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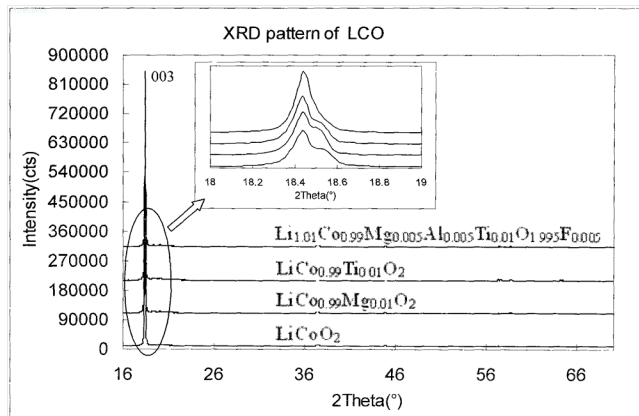
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Titles [MT] A kind of lithium ion battery and positive electrode active material thereof [ZH] 一种锂离子电池及其正极活性材料

Abstract

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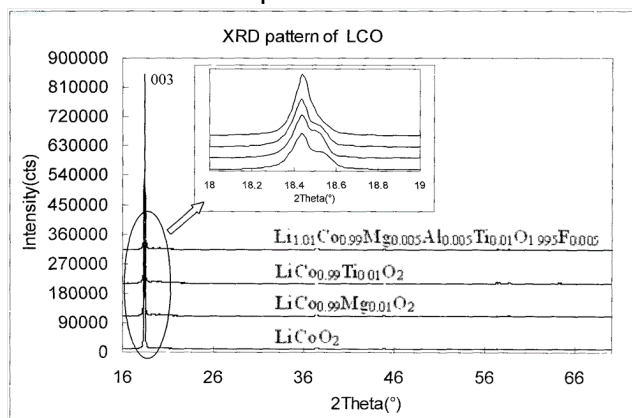
ZH

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， $0.95 \leq a \leq 1.05$ ， $0.001 \leq b \leq 0.02$ ， $0.001 \leq c \leq 0.02$ ， $0.003 \leq b+c \leq 0.03$ ， $0 \leq d \leq 0.01$ ，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。



