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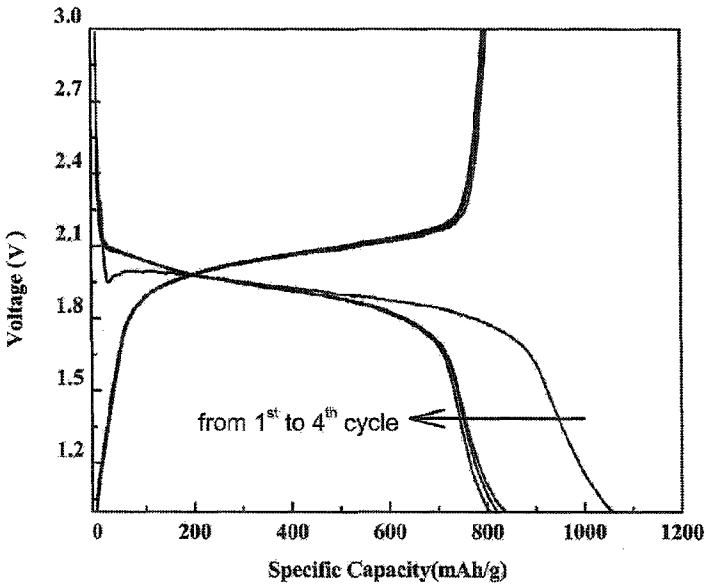
(54) Titre : PROCEDE DE PREPARATION ET D'APPLICATION DE COMPOSITES DE CARBONE-SELENIUM

(54) Title: METHOD OF PREPARING AND APPLICATION OF CARBON-SELENIUM COMPOSITES



(57) Abrégé/Abstract:
Disclosed is method of preparing a selenium carbon composite material and a use of the selenium carbon composite material in a cathode of a lithium selenium secondary battery. A battery formed with a cathode of the disclosed selenium carbon composite material has high energy density and stable electrochemical performance. The disclosed selenium carbon composite material can effectively shorten the migration distance of lithium ions during charging and discharging of the battery and improve conductivity and utilization of selenium after compounding carbon and selenium. Multiple batteries formed with cathodes of the disclosed selenium carbon composite material can be assembled into a lithium selenium pouch-cell battery having stable electrochemical performance and high energy density.

Abstract

Disclosed is method of preparing a selenium carbon composite material and a use of the selenium carbon composite material in a cathode of a lithium selenium secondary battery. A battery formed with a cathode of the disclosed selenium carbon composite material has high energy density and stable electrochemical performance. The disclosed selenium carbon composite material can effectively shorten the migration distance of lithium ions during charging and discharging of the battery and improve conductivity and utilization of selenium after compounding carbon and selenium. Multiple batteries formed with cathodes of the disclosed selenium carbon composite material can be assembled into a lithium selenium pouch-cell battery having stable electrochemical performance and high energy density.

Date Reçue/Date Received 2023-06-21

METHOD OF PREPARING AND APPLICATION OF CARBON-SELENIUM COMPOSITES

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to the field of lithium secondary batteries of high energy density, particularly relates to a novel preparation method of carbon-selenium nanocomposite materials and their applications.

Description of Related Art

With the increasing human demand for energy, secondary batteries with high energy density and high volume energy density, such as lithium-sulfur batteries and lithium-selenium batteries, have attracted widespread interests. Group 6A elements in the periodical table, such as sulfur and selenium, have shown two-electron reaction mechanisms in the electrochemical reaction process with lithium. Despite the theoretical mass energy specific capacity of selenium (675 mA h/g) is lower than that of sulfur (1675 mA h / g), selenium has a higher density (4.82 g/cm^3) than sulfur (2.07 g/cm^3); therefore the theoretical volume energy density of selenium (3253 mAh/cm^3) is close to the theoretical volumetric energy density of sulfur (3467 mAh/cm^3). At the same time, as compared with sulfur, close to an electrically insulated material, selenium is semi-conductive electrically and shows better electrically conductive property. Therefore, as compared to sulfur, selenium can demonstrate a higher level of activity and better utilization efficiency even at a higher loading level, leading to high surface density battery systems. Moreover, selenium-carbon composite can have a further improvement

Date reçue / Date received 2021-11-09

in the electrical conductivity over sulfur-carbon composite to obtain a higher activity electrode material. As described in the patent CN104393304A, by passing hydrogen selenide gas through graphene dispersion solution, the solvent heat reduces the graphene oxide into graphene while oxidized the hydrogen selenide into selenium. The such prepared selenium graphene electrode materials pairs with ethers electrolyte system, 1.5M lithium bi-trifluoromethane sulfonimide (LiTFSI) / 1,3-dioxolane (DOL) + dimethyl ether (DME) (Volume ratio 1: 1); the charging specific capacity reaches 640 mA h/g (approaching selenium theoretical specific capacity) in the first cycle. But in the charge-discharge process, polyselenide ions dissolve in the electrolyte, showing significant amounts of the shuttling effect, which causes the subsequent capacity decay. At the same time, the procedures for preparing the graphene oxide raw material that is used in this process are complicated, not suitable for industrial production. CN104201389A patent discloses a lithium-selenium battery cathode material, utilizing a nitrogen-containing layered porous carbon composite current-collector which was compounded with selenium. In preparing nitrogen-containing layered porous carbon composite current collector, nitrogen-containing conductive polymer is first deposited or grown on the surface of a piece of paper, followed by alkali activation and high temperature carbonization, resulting in a nitrogen-containing layered porous carbon composite current collector with carbon fiber as network structure that supports itself; and such nitrogen-containing layered porous carbon composite current collector is then further compounded with selenium. The deposition method for preparing a conductive polymer is complicated and the process for film formation or growth is hard to control. The preparation process is complicated, which associates with undesirably high costs.

