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(71) Applicant: Ningde Amperex Technology Limited

No.1 Zhenggang Road, Dongqiao Economic Development Zone, Ningde, Fujian, China,
352100

10 Applicant: Dongguan Amperex Technology Limited

(72) Inventors: Leimin Xu, Mengyao Wu, Na Liu

(74) Representative: Bei & Ocean Patent and Trademark Firm, Tianjin, China 12201

Patent attorney, Yuping Cao

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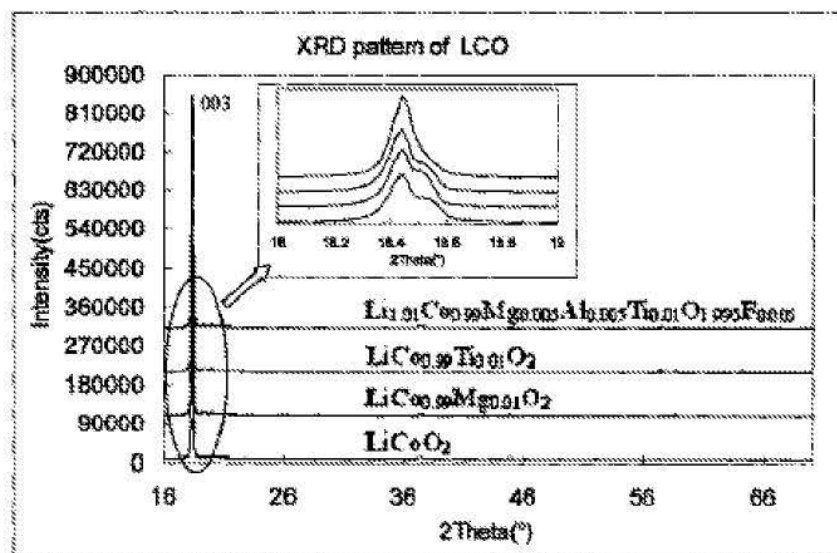
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20 (54) Title of the Invention: LITHIUM-ION BATTERY AND POSITIVE ELECTRODE
ACTIVE MATERIAL THEREOF

(57) Abstract

A positive electrode active material for a lithium ion battery, its structural
formula is $\text{Li}_a\text{Co}_{1-b-c}\text{A}_b\text{B}_c\text{O}_{2-d}\text{C}_d$, where A is at least one element of Mg, Al, Ga and B, B
25 is at least one element of Ti, Zr and Hf, and C is F or P, $0.95 \leq a \leq 1.05$, $0.001 \leq b \leq 0.02$,
 $0.001 \leq c \leq 0.02$, $0.003 \leq b + c \leq 0.03$, $0 < d \leq 0.01$, the element A is uniformly distributed in a
bulk phase of the positive electrode active material, Most of the element B is distributed
on a surface of the positive electrode active material, and the element C is distributed on
the surface of the positive electrode active material, when the positive electrode active
30 material is charged above 4.4V, a 003 peak in an X-ray diffraction spectrum with Cu-K α
remains intact and unsplit.



CLAIMS

1. A positive electrode active material for a lithium ion battery, its structural formula is $\text{Li}_a\text{Co}_{1-b-c}\text{A}_b\text{B}_c\text{O}_{2-d}\text{C}_d$, and characterized in that: A is at least one element of Mg, Al, Ga and B, B is at least one element of Ti, Zr and Hf, and C is F or P, $0.95 \leq a \leq 1.05$, $0.001 \leq b \leq 0.02$, $0.001 \leq c \leq 0.02$, $0.003 \leq b + c \leq 0.03$, $0 < d \leq 0.01$, the element A is uniformly distributed in a bulk phase of the positive electrode active material, at least 80% of the element B is distributed within a range of 0 to 100 nm from the surface, and the element C is distributed on the surface of the positive electrode active material, when the positive electrode active material is charged above 4.4V, a 003 peak in an X-ray diffraction spectrum with Cu-K α remains intact and unsplit.

2. The positive electrode active material for a lithium ion battery according to claim 1, characterized in that: the element A is uniformly distributed in the bulk phase of the positive electrode active material, and no peak of an oxide of the element A appears in the X-ray diffraction spectrum with Cu-K α .

3. The positive electrode active material for a lithium ion battery according to claim 1, characterized in that: at least 80% of the element B is distributed within a range of 0 to 100 nm from the surface, no peak of an oxide of the element B appears in the X-ray diffraction spectrum with Cu-K α .

4. The positive electrode active material for a lithium ion battery according to claim 1, characterized in that: the element C is distributed on the surface of the positive electrode active material and replaces the position of O, no peak of a compound of the element appears in the X-ray diffraction spectrum with Cu-K α ,

5. The positive electrode active material for a lithium ion battery according to claim 1, characterized in that: a Li_2CO_3 content is less than 0.1% and a LiOH content is less than 0.1% in the positive electrode active material.

6. The positive electrode active material for a lithium ion battery according to claim 1, characterized in that: a BET of the positive electrode active material is in a range of 0.1 to 0.4 m^2/g .

7. The positive electrode active material for a lithium ion battery according to claim 1, characterized in that: when the positive electrode active material is charged to 4.4V to 4.6V, a 003 peak in an X-ray diffraction spectrum with Cu-K α remains intact and

unsplit.

8. The positive electrode active material for a lithium ion battery according to claim 1, characterized in that: the positive electrode material is $\text{Li}_{1.01}\text{Co}_{0.99}\text{Mg}_{0.005}\text{Al}_{0.005}\text{Ti}_{0.01}\text{O}_{1.995}\text{F}_{0.005}$.

5 9. A lithium ion battery comprising:

a positive electrode sheet, a negative electrode sheet, a separation film spaced between the positive and negative electrode sheets, and characterized in that: the positive electrode sheet is formed by uniformly mixing the positive electrode active material for a lithium ion battery according to any one of claims 1 to 8 and a conductive carbon powder
10 and a binder.

10. The lithium ion battery according to claim 9, an application charge cut-off voltage is higher than 4.2V.

SPECIFICATION
LITHIUM-ION BATTERY AND POSITIVE ELECTRODE ACTIVE MATERIAL
THEREOF

5 TECHNICAL FIELD

[0001] The present invention relates to a positive electrode active material for a lithium ion battery and a lithium ion battery using the material.

BACKGROUND ART

10 [0002] With the miniaturization and thinness of mobile devices such as mobile phones, digital cameras, laptops, and portable DVD players day by day, the market's demand for mobile energy is getting higher and higher. A lithium-ion has attracted attention as a battery having the highest energy density in the current commercial energy.

[0003] A lithium-ion battery generally include: a positive electrode sheet, a negative
15 electrode sheet, a separation film spaced between the positive and negative electrode sheets, and an electrolyte, wherein positive electrode sheet includes a positive electrode current collector and a positive electrode active material distributed on the positive electrode current collector, the negative electrode sheet includes a negative electrode current collector and a negative electrode active material distributed on the negative
20 electrode current collector. At present, a commonly used positive electrode active material for a lithium ion battery includes multi-materials such as a layered structure such as LiCoO_2 and LiNiO_2 , a spinel structure such as LiMn_2O_4 , and LiNiCoMnO_2 . The above positive electrode active materials each have disadvantages: charging voltage of LiCoO_2 cannot exceed 4.2V, structure of the LiNiO_2 is unstable, a storage performance is
25 poor, performance of LiMn_2O_4 at high temperature is not good, and an energy density is low, an energy density of LiNiCoMnO_2 is low, and they all cannot meet requirements for energy density and safety performance of high-end products, therefore, a new way of increasing energy density is urgently needed.

[0004] For the improvement of energy density, there are mainly two ways from the point
30 of view of materials: one is the development of new high-capacity materials, for example, a lithium-rich manganese-based material developed by the Argon Laboratory in the United States, which can reach 300mAh/g in the charge and discharge range of 2 to 4.8V,

is a currently the material with the highest energy density, but it has natural defects, a cycle performance and a rate performance are poor. There are many problems that cannot be solved now in practical use process. It takes more time to reach commercialization; another way is to increase the charge cut-off voltage of the positive electrode material, for example, LiCoO₂ is a very effective method to increase energy density, which can increase a voltage from the current commonly used voltage of 4.2V, with an increase by 0.1V, the energy density increases by about 10%, but with the increase of the charge cut-off voltage, the delithiation amount of the material increases, and its structure becomes extremely unstable. Many documents report that when LiCoO₂ is cycled above 4.2V, its hexagonal phase is irreversibly changed to monoclinic, side reactions with an electrolyte increase, and the cycle performance becomes poor.

[0005] In order to solve a series of problems caused by increasing the charge cut-off voltage, a great deal of work has been done by the scientific and industry community. United States Patent No. 7135251 discloses that LiCoO₂ coated with AlPO₄ has a significantly improved cycle performance compared to uncoated LiCoO₂ at 4.3V. The relevant document proves that after a high temperature treatment is performed on LiCoO₂ coated with AlPO₄, the phases of LiAlO₂ and Li₃PO₄ are formed on a surface of LiCoO₂, an AlF₃ phase is formed by reaction with the electrolyte in the cycle process and is attached to the surface of LiCoO₂, therefore a cycle performance is improved. Although the coating can improve the cycle performance, the surface coating layer is an electronic insulator, in the practical use, the conductive carbon content in the cathode is not enough to compensate for the increase in the cathodic polarization of the coating layer during the charge and discharge process, and inevitably causes problems such as degradation of voltage platform and the rate performance, so that the energy density is reduced. United States Patent No. 7018741 discloses a doped LiCoO₂, doping elements is distributed on a surface of the material and forms a solid solution with Co, thereby solving the problems of low voltage platform and poor rate performance in United States Patent No. 7135251, but there are a problem of high temperature storage. After the coating element is combined with LiCoO₂, the contact between Co and the electrolyte cannot be completely prevented, and more side reactions inevitably occur during the storage process, therefore, the high-temperature storage performance is slightly worse.

