

镍基三元正极材料储存性能与改性研究进展

孔祥邦， 赵金保

(厦门大学 化学化工学院, 福建 厦门 361005)

摘要:镍基三元正极材料因为其能量密度高、循环性能好等优点越来越受到人们的关注。但是其在空气条件下的储存性能较差,容易和空气中的水分、二氧化碳等成分反应生成杂质,从而较大程度地增加了其在生产、运输和储存过程中的成本。讨论了镍基三元材料在储存过程中发生劣化的原因、劣化的影响以及改进措施,并对镍基三元正极材料储存性能的进一步提升做了展望。

关键词: 锂离子电池; 镍基三元正极材料; 储存性能

中图分类号:TM 912.9

文献标识码:A

文章编号:1002-087 X(2020)04-0613-05

DOI: 10.3969/j.issn.1002-087X.2020.04.034

Progress of storage performance and modification research of nickel-based ternary cathode materials

KONG Xiang-bang, ZHAO Jin-bao

(College of Chemistry and Chemical Engineering, Xiamen University, Xiamen Fujian 361005, China)

Abstract: Nickel-based ternary cathode materials have attracted more and more attention because of their high energy density and good cycle performance. However, their storage performance in air is poor, and it is easy for them to react with moisture, carbon dioxide and other components in air to form impurities, which greatly increases the cost in the production, transportation and storage process. The causes, effects and improvement measures of the deterioration of nickel-based ternary materials during storage process were discussed, and the prospects for further improvement of the storage properties of nickel-based ternary cathode materials were proposed.

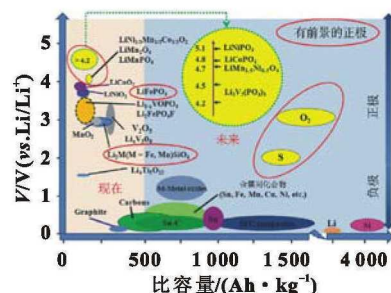
Key words: lithium ion batteries; nickel-based ternary cathode material; storage performance

近年来,随着环境和能源问题的不断加剧,以煤、石油和天然气等传统化石能源为主的能源结构面临着日益严峻的挑战。与此同时,清洁环保的新能源汽车在市场中越来越受到人们的关注,尤其是最近一段时间以来,世界多个国家都制定了逐步禁售传统燃油车的规则和年限,新能源汽车逐步替代传统燃油车的趋势不可阻挡。而新能源汽车的核心组件之一就是动力电源装置,锂电池因为其能量密度高、循环寿命长、自放电小等优势成为了新能源汽车动力电源装置的首选。

在锂离子电池的结构中,正极、负极、隔膜和电解质是其核心组成。其中,正极材料作为锂离子电池的重要组成部分,不仅参与电池的电化学反应,还为电池的循环提供锂离子源,对锂离子电池的容量和成本等有着重要影响^[4]。而在目前阶段,电池中负极材料的质量比容量要普遍高于正极材料的质量比容量,因而提高正极材料的比容量成为了提升电池续航能力的关键。目前常见的锂离子电池正极材料(图1)主要有锰酸锂(LiMnO_2)、尖晶石锰酸锂(LiMn_2O_4)、钴酸锂(LiCoO_2)、镍酸

锂(LiNiO_2), 镍基三元材料($\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$), 磷酸铁锂(LiFePO_4)和富锂锰基材料 $[\text{xLi}_2\text{MnO}_3 \cdot (1-\text{x})\text{LiMO}_2]$ 等。

在众多的正极材料中,镍基三元正极材料因为其相对较高的比容量(图 1)以及较成熟的生产工艺,越来越受到电池厂商的关注。但是对于镍基三元正极材料而言,由于其在空气中储存时,表面会与空气中的成分反应,生成杂质,因而其电化学性能会受到极大影响。本文综述了镍基三元材料在储存过程生成杂质的机理与影响,并对目前储存性能改性的相关研究进行总结与展望。

图 1 目前常见的锂离子电池正极材料对比^[2]

1 镍基三元材料在储存时的劣化

在实际生产过程中,为了使得三元材料保持良好的有序结构,往往会加入稍微过量的钾源,但是 Cho 等^[20]指出,未反应

收稿日期:2019-12-02

基金项目:国家自然科学基金项目(21621091);国家重点研发计划项目(2017YFB0102000)

