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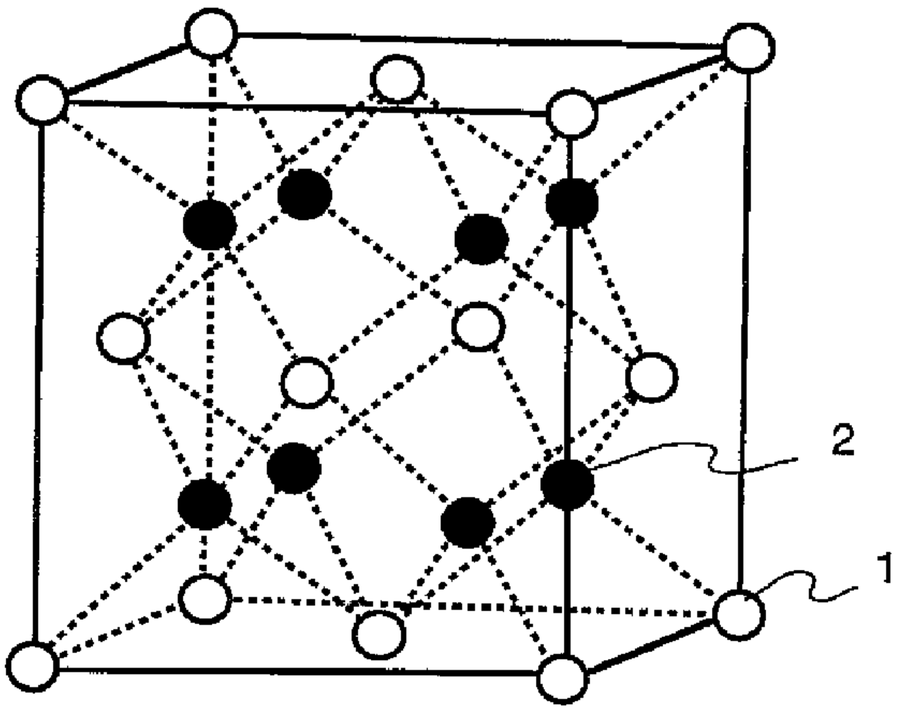
(54) **BATTERIE D'ACCUMULATEURS A ELECTROLYTE NON AQUEUX ET MATERIAU DE CONSTITUTION DE L'ELECTRODE NEGATIVE**

(54) **NONAQUEOUS SECONDARY BATTERY AND NEGATIVE ELECTRODE MATERIAL THEREFOR**




(57) A nonaqueous secondary battery achieves a long life-time and a high capacity density by increasing the discharging capacity and extending the life-time of the negative electrode. The battery has a positive electrode and a negative electrode reversibly absorbing and discharging an alkaline metal and a nonaqueous electrolyte. The negative electrode is made of an inter-metallic compound containing at least one element selected from the group consisting of 4B group elements, P and Sb. The inter-metallic compound has any one of $CaF_2$ type, ZnS type and AlLiSi type crystal structures. The $CaF_2$ type structure is either an inverse-fluorite structure or a fluorite structure having a lattice constant larger than 6.36 Å.

**Abstract**

A nonaqueous secondary battery achieves a long life-time and a high capacity density by increasing the discharging capacity and extending the life-time of the negative electrode. The battery has a positive electrode and a negative electrode reversibly absorbing and discharging an alkaline metal and a nonaqueous electrolyte. The negative electrode is made of an inter-metallic compound containing at least one element selected from the group consisting of 4B group elements, P and Sb. The inter-metallic compound has any one of $CaF_2$ type, ZnS type and AlLiSi type crystal structures. The $CaF_2$ type structure is either an inverse-fluorite structure or a fluorite structure having a lattice constant larger than 6.36 Å.

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# NONAQUEOUS SECONDARY BATTERY AND NEGATIVE ELECTRODE MATERIAL THEREFOR

The present invention relates to a nonaqueous secondary battery, and, more particularly, to a long life-time and high energy-density nonaqueous secondary battery, and to a negative electrode material therefor, suitable for a portable device power source.

A nonaqueous secondary battery comprises a negative electrode made of an alkaline metal having a low ionization potential. Such a nonaqueous secondary battery can attain a high energy density compared to a conventional aqueous secondary battery. Among secondary batteries of such a kind, a lithium secondary battery is light in weight and high in energy density, and promises to be utilized as a power source for portable devices such as a notebook-type personal computer, a video camera, a cellular phone or the like, because lithium is the lightest metal and has the lowest electric potential of base metals.

The lithium secondary battery using the simple substance of lithium metal as the negative electrode has problems in safety and the life-time of the battery, because the lithium deposition on the surface of the negative electrode during charging is of dendrite which causes an inner short-circuit with the positive electrode or an inactivation reaction with the electrolyte.

Therefore, materials used for the negative electrode are lithium alloys or lithium compounds, instead of the single element lithium. These materials prevent the dendritic deposition of lithium by chemically reacting the deposited lithium during charging with the base material, and by containing the lithium inside the chemical compound.

Such materials that have been studied are lithium alloys, such as Li-Al, Li-Cd, Li-In, Li-Pb, Li-Bi and the like and Li-C. For example lithium alloys are disclosed in USP 4,002,492 and USP 5,294,503, and Li-C is disclosed in Japanese Patent

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Application Laid-open No. 62-23433. However, in the cases of the lithium alloys, sufficient life-time for charging and discharging is not attained. In the case of the Li-C, the energy capacity density per weight is one-tenth as small as those of the single element lithium metal electrode, and accordingly the lithium characteristic of high energy capacity density per weight is not utilized.

In connection with the negative electrode in a secondary battery, it is required to improve the energy density of the battery by increasing its charging capacity and its discharging capacity. In addition to improvement of the energy density of the battery, it is also required to increase its life-time.

It has been difficult to improve both the energy density of the battery and its life-time at the same time. Large change of lithium concentration in the conventional alloy during charging and discharging causes a change in crystal structure over a plurality of different phases, since the width of the lithium concentration range allowable for one kind of the phases is small.

When the battery is operated at room temperature, a mixture of plural phases having different structures appears in the alloy electrode, and the electrode alloy is pulverized by stress and strain produced in the boundaries between different phases, because a thermal equilibrium state is not attained.

The pulverization increases the electrically isolating portions. This causes a decrease in the capacity of the battery at repeated charge and discharge. Therefore, such a material for the negative electrode cannot attain sufficient reversibility.

An example of a base material having sufficient reversibility is carbon, of which the upper limit of the capacity is 372 mAh/g where the inter-granular compound of $LiC_6$ is formed. However, further increase of the capacity brings accompanying problems, although various attempts have been made to avoid these.

As to the essential characteristics of the material of the negative electrode in a secondary battery, that is, a long life-time and a high energy capacity, in the conventional technology, the lithium alloys cannot satisfy the long life-time condition, and Li-C cannot attain the sufficient energy capacity condition, as described above.

An object of the present invention is to provide a high energy capacity and long life-time nonaqueous secondary battery and a negative electrode material therefor by using a lithium alloy for the negative electrode that has an energy capacity higher than that of Li-C and has a long life-time.

In a nonaqueous secondary battery having a positive electrode and a negative electrode reversibly absorbing and discharging an alkaline metal and a nonaqueous electrolyte, the present invention is characterized by the fact that the discharging capacity of the negative electrode during a period is 1000 to 2500 $mAh/cm^3$, this period being from a time when the battery starts to be discharged in the condition of a steady-state current of 0.5 $mA/cm^2$ after having been charged to a time when the voltage between the negative electrode and the positive electrode became 1.0 V.

The negative electrode may be made of an inter-metallic compound containing at least one element selected from the group consisting of 4B group elements, P and Sb, the inter-metallic compound having any one of $CaF_2$ type, ZnS type and AlLiSi type crystal structures, the $CaF_2$ type structure being either an inverse-fluorite structure or a fluorite structure having a lattice constant larger than 6.36 Å.

In another aspect the negative electrode is made of an inter-metallic compound of a cubic crystal system, the inter-metallic compound having any one of $CaF_2$ type, ZnS type and AlLiSi type crystal structures, the $CaF_2$ type structure being either an inverse-fluorite structure or a fluorite structure having a lattice constant larger than 6.36 Å.

The negative electrode may be made of an inter-metallic compound having any one of $CaF_2$ type, ZnS type and AlLiSi type crystal structures, the $CaF_2$ type structure being either an

inverse-fluorite structure or a fluorite structure having a lattice constant larger than 6.36 Å.

The negative electrode may be made of an inter-metallic compound in which the space group of the crystal lattice of the inter-metallic compound is F4-3m.

The negative electrode may be made of any one of inter-metallic compounds $Mg_2Sn$, $Mg_2Pb$, $NiSi_2$, AlP, AlSb, CuMgSb, $Mg_2Ge$ and $CoSi_2$.

It is preferable that the negative electrode material have a charging capacity per volume of 1000 to 3500 $mAh/cm^3$.

It is further preferable that the negative electrode material have a charging capacity per volume of 2200 to 3500 $mAh/cm^3$.

It is preferable that the negative electrode material has a charging capacity per weight of 380 to 1400 mAh/g.

The negative electrode material has a discharging capacity for a period of 1000 to 2500 $mAh/cm^3$. The period is from a time when the battery starts to be discharged in the condition of a steady-state current of 0.5 $mA/cm^2$ after having been charged to a time when the voltage between the negative electrode and a positive electrode in the battery became 1.0 V.

By using an inter-metallic compound as the base material of a negative electrode for absorbing and discharging lithium, lithium can be reversibly absorbed into and discharged from the base alloy of the negative electrode during charging and discharging of the battery, and the absorbed and discharged amount of lithium is larger than that in carbon material. Therefore, it is possible to realize a nonaqueous secondary battery that is good in charging and discharging characteristic and high in energy capacity.

Actually, the lithium concentration in the lithium alloy varies largely during charging and discharging the battery. When using a conventional negative electrode material of lithium alloy, such as LiAl, the width of the lithium concentration range allowable for one kind of phase is narrow. Accordingly the lithium alloy absorbs or discharges lithium

while the phase of the lithium alloy is varying corresponding to the lithium concentration of the lithium alloy during charging and discharging of the battery. Since the battery is operated at room temperature, it is difficult to attain thermal equilibrium in the solid metallic material, and the distribution of lithium concentration in the alloy is apt to become non-uniform. Therefore, the electrode alloy is pulverized by stress and strain produced in the boundaries between different phases, and consequently the energy capacity of the electrode is reduced due to an increase in the number of the pulverized portions that are electrically isolated. Conventional alloys for a negative electrode are a binary alloy of lithium and a single metallic element, such as Li-Al or Li-Pb, or an alloy made by adding a third element to the binary alloy in order to stabilize the phases. Since the phase of the alloy during absorbing lithium and the phase during discharging lithium have different crystal structures, a discontinuous and sharp volume change occurs depending on the change in the lithium concentration. The volume of the alloy Li-Al swells nearly twice as much during absorbing lithium and shrinks one, one half as small during discharging lithium. The volume of the alloy Li-Pb increases by 20% during absorbing lithium, due to reaction from $Li_8Pb_3$ to $Li_7Pb_2$, and decreases by 17% during discharging lithium. Therefore, in such negative electrode active substances, sufficient reversibility cannot be obtained for charging and discharging of the battery, and accordingly the life cycle of the battery is short.

In order to prevent such a phenomenon, the negative electrode active substance employed in the preferred forms of the present invention is an inter-metallic compound of which the frame structure of the crystal lattice does not change with a large change in the lithium concentration during charging and discharging of the battery. In other words, the inter-metallic compound is such that the deformation caused during charging and discharging of the battery is only expansion or contraction. The inter-metallic compound

containing 4B group element, P or Sb can contain lithium in its solid matrix without destroying its basic crystal frame. Therefore, the crystal structure is not changed, and the volume change is caused only by expansion and contraction of the crystal lattice and is accordingly small.

This yields good reversibility, both for the alloy itself and for the electrode construction as an assembly of the alloy.

Although materials applicable for the negative electrode other than the 4B group elements, P and Sb, are As, Se, Te, these latter elements are not preferable because of their toxicity. Further, in addition to this, preferable materials for the negative electrode are of light weight metal or of small atomic number. Furthermore, it is preferable that the crystal structure of the inter-metallic compound be of cubic crystal system. The cubic crystal has three-dimensional diffusion paths for lithium atoms and has a larger freedom of lithium diffusion compared to an inter-layer compound that has two-dimensional diffusion paths. In addition to this, since the cubic crystal isometrically deforms in three directions, the amount of deformation in one direction is small, so that the reversibility of absorbing and discharging of lithium is better. Further, it is preferable that the lattice constant of the crystal be large. Since the space inside the lattice is larger, as the lattice constant is larger, the activation energy of diffusion is low and the lithium atoms easily diffuse. Thereby, lithium is taken into the solid in a short time when the lithium is electrolytically deposited on the surface of the alloy during charging of the battery, and, at the same time, the inactivation reaction of the lithium with the electrolyte on the surface of the alloy can be suppressed. Since the deformation rate of the lattice can be kept small, the expansion and contraction of the alloy can also be kept small, so that the structure of the electrode is not significantly destroyed.

To enable the invention to be further described with the aid of diagrams, the figures of the drawings will first be listed.

FIG. 1 is a view showing the space lattice of a face centered cubic crystal and the positions of tetrahedrons.

FIG. 2 is a graph showing the interstice ratio of cubic crystal structures according to the solid sphere model.

FIG. 3 is a view showing the construction of a battery used for a test.

FIG. 4 is a graph showing the relationship between capacity density per weight and capacity density per volume for inter-metallic compounds.

