First-Principles Intelligent Modeling and Research of High-Voltage Lithium-Free LixCoO2

Lili Wang *
Shanghai University of Engineering Science
School of Mathematics Physics and Statistics
Shanghai, 201620, China

Ye Liu
Shanghai University of Engineering Science
School of Mathematics Physics and Statistics
Shanghai, 201620, China

Abstract:In this paper, intelligent modeling and analysis of the first principles of high-voltage delithiation of titanium are carried out. The bulk structure of lithium-ion battery cathode materials is simulated and calculated. In order to obtain more accurate lattice constants, we first use the program software package to optimize its structure. Using first principles to delithiate the lithium-ion battery cathode materials the product LixCoO2 and the volume geometry and electronic structure of LixCoO2 have been studied and analyzed in detail. The first principles method based on density functional theory was used to intelligently model the delithiated oxygen vacancies, and the results showed that the accuracy was 96.2%.

Keywords: High-Voltage System, Lithium-Free Model, First-Principles Intelligent, Smart Material

1. INTRODUCTION

When LiCoO2 is used as the cathode material of lithium-ion batteries, the charge and discharge curve have a main charging platform at 3193V, and a small platform at 4107V and 4119V. The appearance of the voltage platform is related to the change in the crystal structure of LixCoO2. In the coexistence zone, the platform turning point is the phase transition point. According to the literature, due to the extraction of Li, holes are generated on the t2 band, and the conductivity increases rapidly, and the transition from semiconductor behavior to metal conductor behavior occurs. This transition is a two-phase region. The driving force for existence. This is consistent with the experimental results of Imanishi et al. In 1992, Reimers first proposed that the LixCoO2 high-lithium region ($0175<x<0193$) is the coexistence of the lithium-poor hexagonal phase and the lithium-rich hexagonal phase, and the hexagonal phase at x=015 The coexistence of monoclinic and monoclinic phases. Yang et al. believed that monoclinic and hexagonal phases coexist in the low-lithium region, but Amatacci believes that there is only monoclinic phase in this region. In 1998, Ven used first-principles calculations to show that in high lithium There is no two-phase region. There is still much controversy about the change of the crystal structure of LixCoO2 with the value of x [1-8].

The synthesis temperature of LiCoO2, the cathode material of lithium ion batteries, is often selected based on the characteristics of the X-ray diffraction pattern of the product, which conforms to the stoichiometry. The lithium atomic layer and the cobalt atomic layer are alternately distributed on both sides of the cubic densely packed oxygen atomic layer. The crystal structure of LiCoO2 has the best charge and discharge performance. However, when the reaction temperature changes in a large range ($750℃\sim950℃$), the X-ray diffraction pattern and charge-discharge performance change little, so the selection has a large randomness. The change of LiCoO2 crystal structure in such a wide temperature range is still inconclusive. Since the performance is closely related to the crystal structure, clarifying the characteristics of the crystal structure of LiCoO2 in this temperature range can provide a theoretical basis for a reasonable choice of synthesis temperature. In addition, clarifying the change of LiCoO2 crystal structure during

charging can help to take measures to effectively improve the overcharge resistance of LiCoO2 [8-14].

The electron diffraction results of LixCoO2 did not support the existence of this ordering phenomenon. Recently, Yang et al. used X-ray diffraction and electron diffraction to study the distortion of the monoclinic phase of the crystal lattice when the HT-LiCoO2 was removed from Li to Li015CoO2, and lithium the phenomenon of ordering of ions and vacancies. They believe that the splitting of the observed diffraction peaks is mainly due to the transformation to the monoclinic crystal system caused by the shear deformation of the rhombohedral (i.e., trigonal) oxygen lattice. The appearance of additional diffraction spots on the electron diffraction spectrum of monoclinic Li015CoO2 proves the idea of ordered arrangement of lithium/vacancies in the layer proposed by Reimers and Dahn. Yang et al. assumed that these reflect the spinel structure. The electron diffraction pattern can be fully explained by the special microstructure formed in Li015CoO2 and the ordering of lithium, but they still believe that there is not enough experimental evidence to show that LixCoO2 changes from a layered to a spinel structure when Li is removed. Choi and Manthiran found Heating Li015CoO2 above 200e still maintains the layered structure, which proves the conclusion of Yang et al [16-19].