[0006] These published documents or patents can more or less solve some problems at

high voltage ($> 4.2\text{V}$), but they only pay attention to the problems of the surface of LiCoO_2 , but not pay enough attention to a bulk phase change, so they can only be used in a voltage such as 4.3 V and 4.4V . It is well known that during the desorption process of LiCoO_2 , the lattice expands first and then decreases, a voltage of 4.45 to 4.5V is a turning point. A large number of documents have reported that the coating can inhibit the lattice expansion to a certain extent, therefore, the coated LiCoO_2 has better cycle performance at 4.45 or less, once the voltage exceeds 4.45V , the cycle performance decreases sharply, this is because the coating cannot prevent the internal shrinkage and is due to the unstable internal structure, therefore, an effective method to stabilize the internal lattice structure is needed to improve cycle performance at $> 4.45\text{V}$.

[0007] Based on the above reasons, this patent discloses a positive electrode material LiCoO_2 which has good cycle performance and storage performance at high voltage.

SUMMARY OF THE INVENTION

[0008] The purpose of the present invention is to provide a positive electrode material LiCoO_2 to solve the high temperature storage performance and cycle performance in high-voltage applications, especially when the charge cut-off voltage is higher than 4.4V .

[0009] The present invention discloses a positive electrode active material for a lithium ion battery, its structural formula is expressed as $\text{Li}_a\text{Co}_{1-b-c}\text{A}_b\text{B}_c\text{O}_{2-d}\text{C}_d$, which has a layered structure, where A is at least one element of Mg, Al, Ga, and B, because the addition of the element Mg can improve the conductivity of LiCoO_2 , its rate performance is improved, and at the same time its bulk structure can be stabilized, the element Al can form a perfect solid solution with LiCoO_2 , and the bond energy of Al-O bond is greater than that of Co-O bond, it is helpful to improve the stability of its bulk structure, and the ionic radius of Ga is the same as that of Co^{3+} , which can perfectly replace the position of Co^{3+} and improve the bulk structure stability; B-O bond has the highest bond energy, the element B can effectively inhibit the side reaction between LiCoO_2 and a electrolyte. The B is at least one element of Ti, Zr and Hf. These elements can make the stability of a contact interface between LiCoO_2 and the electrolyte fine, and effectively reduce increase of internal resistance in the cycle process, and thus a cycle performance is improved. The C is F or P, because F or P replaces the position of O on the surface of LiCoO_2 , it has a more stable surface at high voltage, thereby reducing the risk of oxygen

release, $0.95 \leq a \leq 1.05$, $0.001 \leq b \leq 0.02$, $0.001 \leq c \leq 0.02$, $0.003 \leq b + c \leq 0.03$, $0 < d \leq 0.01$, the values of these elements all have a certain range, exceeding this range affects its structural stability and reduce the cycle performance; the element A is uniformly distributed in the bulk phase of the positive electrode active material, because the element A needs to form a perfect solid solution with LiCoO_2 , the A replaces the position of Co, thereby the structural stability can be improved, if the distribution is not uniform, the distribution of the bulk phase charge is uneven, and it is easy to cause local damage and affect the cycle performance; the element B is mostly distributed on the surface of the positive electrode active material, the element B is to improve the contact interface between LiCoO_2 and the electrolyte and to suppress the irreversible expansion of the lattice during the charge and discharge process, so it needs to be concentrated on the surface of LiCoO_2 ; the element C is distributed on the surface of the positive electrode active material, the element C replaces the position of O on the surface of LiCoO_2 , reduces the amount of oxygen released under the state of excessive delithiation, and improves safety performance; when the positive electrode active material is charged above 4.4V, the 003 peak in an X-ray diffraction spectrum with Cu-K α remains intact and unsplit, during the charging process of LiCoO_2 , it starts at about 4.3V that the peaks of each crystal plane in the X-ray diffraction spectrum appear to be shifted and widened to a certain extent, the 003 peak is the peak with the strongest peak intensity. A shoulder peak appears at the position of the 003 peak, which indicates that the phase of CoO_2 is generated, and then the shoulder peak slowly become higher. The main peak gradually weaken and the two peaks separate. This phenomenon is called a split peak. When the lithium is completely removed, the 003 peak at this time completely shows the peak of CoO_2 , therefore, the split peak at 003 is due to the generation of the phase of CoO_2 in LiCoO_2 lattice. This is caused by the non-uniformity of delithiation and changes in the internal structure and structure. Below 4.4V, this phase change after the surface coating is reversible. Above 4.4V, the expand of lattice changes to contract, if the bulk phase structure is not stable enough, the phase transition becomes irreversible, which may cause the cycle to decay rapidly. Therefore, the occurrence of this phase transition needs to be suppressed or delayed to make the cycle at $> 4.4\text{V}$ stable, and this phase change occurs from the surface of LiCoO_2 first, and then diffuses internally. The CoO_2 on the surface greatly affects oxidation of the electrolyte, so it makes the high-temperature storage

performance very poor. From these two points, the 003 peak should not appear as a split peak at $> 4.4\text{V}$, thus the cycle and storage performance at high voltage can be solved completely.

[0010] In the positive electrode active material for a lithium ion battery, the element A is uniformly distributed in the bulk phase of the positive electrode active material, and no peak of an oxide of the element A appears in the X-ray diffraction spectrum with $\text{Cu-K}\alpha$. If the element A is distributed non-uniformly, an enrichment of the element A inevitably occur in the bulk phase, and a corresponding peak must exist in the X-ray diffraction spectrum. At the same time, the enriched A inevitably cause the phenomenon of local structural instability and affect the overall performance.

[0011] In the positive electrode active material for a lithium ion battery, at least 80% of the element B is distributed within a range of 0 to 100 nm from the surface. The main function of the element B is to improve the interface, the distribution in the bulk phase can also stabilize the structure, but the effect is not as significant as the distribution on the surface, so it needs to be concentrated within the range of 100nm of the surface. Furthermore, no peak of an oxide of the element B appears in the X-ray diffraction spectrum with $\text{Cu-K}\alpha$, which indicates that it needs to be uniformly distributed. If the local concentration makes Li^+ transfer non-uniform, the rate performance is affected, and the local structure is damaged.

[0012] In the positive electrode active material for lithium ion batteries, the element C is distributed on the surface of the positive electrode active material and replaces the position of O, no peak of a compound of the element C appears in the X-ray diffraction spectrum with $\text{Cu-K}\alpha$, which indicates that a uniform distribution is required to obtain the best effects.

[0013] In the positive electrode active material for a lithium ion battery, its Li_2CO_3 content is less than 0.1% and a LiOH content is less than 0.1%. Li_2CO_3 reacts with HF in the electrolyte to generate CO_2 and causes flatulence, therefore the Li_2CO_3 content needs to be less than 0.1%, while LiOH reacts with HF to generate water, which accelerates the decomposition of the electrolyte and causes flatulence, therefore the LiOH content needs to be less than 0.1%.

[0014] A BET of the positive electrode active material is in a range of 0.1 to 0.4 m^2/g , if the BET is too large or too small, it affects the performance of LiCoO_2 . If the BET is

too small, its rate performance is very poor and cannot meet the requirements of normal applications, if the BET is too large, a reaction with the electrolyte is very violent, and the high-temperature storage performance is poor.

[0015] When the positive electrode material is charged to 4.4V to 4.6V, the 003 peak in the X-ray diffraction spectrum with Cu-K α has no split peaks, 4.4V to 4.6V is the key potential where the expand of lattice of LiCoO₂ changes to contract, it can clearly characterize whether the structure is stable. Above 4.6V, because the degree of delithiation is too high, a CoO₂ phase appears on that side.

[0016] The positive electrode material is Li_{1.01}Co_{0.99}Mg_{0.005}Al_{0.005}Ti_{0.01}O_{1.995}F_{0.005}. This structural formula is an optimized result in which comprehensive performance such as various electrochemical performance, storage performance, and cycle performance are optimized.

[0017] A lithium ion battery, it includes a positive electrode sheet, a negative electrode sheet, a separation film spaced between the positive and negative electrode sheets, and an electrolyte, and is characterized in that the positive electrode sheet is formed by uniformly mixing the foregoing positive electrode active material for the lithium ion battery, a conductive carbon powder and a binder.

[0018] The lithium-ion battery, it applies charge cut-off voltage higher than 4.2V,

[0019] The lithium-ion battery is used at higher voltage, which can greatly increase energy density, but causes storage, cycle, and safety performance degradation, the materials disclosed by the invention not only have good cycle performance at high voltage, but also solve the storage and safety problems when used at high voltage, which cannot be taken into account by the materials simply modified in coating or doping, the present invention also discloses the characteristics of this material, that is, the structure is stable at high voltage and provides the manufacturing process and method of the materials that produce these features. These processes and methods are easy to achieve mass production and have high economic benefits.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] FIG. 1 is an XRD spectrum of LiCoO₂ from 4.2V to 4.6V measured by using an X-ray diffractometer with Cu-K α .

[0021] FIG. 2 is a comparison of XRD spectra of

$\text{Li}_{1.01}\text{Co}_{0.99}\text{Mg}_{0.005}\text{Al}_{0.005}\text{Ti}_{0.01}\text{O}_{1.995}\text{F}_{0.005}$ and LiCoO_2 measured by using an X-ray diffractometer with Cu-K α .

[0022] FIG. 3 is the rate performance of $\text{Li}_{1.01}\text{Co}_{0.99}\text{Mg}_{0.005}\text{Al}_{0.005}\text{Ti}_{0.01}\text{O}_{1.995}\text{F}_{0.005}$ in a button cell.

