to form a synthesized product at elevated temperatures within a furnace absent a controlled atmosphere, comprising

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providing a furnace that is open to air of the atmosphere, with gases within the furnace consisting essentially of gases resulting from heating the materials of the synthesizing process and air of the atmosphere entering the furnace, placing precursors into a vessel, having at least one opening, so as to have the precursors contained in the vessel, for the synthesizing process, 5 placing a solid reductive material in combination with the vessel so that materials of the synthesizing process are separated from the air of the atmosphere of the furnace by at least one of the vessel and the solid reductive material, placing the contained precursors in the furnace, and heating the contained precursors to a synthesizing temperature to form a synthesized product.

10 One embodiment of the present invention may provide a unit, for use within a furnace absent a controlled atmosphere, in a synthesizing process for synthesizing precursors to form a synthesized product at elevated temperatures. The unit has a vessel, having at least one opening, for containing materials of the synthesizing process, and a solid reductive material, wherein the materials of the synthesizing process are separated from the atmosphere 15 of the furnace by either the vessel or the reductive material.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will become more readily apparent from the following description of preferred embodiments thereof shown, by way of example only, in the accompanying drawings, wherein:

Figs. 1(a) and 1(b) are illustrations of a first embodiment of the unit of the invention;

Figs. 1(c) and 1(d) are illustrations of a second embodiment of the unit of the invention;

Fig. 1(e) is an illustration of a third embodiment of the unit of the invention.

Fig. 2(a) is an illustration of units of the first and/or second embodiments in a furnace for carrying out a synthesizing process;

Fig. 2(b) is an illustration of units of the third embodiment in a furnace for carrying out a synthesizing process;

Fig. 3 is a graph of an x-ray diffraction pattern for a representative sample of a synthesized electrode material prepared using units of the invention;

Fig. 4 is a graph for showing battery test data for the same material as in Fig. 3;

Fig. 5 is a graph of x-ray diffraction patterns for 5 similar synthesized electrode materials prepared using units of the invention; and

Fig. 6 is a graph for showing battery test data for 10 similar synthesized electrode materials prepared using units of the invention.

DETAILED DESCRIPTION OF THE INVENTION

Figs. 1(a) - 1(e) show schematic diagrams of individually sealed units (ISU) containing materials that are subjected to the synthesizing heat treatments. Designs of furnaces that contain the ISUs of different geometries are shown in Figs. 2(a) and 2(b).

In Figs. 1(a) and 1(b) the ISU 1 is a vessel having one end 2 completely sealed while the other end 3 is open to the atmosphere. Precursors to be synthesized to form an electrode

material are contained at 4. The precursors, intermediate products, and resulting material of the synthesizing process are referred to as materials of the synthesizing process throughout the description. The materials of the synthesizing process, contained at 4, are protected from the atmosphere of the furnace, into which ISUs are placed for heating, by either the material of the vessel 1, or a solid reductive material layer 5 that limits the permeation of air from the furnace atmosphere. It should be mentioned that since the reductive material (e.g. carbon black) is usually porous, the porosity of the reductive material layer would allow the permeation of any gas by-product released from the material being synthesized, to the atmosphere. In general, either the gas by-product or the oxidation of the reductive material would generate gas and keep the pressure within the ISU positive, compared to the atmosphere. However, if the material being synthesized does not generate gas as a by-product, a decrease of the porosity of the reductive material layer (by means of tapping, for example) would ensure separation from the atmosphere.

In Figs. 1(c) and 1(d) each ISU of a second embodiment is a vessel 1 having both ends 6 open to the environment. Precursors to be synthesized to form an electrode material are contained at 4. The materials of the synthesizing process, contained at 4, are protected from the atmosphere of the furnace, into which ISUs are placed for heating, by solid reductive material layers 5 that limit the permeation of air from the furnace atmosphere. As mentioned above, the solid reductive material is usually porous to allow permeation of any gases resulting from the synthesizing process.

In both of the embodiments, a divider 11 can be used to separate the reductive material 5 from the material 4 of the synthesizing process. The divider preferably is inert to the materials being separated and porous to any gases being generated. Also, as shown in Figs. 1(a) - 1(d), at 7, a high-temperature durable glass fiber packing can be used to hold all of the materials in the vessels.

Similar characteristics can be observed in a third embodiment of an ISU shown in Fig.

1(e). From Fig. 1(e), it can be seen that the materials to be synthesized 4 are contained in a crucible 8. The path of airflow from any open side of a vessel 9 is controlled by the presence of reductive material 10. A bottom of the crucible separates the reductive material from the materials of the synthesizing process. A tray 12 facilitates handling of the unit. Vessel 9 is not sealed tightly against tray 12 in order that gases can flow freely to or from the reductive material, as shown at 18.

Figs. 2(a) and 2(b) show the various embodiments of the invention as utilized in a furnace to carry out the synthesizing process.

In Fig. 2(a) first embodiments and/or second embodiments are shown in furnace 13. Heating elements of the furnace are shown at 14.

In Fig. 2(b) four units of the third embodiment of the invention are shown at 15 in furnace 16. Heating elements of the furnace are shown at 17. As mentioned above, the furnaces are not required to be sealed and a controlled inert or reducing environment is not necessary.

The common structures of the ISUs are as follows:

- a. An ISU includes a space that contains the materials being subjected to the synthesizing heat treatment;
- b. An ISU includes a space that contains the reductive material;
- c. The reductive material is placed in the vessel in a manner as:

Uncontrolled atmosphere/reductive material/synthesized material (Figs. 1(a) and 1(b)), or

uncontrolled atmosphere/reductive material/synthesized material/ reductive material/uncontrolled atmosphere (Figs. 1(c) and 1(d));

- d. The reductive material can be placed on top of the synthesized material as shown in Figs. 1(a) -1(d) or somewhere else in contact with the outer atmosphere as shown in Fig. 1 (e);

- e. The ISU can dissipate gas generated by the synthesizing reaction.

In the embodiments of Figs. 1(b) and 1(d) the flow of gases is from the materials of the synthesizing process, through the reductive material to the uncontrolled atmosphere, or the reverse of same.

In the embodiments of Figs. 1(a) and 1(c) the flow of gases is from the materials of the synthesizing process, through the separator, through the reductive material to the uncontrolled atmosphere, or the reverse of the same.

In the embodiment of Fig. 1(e) the flow of gases is from the materials of the synthesizing process, through the separation between the crucible and the vessel, through the reductive material to the uncontrolled atmosphere, or the reverse of same.

Other advantages provided by the utilization of ISUs include:

- A. No need for an inert atmosphere in the furnace, thus resulting in:
- i. Easy scale up for production;
 - ii. Much lower cost of a furnace since a gas-tight furnace becomes unnecessary;
 - iii. The cost of inert gas can be saved;
 - iv. Overall cost of the synthesis protocol is reduced; and
 - v. Easy control of the quality of the resultant synthesized materials.

