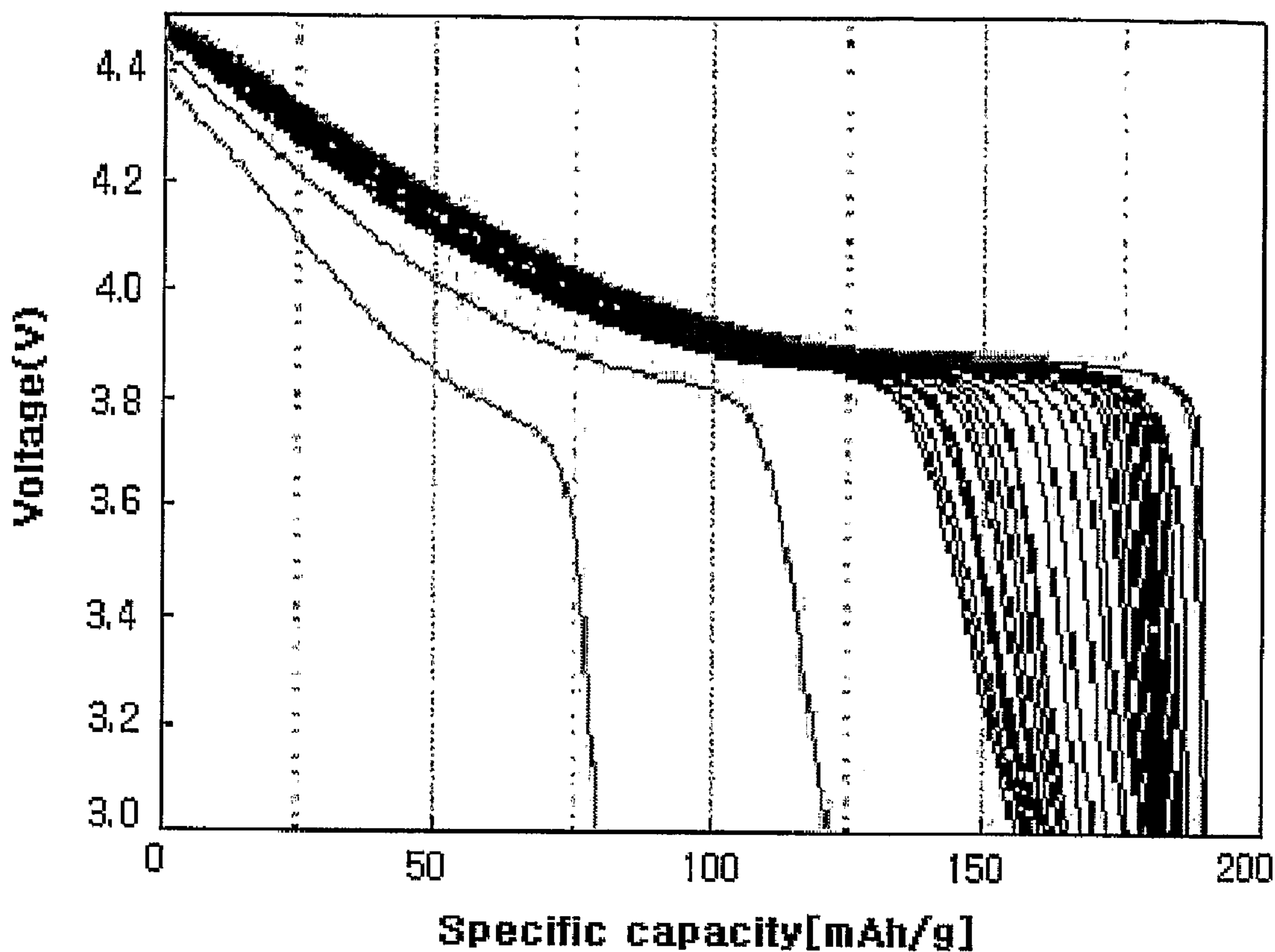




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 (54) Title: ELECTRODE ACTIVE MATERIAL WITH HIGH STABILITY AND ELECTROCHEMICAL DEVICE USING THE
 SAME



(57) Abrégé/Abstract:

Disclosed are an electrode active material, of which the stability is improved by adjusting an acid site of a surface of the electrode active material, an electrode containing the electrode active material, having a surface coated with a compound having an acid site,

(72) Inventeurs(suite)/Inventors(continued): CHANG, JONG-SAN, KR; KIM, DEOK-KYU, KR; JHUNG, SUNG-HWA, KR

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or mixed with the compound having the acid site and an electrode material, and an electrochemical device having the electrode to enhance its performance. By adjusting the acid site on the surface of the electrode active material, the side reaction with the electrolyte is decreased, and the structure stability of the electrode active material is secured, thereby enhancing the performance of the battery.

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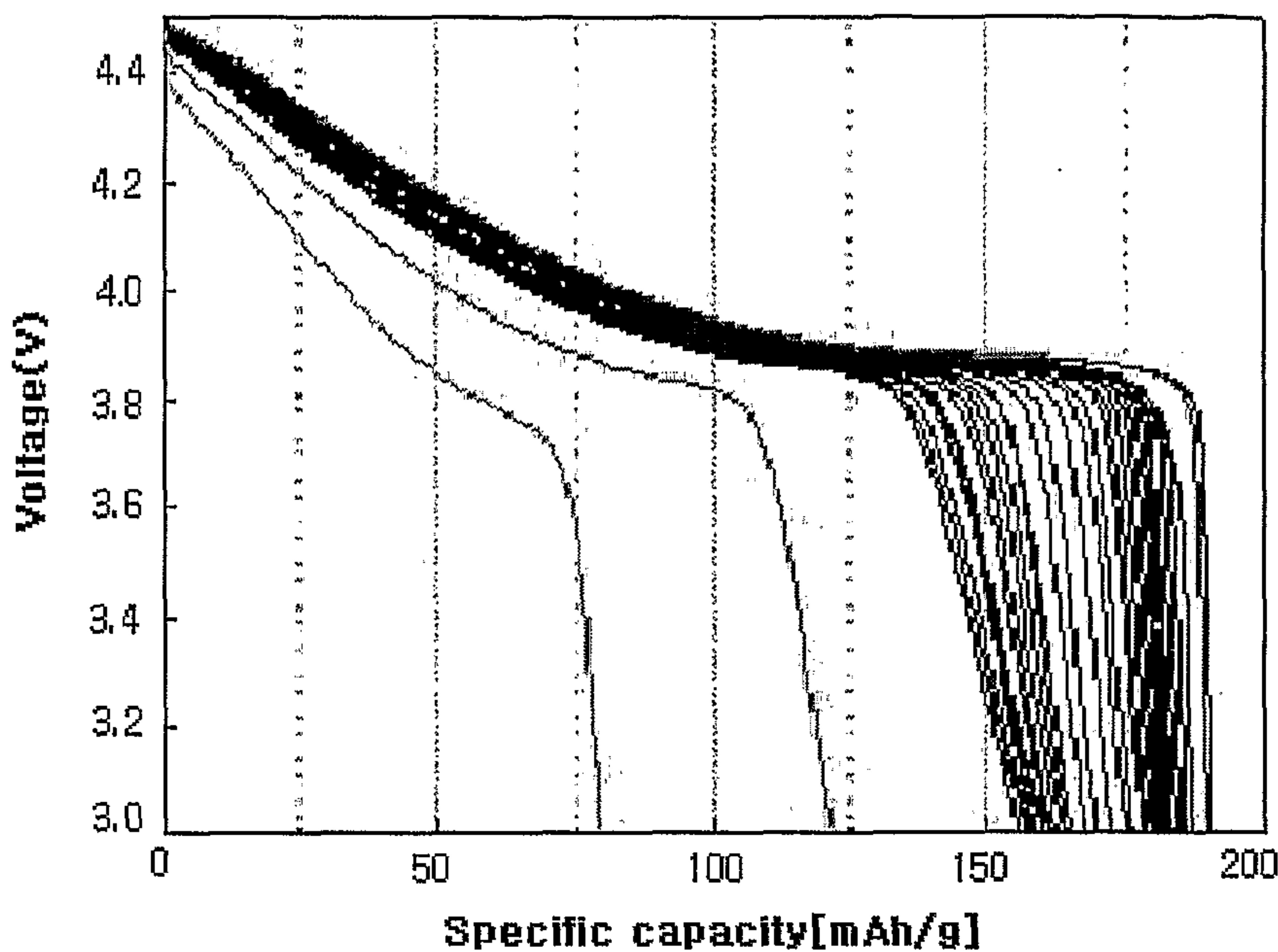
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[Continued on next page]

(54) Title: ELECTRODE ACTIVE MATERIAL WITH HIGH STABILITY AND ELECTROCHEMICAL DEVICE USING THE SAME



(57) Abstract: Disclosed are an electrode active material, of which the stability is improved by adjusting an acid site of a surface of the electrode active material, an electrode containing the electrode active material, having a surface coated with a compound having an acid site, or mixed with the compound having the acid site and an electrode material, and an electrochemical device having the electrode to enhance its performance. By adjusting the acid site on the surface of the electrode active material, the side reaction with the electrolyte is decreased, and the structure stability of the electrode active material is secured, thereby enhancing the performance of the battery.

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Description

ELECTRODE ACTIVE MATERIAL WITH HIGH STABILITY AND ELECTROCHEMICAL DEVICE USING THE SAME

Technical Field

- [1] The present invention relates to an electrode active material, of which the stability is improved by adjusting an acid site of a surface of the electrode active material, an electrode containing the electrode active material, having a surface coated with a compound having an acid site, or mixed with the compound having the acid site and an electrode material, and an electrochemical device, such as a lithium secondary battery, having the electrode to enhance its performance.

