



富镍三元层状过渡金属氧化物正极材料的 改性方法研究综述

殷志刚¹, 王 静¹, 郝彦忠², 栗靖琦², 钱 近²

(1.北京智行鸿远汽车有限公司,北京 102202;2.河北科技大学理学院,河北石家庄 050018)

摘 要:富镍三元层状过渡金属氧化物正极材料因具有比容量高、价格低廉以及对环境友好等特性而备受关注,但受锂镍混排、相变反应、产气、微裂纹、过渡金属溶出、表面结构等影响,材料本身存在循环容量衰减等问题。针对正极材料循环容量衰减过快、高温性能不佳等问题,总结了近年来国内外关于富镍三元层状过渡金属氧化物正极材料的改性方法,包括表面包覆材料合成、元素掺杂材料制备、核壳结构材料开发、浓度梯度材料设计等优化方法,指出高镍层状过渡金属氧化物正极材料的应用需要从不断完善材料制备方法、改变材料性状、降低材料成本等方面入手,开发高能量密度的锂离子电池,使富镍三元层状过渡金属氧化物正极材料在动力电池领域尽早得到广泛应用。

关键词:电化学;富镍正极;过渡金属氧化物;改性研究;容量衰减

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Research summary of modification of nickel-rich ternary layered transition metal oxides positive materials

YIN Zhigang¹, WANG Jing¹, HAO Yanzhong², LI Jingqi², QIAN Jin²

(1.Beijing Idrive Automotive Company Limited, Beijing 102202, China; 2. School of Science, Hebei University of Science and Technology, Shijiazhuang, Hebei 050018, China)

Abstract: Nickel-rich ternary layered transition metal oxide positive materials have attracted much attention due to their high specific capacity, low price and environmental friendliness. However, the material itself has problems such as cyclic capacity degradation, which are caused by Li/Ni mixing, phase change reaction, gas generation, microcracks, transition metal dissolution and surface structure changes. In order to solve the problems of rapid capacity degradation and poor high-temperature performance of positive materials, modification methods of nickel-rich ternary layered transition metal oxide positive materials at home and abroad in recent years were summarized, including optimization methods such as surface coating material synthesis,

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第一作者简介:殷志刚(1978—),男,河北唐山人,工程师,博士,主要从事高能量密度电池开发和相关机理方面的研究。

通讯作者:郝彦忠教授。E-mail:yzhao@hebust.edu.cn

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element doping material preparation, core-shell structure material development, and concentration gradient material design, etc. It is pointed out that the wide application of high nickel layered transition metal oxide anode materials needs to start from the aspects of continuously improving the material preparation method, changing the material properties, and reducing the material cost, etc. to develop high energy density lithium ion batteries, so that nickel-rich ternary layered transition metal oxide anode materials can be applied in the field of power batteries as soon as possible.

Keywords: electrochemistry; nickel-rich positive; transition metal oxides; modification research; capacity degradation

当前,人类社会的可持续性发展与能源和环境保护密不可分。社会的快速发展和文明进步需要消耗大量常规化石能源,而常规化石能源的过度消耗又将导致环境恶化,这与环境保护相悖^[1-3]。因此,既要保障社会发展文明进步,又要尽量节省能源,减少碳排放。节能减排的重要方式之一就是大力发展电动汽车产业^[4-5]。锂离子电池(LIBs)作为当前能量密度和功率密度较高的储能装置,在电动汽车领域得到了快速发展^[6-7]。目前,锂离子电池还不能很好地满足电动汽车续航里程的需求。商业化 LIBs 仅具有 $250 \text{ W} \cdot \text{h}/\text{kg}$ 左右的能量密度,对于安装重达 800 kg 电池组的电动车来说相当于额外需要 400 km 的电能储量^[8-9]。毋庸置疑,引入更多的电池可以延长行驶距离,然而车体空间受到压缩以及车身总重量的增加将导致乘坐舒适度的下降和相关运行成本的升高。为满足需求,各国纷纷鼓励开发高能量密度电池^[10-11]。

