

(19)



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

(11)

N° de publication :

LU500935

(12)

BREVET D'INVENTION**B1**

(21)

N° de dépôt: LU500935

(51)

Int. Cl.:

H01M 4/02, H01M 10/04, H01M 10/0525

(22)

Date de dépôt: 01/12/2021

(30)

Priorité:

(72)

Inventeur(s):

ZONG LINGBO – Chine, WANG LEI – Chine, LIU KANG –
Chine, LIN HAIFENG – Chine, LIU YANRU – Chine, DU
YUNMEI – Chine

(43)

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

(47)

Date de délivrance: 01/06/2022

(74)

Mandataire(s):

KIRKPATRICK SA / NV – 1310 LA HULPE (Belgique)

(73)

Titulaire(s):

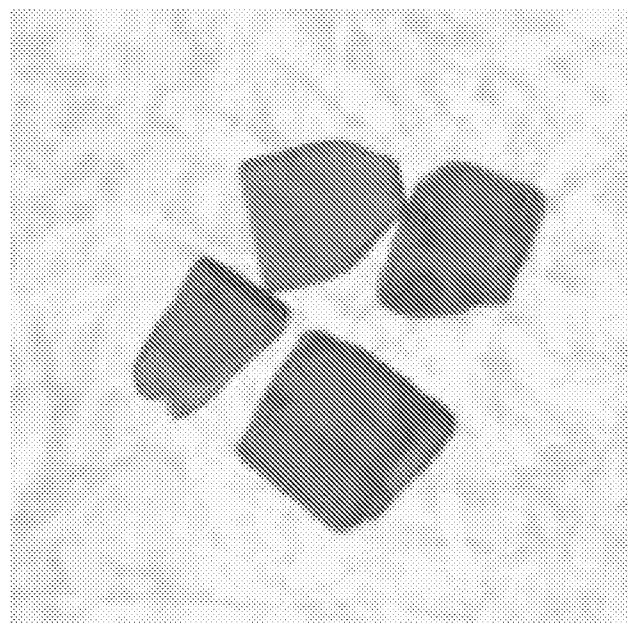
QINGDAO UNIVERSITY OF SCIENCE AND TECHNOLOGY
– 266000 Qingdao, Shandong (Chine)

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ELECTRODE MATERIAL COBALT VANADATE AS WELL AS PREPARATION AND USE THEREOF.

(57)

The present disclosure provides a preparation of an electrode material cobalt vanadate and the obtained cobalt vanadate as well as use thereof in a negative electrode material of a lithium battery. The preparation method of the electrode material cobalt vanadate is as follows: based on 4'4-bipyridine as a template, by using a hydrothermal method, an inorganic-organic hybrid material containing metal vanadium cobalt is prepared, and then thermal treatment was carried out at a high temperature, so as to obtain cluster-shaped rod-like porous CoV₂O₆. The method provided by the present disclosure is rich in raw material sources and low in cost, the obtained cobalt vanadate has high purity and porous surface.

**FIG. 1**

ELECTRODE MATERIAL COBALT VANADATE AS WELL AS PREPARATION AND USE THEREOF

TECHNICAL FIELD

5 The present disclosure belongs to the field of materials, particularly to an electrode material cobalt vanadate as well as a preparation method and use thereof.

BACKGROUND

As market demands of hybrid power electric vehicles, electric automobiles and large
10 accumulation systems gradually increase, lithium ion batteries (LIBs) and supercapacitors (SCs) have been attracted by more and more scientific research workers; however, their performances still fall behind increase in application demands. Urgent need on energy storage has always stimulated researchers all over the world to seek materials with both high energy and power density. Nevertheless, in order to counteract excess dependence on
15 graphite electrodes and environmental problems and realize higher energy density, development of replaced anodes is still crucial to vehicle application. Mixed transition metal oxides are deemed as the promising candidates in many fields such as catalysis, lithium ion batteries and supercapacitors, because of complicated chemical components, high theoretical capacity, low cost, high conversion mechanism stability, interface effects and synergistic
20 effects among multiple metal substances. The metal vanadium oxides have an outstanding exhibition in the aspect of electrochemistry, are expected to replace current commercial graphite and become a novel negative electrode material of a lithium ion battery. The metal vanadates attract people's more and more attentions in the aspects of synthesis and morphological control. Reliable designing a nano structure of metal vanadate is extremely
25 necessary for improving the conductivity of electrons and ions.