Since one ISU can be considered as one furnace.

B. Good performance of the synthesized material as demonstrated in the following examples.

C. Consistency in performance of the synthesized material, which is extremely important for battery applications.

Owing to the advantage of the controlled heat treatment environment provided by the ISUs, materials that require heat treatment under an inert atmosphere can be obtained easily and cost efficiently. Following are examples of materials synthesized in an ISU of the

invention, in order to better describe use of the invention.

EXAMPLE 1. Synthesis of LiFePO_4 using methods and devices of the invention

In order to demonstrate the novelty of the ISUs disclosed in the present patent application, the synthesis of conventional LiFePO_4 in bulk quantity is used. 12kg (75 moles) of Fe_2O_3 and 5.55kg (75 moles) of Li_2CO_3 and 1.8kg (150 moles) of Super P (carbon black, available from MMM Carbon, Belgium), molar ratio of (1:1:2), were mixed together with the addition of a suitable amount of water to form a paste. After mixing thoroughly, the proper stoichiometric amount of phosphoric acid was added and extended mixing was utilized (6 hours). Finally, the slurry was dried in air at 150°C for 10 hours, followed by further heat treatment at 400°C for 10 hours until chunks of materials were obtained. The as-prepared material was then subjected to grinding and ball milling for about 12 hours. The ground powdery materials was then loaded into several ISUs as shown in Fig. 1(a) with the addition of a carbonaceous material placed directly on top of the ground powdery material for heat treatment. In practice, the carbonaceous material can be placed directly on top of the synthesized material or separated by a thin layer of porous glass fiber fabrics or other inert plate. The ISUs were then placed in a furnace as shown in Fig. 2(a).

The heat treatment was conducted at 650°C for 24 hours resulting in the synthesized material. After the heat treatment step, slight grinding and sieving were conducted on the synthesized material. The post-heat treated materials were then ready for further tests, as will be described below.

The utilization of ISUs is not limited to the synthesis of lithium iron phosphate, or limited to the choice of starting materials and precursor processing steps described for the synthesis of lithium iron phosphate of the present example.

X-ray diffraction pattern data of the synthesized material is shown in Fig. 3. It is observed that phase pure material was obtained using the processing methods and devices

presented in this example, without the use and control of an inert gas, such as nitrogen or argon. Battery test data (obtained using a three electrode design test battery and lithium is utilized as the reference electrode) are shown in Fig. 4. From Fig. 4 it can be seen that the capacity is high during the first charge-discharge cycle ($\sim C/5$ rate, $0.23\text{mA}/\text{cm}^2$). The material synthesized in the present case is comparable or superior to the prior art material disclosed in U.S. Patent No. 6,723,470, which was obtained using an inert atmosphere as a heat treatment environment.

EXAMPLE 2. Demonstration of consistently the synthesized LiFePO_4 using methods and devices of the invention

In the present example, ten batches of materials synthesized using the ISUs shown in Fig. 1(a) were tested for quality consistency. The precursor processing procedures for each batch were the same as the procedures described in example 1. The ten different batches were subjected to 10 identical heat treatment procedures in ISUs. From the ten batches, five batches were subjected to the x-ray diffraction pattern analyses and the results are shown in Fig. 5. Also, a stack of the 1st cycle data for each batch is shown in Fig. 6. More accurate numerical data is provided in Table 1. From Fig. 5 it can be seen that all of the materials are phase pure in nature. The peak intensity and peak positions for each sample are similar, as shown and indicated in Fig. 5. In Fig. 6, the 1st charge and discharge plot for each sample is again very similar. The 1st charge capacity ranges from 132~137mAh/g and the 1st discharge capacity ranges from 118~124mAh/g. All these data suggest that the consistency of the materials synthesized using the ISUs is insured.

Table 1. The detailed electrochemical data of the ten batches heat treated using the ISUs.

Batch Names	1 st charge capacity (mAh/g)	1 st discharge capacity (mAh/g)	1 st charge average voltage (V)	1 st discharge average voltage (V)	1 st cycle Coulomb efficiency
AE11021	133.97	118.69	3.5083	3.3800	0.8859
AE11031	132.15	118.64	3.5070	3.3805	0.8978
AE11041	137.30	124.11	3.5016	3.3845	0.9039
AE11051	135.29	118.60	3.5088	3.3778	0.8766
AE11061	133.03	119.06	3.5066	3.3810	0.8950
AE11121	132.14	118.75	3.5071	3.3608	0.8987
AE11131	133.19	120.19	3.5083	3.3791	0.9024
AE11141	135.69	122.59	3.5189	3.3794	0.9035
AE11151	136.43	122.55	3.5109	3.3776	0.8983
AE11161	134.71	120.52	3.5090	3.3778	0.8947

The devices of the present invention provide the following advantages. There is no need for the use of an inert gas in the furnace, such as nitrogen or argon, or forming gas (nitrogen plus hydrogen), thus a completely sealed furnace is not required. The ISUs are semi-open to the atmosphere of the furnace, thus sealing of the ISUs is not difficult. There is a short thermal diffusion distances from the heat source to the material being synthesized. With use of the reductive material, such as carbon black or carbonaceous materials for air permeation prevention, even if a small amount of air permeation occurs during heat treatment, oxidation of the carbonaceous material prevents further oxidation of the material being synthesized. The reductive material can be porous so to allow the dissipation of gas produced by the

materials that are subjected to the heat treatment. The depth of the ISUs shown in Fig. 1(a) and 1(b) are adjustable for the prevention of oxidation, for example a longer depth would give a better-isolated environment. Also, the geometry of the ISUs is flexible to accommodate the design of the furnaces, such as shown in Figs. 2(a) and 2(b).

While specific materials, dimensional data, etc. have been set forth for purposes of describing embodiments of the invention, various modifications can be resorted to, in light of the above teachings, without departing from applicant's novel contributions; therefore in determining the scope of the present invention, reference shall be made to the appended claims.

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CLAIMS:

1. A system for use in a synthesizing process for synthesizing precursors to form a synthesized product at elevated temperatures, comprising

 materials of the synthesizing process,

5 a furnace that is open to air of the atmosphere, with gases within the furnace chamber consisting essentially of gases resulting from heating the materials of the synthesizing process and air of the atmosphere entering the furnace,

 a vessel, having at least one opening, for containing the materials of the synthesizing process, and

10 a solid reductive material, wherein

 said materials of the synthesizing process are completely separated from the air of the atmosphere within the furnace by at least one of the vessel and the solid reductive material.
2. The system of claim 1, wherein

15 said vessel and said reductive material are arranged such that said materials of the synthesizing process are in contact with said solid reductive material.
3. The system of claim 1, further comprising

 a divider for separating the materials of the synthesizing process from the solid reductive material, wherein

20 the divider is of a material substantially inert to the materials being separated.

