(19) LE GOUVERNEMENT
DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Économie

(11) N° de publication : **LU500937**

(12) **BREVET D'INVENTION** **B1**

(21) N° de dépôt: LU500937

(22) Date de dépôt: 01/12/2021

(51) Int. Cl.:
H01M 10/0525, H01M 4/42

(30) Priorité:

(43) Date de mise à disposition du public: 01/06/2022

(47) Date de délivrance: 01/06/2022

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(54) MICRO-SPHERICAL ZINC VANADATE AS WELL AS PREPARATION METHOD AND USE THEREOF.

(57) The present disclosure discloses a micro-spherical zinc vanadate. The zinc vanadate has a chemical formula of Zn2V2O7, an average diameter of less than 3 μm and a porous surface structure. The present disclosure also discloses a preparation method of micro-spherical zinc vanadate, comprising the following steps: (1) putting zinc nitrate and zinc metavanadate both 10 of which have a purity of 99.9% into a breaker; (2) adding ethylene glycol into the breaker, evenly stirring, and then adding DMF, so as to obtain a mixed solution; (3) transferring the above mixed solution into a hydrothermal reactor to be heated, and then cooling to room temperature to obtain a product; and (4) centrifuging the obtained product, collecting the centrifuged product, drying, and then calcining to obtain the micro-spherical zinc vanadate. 15 The micro-spherical zinc vanadate of the present disclosure is uniform in size and good in crystallinity.

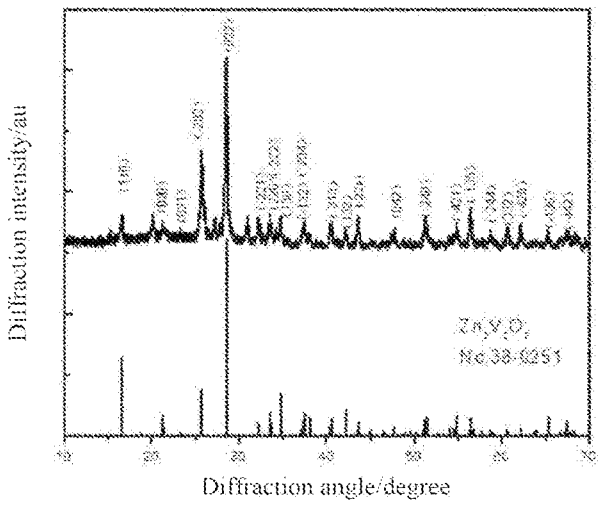


FIG.1

MICRO-SPHERICAL ZINC VANADATE AS WELL AS PREPARATION METHOD AND USE THEREOF

TECHNICAL FIELD

The present disclosure belongs to the technical field of battery materials, particularly to a micro-spherical zinc vanadate as well as a preparation method and use thereof.

BACKGROUND

Energy issues have become the most important theme in the 21st century. The increasing energy demand in the world has been significantly challenged in today's society. It is caused by continuous increase in population, continuous increase in gasoline prices, continuous depletion of non-renewable resources such as fossil energy and a mission proposed by China that the emission of CO_2 is reduced to the minimum. All of them continuously encourage us to find new renewable resource technologies to replace traditional technologies so as to meet people's needs in life, such as nuclear energy, wind energy, solar energy, tidal energy and fuel cells. In order to deal with these challenges, the storage and conversion of the electrochemical energy of the system is considered to be a feasible energy storage system due to its advantages of high output power, low cost, and environmental protection. For example, lithium-ion batteries, lithium-oxygen batteries, fuel cells and supercapacitors. Since Sony company launched the first-generation lithium-ion battery in 1990, it together with a nickel hydrogen battery has been used as a power source for small electronic products, and has occupied an important position ever since.

An electrode material directly or indirectly participates in catalyzing electrochemical reaction, and plays a key role in improving the capacity of energy storage. Graphite carbon has always been the best candidate for the anode material of the lithium-ion battery and has many advantages, including low cost, easy processing, and good chemical stability. In addition, graphitic carbon also has some shortcomings: its theoretical capacity is relatively low, for example, the power output per unit mass or volume is limited, hindering the development of some high-tech industries. Therefore, it is particularly important to use structural design and develop functional advanced electrode materials. Metal oxides, mixed metal oxides, sulfides and hydroxides are all potential advantages for the development of lithium-ion batteries.