5 [0023] FIG. 4 is a cycle performance at 4.6V of $\text{Li}_{1.01}\text{Co}_{0.99}\text{Mg}_{0.005}\text{Al}_{0.005}\text{Ti}_{0.01}\text{O}_{1.995}\text{F}_{0.005}$ in a button cell.

[0024] FIG. 5 is an XRD spectrum of $\text{Li}_{1.01}\text{Co}_{0.99}\text{Mg}_{0.005}\text{Al}_{0.005}\text{Ti}_{0.01}\text{O}_{1.995}\text{F}_{0.005}$ at 4.5V using a Cu-K α X-ray diffractometer to test the positive electrode material.

10 [0025] FIG. 6 is a cycle performance at 4.4V of $\text{Li}_{1.01}\text{Co}_{0.99}\text{Mg}_{0.005}\text{Al}_{0.005}\text{Ti}_{0.01}\text{O}_{1.995}\text{F}_{0.005}$ in a full cell.

[0026] Hereinafter, the surface-coated positive electrode material for the lithium ion battery of the present invention and a preparation method thereof will be described in detail with reference to the drawings and specific embodiments.

15 BEST MODE FOR CARRYING OUT THE INVENTION

[0027] The performance of the positive electrode material of the lithium ion battery of the present invention and its preparation method will be described in detail with reference to various Examples.

[0028] Example 1

20 [0029] A certain amount of $\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{Al}(\text{OH})_3$, Co_3O_4 and LiOH powders were weighed, and they are mixed and milled thoroughly in an agate mortar. The average particle size of the milled particles was less than 2 μm , and then calcining was performed at 900 ° C for 10 hours, nano-scale LiF and TiO_2 were added to the calcined mixture, an ethanol was used as a solvent, a ball mill treatment was performed for 10 hours, and then
25 calcining was performed at 800 ° C for 6 hours to obtain a positive electrode material $\text{Li}_{1.01}\text{Co}_{0.99}\text{Mg}_{0.005}\text{Al}_{0.005}\text{Ti}_{0.01}\text{O}_{1.995}\text{F}_{0.005}$, a BET was 0.22 m^2/g , a Li_2CO_3 content was 0.05%, a LiOH content was 0.01%.

[0030] FIG. 2 shows the XRD spectrum of the positive electrode material measured by using an X-ray diffractometer with Cu-K α , compared with LiCoO_2 , all characteristic
30 peaks are consistent. No characteristic diffraction peaks of compounds such as MgO , Al_2O_3 , MgF_2 , AlF_3 , TiO_2 , TiF_4 appears, this indicates that various elements are dispersed

uniformly, and a perfect solid solution is formed.

[0031] FIG. 3 is the rate performance of this material in a button cell, compared with LiCoO_2 , $\text{LiCo}_{0.99}\text{Mg}_{0.01}\text{O}_2$ and $\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$, the rate performance has advantages.

[0032] FIG. 4 shows the cycle performance at 4.6V of this material in a button cell.
5 Compared with LiCoO_2 , $\text{LiCo}_{0.99}\text{Mg}_{0.01}\text{O}_2$ and $\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$, the cycle performance has a very obvious advantage.

[0033] FIG. 5 is an XRD spectrum of the material in the positive electrode material measured by using an X-ray diffractometer with Cu-K α at 4.5V, compared with LiCoO_2 , $\text{LiCo}_{0.99}\text{Mg}_{0.01}\text{O}_2$ and $\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$, the 003 peak does not appear as a split peak, this
10 indicates that the structure is very stable at 4.5V.

[0034] Table 1 shows the high-temperature storage expansion data at 4.4V of the material in a full cell, compared with LiCoO_2 , $\text{LiCo}_{0.99}\text{Mg}_{0.01}\text{O}_2$ and $\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$, the high-temperature storage performance has obvious advantages.

[0035] Example 2

15 [0036] $\text{LiCo}_{0.99}\text{Al}_{0.01}\text{Zr}_{0.01}\text{O}_{1.99}\text{F}_{0.01}$ was prepared according to the method of Example 1, the BET was $0.42\text{m}^2/\text{g}$, a Li_2CO_3 content was 0.15%, a LiOH content was 0.01%, its capacity, rate performance, cycle performance and storage performance are listed in Table 2.

[0037] Example 3

20 [0038] $\text{LiCo}_{0.99}\text{Al}_{0.02}\text{Zr}_{0.01}\text{O}_{1.99}\text{F}_{0.01}$ was prepared according to the method of Example 1, the BET was $0.25\text{m}^2/\text{g}$, a Li_2CO_3 content was 0.05%, and a LiOH content was 0.1%, its capacity, rate performance, cycle performance and storage performance are listed in Table 2.

[0039] Example 4

25 [0040] $\text{LiCoLi}_{0.99}\text{Al}_{0.02}\text{Zr}_{0.02}\text{O}_{1.99}\text{F}_{0.01}$ was prepared according to the method of Example 1, the BET was $0.39\text{m}^2/\text{g}$, a Li_2CO_3 content was 0.05%, a LiOH content was 0.01%, its capacity, rate performance, cycle performance and storage performance are listed in Table 2.

[0041] Example 5

30 [0042] $\text{LiCo}_{0.99}\text{Al}_{0.02}\text{Zr}_{0.02}\text{O}_{1.99}\text{F}_{0.02}$ was prepared according to the method of Example 1, the BET was $0.12\text{m}^2/\text{g}$, a Li_2CO_3 content was 0.1%, and a LiOH content was 0.1%, its capacity, rate performance, cycle performance and storage performance are listed in Table

2.

[0043] The data in Table 2 shows that the increase of the elements A, B and C significantly reduce the capacity and rate performance, but there is no significant improvement in the high temperature storage performance.

5 [0044] Example 6

[0045] $\text{LiCo}_{0.99}\text{B}_{0.01}\text{Hf}_{0.01}\text{O}_{1.995}\text{P}_{0.005}$ was prepared according to the method of Example 1, the BET was $0.32\text{m}^2/\text{g}$, a Li_2CO_3 content was 0.1%, and a LiOH content was 0.05%, is capacity, rate performance, cycle performance and storage performance are listed in Table 2.

10 [0046] Example 7

[0047] An positive electrode sheet which was formed by uniformly mixing the positive electrode active material in Example 1, a conductive carbon powder and a binder was employed. The positive electrode sheet, a separator, and the negative electrode were wound into a cell, and then the cell was subjected to encapsulation, injection formation, and capacity tests, so that the lithium ion battery was formed. FIG. 6 shows the cycle performance at 3.0 to 4.4V of the full cell.

[0048] Comparative Example 1

[0049] LiCoO_2 was prepared according to the method of Example 1 and was compared with Example 1.

20 [0050] FIG. 1 is the XRD spectrum of LiCoO_2 when it is charged from 4.2V to 4.6V. It can be seen from the figure that the various peaks are shifted, split, and it disappears finally. The change of the 003 peak is the most intuitive.

[0051] Comparative Example 2

25 [0052] $\text{LiCo}_{0.99}\text{Mg}_{0.01}\text{O}_2$ was prepared according to the method of Example 1 and was compared with Example 1.

[0053] Comparative Example 3

[0054] $\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$ was prepared according to the method of Example 1 and was compared with Example 1.

[0055] Table 1

30 [0056]

material	rate of change in thickness at 85°C8/h
$\text{Li}_{1.0}\text{Co}_{0.99}\text{Mg}_{0.005}\text{Al}_{0.005}\text{Ti}_{0.01}\text{O}_{1.995}\text{F}_{0.005}$	12%
LiCoO_2	230%
$\text{LiCo}_{0.99}\text{Mg}_{0.01}\text{O}_2$	180%
$\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$	130%

[0057] Table 2

[0058]

material	capacity (mAh/g)	rate				40 循环后 容量保持率	rate of change in thickness at 85°C8/h
		0.2C	0.5C	1C	2C		
$\text{LiCo}_{0.99}\text{Al}_{0.01}\text{Zr}_{0.01}\text{O}_{1.99}\text{F}_{0.01}$	181.4	99.1%	97.7%	95.5%	79.5%	95.2%	16%
$\text{LiCo}_{0.99}\text{Al}_{0.01}\text{Zr}_{0.01}\text{O}_{1.99}\text{F}_{0.01}$	178.6	99%	97.3%	93.8%	77.1%	95.3%	16%
$\text{LiCo}_{0.99}\text{Al}_{0.01}\text{Zr}_{0.01}\text{O}_{1.99}\text{F}_{0.01}$	177.9	98.9%	97.2%	93.4%	77%	95.3%	14%
$\text{LiCo}_{0.99}\text{Al}_{0.01}\text{Zr}_{0.01}\text{O}_{1.99}\text{F}_{0.01}$	176.3	98.9%	97.1%	93.3%	76.8%	95.2%	13%
$\text{LiCo}_{0.99}\text{P}_{0.01}\text{Hf}_{0.01}\text{O}_{1.99}\text{F}_{0.01}$	181.6	99%	97.8%	95.6%	80%	94.7%	17%