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4. The system of claim 1, further comprising

a crucible, disposed within said vessel, for holding materials of the synthesizing process and separating the materials of the synthesizing process from said vessel and from said reductive material.

5 5. The system of claim 1, wherein

the solid reductive material is porous to gases resulting from the synthesizing process and gases resulting from oxidation of the reductive material.

6. The system of claim 3, wherein

10 the reductive material is porous to gases resulting from the synthesizing process and gases resulting from oxidation of the reductive material, and the divider is porous to gases resulting from the synthesizing process.

7. The system of claim 5, wherein

15 a combination of the porosity and separating thickness of the solid reductive material substantially prevents the atmosphere of the furnace from entering the synthesizing process.

8. The system of claim 7, wherein

the solid reductive material has a separating thickness of 5-10 centimeters.

9. The system of claim 1, wherein

20 the solid reductive material is carbon black, coal, coke or metal powder.

10. The system of claim 9, wherein

the solid reductive material is carbon black.

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11. The system of claim 1, wherein

the vessel is of a material substantially inert to the materials of the synthesizing process and the solid reductive material.

12. The system of claim 11, wherein

5 the material of the vessel is stainless steel.

13. A process for use in a synthesizing process for synthesizing precursors to form a synthesized product at elevated temperatures within a furnace absent a controlled atmosphere, comprising

10 providing a furnace that is open to air of the atmosphere, with gases within the furnace consisting essentially of gases resulting from heating the materials of the synthesizing process and air of the atmosphere entering the furnace,

placing precursors into a vessel, having at least one opening, so as to have the precursors contained in the vessel, for the synthesizing process,