Oxides of cobalt, such as Co_3O_4 and CoO , have high theoretical capacities which are 890 mAhg^{-1} and 715 mAhg^{-1} , respectively. In recent years, Co_3O_4 -based nano materials are synthesized to serve as anode materials of a lithium battery, including mesoporous Co_3O_4 ,
30 porous Co_3O_4 nano sheets, Co_3O_4 nano wire arrays, needle-like Co_3O_4 nano tubes, multi-walled carbon nano tubes/ Co_3O_4 nano composites and Co_3O_4 nano rod composite vanadium oxides, and the vanadates have outstanding theoretical capacity because of multi-step reduction electron transfer after lithium intercalation. However, at present, the

above electrode material shows poor cycle performance.

SUMMARY

In order to overcome the technical problem in the prior art that the cycle performance of the electrode material is poor, the present disclosure provides a preparation method of an electrode material cobalt vanadate with a high first discharge capacity and the obtained cobalt vanadate as well as use thereof. The above cobalt vanadate is cluster-shaped rod-like porous material cobalt vanadate obtained by using 4'4-bipyridine as a template, reacting vanadium pentoxide with cobalt chloride hexahydrate under a hydrothermal condition to form an organic-inorganic hybrid material containing metal vanadium cobalt and then carrying out thermal treatment at a high temperature. The cobalt vanadate has excellent electrochemical performances.

The objective of the present disclosure is to provide a preparation method of an electrode material cobalt vanadate.

Another objective of the present disclosure is to provide a material cobalt vanadate obtained by the above method.

Still another objective of the present disclosure is to provide use of the above cobalt vanadate in a negative electrode material of a lithium battery.

The present disclosure provides a preparation method of an electrode material cobalt vanadate, comprising the following steps:

(1) transferring vanadium pentoxide and cobalt chloride hexahydrate into a Teflon lining of a reactor, adding water, evenly stirring, adding 4'4-bipyridine, heating to 190-200°C at the temperature rising rate of 5-10°C/min, preserving for 155-160 h, cooling to room temperature, filtering to obtain a precipitate, washing, filtering, and drying to obtain a crystallized precursor; and

(2) heating the precursor obtained in step (1) to 550-580°C at the temperature rising rate of 2-5°C/min, and calcining for 100-140 min at an air atmosphere to obtain cobalt vanadate.

Preferably, in step (1), a mass ratio of vanadium pentoxide to cobalt chloride hexahydrate to 4'4-bipyridine is 8-9: 15-20:4.4.

Preferably, in step (1), the temperature rising rate of the heating is 5-10°C/min.

Preferably, in step (1), the time of the preservation reaction is 155-160 h.

Preferably, in step (2), the temperature rising rate of the heating is 2-5°C/min.

Preferably, in step (2), the calcination atmosphere is air atmosphere.

5

The present disclosure provides the electrode material cobalt vanadate obtained by the preparation method of the above electrode material cobalt vanadate.

Preferably, the cobalt vanadate is of a cluster-shaped rod-like structure with an average width of 8-12 μm .

10 Preferably, there are a plurality of hole channels on the surface of the rod-like structure of cobalt vanadate.

The electrode material cobalt vanadate provided by the present disclosure can be applied to preparation of a negative electrode material of a lithium ion battery.

15 The present disclosure has the beneficial effects:

The present disclosure provides a preparation method of an electrode material cobalt vanadate and the obtained cobalt vanadate as well as use thereof in the negative electrode material of the lithium battery. In the preparation method of the electrode material cobalt vanadate, 4',4'-bipyridine is used as the template, a hydrothermal method is used, the
20 inorganic-organic hybrid material containing metal vanadium cobalt is prepared and then thermal treatment is carried out at the high temperature so as to obtain cluster-shaped rod-like porous CoV_2O_6 . The method provided by the present disclosure is rich in raw material sources and low in cost, the obtained cobalt vanadate has high purity and porous surface. When the obtained cobalt vanadate is used as the electrode, the transportation path of
25 electrons is effectively shortened, and the first discharge capacity of the battery is greatly improved. When being used for the negative electrode material of the lithium ion battery, the electrode material cobalt vanadate provided by the present disclosure has the first discharge capacity of 1107 under the current density of $100 \text{ mAh}^{-1} \cdot \text{g}^{-1}$ and has good cyclic stability.

30 **BRIEF DESCRIPTION OF THE DRAWINGS**

For more clearly illustrating the embodiments of the present disclosure or technical solution in the prior art, drawings required to be used in the embodiments or technical solution will be simply discussed below. Obviously, the drawings described below are only some

embodiments of the present disclosure, and other drawings can also be made by persons of ordinary skill in the art without creative efforts according to these drawings.