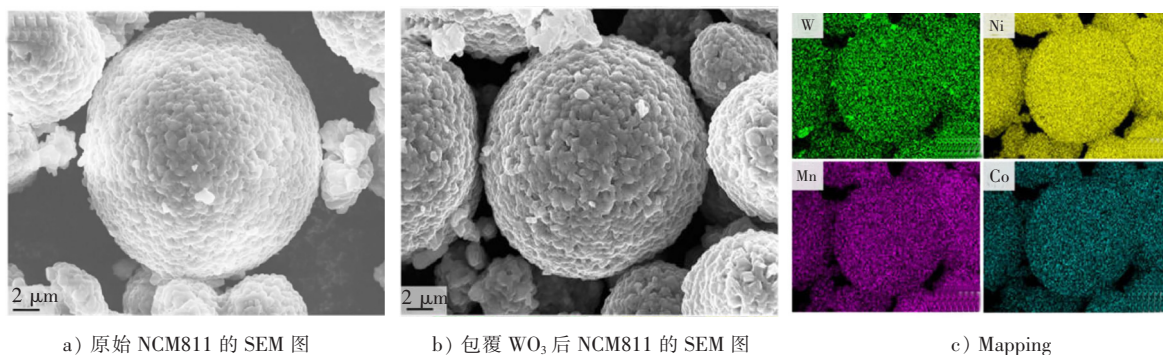
锂离子电池正负极材料的比容量与能量密度直接相关,当正极材料比容量与负极材料比容量相等时,电池具有最佳的能量密度^[12-13]。当前,电池负极材料石墨占比最高,负极石墨材料的比容量在 $355 \text{ mA} \cdot \text{h}/\text{g}$ 左右,而正极材料的比容量要明显低于负极材料的比容量^[14-15],因此,提高正极材料的比容量是比较理想的选择。理想正极材料需要满足以下几方面的特点:一是高的正极电势,确保电池能够提供高的输出电压;二是优良的锂离子可逆插入-脱嵌能力,保证正极材料有较高的可逆容量;三是稳定的材料结构,避免不可逆相转变;四是高离子电子电导性,保证具有高的电流充电、放电性能;五是材料不与电解液反应,并且材料要具有高的电解液兼容性;六是具有低廉的原材料价格、低制备成本和环境友好等特点。当前没有一种正极材料满足上述所有条件,最具优势的材料是富镍三元层状过渡金属氧化物。

富镍 $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ (NCM), $\text{LiNi}_{1-x-y}\text{Co}_x\text{Al}_y\text{O}_2$ (NCA) ($1-x-y \geq 0.6$) 三元层状过渡金属氧化物正极材料表现出比容量高、价格低廉、毒性小等特点,是最具潜力的正极材料体系^[16-20]。尽管富镍三元层状过渡金属氧化物正极材料比容量高,但在循环过程中易发生容量衰减快、高温热稳定性差等问题,增大了富镍材料商业化的难度^[21-23]。这些问题是由于富镍三元层状过渡金属氧化物正极材料在循环过程中发生了相变化^[24-25]、锂镍混排^[26-27]、产气^[28-29]、过渡金属溶出^[30-31]、微裂纹^[32-33]等原因引起的。为了克服这些缺陷,科研工作者尝试了多种方法制备高比容量和高稳定性的正极材料。本文总结了近年来国内外关于富镍三元层状过渡金属氧化物正极材料的改性方法,解决正极材料循环容量衰减过快、高温性能不佳等问题,以期富镍三元层状过渡金属氧化物正极材料在动力电池领域的早日应用提供解决问题的思路。

1 表面包覆材料的合成

富镍三元层状过渡金属氧化物正极材料是最有可能取代 LiCoO_2 成为主流正极的材料,然而这些正极材料普遍存在容量衰减、热稳定性差等问题。大量研究表明,正极材料性能恶化的原因来源于表面结构的变化,因此解决这些问题行之有效的方法是进行表面包覆处理^[34-36]。BECKER 等^[37]采用钨酸铵作为包覆原材料,在大量生产的 NCM811 材料表面包覆一层氧化钨,材料表面的残碱能够与氧化钨反应生成钨酸锂。此方法的优点是既能消耗材料的潜在产气源,又能对材料进行表面包覆。通过 ICP-OES 分析表征,材料的包覆量在 1% 左右。XRD 精修分析结果表明,包覆材料具有更低的阳离子(锂镍)混排程度,因此表面包覆能够加强材料的结构稳定性。图 1 a) 和图 1 b) 是 NCM811 材料未包覆和包覆后的扫描电镜照片,从图 1 b) 能够看到材料表面包覆了一层物质。Mapping 结果见图 1 c),表明 W 元素均匀分布在材料表面,其他元素也是均匀分布。