Background Art

- [2] Since a lithium secondary battery has been commercialized, the development of such a battery mainly aims to prepare a cathode active material with electrochemical properties such as high capacity, long lifespan, and the like. In addition to the electrochemical properties, the development of the cathode active material with improved stability is really needed to secure the stability and reliability of a battery system under abnormal conditions such as thermal exposure, burning, or overcharge.
- [3] LiMO_2 (M is a transition metal comprising Ni, Mn, Co, and so forth), which is widely used as the cathode active material of the lithium secondary battery, is reacted with an electrolyte in a charge state or an overcharge state to generate by-products or break down the structure of the electrode active material, thereby causing reduction of the battery performance. Consequently, many scientists have been conducting researches to enhance the performance of active material by treating the surface of the active material with stable oxide, but they are unable to enhance the stability and performance simultaneously in the electrode active material.

Disclosure of Invention

Technical Problem

- [4] Meanwhile, in case of utilizing a conventional surface modifying method that coats a particle surface of the electrode active material with a compound having low reactivity, the inventors found that the stability of the electrode active material is assured, but the performance of the battery is inevitably induced. Consequently, coating of the surface of the electrode active material with compound having adjusted acid strength can not only improve the structure stability of the electrode active material, but also prevent change of its physical properties, instead of utilizing a conventional surface modifying method. Consequently, the inventors have attempted to adopt a new surface modifying method which significantly reduces the reactivity with the electrolyte to enhance the

performance of the battery.

Technical Solution

- [5] An object of the present invention is to provide an electrode active material comprising an acid site partially or wholly formed on its surface, an electrode comprising the electrode active material, and an electrochemical device, such as a lithium secondary battery, having the electrode.
- [6] According to an aspect of the present invention, there are provided an electrode having a surface coated with a compound having an acid site or comprising the compound, and an electrochemical device, such as a lithium secondary battery, having the electrode.
- [7] In another aspect of the present invention, there is provided a method for manufacturing an electrode active material having a coating layer with adjusted acid strength, which comprises the steps of: (i) reacting (a) a compound capable of donating or accepting proton, or a compound capable of donating or accepting electron-pair, with (b) a compound having an acid site; and (ii) coating the result of step (i) onto a surface of the electrode active material and drying the coating layer.
- [8] The present invention is characterized in that an acid site is partially or wholly formed on a particle surface of an electrode active material capable of intercalating/deintercalating lithium ions or inserting/deinserting the lithium ions, thereby modifying electrochemical physical properties of the electrode active material.
- [9] The acid site is generally known as a reaction active site existed on a solid acid catalyst, such as zeolite, which induces a chemical reaction, for example, decomposition reaction. In the present invention, however, the acid site means an active region indicative of specific acid strength at a surface modified portion which is partially or wholly formed on the surface of the active material through the new surface modifying method.
- [10] The acid strength is determined depending upon how to easily donate proton or how to easily accept electron-pair. Consequently, the characteristic of the acid site is generally associated not with the surface structure, but with the electronic property between atoms configuring the surface.
- [11] The electrode active material with the acid site formed on the surface thereof reacts like a common acid material having positive charge partially, because of the possession of positive charge or an electronegativity difference. Therefore, since the reaction with Brønsted acid serving as a proton donor or Lewis acid serving as an electron-pair acceptor is significantly reduced, it can enhance the performance of the battery, which can be presumed as follows.
- [12] 1) Firstly, the surface of a conventional electrode active material indicates weak basic through lithium byproduct or hydrophilic surface treatment. Accordingly, there is little

recognition about the acid site.

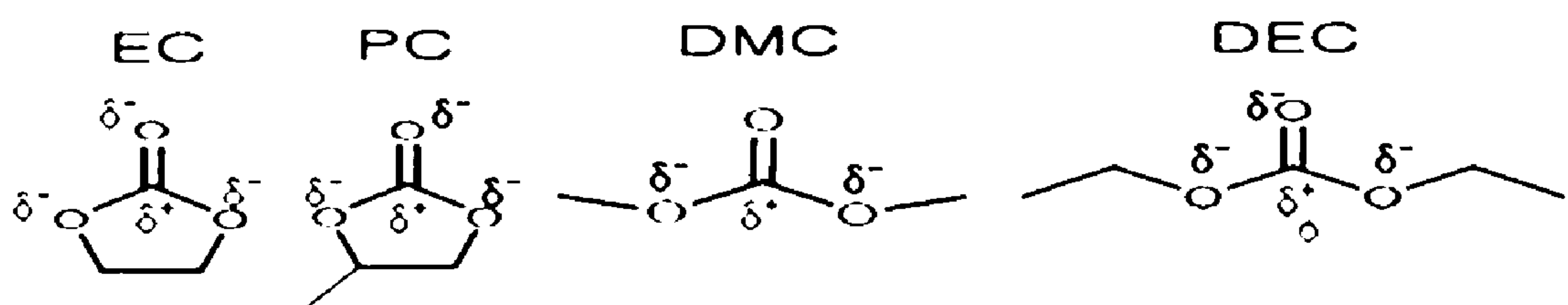
[13] In a battery utilizing the conventional electrode active material, especially cathode active material, moistures existed in an electrode or electrolyte is reacted with lithium salt (e.g., LiPF_6) to create strong acid HF. The created HF is spontaneously reacted with the electrode active material indicating weak basic to dissolve and degrade the electrode active material component. Also, LiF is created on a surface of an cathode, and electric resistance is increased in the electrode, thereby generating a gas and thus shortening a lifespan of the battery. In particular, since a dissolution speed of the electrode due to HF is increased at high temperature, HF is a major factor in the lifespan and maintenance of the battery.

[14] By contrast, since the electrode active material of the present invention carries the acid site on the surface thereof, it serves as an acid material. Consequently, the reaction with strong acid HX (X means a halogen element) is decreased, so that the above problem is substantially solved to secure the structure stability of the electrode active material and enhance the performance of the battery.

[15] And, 2) secondary, a carbonate-based nonaqueous solvent is used as an electrolyte for a conventional battery. The carbonate-based nonaqueous solvent has carbon of a positive charge and oxygen of a negative charge in view of dipole moment, as disclosed in Equation 1 below. In this instance, in case that Lewis base capable of donating unshared electron pair is existed on the surface of the electrode active material, the Lewis base attacks the carbon having the positive charge, thereby further activating the electrophilic decomposition reaction of the electrolyte.

[16] By contrast, the electrode active material of the present invention having the acid site is Lewis acid capable of not donating unshared electron pair but accepting the unshared electron pair. Thus, the above side reaction with the electrolyte is significantly reduced, thereby minimizing the deterioration of the performance of the battery.

[17] [reaction equation 1]



[18] The acid site partially or wholly formed on the surface of the electrode active material according to the present invention means a common acid site widely known in the art. For example, it may be Brønsted acid capable of donating proton (i.e., proton donor) or Lewis acid capable of accepting unshared electron pair (i.e., electron-pair acceptor).

- [19] The acid strength may be indicated by H_0 (Hammett indicator), and is adjustable within a range generally known in the art, for example, the range of -20 to 20. Preferably, H_0 is in the range of -10 to 10, so as to prevent degradation of the electrode active material and suppress the side reaction with the electrolyte, through the adjustment of the acid site.
- [20] A method of forming the acid site on the surface of the electrode active material is not limited, but two embodiment modes will be described by way of example.
- [21] 1) Embodiment Mode 1
- [22] In the embodiment mode, the surface of the electrode active material is treated with an inorganic substance.
- [23] The inorganic substance treated on the surface of the electrode active material changes the electron distribution on the surface of the electrode active material due to the electronegativity difference of hetero-metal elements and/or the functional group of the proton donor partially or wholly existed on the surface of the inorganic substance, so that the acid site is formed on the surface of the electrode active material.
- [24] The inorganic substance is widely known in the art, for example, ceramic, metal, or a compound thereof. If the electrochemical property of the surface of the electrode active material is changed when the inorganic substance is existed on the surface, it is not limited. Especially, a compound containing an element (e.g., B, Al, Ga, In, Ti or the like) of Group 13, Group 14, Group 15, or a mixture thereof, which can improve the structure stability of the electrode due to intercalation of Li is preferable, since it is easily doped on the surface of the electrode active material due to its atomic size.
- [25] Examples of the available inorganic substance may comprise an element of Group 13, and a compound of an element of Group 13 and at least one selected from the group consisting of alkaline earth metal, alkaline metal, an element of Group 14, an element of Group 15, transition metal, lanthanide metal, and actinide metal, which does not limit the scope of the present invention. As an example, the inorganic substance may be $M_{1-x}Si_xO_2$ (M is at least one element selected from the group consisting of transition metal; $0 \leq x < 1$). As other examples according to the present invention, the inorganic substance may be silane, hydrogenated silicon, monosilane.
- [26] The inorganic substance having the acid site may be formed through heat treatment after modifying the surface of the electrode active material. In this instance, the heat treatment temperature is not specially limited, even if it is above a temperature to form the acid site. If a hydroxyl group is still existed on the surface, it is not possible to form strong Lewis acid site. Consequently, the temperature of 400 °C or more is preferable so as to eliminate the hydroxyl group.
- [27] The above grain size and contents of the inorganic substance are not specially limited, and can be properly adjusted in the common range widely known in the art.
- [28] 2) Embodiment Mode 2