作者简介:孔祥邦(1994—),男,江苏省人,博士,主要研究方向为锂离子电池用高容量三元正极材料。

通信作者:赵金保

的锂源会附着在三元正极材料的表面,并以 Li_2O 的形式存在,与空气中的 H_2O 和 CO_2 等成分发生反应,形成 LiOH 和 Li_2CO_3 等杂质(图 2)。根据文献[4],本课题组将在 55°C , 80% 相对湿度下存放 28 d 以后的 $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ 材料进行热重测试,结果显示,储存以后的材料在 $35\sim 850^\circ\text{C}$ 的温度区间内会出现三次明显的质量下降,第一次是 $200\sim 500^\circ\text{C}$,第二次为 $668\sim 780^\circ\text{C}$,第三次则发生在高于 800°C 的温度。这一结果与 Zhang 等^[9]的实验结果相一致,并且这三个发生质量下降的温度段分别对应吸附系(碳酸氢盐和易分解的碳酸盐)的解吸及分解, Li_2CO_3 的热分解和活性材料的热分解。

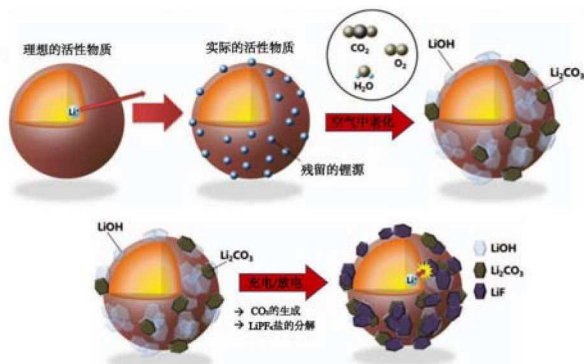


图2 三元正极材料储存失效机理^[9]

与此同时,早在 2004 年,Zhuang 等^[6]就提出,由于长时间暴露在空气中, $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ 颗粒上形成了由 Li_2CO_3 组成的表面附着物。该附着物来自于大气中二氧化碳与材料中的氧化锂残余物的反应以及来自 $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ 活性材料的 Li 反应而形成的,它对锂离子电池中正极的容量和功率特性产生严重的不良影响。非原位 XRD 研究显示在严重污染的正极中具有明显的双峰电荷分布,导致材料的反应非常缓慢。作者进一步提出了由于表面生成 Li_2CO_3 而引起的颗粒分离导致了电极的功率和容量损失的机制。为了进一步验证镍基三元材料在储存时表面生成的杂质的成分,本课题组^[4]使用了红外和拉曼测试(图 3)进行分析。红外测试中,储存前后的材料都出现了 O-H 的伸缩振动峰,主要来自于 LiOH ^[7]。与此同时,储存后的材料出现了明显的 CO_3 的弯曲振动吸收和 C-O 的对称与反对称伸缩振动峰,主要来自于储存后材料表面生成的 Li_2CO_3 ^[6,8]。并且随着储存时间的增加,该波数的吸收峰强度不断增加,说明随着储存时间的延长,表面生成的 Li_2CO_3 量增加。同时在拉曼测试中,也观察到了与储存时间正相关的 Li-OH 和 Li_2CO_3 吸收峰^[9]。综合红外与拉曼的测试结果,我们可以得知,储存之后,在 NCM622 表面杂质有 LiOH 和 Li_2CO_3 两种。因此,在储存过程中, $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ 材料表面生成的杂质主要为吸附系杂质、 LiOH 和 Li_2CO_3 。

一般认为,在 $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ 材料中,Ni 元素的价态为 2+,Co 元素的价态为 3+,Mn 元素的价态为 4+,例如 $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM333) 和 $\text{LiNi}_{1/4}\text{Co}_{1/2}\text{Mn}_{3/4}\text{O}_2$ (NCM424); 在 $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ (Ni/Mn>1) 中,Ni 的价态为 2+ 和 3+,Co 的价态为 3+,Mn 的价态为 4+,例如 $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM523)、 $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NCM622) 和 $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NCM811); 在