The electrochemical performance of metal organic oxides is relatively prominent, and it is expected to replace the current commercial graphite and become a new type of lithium-ion battery anode material. Metallic organic acid salts have received more and more attention in terms of synthesis and morphology control. A reasonable design of the nanostructure of the metallic organic acid salt is very necessary to improve the electronic and ionic conductivity.

In view of the above reasons, the present disclosure is put forward.

SUMMARY

In order to solve the above problems existing in the prior art, the first objective of the present disclosure is to provide to a micro-spherical zinc vanadate, wherein the zinc vanadate has a chemical formula of $Zn_2V_2O_7$, an average diameter of less than 3 μm and a porous surface structure.

The zinc vanadate prepared by the present disclosure can be used as a negative electrode of a lithium battery, which can improve the electrochemical property, increase the first discharge capacity and cycle performance stability, wherein the porous structure is beneficial to penetration of lithium ions.

The second objective of the present disclosure is to provide a preparation method of the micro-spherical zinc vanadate, the method comprising the following steps:

(1) putting zinc nitrate and zinc metavanadate both of which have a purity of 99.9% into a breaker;

(2) adding ethylene glycol into the breaker, evenly stirring, and then adding DMF, so as to obtain a mixed solution;

(3) transferring the above mixed solution into a hydrothermal reactor to be heated, and then cooling to room temperature to obtain a product; and

(4) centrifuging the obtained product, collecting the centrifuged product, drying, and then calcining to obtain the micro-spherical zinc vanadate.

According to the present disclosure, zinc nitrate and zinc metavanadate are used as raw materials, the micro-spherical zinc vanadate with an uniform size is prepared by solvent

thermal and solid sintering methods, the surface of the microsphere is in a porous structure, such the porous structure is beneficial to penetration of lithium ions, a molecular formula is $Zn_2V_2O_7$. The zinc vanadate material prepared by this method, as the negative material of the lithium ion battery, shows excellent discharge capacity and stable cycle performance.

Further, in step (1), a molar ratio of zinc nitrate to zinc metavanadate is 1:2.

Further, in step (3), a molar volume of zinc nitrate to ethylene glycol to DMF is 1 mmol: 30ml: 5ml.

Further, in step (3), a volume ratio of water to ethylene glycol in the hydrothermal reactor is 5:3.

Further, in step (3), heating is conducted to 170~190°C which is maintained for 22~26 h, and the heating rate is 3~7°C/min, preferably, heating is conducted to 180°C which is maintained for 24 h, and the heating rate is 5°C/min.

Further, in step (4), the cooling rate is 3~7°C/min, preferably, the cooling rate is 5°C/min.

Further, in step (4), the drying time is 10~14 h, and the drying temperature is 78~82°C, preferably, the drying time is 12 h, and the drying temperature is 80°C.

Further, in step (4), calcination is conducted for 1.5~2 h at 380~420°C at the heating rate of 0.8~1.2°C/min.

The micro-spherical zinc vanadate of the present disclosure is directly composited under the condition of solvent thermal without any templates or surface modifiers, has simple experimental operation process, low cost and high yield. The sample prepared by using the method of the present disclosure is uniform in size and high in purity, and has good charge and discharge performances as the negative material of the lithium ion battery and excellent cycle stability.

The third objective of the present disclosure is to provide use of the micro-spherical zinc vanadate in a battery. The micro-spherical zinc vanadate, when being applied to the negative electrode of the lithium ion battery, under the current density of 100 mAh • g^{-1}, has the first charge and discharge specific capacities of 779.2 mAh· g^{-1} and 1075.3 mAh· g^{-1} respectively and a coulomb efficiency is 72.5%, and has the specific capacity of greater than 860 mAh· g^{-1} after charge and discharge for 50 times.

