

学校编码: 10384

密级_____

学号: 20520110153716

厦 门 大 学

博 士 学 位 论 文

锂离子电池高电压正极材料镍锰酸锂的制
备和改性研究

Synthesis and Modification of High-voltage Lithium Nickel
Manganese Oxide Cathode Material for Lithium-ion
Batteries

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专 业 名 称: 应用化学

论文提交日期: 2014 年 12 月

论文答辩日期: 2014 年 12 月

2014 年 12 月

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Synthesis and Modification of High-voltage Lithium Nickel Manganese Oxide Cathode Material for Lithium-ion Batteries



A Dissertation Submitted to the Graduate School of Xiamen
University for the Degree of
Doctor of Science

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December, 2014

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摘要

随着锂离子电池的应用从手机、数码相机和笔记本电脑等电子仪器领域扩展至电动汽车、通信技术和移动存储设备等领域，人们对锂离子电池的性能，特别是对功率密度和工作电压，提出了越来越高的要求。锂离子电池工作电压和功率密度等性能，主要由正极材料决定。因此，发展高电压正极材料是发展高能量密度锂离子电池重要的研究方向之一。

LiMn_2O_4 (LMO)具有低成本、低毒性和良好的安全性能等优点，被认为是一种理想的正极材料。然而 LMO 能量密度低，研究表明当向 LMO 掺杂一定量的镍形成镍锰酸锂 $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO)后，其放电平台从 4.1 V 提高至 4.7 V，与传统的正极材料如 LiCoO_2 、 $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ 和 LiFePO_4 ，LNMO 的重量比能量得到很大提高。LNMO 不仅可以满足新一代个人消费电子产品和大型电气设备功率要求，也可以兼容高工作电压的负极材料，如 $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ，以提高电池的安全性能，使它成为下一代先进锂离子电池正极材料之一。

本文针对 LNMO 存在导电性低、金属离子在电解液中溶解、容量衰减和倍率放电性能亟待改善和提高这些关键问题，开展制备和改性研究。主要内容分为三部分。第一部分，通过浸渍法制备了由纳米一次颗粒聚集而成的二次微米级球状颗粒 LNMO，LMO，LMO 和 LNMO 共生的 LMO-LNMO I；考察了 LNMO 中微量 Mn^{3+} 对其电化学行为的影响；与 LNMO 和 LMO 相比，LMO-LNMO I 的容量、倍率性能和热稳定性都得到了很大提高。第二部分，在相同的制备方法和焙烧过程下合成了纳米级和微米级的 LNMO，考察了材料的粒径大小与电化学性能的关系，发现纳米级的 LNMO 电化学综合性能没有微米级的 LNMO 好。在接下来的第三部分对纳米的 LNMO 进行了掺杂和包覆的改性研究。(1) 采用简单易行的方法首次实现对 LNMO 的 Na 掺杂，提高了材料的导电性，改善了材料的电化学循环。(2) 首次实现了对 LNMO 的 V_2O_5 包覆，提高了 LNMO 的锂离子扩散系数和减轻了材料在电解液中金属离子的溶解。(3) 对 LNMO 进行了 CuO 表面修饰的研究，改善了电化学循环。本文具体内容如下：

一、浸渍法合成多孔的微米球状的 LMO、LNMO 和 LMO-LNMO I 及其电化学性能的研究。

1. 在本文的第三章,合成了以板栗壳状的 MnO_2 为锰源通过浸渍方法合成了微米球状的 LNMO 材料,该材料的颗粒是由纳米级的多面体聚集而成的。这对电解液的浸入和锂离子的嵌入和脱出是有利的,且可以适应材料在充放电过程中的体积变化,减小材料颗粒之间的张力。通过进一步控制焙烧氛围空气或氧气,分别得到含有痕量 Mn^{3+} 和不含 Mn^{3+} 的 LNMO 材料。通过对其电化学性能的对比,创新性地提出了含有微量 Mn^{3+} 的 LNMO (LNMO-Air) 电化学性能更优。特别是在高温和高倍率下 (5 C 和 55 $^{\circ}\text{C}$), LNMO-Air 的充放电循环 80 圈后放电比容量还能保持在 107 mAh g^{-1} , 容量保持率接近 100%。