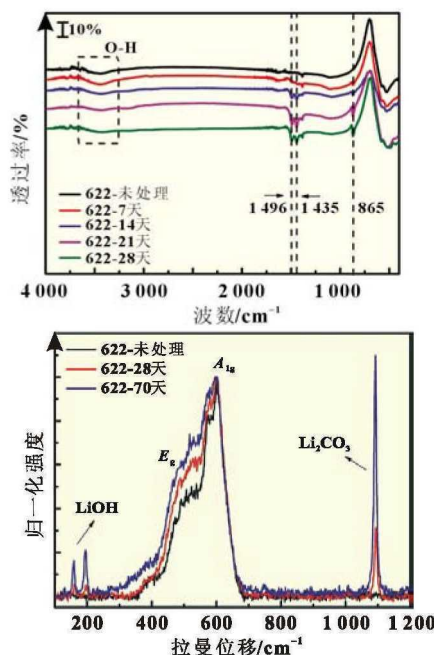


图3 三元正极材料储存前后红外、拉曼测试结果^[4]

$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) 中,Ni、Co、Al 的价态均为 3+。Kenji Shizuka 等^[10]曾经报道,当镍基三元材料中的 Ni^{3+} 含量越高时,材料在空气中储存的稳定性越差,越容易受到空气的影响,导致材料的质量增加更为明显,这一结果也与 You 等^[11]的实验结果相一致。与此同时,Liu 等^[12]也在研究中指出,镍基材料在空气中的劣化机理是 Ni^{3+} 向 Ni^{2+} 的转变,并且在劣化的过程中伴随着晶格锂和晶格氧的脱出。因此,当材料中的 Ni^{3+} 含量更高时,材料更容易和空气中的成分反应,生成杂质,并带来材料结构的转变,如 NCM523^[13]与 NCM622^[4]材料;相反的,当材料中含有更多的 Ni^{2+} 时,材料在空气中的储存更为稳定,不易劣化,如 NCM333^[10]与 NCM424^[14]。

因此,当镍基材料中的 Ni^{3+} 含量较高时,三元材料因为其表面较高的碱度,在空气中储存时容易和空气中的 H_2O 和 CO_2 等成分发生反应,导致劣化,并且容易在表面生成 LiOH 、 Li_2CO_3 以及吸附性杂质。

2 储存劣化对镍基三元材料的影响

2.1 储存对镍基三元材料电化学性能的影响

Cho 等^[15]、Liu 等^[16]、Zheng 等^[17]、Pilgun 等^[18]、Yang 等^[19]在研究中都指出,对于镍基三元材料而言,随着储存时间的增加,三元材料电化学性能衰减严重。原始未进行储存的材料有着良好的循环稳定性,而储存后的材料,在电化学循环过程中,性能会出现断崖式的下跌,并且当储存到达一定时间以后,容量有可能降至 0 左右。对于其他镍基三元材料,电化学性能与储存情况也存在着类似的变化关系,且电化学性能衰减的剧烈程度与材料中镍元素的含量有关,镍元素含量越高,其在储存后的电化学性能衰减越严重,镍元素含量越低,储存对其性能造成的影响则越小。

根据 Lebens 等^[20]报道,当材料表面附着上一些离子/电子导电性较差的异物时,可能会对一些活性颗粒形成隔离效应,从而导致更高的充电电压平台,更低的放电电压平台以及

突然下降的初始放电电压。这一现象在正极材料储存以后同样也会出现^[9,13],主要是因为储存之后材料表面生成的吸附物质及杂质,具有较低的离子/电子导电性,在充放电过程中孤立部分活性颗粒,导致材料的容量下降且极化增加,出现充电平台升高,放电平台下降的现象,从而使得电化学性能降低。而将储存后裂化的材料进行氧气氛围的煅烧,除去表面的杂质成分时,三元材料的电化学性能也能够得到恢复^[4]。因此,镍基三元材料在储存后电化学性能的衰退主要是由于表面低离子/电子导电性的杂质包裹导致部分活性颗粒孤立失活,在除去杂质后,三元材料的电化学性能可得以恢复。

2.2 储存对镍基三元材料结构的影响

镍基三元材料具有典型的 α - NaFeO_2 类型的R-3m的空间群结构^[9,21]。本课题组^[4]将储存前后的三元材料进行了XRD测试,测试结果(见图4)表明,随着储存时间的延长,三元材料(003)晶面的衍射峰向低布拉格角度偏移,且储存的时间越长,偏移的角度越大。一般认为,在镍基三元材料中,(003)晶面衍射峰代表相邻两层过渡金属层对X射线的衍射。Reimers等^[22]、Li等^[23]、Balasubramanian等^[24]、Xiao等^[25]、Dolotko等^[26]都发现,在原位XRD测试中,充电(脱锂)初期,Li的脱出导致相邻的氧层静电斥力增大,层间距增加,最终使过渡金属层间距增大,致