- [29] In the embodiment mode, the surface of the electrode active material is treated with a hybrid of organic metalloid compound or organic metal compound, and an inorganic substance.
- [30] The hybrid of the organic metalloid compound or the organic metal compound, and the inorganic substance treated on the surface of the electrode active material changes the electrochemical physical property of the surface due to the electronegativity difference between the organic metalloid (metal) compound and the inorganic substance which are bonded to each other and/or the organic substance bonded to the organic metalloid (metal) compound, so that the acid site can be formed on the surface of the electrode active material.
- [31] In the hybrid, the organic metalloid (metal) compound and the inorganic substance are bonded to each other through chemical bonding, and a shape and kind of the chemical bonding are not specially limited. For example, it may be covalent bond or coordinate covalent bond.
- [32] In case of using the hybrid of the organic metalloid compound or the organic metal compound, and the inorganic substance as the surface modifying agent of the electrode active material or the electrode, a hydrolysis speed of the inorganic component (e.g., inorganic alkoxide compound) can be decelerated. Also, it can not only create the more uniform surface, but also maintain the created surface continuously. Consequently, it can minimize the deterioration of the performance of the battery due to the lowered structural stability of the electrode active material and the collapsed structure thereof, with the progress of charge and discharge. In addition, it can effectively enhance the electric conductivity of the electrode active material by introducing the surface-modified layer using the inorganic compound contained in the organic-inorganic hybrid.
- [33] The organic-inorganic hybrid induced in the surface of the electrode active material reacts with the moistures or carbon dioxide contained in the air to generate Li byproducts, thereby preventing aging characteristics which causes the side reaction. In particular, nickel-based cathode active material which is seriously changed by the moistures is more effective.
- [34] Further, it reduces the side reactive contact surface between a cathode and an electrolyte in a battery consisting of a conventional electrode active material, with its surface being not modified, thereby improving the stability of the battery.
- [35] As described above, one of the organic-inorganic hybrid capable of creating the acid site partially or wholly on the particle surface of the electrode active material may be a conventional organic metalloid compound or organic metal compound which is widely known in the art. In order to increase the effects of adjusting the acid strength and preventing the aging characteristics, it is preferable to contain an electron donating

group for increasing the Brønsted acid site. The electron donating group is not specially limited to structural formula, substituent, and a range of carbon number. For example, hydrogen or hydrocarbon may be.

- [36] Examples of the available organic metalloid compound or organic metal compound may comprise an element of Group 14, or a compound of an element of Group 14 and at least one selected from the group consisting of alkaline earth metal, alkaline metal, an element of Group 13, an element of Group 15, transition metal, lanthanide metal, and actinide metal, which does not limit the scope of the present invention. The organic metalloid compound or the organic metal compound is preferably a compound containing silicon (e.g., silylizing agent, silane coupling agent, silane polymer, or mixtures thereof).
- [37] The organic metalloid compound may be represented by any one of following Formulas 2 to 7. There is no limitation in the organic metalloid compound or the organic metal compound.
- [40] [Formula 2]
- [41] $\text{Si}(\text{OR})_{4-x} \text{R}_x$ ($0.1 \leq x \leq 3$)
- [42] [Formula 3]
- [43] $\text{Si}(\text{OR})_{4-(x+y)} \text{R}_x \text{Z}_y$ ($0.1 \leq x+y \leq 3.9$)
- [44] [Formula 4]
- [45] $\text{Si}(\text{OR})_{4-x} \text{R}_x \text{Si}$ ($0.1 \leq x \leq 3$)
- [46] [[Formula 5]
- [47] $\text{Si}(\text{OR})_{4-(x+y)} \text{R}_x \text{Z}_y \text{Si}$ ($0.1 \leq x+y \leq 3.9$)
- [48] [Formula 6]
- [49] $\text{R}_x \text{M}(\text{OR})_{4-x}$ ($1 \leq x \leq 3$)
- [50] [Formula 7]
- [51] $\text{R}_x \text{MZ}_y (\text{OR})_{4-(x+y)}$ ($0.1 \leq x+y \leq 3.9$)
- [52] wherein, Z is one element selected from the group consisting of halogen atoms;
- [53] M is at least one element selected from the group consisting of alkaline earth metal, alkaline metal, transition metal, lanthanide metal, and actinide metal; and
- [54] R is a substituent selected from the group consisting of C1 to C20 alkyl group, alkenyl group, alkynyl group, vinyl group, amino group, and mercapto group, the group is/are substituted or non-substituted by a halogen element.
- [55] Another one of the organic-inorganic hybrid capable of creating the acid site partially or wholly on the particle surface of the electrode active material may be a common inorganic substance which can create the acid site due to a chemical bonding number difference between the above organic metalloid (metal) compound and the inorganic

substance. Any compound containing inorganic instance may be used with no particular limitation. As an example, the above inorganic component may be used. In this instance, in order to prevent lowering of the conductivity of the electrode active material due to induction of the organic-inorganic hybrid, it is preferable to use conductive metal, oxide containing conductive metal, hydroxide containing conductive metal, or a mixture thereof.

[56] The organic-inorganic hybrid consisting of the organic metalloid (metal) compound and the inorganic substance is not a simple mixture of an organic substance and an inorganic substance, but is a chemically bonded mixture thereof. As an example, it may comprise a metal-organic metalloid (metal) compound, a metal oxide-organic metalloid (metal) compound ($\text{Al}_2\text{O}_3\text{-SiOCH}_3$), and a hydroxide-organic metalloid (metal) compound (AlOOH-Si-CH_3).

[57] In the compound creating the acid site, a component ratio of the organic metalloid (metal) compound to the inorganic substance may be in the range of 0wt% ~ 95wt% to 5wt% ~ 100wt%.

[58] Also, the organic-inorganic compound of the present invention may comprise additives which are generally known in the art, in addition to the above components.

[59] There is no particular limitation in methods for manufacturing the electrode active material comprising an organic-inorganic hybrid coating layer. In one embodiment, the surface of an electrode active material is partially or wholly coated with a compound comprising an acid site.

[60] According to a preferred embodiment, the process may comprise the steps of (i) mixing a compound containing an inorganic substance or a compound containing an organic substance and an organic metalloid (metal) compound or dispersing them into a solvent, and (ii) adding an electrode active material into the mixture or dispersed solution and stirring and drying it.

[61] The compound containing the inorganic substance may be used a conventional water soluble or non-water soluble compound containing at least one element described above (e.g., alkoxide, nitrate, acetate, or the like, which contains the above inorganic substance).

[62] The solvent may comprise a conventional solvent widely known in the art (e.g., an organic solvent such as water, alcohol, or a mixture thereof).

[63] The electrode active material coated with the above prepared compound may be used a conventional cathode active material and a conventional anode active material, which are widely known in the art.

[64] In this instance, the method of coating the surface of the electrode active material with the compound solution mixed with the inorganic substance with the organic metalloid (metal) compound may comprise a solvent evaporation, a coprecipitation

method, a precipitation method, a sol-gel method, an absorption and filtering method, a sputtering method, a CVD method, and the other. Among these methods, a spray coating method is preferable.

- [65] When the mixed solution of the organic metalloid (metal) compound and the inorganic substance or the compound containing the inorganic substance is added in the electrode active material, preferably, 0.05 to 20 parts by weight of the mixed solution is added based on 100 parts by weight of the electrode active material, which does not limit the scope of the present invention. If the mixed solution is excessive, a lot of surface treated layers are existed on the surface of the electrode active material, so that lithium is not smoothly shifted to the electrode active material, thereby deteriorating the electrochemical characteristic thereof. Also, if the mixed solution is too insufficient, the acid site effect is slight. Then the coated electrode active material may be dried through a common method.
- [66] In necessary, a process of annealing the dried electrode active material may be added. In this instance, the range of heat treating temperature is above 100 °C, but is not especially limited. Preferably, the range is 100 °C to 600 °C. Also, the heat treating may be conducted under conditions of atmosphere or inert gas.
- [67] The conventional method does not obtain the wanted effect, since the organic substance is thermally unstable and/or is partially burnt, during a hot firing process. Consequently, the firing temperature is limited. By contrast, in the present invention, the thermal instability of the organic substance is compensated by the inorganic component, thereby providing the electrode active material with the thermal stability. Also, since it can prepare the electrode active material through a conventional drying process or a low temperature firing process, it can improve the economical efficiency and achieve the mass, by simplifying the preparing method.
- [68] The electrode active material prepared by the above method is provided with the inorganic or organic-inorganic hybrid layer on its surface, in which the inorganic or organic-inorganic hybrid creates the acid site.
- [69] It can be verified from experiments that the surface of the electrode active material modified by the inorganic or organic-inorganic hybrid has the acid site. In particular, the organic-inorganic hybrid not only appears the bonding state of the organic substance and the inorganic substance, but also relatively increases the Brønsted acid site of the inorganic substance by a electron donating group existed in the organic substance in the compound, so that the acid strength of the electrode active material is increased.
- [70] The present invention provides an electrode containing the electrode active material described above. In this instance, it is preferable that the electrode is a cathode which is seriously changed due to HF or moistures.