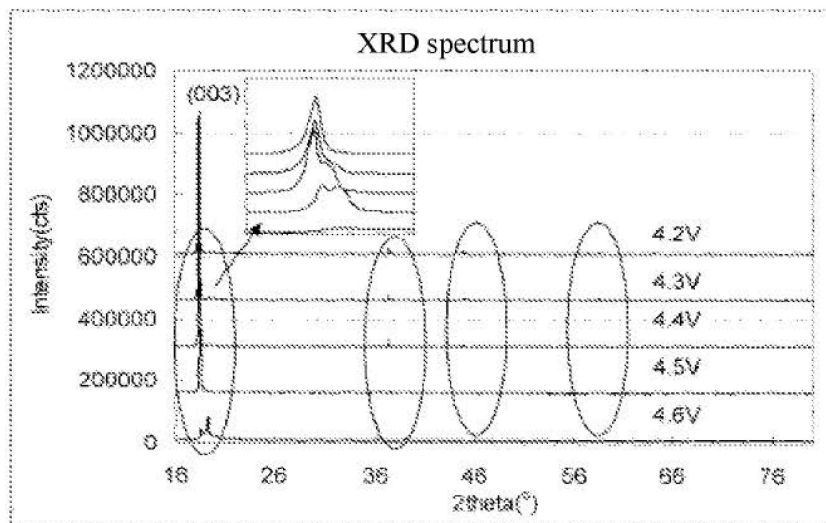


FIG.1

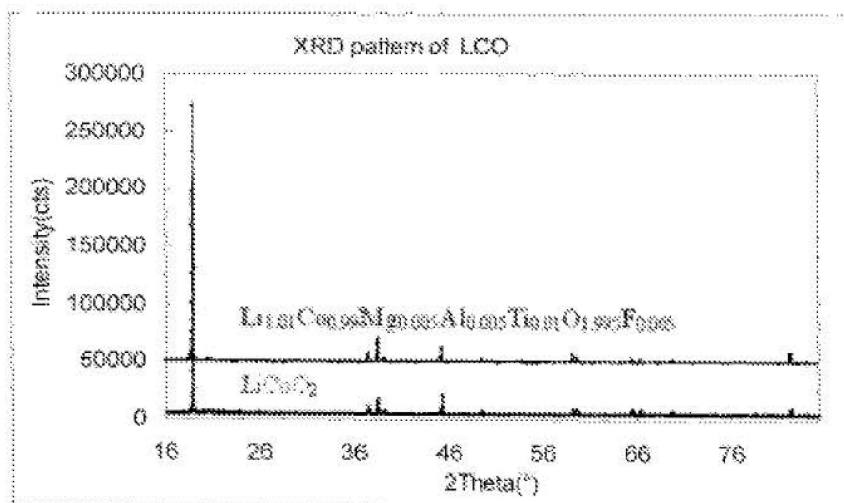


FIG.2

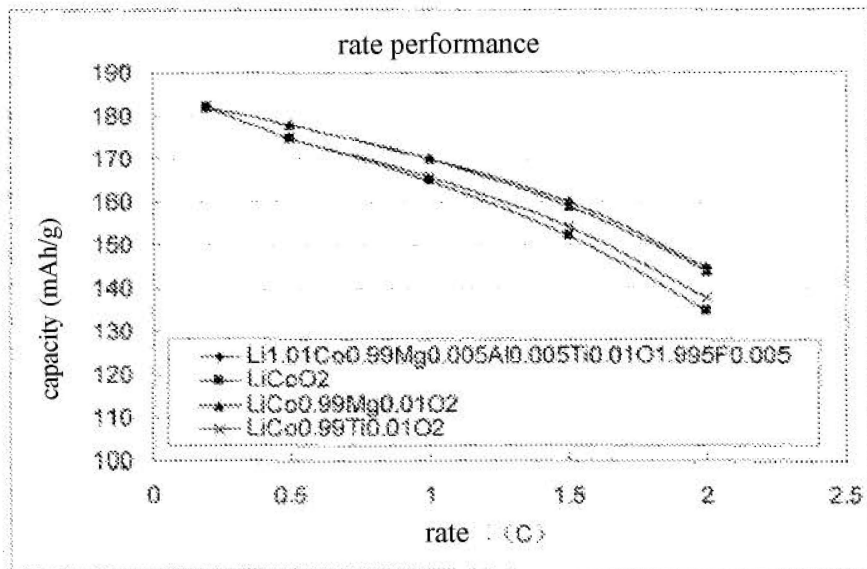


FIG.3

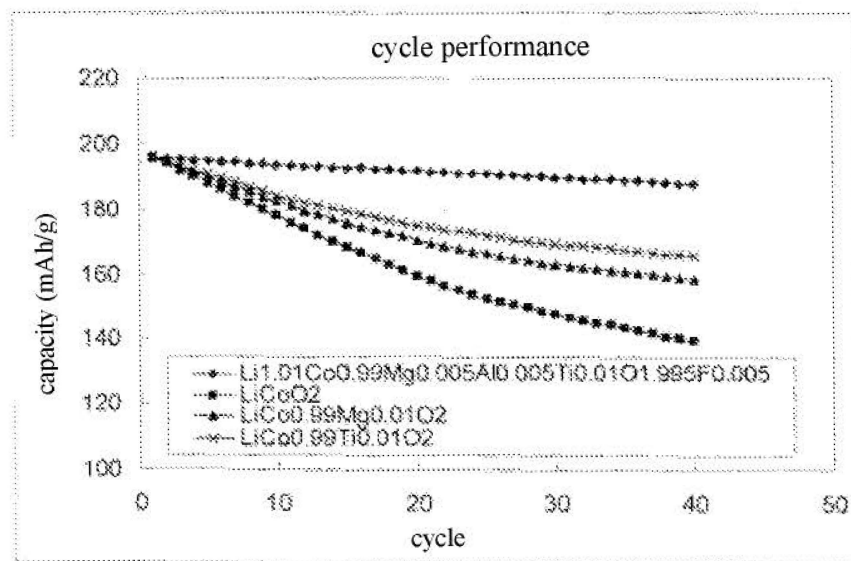


FIG.4

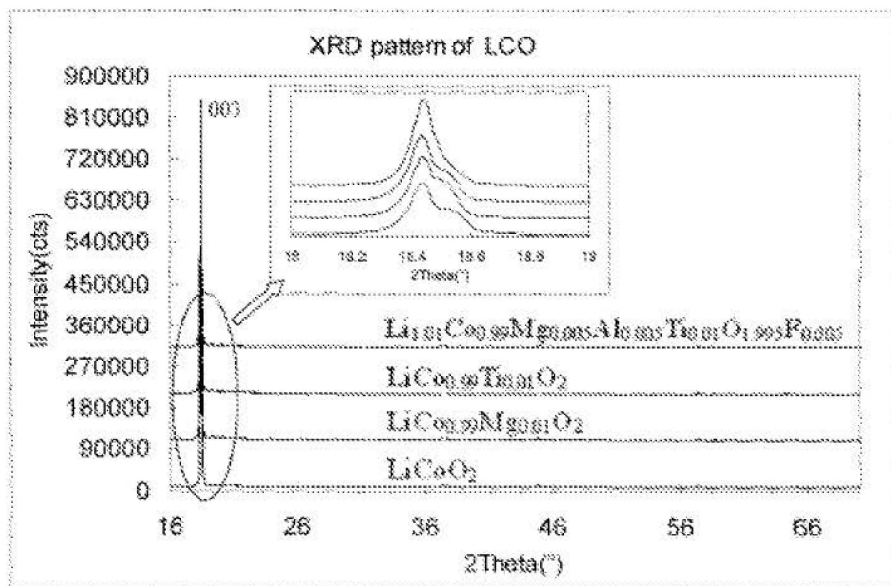


FIG.5

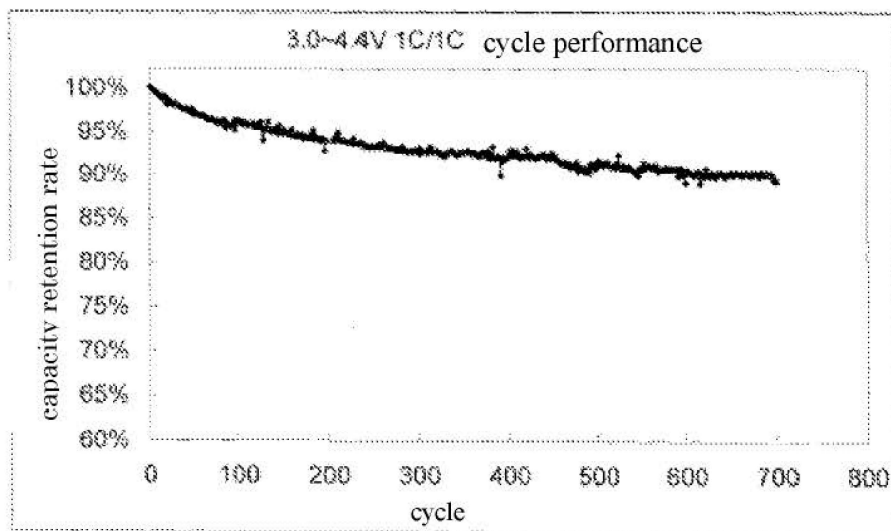
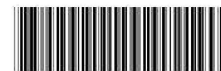


FIG.6



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(71) 申请人 宁德新能源科技有限公司

地址 352100 福建省宁德市东侨经济开发区
郑港路 1 号

申请人 东莞新能源科技有限公司

(72) 发明人 徐磊敏 吴梦尧 柳娜

(74) 专利代理机构 天津市北洋有限责任专利代
理事务所 12201

代理人 曹玉平

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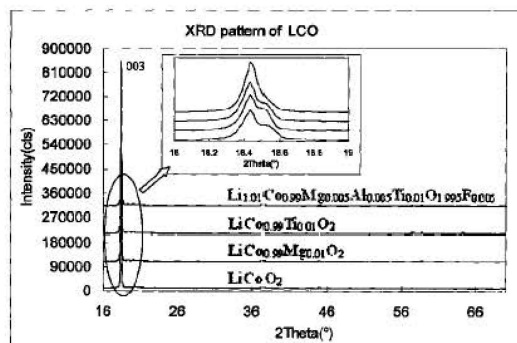
权利要求书 1 页 说明书 5 页 附图 3 页