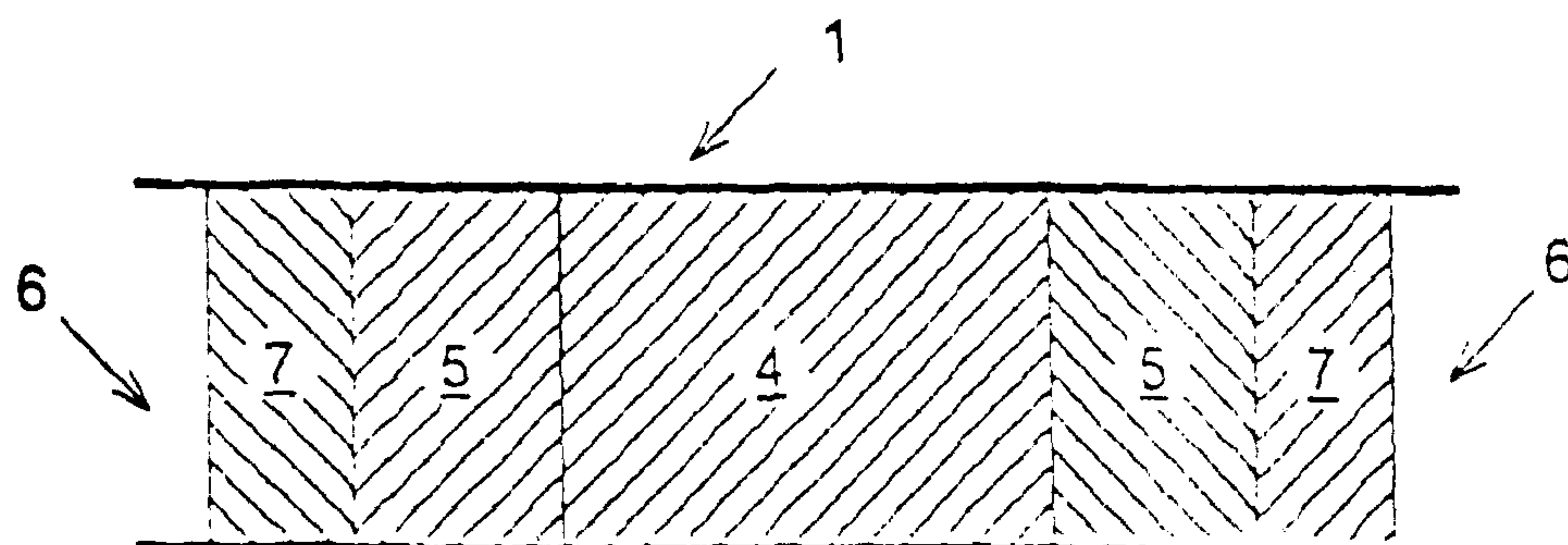
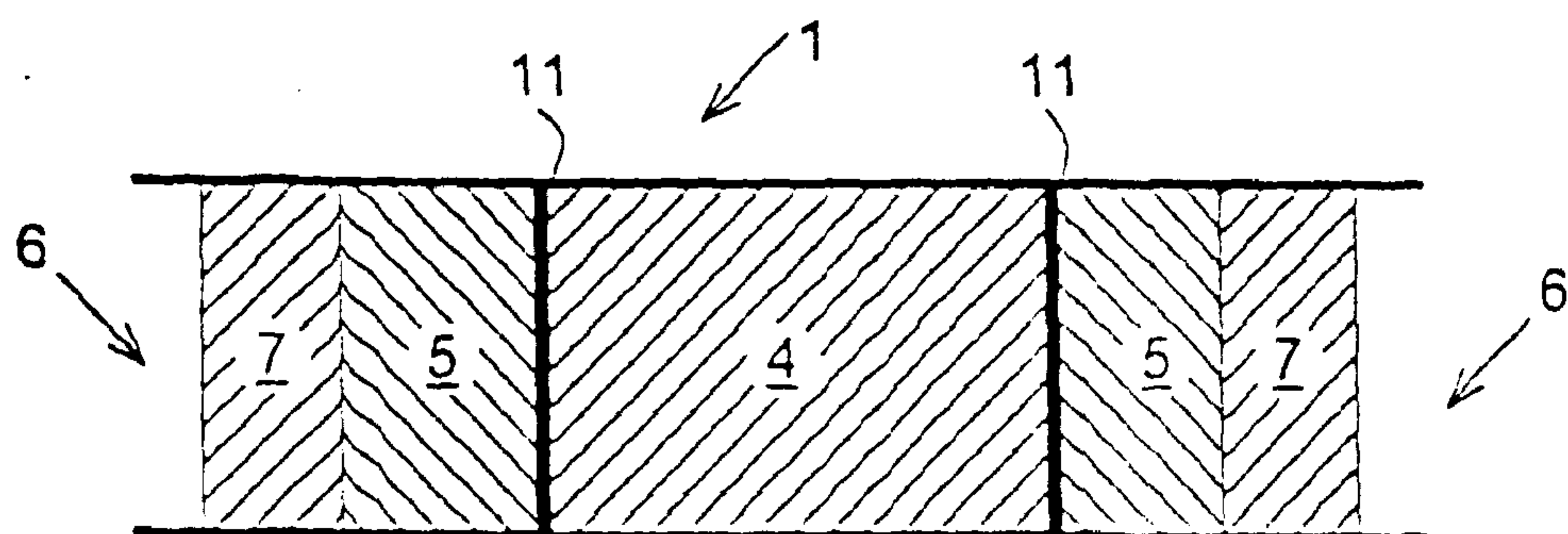
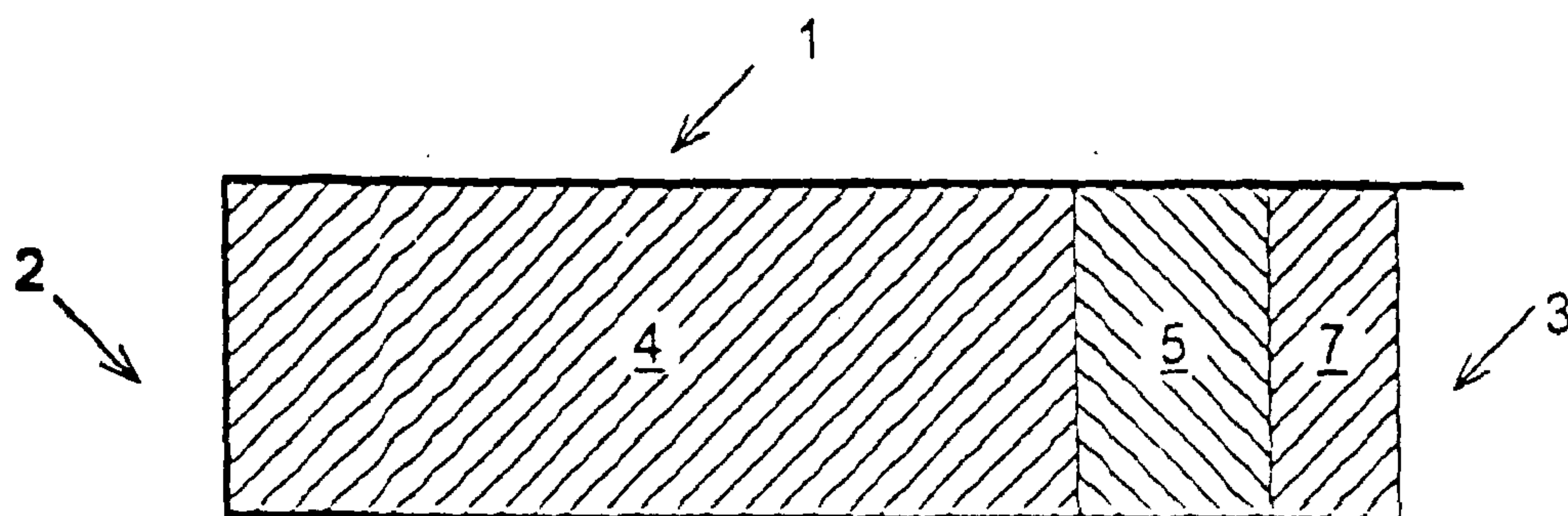
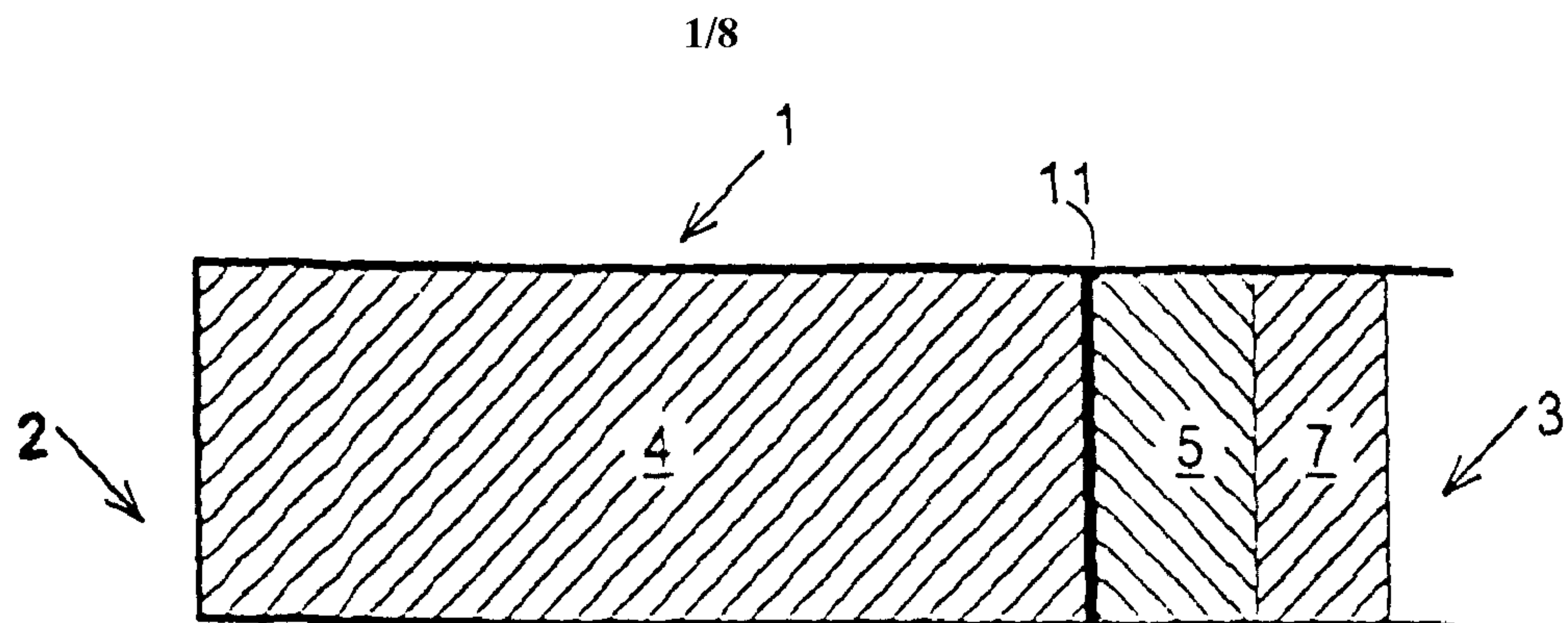
15 placing a solid reductive material in combination with the vessel so that materials of the synthesizing process are separated from the air of the atmosphere of the furnace by at least one of the vessel and the solid reductive material,

placing the contained precursors in the furnace, and

heating the contained precursors to a synthesizing temperature to form a synthesized product.

20 14. The process of claim 13, wherein

the precursors comprise Fe_2O_3 , Li_2CO_3 , carbon black, and phosphoric acid, the precursors are heated to a temperature greater than 600°C , and the synthesized product is LiFePO_4 .



