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锂镍钴氧化物系列正极材料的结构性能和  
第一性原理计算研究

**Structure, Performance and First-principle Calculation of  
Li-Ni-Co-O Compounds as Cathode Materials for Lithium  
Ion Batteries**

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**Structure, Performance and First-principle Calculation of  
Li-Ni-Co-O Compounds as Cathode Materials for Lithium  
Ion Batteries**



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中文摘要.....	I
英文摘要.....	II
<b>第一章 锂离子电池正极材料研究进展 .....</b>	<b>1</b>
<b>1.1 锂离子电池的工作原理及组成.....</b>	<b>1</b>
1.1.1 工作原理 .....	1
1.1.2 组成部分 .....	2
<b>1.2 正极材料的研究进展.....</b>	<b>4</b>
1.2.1 LiCoO <sub>2</sub> .....	4
1.2.2 LiNiO <sub>2</sub> .....	6
1.2.3 锂镍钴氧化物 (LiNi <sub>y</sub> Co <sub>1-y</sub> O <sub>2</sub> ) .....	8
<b>1.3 目前存在的问题.....</b>	<b>41</b>
<b>1.4 本论文工作的研究内容与研究意义.....</b>	<b>42</b>
1.4.1 研究内容 .....	42
1.4.2 研究意义 .....	42
<b>1.5 本论文工作的创新点.....</b>	<b>43</b>
<b>第二章 实验材料、研究方法和设备 .....</b>	<b>44</b>
<b>2.1 正极材料的合成.....</b>	<b>44</b>
<b>2.2 正极材料的表征.....</b>	<b>45</b>
2.2.1 热性能测定 .....	45
2.2.2 结构的测定 .....	45
2.2.3 表面及化学分析 .....	47

2.2.4	电导率测定.....	47
2.2.5	电化学性能测试.....	48
2.3	正极材料的计算.....	49
<b>第三章</b>	<b>实验结果.....</b>	<b>51</b>
3.1	热分析结果.....	51
3.2	结构分析.....	53
3.2.1	非原位 XRD 谱图分析.....	53
3.2.2	原位 XRD 谱图分析.....	62
3.3	表面和化学分析.....	69
3.3.1	非现场 FTIR.....	69
3.3.2	现场 Raman.....	73
3.4	形貌特性.....	76
3.4.1	LiNi <sub>3/4</sub> Co <sub>1/4</sub> O <sub>2</sub> 电极材料的变温表面形貌.....	76
3.4.2	不同掺镍量正极材料的表面形貌.....	77
3.5	导电特性.....	78
3.6	电化学性能.....	79
3.6.1	首次充放电性能.....	79
3.6.2	循环性能.....	82
3.7	本章小结.....	85
<b>第四章</b>	<b>掺杂化合物的理论模型和计算结果.....</b>	<b>86</b>
4.1	晶体结构模型.....	86
4.2	计算参数.....	94

<b>4.3</b>	<b>计算结果</b> .....	<b>95</b>
4.3.1	晶体结构 .....	95
4.3.2	能带结构 .....	108
4.3.3	态密度 .....	110
<b>4.4</b>	<b>本章小结</b> .....	<b>115</b>
<b>第五章</b>	<b>结果讨论</b> .....	<b>116</b>
<b>5.1</b>	<b>镍掺杂对晶体结构的影响</b> .....	<b>116</b>
<b>5.2</b>	<b>镍掺杂对化学计量比的影响</b> .....	<b>117</b>
<b>5.3</b>	<b>镍掺杂对电导率的影响</b> .....	<b>122</b>
5.3.1	能带结构对电导率的影响 .....	122
5.3.2	态密度对电导率的影响 .....	127
5.3.3	价态变化对电导率的影响 .....	132
5.3.4	本节小结 .....	137
<b>5.4</b>	<b>镍掺杂对电化学性能的影响</b> .....	<b>138</b>
5.4.1	晶体结构对电化学性能的影响 .....	138
5.4.2	Jahn-Teller 畸变对电化学性能的影响 .....	139
<b>5.5</b>	<b>本章小结</b> .....	<b>142</b>
<b>第六章</b>	<b>结论</b> .....	<b>143</b>
<b>第七章</b>	<b>对未来研究工作的设想和建议</b> .....	<b>145</b>
	参考文献 .....	147
	攻读博士期间发表的论文 .....	156
	致 谢 .....	158