Compared with the prior art, the present disclosure has the beneficial effects:

(1) the micro-spherical zinc vanadate of the present disclosure is uniform in size and good in crystallinity, and has a micro-spherical diameter of less than 3 μm and a porous surface structure;

(2) the micro-spherical zinc vanadate of the present disclosure is prepared by solvent thermal and solid sintering methods without any templates or surface modifiers, and has simple experimental operation process, low cost and high yield;

(3) when being applied to the negative material of the lithium ion battery, the micro-spherical zinc vanadate of the present disclosure has good first charge and discharge performances and has excellent cycle stability, the first charge and discharge specific capacities are respectively 779.2 $mAh\cdot g^{-1}$ and 1075.3 $mAh\cdot g^{-1}$, the coulomb efficiency is 72.5%, and the specific capacity is greater than 860 $mAh\cdot g^{-1}$ after charge and discharge for 50 times.

BRIEF DESCRIPTION OF THE DRAWINGS

For more clearly illustrating the embodiments of the present disclosure or the technical solution in the prior art, drawings required to be used in the embodiments or the prior art will be simply discussed below, obviously, the drawings described below are only some embodiments of the present disclosure, other drawings can also be made by persons of ordinary skill in the art without creative efforts according to these drawings.

Fig.1 is an X-ray diffraction (XRD) graph of micro-spherical zinc vanadate prepared in example 1.

Fig.2 is a scanning electron microscope (SEM) graph of micro-spherical zinc vanadate prepared in example 1.

Fig.3 is an SEM amplified graph of micro-spherical zinc vanadate prepared in example 1.

Fig.4 is a voltage-specific capacity graph of micro-spherical zinc vanadate prepared in example 1 as an electrode material.

Fig.5 is a cycle performance graph of micro-spherical zinc vanadate prepared in example 1 as an electrode material.

DESCRIPTION OF THE EMBODIMENTS

To make the purpose, the technical solutions and the advantages of the present disclosure more apparent, a more detailed description will be provided to the technical solution of the

present disclosure. Obviously, the described embodiments are only a part of embodiments of the present disclosure but not all the embodiments. Based on the embodiments of the present disclosure, all other embodiments obtained by persons of ordinary skill in the art without creative efforts are included within the protective scope of the present disclosure.

Example 1

A preparation method of micro-spherical zinc vanadate comprises the following steps:

(1) 297.5 mg of zinc nitrate with a purity of 99.9% and 234.0 mg of zinc metavanadate with a purity of 99.9% were put into a breaker;

(2) 30 ml of ethylene glycol was added into the breaker and stirred for 20 min, and then 5 ml of DMF was added, so as to obtain a mixed solution;

(3) the above mixed solution was transferred into a 50 ml hydrothermal reactor to be heated to 180°C at the heating rate of 5°C/min, and then cooled to room temperature at the cooling rate of 5°C/min to obtain a product; and

(4) the obtained product was centrifuged, collected, dried for 12 h at 80°C, and then calcined for 2 h in a vacuum tubular furnace at 400°C under an air atmosphere at the heating rate of 1°C/min to obtain the micro-spherical zinc vanadate.

The XRD spectroscopy of the obtained micro-spherical zinc vanadate is shown in Fig.1. It can be seen that the intensities and positions of the diffraction peaks of the micro-spherical zinc vanadate prepared in this example are matched with those of $Zn_2V_2O_7$ standard card JCPDS No.38-0251, lattice constants a=7.437, b=8.331, and c=10.100, and strong and sharp diffraction peaks show that the prepared sample has good crystalinity. By SEM test, the morphology of the obtained micro-spherical zinc vanadate is of a regular microsphere, as shown in Fig.2, has a uniform size. As shown in Fig.3, after being further magnified, the microsphere has a diameter of less than 3 μm, and pore channels with various sizes.

The above micro-spherical zinc vanadate was prepared into a battery according to the following steps:

(1) 70 mg of prepared zinc vanadate was sufficiently grinded with 20 mg of carbon black for 40 min, and 10 mg of polyvinylidene fluoride and N-methyl pyrrolidone were added to be sufficiently grinded for 30 min;

(2) the slurry was coated on copper foil wiped by ethanol, and then put in a vacuum oven to be dried in vacuum for 6 h at 120°C, and further dried after tabletting and weighing;

(3) the metal lithium was used as an electrode, a Celgard membrane was used as a

diaphragm, EC+DMC+DEC (a volume ratio was 1:1:1) dissolved with $LiPF_6$ (1 mol/L) was used as an electrolyte, and assembling was conducted in an glove box in an argon atmosphere to form a CR2032 battery.