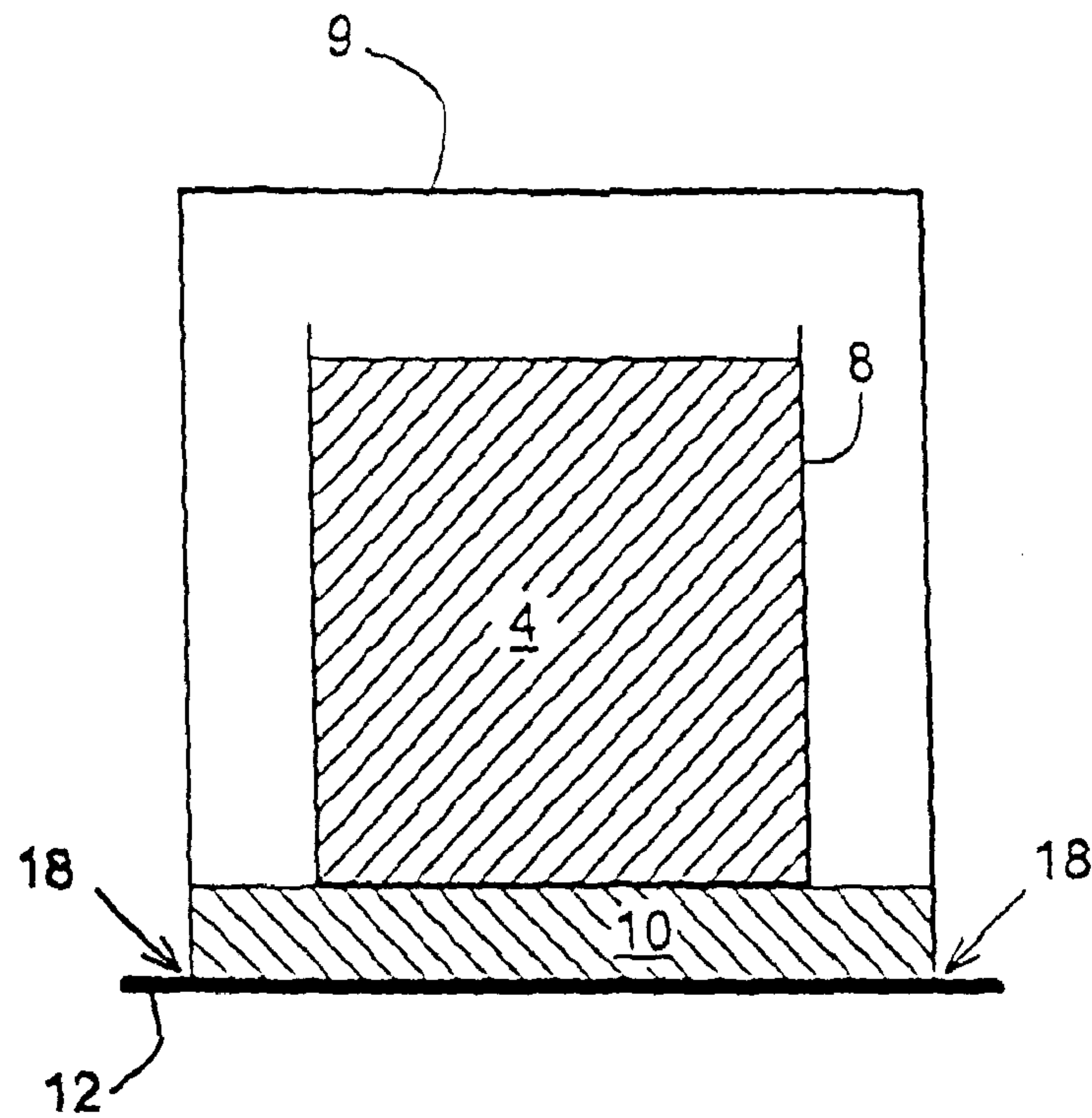


Fig. 1(e)