According to the atomic percentage of Li and Co of 1:1, 1.8g of Li2CO3 and 3.9g of Co3O4 were fully ball-milled and mixed, then packed in a porcelain boat, and synthesized by solid-phase reaction in a horizontal tubular resistance furnace. Firstly, pre-sintered at 650℃ for 8h, and then sintered at 750℃, 800℃, 850℃ and 900℃ for 8h to obtain the synthesized product LiCoO2. After cooling in the furnace, the product aggregates were rolled and dispersed to obtain samples for analysis. In order to solve the problems of lithium secondary batteries, lithium ion batteries have emerged. The principle of lithium battery and lithium ion battery is very similar, and the cathode material and electrolyte used are almost the same. However, the negative electrode materials they choose are quite different. The negative electrode material selected for lithium-ion batteries is carbon. Due to the layered properties of carbon, the reversible behavior can be guaranteed. Lithium batteries use metal as the negative electrode material. At the end of the decade, French scientists proposed two solutions to solve the problems in lithium

secondary batteries: all solid-state lithium metal secondary batteries, which are prepared using polymer solid electrolytes. The metal lithium electrode material can be replaced by materials containing lithium ions [21-24].

2. THE PROPOSED METHODOLOGY

2.1 The High-voltage LixCoO2 LixCoO2

In recent years, a large number of studies have stabilized the layered structure of LiCoO2 by doping LiCoO2 with transition metal elements such as Ni, Mn, and V, so that more lithium ions can be released during the charging process without destroying the structure, thereby Improve the anti-overcharge performance of LiCoO2. In addition, the multiple phase transitions of the lithium ion insertion and extraction process have an important impact on the electrode performance. The structural changes in the phase transition process reduce the long-term cycle stability of the electrode, resulting in capacity decay and shortened life, and charging significant irreversible capacity loss will occur in the later stage. The doping modification suppresses the phase change caused by the insertion and extraction of lithium ions, thereby changing the electrode potential of the bulk material. The root cause is the change of the electronic energy level. Cender et al. used ab initio and first principle calculations and other theories. The study believes that the charge and discharge voltage is determined by the degree of oxygen ions involved in the exchange of electrons. This article studies the influence of the lithium ion insertion and extraction process on the crystal structure of LixCoO2, which provides a basis for the design of new electrode materials. The electrode is the core of the lithium ion battery, and the positive electrode as one of the most important parts of the electrode, the material directly affects the performance of the battery. Therefore, for more than two decades, cathode materials have been the focus of research on lithium-ion batteries. For lithium-ion batteries, the positive electrode material should meet the following requirements to have good electrochemical activity, that is, the reversibility of the charge and discharge reaction is good, and its structure can remain stable when the electrode materials are deintercalated. This can make the battery cycle performance better and longer service life. With a higher electrode potential, that is, a higher discharge platform, the battery can have a higher specific energy and energy density, which is conducive to the development of the battery in the direction of miniaturization and light weight.

2.2 The First Principle Of High Voltage Delithiation State LixCoO2

First-principles calculations are ab initio calculation methods that can derive the properties of the system without any empirical parameters. The development of first-principles calculation methods originated from the discovery of electrons in the century. The interaction problem is one of the hotspots of physics research, and some theories and calculation methods have been produced to deal with these problems. First-principles calculations were developed during this period.

The first principles are based on quantum mechanics and some basic laws of physics. According to the atomic composition of the studied material, self-consistent calculation methods are used to predict some properties of the structure, such as thermodynamic properties, optical properties, electronic structure, geometric structure and Transport performance, etc. The basic idea is to consider the solid as a multi-particle system composed of electrons and atomic nuclei, and then to maximize the "non-empirical"

processing and calculation of the problem based on the principles of quantum mechanics. Generally, first-principles calculations do not include any empirical parameters, but only involve the electronic structure of each component element and basic physical constants. Some physical properties of the material can be predicted. Compared with the experimental value, the error of the unit cell size calculated by the first principles is only a few percentage points. Other properties are also in good agreement with the experimental results, reflecting the maturity and reliability of the theory. Chemical extraction of alkali metal ions from alkali metal oxides There have been literature studies that chemically extract lithium ions from LiCoO2 instead of charging lithium-ion batteries to obtain LixCoO2 in a delithiated state, which greatly simplifies the preparation of X-ray diffraction and electron diffraction samples.