(54) 发明名称

一种锂离子电池及其正极活性材料

(57) 摘要

一种锂离子电池用正极活性材料,其结构式为 $\text{Li}_a\text{Co}_{1-b-c}\text{A}_b\text{B}_c\text{O}_{2-d}\text{C}_d$, 其中 A 至少为 Mg, Al, Ga, B 中的一种元素, B 至少为 Ti, Zr, Hf 中的一种元素, C 为 F 或者 P, $0.95 \leq a \leq 1.05$, $0.001 \leq b \leq 0.02$, $0.001 \leq c \leq 0.02$, $0.003 \leq b+c \leq 0.03$, $0 < d \leq 0.01$, 元素 A 均匀地分布在所述正极活性材料的体相, 元素 B 大部分分布在所述正极活性材料的表面, 元素 C 分布在所述正极活性材料的表面, 所述正极活性材料在充电至 4.4V 以上时, 在 Cu-K α 的 X 射线衍射谱图上的 003 峰保持完整, 未分裂。



1. 一种锂离子电池用正极活性材料, 其结构式为 $\text{Li}_a\text{Co}_{1-b-c}\text{A}_b\text{B}_c\text{O}_{2-d}\text{C}_d$, 其特征在于: A 至少为 Mg, Al, Ga, B 中的一种元素, B 至少为 Ti, Zr, Hf 中的一种元素, C 为 F 或者 P, $0.95 \leq a \leq 1.05$, $0.001 \leq b \leq 0.02$, $0.001 \leq c \leq 0.02$, $0.003 \leq b+c \leq 0.03$, $0 < d \leq 0.01$, 元素 A 均匀地分布在所述正极活性材料的体相, 元素 B 至少有 80% 分布在距离表面 0 ~ 100nm 范围之内, 元素 C 分布在所述正极活性材料的表面, 所述正极活性材料在充电至 4.4V 以上时, 在 Cu-K α 的 X 射线衍射谱图上的 003 峰保持完整, 未分裂。

2. 根据权利要求 1 所述的锂离子电池用正极活性材料, 其特征在于: 所述的 A 元素均匀地分布在正极活性材料的体相, 在 Cu-K α 的 X 射线衍射谱图上未发现 A 元素的氧化物的峰。

3. 根据权利要求 1 所述的锂离子电池用正极活性材料, 其特征在于: 所述的 B 元素至少有 80% 分布在距离表面 0 ~ 100nm 范围之内, 在 Cu-K α 的 X 射线衍射谱图上未发现 B 元素的氧化物的峰。

4. 根据权利要求 1 所述的锂离子电池用正极活性材料, 其特征在于: 所述 C 元素分布在正极活性材料的表面并取代 O 的位置, 在 Cu-K α 的 X 射线衍射谱图上未发现元素的化合物的峰。

5. 根据权利要求 1 所述的锂离子电池用正极活性材料, 其特征在于: 所述正极活性材料的 Li_2CO_3 含量低于 0.1%, LiOH 含量低于 0.1%。

6. 根据权利要求 1 所述的锂离子电池用正极活性材料, 其特征在于: 所述正极活性材料的 BET 在 0.1 ~ 0.4 m^2/g 之间。

7. 根据权利要求 1 所述的锂离子电池用正极活性材料, 其特征在于: 所述的正极材料在充电至 4.4V ~ 4.6V 时, Cu-K α 的 X 射线衍射谱图上的 003 峰保持完整, 未分裂。

8. 根据权利要求 1 所述的锂离子电池用正极活性材料, 其特征在于: 所述的正极材料为 $\text{Li}_{1.01}\text{Co}_{0.99}\text{Mg}_{0.005}\text{Al}_{0.005}\text{Ti}_{0.01}\text{O}_{1.995}\text{F}_{0.005}$ 。

9. 一种锂离子电池, 其包括正极片、负极片、间隔于正负极片之间的隔离膜, 以及电解液, 其特征在于: 所述正极片由权利要求 1-8 任意一项所述的锂离子电池用正极活性材料与导电碳粉、粘结剂均匀混合制成。

10. 根据权利要求 9 所述的一种锂离子电池, 其应用的充电截止电压高于 4.2V。

一种锂离子电池及其正极活性材料

技术领域

[0001] 本发明涉及一种锂离子电池用正极活性材料及使用该材料的锂离子电池

背景技术

[0002] 随着手机、数码相机、笔记本电脑和便携式 DVD 等移动设备的日益小型化和轻薄化,市场对于移动能源的需求越来越高,锂离子作为目前商业化能源中能量密度最高的一类电池备受关注。

[0003] 锂离子电池一般包括:正极片、负极片、间隔于正负极片之间的隔离膜,以及电解液,其中,正极片包括正极集流体和分布在正极集流体上的正极活性材料,负极片包括负极集流体和分布在负极集流体上的负极活性材料。目前,常用的锂离子电池的正极活性材料有层状结构 LiCoO_2 和 LiNiO_2 、尖晶石结构 LiMn_2O_4 ,以及 LiNiCoMnO_2 等多元材料。上述正极活性材料都有各自的缺点: LiCoO_2 充电电压不能超过 4.2V, LiNiO_2 的结构不稳定,存储性能差, LiMn_2O_4 的高温性能不好,能量密度低, LiNiCoMnO_2 的能量密度低,都无法满足高端产品对能量密度和安全性能的要求,因此,迫切需要新的能量密度增长方式。

[0004] 对于能量密度的提升,从材料角度出发,主要有两种方式:一为新的高容量材料的开发,如美国 Argon 实验室开发的富锂锰基材料,在 2 ~ 4.8V 的充放电范围内可以达到 300mAh/g,为目前能量密度最高的材料,但是其具有天然的缺陷,循环性能以及倍率性能都较差,实际应用过程中存在很多目前无法解决的问题,距离商业化还有很长一段距离;另一种方式为提升正极材料的充电截止电压,如 LiCoO_2 ,从目前的常用电压 4.2V 往上提升,每升高 0.1V,能量密度增长约 10%,是一种非常有效的能量密度提升方式,但是随着充电截止电压的提升,材料的脱锂量增加,其本身结构变得极其不稳定,大量文献报道,当 LiCoO_2 在 4.2V 以上循环时,其六方晶相会向单斜晶相发生不可逆的转变,与电解液之间的副反应增多,循环性能会变得很差。

[0005] 为了解决提升充电截止电压所带来的一系列问题,科学界和工业界做了大量的工作。美国专利 7135251 公开了采用 AlPO_4 包覆的 LiCoO_2 在 4.3V 下相对于未包覆的 LiCoO_2 具有非常明显的循环性能的提升,相关文献证明 AlPO_4 包覆的 LiCoO_2 经过高温处理后,在 LiCoO_2 的表面形成了 LiAlO_2 和 Li_3PO_4 的相,同时在循环过程中与电解液反应形成 AlF_3 相附在 LiCoO_2 的表面,从而提升其循环性能。包覆虽然能够提升循环性能,但是表面包覆层为电子绝缘体,在实际应用中,阴极导电碳的含量不足以弥补充放电过程中包覆层对阴极极化的增加,势必会带来电压平台的降低以及倍率性能的变差,如此会降低能量密度。美国专利 7018741 公开了一种掺杂的 LiCoO_2 ,将掺杂元素分布于材料的表面,与 Co 形成固溶体,从而解决了美国专利 7135251 中的电压平台低,倍率性能差等问题,但是存在高温存储的问题,包覆元素与 LiCoO_2 结合后,就不能完全阻止 Co 与电解液的接触,在存储过程必然会有较多的副反应放生,因此,高温存储性能会稍差。

[0006] 这些公开的文献或者专利都能或多或少的解决高电压 (> 4.2V) 下的一些问题,但是它们都只关注了 LiCoO_2 的表面问题,而对体相变化关注不足,因此只能在 4.3V,

4.4V 等电压下进行应用。众所周知, LiCoO_2 在脱离过程中, 其晶格是先膨胀后减小, 电压 4.45 ~ 4.5V 时为转折点, 大量文献报道包覆可以在一定程度上抑制晶格膨胀, 因此包覆后的 LiCoO_2 在 4.45 以下具有较好的循环性能, 一旦电压超过 4.45V, 循环性能急剧降低, 这是因为包覆无法阻止经过内部的收缩, 内部结构不稳定所导致, 因此需要一种有效手段稳定其内部晶格结构, 改善在 > 4.45V 的循环性能。