- [71] Also, the present invention provides an electrode having a surface coated with the compound having the acid site or containing the compound having the acid site.
- [72] The method of preparing the electrode containing the compound having the acid site as a constituent component of the electrode is not specially limited, and the electrode may be prepared by a conventional method. In a preferred embodiment, the compound containing the inorganic substance or the compound containing the organic substance and the organic metalloid (metal) compound are mixed or dispersed into the solvent, and the electrode active material is added into the mixed or dispersed solution to form electrode slurry. Then, the slurry is applied on a collector to manufacture the electrode, and the electrode is dried.
- [73] In this instance, in the mixing process, after the mixed or dispersed solution is mixed with the electrode active material to prepare the electrode slurry, the slurry is applied on the collector.
- [74] The method of manufacturing the electrode by using the organic-inorganic hybrid as a coating component of the electrode according to the present invention may be carried out by a conventional process. As an example, the compound containing the inorganic substance or the compound containing the organic substance and the organic metalloid (metal) compound are mixed, and the mixture is applied on the surface of the preliminarily formed electrode, and then the electrode is dried. In this instance, the preliminary formed electrode may be manufactured by a conventional method known in the art.
- [75] Also, the present invention provides an electrochemical device comprising an anode, a cathode, a separator, and an electrolyte, wherein either or both of the anode and/or cathode contains the above electrode active material or above electrode.
- [76] The electrochemical devices include all devices that perform electrochemical reactions, and specific examples thereof include all kinds of primary and secondary batteries, fuel cells, solar cells, and capacitors. Among the secondary batteries, preferred are lithium secondary batteries, including lithium metal secondary batteries, lithium ion secondary batteries, lithium polymer secondary batteries and lithium ion polymer secondary batteries.
- [77] The electrochemical device of the present invention can be fabricated according to any conventional method known in the art. In one embodiment, the electrochemical device can be manufactured by interposing a porous separator between the cathode and the anode within a battery case and then injecting the electrolyte into the electrochemical device case.
- [78] The electrolyte and the separator which are used for the electrode are not specially limited, and those generally used in the electrochemical device may be used.
- [79] The electrochemical device (e.g., lithium secondary battery) manufactured by the

present invention may be formed in a cylinder, coin, prism or pouch shape, but it is not limited to the shape.

[80] Additionally, the present invention provides a manufacturing method of an electrode active material, of which the acid strength of the surface is adjusted. In one embodiment, the method comprises the steps of (i) reacting (a) a compound capable of donating or accepting proton, or a compound capable of donating or accepting electron-pair, with (b) a compound having an acid site; and (ii) coating the result of step (i) onto a surface of the electrode active material and drying the coating layer. But the present invention is not limited thereto.

[81] The compound capable of donating proton (or electron-pair) or accepting proton (electron-pair) is used as a factor to adjust the acid strength of the conventional compound in a specific range. In this instance, it can adjust the acid strength by controlling contents of the compound, the functional group existed in the compound, and a composition thereof.

[82] There are no particular limitations in the compound capable of donating proton (or electron-pair) or accepting proton (electron-pair) that may be used in the present invention, as long as the compound can donate proton (or electron-pair) or accept proton (electron-pair). The adjusted acid strength of the surface of electrode active material is preferably adjusted within the range of -20 to 20 (i.e., $-20 < H_0 < 20$), preferably -10 to 10 (i.e., $-10 < H_0 < 10$).

Description of Drawings

[83] The foregoing and other objects, features and advantages of the present invention will become more apparent from the following detailed description when taken in conjunction with the accompanying drawings in which:

[84] FIG. 1 is a graph showing a charge/discharge capacity of a lithium secondary battery manufactured by using a cathode active material of Example 1;

[85] FIG. 2 is a graph showing a charge/discharge capacity of a lithium secondary battery manufactured by using a cathode active material of Example 2;

[86] FIG. 3 is a graph showing a charge/discharge capacity of a lithium secondary battery manufactured by using a cathode active material of Example 3;

[87] FIG. 4 is a graph showing a charge/discharge capacity of a lithium secondary battery manufactured by using a cathode active material of Comparative Example 1;

[88] FIG. 5 is a graph showing a charge/discharge capacity of a lithium secondary battery manufactured by using a cathode active material of Comparative Example 2;

[89] FIG. 6 is a graph showing a charge/discharge capacity of a lithium secondary battery manufactured by using a cathode active material of Comparative Example 3;

[90] FIG. 7 is an IR spectrometer graph showing surface characteristic variations according to temperature and measuring conditions of the cathode active material

prepared in Example 1;

[91] FIG. 8 is an IR spectrometer graph showing surface characteristic variations according to temperature and measuring conditions of the cathode active material prepared in Comparative Example 1; and

[92] FIG. 9 is an IR spectrometer graph showing acid sites of the cathode active materials of Examples 1 to 3 and Comparative Examples 1 to 3, and acid strength thereof.

Mode for Invention

[93] Hereinafter, the present invention will be described in further detail with reference to examples and comparative examples. It is to be understood, however, that these examples are illustrative only and the scope of the present invention is not limited thereto.

[94] **Example 1**

[95] **1-1. Preparation of cathode active material**

[96] 0.8 mol% Al-isopropoxide and 0.8 mol% $\text{CH}_3\text{Si}(\text{OCH}_3)_3$ were put in 200ml dehydrated alcohol, and then were stirred during 18 hours. After that, 100g LiCoO_2 was put in the mixture, and then the mixture was stirred during 80 minutes. The mixture was filtered by use of a vacuum filter to obtain an electrode active material. The obtained electrode active material was dried in a vacuum oven at 130 °C, thereby preparing an active material with a treated surface.

[97] **1-2. Manufacture of cathode**

[98] The prepared cathode active material, a conductive agent, and a binder were put in an NMP solvent in a ratio of 95:2.5:2.5 to prepare cathode slurry. After the slurry was applied on an Al foil of 20 μm , the Al foil was dried in a vacuum oven at 130 °C to manufacture an cathode.

[99] **1-3. Manufacture of lithium secondary half cell**

[100] After the obtained electrode was worked by a rolling process to have porosity of 25%, it was punched in a coin shape to form a coin-shaped battery. At that time, an opposite electrode was made of Li metal, and an electrolyte, in which 1M LiPF_6 was solved in a solvent containing EC and EMC in a ratio of 1:2, was used.

[101] **Example 2**

[102] A cathode active material was obtained by the same process as Example 1, except that the dried active material was additionally annealed at 300 °C. And then, a cathode active material, a cathode using the cathode active material, and a coil-shaped battery having the cathode were manufactured the same process as Example 1.

[103] **Example 3**

[104] A cathode active material was obtained by the same process as Example 1, except that the cathode active material prepared only using Al-isopropoxide was additionally annealed at 400 °C. And then, a cathode active material, a cathode using the cathode

active material, and a coil-shaped battery having the cathode were manufactured the same process as Example 1.

[105] **Comparative Example 1**

[106] A cathode and a coil-shaped battery having the cathode were manufactured the same process as Example 1, except that conventional LiCoO_2 was used as a cathode active material instead of the cathode active material with a treated surface.

[107] **Comparative Example 2**

[108] A cathode active material was obtained by the same process as Example 1, except that the cathode active material was prepared only using Al-isopropoxide. And then, a cathode active material, a cathode using the cathode active material, and a coil-shaped battery having the cathode were manufactured the same process as Example 1.

[109] **Comparative Example 3**

[110] A cathode active material was obtained by the same process as Example 1, except that the cathode active material was prepared only using $\text{CH}_3\text{Si}(\text{OCH}_3)_3$. And then, a cathode active material, a cathode using the cathode active material, and a coil-shaped battery having the cathode were manufactured the same process as Example 1.

[111] **Experimental Example 1: Analysis for surface physical properties of electrode active material**

[112] The following experiment was performed to analyze the physical properties of the surface-modified electrode active material according to the present invention.

[113] A cathode active material with a surface modified by the organic-inorganic compound obtained by Example 1 was used as a sample, and a conventional cathode active material (i.e., LiCoO_2) was used as a control.

[114] The above cathode active materials were respectively observed in states of room temperature and atmosphere, room temperature and vacuum, 50 °C and vacuum, 100 °C and vacuum, 200 °C and vacuum, and 300 °C and vacuum, by use of an IR spectrometer. As a result, an alkyl group ($-\text{CH}_2\text{CH}_3$) appearing in the vicinity of 2800 to 3000 cm^{-1} is not appeared in the cathode active material of Comparative Examples 1 and 2 (see FIG. 8), but an alkyl group is appeared in the cathode active material of the present invention (see FIG. 7). Therefore, it can be verified that the hybrid of the organic substance and the inorganic substance is existed in the surface modified material existed in the cathode active material of the present invention.

[115] **Experimental Example 2: Analysis for acid site of electrode active material**

[116] The following experiment was performed to analyze the surface properties of the surface-modified electrode active material according to the present invention.

[117] A cathode active material with a surface modified by the organic-inorganic hybrid obtained by Example 1 and the cathode active material with a surface modified by the inorganic substance having the acid site obtained by Example 3 were used as samples,

and a conventional cathode active material (i.e., LiCoO_2) obtained by Comparative Example 1 and the cathode active material with a surface modified only by the inorganic substance or the organic substance each obtained by Comparative Example 2 and 3 were used as controls.

[118] The above cathode active materials were absorbed with a CH_3CN compound, and then the acid sites thereof were respectively measured by use of an IR spectrometer. For reference, since the CH_3CN compound is a basic compound having unshared electron pair, and thus is surface absorbed by neutralization with the compound having the acid site, a peak change may be appeared in IR spectrum. Consequently, the acid strength of the compound having the acid site can be measured.