对包覆前后材料进行的半电池性能测试结果如图 2 所示^[37]。不管是选取 4.3 V 上限截止电压还是 4.5 V 上限截止电压,表面包覆一层氧化钨材料的循环性能都优于未包覆材料的循环性能。在 4.3 V 上限截止电压进行循环时,包覆材料循环次数是未包覆材料循环次数的近 2 倍,即使是 4.5 V 的上限截止电压,包覆材



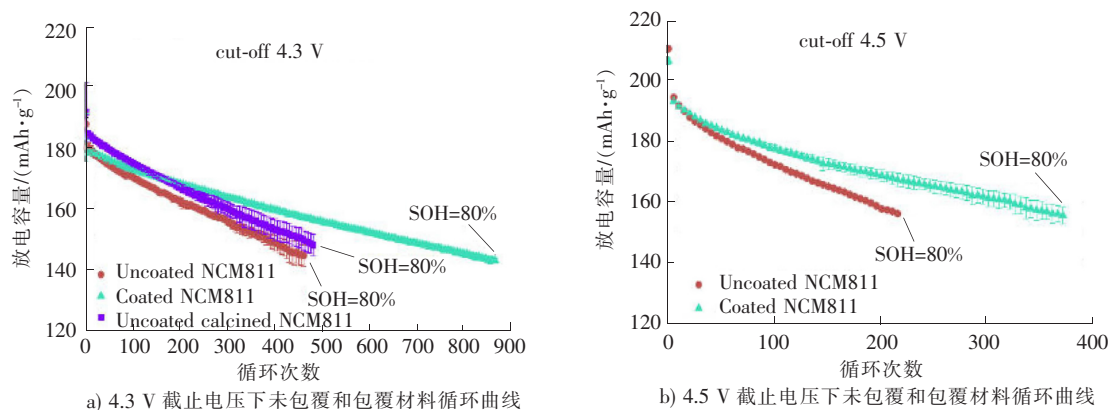
a) 原始 NCM811 的 SEM 图

b) 包覆 WO_3 后 NCM811 的 SEM 图

c) Mapping

图 1 不同样品的 SEM 图

Fig.1 SEM images of different samples



a) 4.3 V 截止电压下未包覆和包覆材料循环曲线

b) 4.5 V 截止电压下未包覆和包覆材料循环曲线

图 2 不同截止电压下未包覆与包覆材料的循环曲线

Fig.2 Cycle curves of uncoated and coated materials at different cut-off voltages

料循环次数也是未包覆材料循环次数的 1.6 倍以上。这表明包覆对改善正极材料起到了显著作用,对于高镍材料而言,包覆能降低材料的锂镍混排,抑制材料不可逆相变化,降低产气。对循环后的材料进行的断面扫描测试结果表明,未包覆材料循环后出现明显通透裂纹,而包覆材料循环后未出现明显微裂纹。因此,对正极材料进行包覆处理能够改善材料的性能。

LIU 等^[38]将硝酸铟溶解到无水乙醇中,再将商业 NCM811 材料加入到完全溶解的硝酸铟-乙醇溶液中,分别配制成 $\text{In}_2\text{O}_3/(\text{In}_2\text{O}_3 + \text{NCM811})$ 质量分数为 1%, 2%, 3% 的溶液。于 100 °C 干燥样品,再于 600 °C 空气氛围下退火制得最终产物。2% 的包覆材料具有最佳形貌,表面未发现缺陷。经过分析表征发现,生成的最终产物相对于未包覆材料的表面残碱量(LiOH 和 Li_2CO_3)更低,且材料的层状结构和原始形貌得到了保持。XRD 和 HRTEM 分析表明材料包覆层为 In_2O_3 和 LiInO_2 。包覆材料的首次库仑效率为 90.86%, 明显大于未包覆材料的首次库仑效率(89.41%), 表明包覆材料表面的副反应要明显小于未包覆材料的副反应。图 3 a) 是材料倍率性能曲线。结果显示, 2% 包覆材料在测试倍率条件下均具有最佳的倍率性能, 表明包覆材料具有更高的离子-电子导电性。选取 1 C 电流密度来对比不同材料的长循环, 发现 2% 的包覆材料性能最佳, 而未包覆材料发生了明显的容量衰减。循环后拆解结果表明, 包覆材料保持初始形貌, 未出现明显微裂纹, 而未包覆材料的微裂纹较为明显。这些结果均表明, 包覆能够改善材料的锂镍混排程度和材料微裂纹。2% 包覆材料在 5 C 电流密度下循环 300 次后仍能保持 86.4% 的容量, 表明表面包覆 In_2O_3 材料对 NCM811 主体材料的性能有明显的改善。除了上述包覆材料外, 还有许多其他材料可用, 如 Al_2O_3 ^[39-41], $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ^[42-43], Li_2TiO_3 ^[44], TiO_2 ^[45], ZrO_2 ^[46] 以及金属氟化物^[47-49] 和金属磷酸盐^[50-52] 等。这些表面包覆材料不仅可以作为电解液与主体材料隔离的保护层, 还能够抑制循环过程中的副反应, 有些包覆层还是优良