使(003)晶面衍射峰向低布拉格角偏移。因此,存储材料的(003)峰位置向较低角度移动是由于锂离子从晶格迁移出来并在存储过程中形成杂质 Li_2CO_3 和 LiOH ,从而使得氧层之间产生的静电排斥增强并导致过渡金属层间距增大,使材料在某种程度上处于脱锂状态^[27]。

同时,课题组在研究工作中也发现,随着储存时间的增加,在拉曼测试中,镍基三元材料的 A_{1g}/E_g 比值会出现下降的情况。Lanz等^[28]在研究中指出,由于锂的脱出,局部的 $\nu(\text{MO}_6)$ 模式受到影响, A_{1g} 振动模式更直接地反应此种作用, E_g 模式受到的影响较小,因此在充电初期, LiMO_2 的 A_{1g} 振动模式的强度迅速衰减,而 E_g 振动模式保持稳定, A_{1g}/E_g 的强度比值迅速下降。储存以后的材料的 A_{1g}/E_g 比值较原始材料降低,说明在储存过程中表面晶格的锂脱出。因此,从XRD和拉曼的测试结果,我们都可以看出,储存会导致镍基三元材料中晶格锂的脱出,造成结构的破坏。

3 镍基三元材料储存性能的改性研究

随着镍基三元材料越来越受到人们的关注,其在商业市场上的生产规模也在不断扩大,而在生产、运输和储存过程中,材料和空气的接触很难避免,因此,改进镍基三元材料的储存性能就显得尤为重要。

为了提高镍基三元材料的储存性能,人们一般采用表面包覆的方法。包覆可以有效阻隔镍基三元材料表面与空气的接触,很大程度上抑制材料表面和正极材料之间的反应。按照包覆物质的种类进行划分,可以将包覆分为无机包覆与有机包覆,其中,无机包覆又可以分为非锂活性物质与锂活性物质包覆。对于非锂活性物质而言,一般为金属氧化物,如 Al_2O_3 ^[29-35]、 MgO ^[36-37]、 ZnO ^[38-39]等;非金属氧化物,如 SiO_2 ^[40-44]等;金属或非金属其他化合物,如 MPO_4 ^[45-47]、 AlF_3 ^[48-50]等。锂活性物质包覆一般会在材料表面包覆一层锂离子导体,并且这部分包覆物质会贡献一部分容量,例如 LiCoO_2 ^[16,51]、 Li_2ZrO_3 ^[52-53]、 LiMPO_4 ^[47,54-55]等。有机包覆则往往会选择在材料表面包覆上一层导电有机物,如 PPy ^[56-58]和 PEDOT ^[30,59]等。例如,Liu等^[16,60]在NCA表面包覆一层 LiCoO_2 ,在常温空气中的储存性能得到明显改善。Pilgun等^[18]使用尖晶石 $\text{LiMn}_{1.9}\text{Al}_{0.1}\text{O}_4$ 在 $\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ 表面形成一层包覆层,在空气中存放一个月后电化学性能仍然得到了较好的保持。Zhang等^[61]在 $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ 表面包覆一层 Li_2MnO_3 ,在空气中储存两个月后,与原材料相比,表面生成的杂质质量大幅减小,电化学性能也有很大的提升。本课题组近日开发出一种简单有效且能大规模使用的提高镍基三元材料的储存性能的方法,预先将导电剂颗粒与三元材料进行共混,并进行一定温度的煅烧,利用导电剂颗粒细小的特点,将其填充进三元材料一次颗粒的间隙之间,抑制三元材料在储存中与空气反应的活性位点,从而极大提升了三元材料的储存性能^[62]。