FIG. 5 is a graph showing discharge characteristics of inter-metallic compounds.

FIG. 6 is a graph showing charge and discharge cycle characteristics of inter-metallic compounds.

FIG. 7 is a graph showing the volume change of $Mg_2Ge$ during charging and discharging.

FIG. 8 is a view showing the space lattice of a $CaF_2$ type structure.

FIG. 9 is a view showing the space lattice of a ZnS type structure.

FIG. 10 is a view showing the space lattice of an AlLiSi type structure.

FIG. 11 is a chart showing an X-ray diffraction image of $Mg_2Ge$ (before and after absorbing Li).

FIG. 12 is a chart showing a change in an X-ray diffraction image of $Mg_2Ge$ (absorbing and discharging Li).

FIG. 13 is a graph showing the relationship between the number of Li elements in a unit cell of a lattice and the interstitial volume in a unit cell of a lattice.

FIG. 14 is a graph showing the relationship between the discharge capacity and the number of cycles.

FIG. 15 is a cross-sectional view showing a coil battery.

FIG. 16 is a cross-sectional view showing a cylindrical battery.

The preferable crystal structure is that all or a part of the eight positions of the tetrahedrons inside the face centered cubic lattice shown in FIG. 1 are occupied. The structures in which all or a part of the eight positions of the tetrahedrons inside a face centered cubic lattice are occupied are of the $CaF_2$ type structure shown in FIG. 8, ZnS type structure shown in FIG. 9 and AlLiSi type structure shown in FIG. 10 which have large porosities in the crystal lattice.

It can be understood from FIG. 2 that the $CaF_2$ type structure, the ZnS type structure and the AlLiSi type structure have large porosities in crystal lattice compared to the closest packed cubic structure, body centered cubic structure and simple cubic structure, and have consequently better diffusivities of lithium inside the solid and better lithium containing abilities. The porosities in the crystal lattice are nearly 26% for the closes packed cubic structure, nearly 32% for the body centered cubic structure and nearly 48% for the simple cubic structure, while being nearly 51% for the $CaF_2$ type structure and the AlLiSi type structure, and nearly 66% for the ZnS type structure.

It can be understood that the simple cubic structures, i.e. the $CaF_2$ type structure, the ZnS type structure and the AlLiSi type structure, have large porosities in the crystal lattice above 40%, which is larger than those of the closest packed cubic structure and the body centered cubic structure, and have consequently better diffusivities of lithium inside the solid and better lithium containing abilities.

The ZnS type structure and the AlLiSi type structure are space groups of crystal lattice of F4-3m, which have large porosities in the crystal lattice and have consequently better diffusivities of lithium inside the solid and better lithium containing abilities.

That is, the discharging capacity of the negative electrode material can be increased and its life time can be increased by setting the discharging capacity of the material obtained from time-integration of the current during a period to 1000 to 2500 $mAh/cm^3$, the period being from a time when the

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battery starts to be discharged in a condition of a steady-state current of 0.5 mA/cm$^2$ after having been charged to a time when the voltage between the negative electrode and the lithium metal reference electrode became 1.0 V. By using this negative electrode material in a nonaqueous secondary battery, it is possible to provide a long life-time and high energy battery.

**Detailed Description of the Preferred Embodiments**

Table 1 shows examples of inter-metallic compounds that contain at least one of the 4B group elements of Si, Ge, Sn, Pb and P and Sb, and have cubic crystal structures.

Table 1

| ELEMENT | INTER-METALLIC COMPOUND | CRYSTAL STRUCTURE |
|---|---|---|
| Si | $NiSi_2$ | $CaF_2$ type structure (inverse fluorite structure) |
| | $CoSi_2$ | $CaF_2$ type structure (inverse fluorite structure) |
| | $Mg_2Si$ | $CaF_2$ type structure (inverse fluorite structure) |
| Ge | $Mg_2Ge$ | $CaF_2$ type structure (inverse fluorite structure) |
| Sn | $Mg_2Sn$ | $CaF_2$ type structure (inverse fluorite structure) |
| Pb | $Mg_2Pb$ | $CaF_2$ type structure (inverse fluorite structure) |
| P | AlP | ZnS type structure |
| | GaP | ZnS type structure |
| | InP | ZnS type structure |
| Sb | AlSb | ZnS type structure |
| | GaSb | ZnS type structure |
| | InSb | ZnS type structure |
| | CuMgSb | AlLiSi type structure |
| | MgPdSb | AlLiSi type structure |
| | MgNiSb | AlLiSi type structure |

AlP, AlSb and CuMgSb are space groups of crystal lattice of F4-3m.

Manufacturing and measurement of all cells for test evaluation were performed in an argon gas environment.

An electrode was formed as a complex electrode according to the geometries of the electrode used in an actual battery by mixing a powder alloy with a binding agent and carbon.

Each of the following test result shows the combined characteristics of the physical property of each alloy itself and the manufacturing process of the electrode, and consequently is equivalent to a test result of an actual battery using each of the alloys.

The inter-metallic compound powders $NiSi_2$, $Mg_2Ge$, $Mg_2Sn$, $Mg_2Pb$, AlP, AlSb, CuMgSb for the negative electrodes were prepared by vacuum-melting the materials and pulverizing them under an argon environment to form powders having a grain size below 45 $\mu$m.

These powders were analyzed by an Z-ray diffraction method, and it was confirmed that $NiSi_2$, $Mg_2Ge$, $Mg_2Sn$, $Mg_2Pb$ were of the $CaF_2$ type structure, AlP, AlSb were of the ZnS type structure and CuMgSb had the AlLiSi type structure.

Pastes of mixed agents were prepared by mixing and kneading these powders with an ethylene-propylene-diene ternary co-polymer (EPDM) (concentration of 40 g/l dissolved with xylene) of 5.0 wt% as a binding agent and heat-dehydrated acetylene black having a specific surface area of 61 $m_2$ of 10 wt% as a conductivity adding powder.

The paste of mixed agent was applied to a collector copper film and vacuum-dried at room temperature for 2 hours, and then pressed with 500 kg/cm$^2$ for 10 minutes and cut into a disk-shape having a diameter of 15 mm to form a negative electrode.

A positive electrode was formed by mixing and kneading $LiCoO_2$ of 80 wt% with acetylene black of 15 wt% and tetra-fluoro-ethylene (PTFE) of 5 wt% to prepare a mixed agent, and pressing the mixed agent of 0.2 g with 200 kg/cm$^2$ using a

piston and cylinder having a diameter of 15 mm to form into a disk shape.

A test battery shown in FIG. 3 was manufactured using both of the aforementioned electrodes, a fine porous poly-propylene film as a separator, a mixture of $LiPF_8$/propylene carbonate of 1 mol/l concentration + 1, 2 dimethoxy ethane (50 % solution) as an electrolyte, and a lithium metal reference electrode. Referring to FIG. 3, the test battery includes the negative electrode 4, the positive electrode 5, the separators 6, the lithium metal reference electrode 7, stainless steel plates 8 for fixing both the positive electrode and the negative electrode, wires 9, a vessel 10, a cover 11, the electrolyte 12 and a positive electrode side collector 13.

The test electrode faces the opposed electrode of lithium metal through a porous poly-propylene separator, and is located between and pressed by the stainless steel separators.

This construction is to prevent the mixed agent from swelling by absorbing the electrolyte and for suppressing the occurrence of poor contact between the constituent parts to produce electrically isolated portions inside the electrode due to a volume change caused by lithium absorption and discharge of the alloy powder during charging and discharging of the battery.

Lithium metal was used for the reference electrode to measure an electric potential of the test electrode in the base of the electric potential of the ($Li/Li^+$). Measurement of the charging capacity of the negative electrode using the battery was conducted by performing under the condition of a steady-state charging current of 0.1 $mA/cm^2$, and measuring the time until the electric potential became 0 Volt between the negative electrode and the lithium metal reference electrode, and then determining the amount of lithium absorbed in the negative electrode, that is to say, the electrolytic depositing amount of lithium by time-integration of the conducted current.

The volume of the inter-metallic compound was determined by subtracting the known volume of the acetylene black from the volume of the negative electrode.

Results of X-ray diffraction analyses of the negative electrodes in the charged states suggested that each of the diffraction image patterns before charging for the inter-metallic compounds was maintained and the space lattice was uniformly expanded, and that accordingly lithium atoms were contained between the lattice of the crystal structure without the crystal structure before charging being destroyed.

FIG. 4 and Table 2 show the relationship between the charging capacity per weight and the charging capacity per volume for the inter-metallic compounds.

Table 2

| INTER-METALLIC COMPOUND | $MoSi_2$ | $TiSi_2$ | $NiSi_2$ | $NiSi_2$ | $Mg_2Sn$ |
|---|---|---|---|---|---|
| Charging capacity per weight (mAh/g) | 36 | 200 | 138 | 499 | 788 |
| Charging capacity per volume ($mAh/cm^3$) | 225 | 804 | 997 | 2445 | 2837 |
| INTER-METALLIC COMPOUND | $Mg_2Pb$ | $Mg_2Ge$ | AlP | AlSb | CuMgSb |
| Charging capacity per weight (mAh/g) | 524 | 1139 | 1386 | 795 | 382 |
| Charging capacity per volume ($mAh/cm^3$) | 2786 | 3531 | 2911 | 3418 | 2292 |

For the purpose of comparison, from silicon inter-metallic compounds having crystal structures other than a cubic crystal structure, negative electrodes of $MoSi_2$ (tetragonal crystal structure), $TiSi_2$ (orthorhombic crystal structure) and $Ni_2Si$ (orthorhombic crystal structure) were manufactured and evaluated by the same methods.

Each of the inter-metallic compounds NiSi, $Mg_2Sn$, $Mg_2Pb$, AlP, AlSb and CuMgSb, has a large charging capacity, which is larger than the theoretical capacity of the typical negative material, carbon, that is 372 (mAh/g) and 837 ($mAh/cm^3$).

The charging capacity per weight and the charging capacity per volume for each of the negative electrodes are

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compared with those of the theoretical capacities for carbon, and the results are shown in Table 3.

As shown in Table 3, the charging capacities per weight of the negative electrodes are nearly 1.03 to 3.73 times as large as the theoretical value of the carbon electrode and the charging capacities per volume of the negative electrodes are nearly 2.74 to 4.08 times as large as the theoretical value of the carbon electrode. Especially, the charging capacities per weight of five kinds of the negative electrodes for AlP, $Mg_2Ge$, AlSb, $Mg_2Sn$ and $Mg_2Pb$ are more than twice as large as the theoretical value of the carbon electrode and the charging capacities per volume of the negative electrodes are more than three times as large as the theoretical value of the carbon electrode.

A discharging test was performed by discharging in the condition of a steady-state current of 0.5 $mA/cm^2$ after being charged and the discharging capacity of the negative electrode material was obtained from time-integration of the current during a period from a time when the battery started to be discharged to a time when the voltage between the negative electrode and the lithium metal reference electrode becomes 1.0 V.

Table 3

| Material of Negative electrode | Magnitude of Charging Capacity to Theoretical Capacity of Carbon (Times) | | Discharging Capacity ($mAh/cm^3$) |
|---|---|---|---|
| | Weight | Volume | |
| C | | | 700 |
| Li-$NiSi_2$ | 1.34 | 2.92 | 1380 |
| Li-$Mg_2Ge$ | 3.06 | 4.21 | 1420 |
| Li-AlP | 3.73 | 3.48 | 1910 |
| Li-AlSb | 2.14 | 4.08 | 2250 |
| Li-CuMgSb | 1.03 | 2.74 | 1910 |
| Li-$Mg_2Sn$ | 2.12 | 3.39 | 1807 |
| Li-$Mg_2Pb$ | 1.41 | 3.33 | 1775 |

FIG. 5 shows the change in electrical potential during the discharging process and the attainable discharging capacity for each of the batteries having the inter-metallic compounds and carbon, until the electric potential becomes 1.0 V.

The discharging curve for carbon changes slowly in the electrical potential range from 0 to approximately 0.2 V, and steeply changes when the discharging capacity exceeds approximately 500 $mAh/cm^3$, and then the discharging capacity reaches approximately 700 $mAh/cm^3$ at the potential of 1.0 V.

The discharging curve for Li-$NiSi_2$ changes gradually in the potential range from 0 to approximately 0.4 V, changes slowly in the range from approximately 0.4 to approximately 0.5 V, and steeply when the discharging capacity exceeds approximately 1100 $mAh/cm^3$. The discharging capacity reaches approximately 1380 $mAh/cm^3$ at the potential of 1.0 V.

The discharging curve for Li-$Mg_2Ge$ changes gradually until a point of discharging capacity of approximately 40 $mAh/cm^3$ and then enters a plateau at a level of approximately 0.25 V. After discharging approximately 300 $mAh/cm^3$ at the plateau, the curve changes steeply and enters another plateau at a level of approximately 0.65 V. After discharging approximately 200 $mAh/cm^3$ at the second plateau, the curve changes steeply again and then the discharging capacity reaches approximately 1420 $mAh/cm^3$ at the potential of 1.0 V.

The discharging curve for Li-$Mg_2Pb$ changes gradually, and after discharging approximately 1600 $mAh/cm^3$ the discharging capacity reaches approximately 1775 $mAh/cm^3$ at the potential of 1.0 V.

The discharging curve for Li-$Mg_2Sn$ changes gradually, and after discharging approximately 1700 $mAh/cm^3$ the discharging capacity reaches approximately 1807 $mAh/cm^3$ at the potential of 1.0 V.

The discharging curve for Li-AlP changes gradually, and the discharging capacity reaches approximately 1910 $mAh/cm^3$ at the potential of 1.0 V.

