

The First Principle Study of Li_xCoO_2 at High Voltage

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Abstract: This is an important research direction to further increase the capacity of LiCoO_2 , a mature electrode material for lithium-ion batteries. By using the first principle method based on the density function theory, the properties of electronic structure and crystal structure of Li_xCoO_2 ($x = 0.75$) are studied. Structure provides the foundation. The calculation shows that the CO in LiCoO_2 material exists in the form of common valence + trivalence. When a small amount of lithium is removed, a small part of CO^{3+} will change from +3 to +4 because of the further loss of electrons. The valence of CO_3^{2-} re increases with the depth of lithium removal ($x = 0.75$), but some of the $o-2p$ orbitals lose electrons, resulting in two oxygen ions O and O_2 , O_2 ions accounting for 1/3, O_2 ions accounting for 2/3. There are obvious differences in the binding length between CO and different oxygen ions. Compared with CO_3^{2-} , CO_4^{2-} and oxygen ions will accumulate a lot of electrons, and their interaction force is stronger than that of CO_3^{2-} and oxygen ions.

1. Introduction

Lithium ion battery has the advantages of high energy consumption, small self discharge and long life. They are the most practical power batteries for electric vehicles. Electric vehicles will bring great challenges to the energy density of lithium-ion batteries. The initial appearance of LiCoO_2 cathode material for lithium-ion batteries can be traced back to the mid-1950s [1]. It is also the first generation of cathode materials widely used in commercial lithium-ion batteries. It is used in the lithium-ion battery industry of electronic equipment, and electric vehicles are widely used [2], which has been widely studied in the past 30 years. When all Li^+ in LiCoO_2 is completely removed from the material, its theoretical capacity reaches 274 MAH / g. When the voltage is 3.0 ~ 4.3v (for Li / Li^+ , the actual capacity can reach 160mah / g. In the process of charge and discharge, about 0.55 Li^+ are released from each LiCoO_2 unit of formula . During charging, when each molecular formula LiCoO_2 unit has 0.65 to 0.70 Li^+ , it corresponds to a voltage of about 4.5 v. This is one of the important research directions in the field of LiCoO_2 cathode materials, which is to further improve the battery energy. One of the important methods of density.

2. Correlation Theory

In the past, many different research methods have been used to study the structural phase transition of LiCoO_2 in silicones. The structure and theory of $\text{Li}_{1-x}\text{CoO}_2$ desaturation system in the range of $0 < x < 1.0$ were studied. It was found that when $0 < x < 0.05$, Li_xCoO_2 was hexagonal crystal structure (H1 phase), $0.05 < x < 0.25$ [3]. The two-phase coexistence region of two hexagonal crystal structures (H1 and H2 have the same crystal symmetry, but have different lattice constant properties, but the a value of two phases is almost the same, while the c axis of H2 phase is slightly larger than H1 phase), $0.25 < x < 0.50$. H2 and X have irregular phase transition near 0.50. $0.50 < x < 0.75$ is single-phase inversion domain. With the increase of X, the value of C continued to increase. At this time, it was basically maintained in the H2 phase. At $0.75 < x < 1.0$,

the rate of lithium almost complete deallocation ($x > 0.7$), and the M2 monoclinic phase of LiCoO_2 reappeared. In previous literature, van zerven et al. It is suggested that the monoclinic phase is actually a mixture of O1 and O3. In order to understand the physical and electrochemical structure of LiCoO_2 in the process of desalination, it is necessary to understand the phase transition of Li_xCoO_2 in the process of lithium decomposition[4]. At present, the reasonable information about the crystal structure and electronic structure of Li_xCoO_2 is very difficult to reach $x = 0.75$. In addition, the deep desalting phase is very unstable, which increases the difficulty of the experiment. In this paper, the first principle theory method of calculating the geometry of cathode materials for Li_xCoO_2 high-voltage lithium-ion batteries for deep lithium removal is used to carry out the electronic energy band based on the atomic structure. A more comprehensive calculation of the structure, electronic state density and charge density characteristics provides a theoretical basis for further understanding of the electronic structure of this high voltage material.

3. Calculation Method the First Principle Method Based on Density Universal Function Method is Adopted in This Paper

VASP representation (PAW) and exchange correlation potential were used in the package. As we know, it is more accurate to use GGA to calculate the structural characteristics of the doped composite, but it greatly underestimates the band gap width and voltage of the material[5]. Therefore, to improve the defect caused by GGA calculation of GGA + U machining method, it is usually necessary to calculate the band gap width and voltage of the inserted composite more accurately. Considering the better U value, the Herbert - ueff value of cobalt is set to 5ev, indicating that the calculation is suitable for Li_xCoO_2 series. In addition, the cutoff of plane wave energy is 500 ev. The integration of Brillouin region uses the special k-point sampling method of monkhorst Pak. $5 \times 5 \times 2K$ grid points are used in the calculation of electronic structure[6]. Before calculating the electronic structure of the layered material Li, the lattice constant and the total atomic position have been fully relieved until the force on each atom converges to 0.1ev/nm. The magnetic properties of CO atoms have an important influence on the electronic structure properties of materials, so all calculations are carried out in the framework of the pan function theory of spin polarization density.