After standing for 6 h, a constant-current charging and discharging test was performed by using a LANHE CT 2001A test system. The test voltage selected 0.01-3 V. Fig.4 is the voltage-specific capacity graph of the negative material of the prepared micro-spherical $Zn_2V_2O_7$ lithium ion battery when charging and discharging for the first, second and fifth under the current density of 100 mA/g under the condition that the voltage window is 0-3 V. The first charge and discharge specific capacities are respectively 779.2 $mAh\cdot g^{-1}$ and 1075.3 $mAh\cdot g^{-1}$, and the coulomb efficiency is 72.5%; and the specific capacity is maintained to be greater than 860 $mAh\cdot g^{-1}$ after charge and discharge for 50 times.

Fig. 5 shows a constant-current cycle performance test of this sample as a negative material of a lithium ion battery. The current density is 100 mA/g, and the voltage window is 0-3V. With the increase of cycle times, the specific capacity is correspondingly increased, which is because an active material is continuously activated with the increase of charging and discharging times, the application of this material in the field of battery materials explores the research scope of the existing material, and provides experimental data to development of new lithium ion battery materials.

Example 2

A preparation method of micro-spherical zinc vanadate comprises the following steps:

(1) 595 mg of zinc nitrate with a purity of 99.9% and 468 mg of zinc metavanadate with a purity of 99.9% were put into a breaker;

(2) 60 ml of ethylene glycol was added into the breaker and stirred for 20 min, and then 10 ml of DMF was added, so as to obtain a mixed solution;

(3) the above mixed solution was transferred into a 100 ml hydrothermal reactor to be heated to 170°C at the heating rate of 3°C/min, and then cooled to room temperature at the cooling rate of 3°C/min to obtain a product; and

(4) the obtained product was centrifuged, collected, dried for 14 h at 78°C, and then calcined for 2.5 h in a vacuum tubular furnace at 380°C under an air atmosphere at the heating rate of 0.8°C/min to obtain the micro-spherical zinc vanadate.

The XRD graph and SEM graph of the micro-spherical zinc vanadate prepared in this example are basically the same as those in example 1.

The preparation method of the battery in example 1 was used, and the zinc vanadate prepared in example 2 was used as the negative material of the lithium ion battery. After standing for 6 h, a constant-current charge and discharge test was performed by using a LANHE CT 2001A test system. The test voltage selected 0.01-3 V. A constant-current cycle performance test was performed. The results are basically the same as those in example 1.

Example 3

A preparation method of micro-spherical zinc vanadate comprises the following steps:

(1) 297.5 mg of zinc nitrate with a purity of 99.9% and 234.0 mg of zinc metavanadate with a purity of 99.9% were put into a breaker;

(2) 30 ml of ethylene glycol was added into the breaker, stirred for 20 min, and then 5 ml of DMF was added, so as to obtain a mixed solution;

(3) the above mixed solution was transferred into a 50 ml hydrothermal reactor to be heated to 190°C at the heating rate of 7°C/min, then cooled to room temperature at the cooling rate of 7°C/min to obtain a product; and

(4) the obtained product was centrifuged, collected, dried for 10 h at 82°C, and then calcined for 1.5 h in a vacuum tubular furnace at 420°C under an air atmosphere at the heating rate of 1.2°C/min to obtain the micro-spherical zinc vanadate.

The XRD graph and SEM graph of the micro-spherical zinc vanadate prepared in this example are basically the same as those in example 1.

The preparation method of the battery in example 1 was used, and the zinc vanadate prepared in example 2 was used as the negative material of the lithium ion battery. After standing for 6 h, a constant-current charge and discharge test was performed by using a LANHE CT 2001A test system. The test voltage selected 0.01-3 V. A constant-current cycle performance test was performed. The results are basically the same as those in example 1.

The above descriptions are only specific embodiments of the present disclosure, but the protective scope of the present disclosure is not limited thereto. Within the technical scope disclosed by the present disclosure, those skilled in the art can easily conceive that variations or replacements are all included within the protective scope of the present disclosure. Therefore, the protective scope of the present disclosure should be based on the protective scope of the appended claims.