The discharging curve for Li-AlSb changes gradually, and the discharging capacity reaches approximately 2250 mAh/cm$^3$ at the potential of 1.0 V.

The discharging curve for Li-CuMgSb changes slowly in the range from 0 to approximately 0.3 V, gradually when the discharging capacity exceeds approximately 750 mAh/cm$^3$, and steeply when the discharging capacity exceeds approximately 1500 mAh/cm$^3$, and then the discharging capacity reaches approximately 1890 mAh/cm$^3$ at the potential of 1.0 V.

Comparing these with the discharging capacity of carbon of approximately 700 mAh/cm$^3$ at the potential of 1.0 V, the discharging capacity for Li-$NiSi_2$ is approximately 1.97 times as high, the discharging capacity for Li-$Mg_2Ge$ is approximately 1.70 times as high, the discharging capacity for Li-$Mg_2Sn$ is approximately 2.15 times as high, the discharging capacity for Li-$Mg_2Pb$ is approximately 2.12 times as high, the discharging capacity for Li-AlP is approximately 2.72 times as high, the discharging capacity for Li-AlSb is approximately 3.21 times as high, and the discharging capacity for Li-CuMgSb is approximately 2.70 times as high. It can be understood that the discharging capacities for the negative electrode materials used in the present invention are approximately two to three times larger than for carbon.

As described above, in comparing to the conventional carbon electrode, the charging capacities per weight of the negative electrodes according to this embodiment is approximately 1.03 to 3.73 times as large and the charging capacities per volume of the negative electrodes according to this embodiment is approximately 2.74 to 4.08 times as large. The discharging capacities are approximately 2 to 3 times larger than that of carbon.

[Embodiment 2]

The inter-metallic compounds shown in Table 4 were manufactured by the same method as in Embodiment 1 and the same tests as in Embodiment 1 were performed using the battery shown in FIG. 3. The results are shown in Table 4.

According to the X-ray diffraction images of the negative electrodes in the charged states, the x-ray diffraction image pattern before charging for each of the inter-metallic compounds was maintained, but the pattern was shifted to the low angle side. Therefore, it was suggested that each of the diffraction image patterns before charging for the inter-metallic compounds was maintained, and the space lattice was uniformly expanded. Accordingly, lithium atoms were contained between the lattice of the crystal structure without the crystal structure that existed before charging being destroyed.

Table 4

| MATERIAL OF NEGATIVE ELECTRODE | CHARGING CAPACITY PER WEIGHT (mAh/g) | CHARGING CAPACITY PER VOLUME (mAh/cm$^3$) | MAGNITUDE OF CHARGING CAPACITY TO THEORETICAL CAPACITY OF CARBON (TIMES) | | CRYSTAL STRUCTURE |
|---|---|---|---|---|---|
| | | | CHARGING CAPACITY PER WEIGHT | CHARGING CAPACITY PER VOLUME | |
| $NiSi_2$ | 499 | 2445 | 1.34 | 2.92 | cubic |
| $Mg_2Si$ | 1607 | 3053 | 4.32 | 3.65 | cubic |
| $Mg_2Ge$ | 1095 | 3384 | 2.94 | 4.04 | cubic |
| $Mg_2Sn$ | 788 | 2837 | 2.12 | 3.39 | cubic |
| $Mg_2Pb$ | 524 | 2786 | 4.41 | 3.33 | cubic |
| AlSb | 795 | 3418 | 2.14 | 4.08 | cubic |
| $CoSi_2$ | 108 | 539 | 0.29 | 0.64 | cubic |
| $MoSi_2$ | 58 | 363 | 0.16 | 0.43 | tetragonal |
| $TiSi_2$ | 252 | 1013 | 0.76 | 1.21 | ortho-rhombic |
| $Ni_2Si$ | 138 | 997 | 0.37 | 1.19 | ortho-rhombic |

FIG. 13 is a graph showing the relationship between the number of Li atoms in a unit cell of a lattice determined from the charging capacity and the interstitial volume in a unit cell of a lattice for each of the inter-metallic compounds. The interstitial volume in a unit cell of a lattice can be determined from the crystal structure and the lattice constant. In the tetragonal crystal structure and the

orthorhombic crystal structure, the number of Li atoms entered into a unit cell of a lattice is few, and, even in a case where the interstitial volume in a unit cell of a lattice is large, the number of Li atoms capable of entering into a unit cell of a lattice increases very little. On the other hand, in the cubic crystal structure, in a case where the interstitial volume in a unit cell of a lattice is large, the number of Li atoms capable of entering into a unit cell of a lattice increases greatly. From the above facts, in order to increase the charging capacity, it is preferable that the negative electrode be made of an inter-metallic compound, the crystal structure of the inter-metallic compound, the crystal structure of the inter-metallic compound be cubic, and the lattice constant of the cubic crystal structure be large.

By employing an inter-metallic compound of lithium interstitial-lattice type having a cubic crystal structure as described above, in comparison to the conventional carbon electrode, the charging capacities per weight of the negative electrodes according to this embodiment are approximately 1.03 to 3.73 times as large and the charging capacities per volume are approximately 2.74 to 4.08 times as large.

[Embodiment 3]

From the diffraction image shown in FIG. 11, it was confirmed that a test sample of $Mg_2Ge$ was nearly a single phase sample of $Mg_2Ge$ having a cubic crystal of the $CaF_2$ type structure. A charging test was performed using the same test electrode and the same construction of battery as in Embodiment 1 with a charging current density of 0.1 $mA/cm^2$. The diffraction image of the sample after lithium absorption was shifted to the low angle side, while the diffraction peaks were maintained. From the result, it was considered that lithium atoms entered the lattice without changing the frame structure. The linear expansion rate was approximately 0.47% and the volume expansion rate was approximately 1.42%.

A lithium-free sample was made by removing lithium from a lithium absorbed sample, and the structure change was studied using the lithium-free sample. An alloy after absorbing

A

lithium was discharged at the same current density as the current density at which lithium was absorbed in the alloy until the electrical potential became 1.0 V, and then further discharged for 1.3 days while the discharge current was exponentially decreased so as to maintain the potential at 1.0 V.

As shown in FIG. 12, the diffraction image of the above sample maintains the diffraction peaks before absorbing lithium, and the peaks are shifted to the higher angle side compared to the sample before absorbing lithium.

This means that the frame structure of the lattice was maintained but has contracted in this case.

That is, the results can be summarized as follows.

FIG. 7 shows the volume change of $Mg_2Ge$ during charging and discharging.

The lattice constant of $Mg_2Ge$ before absorbing lithium is 6.386 Å, and the lattice constant after absorbing lithium increased by 1.004697776 times and became 6.416 Å. then, after discharging, the lattice constant returned to 6.386 Å. Since the change in lattice constant was small, the volume change due to absorbing lithium and discharging was small.

Further, in the case of removing lithium from the sample of $Mg_2Ge$, the lattice constant changed by the order of $10^{-3}$ Å, and therefore, $Mg_2Ge$ had sufficient reversibility for the charging and discharging reaction.

A charging and discharging cycle life-time test was performed. After charging was performed using the same test electrode and the same construction of battery as in Embodiment 1 with a charging current density of 0.1 $mA/cm^2$, the test was performed by setting the discharging depth to a constant value of 160 mAh/g, charging and discharging terminal electrical potentials to 0 V and 1.0 V, respectively, and a current density to 20 mA/g.

For the purpose of comparison, a Li-Pb alloy, not of the lithium interstitial-lattice type was also used.

FIG. 6 shows the results. The reference character a indicates the charge and discharge cycle life-time

A

characteristic of Li-Pb and the reference character b indicates the charge and discharge cycle life-time characteristics of inter-metallic compounds in accordance with the present invention, that is, NiSi, $Mg_2Ge$, $Mg_2Sn$, $Mg_2Pb$, AlP, AlSb and CuMgSb.

The alloys for negative electrode materials according to the present invention show stable charge and discharge cycle life-time characteristics. On the other hand, in Li-Pb, which is not of the lithium interstitial-lattice type, there is a large volume change of the negative electrode alloy at charging and discharging, and the discharging capacity density steeply decreases.

The charge and discharge cycle life-time characteristic curve for Li-Pb maintains 160 mAh/g until 8 cycles, but steeply decreases after that and becomes 60 mAh/g at 18 cycles. It can be understood that the discharging capacity density decreases to 37.5 % at nearly 20 cycles, and the life-time of Li-Pb is short.

The charge and discharge cycle life-time characteristic curves for the inter-metallic compounds in accordance with the present invention, that is, NiSi, $Mg_2Ge$, $Mg_2Sn$, $Mg_2Pb$, AlP, AlSb and CuMgSb maintain 160 mAh/g until 20 cycles and further maintain 160 mAh/g even for 50 cycles. The inter-metallic compounds in accordance with the present invention can maintain the initial discharging capacity at cycles of more than 50, and the life-time can be substantially extended.

It can be understood that the number of cycles capable of maintaining 160 mAh/g for the inter-metallic compounds in accordance with the present invention is more than 50 cycles which is approximately 6.25 times as much as the 8 cycles capable of maintaining 160 mAh/g for Li-Pb.

[Embodiment 4]

A charging and discharging cycle life-time test was performed using the same test electrode and the same construction of battery as in Embodiment 1 under the condition that the charging current density was set to 0.5 $mA/cm^2$, charging and discharging terminal electric potentials were set

to 0 V and 1.0 V with respect to the potential of ($Li/Li^+$), respectively, and a 30-minute pause was provided between charging and discharging. This condition is for a high capacity discharging test, since discharging is performed up to a high potential of 1.0 V and there is no limitation in the electrical capacity during discharging.

Table 5 shows the lattice constants of the cubic crystal inter-metallic compounds.

That is, the lattice constant for $Mg_2Pb$ is 6.836 Å, the lattice constant for $Mg_2Sn$ is 6.77 Å and the lattice constant for $Mg_2Si$ is 6.35 Å.

Table 5

| INTER-METALLIC COMPOUND | $NiSi_2$ | $Mg_2Si$ | $Mg_2Sn$ | $Mg_2Pb$ |
|---|---|---|---|---|
| LATTICE CONSTANT (Å) | 5.38 | 6.35 | 6.77 | 6.836 |

FIG. 14 is a graph showing cycle characteristics for $NiSi_2$, $Mg_2Si$, $Mg_2Sn$ and $Mg_2Pb$. In the high capacity discharging test condition, the discharging capacities for $NiSi_2$ and $Mg_2Si$ having small lattice constants decrease steeply as the cycles increase, the discharging capacity for $NiSi_2$ decreases to below 10% of the initial discharging capacity at 10 cycles and the discharging capacity for $Mg_2Si$ decreases to 20% of the initial discharging capacity at 10 cycles. However, although the discharging capacities for $Mg_2Sn$ and $Mg_2Pb$ having lattice constants of above 6.36 Å decrease in several initial cycles, the discharging capacity for $Mg_2Sn$ can maintain 900 Ah/l above 70 cycles and the discharging capacity for $Mg_2Pb$ can maintain 930 Ah/l above 70 cycles. That is to say, by employing an alloy of an inter-metallic compound having a cubic crystal structure of which the lattice constant is above 6.36 Å, and an alkaline metal, the life-time of the negative electrode material can be substantially extended.

[Embodiment 5]

A coin-type battery shown in FIG. 15 was manufactured using a positive electrode and a negative electrode

manufactured in the same method as in Embodiment 1. The coin-type battery includes a negative electrode 22, a positive electrode 23, a separator 24, a negative electrode side case 25 and a positive electrode side case 26. Although in Embodiment 1 the negative electrode material paste was applied to a copper film, in this embodiment the negative electrode material was formed in a disk-shape as the positive electrode.

The non-aqueous electrolyte liquid 14 used was a solution containing 1 mol/litre concentration of $LiPE_6$ added to a mixture of equal volumes of propylene carbonate (PC) and 1,2-dimethoxy ethane (DME).

The separator 24 was a porous propylene film. An aluminum plate is used for a positive electrode side collector 10 and a nickel plate was used for a negative electrode side collector 20. The battery vessel was composed of the positive electrode side case 26 and the negative electrode side case 25. Both were made of stainless steel (SUS304), and a gasket 16 made of poly-propylene was provided for fixing the cases 26 and 25.

In this coin-type battery, the discharging capacity was increased and the life-time was also extended.

In making an alloy of lithium and the inter-metallic compound containing any one of 4B group elements and P and Sb, only the electro-chemical method has been described in the embodiments. In the electro-chemical method, the inter-metallic compound is electrolytically reduced in an electrolyte liquid containing a lithium salt in a battery. However, a metallurgical method may also be applied.

The other positive active materials which can be used are transition metal chalcoganides such as $TiS_2$, $MoS_2$ and the like, and transition metal oxide compositions such as $LiMn_2O_4$, $LiNiO_2$ and the like.

The electrolytes that may be used are an organic electrolyte liquid made by dissolving a lithium salt such as $LiPF_6$, $LiClO_4$, $LiAlCl_4$, $LiBF_4$, $LiAsF_4$ and so on, in at least one kind of aprotic polar organic solvent, such as propylene carbonate, 2-methyl-tetra-hydrofuran, dioxolene, tetra-

hydrofuran, 1,2-dimethoxy-ethane, ethylene carbonate, γ-butylo-lactone, dimethyl-sulfoxide, acetnitrile, formamide, dimethyl-formamide, nitro-methane and so on, or a solid electrolyte, or a molten salt having lithium ions as a conductive substance, or a well-known electrolyte commonly used in a battery using an alkaline metal.

As described above, it can be confirmed from this embodiment that the negative electrode is hardly damaged even after repeated charing and discharging, since the volume change of the material is small, and it can be confirmed from the result of the cycle test that the life-time of the negative electrode material can be extended, that is, the life-time of a non-aqueous secondary battery can be extended.

