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锂离子电池三元正极材料的首圈分析和改性研究

First cycle analysis and modification study on NMC cathode  
material for lithium ion batteries

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## 摘要

随着对锂离子电池能量密度的要求越来越高，如何进一步提高锂离子电池能量密度是人们面临的挑战。三元正极材料具有较高比容量和成本低等优点，使其在动力电池、储能领域具有很大的应用前景。但是三元材料的首圈不可逆容量损失问题、高电压下循环性能差以及倍率性能不好等问题仍亟待解决。

本文选择  $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$  材料为研究对象，初步分析了三元材料在循环过程中首圈不可逆容量损失的原因，并采用包覆改性的方法，探究包覆对库伦效率的影响及提高材料在高电压下的电化学性能。主要内容如下：

1. 对材料的首圈充放电过程以及材料表面及结构变化进行分析，表明充放电过程首圈不可逆容量损失来源于两方面：高电位下副反应和充放电过程材料自身动力学因素导致的不可逆容量损失；

2. 利用原位 XRD 表征进一步分析了首圈充放电过程的不可逆结构变化；通过分析低电位下材料首圈的容量损失，表明材料本身结构和动力学因素是导致容量损失的主要因素，占整个不可逆容量中的 60% 以上，电解液副反应的影响主要体现在高电位(>4.3V)。

3. 研究包覆改性对材料在高电压下电化学性能的影响。通过液相包覆的方法在  $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$  材料表面包覆了偏硼酸锂( $\text{LiBO}_2$ )。研究表明当包覆量为 2wt% 时，对材料的电化学性能提高最明显，在 3.0 V-4.5 V 电压区间，0.2C 倍率下循环 50 周后，放电比容量为  $171.2 \text{ mAh}\cdot\text{g}^{-1}$ ，容量保持率为 91.23%。未包覆改性的材料容量保持率仅为 53.19%；倍率性能测试表明，2wt% 包覆量的材料在 10C 倍率下放电比容量达到  $114.7 \text{ mAh}\cdot\text{g}^{-1}$  是未改性材料同倍率下放电比容量的 2 倍。高温测试表明， $\text{LiBO}_2$  包覆后材料的高温循环性能优于未改性材料。

4. 采用  $\text{Al}_2\text{O}_3$  和岩盐相  $\text{LiTiO}_2$  包覆后，材料电化学性能得到一定程度提高， $\text{Al}_2\text{O}_3$  包覆有效提高了循环性能，0.2C 倍率，50 圈后容量保持率为 90.23%；但是对倍率性能的提升不明显； $\text{LiTiO}_2$  包覆后，材料首圈库伦效率提高到 86.90%，高出未包覆材料近 5%。

**关键词：**  $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ ；高电压；库伦效率；包覆改性

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## Abstract

With the energy density requirements getting higher and higher, further improving the energy density of lithium-ion battery has been a hotspot. However, the problem of irreversible capacity of materials, as well as cycle performance and rate capability at high cutoff potential, remains to be solved.

In this paper,  $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$  was chosen as the object of study, and the reason of the irreversible capacity loss of the NMC material during the cycle was analyzed. The effect of surface coating on the Coulombic efficiency and electrochemical properties of the material under high voltage were investigated. The main contents are as follows:

1. The analysis of the charge/discharge process, the surface and structure of the material shows that the irreversible capacity of the first cycle comes from two aspects: the side reaction and the dynamics factors during charge and discharge process at high potential;
2. In-situ XRD characterization was used to further analyze the irreversible structural changes of the initial charge-discharge process. The capacity loss analysis of the material under different lithium-off conditions at low potential showed that the capacity loss caused by the structural and kinetic factors of the material itself accounts for more than 60% of the total irreversible capacity, the impact of electrolyte side effects is mainly reflected in the high potential ( $> 4.3\text{V}$ ).
3. The effect of coating modification on the electrochemical properties of the material under high voltage was studied.  $(\text{LiBO}_2)$  was coated on the surface of  $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$  by liquid-phase coating. The results showed that the electrochemical performance could be enhanced obviously when the coating amount is 2wt%. After 50 cycle, the discharge specific capacity is  $171.2 \text{ mAh}\cdot\text{g}^{-1}$  in the voltage range of 3.0 V-4.5 V with the capacity retention rate was 91.23% while the capacity retention rate of bare was only 53.19%. The rate test showed that the specific capacity of the 2wt% coating material reached  $114.7 \text{ mAh}\cdot\text{g}^{-1}$  at 10C rate which was almost two times of bare sample. Thermal test showed that the  $\text{LiBO}_2$  coated material

was better than that of unmodified one.

4. The electrochemical performance of the composites was improved by Al<sub>2</sub>O<sub>3</sub> and rock salt LiTiO<sub>2</sub> coating. The Al<sub>2</sub>O<sub>3</sub> coating improved the cycle performance effectively with the capacity retention of 90.23% at 0.2C current after 50 cycles, however, the improvement of the rate capability was not obvious. After LiTiO<sub>2</sub> coating, the efficiency of the initial Coulombic efficiency increased to 86.90%, nearly 5% higher than the uncoated material.

**Keywords:** LiNi<sub>0.5</sub>Mn<sub>0.3</sub>Co<sub>0.2</sub>O<sub>2</sub>; high voltage; coulombic efficiency; surface coating

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