CLAIMS

1. A micro-spherical zinc vanadate, wherein the zinc vanadate has a chemical formula of $Zn_2V_2O_7$, an average diameter of less than 3 μm and a porous surface structure;

wherein, a preparation method of the micro-spherical zinc vanadate comprises the following steps:

(1) putting zinc nitrate and zinc metavanadate both of which have a purity of 99.9% into a breaker, a molar ratio of zinc nitrate to zinc metavanadate being 1:2;

(2) adding ethylene glycol into the breaker, evenly stirring, and then adding DMF, so as to obtain a mixed solution;

(3) transferring the above mixed solution into a hydrothermal reactor to be heated to 170°C~190°C at the heating rate of 3-7°C/min, and maintaining for 22~26 h, a molar volume of zinc nitrate to ethylene glycol to DMF being 1 mmol: 30ml: 5ml, a volume ratio of water to ethylene glycol in the hydrothermal reactor being 5:3, and then cooling to room temperature at the cooling rate of 3-7°C/min to obtain a product; and

(4) centrifuging the obtained product, collecting the centrifuged product, drying, and then calcining to obtain the micro-spherical zinc vanadate.

2. The micro-spherical zinc vanadate according to claim 1, wherein in step (3), heating is conducted to 180°C which is maintained for 24 h, and the heating rate is 5°C/min.

3. The micro-spherical zinc vanadate according to claim 1, wherein in step (3), the cooling rate is 5°C/min.

4. The micro-spherical zinc vanadate according to any one of claims 1-3, wherein in step (4), the drying time is 10~14 h, and the drying temperature is 78~82°C.

5. The micro-spherical zinc vanadate according to claim 4, wherein the drying time is 12 h, and the drying temperature is 80°C.

6. A use of the micro-spherical zinc vanadate according to any one of claims 1-5 in a battery, wherein the micro-spherical zinc vanadate, when being applied to a negative electrode of a lithium ion battery, under the current density of 100 $mAh \cdot g^{-1}$, has the first

charge-discharge specific capacities of 779.2 $mAh \cdot g^{-1}$ and 1075.3 $mAh \cdot g^{-1}$ respectively and has a coulomb efficiency of 72.5%, and has the specific capacity of greater than 860 $mAh \cdot g^{-1}$ after charge and discharge for 50 times.

ANSPRÜCHE

1. Mikrokugelförmiges Zinkvanadat, wobei das Zinkvanadat die chemische Formel $Zn_2V_2O_7$, einen durchschnittlichen Durchmesser von weniger als 3 μm und eine poröse Oberflächenstruktur aufweist;

wobei ein Herstellungsverfahren des mikrosphärischen Zinkvanadats die folgenden Schritte umfasst:

(1) Einbringen von Zinknitrat und Zinkmetavanadat, die beide eine Reinheit von 99,9 % aufweisen, in einen Brecher, wobei das molare Verhältnis von Zinknitrat zu Zinkmetavanadat 1:2 beträgt;

(2) Zugeben von Ethylenglykol unter gleichmäßigem Rühren in den Brecher und dann Hinzufügen von DMF, um eine gemischte Lösung zu erhalten;

(3) Überführen der oben gemischten Lösung in einen hydrothermalen Reaktor, die mit einer Erhitzungsgeschwindigkeit von 3-7°C/min auf 170°C~190°C erhitzt wird, und Aufrechterhalten für 22~26 h, wobei das molare Volumen von Zinknitrat zu Ethylenglykol zu DMF 1 mmol: 30ml: 5 ml beträgt: Wobei in Volumenverhältnis von Wasser zu Ethylenglykol in dem hydrothermalen Reaktor von 5:3 und anschließendes Abkühlen auf Raumtemperatur mit einer Abkühlgeschwindigkeit von 3-7°C/min, um ein Produkt zu erhalten; und

(4) Zentrifugieren des erhaltenen Produkts, Sammeln des zentrifugierten Produkts, Trocknen und anschließendes Kalzinieren, um das mikrokugelförmige Zinkvanadat zu erhalten.