[Embodiment 6]

A cylindrical battery shown in FIG. 16 was manufactured by applying the paste of the negative electrode material shown in Embodiment 1 onto a copper film with a doctor blade and applying the paste made of the positive electrode material in a similar manner to the negative electrode material onto an aluminum film with a doctor blade, and interposing a propylene separator impregnated with an electrolyte between the electrodes to form a rolled body.

The rolled body was contained in a battery can 31 of a nickel plated steel cylinder with a bottom head serving as a negative electrode terminal. An electrolyte liquid was poured into the battery can. The electrolyte liquid was a solution containing 1 mol/litre concentration of $LiPE_6$ added to a mixture of ethylene carbonate, butylene carbonate and dimethyl carbonate in a volume ratio of 2: 2: 6. A top head 32 with a positive electrode terminal was fixed to the battery can through a gasket 33 by crimping the battery can to form the cylindrical battery. The positive electrode terminal 32 and the battery can 31 were connected to a positive electrode sheet 38 and a negative electrode sheet 9 using lead terminals in advance, respectively. The reference character 34 indicates a safety valve.

A

In this embodiment, the discharging capacity was increased and the life-time was extended, the same as in Embodiment 1.

The effects of the present invention are as follows.

(1) The discharging capacity of the negative electrode material can be increased by setting the discharging capacity of the negative electrode during a period to 1000 to 2500 $mAh/cm^3$, the period being from a time when the battery starts to discharge in the condition of a steady-state current of 0.5 $mA/cm^2$ after having been charged, to a time when the voltage between the negative electrode and the positive electrode becomes 1.0 V.

(2) The life-time of the negative electrode can be extended.

CLAIMS:

1. A nonaqueous secondary battery having a positive electrode and a negative electrode reversibly absorbing and discharging an alkaline metal and a nonaqueous electrolyte, wherein the discharging capacity of the negative electrode during a period is 1000 to 2500 $mAh/cm^3$, said period being from a time when the battery starts to be discharged in the condition of a steady-state current of 0.5 $mA/cm^2$ after having been charged, to a time when the voltage between said negative electrode and said positive electrode became 1.0 V.

2. A nonaqueous secondary battery having a positive electrode and a negative electrode reversibly absorbing and discharging an alkaline metal and a nonaqueous electrolyte, wherein said negative electrode being comprised of an inter-metallic compound containing at least one element selected from the group consisting of 4B group elements, P and Sb, said inter-metallic compound having any one of $CaF_2$ type, ZnS type and AlLiSi type crystal structures, said $CaF_2$ type structure being either an inverse-fluorite structure or a fluorite structure having a lattice constant larger than 6.36 Å.

3. A nonaqueous secondary battery having a positive electrode and a negative electrode reversibly absorbing and discharging an alkaline metal and a nonaqueous electrolyte, wherein said negative electrode being comprised of an inter-metallic compound of a cubic crystal system, said inter-metallic compound having any one of $CaF_2$ type, ZnS type and AlLiSi type crystal structures, said $CaF_2$ type structure being either an inverse-fluorite structure or a fluorite structure having a lattice constant larger than 6.36 Å.

4. A nonaqueous secondary battery having a positive electrode and a negative electrode reversibly absorbing and discharging an alkaline metal and a nonaqueous electrolyte, wherein said negative electrode being comprised of an inter-

metallic compound, said inter-metallic compound having any one of $CaF_2$ type, ZnS type and AlLiSi type crystal structures, said $CaF_2$ type structure being either an inverse-fluorite structure or a fluorite structure having a lattice constant larger than 6.36 Å.

5. A nonaqueous secondary battery having a positive electrode and a negative electrode reversibly absorbing and discharging an alkaline metal and a nonaqueous electrolyte, wherein said negative electrode being comprised of an inter-metallic compound in which the space group of the crystal lattice of said inter-metallic compound is F4-3m.

6. A nonaqueous secondary battery having a positive electrode and a negative electrode reversibly absorbing and discharging an alkaline metal and a nonaqueous electrolyte, wherein said negative electrode being comprised of any one of inter-metallic compounds $Mg_2Sn$, $Mg_2Pb$, $NiSi_2$, AlP, AlSb, CuMgSb, $Mg_2Ge$ and $CoSi_2$.

7. A nonaqueous secondary battery according to any one of claim 2 to 6, wherein said negative electrode material has a charging capacity per volume of 1000 to 3500 $mAh/cm^3$.

8. A nonaqueous secondary battery according to any one of claim 1 to 6, wherein said negative electrode material has a charging capacity per volume of 2200 to 3500 $mAh/cm^3$.

9. A nonaqueous secondary battery according to any one of claim 1 to 8, wherein said negative electrode material has a charging capacity per weight of 380 to 1400 mAh/g.

10. A negative electrode material for a nonaqueous secondary battery reversibly absorbing and discharging an alkaline metal, wherein the discharging capacity of the negative electrode during a period is 1300 to 2500 $mAh/cm^3$, said period being from a time when the battery starts to be

B

discharged in the condition of a steady-state current of 0.5 $mA/cm^2$ after having been charged, to a time when the voltage between a negative electrode and a positive electrode the battery became 1.0 V.

11. A negative electrode material for a nonaqueous secondary battery reversibly absorbing and discharging an alkaline metal, said negative electrode material comprising an inter-metallic compound containing at least one element selected from the group consisting of 4B group elements, P and Sb, said inter-metallic compound having any one of $CaF_2$ type, ZnS type and AlLiSi type crystal structures, said $CaF_2$ type structure being either an inverse-fluorite structure or a fluorite structure having a lattice constant larger than 6.36 Å.

12. A negative electrode material for a nonaqueous secondary battery reversibly absorbing and discharging an alkaline metal, said negative electrode material comprising an inter-metallic compound of a cubic crystal system, said inter-metallic compound having any one of $CaF_2$ type, ZnS type and AlLiSi type crystal structures, said $CaF_2$ type structure being either an inverse-fluorite structure or a fluorite structure having a lattice constant larger than 6.36 Å.

13. A negative electrode material for a nonaqueous secondary battery reversibly absorbing and discharging an alkaline metal, said negative electrode material comprising an inter-metallic compound, said inter-metallic compound having any one of $CaF_2$ type, ZnS type and AlLiSi type crystal structures, said $CaF_2$ type structure being either an inverse-fluorite structure or a fluorite structure having a lattice constant larger than 6.36 Å.

14. A negative electrode material for a nonaqueous secondary battery reversibly absorbing and discharging an alkaline metal, said negative electrode material comprising an

inter-metallic compound in which the space group of the crystal lattice of said inter-metallic compound is F4-3m.

15. A negative electrode material for a nonaqueous secondary battery reversibly absorbing and discharging an alkaline metal, said negative electrode material comprising any one of inter-metallic compounds $Mg_2Sn$, $Mg_2Pb$, $NiSi_2$, AlP, AlSb, CuMgSb, $Mg_2Ge$ and $CoSi_2$.

16. A negative electrode material for a nonaqueous secondary battery according to any one of claims 11 to 15, of which the charging capacity per volume is 1000 to 3500 $mAh/cm^3$.

17. A negative electrode material for a nonaqueous secondary battery according to any one of claims 11 to 15, of which the charging capacity per volume is 2200 to 3500 $mAh/cm^3$.

18. A negative electrode material for a nonaqueous secondary battery according to any one of claims 11 to 17, of which the charging capacity per weight is 380 to 1400 mAh/g.

19. A nonaqueous secondary battery according to claim 7, wherein said negative electrode material has a charging capacity per weight of 380 to 1400 mAh/g.

20. A nonaqueous secondary battery according to claim 8, wherein said negative electrode material has a charging capacity per weight of 380 to 1400 mAh/g.

21. A negative electrode material for a nonaqueous secondary battery according to claim 16, of which the charging capacity per weight is 380 to 1400 mAh/g.

22. A negative electrode material for a nonaqueous secondary battery according to claim 17, of which the charging capacity per weight is 380 to 1400 mAh/g.

B

23. A nonaqueous secondary battery according to claim 6, wherein the inter-metallic compound is selected from the group consisting of AlP, $Mg_2Ge$, AlSb, $Mg_2Sn$ and $Mg_2Pb$.

24. A negative electrode material according to claim 15, wherein the inter-metallic compound is selected from the group consisting of AlP, $Mg_2Ge$, AlSb, $Mg_2Sn$ and $Mg_2Pb$.

B

FIG. 1

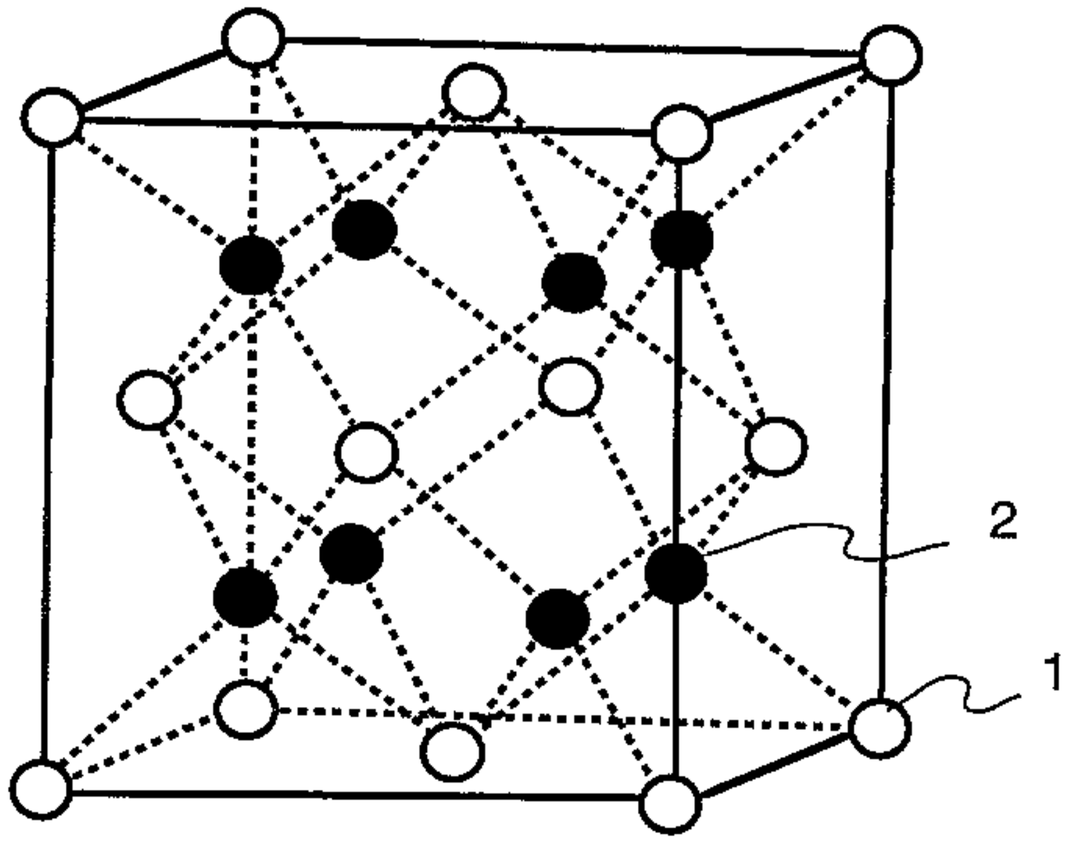

2
1

FIG. 2

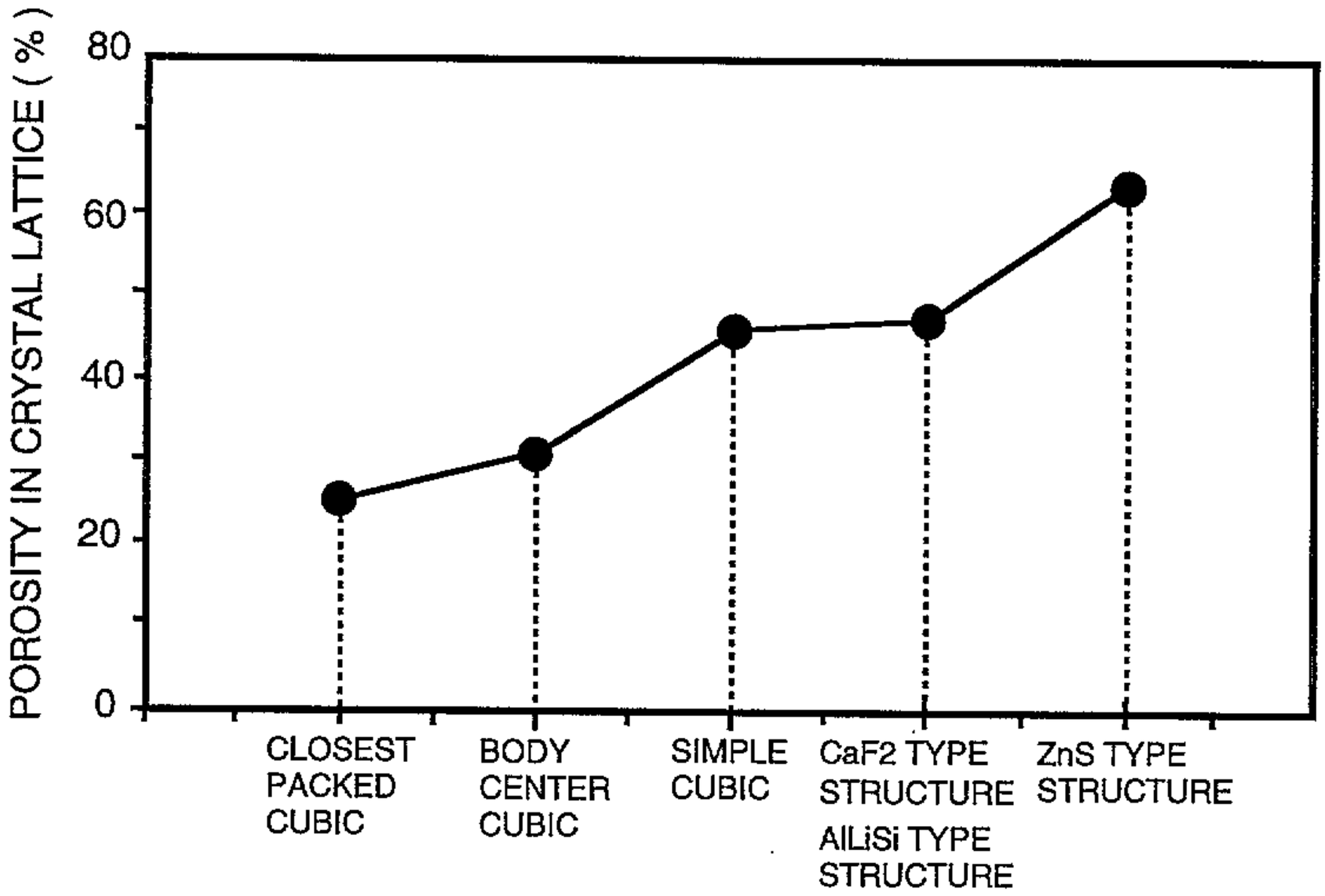

POROSITY IN CRYSTAL LATTICE ( % )
80
60
40
20
0
CLOSEST PACKED CUBIC
BODY CENTER CUBIC
SIMPLE CUBIC
CaF2 TYPE STRUCTURE
AlLiSi TYPE STRUCTURE
ZnS TYPE STRUCTURE