4 总结与展望

随着人们对于锂离子电池续航里程要求的不断增加,高容量的镍基三元正极材料越来越受到人们的青睐,而在获得

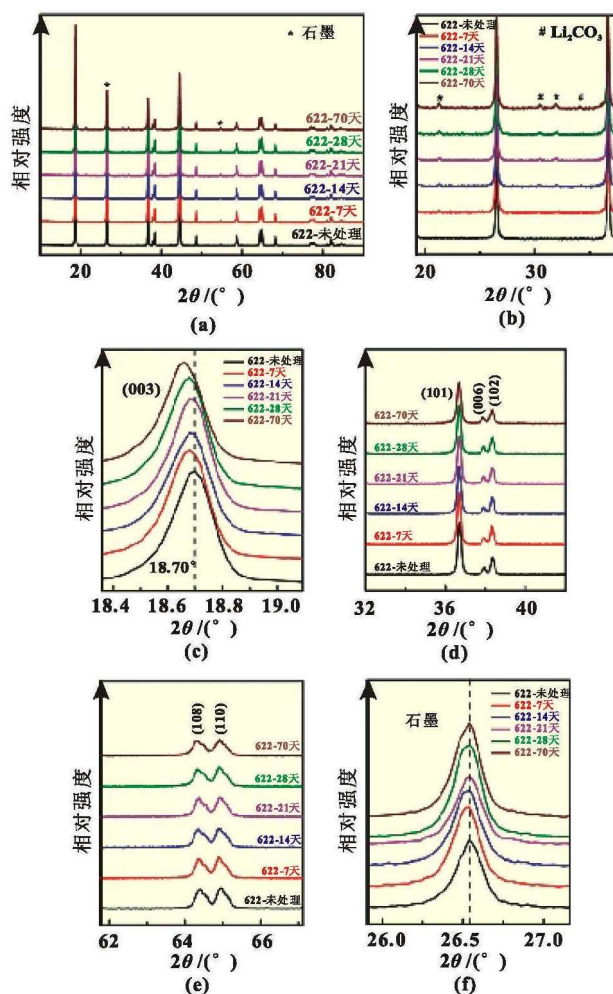


图4 三元正极材料储存前后XRD测试结果^[4]

其容量优势的同时,欠佳的储存性能也给实际生产带来不便。镍基三元正极材料因为其表面残碱的存在,在空气中暴露存放时会与水分、二氧化碳等成分反应,生成 Li_2CO_3 、 LiOH 以及吸附性杂质,这些杂质的存在破坏了正极材料的结构,降低了材料活性,并带来了电化学性能的极大衰退。因此,对于镍基三元正极材料的储存性能改性研究已经刻不容缓。虽然目前在该领域已经有了一些研究进展,但是这些改性手段仍然存在着工艺复杂、难以在实际生产中使用等问题。针对镍基三元正极材料储存性能的改性,不仅需要有效提升其储存性能,还需要做到工艺简单、利于实际生产,仍然需要研究者们做出进一步的努力。

参考文献:

- ARMAND M, TARASCON J M. Building better batteries [J]. *Nature*, 2008, 451: 652-657.
- XU J, DOU S, LIU H, et al. Cathode materials for next generation lithium ion batteries [J]. *Nano Energy*, 2013, 2(4): 439-42.
- CHO D H, JO C H, CHO W, et al. Effect of residual lithium compounds on layer Ni-rich $\text{Li}[\text{Ni}_{0.7}\text{Mn}_{0.3}]\text{O}_2$ [J]. *Journal of the Electrochemical Society*, 2014, 161(6): A 920-A 926.
- CHEN Z, WANG J, HUANG J, et al. The high-temperature and high-humidity storage behaviors and electrochemical degradation mechanism of $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode material for lithium ion batteries [J]. *Journal of Power Sources*, 2017, 363: 168-176.
- LIU H, YANG Y, ZHANG J. Investigation and improvement on the storage property of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ as a cathode material for lithium-ion batteries [J]. *Journal of Power Sources*, 2006, 162(1): 644-650.
- ZHUANG G V, CHEN G, SHIM J, et al. Li_2CO_3 in $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathodes and its effects on capacity and power [J]. *Journal of Power Sources*, 2004, 134(2): 293-297.
- XIONG X, WANG Z, YUE P, et al. Washing effects on electrochemical performance and storage characteristics of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ as cathode material for lithium-ion batteries [J]. *Journal of Power Sources*, 2013, 222: 318-325.
- OSTROVSKII D, RONCI F, SCROSATI B, et al. Reactivity of lithium battery electrode materials toward non-aqueous electrolytes: Spontaneous reactions at the electrode-electrolyte interface investigated by FTIR [J]. *Journal of Power Sources*, 2001, 103(1): 10-17.
- ZHANG X, JIANG W J, ZHU X P, et al. Aging of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ cathode material upon exposure to H_2O [J]. *Journal of Power Sources*, 2011, 196(11): 5102-5108.
- SHIZUKA K, KIYOHARA C, SHIMA K, et al. Effect of CO_2 on layered $\text{Li}_{1-x}\text{Ni}_{1-2x}\text{Co}_x\text{M}_2\text{O}_2$ ($\text{M}=\text{Al}, \text{Mn}$) cathode materials for lithium ion batteries [J]. *Journal of Power Sources*, 2007, 166(1): 233-238.
- YOU Y, CELIO H, LI J, et al. Modified high-nickel cathodes with stable surface chemistry against ambient air for lithium-ion batteries [J]. *Angewandte Chemie*, 2018, 57(22): 6480-6485.
- LIU H S, ZHANG Z R, GONG Z L, et al. Origin of deterioration for LiNiO_2 cathode material during storage in air [J]. *Electrochemical and Solid-State Letters*, 2004, 7(7): A 190.
- CHEN Z, LIU C, SUN G, et al. Electrochemical degradation mechanism and thermal behaviors of the stored $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ cathode materials [J]. *ACS Appl Mater Interfaces*, 2018, 10(30): 2554-2564.
- LI J, ZHENG J M, YANG Y. Studies on storage characteristics of $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$ as cathode materials in lithium-ion batteries [J]. *Journal of the Electrochemical Society*, 2007, 154(4): A 427-A 432.
- EOM J, KIM M G, CHO J. Storage characteristics of $\text{LiNi}_{0.8}\text{Co}_{0.1-x}\text{Mn}_{0.1-x}\text{O}_2$ ($x=0, 0.03$, and 0.06) cathode materials for lithium batteries [J]. *Journal of the Electrochemical Society*, 2008, 155(3): A 239.
- LIU W, HU G, DU K, et al. Enhanced storage property of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ coated with LiCoO_2 [J]. *Journal of Power Sources*, 2013, 230: 201-206.
- ZHENG X, LI X, WANG Z, et al. Investigation and improvement on the electrochemical performance and storage characteristics of LiNiO_2 -based materials for lithium ion battery [J]. *Electrochimica Acta*, 2016, 191: 832-840.
- OH P, SONG B, LI W, et al. Overcoming the chemical instability on exposure to air of Ni-rich layered oxide cathodes by coating with spinel $\text{LiMn}_{1.5}\text{Al}_{0.5}\text{O}_4$ [J]. *Journal of Materials Chemistry A*, 2016, 4(16): 5839-5841.
- LI J, ZHENG J M, YANG Y. Studies on storage characteristics of $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$ as cathode materials in lithium-ion batteries [J]. *Journal of the Electrochemical Society*, 2007, 154(5): A 427.
- LEBENS-HIGGINS Z W, SALLIS S, FAENZA N V, et al. Evolution of the electrode-electrolyte interface of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ electrodes due to electrochemical and thermal stress [J]. *Chemistry of Materials*, 2018, 30(3): 958-969.
- JUNG S K, GWON H, HONG J, et al. Understanding the degradation mechanisms of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ cathode material in lithium ion batteries [J]. *Advanced Energy Materials*, 2014, 4(1): 1300787.
- REIMERS J N, DAHN J R. Electrochemical and in situ x-ray diffraction studies of lithium intercalation in Li_xCoO_2 [J]. *Journal of the Electrochemical Society*, 1992, 139(8): 2091-2097.
- LI W, REIMERS J N, DAHN J R. In situ x-ray diffraction and electrochemical studies of $\text{Li}_{1-x}\text{NiO}_2$ [J]. *Solid State Ionics*, 1993, 67(1/2): 123-130.
- BALASUBRAMANIAN M, SUN X W, YANG X Q, et al. In situ x-ray diffraction and x-ray absorption studies of high-rate lithium-ion batteries [J]. *Journal of Power Sources*, 2001, 92(1/2): 1-8.
- XIAO Q Y, MCBREEN J, YOON W S, et al. Crystal structure changes of $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ cathode materials during charge and discharge studied by synchrotron based in situ XRD [J]. *Electrochemistry Communications*, 2002, 4(8): 649-654.
- DOLOTKO O, SENYSHYN A, MÜHLBAUER M J, et al. Understanding structural changes in NMC Li-ion cells by in situ neutron diffraction [J]. *Journal of Power Sources*, 2014, 255: 197-203.
- VILLEVIEILLE C, LANZ P, BÜNZLI C, et al. Bulk and surface analyses of ageing of a 5 V-NCM positive electrode material for lithium-ion batteries [J]. *Journal of Materials Chemistry A*, 2014, 2(18): 6488.
- LANZ P, VILLEVIEILLE C, NOVÁK P. Ex situ and in situ Raman microscopic investigation of the differences between stoichiometric LiMO_2 and high-energy $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($\text{M}=\text{Ni}, \text{Co}, \text{Mn}$) [J]. *Electrochimica Acta*, 2014, 130: 206-212.
- LAI F, ZHANG X, WANG H, et al. Three-dimension hierarchical Al_2O_3 nanosheets wrapped LiMn_2O_4 with enhanced cycling stability as cathode material for lithium ion batteries [J]. *ACS Appl Mater Interfaces*, 2016, 8(33): 21656-21665.
- LEE Y S, SHIN W K, KANNAN A G, et al. Improvement of the cycling performance and thermal stability of lithium-ion cells by double-layer coating of cathode materials with Al_2O_3 nanoparticles and conductive polymer [J]. *ACS Appl Mater Interfaces*, 2015, 7(25): 13944-13951.