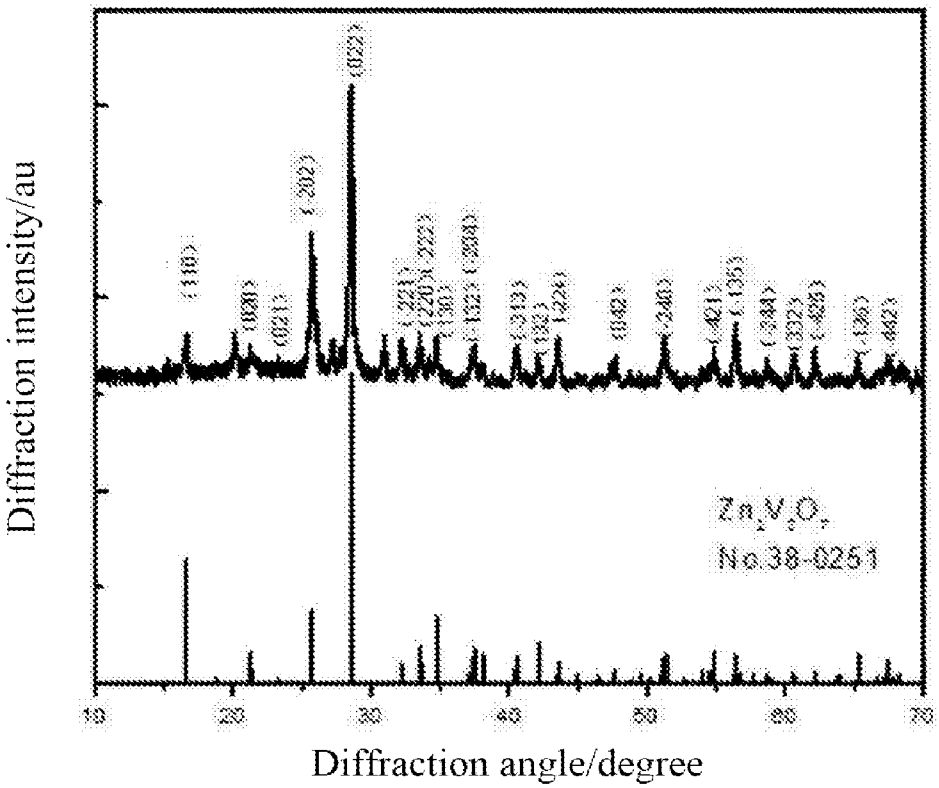
2. Mikrokugelförmiges Zinkvanadat nach Anspruch 1, wobei in Schritt (3) das Erhitzen auf 180°C durchgeführt wird, das 24 Stunden lang beibehalten wird, und die Erhitzungsgeschwindigkeit 5°C/min beträgt.

3. Mikrokugelförmiges Zinkvanadat nach Anspruch 1, wobei in Schritt (3) die Abkühlgeschwindigkeit 5°C/min beträgt.

4. Mikrosphärisches Zinkvanadat nach einem der Ansprüche 1 bis 3, wobei in Schritt (4) die Trocknungszeit 10 bis 14 Stunden und die Trocknungstemperatur 78 bis 82 °C beträgt.

5. Mikrokugelförmiges Zinkvanadat nach Anspruch 4, wobei die Trocknungszeit 12 h und die Trocknungstemperatur 80°C beträgt.

6. Verwendung des mikrokugelförmigen Zinkvanadats nach einem der Ansprüche 1 bis 5 in einer Batterie, wobei das mikrokugelförmige Zinkvanadat, wenn es auf eine negative Elektrode einer Lithium-Ionen-Batterie aufgebracht wird, bei einer Stromdichte von 100 $mAh \cdot g^{-1}$ die spezifischen Kapazitäten der ersten Ladung/Entladung von 779.2 $mAh \cdot g^{-1}$ bzw. 1075.3 $mAh \cdot g^{-1}1$ aufweist und einen Coulomb-Wirkungsgrad von 72,5 % aufweist und die spezifische Kapazität von mehr als 860 $mAh \cdot g^{-1}$ nach 50-maliger Ladung und Entladung aufweist.