[119] As the experimental results, the cathode active material of Comparative Example 1 using a conventional cathode active material, the cathode active material of Comparative Example 2 using the cathode active material with the surface modified only by the inorganic substance, and the cathode active material of Comparative Example 3 using the cathode active material with the surface modified only by the organic substance did not show special change in IR data. By contrast, according to the cathode active material of Example 3, of which the surface was modified only by the inorganic substance having the acid site, and the cathode active material of Example 1, of which the surface was modified by the hybrid of the organic-inorganic compound, the peak for a nitrile group was found in the vicinity of 2200 to 2400cm^{-1} . Thus, it was verified that the acid site is formed on surface of the electrode active material (see FIG. 9).

[120] In particular, comparing the cathode active material of Example 3, of which the surface was modified only by the same inorganic substance, with the cathode active material of Comparative Example 2, although the cathode active material of Comparative Example 2 prevents the side reaction with the electrolyte, the cathode active material does not contribute to the formation of the acid site, thereby deteriorating the performance of the battery (see FIG. 5). However, the performance of the battery using the cathode active material having the acid site of Example 3 is enhanced (see FIG. 3). Thus, it was verified that the formation of the acid site is a factor associated with the performance of the battery.

[121] **Experimental Example 3: Evaluation for performance of Lithium secondary battery**

[122] The following experiment was performed to evaluate the performance of the lithium secondary battery manufactured by using the electrode active material having the acid site on its surface according to the present invention.

[123] The coin-shaped batteries of Examples 1 to 3 which were manufactured by using the cathode active material having the acid site were tested. Meanwhile, the coin-shaped

batteries of Comparative Examples 1 to 3 were tested as corresponding samples, in which the surface was not modified, or the surface were modified only by the inorganic substance or the organic substance.

- [124] Each sample was subjected to charge/discharge cycles by constant current and constant voltage (CC/CV) in the charge/discharge range from 3 to 4.5 V at a current density of 0.5C and a temperature of 50 °C . The obtained results are shown in FIGs. 1 to 6 as a charge/discharge graph for each cycle.
- [125] As test results, in the batteries of Examples 1 to 3 which were manufactured by using the cathode active material having the acid site, the charge/discharge efficiencies were maintained with a lapse of the cycle. In other words, it can be understood that the cycle characteristic is remarkably enhanced (see FIGs. 1 to 3). Meanwhile, in the batteries of Comparative Examples 1 to 3 which were manufactured by using the cathode active material with no acid site on its surface, it can be understood that the charge/discharge characteristic is lowered (see FIGs. 4 to 6).
- [126] While this invention has been described in connection with what is presently considered to be the most practical and preferred embodiment, it is to be understood that the invention is not limited to the disclosed embodiment and the drawings.

Industrial Applicability

- [127] As can be seen from the foregoing, by adjusting the acid site on the surface of the electrode active material, the side reaction of the electrode active material with the electrolyte is decreased, and the structure stability of the electrode active material is secured, thereby enhancing the performance of the battery.

What is claimed is:

1. An electrode active material comprising an acid site, wherein the acid site is partially or wholly formed on a surface of the electrode active material, and the acid site is formed by a hybrid comprising organic metalloid compound or organic metal compound including at least one of an electron donating group and inorganic compound.
2. The electrode active material as claimed in claim 1, wherein the acid site is Brønsted acid or Lewis acid.
3. The electrode active material as claimed in claim 1, wherein a strength of the acid strength is in the range from -10 to 10 in terms of Hammett indicator (H_0).
4. The electrode active material as claimed in claim 1, wherein the acid site is formed due to either or both of an electronegativity difference between the organic metalloid compound and the inorganic compound which are bonded to each other, and an organic substance bonded to the organic metalloid compound or the organic metal compound.
5. The electrode active material as claimed in claim 1, wherein the organic metalloid compound or the organic metal compound comprises (a) an element of Group 14; or (b) a compound of an element of Group 14, and at least one selected from the group consisting of alkaline earth metal, alkaline metal, an element of Group 13, an element of Group 15, transition metal, lanthanide metal, and actinide metal.
6. The electrode active material as claimed in claim 1, wherein the organic metalloid compound is a compound containing silicon.
7. The electrode active material as claimed in claim 6, wherein the organic metalloid compound containing silicon comprises at least one selected from the group consisting of silylizing agent, silane coupling agent, and silane polymer.
8. The electrode active material as claimed in claim 1, wherein the organic metalloid compound or the organic metal compound is represented by any one of following Formulas 2 to 7:

Formula 2

$\text{Si}(\text{OR})_{4-x} \text{R}_x$, wherein $0.1 \leq x \leq 3$;

Formula 3

$\text{Si}(\text{OR})_{4-(x+y)} \text{R}_x \text{Z}_y$, wherein $0.1 \leq x+y \leq 3.9$;

Formula 4

$\text{Si}(\text{OR})_{4-x} \text{R}_x \text{Si}$, wherein $0.1 \leq x \leq 3$;

Formula 5

$\text{Si}(\text{OR})_{4-(x+y)} \text{R}_x \text{Z}_y \text{Si}$, wherein $0.1 \leq x+y \leq 3.9$;

Formula 6

$\text{R}_x \text{M}(\text{OR})_{4-x}$, wherein $1 \leq x \leq 3$; and

Formula 7

$\text{R}_x \text{MZ}_y(\text{OR})_{4-(x+y)}$, wherein $0.1 \leq x+y \leq 3.9$;

wherein, Z is one element selected from the group consisting of halogen atoms; M is at least one element selected from the group consisting of alkaline earth metal, alkaline metal, transition metal, lanthanide metal, and actinide metal; and R is a substituent selected from the group consisting of C1 to C20 alkyl group, alkenyl group, alkynyl group, vinyl group, amino group, and mercapto group, the group is substituted or non-substituted by a halogen element.

9. The electrode active material as claimed in claim 1, wherein a component ratio of the organic metalloid compound or the organic metal compound to the inorganic compound is in the range of 0:100 to 95:5wt%.

10. The electrode active material as claimed in claim 1, wherein a content of the hybrid comprising the organic metalloid compound or the organic metal compound and the inorganic compound is 0.05 to 20 parts by weight based on 100 parts by weight of the electrode active material.

11. An electrode comprising the electrode active material according to any one of claims 1 to 10.
12. The electrode as claimed in claim 11, wherein the electrode is a cathode.
13. The electrode as claimed in claim 11, wherein reactivity between the electrode active material and HX, wherein X is any one of F, Cl, Br, and I, is decreased due to the acid site partially or wholly formed on the surface of the electrode active material.
14. An electrochemical device comprising an anode, a cathode, a separator, and an electrolyte, wherein either or both of the anode and the cathode comprises the electrode active material according to any one of claims 1 to 10.
15. The electrochemical device as claimed in claim 14, wherein the electrochemical device is a lithium secondary battery.
16. A method for manufacturing an electrode active material according to any one of claims 1-10, which comprises the steps of: (i) reacting (a) an organic metalloid compound or an organic metal compound including at least one of an electron donating group with (b) an inorganic compound to form a hybrid comprising organic metalloid compound or organic metal compound including at least one of an electron donating group and inorganic compound; (ii) coating the result of step (i) onto a surface of the electrode active material and drying the coating layer; and (iii) annealing the result of step (ii) between 100°C to 600°C to form an acid site on the surface of the electrode active material.
17. The method as claimed in claim 16, wherein the acid strength is in the range from -10 to 10 in terms of Hammett indicator (H_0).