## TABLE OF CONTENTS

<b>ABSTRACT IN CHINESE</b> .....	I
<b>ABSTRACT IN ENGLISH</b> .....	II
<b>CHAPTER ONE</b>	
<b>Recent Progress in Cathode Materials for Li-ion Batteries</b> .....	1
<b>1.1 Principle and Components</b> .....	1
1.1.1 Principle .....	1
1.1.2 Components .....	2
<b>1.2 Recent Progress in Cathode Materials</b> .....	4
1.2.1 LiCoO <sub>2</sub> .....	4
1.2.2 LiNiO <sub>2</sub> .....	6
1.2.3 LiNi <sub>y</sub> Co <sub>1-y</sub> O <sub>2</sub> (0≤y≤1).....	8
<b>1.3 Summary of the Current Problems</b> .....	41
<b>1.4 Research Contents and Significance</b> .....	42
1.4.1 Research Contents.....	42
1.4.2 Research Significance.....	42
<b>1.5 Research Originalities</b> .....	43
<b>CHAPTER TWO</b>	
<b>EXPERIMENTAL MATERIALS、METHODS AND PROCEDURES</b>	44
<b>2.1 Synthesis of Materials</b> .....	44
<b>2.2 Chatacterization of Materials</b> .....	45



2.2.1	Thermal Analysis.....	45	
2.2.2	Structure Analysis .....	45	
2.2.3	Surface and Chemical Analysis.....	47	
2.2.4	Conductivity Measurements.....	47	
2.2.5	Electrochemical Measurements.....	48	
<b>2.3</b>	<b>Calculation of Materials .....</b>	<b>49</b>	
<b>CHAPTER THREE</b>			
<b>EXPERIMENTAL RESULTS .....</b>			<b>51</b>
<b>3.1</b>	<b>Thermal Property of Materials.....</b>	<b>51</b>	
<b>3.2</b>	<b>Structure of Materials .....</b>	<b>53</b>	
3.2.1	Ex-situ XRD .....	53	
3.2.2	In-situ XRD .....	62	
<b>3.3</b>	<b>Surface and Chemistry of Materials .....</b>	<b>69</b>	
3.3.1	Ex-situ FTIR.....	69	
3.3.2	In-situ Raman.....	73	
<b>3.4</b>	<b>Morphology of Materials .....</b>	<b>76</b>	
3.4.1	In-situ SEM of $\text{LiNi}_{3/4}\text{Co}_{1/4}\text{O}_2$ .....	76	
3.4.2	Ex-situ SEM of Materials.....	77	
<b>3.5</b>	<b>Electrical Conductivity of Materials .....</b>	<b>78</b>	
<b>3.6</b>	<b>Electrochemical Performance of Lithium Batteries .....</b>	<b>79</b>	
3.6.1	First Cycle Charge/Discharge Performance .....	79	
3.6.2	Cycle Performance .....	82	

**3.7 Brief Summary .....85**

**CHAPTER FOUR**

**THEORETICAL MODEL AND CALCULATED RESULTS .....86**

**4.1 Theoretical Model .....86**

**4.2 Parameters of Calculation.....94**

**4.3 Results of Calculation .....95**

4.3.1 Crystal Structure ..... 95

4.3.2 Band Structure..... 108

4.3.3 Density of States (DOS)..... 110

**4.4 Brief Summary ..... 115**

**CHAPTER FIVE**

**DISCUSSION OF RESULTS ..... 116**

**5.1 Effect of Doping on Crystal Structure ..... 116**

**5.2 Effect of Doping on Stoichiometry ..... 117**

**5.3 Effect of Doping on Electrical Conductivity .....122**

5.3.1 Influence of Band Structure..... 122

5.3.2 Influence of DOS ..... 127

5.3.3 Influence of Valence ..... 132

5.3.4 Brief Summary..... 137

**5.4 Effect of Doping on Electrochemical Performance .....138**

5.4.1 Influence of Crystal Structure..... 138

5.4.2 Influence of Jahn Teller Effect..... 139

**5.5 Brief Summary ..... 142**

**CHAPTER SIX**

**CONCLUSIONS ..... 143**

**CHAPTER SEVEN**

**SUGGESTIONS FOR FUTURE WORK..... 145**

**REFERENCES..... 147**

**PUBLICATIONS ..... 156**

**ACKNOWLEDGMENTS ..... 158**

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## 摘要\*

正极材料是目前制约锂离子电池性能进一步提高的主要因素，掺杂改性被认为是解决该问题的一种重要手段。但是迄今为止的绝大部分研究的重点仅是实验研究，对掺杂离子改性机理缺乏更深层次的研究。本论文工作选取了锂镍钴氧化物作为具体的研究对象，试图从电子结构的角度进一步探讨镍掺杂改性机理。

在论文工作中，合成了一系列不同掺镍量的  $\text{LiNi}_y\text{Co}_{1-y}\text{O}_2$  化合物，并利用 TG-DTA, 高温原位和非原位 XRD, 现场和非现场 Raman, FTIR 与 SEM/EDAX 以及四探针等表征和电化学测试技术，获得了九种化合物的晶体结构、化学计量比、电导率及电化学性能随掺杂量变化的实验数据。为了深入阐明掺杂机理，本论文从材料晶体结构的对称性入手，通过考虑掺杂后的稳定结构必须处于宏观平衡状态的要求，建立了合理的超晶胞模型，进而提出了掺杂锂镍钴氧化物的晶体结构需满足结构对称且层间应力为零、层内应力不为零但宏观平衡的超晶胞理论，并利用 VASP 软件对根据该理论构建的九种化合物的超晶胞模型进行了第一性原理计算，获得了这些化合物的理论晶体结构、能带结构、态密度和部分态密度。在上述计算的基础上，建立了适用于锂离子电池正极材料的电导率计算方法；提出了  $\text{LiNi}_y\text{Co}_{1-y}\text{O}_2$  的电荷补偿机制；给出了 Jahn-Teller 畸变强度和掺杂量之间的定量关系。