MT

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



Claims

[ZH]	[MT]
1.一种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$\text{Li}_{1.01}\text{Co}_{0.99}\text{Mg}_{0.005}\text{Al}_{0.005}\text{Ti}_{0.01}\text{O}_{1.995}\text{F}_{0.005}$、$\text{LiCo}_{0.99}\text{Al}_{0.01}\text{Zr}_{0.01}\text{O}_{1.99}\text{F}_{0.01}$、$\text{LiCo}_{0.99}\text{Al}_{0.02}\text{Zr}_{0.01}\text{O}_{1.99}\text{F}_{0.01}$、$\text{LiCo}_{0.99}\text{Al}_{0.02}\text{Zr}_{0.02}\text{O}_{1.99}\text{F}_{0.01}$、$\text{LiCo}_{0.99}\text{Al}_{0.02}\text{Zr}_{0.02}\text{O}_{1.99}\text{F}_{0.02}$或$\text{LiCo}_{0.99}\text{B}_{0.01}\text{Hf}_{0.01}\text{O}_{1.995}\text{P}_{0.005}$，其中，元素Mg、Al及B均匀地分布在所述正极活性材料的体相，在Cu-Kα的X射线衍射谱图上未发现Mg、Al及B元素的氧化物的峰；元素Ti、Zr以及Hf至少有80%分布在距离表面0~100nm范围之内，在Cu-Kα的X射线衍射谱图上未发现Ti、Zr以及Hf元素的氧化物的峰；所述F或P元素分布在正极活性材料的表面并取代O的位置，在Cu-Kα的X射线衍射谱图上未发现F或P元素的化合物的峰；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%，所述正极活性材料的BET在0.1~0.4 m²/g之间，所述正极活性材料在充电至4.4V以上时，在Cu-Kα的X射线衍射谱图上的003峰保持完整，未分裂。	1. A positive electrode active material for a lithium ion battery, characterized in that: the positive electrode material is $\text{Li}_{1.01}\text{Co}_{0.99}\text{Mg}_{0.005}\text{Al}_{0.005}\text{Ti}_{0.01}\text{O}_{1.995}\text{F}_{0.005}$, $\text{LiCo}_{0.99}\text{Al}_{0.01}\text{Zr}_{0.01}\text{O}_{1.99}\text{F}_{0.01}$, $\text{LiCo}_{0.99}\text{Al}_{0.02}\text{Zr}_{0.01}\text{O}_{1.99}\text{F}_{0.01}$, $\text{LiCo}_{0.99}\text{Al}_{0.02}\text{Zr}_{0.02}\text{O}_{1.99}\text{F}_{0.01}$, $\text{LiCo}_{0.99}\text{Al}_{0.02}\text{Zr}_{0.02}\text{O}_{1.99}\text{F}_{0.02}$ or $\text{LiCo}_{0.99}\text{B}_{0.01}\text{Hf}_{0.01}\text{O}_{1.995}\text{P}_{0.005}$, Al and B are evenly distributed in the bulk phase of the positive electrode active material, no peaks of oxides of Mg, Al and B elements are found on the X-ray diffraction spectrum of Cu-Kα; elements Ti, Zr and Hf have at least 80% are distributed within the range of 0 to 100 nm from the surface, and no oxide peaks of Ti, Zr and Hf elements are found in the X-ray diffraction spectrum of Cu-Kα; the F or P elements are distributed in the positive electrode active material surface and replace the position of O, no peaks of compounds of F or P elements are found on the X-ray diffraction spectrum of Cu-Kα; the Li_2CO_3 content of the positive electrode active material is lower than 0.1%, and the LiOH content is lower than 0.1%, the BET of the positive electrode active material is between 0.1 and 0.4 m²/g, and when the positive electrode active material is charged above 4.4V, the 003 peak on the X-ray diffraction spectrum of Cu-Kα remains intact, unsplit.
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：所述的正极材料在充电至4.4V~4.6V时，Cu-Kα的X射线衍射谱图上的003峰保持完整，未分裂。	2. The positive electrode active material for lithium ion battery according to claim 1, characterized in that: when the positive electrode material is charged to 4.4V~4.6V, the 003 peak on the X-ray diffraction spectrum of Cu-Kα Remains intact and unsplit.
3.一种锂离子电池，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或2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。	3. a lithium ion battery, it comprises positive electrode sheet, negative electrode sheet, the separator that is spaced between positive and negative electrode sheet, and electrolytic solution, it is characterized in that: described positive electrode sheet is made of the lithium described in claim 1 or 2 The ion battery is made by uniformly mixing positive electrode active material with conductive carbon powder and binder.
4.根据权利要求3所述的一种锂离子电池，其特征在于：其应用的充电截止电压高于4.2V。	4. A kind of lithium ion battery according to claim 3, is characterized in that: the charging cut-off voltage of its application is higher than 4.2V.

Description

[ZH]	[MT]
技术领域	technical field
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	The invention relates to a positive electrode active material for a lithium ion battery and a lithium ion battery using the material
背景技术	Background technique
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。	With the miniaturization and thinning of mobile devices such as mobile phones, digital cameras, notebook computers and portable DVDs, the market demand for mobile energy is increasing. attention.
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，能量密度地， 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。	Lithium-ion batteries generally include: a positive electrode sheet, a negative electrode sheet, a separator spaced between the positive and negative electrode sheets, and an electrolyte, wherein the positive electrode sheet includes a positive electrode current collector and a positive active material distributed on the positive electrode current collector, and the negative electrode sheet It includes a negative electrode collector and a negative electrode active material distributed on the negative electrode collector. At present, the commonly used cathode active materials for lithium-ion batteries include layered structure LiCoO_2 and LiNiO_2 , spinel structure LiMn_2O_4 , and multi-element materials such as LiNiCoMnO_2 . The above-mentioned positive electrode active materials have their own disadvantages: the charging voltage of LiCoO_2 cannot exceed 4.2V, the structure of LiNiO_2 is unstable, the storage performance is poor, the high temperature performance of LiMn_2O_4 is not good, and the energy density is low, and the energy density of LiNiCoMnO_2 is low, can not meet the energy density and safety performance requirements of high-end products, therefore, there is an urgent need for a new way of increasing energy density.