FIG. 1

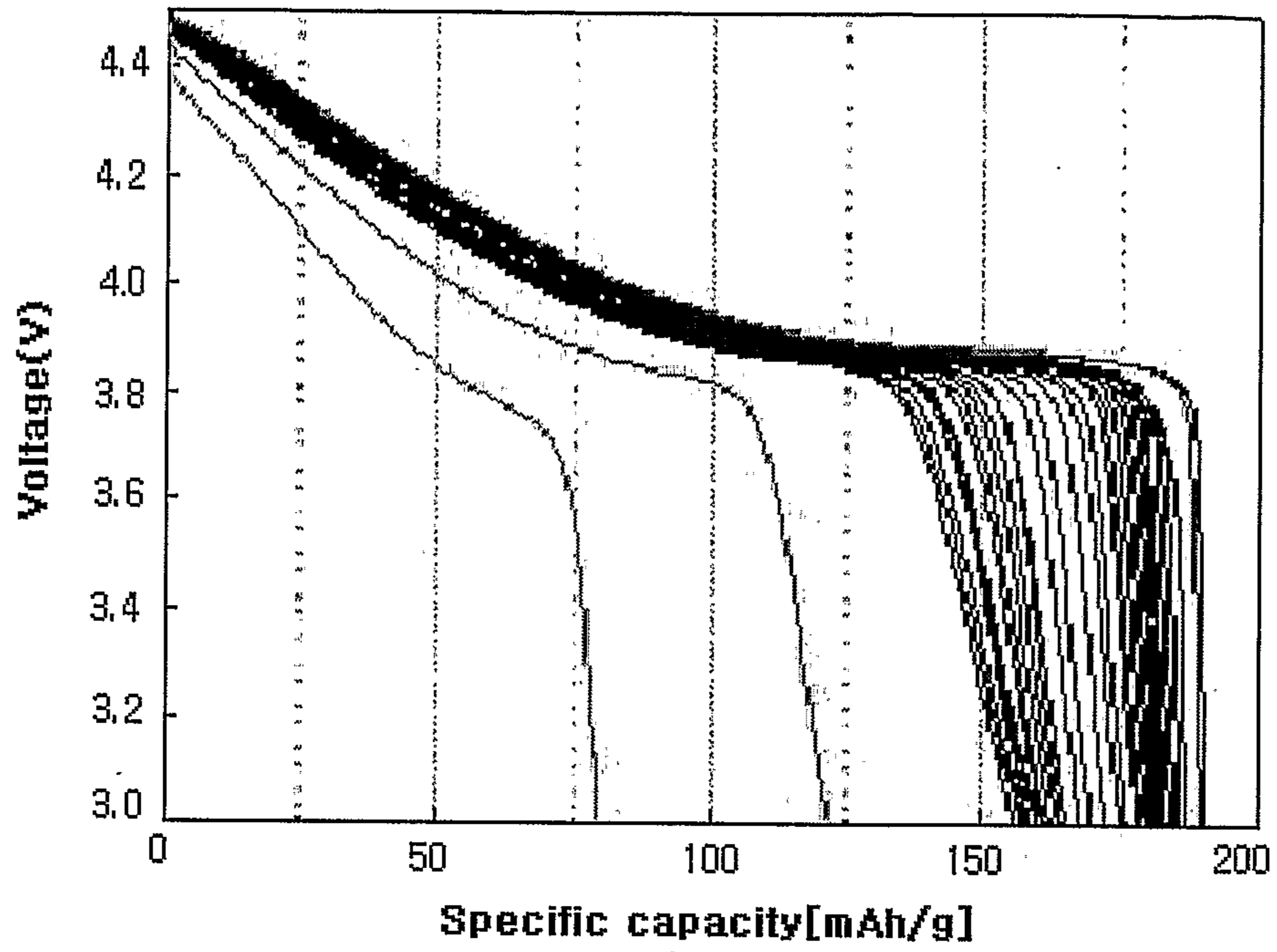


FIG. 2

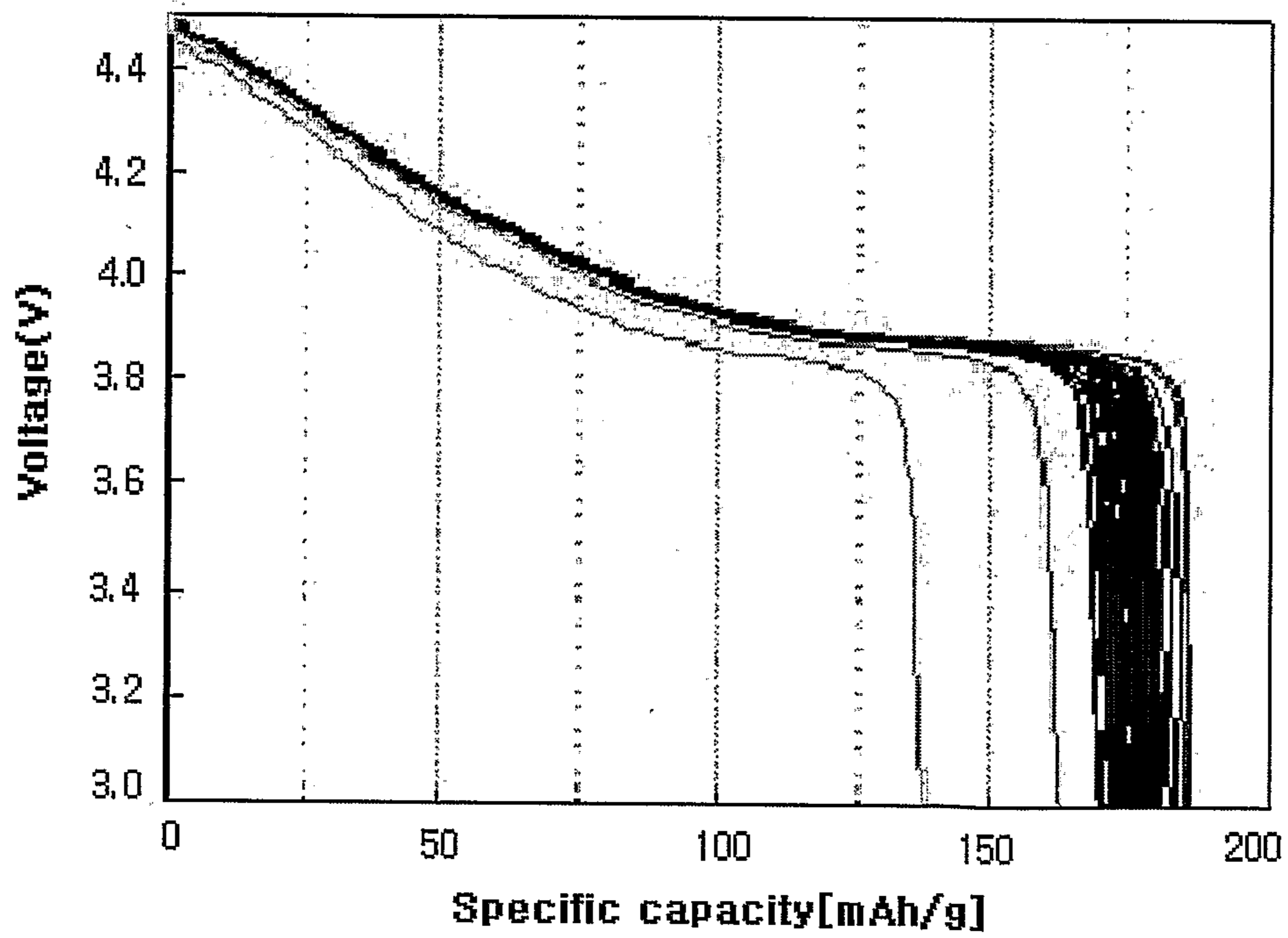


FIG. 3

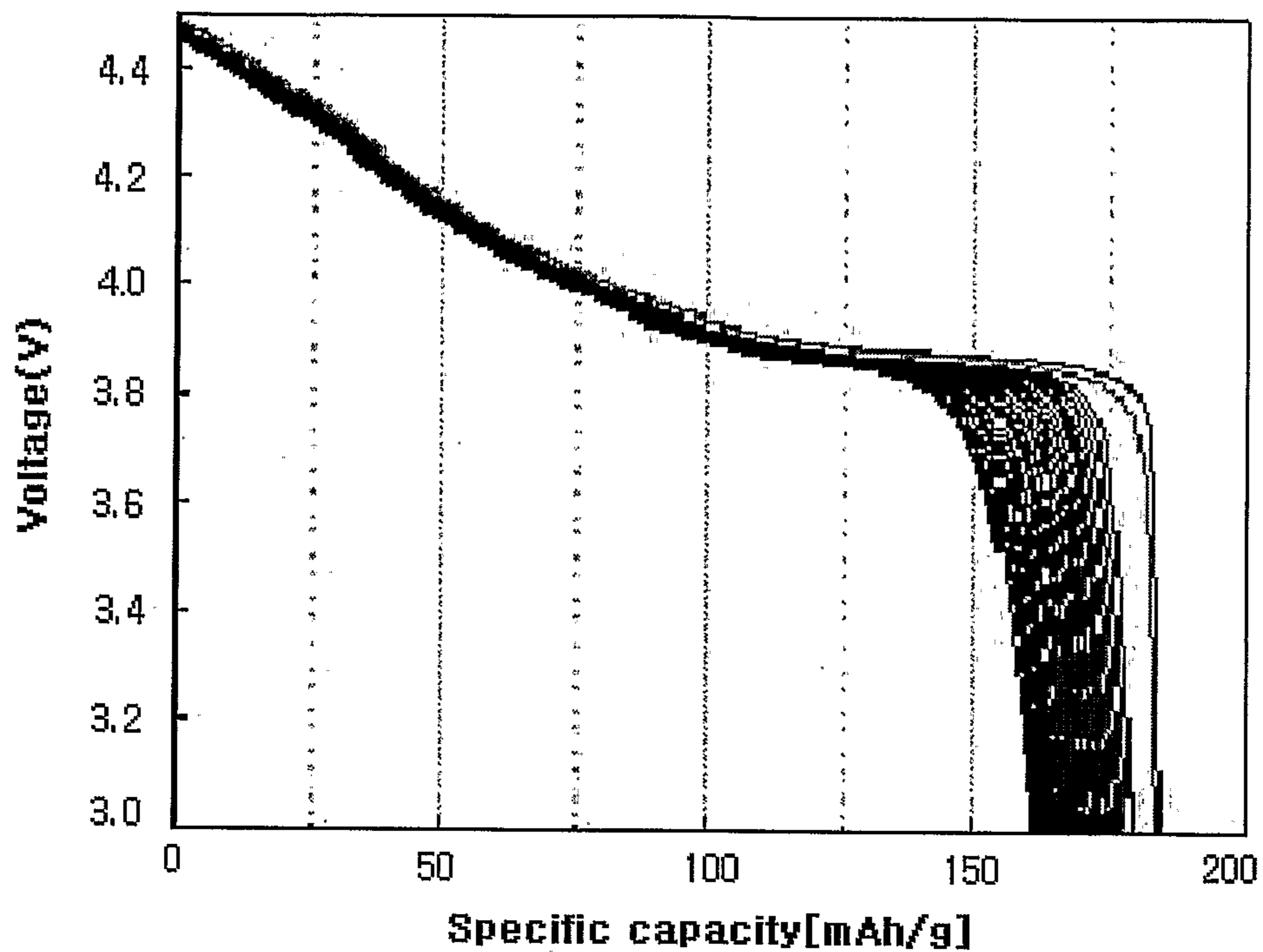


FIG. 4

