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博 士 学 位 论 文

# 锂离子电池正极材料 $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ 及相关 电解液添加剂的性能与表征

**The Investigation of  $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$  as Cathode Materials and  
their corresponding Electrolyte Additive for Lithium-ion Batteries**

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## 中文摘要

### 锂离子电池正极材料 $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ 及其相关电解液添加剂的性能与表征

三元正极材料  $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$  因具有价格低、热稳定性好、对环境友好以及高电位下比容量高等突出优势成为锂离子电池研究的热点之一,引起了研究者的广泛关注。本论文选择该系列材料为研究内容,主要工作集中在优化合成条件,并成功制备出具有良好电化学性能的  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  和  $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$  正极材料,通过多种电化学与谱学手段表征它们的电化学、表面性质、热稳定以及储存等多方面的性能,并重点研究了  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  材料首次不可逆损失严重的原因,以及  $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$  粉末在空气中的储存稳定性等。

在实验技术方面,本论文在国内首次建立了用于锂离子电池研究的原位差分电化学质谱装置(DEMS),自行设计制作 DEMS 用的电解池并搭建了整套系统,并且已将其成功应用于对电解液添加剂的研究中。

在材料合成方面,本论文采用溶胶凝胶预处理高温烧结或共沉淀预处理高温烧结的两种方法,分别制备  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  和  $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$  材料,将烧结温度控制在  $850^\circ\text{C}$ - $900^\circ\text{C}$  范围内可以得到层状结构良好的材料。他们的电化学性能突出,在  $2.5$ - $4.6\text{V}$  里以  $0.1\text{C}$  ( $20\text{mAh/g}$ ) 的倍率充放,首次放电容量均达到  $200\text{mAh/g}$ , 60 圈后仍然具有首次 70% 以上的容量,具有较高的能量密度和较好的循环稳定性。

在有关  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  材料的研究中也发现,该材料第一圈的库仑效率仅有 77%,首次不可逆容量损失比较严重。为了了解出现这一现象的原因,本文选择  $\text{NO}_2\text{BF}_4$  作为脱锂剂,遵循  $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2 + m \text{NO}_2\text{BF}_4 \rightarrow \text{Li}_{1-m}\text{Ni}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2 + m\text{NO}_2 + m\text{LiBF}_4$  反应方程式,用化学方法直接从粉末里氧化脱出定量的锂,希望能够模拟电池的电化学脱锂过程,排除导电剂,粘结剂,集流体的影响,帮助更好的理解三元正极材料的电化学行为。

研究表明,该材料的结构稳定性较好,虽然在脱锂过程中,晶胞的体积发生先膨胀后收缩的变化,但仍维持 O3 的单相结构,并不会随锂的脱出形成新

相。但过渡金属Ni和Co的氧化态却会随锂的脱出持续升高，尤其是在高电位下发生的 $\text{Ni}^{3+} \rightarrow \text{Ni}^{4+}$ 和 $\text{Co}^{3+} \rightarrow \text{Co}^{4+}$ 的变化，其可逆性比较差，给材料的电化学性能带来了负面影响。另外在高脱锂状态下，晶格氧会形成具有活性的氧物种，如： $\text{O}_2^-$ ,  $\text{O}^-$ ,  $\text{O}_2^{2-}$ ，它们会逐渐失去电子形成 $\text{O}_2$ ，进而发生吸附于材料表面甚至脱出氧气的不可逆变化，既打破了材料原来的物料平衡，也会在表面形成阻挡层，影响放电时锂的嵌入。因此如何控制高脱锂状态下过渡金属离子以及氧物种的不可逆变化，是该材料进一步提高电化学性能应该解决的问题。

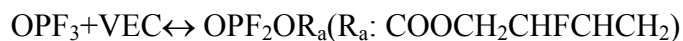
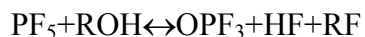
同时相对于 $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ，在保证容量性能的前提下，由于降低了钴的相对含量而进一步降低了成本， $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$ 被认为具有了更好的商业化应用前景，那么材料存储过程中的稳定性就成为一个有意义的研究课题。本文选择4种不同的条件来储存 $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$ (放置在空气中；在空气氛恒温恒湿条件下；在Ar气氛手套箱里；在空气氛除去 $\text{CO}_2$ 的条件下)，通过对比它们存储2个月和8个月后的性能差别来确定该材料的最优储存条件。