2. 在第三章所合成的板栗壳状 MnO_2 可以用来作为锰源和自我模板来合成 LMO, 而 LMO 由于其本身材料中 Mn^{3+} 的 Jahn-Teller 效应, LMO 的电化学循环衰减比较严重。由此出发,在本文的第四章,首次创新性地合成了共生的 $\text{LiMn}_2\text{O}_4\text{-LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LMO-LNMO I), 在共生结构中 LNMO 稳定了 LMO 相的结构,使更多的锂参与了充放电; LMO 提高了材料中 Ni 和 Mn 的无序性,从而提高了 LMO-LNMO I 的导电性。因此与 LNMO、LMO 和它们的共混材料相比, LMO-LNMO I 的放电容量、循环稳定性、高温性能和热稳定性都得到了显著提高。

二、粒径大小对 LNMO 电化学行为的研究。

LNMO 材料的粒径大小会影响它的电化学行为。在本文的第五章,通过严格控制相同的焙烧条件和合成方法合成了微米级和纳米级的镍锰酸锂,研究表明纳米级的 LNMO 没有微米级的电化学性能好。在接下来的第六、七和八章,对纳米级的 LNMO 进行了掺杂和包覆的改性研究。

三、对纳米 LNMO 的改性研究。

1. 在第六章,首次合成了 Na 掺杂的 LNMO。与其他重金属掺杂元素相比,Na 元素储量丰富、廉价和无毒。Na 源采用氢氧化钠,掺杂方法简单有效,可以用于大规模生产。Na 进入活性位 Li 位,Na 掺杂提高了 LNMO 中 Ni 和 Mn 的无序性,增加了材料中的锂离子跃迁途径和电导性,减少了电化学极化和欧姆极化。研究表明当掺杂量为 5% 时,材料的性能最佳。在 1 C 下,材料的放电比容量高达 125 mAh g^{-1} , 循环 100 圈后容量保持率在 93%。甚至在 5 C 和 55 $^{\circ}\text{C}$ 下,5% Na 掺杂的 LNMO 在循环 400 圈后容量还能保持在 82%。

2. 在第七章,首次合成了 V_2O_5 包覆 LNMO 的纳米复合材料 ($\text{V}_2\text{O}_5\text{-LNMO}$),

这种合成方法对仪器和设备要求不高，并且操作简单，可用于大规模生产。 V_2O_5 是一种可以嵌锂的钒的氧化物，界面处的 V_2O_5 可以与镍锰酸锂表面的 $LiOH$ 和 Li_2CO_3 反应形成 LiV_2O_5 ，因此 V_2O_5 与镍锰酸锂形成紧密接触，有利于电子的传递，与其他锂离子惰性的包覆物相比降低了电池的阻抗。 V_2O_5 不仅降低了材料表面的pH值，而且洁净了材料的表面由于吸潮产生的 $LiOH$ 和 Li_2CO_3 等。在组装成电池后， V_2O_5 有效减缓电解液与电极材料的相互作用，并减缓电解液中HF对LNMO的攻击，减轻金属离子的溶解，而且 V_2O_5 还作为锂离子导体提高了镍锰酸锂的锂离子扩散系数。研究发现当包覆量为5%时，材料的性能最佳。在1 C下，材料的放电比容量高达 131.5 mAh g^{-1} ，循环100圈后容量保持率在92.2%，显著提高了LNMO循环稳定性。即使在5 C和55 °C，5% V_2O_5 -LNMO的放电比容量还比LNMO高15%为 126.3 mAh g^{-1} 。

3. 在第八章，采用湿法合成了LNMO表面修饰CuO的纳米复合材料(CuO-LNMO)。CuO在循环过程中会转变成 $LiCuO_2$ ，然后 $LiCuO_2$ 和 Li_2CuO_2 在充放电过程中发生相互转化，这种层状的 Li_xCuO_2 对锂离子的传输是有利的。实验表明当包覆量为1%时，LNMO的性能最佳。在1 C下，材料的放电比容量高达 126.1 mAh g^{-1} ，循环100圈后容量保持率在99.5%。

关键词：镍锰酸锂 球 多孔 共生 纳米 微米 改性 包覆 掺杂 Na V_2O_5

Abstract

With the lithium ion battery expansion from mobile phones, digital cameras, laptop computers and other small electronics to electric vehicle, communication technology and mobile storage devices field, higher requirements for the performance of lithium ion battery, especially the power density and energy density, have been set to satisfy production and people's demands. Performance of lithium-ion batteries, such as working voltage and power density, is mainly determined by the property of the cathode materials. Therefore, the development of high voltage cathode materials is one of important research direction for lithium ion battery with high energy density.