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时间；另一种方式为提升正极材料的充电截止电压，如LiCoO₂，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LiCoO₂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。

For the improvement of energy density, from the perspective of materials, there are mainly two ways: one is the development of new high-capacity materials, such as the lithium-rich manganese-based materials developed by Argon Laboratories in the United States, within the charge and discharge range of 2-4.8V It can reach 300mAh/g, which is the material with the highest energy density at present, but it has natural defects, poor cycle performance and rate performance. There are many problems that cannot be solved in the actual application process, and there is still a long way to go before commercialization Time; Another way is to increase the charge cut-off voltage of the positive electrode material, such as LiCoO₂, which is raised from the current common voltage of 4.2V. For every 0.1V increase, the energy density increases by about 10%, which is a very effective energy However, with the increase of the charge cut-off voltage, the amount of delithiation of the material increases, and its structure becomes extremely unstable. A large number of literature reports that when LiCoO₂ is cycled above 4.2V, its hexagonal crystal phase will change to the unidirectional The oblique crystal phase undergoes an irreversible transformation, and the side reactions with the electrolyte increase, resulting in poor cycle performance.

为了解决提升充电截至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。	In order to solve a series of problems caused by increasing the charging cut-off voltage, the scientific and industrial circles have done a lot of work. U.S. Patent 7135251 discloses that LiCoO_2 coated with AlPO_4 has a very obvious improvement in cycle performance compared with uncoated LiCoO_2 at 4.3V. The surface of LiCoO_2 forms the phases of LiAlO_2 and Li_3PO_4, and at the same time, it reacts with the electrolyte to form AlF_3 phase attached to the surface of LiCoO_2 during the cycle, thereby improving its cycle performance. Although the coating can improve the cycle performance, the surface coating layer is an electronic insulator. In practical applications, the content of conductive carbon in the cathode is not enough to compensate for the increase in the polarization of the coating layer to the cathode during the charging and discharging process, which will inevitably lead to a voltage plateau. The reduction and the deterioration of the rate performance will reduce the energy density. US Patent 7018741 discloses a doped LiCoO_2, which distributes doping elements on the surface of the material and forms a solid solution with Co, thereby solving the problems of low voltage platform and poor rate performance in US Patent 7135251, but there is a high temperature storage The problem is that after the coating element is combined with LiCoO_2, the contact between Co and the electrolyte cannot be completely prevented, and there will inevitably be more side reactions released during the storage process. Therefore, the high-temperature storage performance will be slightly worse.
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。	These published documents or patents can more or less solve some problems under high voltage (>4.2V), but they only pay attention to the surface problem of LiCoO_2, and pay insufficient attention to the bulk phase change, so they can only be used in 4.3V, 4.4V and other voltages for application. It is well known that during the detachment process of LiCoO_2, the crystal lattice first expands and then decreases, and the turning point is when the voltage is 4.45-4.5V. A large number of literatures have reported that coating can inhibit the lattice expansion to a certain extent, so the coated LiCoO_2 It has good cycle performance below 4.45V. Once the voltage exceeds 4.45V, the cycle performance will drop sharply. This is because the coating cannot prevent the internal shrinkage and the internal structure is unstable. Therefore, an effective means is needed to stabilize the internal crystal. Lattice structure, improved cycle performance at >4.45V.