- [31] SHI Y, ZHANG M, QIAN D, et al. Ultrathin Al_2O_3 coatings for improved cycling performance and thermal stability of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ Cathode Material [J]. *Electrochim Acta*, 2016, 203:154-161.
- [32] BETTGE M, LI Y, SANKARAN B, et al. Improving high-capacity $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ -based lithium-ion cells by modifying the positive electrode with alumina [J]. *Journal of Power Sources*, 2013, 233:346-357.
- [33] RILEY L A, VAN ATTA S, CAVANAGH A S, et al. Electrochemical effects of ALD surface modification on combustion synthesized $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ as a layered-cathode material [J]. *Journal of Power Sources*, 2011, 196(6): 3317-3324.
- [34] CAO Z, LI Y, SHI M, et al. Improvement of the cycling performance and thermal stability of lithium-ion batteries by coating cathode materials with Al_2O_3 nano layer [J]. *J Electrochem Soc*, 2017, 164(2): A 475-A 481.
- [35] SCOTT I D, JUNG Y S, CAVANAGH A S, et al. Ultrathin coatings on nano- LiCoO_2 for Li-ion vehicular applications [J]. *Nano Lett*, 2011, 11(2): 414-418.
- [36] OH S M, OH S W, YOON C S, et al. High-performance carbon- LiMnPO_4 nanocomposite cathode for lithium batteries [J]. *Adv Funct Mater*, 2010, 20(19): 3260-3265.
- [37] SHIM J H, LEE S, PARK S S. Effects of MgO coating on the structural and electrochemical characteristics of LiCoO_2 as cathode materials for lithium ion battery [J]. *Chem Mater*, 2014, 26(8): 2537-2543.
- [38] KONG J Z, REN C, TAI G A, et al. Ultrathin ZnO coating for improved electrochemical performance of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ cathode material [J]. *Journal of Power Sources*, 2014, 266:433-439.
- [39] FANG T, DUH J G, SHEEN S R. Improving the Electrochemical Performance of LiCoO_2 cathode by nanocrystalline ZnO coating [J]. *J Electrochem Soc*, 2005, 152(9): A 1701.
- [40] HONG W, MING-CAI C. Modification of LiCoO_2 by surface coating with $\text{MgO/TiO}_2/\text{SiO}_2$ for high-performance lithium-ion battery [J]. *Electrochem Solid-State Lett*, 2006, 9(2): A 82-A 85.
- [41] MOHAN P, KALAIANAN G P. Electrochemical behaviour of surface modified SiO_2 -coated LiNiO_2 cathode materials for rechargeable lithium-ion batteries [J]. *Journal of Nanoscience and Nanotechnology*, 2013, 13(4): 2765-2770.
- [42] CHO W, KIM S M, SONG J H, et al. Improved electrochemical and thermal properties of nickel rich $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode materials by SiO_2 coating [J]. *Journal of Power Sources*, 2015, 282: 45-50.
- [43] CHO Y, CHO J. Significant improvement of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathodes at 60 °C by SiO_2 dry coating for Li-ion batteries [J]. *J Electrochem Soc*, 2010, 157(6): A625.
- [44] ZHOU P, ZHANG Z, MENG H, et al. SiO_2 -coated $\text{LiNi}_{0.95}\text{Co}_{0.05}\text{Al}_{0.01}\text{O}_2$ cathode material for rechargeable Li-ion batteries [J]. *Nano-scale*, 2016, 8(46): 19263-19269.
- [45] CHO J, KIM Y W, KIM B, et al. A breakthrough in the safety of lithium secondary batteries by coating the cathode material with AlPO_4 nanoparticles [J]. *Angew Chem Int Ed Engl*, 2003, 42(14): 1618-1621.
- [46] CHO J, KIM H, PARK B. Comparison of overcharge behavior of AlPO_4 -coated LiCoO_2 and $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ cathode materials in Li-ion cells [J]. *J Electrochem Soc*, 2004, 151(10): A1707.