Fig.1 is a microscope magnification graph of a precursor obtained in example 1.

5 Fig.2 is an X-ray diffraction (XRD) graph of a precursor obtained in example 1.

Fig.3 is an XRD graph of cobalt vanadate obtained in example 1.

Fig.4 is a scanning electron microscope (SEM) graph of cobalt vanadate obtained in example 1, in which the magnification times of a is 600 times, and the magnification times of a is 10000 times.

10 Fig.5 is a cyclic voltammetric curve (CV curve) of a battery obtained in example 4.

Fig.6 is a constant-current charging-discharging curve of the first three cycles of the battery obtained in example 4.

Fig.7 shows 200 cycles of charging and discharging capacities of a battery obtained in example 4 of under a current density of $100 \text{ mA} \cdot \text{g}^{-1}$.

15 Fig.8 is a magnification performance test graph of a battery obtained in example 4 under different current densities.

DESCRIPTION OF THE EMBODIMENTS

To make the purpose, the technical solution and advantages of the present disclosure more
20 clear, the technical solution of the present disclosure will be described in detail. Obviously, the embodiments described are only a part of embodiments of the present disclosure but not all the embodiments.

Based on the embodiments of the present disclosure, other embodiments obtained by persons
25 of ordinary skill in the art without creative efforts are all included within the protective scope of the present disclosure.

Example 1

A preparation method of an electrode material cobalt vanadate comprises the following steps:

30 (1) 0.162 g of V_2O_5 and 0.323 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were successively weighed and then transferred into a Teflon lining of a 10 ml reactor, 5 ml of deionized water was added using a pipette, the above raw materials were evenly stirred, 0.088 g of 4'4-bipyridine was added, the resulting mixture was put into the reactor and then was placed in a 200°C oven at the

temperature rising rate of 5°C/min to be maintained for 160 h; after the reaction was ended, the reaction product was naturally cooled to room temperature, and supernate was discarded, so as to obtain two products which were a red massive crystal and amorphous powder respectively, the products were treated under the ultrasound, washed with water and filtered, and then naturally dried in air to obtain the red massive crystal, namely, a precursor; and (2) the precursor obtained in step (1) was put in a muffle furnace, heated 550°C at the temperature rising rate of 2 °C/min at the air atmosphere, and then calcined for 120 min so as to obtain black powder sample cobalt vanadate.

10 Example 2

A preparation method of an electrode material cobalt vanadate comprises the following steps:

- (1) 0.16 g of V_2O_5 and 0.3 g of $CoCl_2 \cdot 6H_2O$ were successively weighed and then transferred into a Teflon lining of a 10 ml reactor, 5 ml of deionized water was added using a pipette, the above raw materials were evenly stirred, 0.088 g of 4'4-bipyridine was added, the resulting mixture was put into the reactor and then was placed in a 190°C oven at the temperature rising rate of 10°C/min to be maintained for 160 h; after the reaction was ended, the reaction product was naturally cooled to room temperature, and supernate was discarded, so as to obtain two products which were a red massive crystal and amorphous powder respectively, the products were treated under the ultrasound, washed with water and filtered, and then naturally dried in air to obtain the red massive crystal, namely, a precursor; and (2) the precursor obtained in step (1) was put in a muffle furnace, heated to 580°C at the temperature rising rate of 5 °C/min under the air atmosphere, and then calcined for 100 min so as to obtain black powder sample cobalt vanadate.

25 Example 3

A preparation method of an electrode material cobalt vanadate comprises the following steps:

- (1) 0.18 g of V_2O_5 and 0.4 g of $CoCl_2 \cdot 6H_2O$ were successively weighed and then transferred into a Teflon lining of a 10 ml reactor, adding 5 ml of deionized water with a pipette, the above raw materials were evenly stirred, 0.088 g of 4'4-bipyridine was added, the resulting mixture was put into the reactor and then was placed in a 200°C oven at the temperature rising rate of 5°C/min to be maintained for 155 h; after the reaction was ended, the reaction product was naturally cooled to room temperature, and supernate was discarded, so as to obtain two products which were a red massive crystal and amorphous powder respectively,

the products were treated under the ultrasound, washed with water and filtered, and then naturally dried in air to obtain the red massive crystal, namely, a precursor; and

- (2) the precursor obtained in step (1) was put in a muffle furnace, heated to 550°C at the temperature rising rate of 2.5°C/min under the air atmosphere, and then calcined for 140 min so as to obtain black powder sample cobalt vanadate.