[0007] 基于上述原因, 本专利公开了一种在高电压下具有很好循环性能和存储性能正极材料 LiCoO_2 。

发明内容

[0008] 本发明的目的在于提供一种正极材料 LiCoO_2 , 以解决高电压应用下的高温存储性能和循环性能, 尤其是在充电截止电压高于 4.4V 时。

[0009] 本发明公开了一种锂离子电池用正极活性材料, 其结构式表达为 $\text{Li}_a\text{Co}_{1-b-c}\text{A}_b\text{O}_{2-d}\text{C}_d$, 其具有层状结构, 其中 A 至少为 Mg, Al, Ga, B 中的一种元素, 因为 Mg 元素的加入可以提升 LiCoO_2 的电导率, 从而提高其倍率性能, 同时可以稳定其体相结构, Al 元素能与 LiCoO_2 形成完美的固溶体, 同时 Al-O 键的键能大于 Co-O 键, 对于提高其体相结构稳定性有帮助, 而 Ga 的离子半径与 Co^{3+} 相同, 可以完美的取代 Co^{3+} 的位置, 提升体相结构稳定性; B-O 键具有最高的键能, 同 B 元素可以有效抑制 LiCoO_2 与电解液之间的副反应, B 至少为, Ti, Zr, Hf 中的一种元素, 这些元素能够很好的稳定 LiCoO_2 与电解液的接触界面, 有效减少循环过程的内阻增加, 从而提高循环性能。C 为 F 或者 P, 因为 F 或者 P 在 LiCoO_2 的表面取代 O 的位置, 使其在高电压下具有更稳定的表面, 从而降低释氧风险, $0.95 \leq a \leq 1.05$, $0.001 \leq b \leq 0.02$, $0.001 \leq c \leq 0.02$, $0.003 \leq b+c \leq 0.03$, $0 < d \leq 0.01$, 这些元素的取值都有一定范围, 超过这个范围都会影响其结构稳定性, 降低循环性能; 元素 A 均匀地分布在所述正极活性材料的体相, 因为元素 A 需要与 LiCoO_2 形成完美的固溶体, A 取代 Co 的位置, 才能提高结构稳定性, 如果分散不均匀, 造成体相电荷分布不均匀, 容易造成局部破坏, 影响循环性能; 元素 B 大部分分布在所述正极活性材料的表面, 元素 B 在于改善 LiCoO_2 与电解液的接触界面, 抑制充放电过程中晶格的不可逆膨胀, 因此需要集中在 LiCoO_2 的表面; 元素 C 分布在所述正极活性材料的表面, 元素 C 取代 LiCoO_2 表面 O 的位置, 降低过度脱锂状态下的释氧量, 提升安全性能; 所述正极活性材料在充电至 4.4V 以上时, 在 Cu-K α 的 X 射线衍射谱图上的 003 峰保持完整, 不分裂, 在 LiCoO_2 充电过程中, 在 4.3V 左右开始, X 射线衍射谱图上的各个晶面的峰会出现一定程度的位移和宽化, 其中 003 峰是峰强度最强的峰, 在 003 峰的位置会出现一个肩峰, 代表生成了 CoO_2 的相, 然后肩峰慢慢变高, 而主峰会逐渐减弱, 两峰会分离, 这种现象称做为分峰, 到完全脱锂时, 此时的 003 峰完全显示为 CoO_2 的峰, 因此在 003 峰的分峰是因为 LiCoO_2 晶格中产生了 CoO_2 的相, 这是脱锂不均匀以及内部结构结构发生变化造成的, 在 4.4V 以下, 这个相变在表面包覆之后是可逆的, 在 4.4V 以上时, 由于晶格有膨胀转变为收缩, 如果体相结构不够稳定, 相变就变成不可逆的, 这样就造成循环衰减很快, 因此, 需要抑制或者延缓这个相变的发生, 才能使 > 4.4V 时循环稳定, 同时这个相变从 LiCoO_2 的表面先发生, 然后再内部扩散, 表面的 CoO_2 对电解液的氧化性能很强, 因此会使得高温存储性能变得很差, 从这两点出发, 要使 003 峰在 > 4.4V 不出现分裂才能从根本上解决高电压下的循环和存储性能。

[0010] 所述的锂离子电池用正极活性材料中,A元素均匀地分布在正极活性材料的体相,在Cu-K α 的X射线衍射谱图上未发现A元素的氧化物的峰,如果A元素分布不均匀,则在体相中必然出现A元素的富集,在X射线衍射谱中必然有相对应的峰存在,同时富集的A必然造成局部结构不稳定的现象,影响整体性能。

[0011] 所述的锂离子电池用正极活性材料,B元素至少有80%分布在距离表面0~100nm范围之内,B元素的主要功能是改善界面,分布在体相也能稳定结构,但不如分布在表面效果明显,因此需要集中分布在表面100nm的范围内,同时在Cu-K α 的X射线衍射谱图上未发现B元素的氧化物的峰,表示需要均匀分布,如果局部团聚会造成Li⁺迁移不均匀,影响倍率性能,同时造成局部结构被破坏。

[0012] 所述的锂离子电池用正极活性材料,C元素分布在正极活性材料的表面并取代O的位置,在Cu-K α 的X射线衍射谱图上未发现C元素的化合物的峰,表明需要均匀分布才能取得最好的效果。

[0013] 所述的锂离子电池用正极活性材料,其Li₂CO₃含量低于0.1%,LiOH含量低于0.1%。因为Li₂CO₃会与电解液中的HF反应生成CO₂造成胀气,因此Li₂CO₃含量需要低于0.1%,而LiOH会与HF反应生成水,加速电解液的分解,造成胀气,因此LiOH含量需要低于0.1%。

[0014] 所述正极活性材料的BET在0.1~0.4m²/g之间,BET太大或者太小都会影响LiCoO₂的性能,BET太小时,其倍率性能很差,无法满足正常应用要求,BET太大时,与电解液之间的反应很剧烈,高温存储性能较差。

[0015] 所述的正极材料在充电至4.4V~4.6V时,Cu-K α 的X射线衍射谱图上的003峰无分峰,4.4V~4.6V是LiCoO₂晶格有膨胀转为收缩的关键电势,可以清楚地表征其结构是否稳定,高于4.6V以后,因为脱锂程度太高,那面会出现CoO₂的相。

[0016] 所述的正极材料为Li_{1.01}Co_{0.99}Mg_{0.005}Al_{0.005}Ti_{0.01}O_{1.995}F_{0.005},这种结构式是经过优化后,各种电化学性能、存储性能、循环性能综合性能最有的结果。

[0017] 一种锂离子电池,其包括正极片、负极片、间隔于正负极片之间的隔离膜,以及电解液,其特征在于:所述正极片上述的锂离子电池用正极活性材料与导电碳粉、粘结剂均匀混合制成。

[0018] 所述的一种锂离子电池,其应用的充电截止电压高于4.2V,

[0019] 锂离子电池在更高电压下应用,能够大幅度提升能量密度,但是会带来存储、循环、安全等性能的衰减,被发明公开的材料不仅在高电压下具有很好的循环性能,而且还解决了困扰高电压应用的存储、安全问题,这是简单的包覆或者掺杂改性的材料所无法兼顾的,本发明还公开了这种材料所具有的特征,即在高电压下结构稳定性的特征,并且提供了产生这些特征的的材料的制备工艺和方法,这些工艺和方法容易实现量产,具有很高的经济效益。

附图说明

[0020] 图1是使用Cu-K α 的X射线衍射仪测试LiCoO₂从4.2V-4.6V的XRD谱图。

[0021] 图2是使用Cu-K α 的X射线衍射仪测试Li_{1.01}Co_{0.99}Mg_{0.005}Al_{0.005}Ti_{0.01}O_{1.995}F_{0.005}和LiCoO₂的XRD谱图对比。

- [0022] 图 3 是 $\text{Li}_{1.01}\text{Co}_{0.99}\text{Mg}_{0.005}\text{Al}_{0.005}\text{Ti}_{0.01}\text{O}_{1.995}\text{F}_{0.005}$ 在扣式电池中的倍率性能。
- [0023] 图 4 是 $\text{Li}_{1.01}\text{Co}_{0.99}\text{Mg}_{0.005}\text{Al}_{0.005}\text{Ti}_{0.01}\text{O}_{1.995}\text{F}_{0.005}$ 在扣式电池中 4.6V 的循环性能。
- [0024] 图 5 是 $\text{Li}_{1.01}\text{Co}_{0.99}\text{Mg}_{0.005}\text{Al}_{0.005}\text{Ti}_{0.01}\text{O}_{1.995}\text{F}_{0.005}$ 在 4.5V 时使用 Cu-K α 的 X 射线衍射仪测试正极材料的 XRD 谱图。
- [0025] 图 6 是 $\text{Li}_{1.01}\text{Co}_{0.99}\text{Mg}_{0.005}\text{Al}_{0.005}\text{Ti}_{0.01}\text{O}_{1.995}\text{F}_{0.005}$ 在全电池 4.4V 时的循环性能。
- [0026] 下面结合附图和具体实施方式,对本发明锂离子电池表面包覆正极材料及其制备方法进行详细说明。

具体实施方式

[0027] 下面结合各个实施例,详细说明本发明锂离子电池正极材料的性能及其制备方法。

[0028] 实施例 1

[0029] 称取一定量的 $\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{Al}(\text{OH})_3$, Co_3O_4 以及 LiOH 粉末在玛瑙研钵中进行充分混合研磨后,研磨后颗粒的平均粒度小于 $2\mu\text{m}$,然后在 900°C 下煅烧 10h;将煅烧后的混合物中加入纳米级 LiF 和 TiO_2 ,并以乙醇作为溶剂,球磨 10h 后,在 800°C 下煅烧 6h 得到了正极材料 $\text{Li}_{1.01}\text{Co}_{0.99}\text{Mg}_{0.005}\text{Al}_{0.005}\text{Ti}_{0.01}\text{O}_{1.995}\text{F}_{0.005}$, BET 为 $0.22\text{m}^2/\text{g}$, Li_2CO_3 含量为 0.05%, LiOH 含量为 0.01%。

[0030] 图 2 是使用 Cu-K α 的 X 射线衍射仪测试该正极材料的 XRD 谱图,与 LiCoO_2 相比,所有特征峰一致,没有发现 MgO , Al_2O_3 , MgF_2 , AlF_3 , TiO_2 , TiF_4 等化合物的特征衍射峰,说明各种元素分散均匀,形成了完美的固溶体。

[0031] 图 3 是该材料在扣式电池中的倍率性能,与 LiCoO_2 , $\text{LiCo}_{0.99}\text{Mg}_{0.01}\text{O}_2$, $\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$ 相比,倍率性能具有优势。

[0032] 图 4 是该材料在扣式电池中 4.6V 的循环性能,与 LiCoO_2 , $\text{LiCo}_{0.99}\text{Mg}_{0.01}\text{O}_2$, $\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$ 相比,循环性能具有非常明显的优势。