FIG. 3

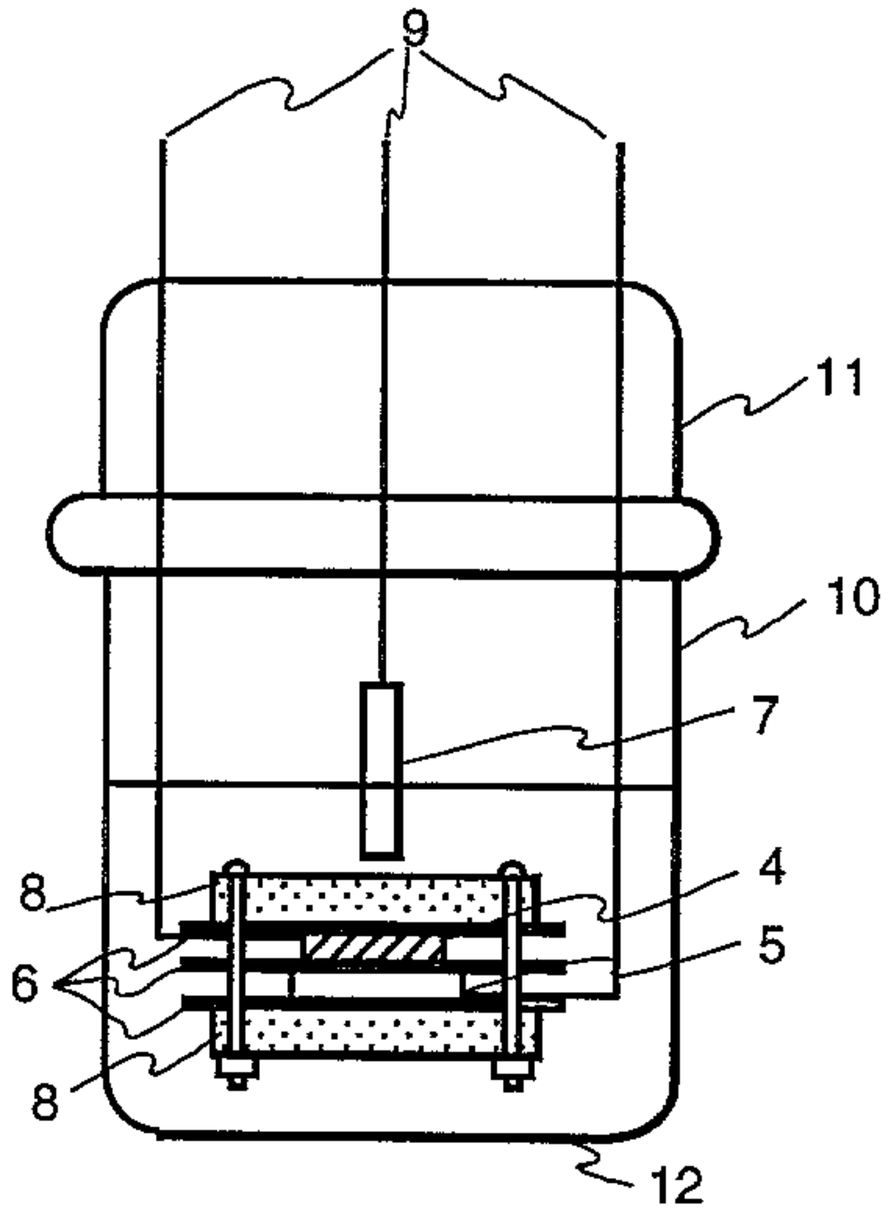

9
11
10
7
8
4
6
5
8
12

FIG. 4

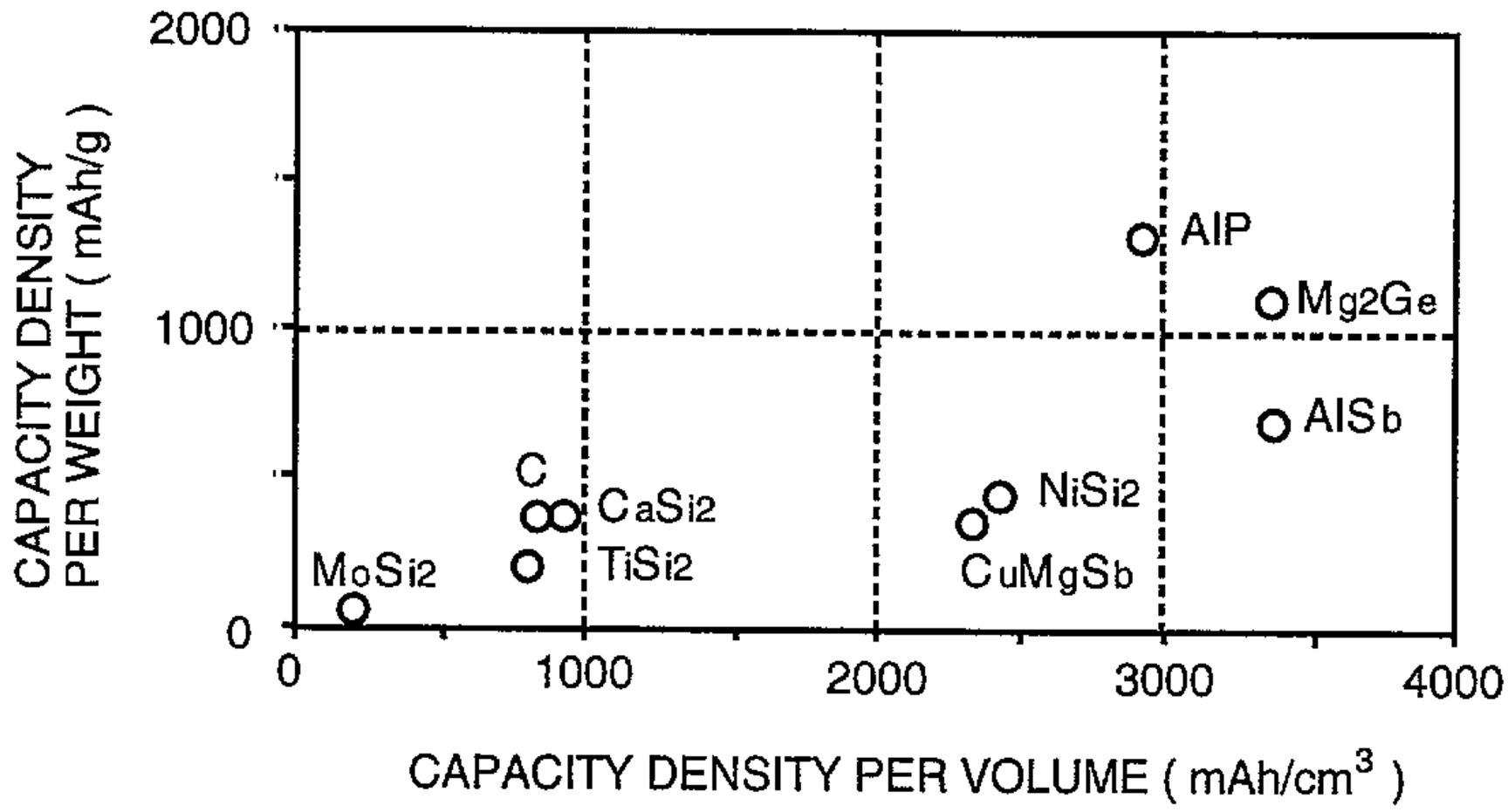

2000
1000
0
0
1000
2000
3000
4000
CAPACITY DENSITY PER WEIGHT ( mAh/g )
CAPACITY DENSITY PER VOLUME ( mAh/cm3 )
AlP
Mg2Ge
AlSb
C
CaSi2
TiSi2
MoSi2
NiSi2
CuMgSb

FIG. 5

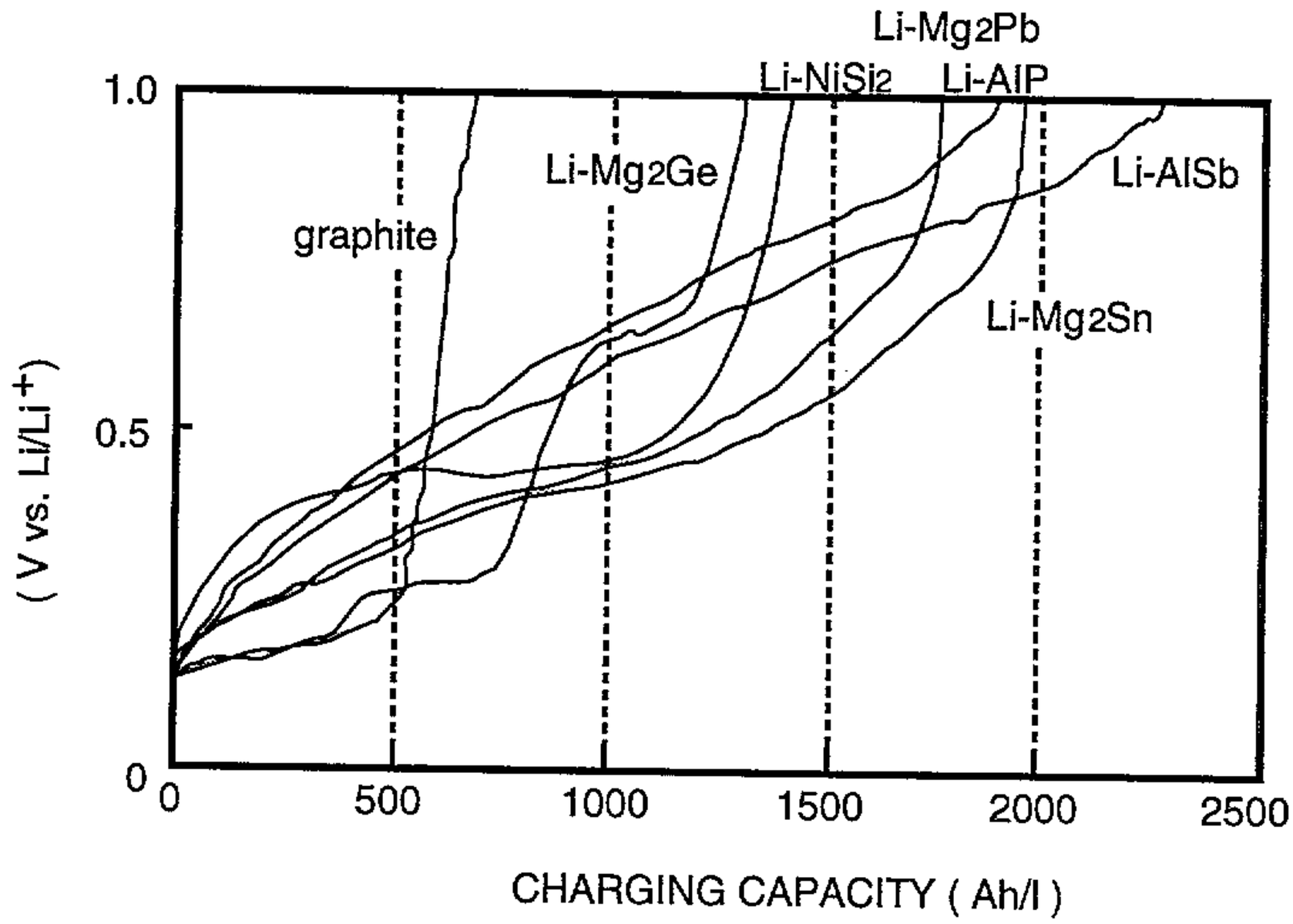

Li-Mg2Pb
Li-NiSi2
Li-AlP
Li-AlSb
Li-Mg2Ge
graphite
Li-Mg2Sn
1.0
0.5
0
( V vs. Li/Li+)
0
500
1000
1500
2000
2500
CHARGING CAPACITY ( Ah/l )

