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# 厦 门 大 学

## 硕 士 学 位 论 文

### 层状-尖晶石复合结构富锂锰基正极材料的 溶剂热合成及其性能研究

**Solvothermal synthesis and properties of Layered/Spinel  
heterostructured Li-rich and Mn-based cathode materials of  
Li-ion batteries**

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**Solvothermal synthesis and properties of  
Layered/Spinel heterostructured Li-rich and Mn-  
based cathode materials of Li-ion batteries**



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## 摘要

随着化石能源的快速消耗和环境污染问题的日益突出,人类社会的可持续发展对于电动汽车的需求日渐迫切。具有较高能量密度的锂离子电池已成为了新能源极为重要的组成部分。相较于负极材料,正极材料是进一步提高锂离子电池能量密度的决定性因素,也决定着锂电池的安全性能及使用寿命。其中,富锂锰基固溶体材料( $\text{Li}_2\text{MnO}_3\cdot\text{LiMO}_2$ )具有较高的放电比容量( $\geq 250 \text{ mAh/g}$ )、低成本、较好的热稳定性等优点受到了广泛关注,并被认为是极具前景的下一代锂离子电池正极材料。但富锂材料存在的一些问题严重制约了其发展应用,例如,首次充放电过程中的容量损失较大、倍率及循环性能不佳、电压衰减严重等。此前的研究主要通过体相掺杂、表面修饰及颗粒纳米化等方式在一定程度上优化材料的性能。本论文通过改变合成条件调控材料结构,一步制备出具有层状-尖晶石复合结构的富锂锰基材料  $\text{Li}_{1.16}\text{Mn}_{0.6}\text{Ni}_{0.12}\text{Co}_{0.12}\text{O}_2$ , 从而显著提升其电化学性能。

本论文研究内容主要包括:

1. 通过溶剂热法一步制备了具有层状-尖晶石复合结构的富锂锰基三元正极材料 (LS)。该材料由粒径为 20~30nm 的纳米颗粒团聚成大小为 3-5 $\mu\text{m}$  的空心球型聚集体。结构分析结果表明, LS 材料中的尖晶石相为  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  结构。与纯相层状富锂材料 (PL) 相比, LS 表现出了更优异的电化学性能, 包括更高的首次库伦效率和更佳的倍率性能。在 2.0~4.8 V 电压区间内, LS 在各个倍率下都给出了比 PL 高出 15% 左右的首次充放电库伦效率, 即更低的容量损失。在 10 C 倍率条件下, LS 的稳定放电容量为 193  $\text{mAh g}^{-1}$ , 比 PL 高 138  $\text{mAh/g}$ 。LS 的优异性能可归因于共生的尖晶石结构提供的 16c 八面体空位及 3D 锂离子扩散通道。一方面, 尖晶石结构的 16c 八面体空位在首次放电过程能容纳更多的  $\text{Li}^+$ , 以缓解  $\text{Li}_2\text{MnO}_3$  在首周活化过程中的不可逆分解带来的较大容量损失; 另一方面, 尖晶石结构中的 3D 锂离子扩散通道能极大地提高  $\text{Li}^+$  的扩散速率, 改善其倍率性能。

2. 针对富锂锰基三元正极材料, 着重研究了不同的煅烧时间对于其层状-尖晶石复合结构的影响。所合成的材料均具有微米球型聚集体形貌, 煅烧时间的改

变对于材料的形貌影响不大。通过 XRD 对其结构表征及精修计算，650 °C 下煅烧 24 h 所得样品 (T24)，相较于 T12 和 T36，具有更高的尖晶石含量和更宽阔的 3D Li<sup>+</sup> 扩散通道。充放电测试结果指出，T24 给出了最优的电化学性能。在 0.2 C 倍率下，T24 的首次库伦效率达到 101%；即使在 2 C 倍率下进行充放电测试，依然高达 92%，各个倍率下的首次库伦效率均高于尖晶石结构含量较低的其他样品。与此同时，T24 还表现出优异的倍率性能。在 5 C 及 10 C 倍率下进行充放电测试，材料分别释放出高达 234 mAh/g 和 206 mAh/g 的放电比容量。PITT 测试结果显示，T24 比 T36 在 4.8~2.0 V 区间内具有更大的锂离子扩散速率。