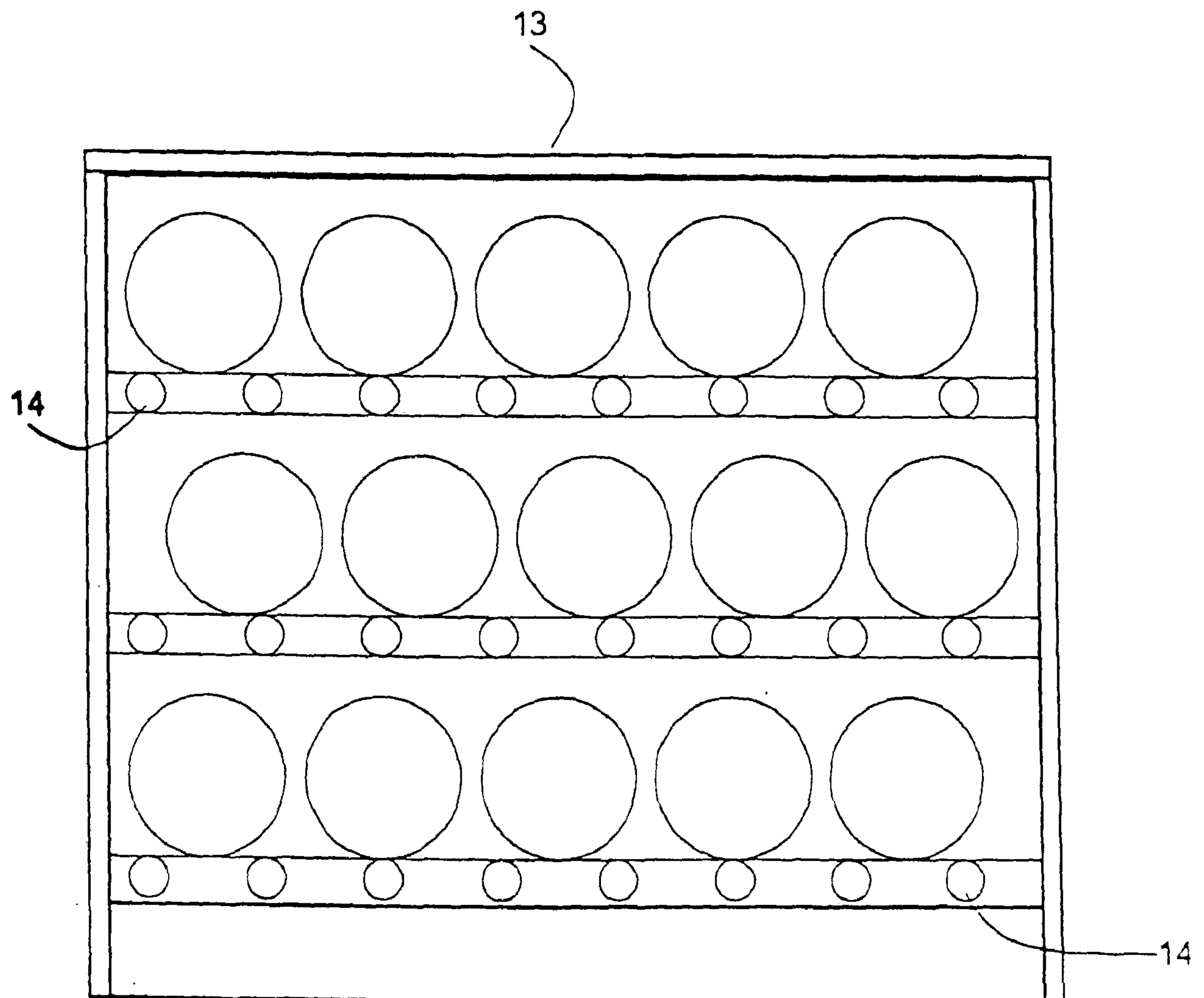


Fig. 2(a)

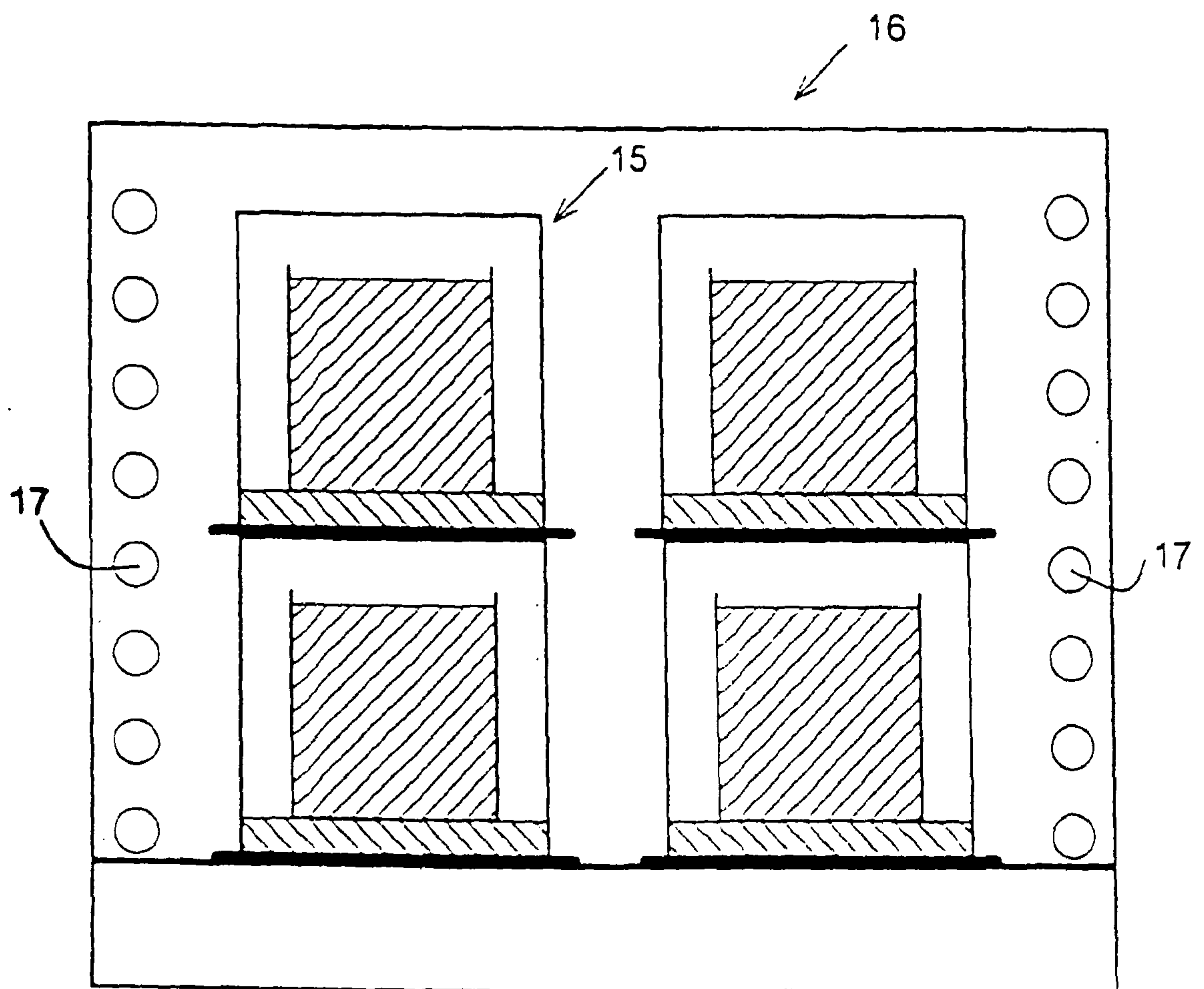


Fig. 2(b)