Because obtaining LixCoO2 in the delithiation state from the latter requires disassembling the charged battery, taking out the positive electrode foil, obtaining the positive electrode material (a mixture of LixCoO2, acetylene black, graphite and binder) from the foil, and separating the positive electrode material to obtain the operation of the active material LixCoO2 is extremely cumbersome. More importantly, the Li content of the positive electrode active material particles obtained by electrochemical delithiation is often very different from the expected. This is due to the different sizes of LiCoO2 particles before charging, and the amount of Li ions removed. Different, the TEM sample prepared in this way cannot select particles with a predetermined Li content on the microgrid when doing electron diffraction. However, repeated experiments have shown that the amount of lithium ions extracted with Na2S2O8 chemically is limited, and the Li content in LiCoO2 cannot be reduced to Less than half.

2.3 The First-Principles Intelligent Modeling

The basic idea of using first principles to intelligently model the electronic ground state of a multi-particle system (material) is as follows: the various physical properties of the material are determined by the multi-particle system composed of atomic nuclei and electrons. In principle, as long as the equations of multi-particle systems are written and intelligently modeled, various physical and chemical properties of solids can be calculated. Therefore, to understand the properties of materials, we must first start from the Schrödinger equation of the many-body system: Since the mass of electrons is much smaller than the mass of the nucleus (about twice), when the electron is moving at high speed, the slow motion of the nucleus can only follow its the distribution of electrons changes.

When considering electrons, one can ignore the nucleus and just treat it as a fixed one. The interaction between the movement of electrons and the movement of the nucleus in Hamilton is regarded as a kind of perturbation, which is the so-called approximation or adiabatic approximation. Due to the approximate treatment, the goal of separating the movement of the nucleus and the movement of the electrons in the multi-particle system is achieved. When considering the movement of electrons, the nucleus is approximately regarded as fixed, and the electrons move in the potential field formed by the nucleus. If the relative position of the nucleus changes, the movement state of the electrons will also change accordingly. Based on this, it is necessary for us to attribute the repulsive energy between nuclei to the energy of the electronic system. Since the repulsive potential between nuclei is only related to the position of the nucleus, as long as

the position of the nucleus is determined, then it only affects the total energy of the electronic system, not the electronic wave function, so we are intelligently modeling electronic energy and electronic wave function At this time, the repulsive energy between the nuclei is not counted first, and finally the repulsive energy between the nuclei is directly added to the electron energy. Therefore, the kinetic energy of the nucleus is zero. After adiabatic approximation, the multi-particle problem is transformed into a multi-electron problem, but the library-enterprise interaction term between electrons and electrons still exists, so the wave function of the system cannot be written as a single-electron wave function product. In the form of, that is, it is impossible to separate the coordinates of one electron from the coordinates of other electrons. Therefore, it is still difficult to model intelligently.

3. CONCLUSIONS

This article mainly focuses on the theoretical research on the physical problems of high-voltage delithiation LiCoO2 when the layered cathode material of lithium-ion batteries is charged. By adopting the first-principles pseudopotential method based on density functional theory to systematically study and analyze the bulk geometry and electronic structure of cathode materials, and theoretically analyze and explain that oxide coating can improve its structure the essence of stability and cycling performance. It provides good reference data for the experimental and theoretical research on improving the cathode material in the future.

4. REFERENCES

[1] Zhao Dongqin. Preparation and performance of lithium primary battery cathode materials [D]. Huazhong University of Science and Technology, 2017.

[2] Lin Mei, Hu Jiaqi, Zhu Zizhong. Electronic structure of high voltage cathode material $Li_{(1-x)}CoO_2(x=0.75)$[J]. Journal of Xiamen University (Natural Science Edition), 2016, 55(03): 73 -77.