本论文从改善富锂材料的合成工艺出发，运用溶剂热方法一步制备出具有层状-尖晶石复合结构的富锂锰基正极材料。首次报道了在未经过任何后续改性手段时，富锂三元正极材料同时表现出优异的首次库伦效率和倍率性能。本论文所采用的溶剂热方法简便易行、重现性高，具有产业化批量生产的前景，而所合成的复合结构富锂锰基材料是极具市场前景的新型锂离子电池正极材料。

**关键词：**锂离子电池 富锂锰基正极材料 层状-尖晶石复合结构 溶剂热合成方法



## Abstract

Recently, the effects of global warming and fluctuation of petroleum prices have forced us to look for alternative energy storage-conversion systems to meet the increasing requirement of practical use, such as electrical vehicles and smart grid. Due to the high energy density, lithium-ion batteries have drawn extensive attractions. Compared to anode materials, cathode materials play a more critical role in the development (*i. e.* energy density, safety and life) of lithium-ion batteries. Considering the advantages of high capacity ( $\geq 250$  mAh/g), low cost and improved safety, Li-rich and Mn-based materials, a solid solution of  $\text{Li}_2\text{MnO}_3$  and  $\text{LiMO}_2$  (M= Mn, Co, Ni *et al.*), have been regarded to be one of the promising cathode candidates for future lithium-ion batteries. However, Li-rich materials still suffer from some intrinsic performance problems, such as huge initial irreversible capacity loss, poor cycleability, inferior rate capability and gradual voltage decay, which hinder their commercialization. Although extensive efforts, such as doping, surface modification and controlling nanoparticles granularity, have been made to address these limitations, previous strategies can only enhance their electrochemical performance to a certain extent. Therefore, with the aim to boost the electrochemical performance by modifying the structural properties, this thesis present effective solution to prepare Li-rich materials  $\text{Li}_{1.16}\text{Mn}_{0.6}\text{Ni}_{0.12}\text{Co}_{0.12}\text{O}_2$  of layered/spinel heterostructure, which show the merits of high initial efficiency and remarkable rate capability, simultaneously.

The main results are given below:

1. Hierarchical Li-rich microspheres of layered/spinel heterostructure (LS) were one-step prepared via a solvothermal strategy combined with calcination process. As for their morphology, nanoparticles with a diameter about 20~30 nm were assembled further into hollow microspheres with a size around 3~5  $\mu\text{m}$ . According to detail structural characterizations and analyses,  $\text{Li}_4\text{Mn}_5\text{O}_{12}$ -type structure was definitely introduced to the LS. In comparison to the pure-layered Li-rich materials (PL), superior electrochemical performance was delivered by the LS. When the voltage range was

between 2.0-4.8V (vs. Li/Li<sup>+</sup>), the LS presented initial efficiencies about 15% higher than that of the PL at varies rates. In other words, much lower capacity loss was obtained in the charge-discharge tests of the LS. Besides, at super-high rate of 10 C, the stable capacity of the LS was about 138 mAh g<sup>-1</sup> higher than that of the PL. The spinel structure with the empty 16c octahedral site and 3D Li<sup>+</sup> diffusion channel is considered as the key to the enhanced electrochemical performances of Li-rich materials.

2. The effects of calcination time on such layered/spinel heterostructured Li-rich cathode materials were systematically studied. In spite of little difference reflected in the morphology of microsphere aggregates, materials experienced various calcination conditions exhibited obvious difference in their structural properties and electrochemical performance. As-prepared heterostructured Li-rich materials calcined at 650 °C for 24 h (T24) deliver the optimal performance. Decent initial coulombic efficiency of 101% at 0.2 C rate and the maximum discharge capacities as high as 206 mAh g<sup>-1</sup> at super-high rate of 10 C were achieved. According to the potentiostatic intermittent titration technique (PITT) tests, the T24 presents larger values of Li<sup>+</sup> chemical diffusion coefficient than the T36. Such superior performances of the T24 should be attributed to its higher spinel contents and broader 3D Li<sup>+</sup> diffusion channels.

This thesis focuses on modifying the synthesis route of Li-rich and Mn-based materials. An improved solvothermal strategy has been adopted to one-step fabricate Li-rich materials of layered/spinel heterostructure. For the first time, without any following modification, synthesized materials share the merits of impressive high coulombic efficiency and remarkable rate capability, simultaneously. The novel heterostructured materials in this thesis could be considered as promising cathode for dynamic lithium-ion batteries.

**Keywords:** Li-ion batteries; Li-rich and Mn-based cathode materials; layered/spinel heterostructure; solvothermal route

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