Example 4

The electrode material cobalt vanadate obtained in example 1 was prepared into a battery according to the following steps: cobalt vanadate, carbon black and polyvinylidene fluoride were mixed in a mass ratio of 8:1:1 and then sufficiently grinded, the grinded powder and solvent N-methyl pyrrolidone were grinded to form slurry, the slurry was coated on copper foil and dried in vacuum for 6 h at 120°C; the CR2032 battery was assembled by using metal lithium as a counter electrode, Celgard film as a diaphragm, and EC+DMC+DEC (a volume ratio of 1:1:1) dissolved with LiPF₆ (1 mol/L) as an electrolyte.

15

Test examples

1. The crystal shape of the precursor obtained in example 1 was observed under the microscope. The results are shown in Fig. 1.
2. XRD characterization was carried out on the precursor obtained in example 1. The results are shown in Fig. 2.
3. XRD characterization was carried out on the electrode material cobalt vanadate obtained in example 1. The results are shown in Fig. 3.
4. SEM characterization was carried out on the electrode material cobalt vanadate obtained in example 1. The results are shown in Fig. 4;
5. After standing for 6 h, the CR2032 battery obtained in example 4 was subjected to a constant-current charge/discharge test with a LANHECT2001A test system. The test voltage was 3-0.01 V. The results are seen in Figs. 5-8.

It can be seen from Fig.1 that the shape of the precursor obtained in example 1 is a crystal with a regular shape and is dark red; it can be seen from Fig.2 that by comparing the XRD graph of the precursor obtained in example 1 with the XRD graph simulated by software, there are highly consistent diffraction peaks at the same angle and no miscellaneous peaks.

It can be seen from Fig.3 that the electrode material cobalt vanadate obtained in example 1 is well matched with standard card, does not have miscellaneous peaks and has narrow half peaks, indicating that the material has good crystallization performance.

5 It can be seen from Fig.4 that the electrode material CoV_2O_6 obtained in example 1 of the present disclosure is of a cluster-shaped rod-like structure, each rod-like structure has a width of about $10\text{ }\mu\text{m}$ and a length of more than $10\text{ }\mu\text{m}$, the tail end of the rod-like structure is not a plane and is slightly inclined; after amplification, the surface of the rod-like structure is shown to have a large amount of hole channels, formation of these hole channels is caused by
 10 a fact that ligand organic matters are burnt and volatilized in the process of thermal treatment calcinations, these hole channels facilitate shuttling back and forth of lithium ions therein to assist the promotion of electrochemical performance.

Fig. 5 shows a three-circle cyclic voltammetry curve (CV curve) of this material in a voltage
 15 window of 0-3 V at the scanning rate of 0.2 mv/s. It can be obviously seen that the shapes of three circles of curves are similar, indicating that the material is very little polarized, the peak value is around 1.75 V, which corresponds to the decomposition reaction ($\text{CoV}_2\text{O}_6 \rightarrow \text{CoV} + \text{V}_2\text{O}_5$) and the lithiation reaction ($\text{V}_2\text{O}_5 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{V}_2\text{O}_5$) of the material; as the lithiation reaction further proceeds, metallic Co ($\text{CoO} + 2\text{Li}^+ + 2e^- \rightarrow \text{Co} + \text{Li}_2\text{O}$)
 20 is formed at about 0.35 V, and meanwhile $\text{Li}_x\text{V}_2\text{O}_5$ further proceeds to form a solid electrolyte interface (SEI). In the process of first charging, corresponding lithium ions were deintercalated from the material at the peak values of 1.37 V and 2.42 V and CoO was formed. In the process of discharging and discharging, the first circle and the last two circles are obviously different, which is because of the irreversible decomposition of electrolyte and
 25 electrode materials.

Fig.6 shows a first three-circle constant-current charging-discharging curve of the material. The range of the voltage is 0-3 V, and the density of the current is $100\text{ mA}\cdot\text{g}^{-1}$ as well. In the process of first discharge, three transient discharge platforms are respectively 0.95 V, 0.75 V
 30 and 0.39 V, which correspond to the CV curve scanning results as described above. The cobalt vanadate having a porous structure provides a relatively high discharge of $1107\text{mAh}\cdot\text{g}^{-1}$, which is equivalent to a fact that 10.6 mol of lithium ions are embedded into the material, the first charge capacity is $565\text{mAh}\cdot\text{g}^{-1}$, and the reversible capacity of 542

$\text{mAh}\cdot\text{g}^{-1}$ occurs. In the subsequent cyclic period, the capacity of discharging is reduced, and the discharge capacity after three cycles is $492\text{ mAh}\cdot\text{g}^{-1}$, which is because reversible capacity loss forms an SEI membrane and some un-decomposed Li_2O .