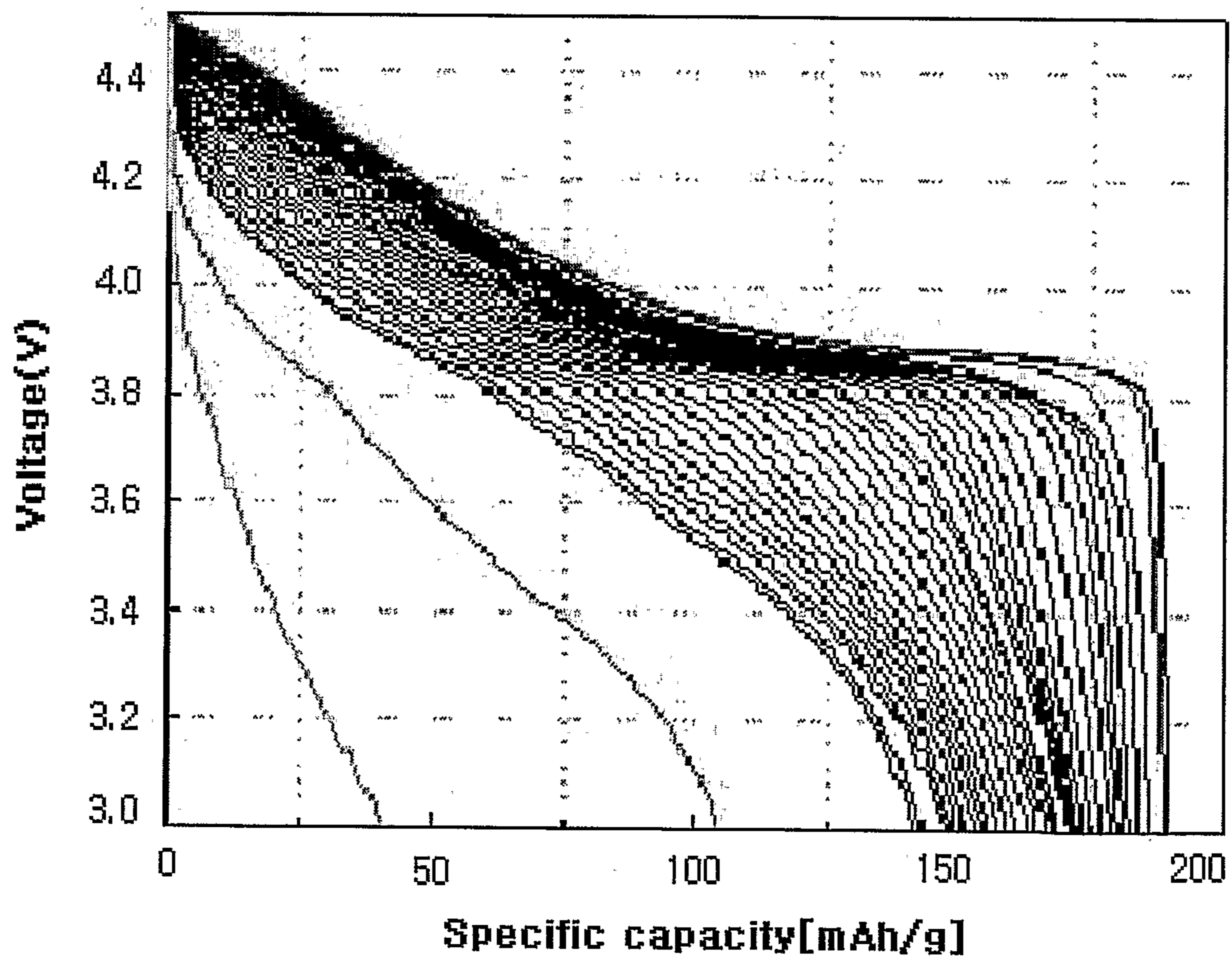


FIG. 5

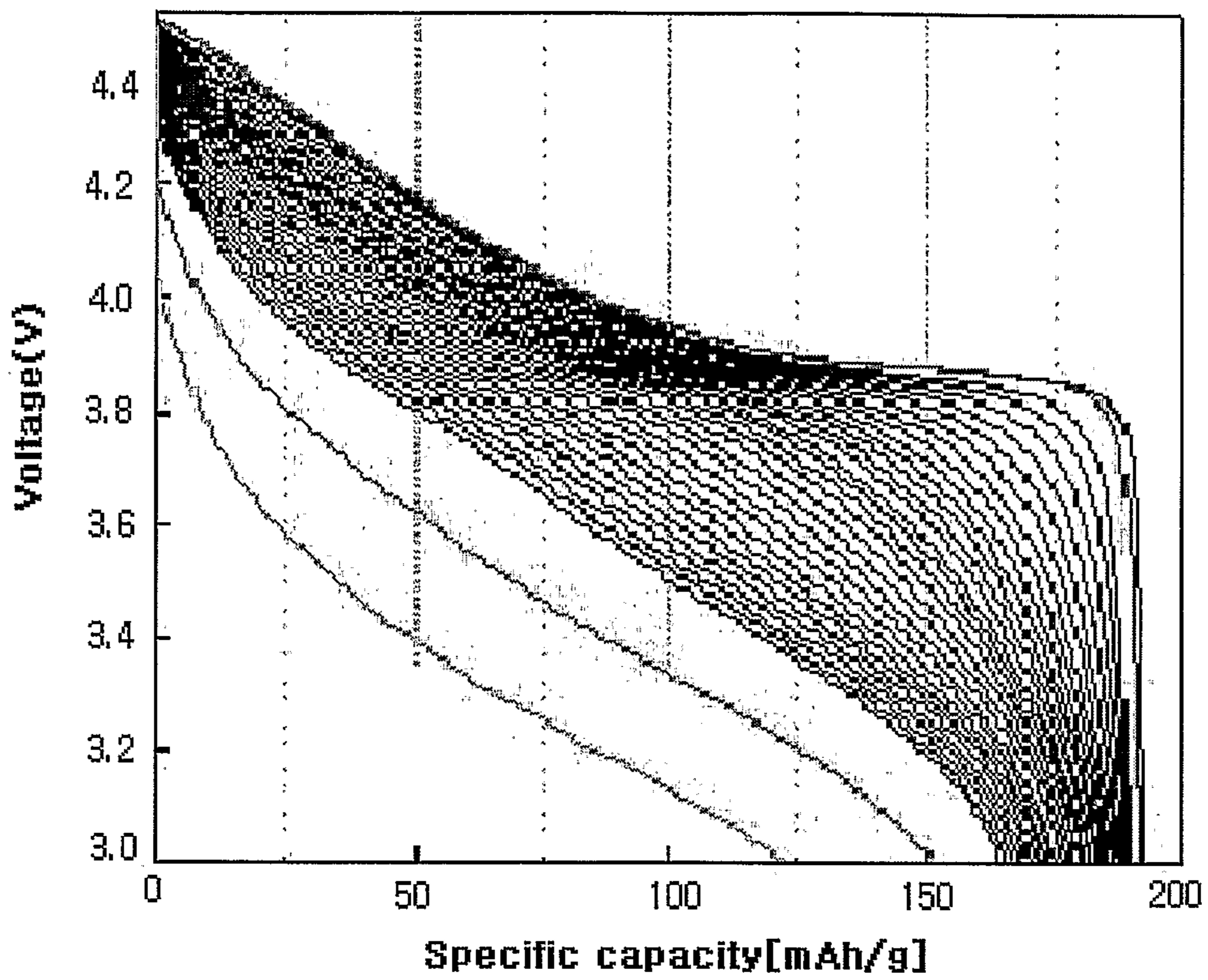
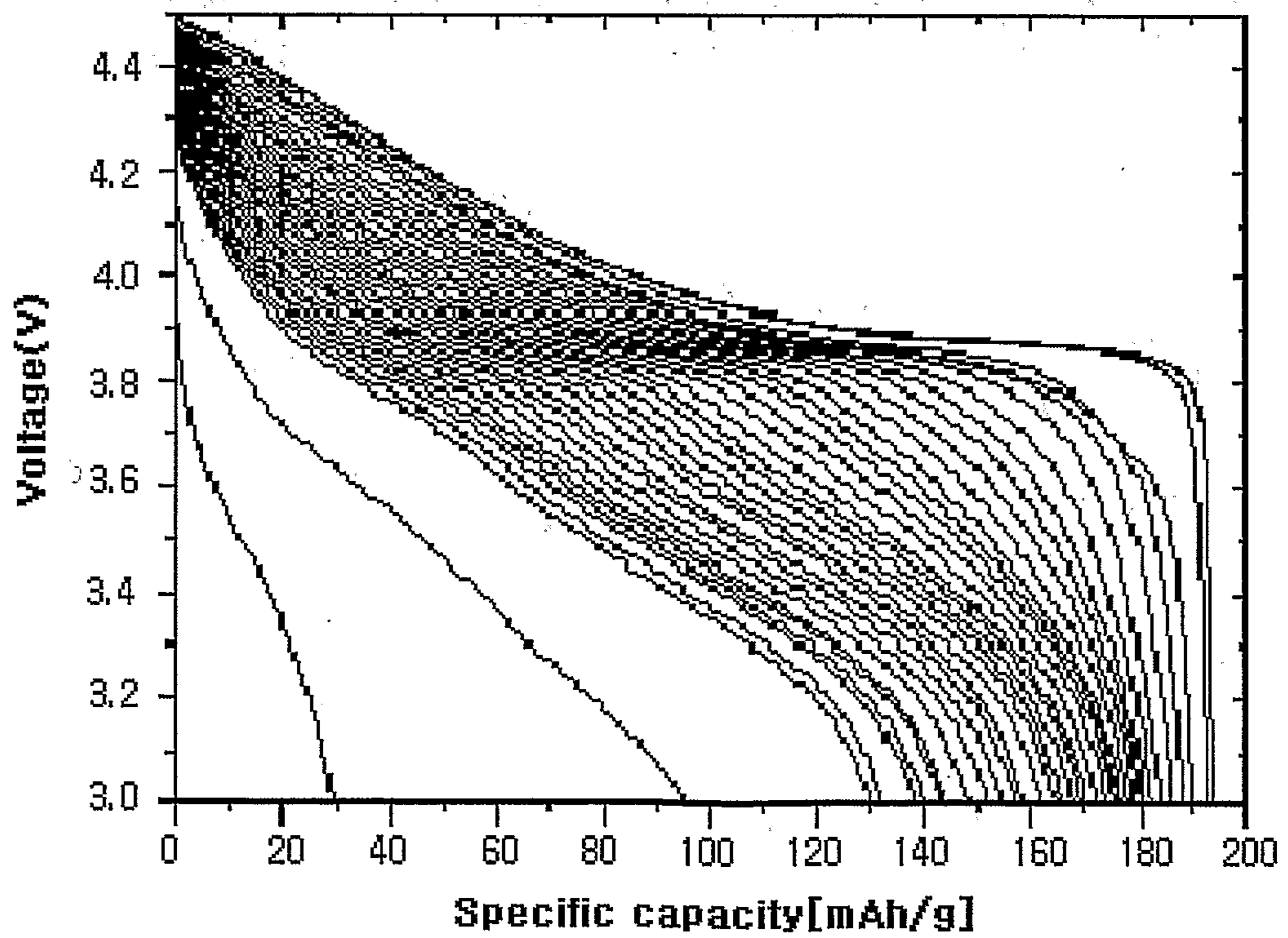
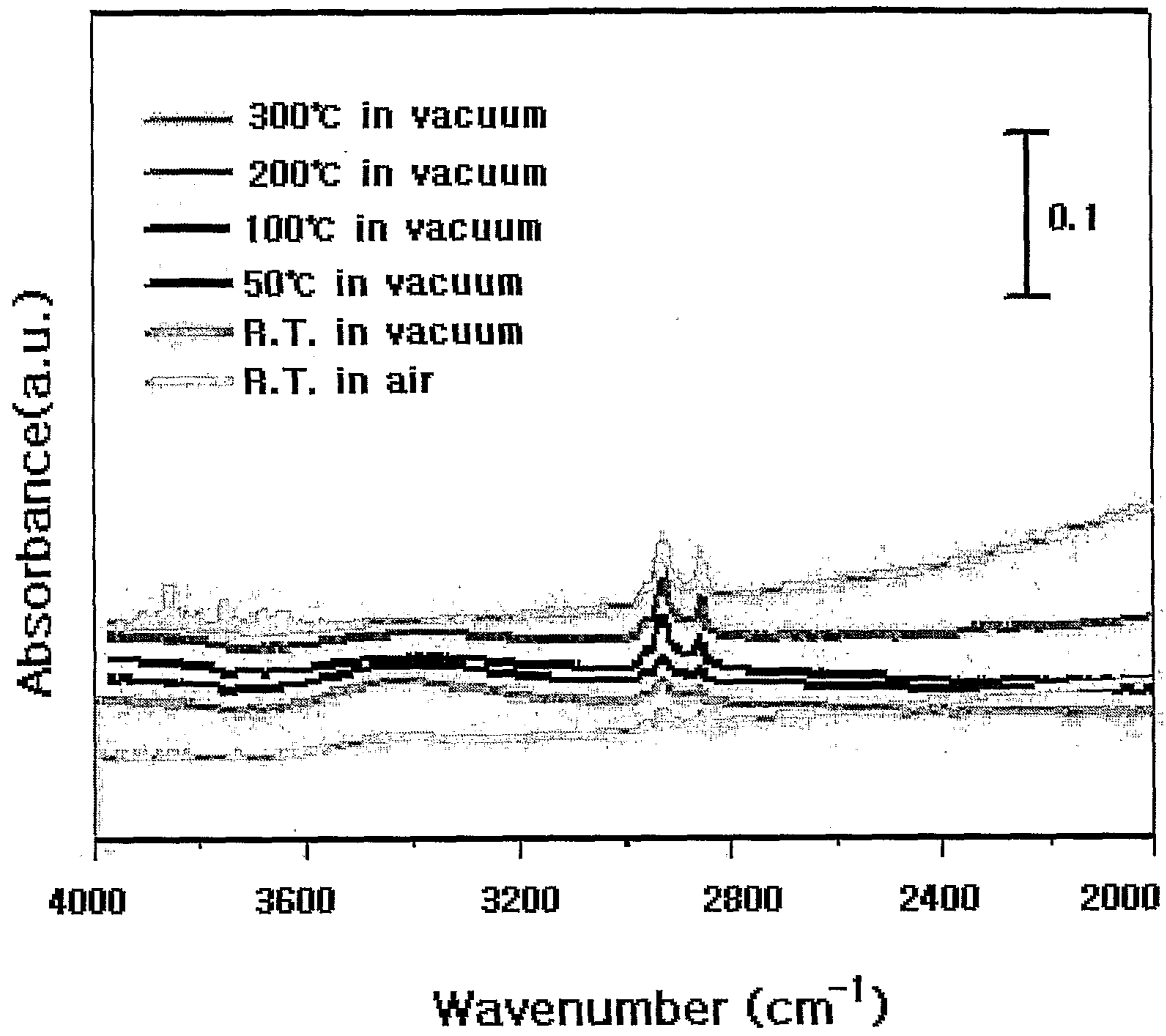