实验结果表明，该材料在空气中的储存性能突出，颗粒表面基本不与空气中的 $\text{CO}_2/\text{H}_2\text{O}$ 发生反应，电化学性能保持良好。但是由于除氧环境(手套箱)提供的氧分压非常低，导致材料表面的氧物种处于非稳定的环境中，易于脱出；为了达到晶格中的电荷平衡，部分过渡金属Mn离子和Co离子就相应降低它们的氧化态而变得活泼性增强，参与电极反应，并溶解到电解液中去。这一不可逆变化使材料表面组分的平衡被打破，导致材料循环稳定性随之降低。因此选择与合成时高温烧结相同的氛围应更有助于材料性能的保持，将该材料生产出来以后只需要进行普通包装，相对那些必须真空包装的材料简化了生产过程，降低了成本。

另外，在对正极的研究中发现，由于这些高电位型正极材料的投入使用对电解液体系也提出了新要求，如何提高电解液在高电位下的稳定性和高温性能等成为拓展锂离子电池应用领域的关键。基于此目的，本文选择碳酸乙烯亚乙酯(VEC)作为锂离子电池电解液添加剂，研究它对正极材料性能的影响，并使用DEMS装置对其改善电池体系的作用机制进行了深入的探讨。

实验表明在 $\text{LiPF}_6/\text{EC}+\text{DMC}$ 的电解液体系中添加2%的VEC能够有效改善锂离子电池正极材料 $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ 的电化学性能，特别是高温( $50^\circ\text{C}$ )下工作的循

环稳定性。它是通过先于 DMC、EC 同  $\text{OPF}_3$  发生反应，抑制本来存在的电解液分解反应来达到的，具体的反应进程为：



反应生成的  $\text{OPF}_2\text{OR}_a (\text{R}_a: \text{COOCH}_2\text{CHFCHCH}_2)$ ；VEC 上的  $\text{C}=\text{C}$  在高温下聚合而成的网状聚合物；以及由 DMC 同  $\text{OPF}_2\text{OR}$  之间不能完全避免的反应产物  $\text{OPFR}_b (\text{R}_b: \text{CH}_2\text{OCOOCH}_3) \text{OCOOCH}_2\text{CHFCHCH}_2$  等一类大分子，少量这类大分子并不会给电池的电化学性能带来负面效应，相反却能成为 SEI 层的有效成分，附于电极(正极)表面，改善电极的表面组成，隔离电极材料和电解液特别是其一系列不稳定分解产物的进一步接触，它们的存在对电池电化学性能的改善起到积极的作用。

**关键词：**锂离子电池、 $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$  正极材料、首次不可逆容量损失、化学脱锂、储存性能、差分电化学质谱、电解液添加剂、VEC

## Abstract

### **The Investigation of $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ as Cathode Materials and their corresponding Electrolyte Additive for Lithium-ion Batteries**

Recently,  $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$  material has become one of the promising cathode material systems for their high capacity, low cost, environmental-friendly, good thermal stability and stable cyclic performance in the lithium ion batteries. In this thesis, two kinds of material in this family, such as  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  and  $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$  with excellent electrolyte performance have been synthesized. Their structure, surface properties, thermal stability and storage performance were also studied in detail by various electrochemical methods and spectral techniques, including structural analysis, surface analysis, thermal analysis and electrochemical techniques. In particular, the origination of the first irreversible capacity of  $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ , and the storage performance of  $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$  were also emphasized.

In addition, we have designed and set up Differential Electrochemical Mass Spectrometer (DEMS) for the first time in the lab for Li-ion batteries study, e.g. investigation of the improvement mechanism of VEC as the electrolyte additive.

$\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  and  $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$  cathode were prepared by sol-gel method and a mixed-hydroxide method with the sintering temperature of 850-900°C, respectively. The oxidation state of Ni, Co and Mn are +2, +3 and +4, both of them have good thermal stability. The electrochemical performances of the materials are excellent, especially at high charging voltage. They all delivered a capacity over 200 mAh/g in the 1<sup>st</sup> discharge process when circling at 18 mA/g between 2.5 V and 4.6 V, and still maintain more than 70% after charge-discharge 60 cycles.