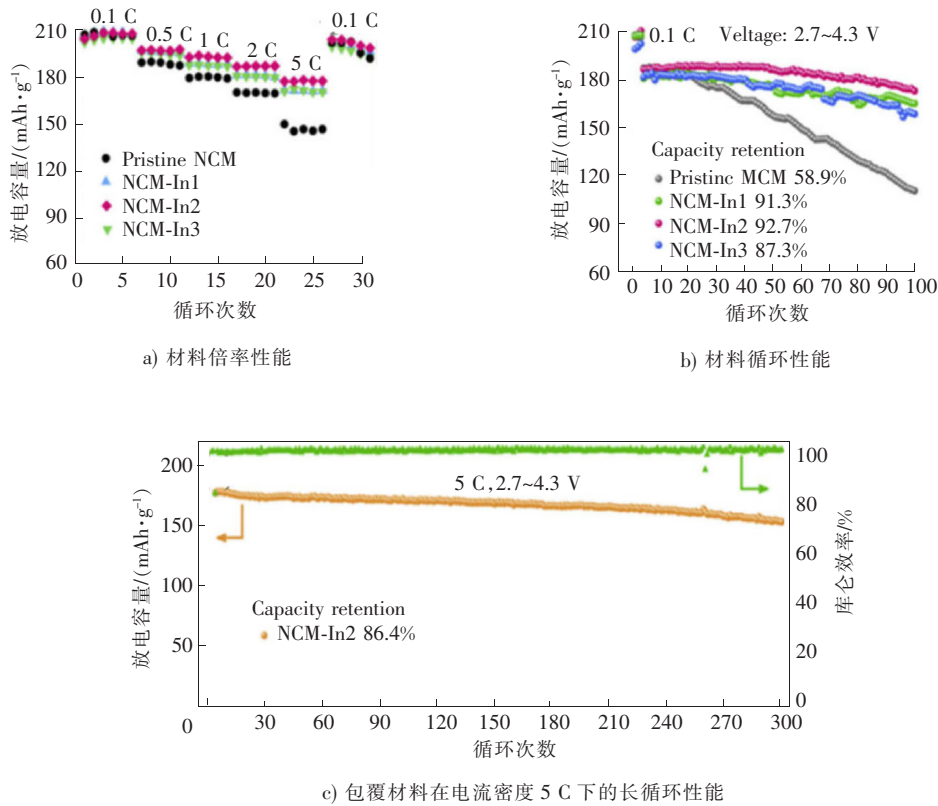


图 3 不同材料倍率性能、循环性能和在 5 C 下的长循环性能

Fig.3 Different material rate performance, cycle performance and long-cycle performance at a current density of 5 C