FIG. 6



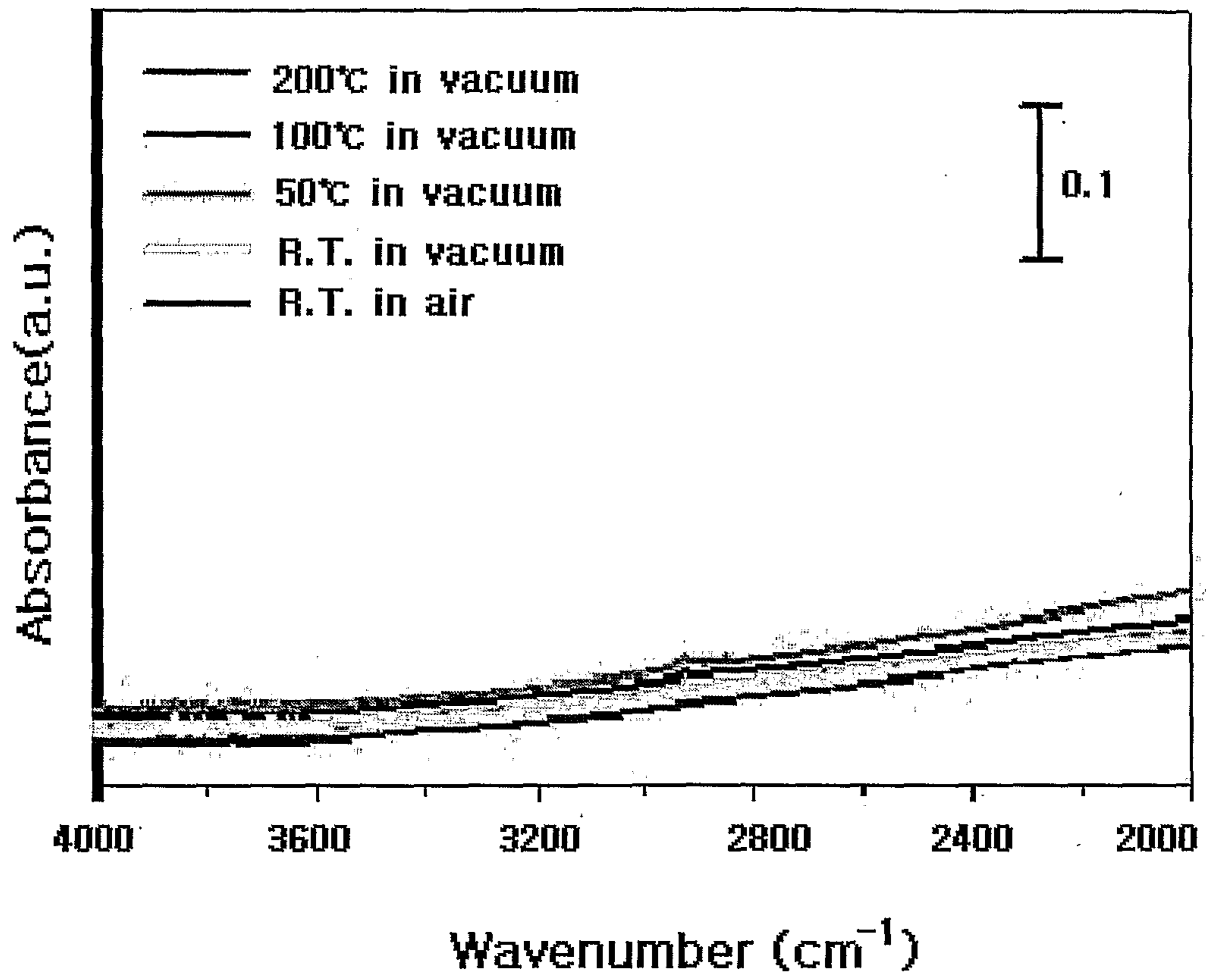
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FIG. 7



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FIG. 8



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FIG. 9

