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成膜添加剂及表面包覆对高电压镍锰酸锂正极材料
性能影响的研究

**A study of the influence of film-formation additive and
surface coating on the performance of Lithium Nickel
Manganese Cathode Material**

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摘要

随着能源和环境问题的日益凸显,锂离子电池作为新的储能方式越来越广泛地应用在电动汽车(EV),混合动力电动汽车(HEV)和插入式混合动力电动汽车(PHEV)等领域。为了获得更高的能量密度和功率密度,开发高电压正极材料如 5 V 尖晶石 $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) 和与之相关的基础研究成为锂离子电池研究的重要方向之一。然而,造成 LNMO 容量衰减的因素主要有两个方面: LNMO 的工作电压超出了电解液的电化学窗口 ($<4.5\text{V}$),造成了电解液溶剂的分解,影响了材料的电化学性能; LNMO 材料也存在着金属离子溶解的问题,循环过程中溶解的金属离子在负极还原,消耗有限的活性锂。

针对以上问题,本文分别从电解液成膜添加剂和材料表面包覆两个方面对 5V $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ 锂离子电池性能进行改善,本论文的主要研究集中以下两个方面:

在第三章,通过在电解液中添加成膜添加剂三(三甲基硅烷)磷酸酯(TMSP),研究了 TMSP 对于商业化 $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ 材料性能的影响。LSV 测试表明 TMSP 能够在 4.2V 氧化分解,优先于电解液溶剂分解,在正极表面形成稳定的 SEI。添加 1wt% TMSP 后 LNMO/Li 半电池的常温循环效率略有增加,55°C 循环的首圈放电容量从 111.8 mAh g^{-1} 增加到 120 mAh g^{-1} ,100 圈循环后的效率从 78.3% 增加到 92.5%。EIS 证明了 TMSP 分解形成的界面层具有更低的界面阻抗,XPS 的结果表明了界面阻抗的降低是由于 TMSP 形成的界面层中 LiF 的含量更少。添加 1wt% TMSP 后能够显著减少 LNMO 材料高温存储时金属离子的溶解,Mn 元素的溶解从 65.3ppm 减少到 29.7 ppm, Ni 元素的溶解量从 11.7 ppm 减低到 4.7 ppm。研究结果证明了 TMSP 能够提高 LNMO 基材料电池的电化学性能。

第四章通过氢氧化物共沉淀法合成了类球形 $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ 正极材料。通过一种溶胶凝胶法在 $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ 材料表面包覆了一层具有良好电化学稳定性、热稳定性和耐酸碱性的 CoAl_2O_4 ,合成了 2% $\text{CoAl}_2\text{O}_4@$ LNMO 材料。结果表明 CoAl_2O_4 包覆层有效缓解电解液与电极材料的相互作用,阻止了电解液中 HF 对 LNMO 的攻击,提高了 LNMO 的电化学性能和热稳定性。在 55°C 高温和 5C 高

倍率下，LNMO 循环 100 圈后容量保持率仅为 83.8%，而包覆后的 2% CoAl_2O_4 @LNMO 循环 100 圈后容量保持率提高到 92.4%。 CoAl_2O_4 包覆后，材料的倍率性能也得到提高。CV 和 EIS 表明 CoAl_2O_4 包覆后材料锂离子嵌/脱的可逆性提高，表面电阻的增加减缓。Ni、Mn 离子溶解量测试表明 CoAl_2O_4 包覆抑制了材料金属离子 Mn、Ni 的溶解。DSC 测试结果表明 CoAl_2O_4 包覆层使材料的放热峰向高温推移，减少了放热量，提高了材料的热稳定性。

关键词：镍锰酸锂 三(三甲基硅烷)磷酸酯 添加剂 铝酸钴 包覆

Abstract

With the energy and environmental issues becoming increasingly serious, Lithium-ion batteries (LIBs) are now widely used in portable electronic devices, hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs) and pure electric vehicles (PEVs), etc.. The application of high-voltage cathode material like $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (LNMO) with a 4.7 V voltage platform has been considered as an effective way to increase energy density storage. However, $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ suffers from serious capacity fading in the long-cycle, which is resulted from the oxidative decomposition of electrolyte solvent at high voltage and the “Mn dissolution” problem that is detrimental to the cell performance.

The effect of the film-formation additive Tris(trimethylsilyl) phosphate(TMSP) on the performance of LNMO is investigated in the first part of the paper. TMSP can decompose in the charge process and form a rigid solid interface film on the surface of LNMO which can prevent the further decomposition of the electrolyte. As indicated by the LSV results, oxidative decomposition of TMSP can occur at 4.2 V prior to the potential electrolyte decomposition. The surface film has been confirmed by SEM and XPS analysis. The r. t. capacity performance of LNMO/Li increased slightly. After 1wt% TMSP has been added to the electrolyte, the first discharge capacity of the half-cell increases from 111.8 mAh g^{-1} to 120 mAh g^{-1} , and the efficiency increasing from 78.3% to 92.5% after 100 cycles at 55°C . EIS results show that the interface impedance is lower in the 1wt% TMSP-containing electrolyte compared with the base electrolyte, which is attributed to the less LiF residue in the interface of LNMO as indicated by XPS results. It is clearly illustrated that TMSP can decompose prior to the electrolyte solvent and form a solid and high performance interface compared to the base electrolyte. In addition, the amount of the metal for Mn element dissolution has decreased from 65.3 ppm to 29.7 ppm, while for Ni element dissolution, the amount reducing from 11.7 ppm to 4.7 ppm in the high temperature storage with 1wt% TMSP. This phenomenon can be attributed to the fact that the interface film formed

by TMSP can prevent direct contact between the LNMO and electrolyte and mitigate the corrosion of the cathode caused by HF.

The aluminum cobalt oxides coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) cathode materials are synthesized via a wet-coating method. The surface coating of LNMO with cobalt aluminum oxides (CoAl_2O_4) does not alter its spinel structure, but greatly affects its thermostability properties. The CoAl_2O_4 coating layer can effectively prevent the LNMO from direct contact with electrolyte and corrosion caused by HF. 2% CoAl_2O_4 @LNMO exhibits an excellent high temperature performance. The capacity retention rate of the half-cell is raised from 83.8% to 92.4% by 2% CoAl_2O_4 coating at 55°C at 5C rate after 100 cycles. The rate performance has also been improved by 2% CoAl_2O_4 coating. As indicated by CV and EIS analyses, CoAl_2O_4 coating can improve the reversibility of the electrochemical intercalation/deintercalation of the material and slow down the increase in interface resistance. In addition, the dissolution amounts of the Mn and Ni elements has also been decreased by certain amount of CoAl_2O_4 coating. DSC/TG analysis has suggested that the exothermic peak of the full-charge material has shifted to a higher level, with lower exothermic value, which demonstrates higher stability.

keywords: LNMO; TMSP; additives; CoAl_2O_4 ; coating

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