实验结果表明，镍掺杂有利于提高材料的结晶度、电导率和首次充电比容量。当掺镍量达到 75% 以上时，电导率提高近一个数量级，首次充电比容量提高了 65%。然而，镍掺杂也带来体积膨胀、相变温度升高和形成大量的中间杂相等问题，降低了材料的化学计量比、充放电容量损失及电池的循环性能。

理论计算表明：1) 镍掺杂不仅导致能带结构中导带和价带之间的带隙变窄，同时也在价带中引入了空穴态，钴和镍的价态发生了变化，出现了混合价态，导致材料的电子结构趋于满足 Zener 的双交换机制，有利于电导率的提高。当掺镍量达到 75% 以上时，价带中的空穴态增加了 4 倍，导带和价带之间的带隙大大变小，这些均导致电导率的大幅度提高。2) 随着镍掺杂量增加，Jahn-Teller 畸变强度线性增加；当镍掺杂量大于 75% 时，Jahn-Teller 畸变达到最大。Jahn-Teller 畸变强度的增加将导致非计量比化合物增加，进一步降低材料的结构稳定性和循环性能。

**关键词：**正极材料；电导率；Jahn-Teller 畸变

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**ABSTRACT\***

Metal doping has been considered as one of the most efficient ways to improve performance of lithium-ion batteries restricted mainly by cathode materials and has been extensively studied in the past. However, little information is available in fundamental understanding of doping nature because of the constraints in experimental approaches adopted in most previous researches. In this work, an effort was directly made to investigate the doping mechanisms of lithium-nickel-cobalt oxides ( $\text{LiNi}_y\text{Co}_{1-y}\text{O}_2$ ,  $0 \leq y \leq 1$ ) based on the electronic structures of  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$ .

A series of  $\text{LiNi}_y\text{Co}_{1-y}\text{O}_2$  compounds were prepared by sol-gel pretreatment and solid-phase formation. The variations of thermal property, crystal structure, stoichiometry, electric conductivity and electrochemical performance with nine levels of nickel doping contents were obtained by TG-DTA, in-situ and ex-situ XRD, in-situ and ex-situ Raman, FTIR, SEM/EDAX, four-probe and electrochemical measurements. In order to interpret the experimental data and to elucidate the doping mechanisms, the first-principle calculations were carried out based on the complete new supercell model developed by ensuring the unchanged structural symmetry and the most stable structure after doping. Accordingly, the supercell theory of lithium-nickel-cobalt oxides was proposed, which states that the crystal structures after metal doping must satisfy both the structure symmetrical characteristics and the macroscopic force equilibrium state through which the net stress among the interlayer structure is zero but the net stress within the inner layer structure is non-zero, and the crystal structure, band structure, density of states (DOS) and partial density of states (PDOS) before and after nickel doping were systematically calculated by employing the VASP software package. The improved formulas applicable to evaluate the electric conductivity of cathode materials as lithium ion batteries were established. The charge compensation mechanisms of  $\text{LiNi}_y\text{Co}_{1-y}\text{O}_2$  were provided based on the computational results. The quantitative relation between the

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doping content and Jahn-Teller distortion were also described according to the PDOS analysis results.

The experimental results revealed that nickel doping enhanced the crystallinity, electric conductivity and first cycle charge capacity. When the nickel content attained 75%, the conductivity improved nearly an order of magnitude and the first cycle charge capacity increased 65%. However, with the increase of nickel content, the volume expansion of crystal structure occurred, and the temperature of phase transformation rose and more impure phases were formed during the courses of synthesis. In addition, the stoichiometry, loss of charge-discharge capacity and cycling performance decreased.

The first-principle calculation results indicated: 1) with nickel doping the energy gap between valence bands and conduction bands became narrower, and the extra holes were introduced into valence bands, both altered the valences of cobalt and nickel, resulting in the mixing valence state which tends to satisfy the Zener's double exchange mechanism. All of these led to the increase of the electric conductivity. When the nickel content reached 75%, the extra holes induced in valence bands jumped four times and this dramatically reduced the energy gap between valence bands and conduction bands, hence, significantly improved the electric conductivity; 2) the strength of the Jahn-Teller distortion increased linearly with the increase of nickel content; when the nickel content was more than 75%, the strength of the Jahn-Teller distortion reached the maximum. Ultimately, this would result in a large amount of the nonstoichiometric compounds, therefore, the stability of material structure and the cycling performance became worse.

**Keywords:** cathode materials; electric conductivity; Jahn-Teller distortion

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