- [47] KIM Y, CHO J. Lithium-reactive $\text{Co}_3(\text{PO}_4)_2$ nanoparticle coating on high-capacity $\text{LiNi}_{0.8}\text{Co}_{0.16}\text{Al}_{0.04}\text{O}_2$ cathode material for lithium rechargeable batteries [J]. *J Electrochem Soc*, 2007, 154(6): A495.
- [48] ZHENG J, GU M, XIAO J, et al. Functioning mechanism of AlF_3 coating on the Li- and Mn-rich cathode materials [J]. *Chem Mater*, 2014, 26(22): 6320-6327.
- [49] YANG K, FAN L Z, GUO J, et al. Significant improvement of electrochemical properties of AlF_3 -coated $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ cathode materials [J]. *Electrochim Acta*, 2012, 63:363-368.
- [50] PARK B C, KIM H B, BANG H J, et al. Improvement of electrochemical performance of $\text{Li}[\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}]\text{O}_2$ cathode materials by AlF_3 coating at various temperatures [J]. *Ind Eng Chem Res*, 2008, 47:3876-3882.
- [51] KIM H, LEE S, CHO H, et al. Enhancing interfacial bonding between anisotropically oriented grains using a glue-nanofiller for advanced Li-ion battery cathode [J]. *Adv Mater*, 2016, 28(23): 4705-4712.
- [52] ZHANG J, LI Z, GAO R, et al. High rate capability and excellent thermal stability of Li^+ -Conductive Li_2ZrO_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ via a synchronous lithiation strategy [J]. *The Journal of Physical Chemistry C*, 2015, 119(35): 20350-20356.
- [53] SONG B, LI W, OH S M, et al. Long-life nickel-rich layered oxide cathodes with a uniform Li_2ZrO_3 surface coating for lithium-ion batteries [J]. *ACS Appl Mater Interfaces*, 2017, 9(11): 9718-9725.
- [54] TANG Z F, WU R, HUANG P F, et al. Improving the electrochemical performance of Ni-rich cathode material $\text{LiNi}_{0.815}\text{Co}_{0.15}\text{Al}_{0.035}\text{O}_2$ by removing the lithium residues and forming Li_3PO_4 coating layer [J]. *J Alloys Compd*, 2017, 693:1157-1163.
- [55] LIANG L, JIANG J, JIANG F, et al. An ordered olivine-type LiCoPO_4 layer grown on $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ cathode materials applied to lithium-ion batteries [J]. *J Alloys Compd*, 2017, 695:1993-1997.
- [56] ZHANG P, ZHANG L, REN X, et al. Preparation and electrochemical properties of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ -PPy composites cathode materials for lithium-ion battery [J]. *Synthetic Metals*, 2011, 161(11/12): 1092-1097.
- [57] YANG Y, LIAO X Z, MA Z F, et al. Superior high-rate cycling performance of LiFePO_4/C -PPy composite at 55 °C [J]. *Electrochem Commun*, 2009, 11(6): 1277-1280.
- [58] WANG G X, YANG L, CHEN Y, et al. An investigation of polypyrrole- LiFePO_4 composite cathode materials for lithium-ion batteries [J]. *Electrochim Acta*, 2005, 50(24): 4649-4654.
- [59] JU S H, KANG I S, LEE Y S, et al. Improvement of the cycling performance of $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode active materials by a dual-conductive polymer coating [J]. *ACS Appl Mater Interfaces*, 2014, 6(4): 2546-2552.
- [60] LIU W, HU G, DU K, et al. Synthesis and characterization of LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode materials [J]. *Materials Letters*, 2012, 83:11-13.
- [61] ZHANG H, LI B, WANG J, et al. Effects of Li_2MnO_3 coating on the high-voltage electrochemical performance and stability of Ni-rich layer cathode materials for lithium-ion batteries [J]. *RSC Advances*, 2016, 6(27): 22625-22632.
- [62] KONG X, PENG S, LI J, et al. Pre-blended conductive agent to effectively improve the storage properties of $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode materials [J]. *Journal of Power Sources*, 2020, 448:227445.