SUMMARY OF THE INVENTION

The present invention uses one-step process to prepare a two-dimensional carbon nanomaterial, which has a high degree of graphitization; the two-dimensional carbon nanomaterials are compounded with selenium to obtain a carbon-selenium composite material, which is used as a cathode material that pairs with anode material containing lithium, resulting in

Date reçue / Date received 2021-11-09

a lithium-selenium battery that has a high energy density and stable electrochemical performances. Similar procedures were used to further assemble a pouch cell, which also demonstrates excellent electrochemical properties.

The aspect of the present invention is to provide a method to prepare selenium-carbon composite material with readily available raw materials and simple preparation procedures.

Selenium-carbon composite material descripted the present invention is obtained from the preparation method that comprises the following steps:

(1) Carbonize alkali metal organic salts or alkaline earth metal organic salts in high temperature, and then wash with dilute hydrochloric acid, and dry to obtain a two-dimensional carbon material;

(2) Mix the two-dimensional carbon material obtained in step (1) with a selenium organic solution, heat and evaporate the organic solvent, and then achieve compounding selenium with the two-dimensional carbon material through a multi-stage heat ramping and soaking procedure to obtain carbon-selenium composite.

Wherein, in the step (1), the alkali metal organic salt is selected from one or several of potassium citrate, potassium gluconate, sucrose acid sodium. The alkaline earth metal organic salt is selected from one or both of calcium gluconate, sucrose acid calcium. The high temperature carbonization is performed at 600-1000 °C, preferably, 700-900 °C; carbonation time for 1-10 hours, preferably for 3-5 hours.

Wherein, step (2) of the organic solvent is selected from one or several of ethanol, dimethylsulfoxide (DMSO), toluene, acetonitrile, N,N-dimethylformamide (DMF), carbon tetrachloride, diethyl ether or ethyl acetate; multi-heat ramping & soaking section is referred as to a ramping rate 2-10 °C / min, preferably 5-8 °C / min, to a temperature between 200 and 300 °C, preferably between 220 and 280 °C, followed by soaking at the temperature for 3-10 hours,

Date reçue / Date received 2021-11-09

preferably, 3-4 hours; then continue to heat up to 400 °C -600 °C, preferably, 430-460°C, followed by soaking for 10-30 hours, preferably 15-20 hours.

Another aspect of the present invention is to provide a lithium-selenium secondary battery that comprises the carbon-selenium composite materials. The said selenium lithium secondary battery further comprises: a lithium-containing anode, a separator, and an electrolyte.

Among them, lithium-containing anode may be one or several of lithium metal, a lithiated graphite anode, lithiated silicon carbon anode materials (through assembling the graphite and silicon-carbon anode materials and lithium anode into a half battery, discharge, to prepare lithiated graphite anode and lithiated silicon carbon anode materials). The separator (membrane) is one of the commercial celgard membrane, Whatman membrane, cellulose membrane, a polymer membrane. The electrolyte is one or several of the carbonate electrolyte, ether electrolyte, and ionic liquids. Carbonate electrolyte is selected from one or several from diethyl carbonate ester (DEC), dimethyl carbonate (DMC), ethylene carbonate (EC), ethyl methyl carbonate (EMC), and propylene carbonate (PC). The solute is selected from one or several from lithium hexafluoro phosphate (LiPF6), lithium bis (trifluoromethanesulfonyl) imide (LiTFSI), lithium perchlorate (LiClO4) and lithium bis(fluorosulfonyl) imide (LiFSI). In ether electrolytic solution, the solvent is selected one or several from 1,3-dioxolane (DOL), ethylene glycol dimethyl ether (DME) and triethylene glycol dimethyl ether (TEGDME); solute is selected in one or more from lithium hexafluorophosphate (LiPF6), lithium bis-(trifluoromethanesulfonyl) imide (LiTFSI), lithium perchlorate (LiClO4) and lithium bis-fluorosulfonylimide (LiFSI). For ionic liquids, the Ionic liquid is one or more from room temperature ionic liquid [EMIm] NTf2 (1-ethyl-3-methylimidazolium bis trifluoromethane sulfonimide salt), [Py13] NTf2 (N-Propyl -N-methylpyrrolidine bis trifluoromethane sulfonimide salt), [PP13] NTf2 (N- propyl-methylpiperidine alkoxy -N-Bis trifluoromethane sulfonimide salts); solute is selected in one or more from lithium hexafluorophosphate (LiPF6), bis(trifluoromethylsulfonyl) imide (LiTFSI), lithium perchlorate (LiClO4) and lithium bis fluorosulfonylimide (LiFSI).

Date reçue / Date received 2021-11-09

The present invention also provides a pouch-cell lithium-selenium battery containing the carbon selenium composite material.

Compared with the prior art, with respect to the method for preparing selenium carbon composite material in the present invention, the two-dimensional carbon material is not only of the advantages in that the raw materials are readily available and low cost, and preparation method is simple, highly practical and suitable for mass production, but also the obtained selenium carbon composite material exhibits excellent electrochemical properties.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a 50,000X scanning electron microscope photograph for carbon material in the example 1.

Figure 2 is a 0.1C charge and discharge curve of the lithium selenium battery in the example 1.

Figure 3 is a 0.1C charge and discharge curve of the lithium selenium battery in the comparative example 2.

Figure 4 is an optical image of the pouch-cell battery case in the example 1.

Figure 5 is a 0.05C charge and discharge curve of the pouch-cell battery case in the example 1.

DESCRIPTION OF THE INVENTION

In conjunction with the specific examples, the present invention will be further described below. Unless otherwise specified, the experimental methods in the following examples are all conventional; the reagents and materials are all available from commercial sources.

Example 1:

(A) Preparation of selenium carbon composite material

After grinding and milling, an appropriate amount of potassium citrate is calcined at 800 °C for 5 hours under an inert atmosphere, and cooled to room temperature.