Because of its low cost, little toxicity and good safety performance, spinel LiMn_2O_4 (LMO) is thought to be an ideal cathode material for lithium ion batteries. Lots of studies have shown that the Fermi energies of the materials could be improved and their electrode potentials could be raised resultantly by doping the spinel LiMn_2O_4 materials with a certain amount of transition metal elements M to prepare $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$ (M=Fe, Co, Ni, Cr etc.). Of the improved cathode materials with spinel structure, the material $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is of an acceptable performance and stable discharge capacity. Because of the discharge platform of LNMO is up to 4.7 V, the specific weight energy of the LNMO could be expected to be greatly improved comparing to the conventional cathode materials such as LiCoO_2 , $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$, LiFePO_4 and so on. The LNMO can not only meet the power demands for personal consumer electronics and electric equipment, but also be compatible with high working voltage anode materials such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and so on. These advances improve the energy density and safety performance of the battery, making it one of the most potential positive electrode material for the next generation of the advanced lithium ion batteries.

The key problems for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ are to improve its electrical conductivity, fading of capacity, dissolution transition metal ions in electrolyte solution and rate capacity. This dissertation attempts to solve these problems. The dissertation includes three major parts. Firstly, micro-sized spherical LNMO, LMO, and intergrown LMO-LNMO I comprised of aggregated nano-polyhedrons were synthesized by an impregnation method. Influence of trace amount of Mn^{3+} in

LNMO on the electrochemical properties was explored. The results show that thermostability, capacity and rate performance of LNMO-LMO I were much improved compared with LNMO and LMO. Secondly, we controllably synthesized nano-sized and micron-sized LNMO to examine the relationship between the particle size and the electrochemical properties of the material. The electrochemical property of nano-sized LNMO is not as good as that of micron-sized LNMO. Then, modification of nano-sized LNMO was carried out in the third part as follows: (1) The Na-doped LNMO was firstly synthesized via a sample method, and the electrical conductivity and cycle performance were improved as a result. (2) V₂O₅-coated LNMO were first demonstrated. Resultantly, the lithium ion diffusion coefficient was increased nearly doubly and dissolution of metal ions in electrolyte was alleviated. (3) The CuO-coated LNMO was synthesized to improve cycle performance. The detailed research contents are as follows:

1. Porous micron-sized sphere LNMO, LNMO and LMO-LNMO I and the electrochemical property of them.

(1) In Chapter 3, the porous micron-sized sphere LiNi_{0.5}Mn_{1.5}O₄ particles were synthesized via an impregnation method based on highly prominent chestnut-cupule-like MnO₂ spheres as the manganese sources. The micrometer particles composed of aggregated nano-sized polyhedron also lead to high loading density and is able to better accommodate the volume change and to reduce the electrode tension upon cycling. In comparison to conventionally ball-milling method, the method presented in the dissertation can be easily operated and is energy-efficient. The electrochemical properties of the sphere LiNi_{0.5}Mn_{1.5}O₄ cathode material was superior to those made from commercial manganese sources and conventional approaches, because of its more porous structure for the enhanced immersion of electrolyte and better structure for insertion/desertion of Li ions. We also studied the effects of the trace amount of Mn³⁺ ions in the structure on its specific capacity and cycle stability. We innovatively proposed that these trace Mn³⁺ ions are beneficial to its rate capability and cycle life, especially at high rates and raised temperature, by improving the conductivities of Li ions and electrons of the LNMO material.

(2) Chestnut-cupule-like shaped MnO₂ synthesized in Chapter 3 can be used as manganese source and self-template to synthesize LMO. Due to Mn³⁺

Jahn-Teller effect, the electrochemical cycle attenuation of LMO is very serious. So, in Chapter 4, we firstly synthesized a kind of intergrown composite, $\text{LiMn}_2\text{O}_4\text{-LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LMO-LNMO I), which are micro-sized spheres consisted of aggregated nano-sized octahedral particles with a well-defined cubic spinel structure. In LMO-LNMO I, LNMO acts as a skeleton to stabilize the structure of LMO, and enables more lithium ions in LMO participate in charge-discharge process along with these in LNMO, leading to that high specific discharge capacities and its thermostability can be more enhanced compared to LNMO due to the high Mn content in LMO-LNMO I. Also LMO in LMO-LNMO I disorders excessively Ni and Mn ion, which induced a superior rate performance of LMO-LNMO I by improve the conductivity of the material. In summary, LMO-LNMO I is superior to LMO, LNMO and the mixture of LMO and LNMO in electrochemical property, rate capacity and thermostability.