Table 1 Structural parameters of $\text{Li}_{1-x}\text{CoO}_2$

System	Lattice constant		Volume	Interlayer spacing	
	a	c		d1	d2
LiCoO_2	0.5862	1.4520	0.4321	0.2640	0.2199
$\text{Li}_{0.25}\text{CoO}_2$	0.5778	1.1054	0.4296	0.2952	0.2004
$\text{Li}_{0.68}\text{CoO}_2$	0.5632	1.4224	0.3861	0.3094	0.2816
$\text{Li}_{0.48}\text{CoO}_2$	0.5622	1.4389	0.3893	0.3178	0.2811
$\text{Li}_{0.35}\text{CoO}_2$	0.5614	1.4389	0.3932	0.3255	0.2809

4. Results

The specific method to determine the position of Li^+ is as follows: the embedded atom potential (EAM) which is used to fit Li_xCoO_2 system. Random numbers are used to generate multiple random structures (the position of each atom is described by three random numbers); EAM is used to calculate the energy of each random structure. Because EAM calculates energy very quickly, we can filter multiple structures generated by random numbers (for example, 10 million random numbers here). Select the appropriate number of low energy structures to continue to ease the atomic position of each structure under the EAM framework[7]. On the basis of structure relaxation, some structures are selected for the first principle calculation of the density universal function theory (including atom relaxation). It is considered that the structure with the lowest energy is the final crystal structure. Table 1 shows that the unit volume calculated by Li_xCoO_2 and Li is slightly larger than the experimental value, and the atomic layer spacing is slightly smaller than the

experimental value. The theoretical calculation is in good agreement with the experimental data. When Li⁺ is removed from the cathode material, the lattice constant *a* does not change much, but *c* increases significantly. This is because the Coulomb interaction between the negative Li⁺ layer and the negative CoO₂ layer is weak. It is found that the interval of O - O layer in desalting is continuous[8]. The distance between the O layers on both sides of the Li⁺ layer and the O-O layers on both sides of the Co layer, Li_xCoO₂ changes from 0.219 nm to 9 nm, and Li_xCoO₂ changes from 0.200 to 4 nm. The Li⁺ optimized structure of Li_xCoO₂ material improved by the above method. Li_xCoO₂, which is full of lithium, has 12 Li⁺ positions[9]. There are only three positions, 25 occupied by Li⁺. CoO₂ is evenly distributed in each layer of the supercell, and distributed through the rebound between Li⁺. This effect is a Li⁺ staggered arrangement of different layers.

Table 2 List of relevant information

	Quality development training	Non intelligent police course
Student role	Active participant	Passive recipient
Learning subject	Students and teachers are the main subjects, but learn Mainly	Student
Learning evaluation	Process and results combined, self-evaluation, mutual Evaluation and teacher evaluation	Based on the results evaluation, using a single Evaluation, teacher evaluation
Learning process	Experience - Review (Process) - Share(Experience) - Communication (Feeling) - Integration (Essence) - Promotion - Application...	Teacher explanation - Student exercises - Focus on learning again - Correct wrong actions - Practice again - Teacher summary
learning result	In addition to completing the functions of traditional physical education, it will also affect thoughts, change behaviors, cultivate good psychological quality and social adaptability, apply what they have learned, and improve their quality and ability.	Enhance physical fitness, cultivate the will of quality and exercise the body, but sometimes learn to use disjoint, high scores and low energy

5. Conclusion

By using the first principle method based on the density function theory, the crystal structure and electronic structure characteristics of Li_{1-x}CoO₂ (*x* = 0.75) in the state of deep detachment are calculated. The results show that the Li⁺ high separation (*x* = 0.75) system still has a laminated structure. In non detached LiCoO₂ materials, CO exists in the form of usual valence + 3. When a small amount of lithium is removed, the corresponding small part of CO₃⁺ will further lose electrons and change from + 3 to + 4. The valence of CO₃⁺ re increases with the depth of lithium removal (*x* = 0.75), but some of the o-2p orbitals lose electrons, resulting in two oxygen ions o 1 and O 2, O 2 ions accounting for 1 / 3, O 2 ions accounting for 2 / 3. Compared with O stores more electrons, and the interaction between CO₃⁺ and oxygen ion is stronger. This interaction is reflected in the obvious difference of the coupling length between CO and different valence states. In order to further improve the energy density of LiCoO₂, it is important to increase the voltage of cathode material. This must be achieved by removing lithium ions from LiCoO₂ materials. At present, the cycle performance of lithium battery is not good[10]. If more than 50% lithium is

released, its structure will become unstable and phase transition will occur. The electronic and crystal structure information of $\text{Li}_{1-x}\text{CoO}_2$ ($x = 0.75$) obtained in this paper is helpful to understand the physical and electrochemical properties of $\text{Li}_{1-x}\text{CoO}_2$ cathode materials. LiCoO_2 with high energy density provides theoretical help for lithium batteries, which have positive materials.

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