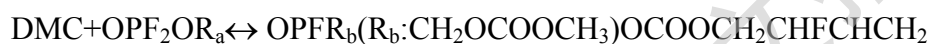
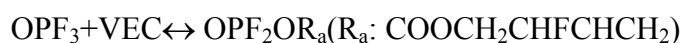
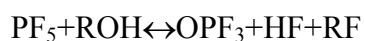
However  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  loses 23% capacity in the first cycle, it is a big problem which affect its practical application. In order to make clearly of this

origination, we took the  $\text{NO}_2\text{BF}_4$  as oxidize, quantitatively extracted some lithium ions from the material which could avoid the interference of carbon, PVDF and current collector in the electrochemical analysis. The reaction is:  $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2 + m \text{NO}_2\text{BF}_4 \rightarrow \text{Li}_{1-m}\text{Ni}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2 + m\text{NO}_2 + m\text{LiBF}_4$ . The investigated results of this series of chemical delithium sample shown that  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  is able to keep its single phase during delithiation process. Oxidation states of Ni and Co increase to +4 when charging the material to high voltage ( $V \geq 4.3\text{V}$ ) i.e.  $\text{Ni}^{3+} \rightarrow \text{Ni}^{4+}$  and  $\text{Co}^{3+} \rightarrow \text{Co}^{4+}$ . These changes happened at the first cycle are partly irreversible, which may cause negative effects on the electrochemical performance of the material. Simultaneously, the active oxygen species such as  $\text{O}_2^-$ ,  $\text{O}^-$ ,  $\text{O}_2^{2-}$  will lose some electrons to form  $\text{O}_2$ , or immigrate to the surface of material at higher charging voltage. Parts of them even release from the delithiated materials. These irreversible changes also break the balance of charge and species in the original materials, affecting insertion of lithium ions into delithiated materials when it is discharged. These results will be very helpful to understand the structural changes of the materials and chemical activity of the lattice oxygen species during the electrochemical delithiation process in  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  cathode materials.

The storage stability of  $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$  material was studied by comparing four materials which stored at different conditions (like exposing to air, or placing in glove box, or storing in a box maintained at  $35^\circ\text{C}$  and 45% HR, or storing in a airtight bottle without  $\text{CO}_2$  which was also put into an incubator) for two and eight months. It is proved that the surface reaction between samples and  $\text{CO}_2/\text{H}_2\text{O}$  is so negligible that it could not affect the electrochemical performance of the materials. However the sample stored in the glove box has shown the worst cycle stability because of the oxygen release from the material surface. After that the Mn and Co ions will decrease their oxidation states, take part in the electrode reaction, and dissolve into electrolyte. The regular ion arrangement on the surface may be destroyed, and the cycle performance of the material becomes poorer. So keeping the storage atmosphere same as the synthesis condition would be a scientific choice for batteries materials. There is no especial request like vacuum-pack for  $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$  material which will be

very valuable for its practical use.

In the end of this thesis, the reason of improvement of VEC as an electrolyte additive was also investigated through the DEMS method. It is proved that adding 2 % VEC to  $\text{LiPF}_6/\text{EC}+\text{DMC}$  electrolyte can significantly improve the cyclic performance of  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  cathode material at elevated temperature such as  $50\text{ }^\circ\text{C}$ . It works through former reacted with  $\text{OPF}_3$  before EC and DMC, which would suppress the decomposition of electrolyte, the possible reactions are:



In summary, the products of  $\text{OPF}_2\text{OR}_a$ , the net high-polymer molecule from self-polymerized of VEC, and  $\text{OPFR}_b\text{OCOOCH}_2\text{CHFCH}_2$  from the unavoidable reaction between DMC and  $\text{OPF}_2\text{OR}_a$  are helpful in forming a stable SEI layer. It could prevent subsequent decomposition of the electrolyte during charge/discharge process, and improve the electrochemical performance of the batteries.

**Key words:** Lithium ion batteries,  $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$  cathode materials, The first irreversible capacity, Chemical delithiation process, Storage performance, Differential electrochemical mass spectrum, Electrolyte additive, Vinyl Ethylene Carbonate



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