Date reçue / Date received 2021-11-09

Washed with dilute hydrochloric acid to a neutral pH; filtered and dried to give a two-dimensional carbon nanomaterial (Figure 1); according to the mass ratio of 50:50, weigh the two dimensional carbon material and selenium, and then stir and mix with the ethanol solution of selenium uniformly; after solvent evaporation, dry the mixture in dry oven; the dried mixture was heated at 5 °C /min to 240 °C and soaked for 3 hours; then continues to heat up at 5 °C /min to 450 °C; soaked for 20 hours; cooled to room temperatures, which resulted in the selenium carbon composite material.

(B) Preparation of the cathode tab

The above-prepared selenium carbon composites are mixed with carbon black Super-P and binder CMC / SBR (1: 1) along with water by a fixed proportions by pulping, coating, drying and other procedures to obtain selenium carbon composite cathode.

(C) Assembling lithium - selenium Battery

The above-prepared selenium carbon composite cathode, lithium foil as anode, celgard diaphragm as separator and 1M LiPF6 in EC/DMC as the electrolyte were assembled into a lithium selenium button cell battery and lithium selenium pouch-cell battery (Figure 4).

(D) Lithium-selenium battery test

Use a charge-discharge apparatus to do constant current charge - discharge test on the said lithium-selenium button cell battery and lithium selenium pouch-cell battery. Test voltage range is between 1.0 and 3.0 V and test temperature is 25 °C. Discharge specific capacity and the level of charge-discharge current are standardly calculated based on the mass of selenium. The charge - discharge current is 0.1C or 0.05C. Lithium selenium button coin battery charge and discharge curve is shown in Figure 2, the specific test results are shown in Table 1. Lithium selenium pouch-cell battery test results are shown in Figure 5.

Date reçue / Date received 2021-11-09

Example 2:

Other experimental conditions are same as in Example 1; only exception is that the raw material carbonized for two-dimensional carbon is sodium citrate. Battery Test results are summarized in Table 1 below.

Example 3:

Other experimental conditions are same as in Example 1; only exception is that the raw material carbonized for two-dimensional carbon is potassium gluconate. Battery Test results are summarized in Table 1 below.

Example 4:

Other experimental conditions are same as in Example 1; only exception is that the high-temperature carbonization temperature for the carbon material is 650°C. Battery Test results are summarized in Table 1 below.

Example 5:

Other experimental conditions are same as in Example 1; only exception is that the dried mixture was heated at 5 °C / min to 300 °C and soaked at this temperature for 3 hours. Battery Test results are summarized in Table 1 below.

Example 6:

Other experimental conditions are same as in Example 1; only exception is that the dried mixture was heated at 5 °C / min to 240 °C and soaked at this temperature for 3 hours, then continued to heat up to 600 °C, and soaked at this constant temperature for 20 hours. Battery Test results are summarized in Table 1 below.

Example 7:

Other experimental conditions are same as in Example 1; only exception is that the lithium-Se battery is packed with lithiated graphite anode, instead of the lithium anode sheet. Battery Test results are summarized in Table 1 below.

Example 8:

Date reçue / Date received 2021-11-09

Other experimental conditions are same as in Example 1; only exception is that the lithium-Se battery is packed with lithiated silicon carbon anode, instead of the lithium anode sheet. Battery Test results are summarized in Table 1 below.

Comparative Example 1:

Other experimental conditions are the same as in Example 1; only exception is that the use of polyacrylonitrile as the raw material. Battery Test results are summarized in Table 1 below.

Comparative Example 2:

Other experimental conditions are the same as in Example 1; only exception is that using one-step compound method to prepare selenium and carbon composite. The dried selenium carbon mixture was heated at 5 °C / min to 500 °C and soaked at this temperature for 23 hours to obtain selenium carbon composite material. The charge-discharge curve of a battery made from the thus obtained selenium carbon composite material is shown in Figure 3; the battery test results are summarized in Table 1 below.

Table 1 summarized Battery Test Results

Numbering	The first cycle discharge capacity (mAh/g)	the first cycle Coulomb efficiency (%)	After cycling 50 laps capacity (mAh/g
Example 1	1,050	78.1	756
Example 2	940	74.6	672
Example 3	962	75.3	683
Example 4	987	72.1	680
Example 5	936	73.2	653
Example 6	972	70	661
Example 7	836	72.5	580

Date reçue / Date received 2021-11-09

Examplc 8	910	73	600
Comparative Example 1	635	55	350
Comparative Example 2	980	40.8	386

Above examples are only for the illustration of the embodiments of the present invention, which by no means is to be used in any form as a limit to the scope of the present invention. Although the present invention has been revealed above as the preferred embodiments, it is not intended to limit the present invention. Anybody with skills in the art can use the revealed technical content by making little changes or substitutions, without departing from the scope of the technical aspect of the present invention, as described above, to derive equivalent of examples of the present invention. But those that do not depart from the nature of the present invention by simple modification of any of the above embodiments or by making equivalent variations and modifications based on the technical nature of the present invention, would fall within the scope of the present invention of the technical solutions.

Date reçue / Date received 2021-11-09

What is claimed is:

1. A lithium selenium secondary battery, comprising:

a selenium carbon composite material as the cathode material, prepared by the method of:

(a) carbonizing an alkali metal organic salt or an alkaline earth metal organic salt at a temperature from 600°C and 1000°C, washing with an acid, and drying to obtain a two-dimensional carbon nanomaterial; and

(b) mixing the two-dimensional carbon nanomaterial obtained in step (a) with an organic solvent and selenium, heating the mixture to evaporate the organic solvent, and then subjecting the organic solvent evaporated mixture to a multistage heat ramping and soaking process to achieve the selenium carbon composite material;

a lithium-containing anode;

a separator; and

an electrolyte.

2. The lithium selenium secondary battery of claim 1, wherein the separator includes at least one of the following:

an inorganic membrane;

a cellulose membrane; and

a polymer membrane.

3. The lithium selenium secondary battery of claim 2, wherein the inorganic membrane is a glass fiber membrane.

4. The lithium selenium secondary battery of any one of claims 1 to 3, wherein the electrolyte is one or more of a carbonate electrolyte, an ether electrolyte, and an ionic liquid.