2. Particle size effect of LNMO.

In Chapter 5, we discussed the LNMO particle size effect on its electrochemical behavior. Nano-sized and micron-sized LNMO materials were synthesized under the same calcination conditions and by the same synthesis method. By comparing the cycle stability of these different sized LNMO, we speculated that capacity and cycle stability of the nano-graded LNMO was not as good as that of micron-sized LNMO. In the following, modification of nano-sized LNMO were implemented to improve the electrical property of spinel.

3. Modification of nano-sized LNMO.

(1) In Chapter 6, the Na-doped LNMO are firstly synthesized via a solid-state method. Na element is cheap, abundant and environmental friendly than other heavy metal dopants. The doping of Na ions increases the disorder degree of nickel and manganese ion in the spinel structure and improves lithium ion diffusion coefficient, and two additional electron hopping paths happened, which contribute to a better charge transfer ability and resultantly relieve the ohmic polarization and electrochemical polarization of the materials. The doping content of Na up to 5% in the spinel structure exhibited the excellent electrochemical cycle, presenting a discharge specific capacity of 125 mAh g^{-1} at 1 C with a retention of 116.2 mAh g^{-1} after 100 cycles. In addition, it also shows remarkable rate capability, the discharge

specific capacity decreased slightly from 121 to 119.4, 118.5, 115.1, 108.4 and 101.3 mAh g⁻¹ at 0.2 C, 0.5 C, 1 C, 2 C, 5 C and 10 C, respectively. Furthermore, it has striking electrochemical property at elevated temperature and great rates. Even at 5 C rate at 55 °C, the discharge capacity of 5% Na-LNMO is up to 119.7 mAh g⁻¹, with a retention of 97.6 mAh g⁻¹ after 400 cycles.

(2) In Chapter 7, we firstly demonstrated a simple method coating a thin layer of V₂O₅ on spinel LNMO surface. V₂O₅ can react with LiOH/Li₂CO₃ impurities and trace Li ions in the bulk layer when annealed at high temperature to form a close contact with core materials, which reduces the impedance for electron transport than other coating materials. Furthermore, the formation of lithium ion intercalated compound LiV₂O₅ lower the pH value of materials and purify LNMO surface by physical adsorption of residue Li₂O/LiOH to enhance the cycle performance at a high voltage. Also, the V₂O₅ layer not only works as an isolating layer to prevent LNMO cathode from electrolyte corrosion, alleviate the dissolved metal ions, but also modifies the surface ion transport properties of LNMO because this thin V₂O₅ coating layer is a kind of lithium ion conductor. The D_{Li} lithium ion diffusion coefficient values of 5% V₂O₅-LNMO is roughly twice of that of the pristine LNMO. The 5% V₂O₅-LNMO (optimal coating content) shows remarkable rate capability, and its discharge specific capacity retention is much improved compared with pristine LNMO. Furthermore, it has superior electrochemical property at elevated temperature and high rates.

(3) In Chapter 8, the CuO-coated LiNi_{0.5}Mn_{1.5}O₄ has been synthesized to use as a cathode material for lithium ion batteries via a wet-method. The coating of CuO on the material does not have significant effect on the basic spinel structure of LNMO, but effectively reduces the interaction between electrolyte and LNMO, and prevent further the dissolution of manganese. During cycling, CuO was transformed into LiCuO₂. Due to electrochemical redox behaviors between LiCuO₂ and Li₂CuO₂, such layer Li_xCuO₂ compounds can be advantageous for the fast Li⁺ ion diffusion. The results show that LNMO with 1% CuO coating has the better electrochemical performance. Its cycle capacity retention at 1 C is up to 99.5% after 100 cycles. Even cycling at 5 C rate, the cell with 1% CuO-LNMO cathode can has 99.4% of capacity retention after 200 cycles, indicating that it is a promising cathode material for lithium ion batteries.

Keywords: LNMO; sphere; porous; intergrown; nano; micron; modification; doping; coating; Na; V₂O₅

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