5 Fig. 7 shows cyclic performance. 200 circles of cycles are reached under the current density of $100\text{ mAh}\cdot\text{g}^{-1}$. In the first 50 cycles, the discharge capacity continuously decreases and then slowly rises, after 200 cycles, the discharge capacity is maintained at $100\text{ mAh}\cdot\text{g}^{-1}$, which is because the diffusion dynamic of lithium is enhanced and the reverse reaction between interior metal particles and electrolyte is gradually activated.

10

Fig.8 is a magnification performance test graph under different current densities ($100\text{ mAh}\cdot\text{g}^{-1}$, $200\text{ mAh}\cdot\text{g}^{-1}$, $500\text{ mAh}\cdot\text{g}^{-1}$, $200\text{ mAh}\cdot\text{g}^{-1}$ and $100\text{ mAh}\cdot\text{g}^{-1}$). In the first 30 cycles, the discharge capacities provided by this structure are $437\text{mAh}\cdot\text{g}^{-1}$, $288\text{ mAh}\cdot\text{g}^{-1}$ and $226\text{mAh}\cdot\text{g}^{-1}$, the discharge capacities are $277\text{mAh}\cdot\text{g}^{-1}$ and $371\text{ mAh}\cdot\text{g}^{-1}$ when $200\text{ mAh}\cdot\text{g}^{-1}$ and $100\text{ mAh}\cdot\text{g}^{-1}$ are returned back again, indicating that the structure stable when the electrochemical reaction is carried out.

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

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CLAIMS

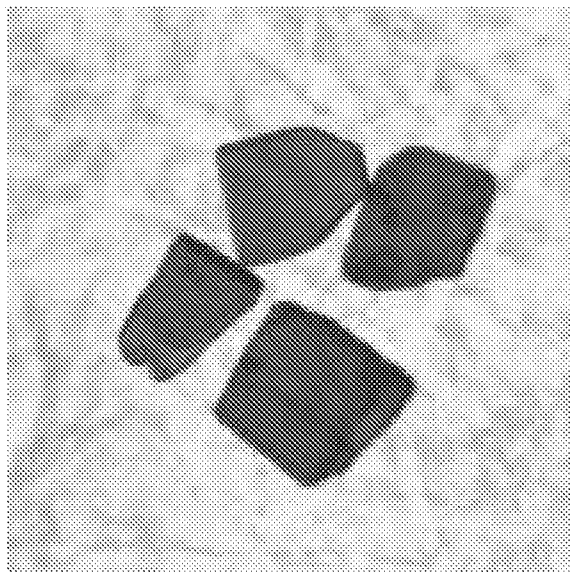
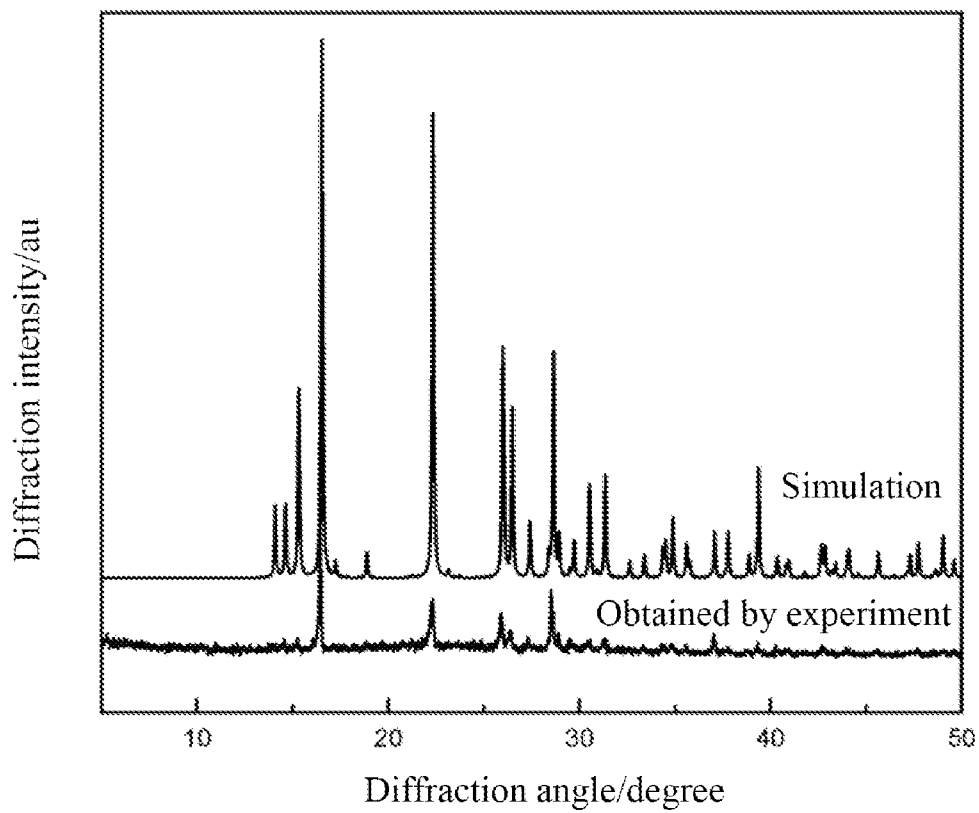
1. A preparation method of an electrode material cobalt vanadate, comprising the
5 following steps:

(1) transferring vanadium pentoxide and cobalt chloride hexahydrate into a Teflon lining of a reactor, adding water, evenly stirring, adding 4'4-bipyridine, heating to 190-200°C at the temperature rising rate of 5-10°C/min, preserving for 155-160 h, cooling to room temperature, filtering to obtain a precipitate, washing, filtering, and drying to obtain a
10 crystallized precursor; a mass ratio of vanadium pentoxide to cobalt chloride hexahydrate to 4'4-bipyridine being 8-9: 15-20:4.4; and

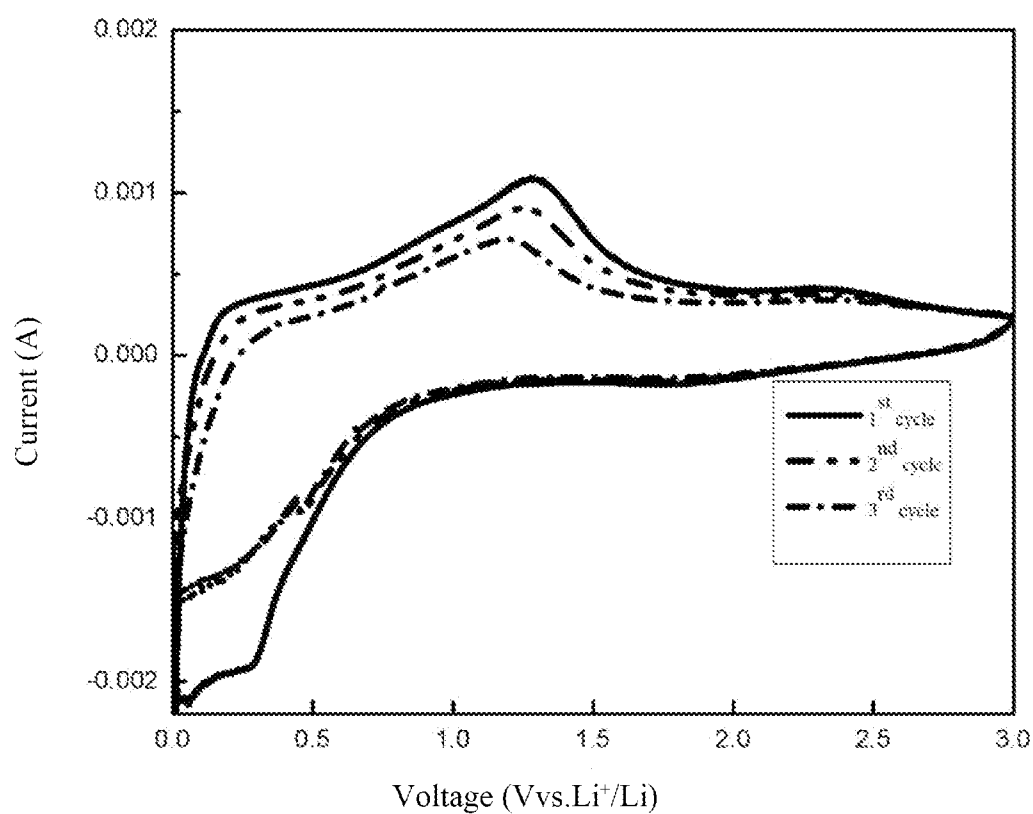
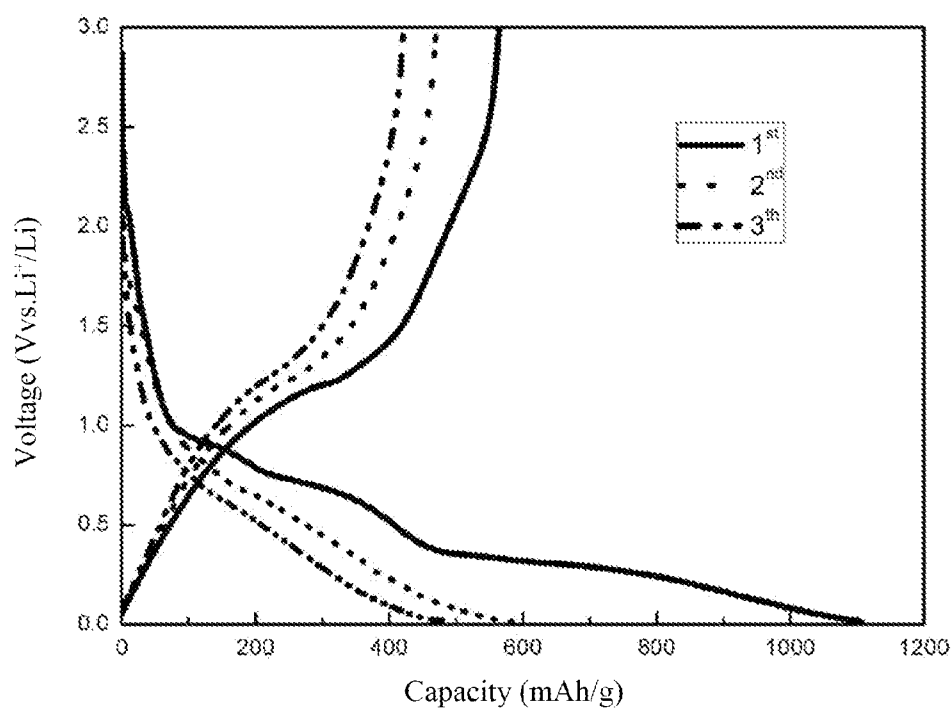
(2) heating the precursor obtained in step (1) to 550-580°C at the temperature rising rate of 2-5°C/min, and calcining for 100-140 min at an air atmosphere to obtain the cobalt vanadate, wherein the cobalt vanadate is in a cluster-shaped rod-like structure with an average width of
15 8-12 μm .