5. The lithium selenium secondary battery of claim 4, wherein:

the carbonate electrolyte comprises:

Date Reçue/Date Received 2023-06-21

a solvent comprising one or more of diethyl carbonate ester (DEC), dimethyl carbonate (DMC), ethylene carbonate (EC), ethyl methyl carbonate (EMC), and propylene carbonate (PC), and

a solute selected from one or several of lithium hexafluorophosphate ($LiPF_6$), Lithium Bis(trifluoromethane)sulfonimide (LiTFSI), lithium perchlorate ($LiClO_4$) and Lithium bis(fluorosulfonyl)imide (LiFSI);

the ether electrolyte comprises:

a solvent comprising one or more of 1,3-dioxolane (DOL), ethylene glycol dimethyl ether (DME) and triethylene glycol dimethyl ether (TEGDME), and

a solute selected from one or more of lithium hexafluorophosphate ($LiPF_6$), lithium bis(trifluoromethanesulfonyl) imide (LiTFSI), lithium perchlorate ($LiClO_4$) and Lithium bis(fluorosulfonyl)imide (LiFSI); and

the ionic liquid comprises:

one or more of room temperature ionic liquids selected from the group consisting of 1-ethyl-3-methylimidazolium bis trifluoromethane sulfonamide salt ([EMIm] NTf2), N-Propyl-N-methylpyrrolidine bis trifluoromethane sulfonamide salts ([Py13] NTf2) and N-propylmethylpiperidine alkoxy-N-Bis trifluoromethane sulfonamide salts ([PP13] NTf2), and

a solute selected from one or more of lithium hexafluorophosphate ($LiPF_6$), Lithium Bis(trifluoromethane)sulfonimide (LiTFSI), lithium perchlorate ($LiClO_4$) and lithium bis fluorosulfonylimide (LiFSI).

6. The lithium selenium secondary battery of claim 4, wherein the carbonate electrolyte comprises a solvent and a solute, wherein

the solvent is one or more of diethyl carbonate ester (DEC), dimethyl carbonate (DMC), ethylene carbonate (EC), ethyl methyl carbonate (EMC), and propylene carbonate (PC); and

the solute is selected from one or more of lithium hexafluoro phosphate ($LiPF_6$), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), lithium perchlorate ($LiClO_4$) and lithium bis(fluorosulfonyl)imide (LiFSI).

7. The lithium selenium secondary battery of claim 4, wherein the ether electrolyte comprises a solvent and a solute, wherein

Date Reçue/Date Received 2023-06-21

the solvent is one or more of 1,3-dioxolane (DOL), ethylene glycol dimethyl ether (DME) and triethylene glycol dimethyl ether (TEGDME); and

the solute is one or more of lithium hexafluorophosphate ($LiPF_6$), lithium bis (trifluoromethanesulfonyl) imide (LiTFSI), lithium perchlorate ($LiClO_4$) and Lithium bis(fluorosulfonyl)imide (LiFSI).

8. The lithium selenium secondary battery of claim 4, wherein the ionic liquid comprises a room temperature ionic liquid and a solute, wherein

the room temperature ionic liquid is one or more of 1-ethyl-3-methylimidazolium bis trifluoromethane sulfonamide salt ([EMIm] NTf2), N- Propyl-N-methylpyrrolidine bis trifluoromethane sulfonamide salts ([Py13] NTf2) and N- propyl-methylpiperidine alkoxy-N-Bis trifluoromethane sulfonamide salts ([PP13] NTf2); and

the solute is one or more of lithium hexafluorophosphate ($LiPF_6$), lithium bis(trifluoromethanesufonyl)imide (LiTFSI), lithium perchlorate ($LiClO_4$) and lithium bis (fluorosulfonyl)imide (LiFSI).

9. A lithium selenium secondary battery of any one of claims 1 to 8, wherein the lithium selenium secondary battery has a discharge specific capacity of at least 580 mAh/g after 50 cycles of a constant current charge-discharge with a test voltage range between 1.0 and 3.0 V and a test temperature of 25°C.

10. The lithium selenium secondary battery of claim 9, wherein the two-dimensional carbon nanomaterial is in the form of a sheet having a thickness $\leq$ 200 nm.

11. The lithium selenium secondary battery claim 1, wherein the alkali metal organic salt is potassium citrate; sodium citrate; or potassium gluconate.

12. The lithium selenium secondary battery of any one of claims 1-11, wherein the cathode further comprises a first binder.

Date Reçue/Date Received 2023-06-21

13. The lithium selenium secondary battery of claim 12, wherein the cathode further comprises at least one of the following:

a second binder; and

carbon black.

14. The lithium selenium secondary battery of claim 12 or claim 13, wherein the first binder comprises a cellulose-based compound or a latex-based compound.

15. The lithium selenium secondary battery of claim 14, wherein:

the cellulose-based compound is carboxymethyl cellulose (CMC); and

the latex-based compound is styrene-butadiene rubber (SBR).

16. The lithium selenium secondary battery of any one of claims 1 to 15, wherein the lithium-containing anode comprises a lithium metal, a lithiated graphite anode material, or a lithiated silicon carbon anode material.

17. A pouch-cell lithium selenium secondary battery comprising a selenium carbon cathode comprising a selenium carbon composite material prepared by the method of:

(a) carbonizing an alkali metal organic salt or an alkaline earth metal organic salt at a temperature from 600°C to 1000°C;

(b) washing the carbonized salt of step (a) with an acid;

(c) drying the washed carbonized salt of step (b) to obtain a two-dimensional carbon nanomaterial;

(d) mixing the two-dimensional carbon nanomaterial of step (c) with selenium and an organic solvent;

(e) heating the mixture of step (d) to evaporate the organic solvent; and

(f) subjecting the organic solvent evaporated mixture of step (e) to a multistage heat ramping and soaking process to achieve the selenium carbon composite material.