2 掺杂材料的制备

通常的掺杂元素具有电化学惰性、高极性、适合的离子半径以及与氧具有强键合能力等特点^[53],掺杂元素既包含阳离子也包括阴离子。掺杂具有如下 4 个特点:一是掺杂离子用于取代可移动的 Ni^{2+} 和 Li^+ ^[54];二是能阻碍 Ni^{2+} 进入到锂层^[55];三是通过增强氧-过渡金属键强度,抑制循环过程中的氧释放^[56];四是增加 Ni^{4+} -O 结合能力,抑制在充电末期材料收缩,降低 O_2^- 的斥力^[57]。具有较小离子半径的 Al^{3+} 在高电压电解液中能保持稳定而不被氧化,因此铝作为稳定晶格掺杂剂在 NCM 富镍正极材料中得到了广泛研究。WOO 等^[58]采用共沉积方法制备 $\text{Li}[\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1-x-y}\text{Al}_x\text{Mg}_y]\text{O}_2$ 材料($x, y = 0.0 \sim 0.02$),经过连续不同操作步骤得到最终产物。不同铝、镁含量的 XRD 精修图和循环性能图见图 4。由图 4 a)可知,随着镁铝离子掺入主体材料,在锂层的 Ni 和 Mg 二价离子含量均减小,表明掺杂能够有效降低材料的锂镍混排程度,镁离子的掺杂能够有效降低 c 轴的晶格常数。这些改变将影响 Li-O 和 M-O 的间距(M 代表金属元素),当单独掺入 Al 元素时,随着掺入量的增加,材料的 Li-O 间距逐渐增加,M-O 间距逐渐减小。单独掺入 Mg 元素时,随着掺入量的增加,材料的 Li-O 间距逐渐减小,M-O 间距逐渐增加。当 Al 和 Mg 元素掺入量均为 0.01 时, Li-O 和 M-O 的间距均最小,详细参数见表 1。随着 Al 掺入量的增加,材料的克容量逐渐下降,但材料的稳定性得到了改善,如图 4 b)所示。图 4 c)显示,随着 Mg 掺入量的增加,材料的克容量也逐渐下降,但材料的克容量发挥要明显高于掺入 Al 后克容量的发挥。如果 Mg 与 Al 共掺杂,则能够明显改善材料的稳定性,共掺杂材料的克容量发挥也明显高于单独掺杂材料。通过对不同掺杂量的材料进行热重分析,发现双掺杂材料的热分解温度明显提高,表明材料的热稳定性得到了有效提升。

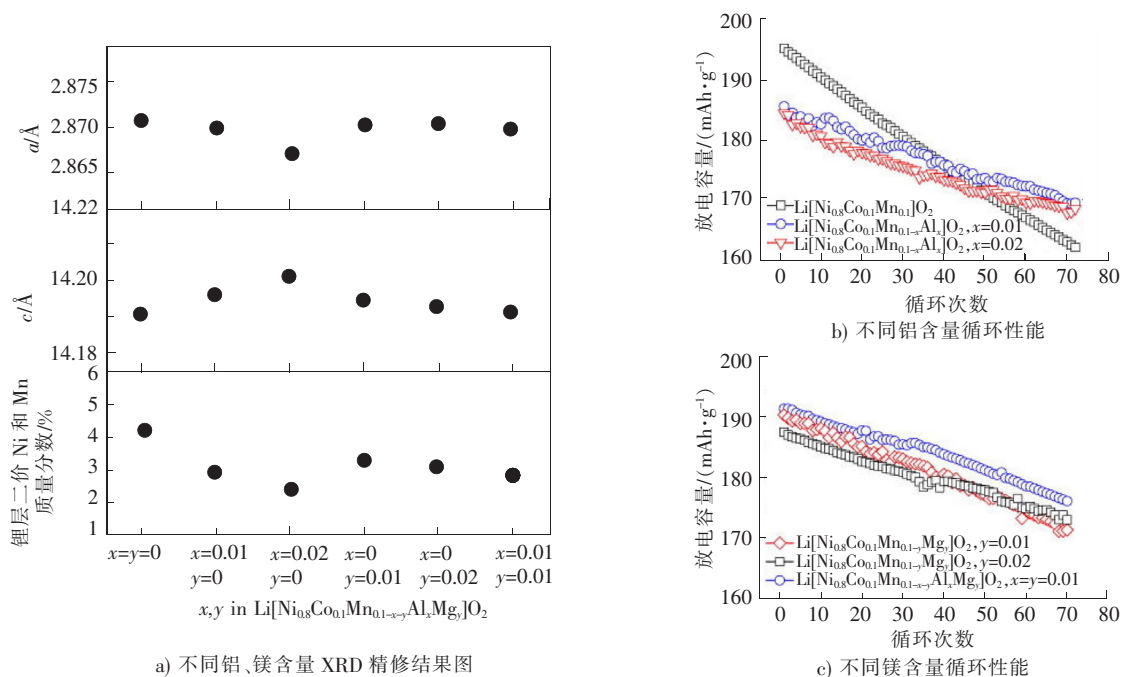


图 4 不同铝、镁含量的 XRD 精修图和循环性能图

Fig.4 XRD and cycle performance graphs of different aluminum and magnesium contents