[0033] 图 5 是该材料在 4.5V 时使用 Cu-K α 的 X 射线衍射仪测试该正极材料的 XRD 谱图,与 LiCoO_2 , $\text{LiCo}_{0.99}\text{Mg}_{0.01}\text{O}_2$, $\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$ 相比,003 峰并没有出现分峰,说明其在 4.5V 时的结构非常稳定。

[0034] 表 1 是该材料在全电池中 4.4V 时的高温存储膨胀数据,与 LiCoO_2 , $\text{LiCo}_{0.99}\text{Mg}_{0.01}\text{O}_2$, $\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$ 相比,高温存储性能有明显优势。

[0035] 实施例 2

[0036] 按照实施例 1 的方法制备了 $\text{LiCo}_{0.99}\text{Al}_{0.01}\text{Zr}_{0.01}\text{O}_{1.99}\text{F}_{0.01}$, BET 为 $0.42\text{m}^2/\text{g}$, Li_2CO_3 含量为 0.15%, LiOH 含量为 0.01% 其容量、倍率性能、循环性能以及存储性能列于表 2 中。

[0037] 实施例 3

[0038] 按照实施例 1 的方法制备了 $\text{LiCo}_{0.99}\text{Al}_{0.02}\text{Zr}_{0.01}\text{O}_{1.99}\text{F}_{0.01}$, BET 为 $0.25\text{m}^2/\text{g}$, Li_2CO_3 含量为 0.05%, LiOH 含量为 0.1% 其容量、倍率性能、循环性能以及存储性能列于表 2 中。

[0039] 实施例 4

[0040] 按照实施例 1 的方法制备了 $\text{LiCoLi}_{0.99}\text{Al}_{0.02}\text{Zr}_{0.02}\text{O}_{1.99}\text{F}_{0.01}$, BET 为 $0.39\text{m}^2/\text{g}$, Li_2CO_3 含量为 0.05%, LiOH 含量为 0.01% 其容量、倍率性能、循环性能以及存储性能列于表 2 中。

[0041] 实施例 5

[0042] 按照实施例 1 的方法制备了 $\text{LiCo}_{0.99}\text{Al}_{0.02}\text{Zr}_{0.02}\text{O}_{1.99}\text{F}_{0.02}$, BET 为 $0.12\text{m}^2/\text{g}$, Li_2CO_3 含量为 0.1%, LiOH 含量为 0.1% 其容量、倍率性能、循环性能以及存储性能列于表 2 中。

[0043] 表 2 中的数据说明 A、B 以及 C 元素的增加会显著降低容量及倍率性能,但是高温存储性能并没有明显改善。

[0044] 实施例 6

[0045] 按照实施例 1 的方法制备了 $\text{LiCo}_{0.99}\text{B}_{0.01}\text{Hf}_{0.01}\text{O}_{1.995}\text{P}_{0.005}$, BET 为 $0.32\text{m}^2/\text{g}$, Li_2CO_3 含量为 0.1%, LiOH 含量为 0.05% 其容量、倍率性能、循环性能以及存储性能列于表 2 中。

[0046] 实施例 7

[0047] 采用实施例 1 中的正极活性材料与导电碳粉、粘结剂均匀混合制成制成正极极片,将正极极片与隔离膜以及负极卷绕成电芯,然后对电芯进行封装、注液、化成、容量测试等制成锂离子电池,图 6 是全电池在 3.0 ~ 4.4V 下的循环性能。

[0048] 对比实施例 1

[0049] 按照实施例 1 的方法制备了 LiCoO_2 与实施例 1 进行比较。

[0050] 图 1 是 LiCoO_2 从 4.2V-4.6V 充电时的 XRD 谱图,从图中可以看出,各种峰都在位移、分峰,直至消失,其中 003 峰的变化最为直观。

[0051] 对比实施例 2

[0052] 按照实施例 1 的方法制备了 $\text{LiCo}_{0.99}\text{Mg}_{0.01}\text{O}_2$ 与实施例 1 进行比较。

[0053] 对比实施例 3

[0054] 按照实施例 1 的方法制备了 $\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$ 与实施例 1 进行比较。

[0055] 表 1

[0056]	材料	85℃/8h 厚度变化率
	$\text{Li}_{1.3}\text{Co}_{0.99}\text{Mg}_{0.005}\text{Al}_{0.005}\text{Ti}_{0.01}\text{O}_{1.995}\text{F}_{0.005}$	12%
	LiCoO_2	230%
	$\text{LiCo}_{0.99}\text{Mg}_{0.01}\text{O}_2$	180%
	$\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$	130%

[0057] 表 2

[0058]

材料	容量 (mAh/g)	倍率				40 循环后 容量保持率	85℃/8h 厚度变化率
		0.2C	0.5C	1C	2C		
$\text{LiCo}_{0.99}\text{Al}_{0.01}\text{Zr}_{0.01}\text{O}_{1.99}\text{F}_{0.01}$	181.4	99.1%	97.7%	95.5%	79.5%	95.2%	16%
$\text{LiCo}_{0.99}\text{Al}_{0.02}\text{Zr}_{0.01}\text{O}_{1.99}\text{F}_{0.01}$	178.6	99%	97.3%	93.8%	77.1%	95.3%	16%
$\text{LiCo}_{0.99}\text{Al}_{0.02}\text{Zr}_{0.02}\text{O}_{1.99}\text{F}_{0.01}$	177.9	98.9%	97.2%	93.4%	77%	95.3%	14%
$\text{LiCo}_{0.99}\text{Al}_{0.02}\text{Zr}_{0.02}\text{O}_{1.99}\text{F}_{0.02}$	176.3	98.9%	97.1%	93.3%	76.8%	95.2%	13%
$\text{LiCo}_{0.99}\text{B}_{0.01}\text{Hf}_{0.01}\text{O}_{1.995}\text{P}_{0.005}$	181.6	99%	97.8%	95.6%	80%	94.7%	17%