Date Reçue/Date Received 2023-06-21

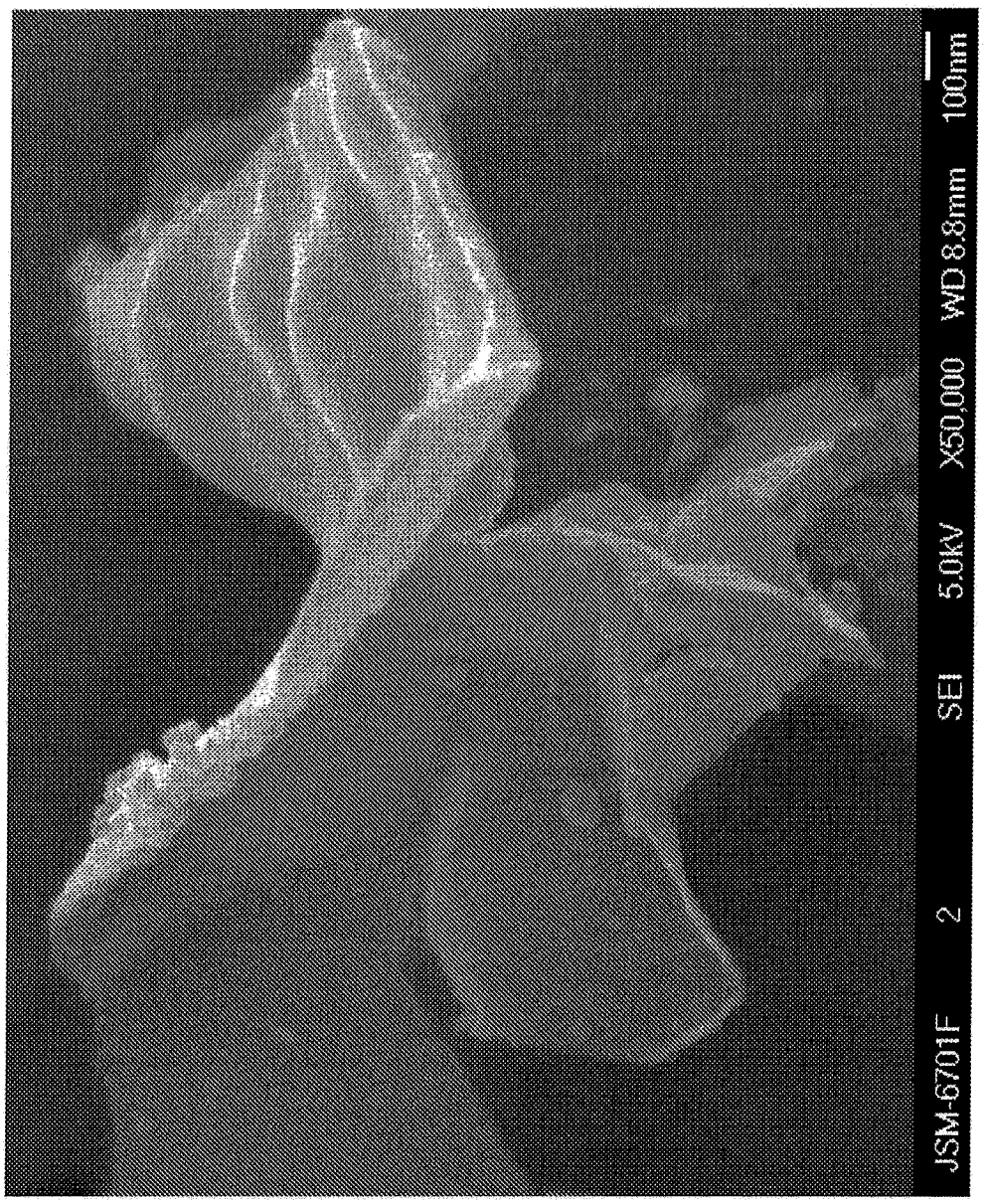
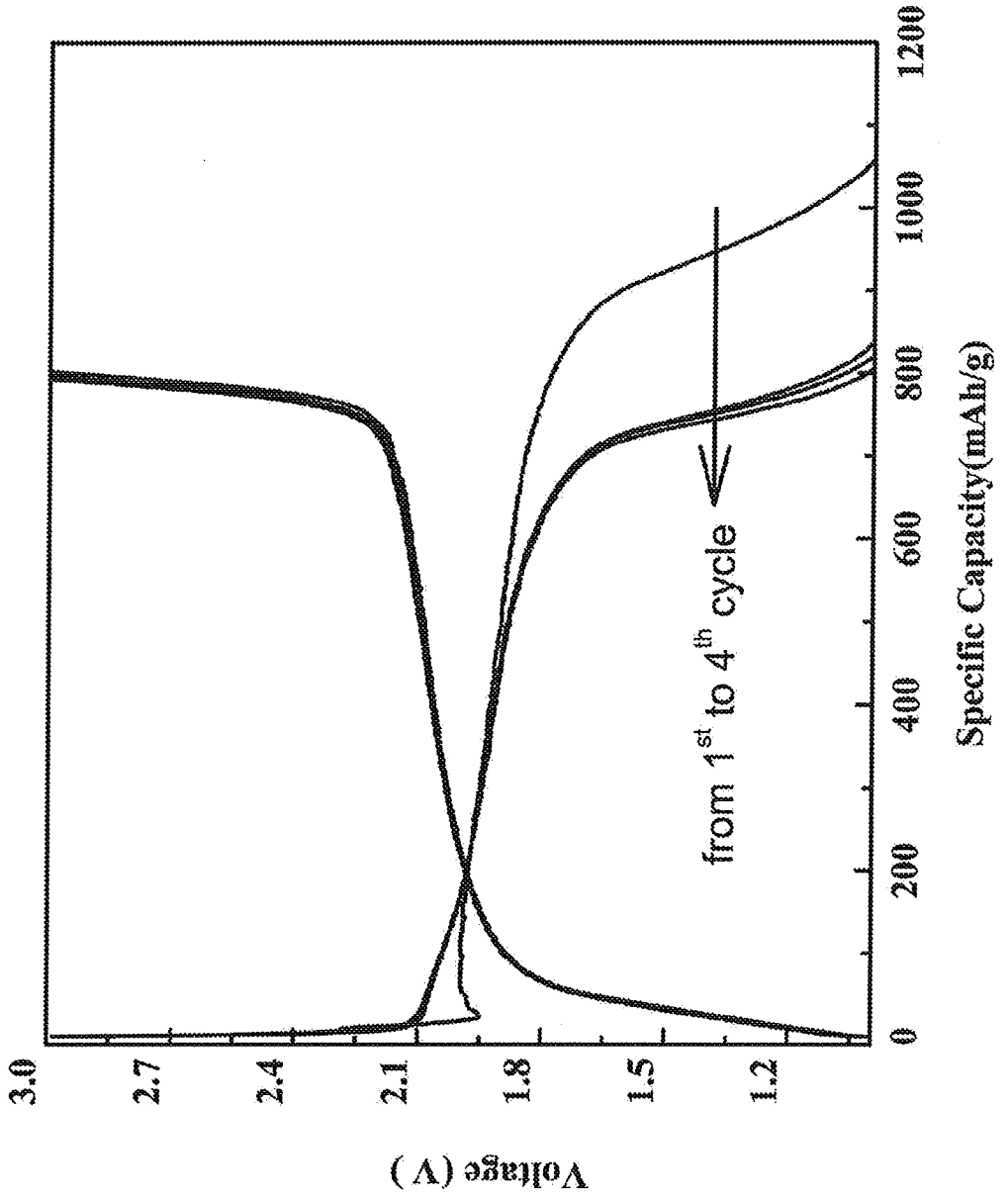