FIG. 6

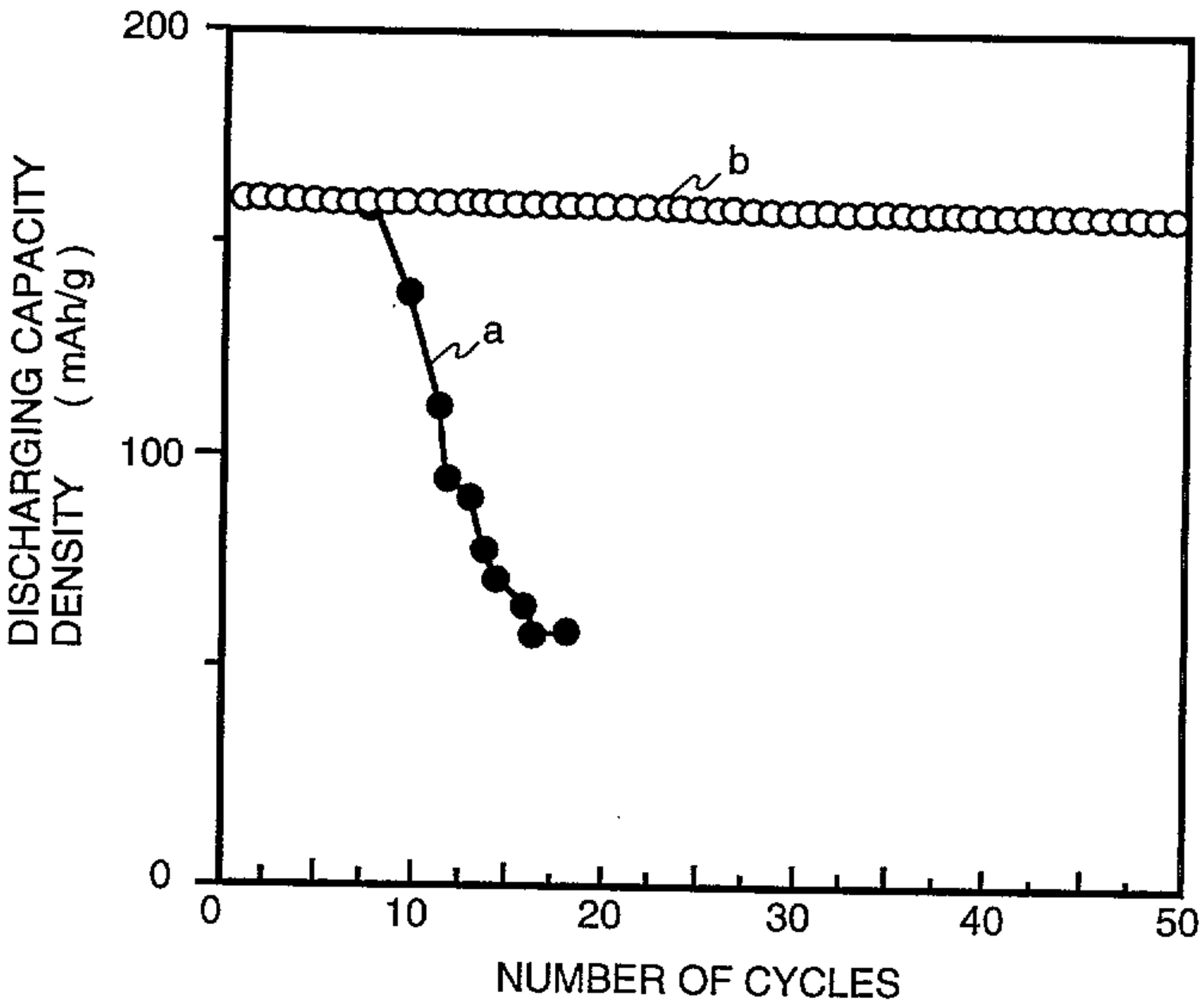

200
100
0
DISCHARGING CAPACITY DENSITY ( mAh/g )
a
b
0
10
20
30
40
50
NUMBER OF CYCLES

FIG. 7

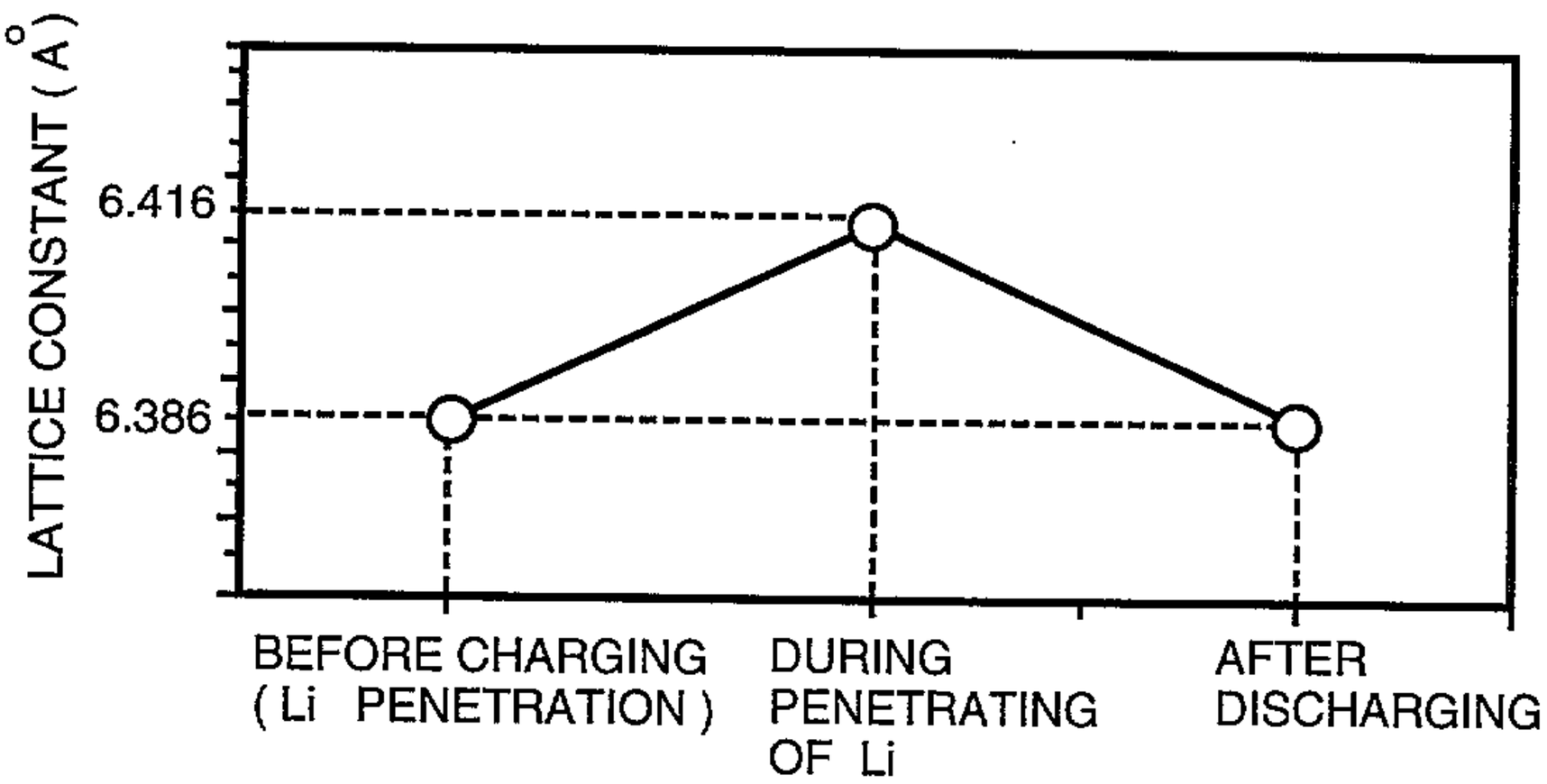

LATTICE CONSTANT ( A° )
6.416
6.386
BEFORE CHARGING
( Li PENETRATION )
DURING
PENETRATING
OF Li
AFTER
DISCHARGING

FIG. 8

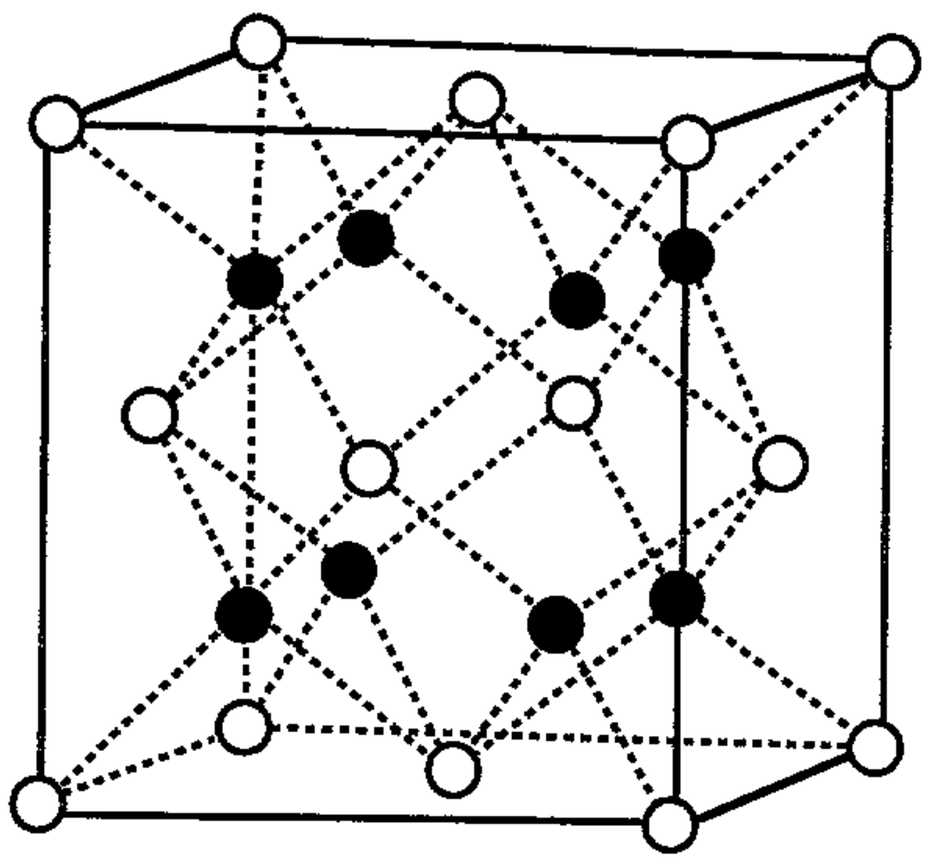


FIG. 9

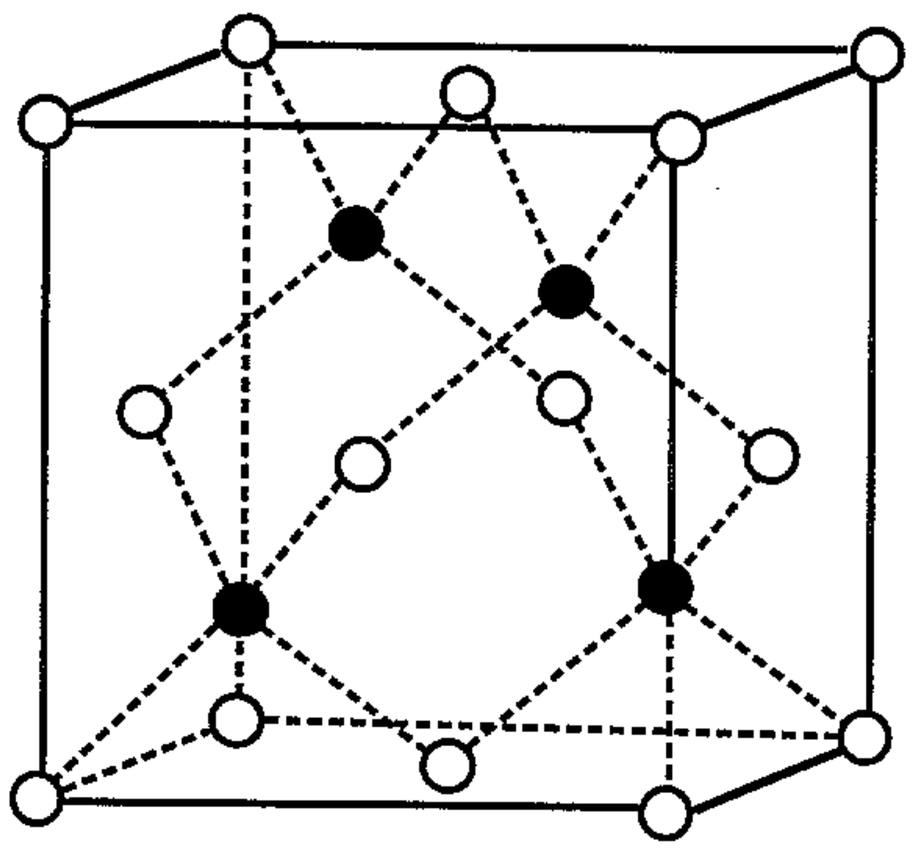


FIG. 10

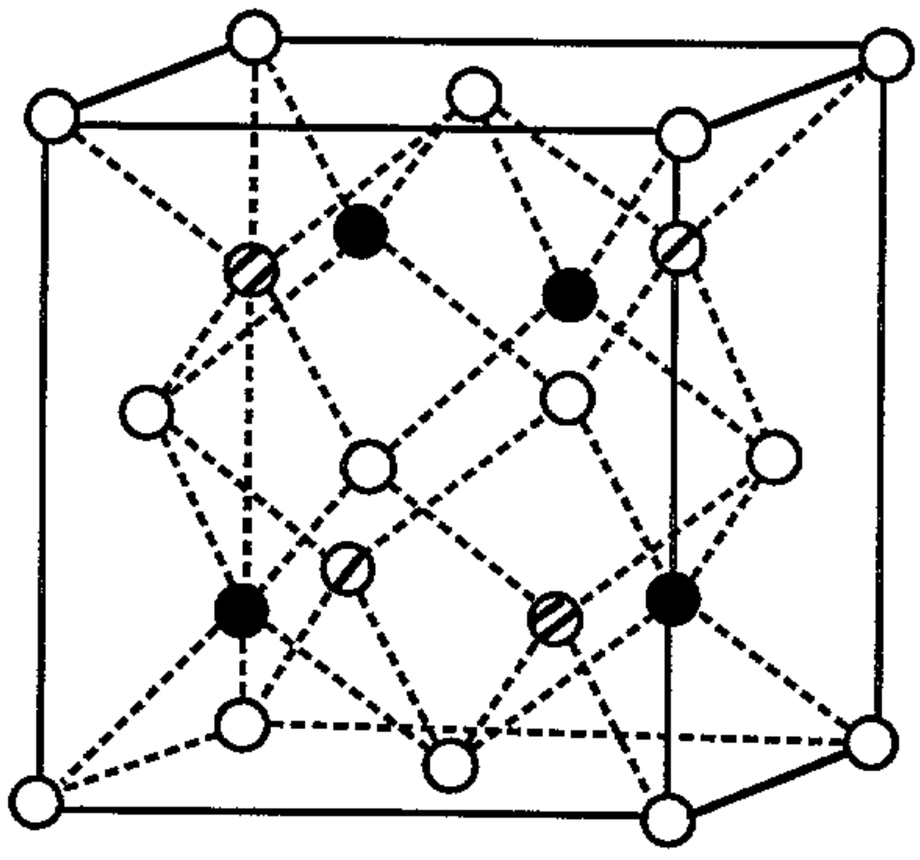


FIG. 11

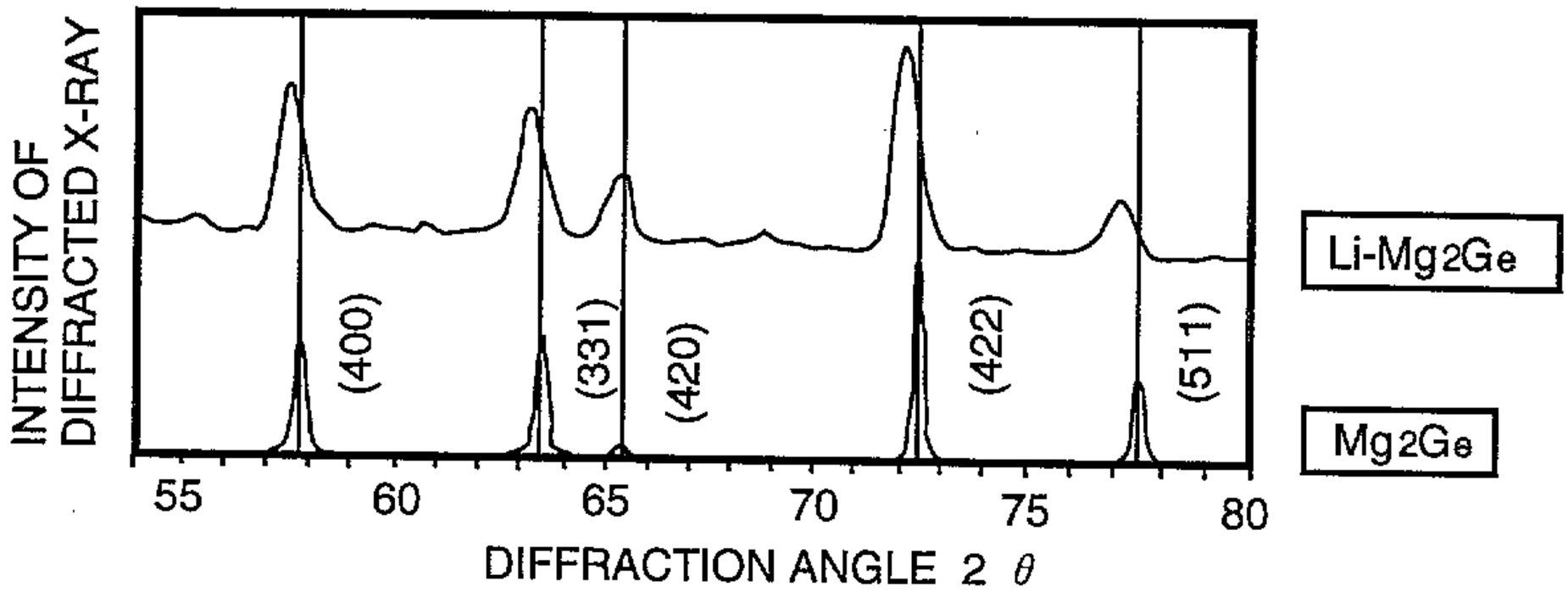

INTENSITY OF DIFFRACTED X-RAY