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LiCoO₂。	Based on the above reasons, this patent discloses a positive electrode material LiCoO₂ with good cycle performance and storage performance under high voltage.
发明内容	Contents of the invention
本发明的目的在于提供一种正极材料LiCoO₂，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。	The purpose of the present invention is to provide a positive electrode material LiCoO₂ to solve the high-temperature storage performance and cycle performance under high-voltage applications, especially when the charge cut-off voltage is higher than 4.4V.
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Li_aCo_{1-b-c}A_bB_cO_{2-d}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LiCoO₂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LiCoO₂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Co³⁺相同，可以完美的取代Co³⁺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LiCoO₂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LiCoO₂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LiCoO₂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≤a≤1.05，0.001≤b≤0.02，0.001≤c≤0.02，0.003≤b+c≤0.03，0<d≤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LiCoO₂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LiCoO₂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LiCoO₂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LiCoO₂表面O的位置，降低过度脱锂状态下的释氧量，提升安全性；所述正极活性材料在充电至4.4V以上时，在Cu-Kα的X射线衍射谱图上的003峰保持完整，不分裂，在LiCoO₂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有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CoO₂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CoO₂的峰，因此在003峰的分峰是因为LiCoO₂晶格中产生了CoO₂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	The invention discloses a positive electrode active material for a lithium ion battery, whose structural formula is expressed as Li_aCo_{1-b-c}A_bB_cO_{2-d}C_d, which has a layered structure, wherein A is at least Mg, Al, Ga, an element in B, because the addition of Mg element can increase the conductivity of LiCoO₂, thereby improving its rate performance, and at the same time can stabilize its bulk phase structure, Al element can form a perfect solid solution with LiCoO₂, while Al-O The bond energy of the bond is greater than the Co-O bond, which is helpful to improve the stability of its bulk structure, and the ion radius of Ga is the same as that of Co³⁺, which can perfectly replace the position of Co³⁺ and improve the stability of the bulk structure; BO The bond has the highest bond energy, and the B element can effectively inhibit the side reaction between LiCoO₂ and the electrolyte. B is at least one element in Ti, Zr, and Hf. These elements can stabilize LiCoO₂ and the electrolytic solution. The liquid contact interface can effectively reduce the internal resistance increase during the cycle, thereby improving the cycle performance. C is F or P, because F or P replaces the position of O on the surface of LiCoO₂, making it have a more stable surface under high voltage, thereby reducing the risk of oxygen release, 0.95≤a≤1.05, 0.001≤b≤0.02, 0.001≤c≤0.02, 0.003≤b+c≤0.03, 0<d≤0.01, the values of these elements have a certain range, exceeding this range will affect its structural stability and reduce cycle performance; element A is evenly distributed in The bulk phase of the positive electrode active material, because the element A needs to form a perfect solid solution with LiCoO₂, and A replaces the position of Co to improve the structural stability. If the dispersion is uneven, the charge distribution of the bulk phase will be uneven, which will easily cause local damage., affect the cycle performance; element B is mostly distributed on the surface of the positive electrode active material, and element B is to improve the contact interface between LiCoO₂ and the electrolyte, and inhibit the irreversible

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。	expansion of the crystal lattice during charge and discharge, so it needs to be concentrated on the surface of LiCoO_2 surface; element C is distributed on the surface of the positive electrode active material, element C replaces the position of O on the surface of LiCoO_2, reduces the amount of oxygen released in the state of excessive delithiation, and improves safety performance; the positive electrode active material is charged to above 4.4V, the 003 peak on the X-ray diffraction spectrum of Cu-Kα remains intact and does not split. During the charging process of LiCoO_2, starting at about 4.3V, the peaks of each crystal plane on the X-ray diffraction spectrum appear to a certain extent. The displacement and broadening of the 003 peak is the peak with the strongest peak intensity, and a shoulder peak will appear at the position of the 003 peak, representing the generation of CoO_2 phase, and then the shoulder peak gradually becomes higher, while the main peak gradually weakens. The two peaks are separated. This phenomenon is called peak splitting. When the delithiation is complete, the 003 peak at this time is completely displayed as the peak of CoO_2. This is caused by uneven delithiation and changes in the internal structure. Below 4.4V, this phase change is reversible after surface coating. When above 4.4V, due to the expansion of the lattice, it changes into contraction. If the bulk phase structure is not stable enough, the phase transition becomes irreversible, which causes the cycle to attenuate rapidly. Therefore, it is necessary to suppress or delay the occurrence of this phase transition in order to make the cycle stable at >4.4V. At the same time, the phase transition from LiCoO_2 first occurs on the surface, and then diffuses inside. The CoO_2 on the surface has a strong oxidation performance on the electrolyte, so it will make the high-temperature storage performance very poor. From these two points, the 003 peak must not. The emergence of splitting can fundamentally solve the cycle and storage performance under high voltage.
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-Kα 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。	In the positive electrode active material for lithium ion batteries, the A element is evenly distributed in the bulk phase of the positive electrode active material, and no peak of the oxide of the A element is found on the X-ray diffraction spectrum of Cu-Kα. If the A element is distributed. If it is not uniform, the enrichment of A element will inevitably appear in the bulk phase, and there must be a corresponding peak in the X-ray diffraction spectrum. At the same time, the enriched A will inevitably cause local structural instability and affect the overall performance.