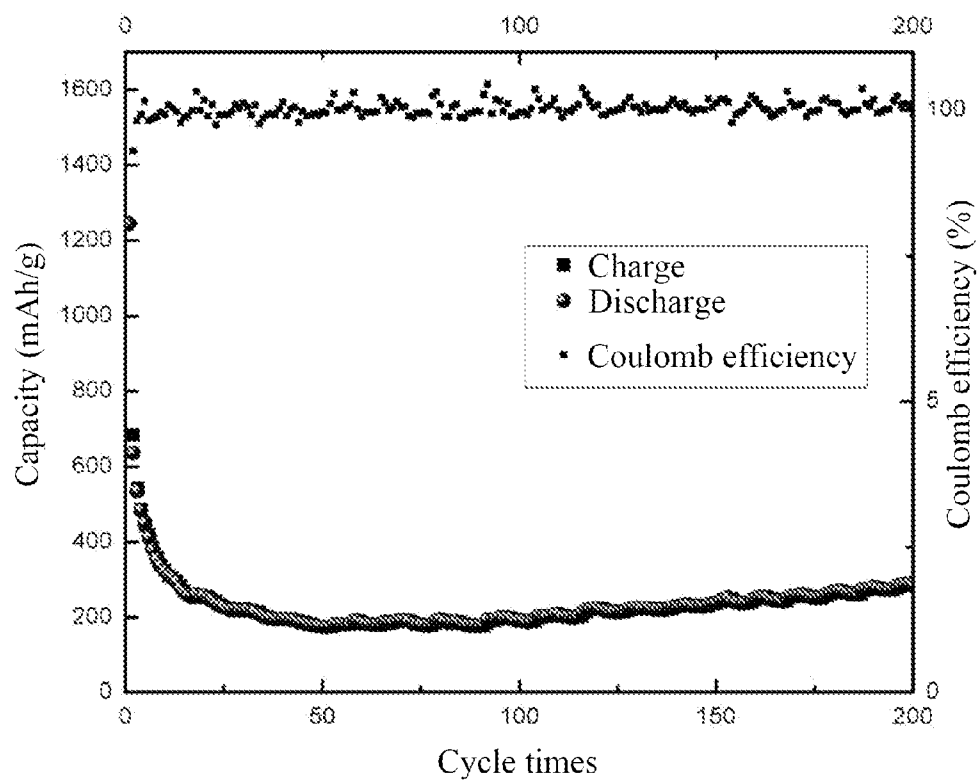
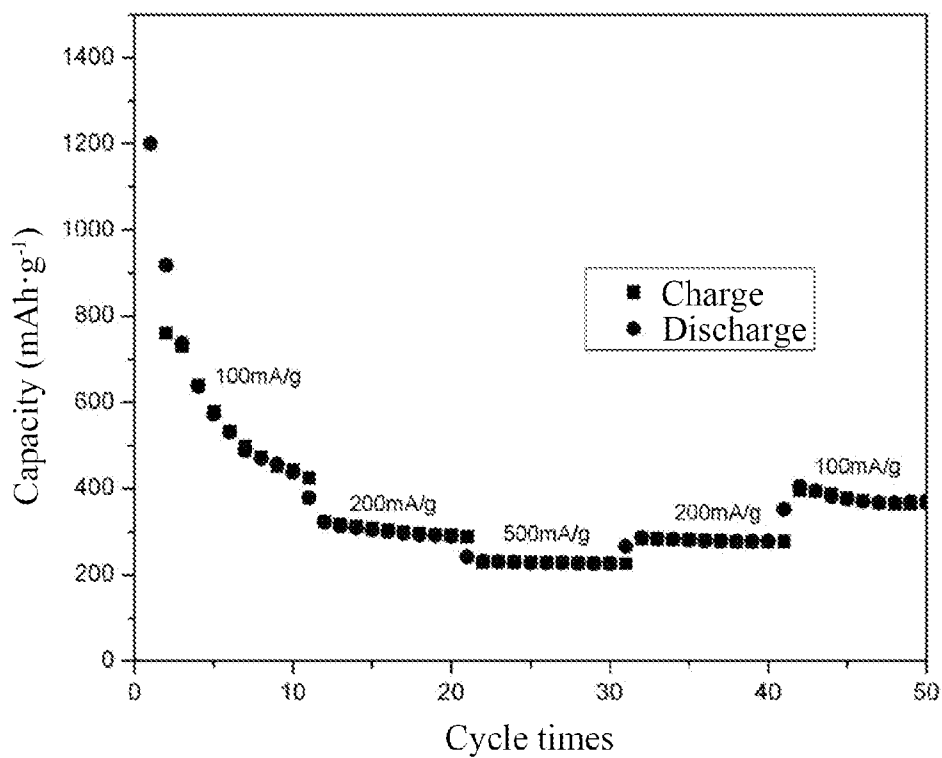
ANSPRÜCHE