[3] Lin Mei. Electronic structure of high voltage cathode material Li1-xCoO2(x=0.75)[D]. Xiamen University, 2016.

[4] Li Lei, Wu Xiao, Mo Junlin, et al. Study on the crystal structure and thermal stability of the charged $Li_{(1-x)}CoO_2$ cathode material[J]. Ship Electric Technology, 2020(6).

[5] Meng Yu. Synthesis and modification of $Li_4Ti_5O_{(12)}$ as anode material for high-performance lithium-ion batteries [D]. Hefei University of Technology, 2016.

[6] Zhang Peng, Zhang Peng. Application of transition metal oxides in non-aqueous lithium-oxygen batteries and research on discharge process[J]. 2016.

[7] Kong Lingming. A first-principles study of modified TiO_2-B as a negative electrode material for rechargeable lithium-ion batteries. Taiyuan University of Technology, 2016.

[8] Xiang Fenghua. First-principles study on the interfacial properties of graphene-enhanced magnesium matrix composites[D]. North University of China, 2016.

[9] Sun Jiayue, Wang Yueting, Ma Liyong, An Zhaojie, Yang Yanan, Wang Jiuqiang, Li Xin. AlP/Mg_2Si heterogeneous nucleation interface modeling method based on first principles[J]. Journal of Hebei Institute of Civil Engineering and Architecture, 2020, v.38;No.136(02):111-115.

[10] Yu Lan, Song Shijin, Shen Yan, et al. A thermally induced voltage material and its application: CN109103324A[P]. 2018.

[11] Zhang Chuanyu, Wang Xuben, Zhao Xiaofeng, et al. Based on first principles to study the physical properties of hydrated iron olivine under high pressure[J]. 2017.

[12] Xu Xi, Jiang Hong. First-principles study of GaN-ZnO solid solution [C]// Abstracts of the 30th Annual Conference of the Chinese Chemical Society-Eighteenth Session: Development and Application of Electronic Structure Theory Methods. 2016.

[13] Wu Yan. Study on the modification of graphite lithium ion battery anode materials[D]. Shandong University, 2018.

[14] Mo Junlin, Wu Jun, Zhu Gang, et al. Research on LiCoO2 delithiation materials as cathode materials for lithium primary batteries[J]. Ship Electric Technology, 2017, 37(004): 34-37.

[15] Meng Yu. Synthesis and modification of $Li_4Ti_5O_{(12)}$ as anode material for high-performance lithium-ion batteries [D]. Hefei University of Technology, 2016.

[16] Meng Yu. Synthesis and modification of $Li_4Ti_5O_{(12)}$ as anode material for high-performance lithium-ion batteries [D]. Hefei University of Technology, 2015.

[17] Wei Lijing. First-principles study on the band gap of ferroelectric photovoltaic materials[D]. Hebei University, 2020.

[18] Li Yao. Research on Amorphous Silicon Modeling and Simulation Based on First Principles [D]. University of Electronic Science and Technology of China, 2016.

[19] Ran Qiyi, Zhang Yun, Zhao Baiqiang. A first-principles study of hydrogen ions and their effects in lithium niobate crystals[J]. Journal of Southwest University (Natural Science Edition), 2015(37): 103.

[20] Liao Li. Process exploration and performance research of 18650 cylindrical $LiNi_{(0.5)}Co_{(0.2)}Mn_{(0.3)}O_2$/$Li_4Ti_2O_{(12)}$ lithium-ion power battery[D]. Chengdu University of Technology, 2019.

[21] Wu Wei. Research on electrical transport mechanism of HfOx memristor based on first principles[D]. Huazhong University of Science and Technology, 2019.

[22] Wu Qingjie. Microstructure and first-principles study of the interface of SiC/Al matrix composites[D]. Zhengzhou University, 2019.

[23] Li Yibo. First-principles study on magnetic induction and regulation of black phosphorous nanoribbons[D]. Zhengzhou University, 2019.

[24] Zhang Qiuyue. First-principles research on donor materials in organic solar cells[D]. Zhengzhou University, 2018.