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-Kα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。	In the positive electrode active material for lithium ion batteries, at least 80% of the B element is distributed within 0 to 100 nm from the surface. The surface effect is obvious, so it needs to be concentrated and distributed within the range of 100nm on the surface. At the same time, no peak of the oxide of B element is found in the X-ray diffraction spectrum of Cu-Kα, which means that it needs to be uniformly distributed. If local agglomeration will cause Li⁺ migration Inhomogeneity affects the rate performance and causes local structure to be destroyed.
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-Kα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。	In the positive electrode active material for the lithium ion battery, the C element is distributed on the surface of the positive electrode active material and replaces the position of O, and no peak of the compound of the C element is found on the X-ray diffraction spectrum of Cu-Kα, indicating that it needs to be evenly distributed to achieve the best results.
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%。	The positive electrode active material for the lithium ion battery has a Li₂CO₃ content of less than 0.1%, and a LiOH content of less than 0.1%. Because Li₂CO₃ will react with HF in the electrolyte to generate CO₂ and cause flatulence, the content of Li₂CO₃ needs to be less than 0.1%, and LiOH will react with HF to generate water, which will accelerate the decomposition of the electrolyte and cause flatulence, so The LiOH content needs to be below 0.1%.
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。	The BET of the positive electrode active material is between 0.1 and 0.4m²/g. If the BET is too large or too small, the performance of LiCoO₂ will be affected. If the BET is too small, the rate performance will be poor and cannot meet the normal application requirements. If the BET is too large When it is used, the reaction with the electrolyte is very violent, and the high-temperature storage performance is poor.
所述的正极材料在充电至4.4V~4.6V时，Cu-Kα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。	When the positive electrode material is charged to 4.4V-4.6V, the 003 peak on the X-ray diffraction spectrum of Cu-Kα has no peaks, and 4.4V-4.6V is the key potential for the LiCoO₂ lattice to expand and contract, can clearly characterize whether its structure is stable. After it is higher than 4.6V, because the delithiation degree is too high, the CoO₂ phase will appear on that side.