1. Verfahren zur Herstellung eines Elektrodenmaterials aus Kobaltvanadat, umfassend die folgenden Schritte:
 - 5 (1) Überführung von Vanadiumpentoxid und Kobaltchloridhexahydrat in eine Teflonauskleidung eines Reaktors, Zugabe von Wasser, gleichmäßiges Rühren, Zugabe von 4'4-Bipyridin, Erhitzen auf 190-200°C bei einer Temperaturanstiegsgeschwindigkeit von 5-10°C/min, Aufbewahren für 155-160 h, Abkühlen auf Raumtemperatur, Filtrieren, um einen Niederschlag zu erhalten, Waschen, Filtrieren und Trocknen, um einen
10 kristallisierten Vorläufer zu erhalten; wobei das Massenverhältnis von Vanadiumpentoxid, Kobaltchloridhexahydrat und 4'4-Bipyridin 8-9:15-20:4.4 beträgt; und
 - (2) Erhitzen des in Schritt (1) erhaltenen Vorläufers auf 550-580°C bei einer Temperaturanstiegsgeschwindigkeit von 2-5°C/min und Kalzinieren für 100-140 min in
15 einer Luftatmosphäre, um das Kobaltvanadat zu erhalten, wobei das Kobaltvanadat in einer clusterförmigen, stäbchenartigen Struktur mit einer durchschnittlichen Breite von 8-12 µm vorliegt.

**FIG. 1****FIG. 2**



**FIG. 5****FIG. 6**

**FIG. 7****FIG. 8**