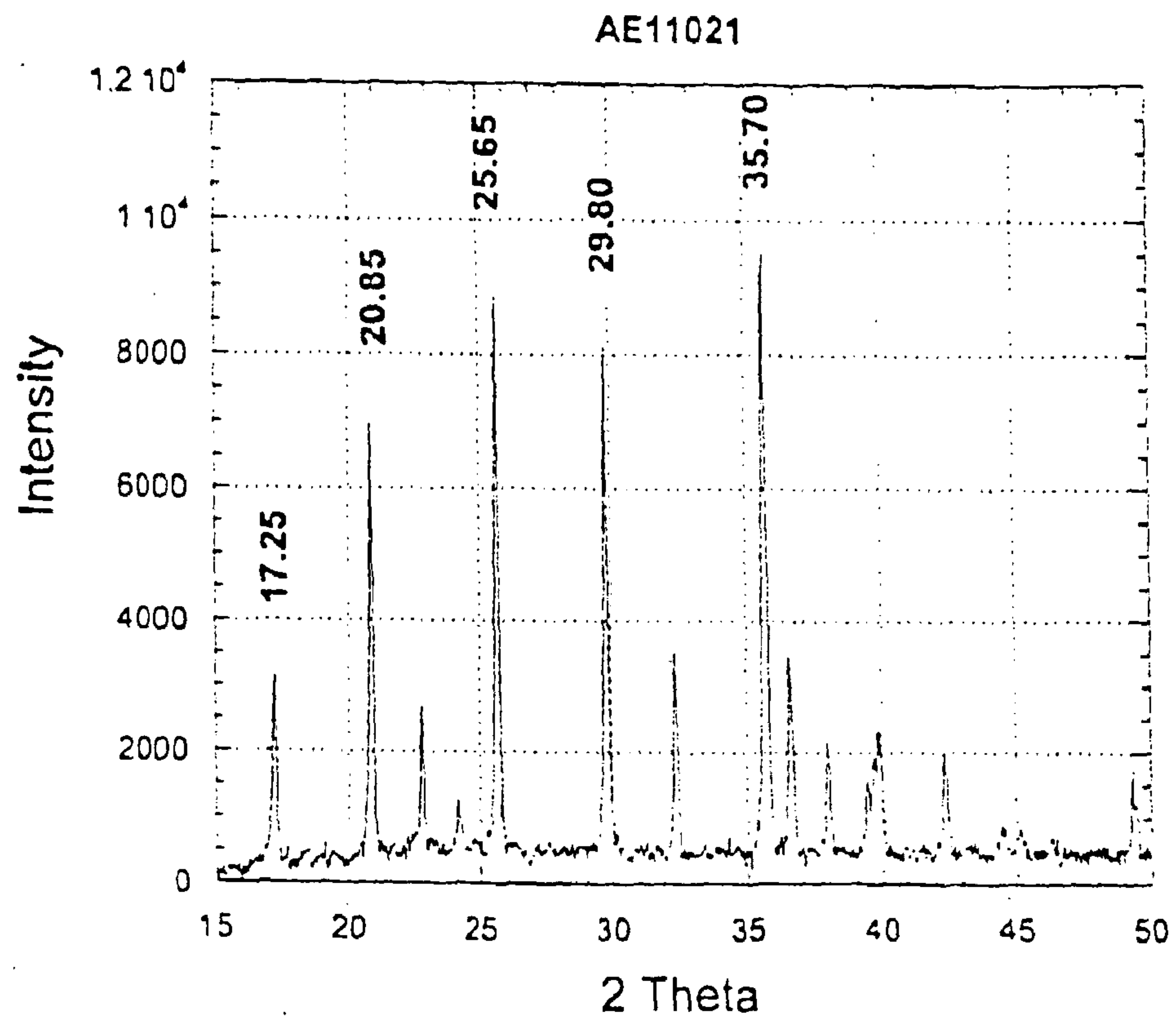


Fig. 3

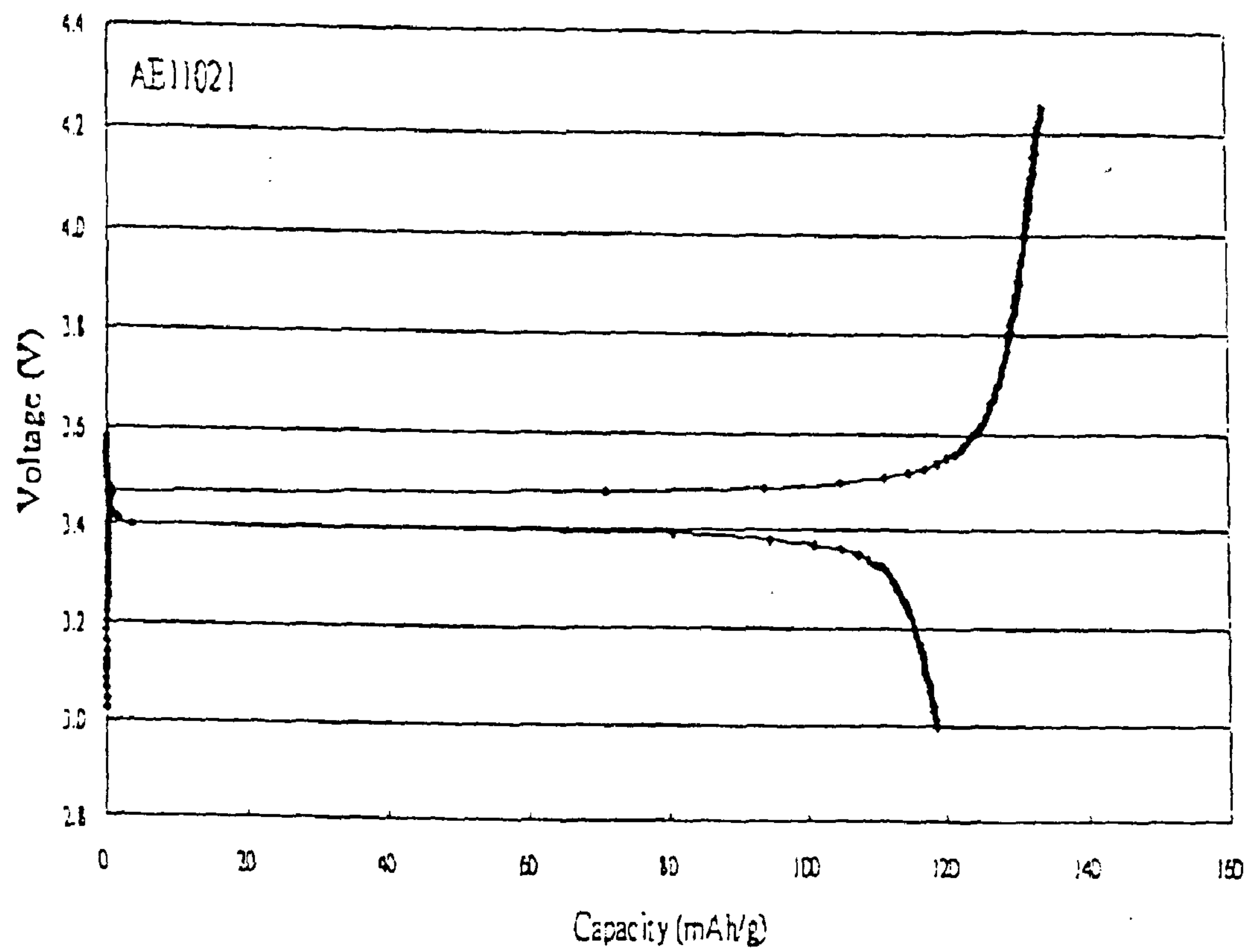


Fig. 4