所述的正极材料为 $\text{Li}_{1.01}\text{Co}_{0.99}\text{Mg}_{0.005}\text{Al}_{0.005}\text{Ti}_{0.01}\text{O}_{1.995}\text{F}_{0.005}$，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。	The positive electrode material is $\text{Li}_{1.01}\text{Co}_{0.99}\text{Mg}_{0.005}\text{Al}_{0.005}\text{Ti}_{0.01}\text{O}_{1.995}\text{F}_{0.005}$, and this structural formula is the most comprehensive result of various electrochemical performances, storage performances and cycle performances after optimization.
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。	A kind of lithium ion battery, it comprises positive electrode sheet, negative electrode sheet, the separating film that is spaced between positive and negative electrode sheet, and electrolytic solution, it is characterized in that: described positive electrode sheet above-mentioned positive electrode active material and conductive carbon for lithium ion battery It is made by uniform mixing of powder and binder.
所述的一种锂离子电池，其应用的充电截止电压高于4.2V，	Described a kind of lithium ion battery, the charging cut-off voltage of its application is higher than 4.2V,
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。	The application of lithium-ion batteries at higher voltages can greatly increase the energy density, but it will cause attenuation of performance such as storage, cycle, and safety. The invented and disclosed materials not only have good cycle performance at high voltages, but also It solves the storage and safety problems that plague high-voltage applications, which cannot be taken care of by simple coating or doping modified materials. The invention also discloses the characteristics of this material, that is, the structure is stable under high voltage characteristics, and provide the preparation process and method of the material with these characteristics, these processes and methods are easy to achieve mass production, and have high economic benefits.
附图说明	Description of drawings
图1是使用Cu-Kα的X射线衍射仪测试LiCoO_2从4.2V-4.6V的XRD谱图。	Figure 1 is the XRD spectrum of LiCoO_2 tested from 4.2V-4.6V using Cu-Kα X-ray diffractometer.
图2是使用Cu-Kα的X射线衍射仪测试$\text{Li}_{1.01}\text{Co}_{0.99}\text{Mg}_{0.005}\text{Al}_{0.005}\text{Ti}_{0.01}\text{O}_{1.995}\text{F}_{0.005}$和$\text{LiCoO}_2$的XRD谱图对比。	Figure 2 is a comparison of the 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 tested by Cu-Kα X-ray diffractometer.
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。	Figure 3 shows 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 coin cell.
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。	Figure 4 shows the cycle 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 coin cell at 4.6V.

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。	Fig. 5 is the 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.
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。	Figure 6 shows the cycle performance of $\text{Li}_{1.01}\text{Co}_{0.99}\text{Mg}_{0.005}\text{Al}_{0.005}\text{Ti}_{0.01}\text{O}_{1.995}\text{F}_{0.005}$ at 4.4V of the full battery.
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。	The surface-coated positive electrode material of the lithium ion battery of the present invention and the preparation method thereof will be described in detail below with reference to the drawings and specific embodiments.
具体实施方式	Detailed ways
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。	The performance and preparation method of the lithium-ion battery positive electrode material of the present invention will be described in detail below in conjunction with various examples.
实施例1	Example 1
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%。	Weigh 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 powder and mix and grind them thoroughly in an agate mortar. The average particle size of the ground particles is less than $2\mu\text{m}$, and then Calcined at $^\circ\text{C}$ for 10h; adding nanoscale LiF and TiO_2 to the calcined mixture, and using ethanol as solvent, ball milled for 10h, then calcined at 800°C for 6h to obtain the positive electrode material $\text{Li}_{1.01}\text{Co}_{0.99}\text{Mg}_{0.005}\text{Al}_{0.005}\text{Ti}_{0.01}\text{O}_{1.995}\text{F}_{0.005}$, BET $0.22\text{m}^2/\text{g}$, Li_2CO_3 content 0.05%, LiOH content 0.01%.
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。	Figure 2 is the XRD spectrum of the positive electrode material tested by Cu-K α X-ray diffractometer. Compared with LiCoO_2 , all the characteristic peaks are consistent, and no MgO , Al_2O_3 , MgF_2 , AlF_3 , TiO_2 , The characteristic diffraction peaks of compounds such as TiF_4 indicate that various elements are uniformly dispersed and form a perfect solid solution.
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。	Figure 3 shows the rate performance of this material in a coin 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.