(400)
(331)
(420)
(422)
(511)
55
60
65
70
75
80
DIFFRACTION ANGLE 2 θ
Li-Mg2Ge
Mg2Ge

FIG. 12

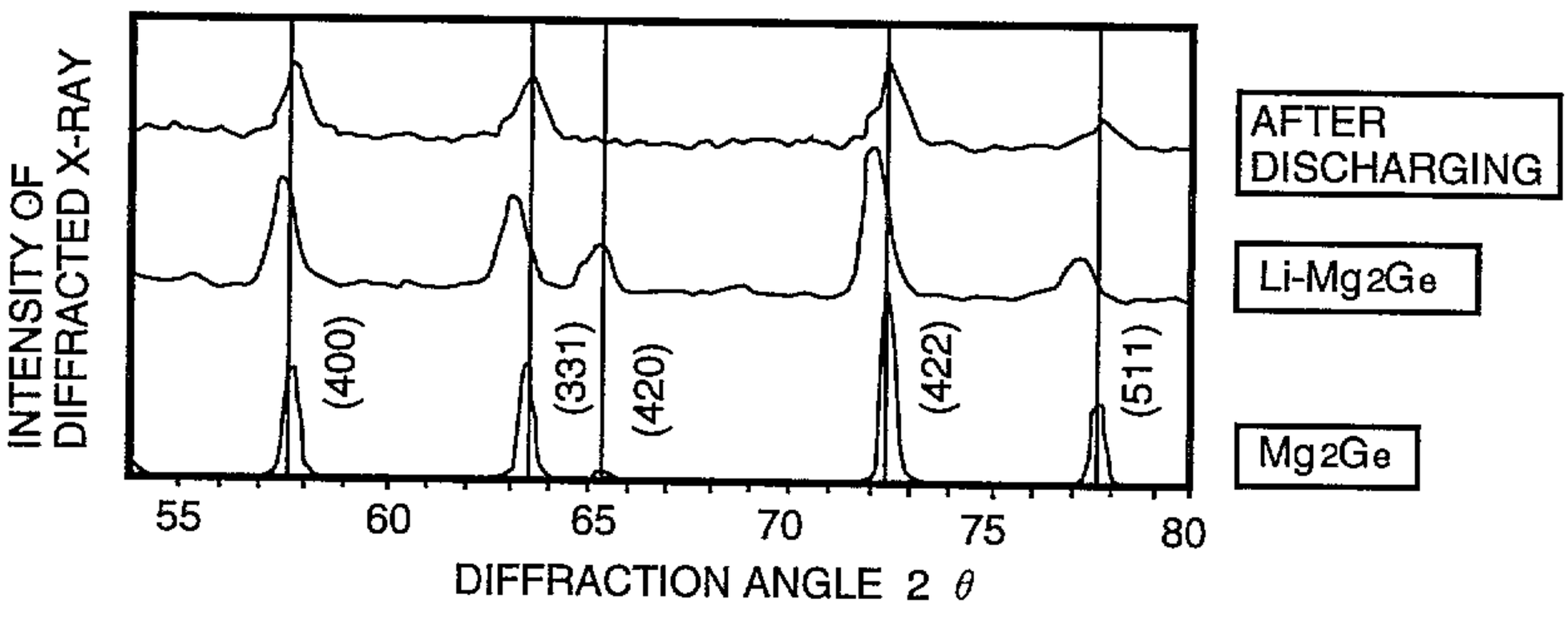

INTENSITY OF DIFFRACTED X-RAY
(400)
(331)
(420)
(422)
(511)
55
60
65
70
75
80
DIFFRACTION ANGLE 2 θ
AFTER DISCHARGING
Li-Mg2Ge
Mg2Ge

FIG. 13

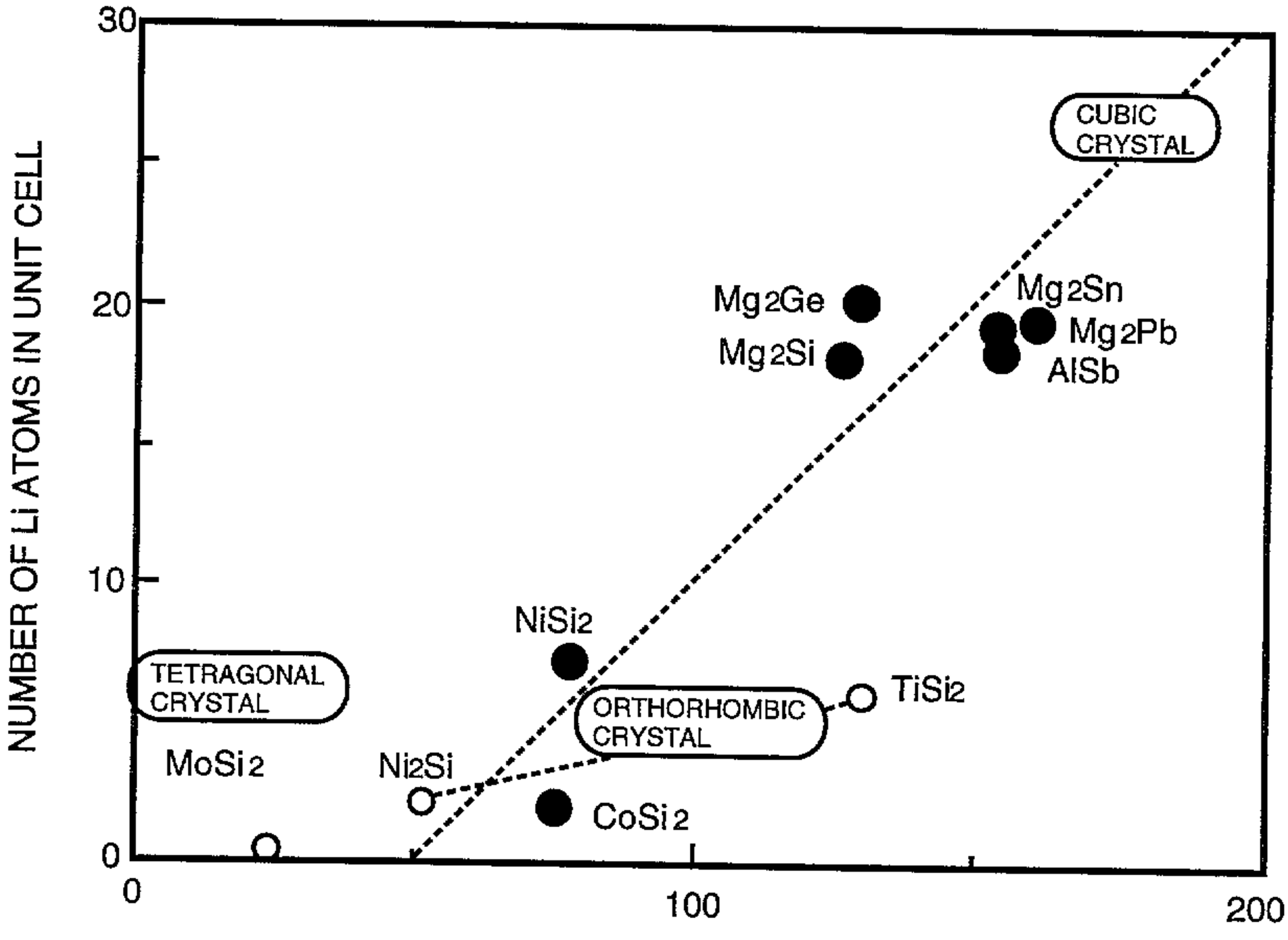

30
20
10
0
NUMBER OF Li ATOMS IN UNIT CELL
CUBIC CRYSTAL
Mg2Ge
Mg2Si
Mg2Sn
Mg2Pb
AlSb
NiSi2
TETRAGONAL CRYSTAL
ORTHORHOMBIC CRYSTAL
TiSi2
MoSi2
Ni2Si
CoSi2
0
100
200
POROSITY IN UNIT ( Å3)