Diffraction intensity/au
(110)
(020)
(021)
(202)
(022)
(221)
(220)
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(132)
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(135)
(244)
(332)
(426)
(136)
(423)
Zn3V2O7
No.38-0251
10
20
30
40
50
60
70
Diffraction angle/degree

FIG.1

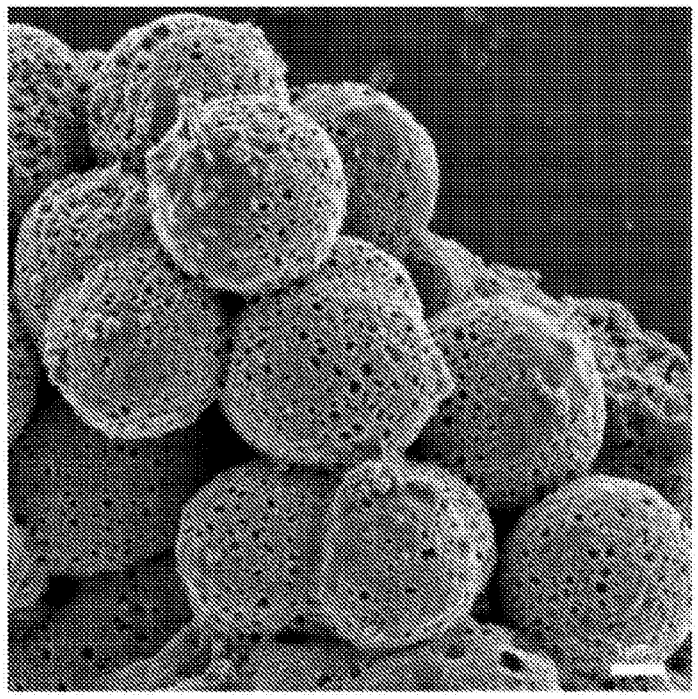

FIG. 2

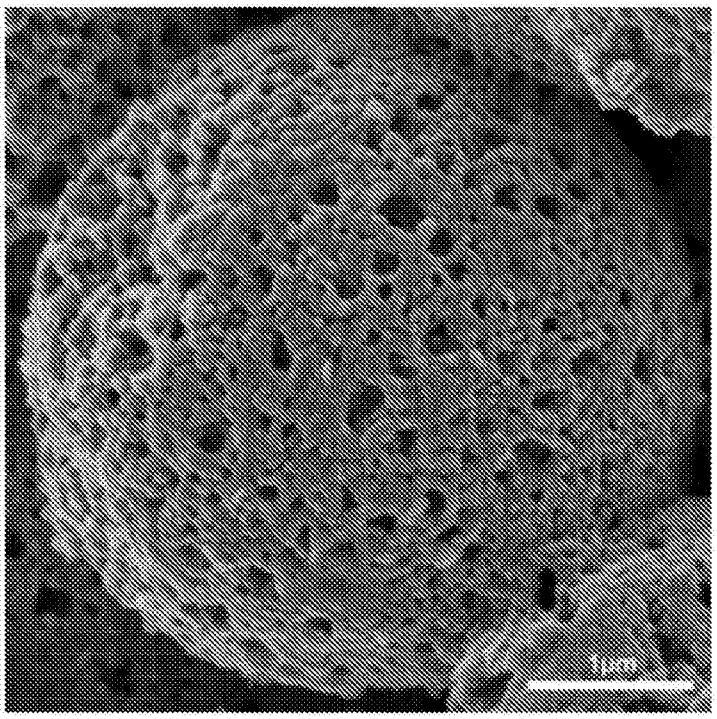

FIG. 3

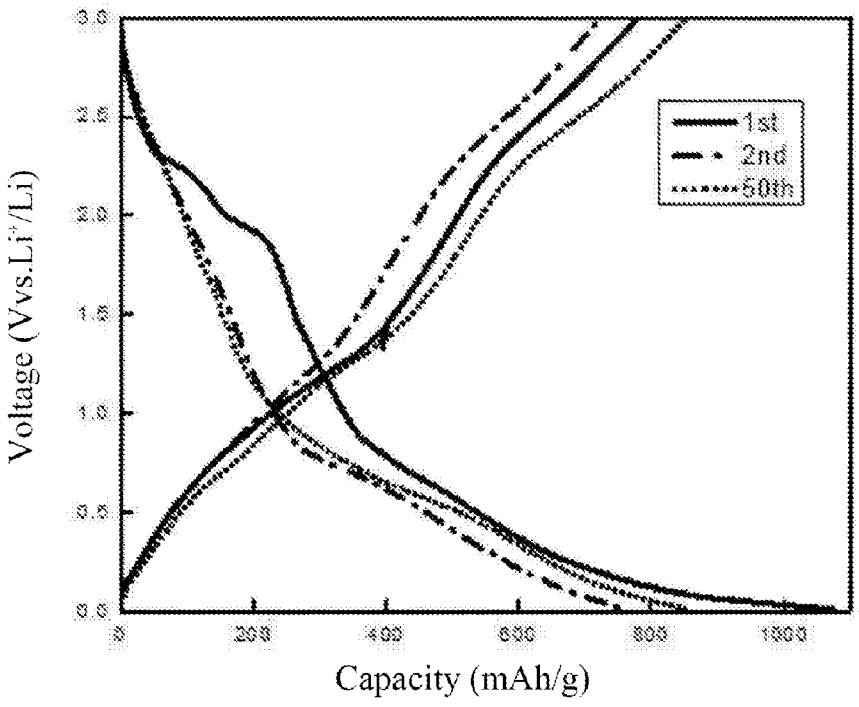

FIG. 4

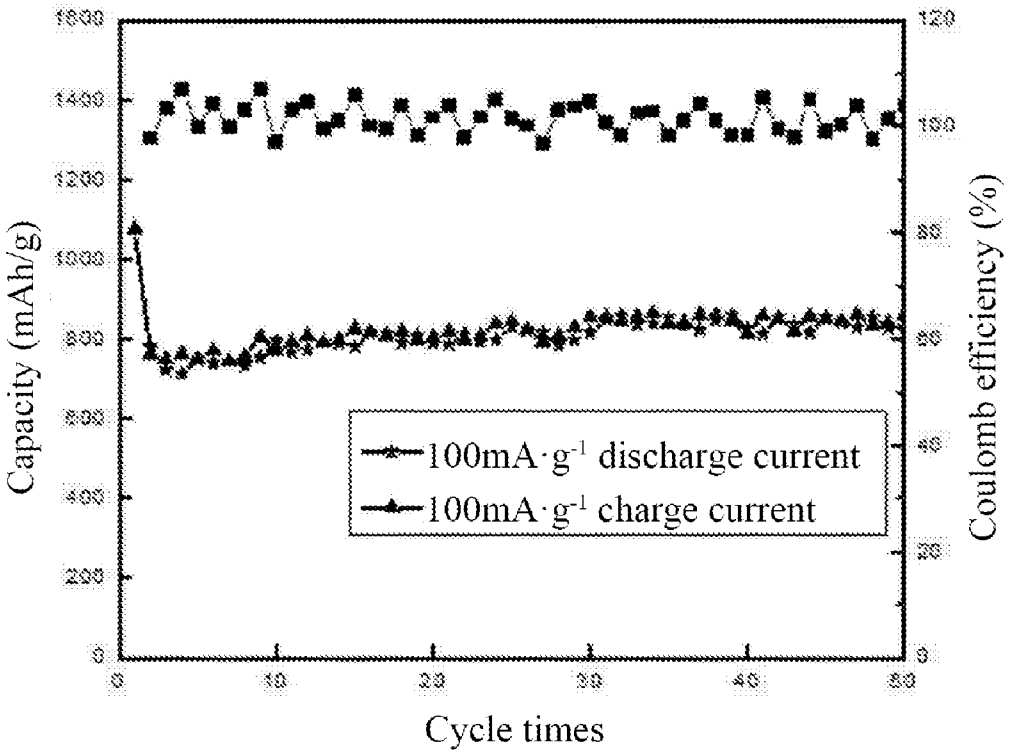
Capacity (mAh/g)
Coulomb efficiency (%)
Cycle times
100mA·g-1 discharge current
100mA·g-1 charge current

FIG. 5