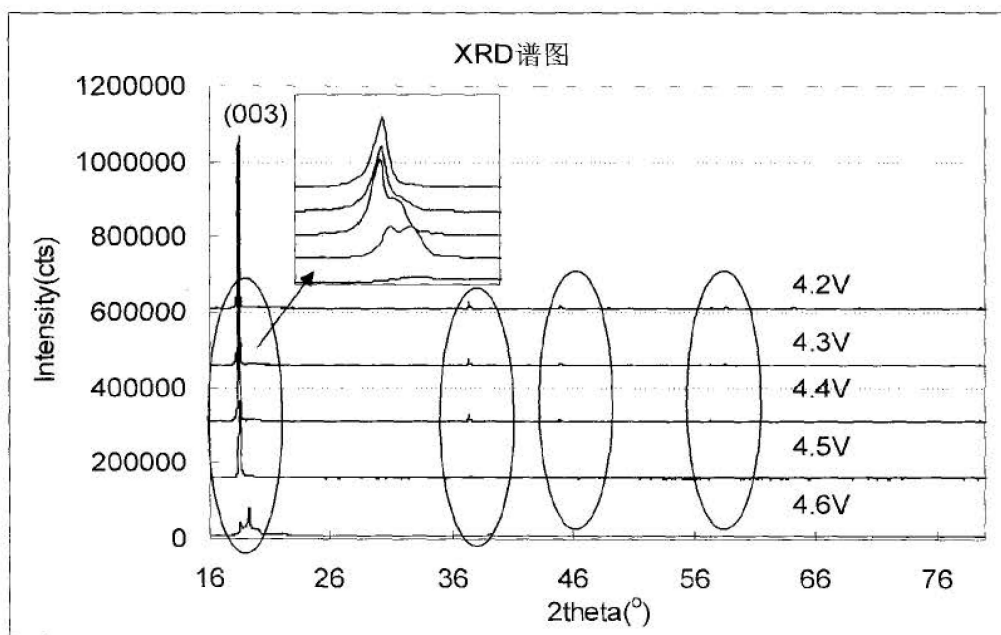


图 1

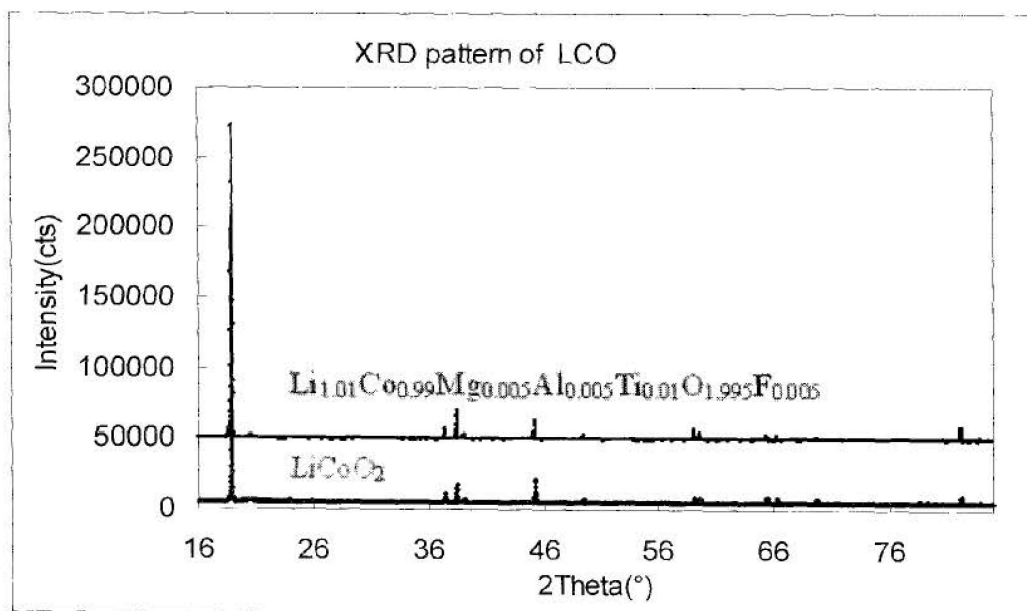


图 2

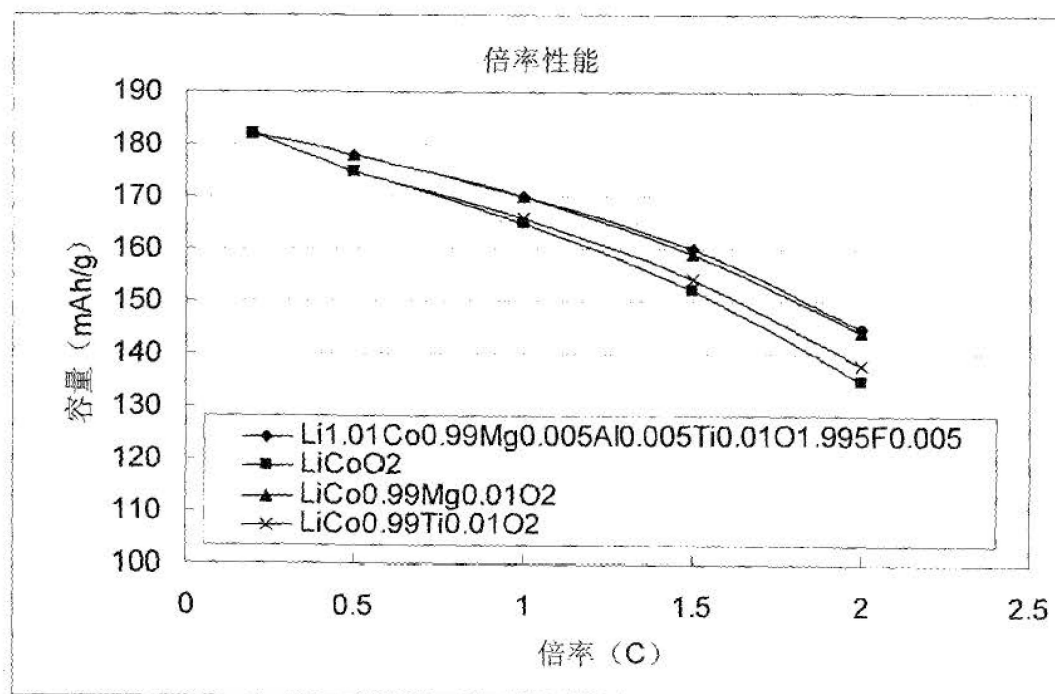


图 3

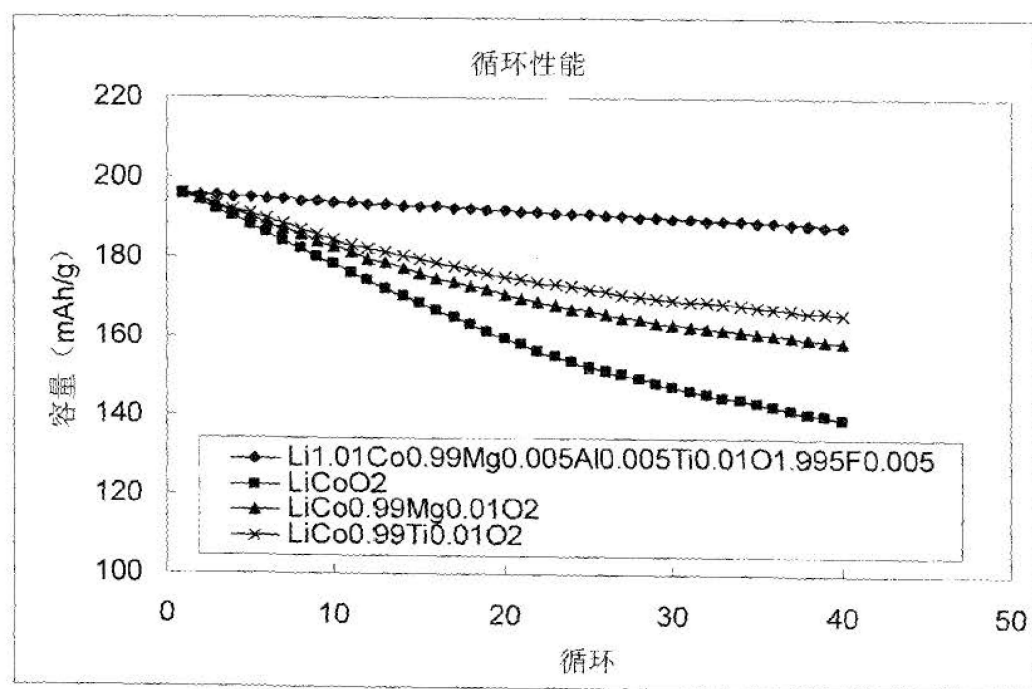


图 4

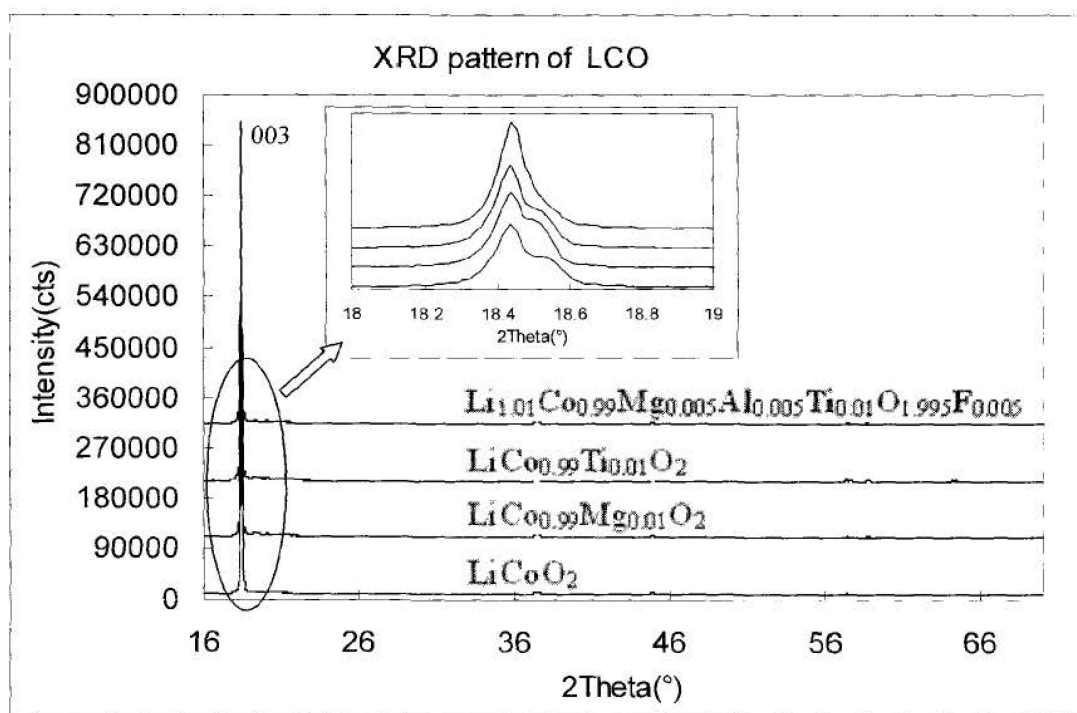


图 5

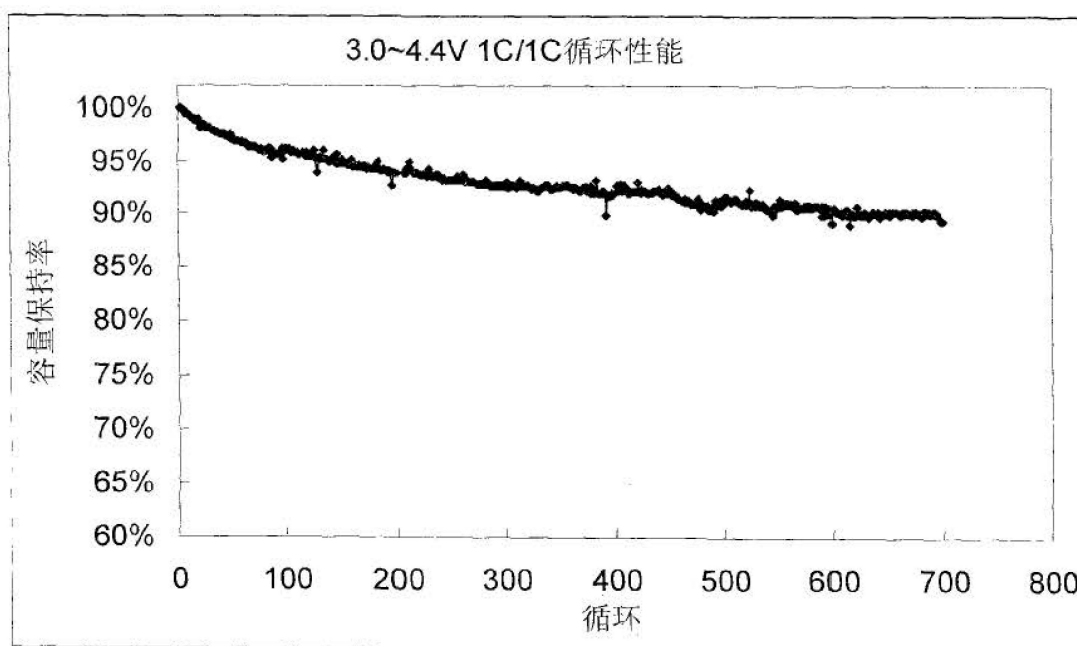


图 6