FIG. 14

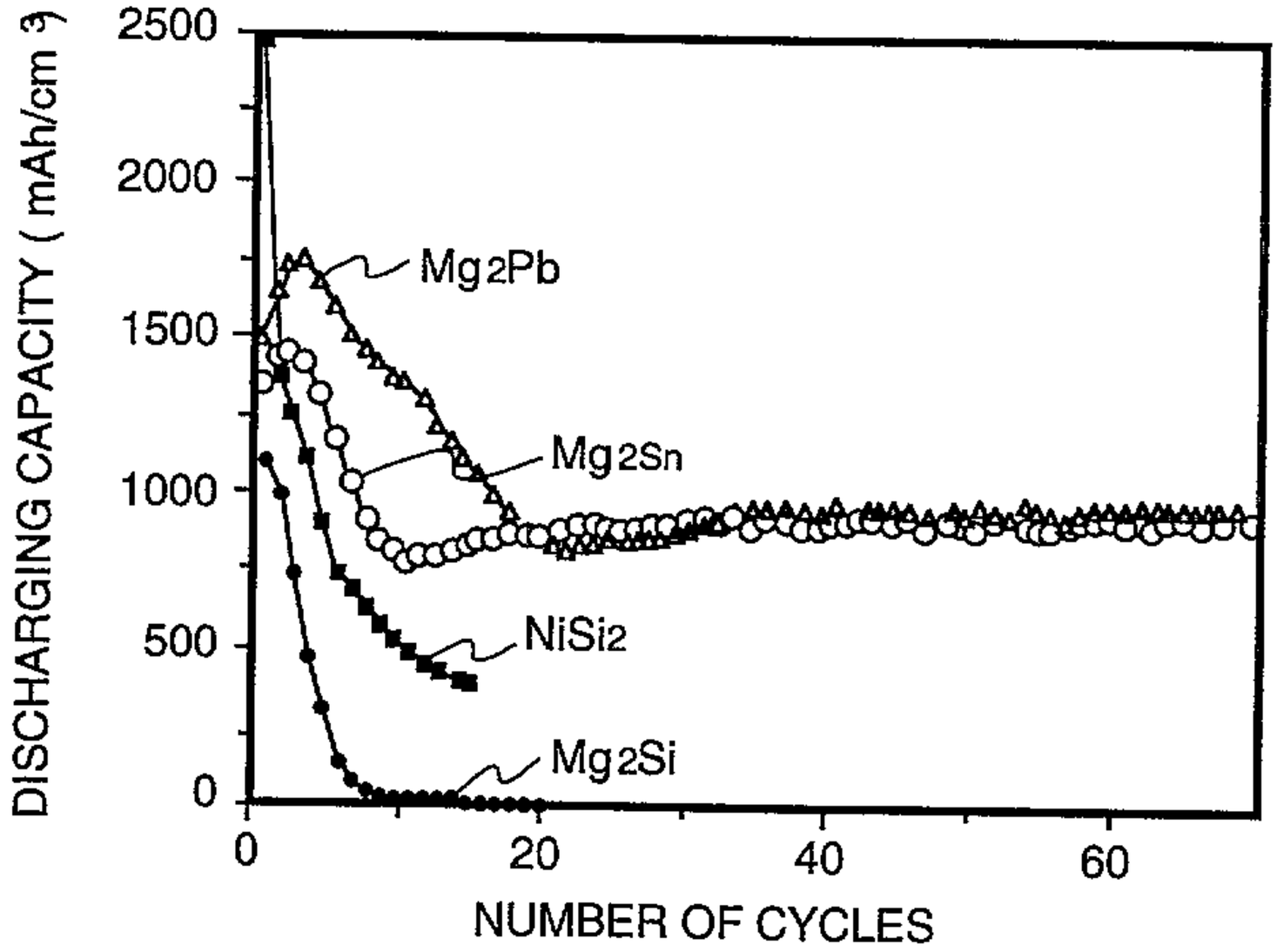

DISCHARGING CAPACITY ( mAh/cm 3)
2500
2000
1500
1000
500
0
Mg2Pb
Mg2Sn
NiSi2
Mg2Si
0
20
40
60
NUMBER OF CYCLES

FIG. 15

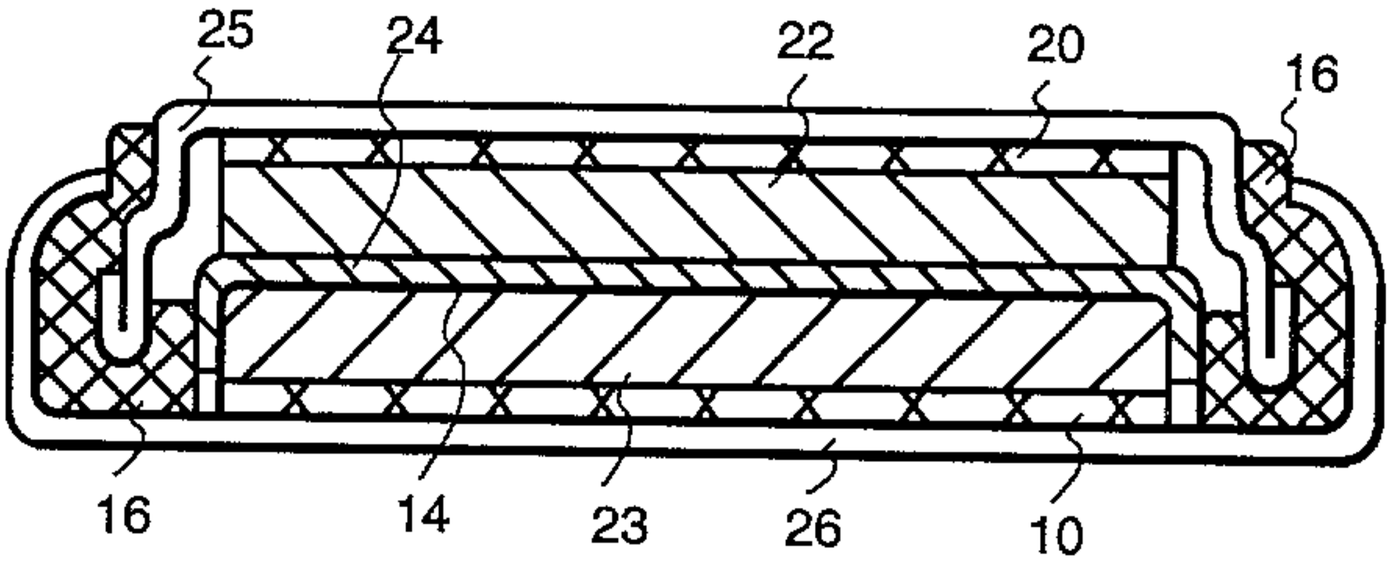
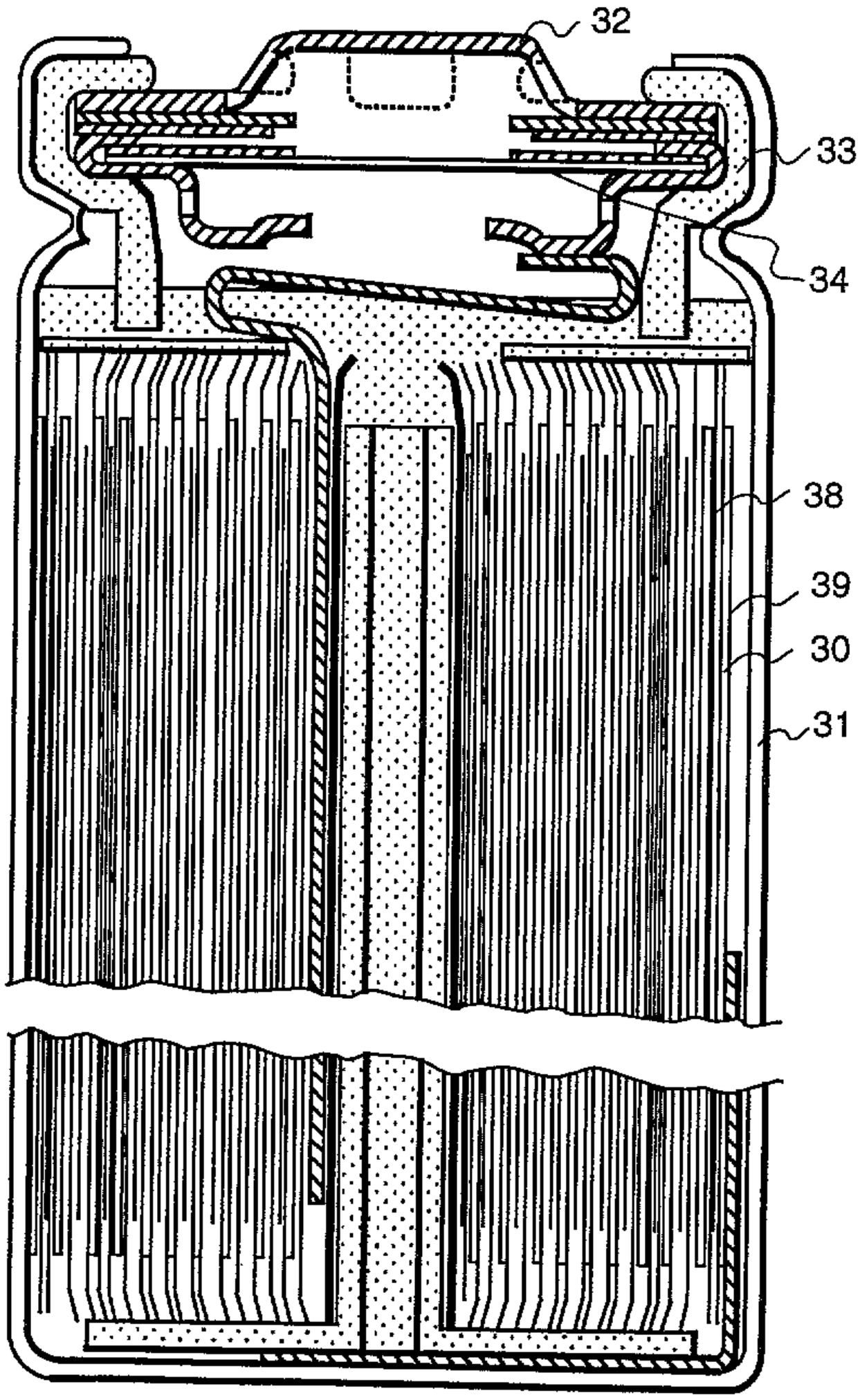
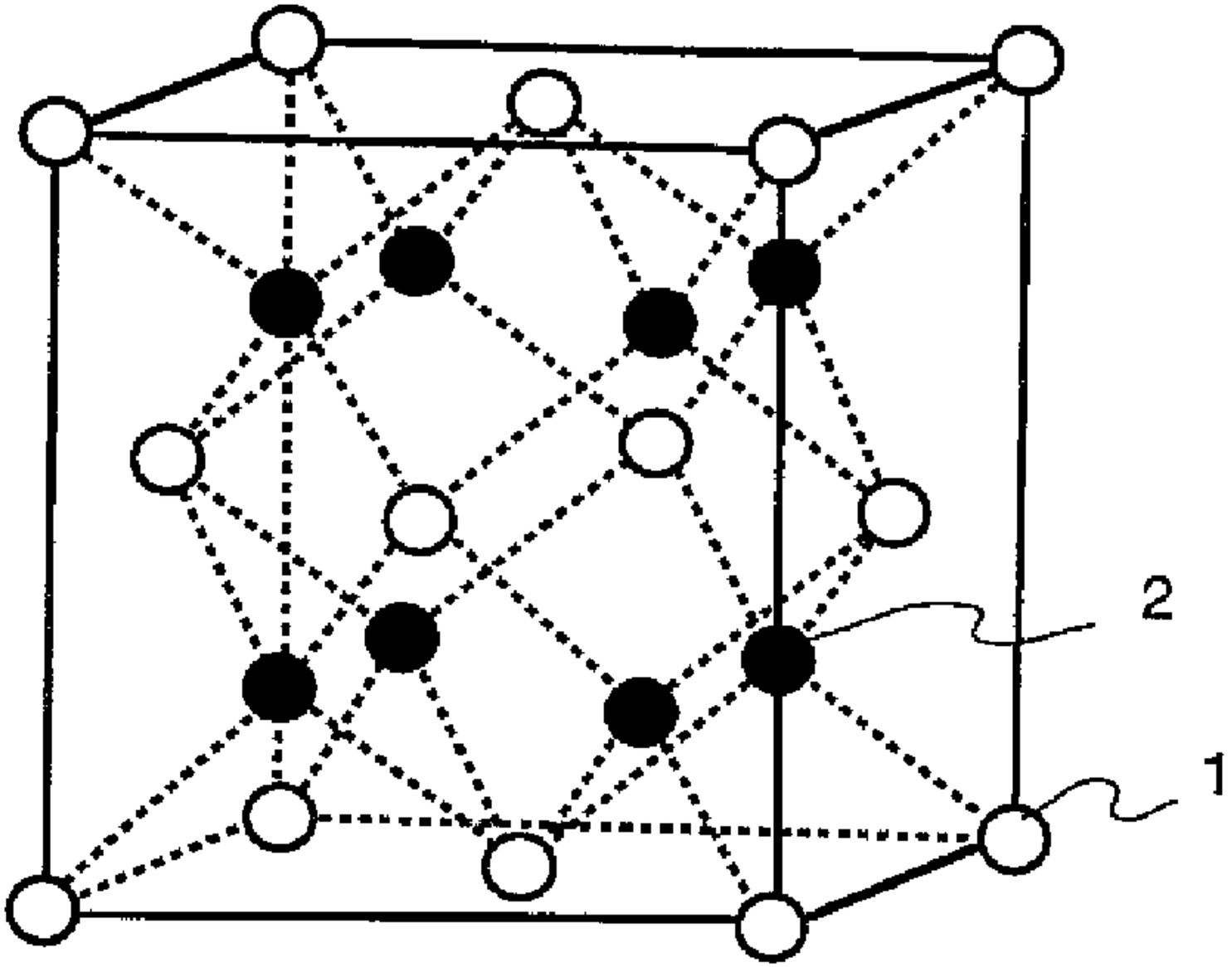



FIG. 16




2
1