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。	Figure 4 shows the cycle performance of this material at 4.6V in a coin 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 cycle performance has a very obvious advantage.
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。	Figure 5 is the XRD spectrum of the positive electrode material tested by Cu-K α X-ray diffractometer at 4.5V. Compared with LiCoO_2 ， $\text{LiCo}_{0.99}\text{Mg}_{0.01}\text{O}_2$ ， $\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$ ，the 003 peak and There is no split peak, indicating that its structure is very stable at 4.5V.
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。	Table 1 shows the high-temperature storage expansion data of this material at 4.4V in a full battery. 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.
实施例2	Example 2
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。	According to the method of Example 1, $\text{LiCo}_{0.99}\text{Al}_{0.01}\text{Zr}_{0.01}\text{O}_{1.99}\text{F}_{0.01}$ was prepared, the BET was $0.42\text{m}^2/\text{g}$, the content of Li_2CO_3 was 0.15%, and the content of LiOH was 0.01%. Its capacity, rate performance, cycle performance and Storage performance is listed in Table 2.
实施例3	Example 3
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。	According to the method of Example 1, $\text{LiCo}_{0.99}\text{Al}_{0.02}\text{Zr}_{0.01}\text{O}_{1.99}\text{F}_{0.01}$ was prepared, the BET was $0.25\text{m}^2/\text{g}$, the content of Li_2CO_3 was 0.05%, and the content of LiOH was 0.1%. Its capacity, rate performance, cycle performance and Storage performance is listed in Table 2.
实施例4	Example 4
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。	According to the method of Example 1, $\text{LiCoLi}_{0.99}\text{Al}_{0.02}\text{Zr}_{0.02}\text{O}_{1.99}\text{F}_{0.01}$ was prepared, the BET was $0.39\text{m}^2/\text{g}$, the content of Li_2CO_3 was 0.05%, and the content of LiOH was 0.01%. Its capacity, rate performance, cycle performance and Storage performance is listed in Table 2.
实施例5	Example 5

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。	According to the method of Example 1, $\text{LiCo}_{0.99}\text{Al}_{0.02}\text{Zr}_{0.02}\text{O}_{1.99}\text{F}_{0.02}$ was prepared, the BET was $0.12\text{m}^2/\text{g}$, the content of Li_2CO_3 was 0.1%, and the content of LiOH was 0.1%. Its capacity, rate performance, cycle performance and Storage performance is listed in Table 2.
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。	The data in Table 2 shows that the increase of A, B, and C elements will significantly reduce the capacity and rate performance, but the high-temperature storage performance has not been significantly improved.
实施例6	Example 6
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。	According to the method of Example 1, $\text{LiCo}_{0.99}\text{B}_{0.01}\text{Hf}_{0.01}\text{O}_{1.995}\text{P}_{0.005}$ was prepared, the BET was $0.32\text{m}^2/\text{g}$, the content of Li_2CO_3 was 0.1%, and the content of LiOH was 0.05%. Its capacity, rate performance, cycle performance and Storage performance is listed in Table 2.
实施例7	Example 7
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。	The positive electrode active material in Example 1 is uniformly mixed with conductive carbon powder and binder to make a positive electrode sheet, and the positive electrode sheet, separator and negative electrode are wound into an electric core, and then the electric core is packaged and injected. Lithium-ion batteries are made by liquid, chemical formation, capacity testing, etc. Figure 6 shows the cycle performance of the full battery at 3.0-4.4V.
对比实施例1	Comparative Example 1
按照实施例1的方法制备了 LiCoO_2 与实施例1进行比较。	LiCoO_2 was prepared according to the method of Example 1 for comparison with Example 1.
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。	Figure 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 various peaks are shifting, splitting, until disappearing, and the change of peak 003 is the most intuitive.
对比实施例2	Comparative Example 2
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。	$\text{LiCo}_{0.99}\text{Mg}_{0.01}\text{O}_2$ was prepared according to the method of Example 1 for comparison with Example 1.

对比实施例3	Comparative Example 3																																																																																																								
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Legal events

Code	Title	Date	Country	Impact	Details
PB01	PUBLICATION	2012-07-25	CN		
C06	PUBLICATION	2012-07-25	CN	+	
SE01	ENTRY INTO FORCE OF REQUEST FOR SUBSTANTIVE EXAMINATION	2012-09-26	CN		
C10	ENTRY INTO SUBSTANTIVE EXAMINATION	2012-09-26	CN		
GR01	PATENT GRANT	2014-11-12	CN	+	
C14	GRANT OF PATENT OR UTILITY MODEL	2014-11-12	CN	+	

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