FIG. 1


Voltage (V)
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2.7
2.4
2.1
1.8
1.5
1.2
Specific Capacity(mAh/g)
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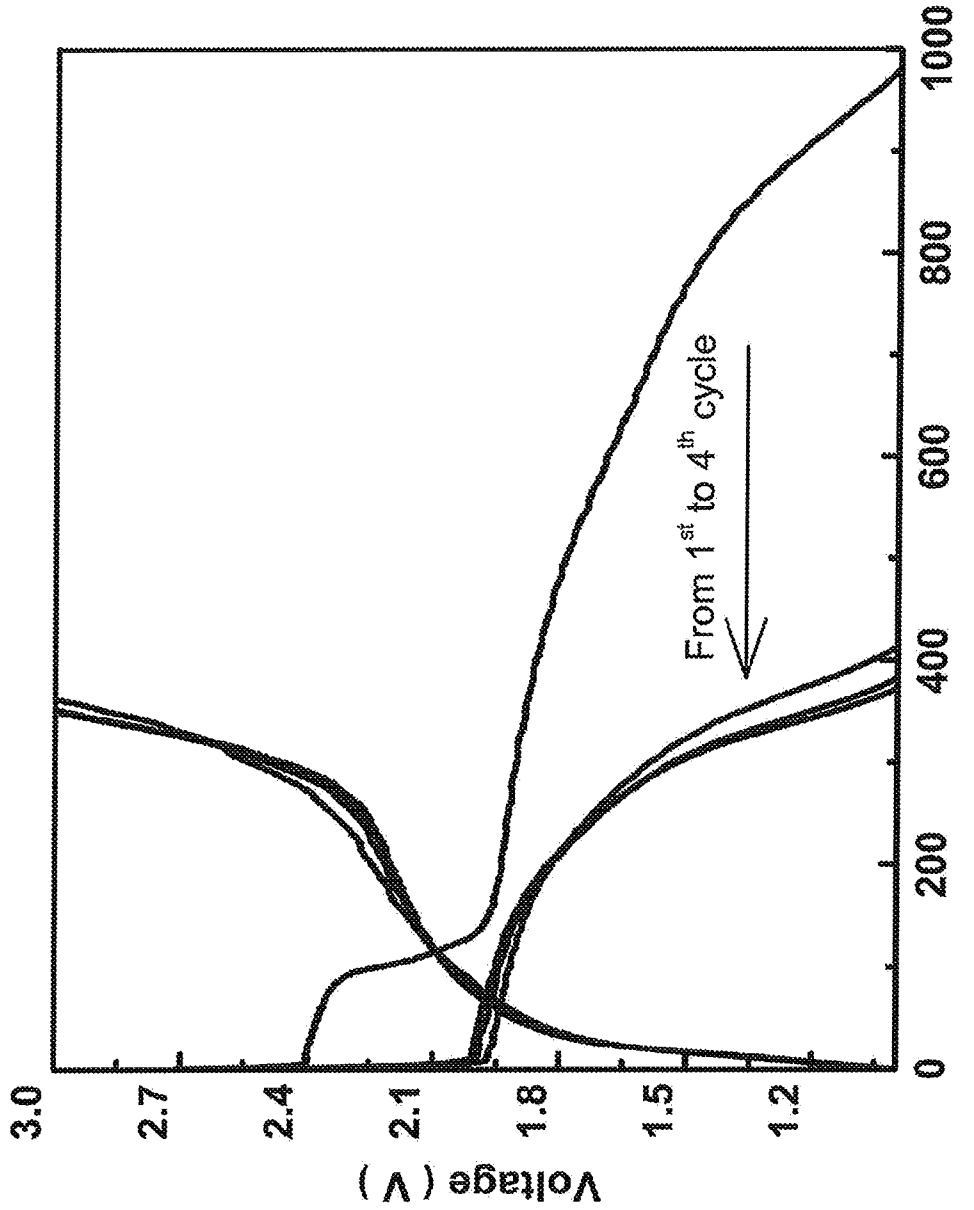
200
400
600
800
1000
1200
from 1st to 4th cycle

FIG. 2


Voltage (V)
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2.7
2.4
2.1
1.8
1.5
1.2
Specific capacity (mA h g^{-1})
0
200
400
600
800
1000
From 1st to 4th cycle