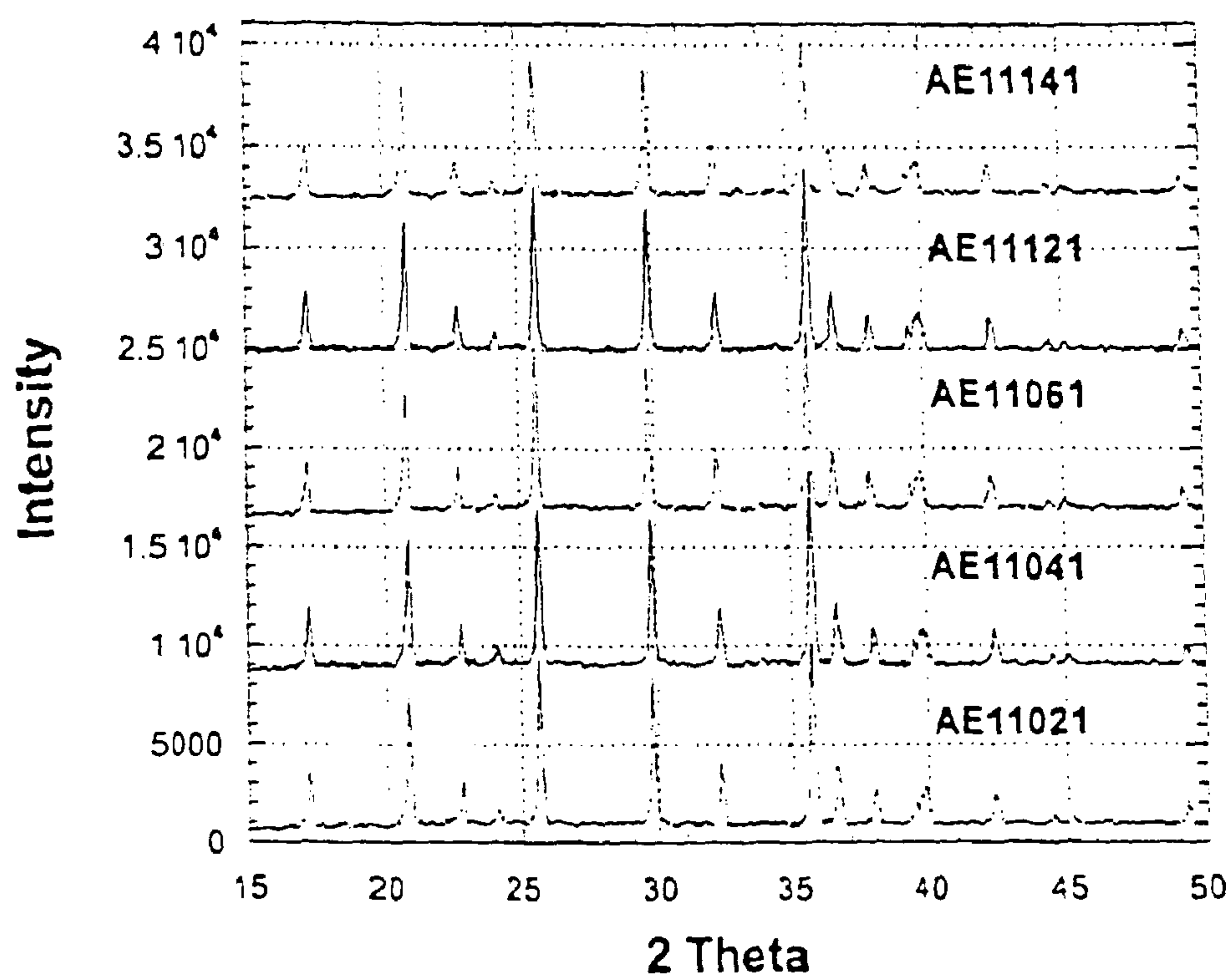


Fig. 5

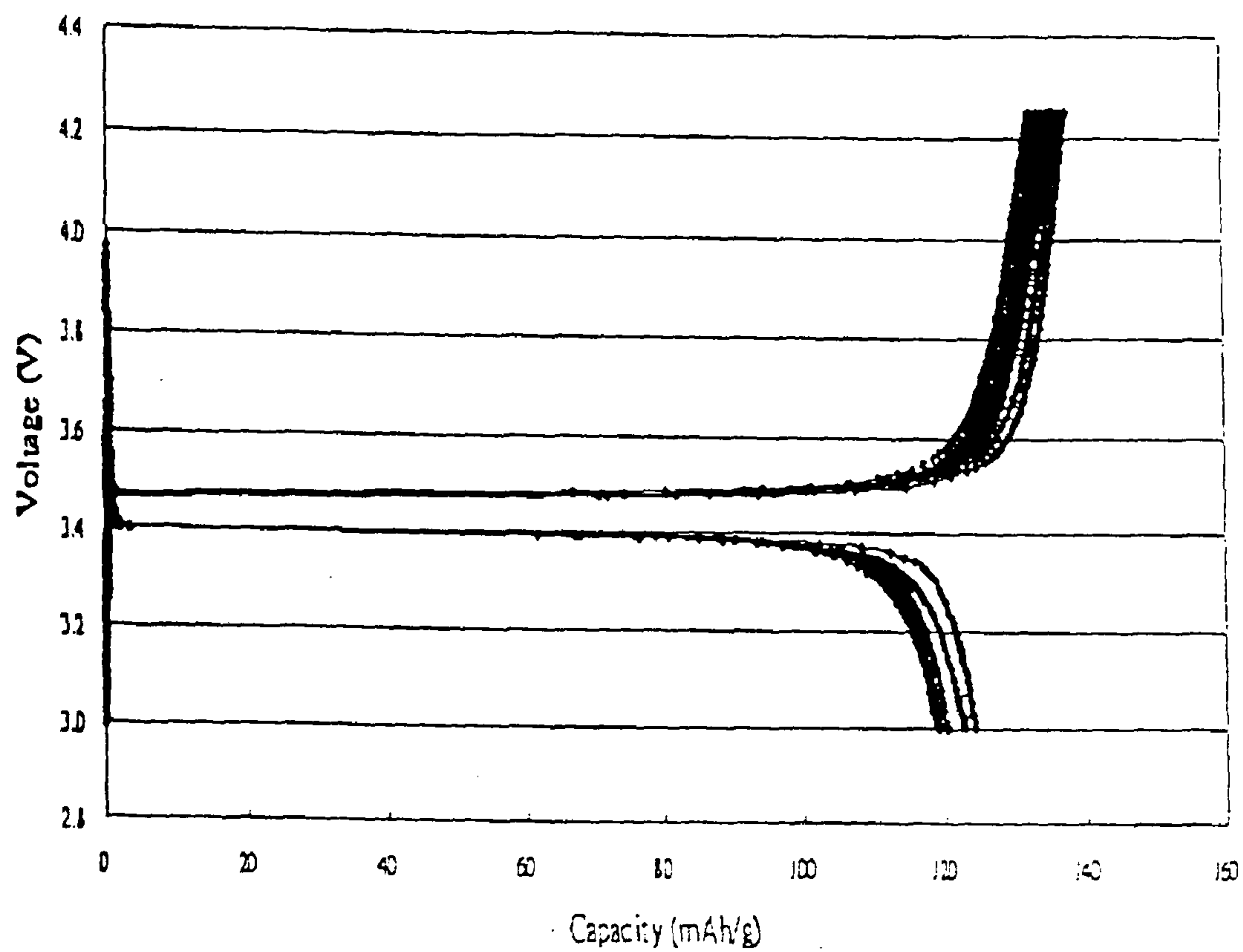


Fig. 6