FIG. 3

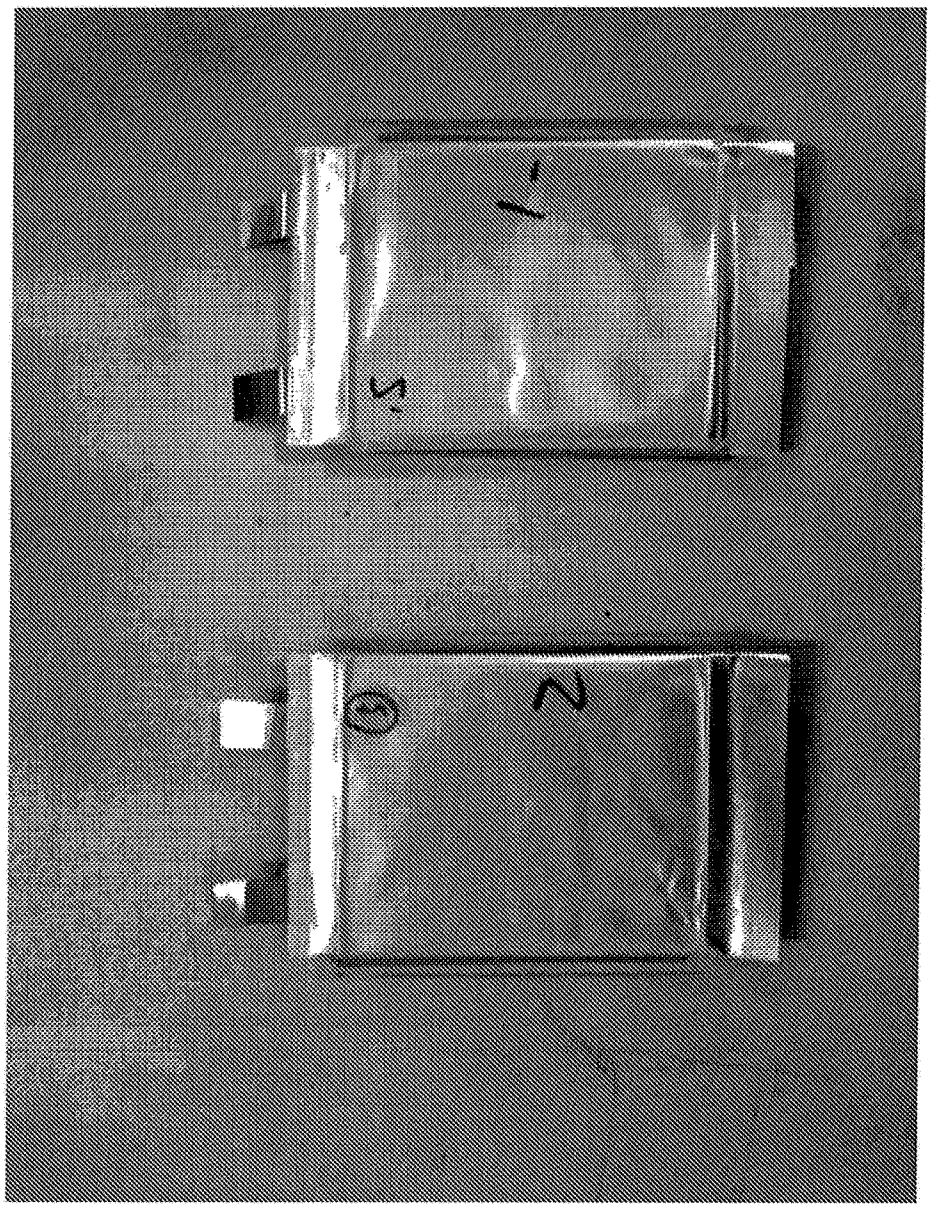
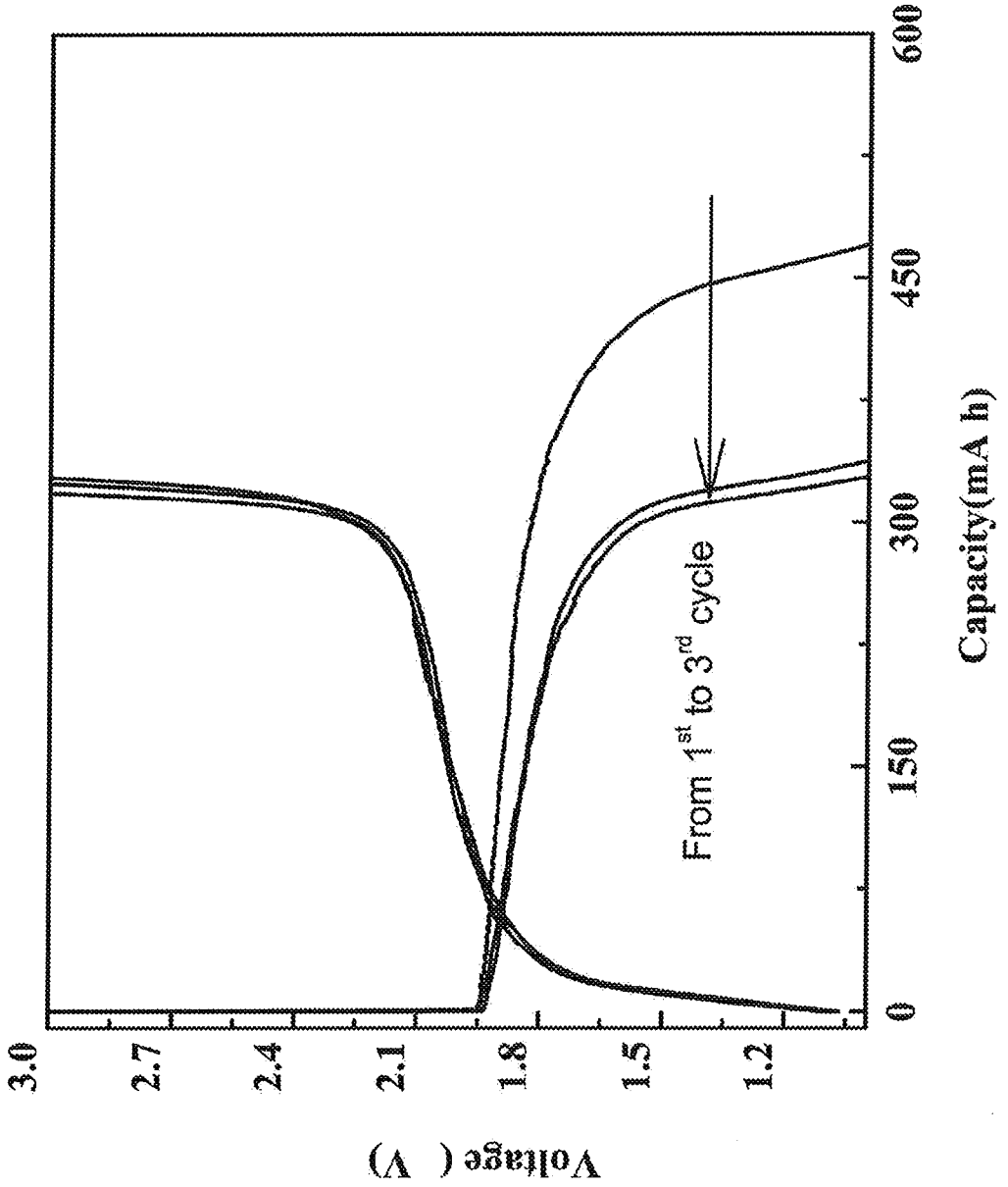


FIG. 4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2.4
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1.8
1.5
1.2
Capacity(mA h)
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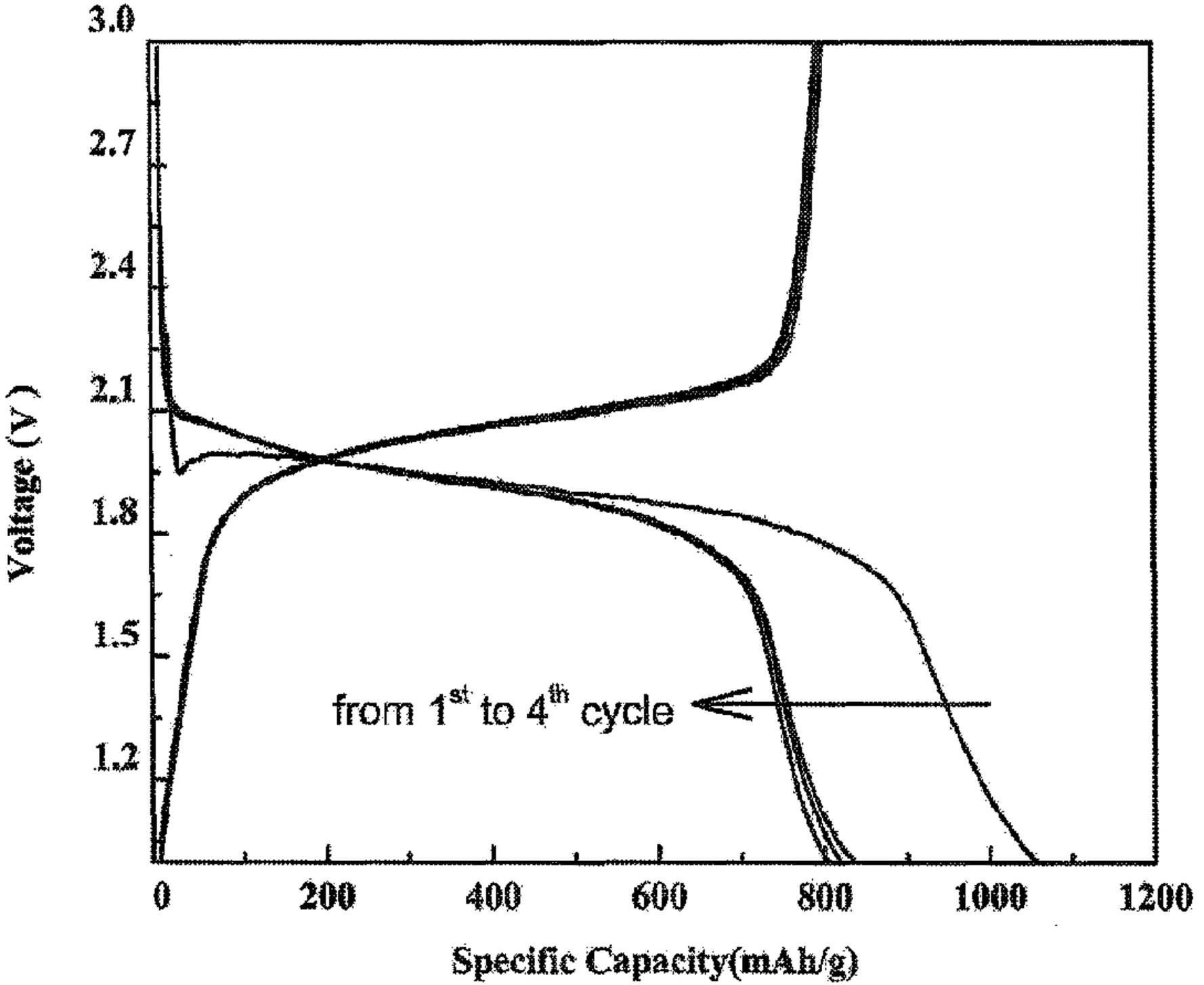
150
300
450
600
From 1st to 3rd cycle

FIG. 5


3.0
2.7
2.4
2.1
1.8
1.5
1.2
Voltage (V)
from 1st to 4th cycle
0
200
400
600
800
1000
1200
Specific Capacity(mAh/g)