表 1 XRD 数据计算得出 Li[Ni_{0.8}Co_{0.1}Mn_{0.1-x-y}Al_xMg_y]O₂ 的金属-氧距离 ($x=0\sim 0.02, y=0\sim 0.02$)Tab.1 Data of metal-oxygen distances of Li[Ni_{0.8}Co_{0.1}Mn_{0.1-x-y}Al_xMg_y]O₂ from XRD ($x=0\sim 0.02, y=0\sim 0.02$)

Li[Ni _{0.8} Co _{0.1} Mn _{0.1-x-y} Al _x Mg _y]O ₂	Li-O 距离/ \AA	M-O 距离/ \AA	$R_{wp}/\%$	$R_p/\%$
$x=0, y=0$	2.109 5(13)	1.967 5(11)	8.73	7.64
$x=0.01, y=0$	2.110 8(12)	1.966 2(12)	8.81	7.49
$x=0.02, y=0$	2.111 5(11)	1.964 4(1)	8.03	6.78
$x=0, y=0.01$	2.110 8(13)	1.966 6(11)	8.24	6.69
$x=0, y=0.02$	2.110 4(15)	1.966 8(12)	9.22	7.93
$x=0.01, y=0.01$	2.110 2(11)	1.966 4(12)	8.45	7.02

一些研究人员把锂镍混排定义为阳离子反位^[59-60],认为阳离子反位的形成不利于正极材料的长期循环性。如果锂位的锂被镍替代,将阻塞锂的扩散路径,影响电池的整体性能。LI 等^[61]提出的阳离子反位机理认为,良好的阳离子反位不仅能够提高正极材料的结构稳定性,而且能提供静电斥力,阻碍更多的过渡金属迁移到锂位,因此适当的阳离子反位对电池的整体性能有利。掺杂卤素元素易于形成卤化物局部八面体结构而诱导反位结构的形成,特别是氟元素更为明显。阳离子反位浓度随着卤元素的增加线性提高,但是过高浓度会导致电子的导电性下降,不可逆相变化提高,破坏主体材料的球形形貌。因此适度的掺杂才是最为合理的选择。相分析和密立根充电表明,氟取代和反位能够增加材料的(003)晶面间距,有利于增加锂离子迁移。图 5 展示了 XRD 精修图和带结构图。从图 5 a)可以发现,氟元素的反位形成能最小,更易于形成 Li/Ni 反位。引入导带 E_{cb} 、价带 E_{vb} 和禁带宽度 E_g 的概念可解释电子传输特性,见图 5 b)。禁带宽度 $E_g = E_{vb} - E_{cb}$, E_g 越大,电子传输性越差。经计算发现,未掺杂氟元素主体材料的禁带宽度为 0.026 5 eV,掺杂 1% 氟的材料禁带宽度为 0.049 1 eV,掺杂 2% 氟的材料禁带宽度为 0.059 3 eV。因此掺杂氟元素会降低材料的电子导电性,需结合离子、电子导电性的需要,选择合适的氟掺杂量。研究人员还对氟掺杂量分别为 0%(PRI),1%(5.7%AS),2%(8.2%AS)的材料分别进行了倍率测试,发现 1% 掺杂量的材料具有最佳倍率性能。在高温和室温条件下测试了 0% 和 1% 掺杂量材料在 1 C 电流密度下的循环性能,见图 6。图 6 a)结果显示,掺杂材料在 55 °C 高温循环后期未出现容量快速衰减现象,拆解结果显示掺杂材料循环后形貌得到保持,未出现明显微裂纹,而未掺杂材料循环衰减严重且材料出现明显裂纹。图 6 b)结果显示,掺杂材料在室温时的循环性能要明显优于未掺杂材料,拆解结果显示掺杂材料循环后形貌得到保持,未出现明

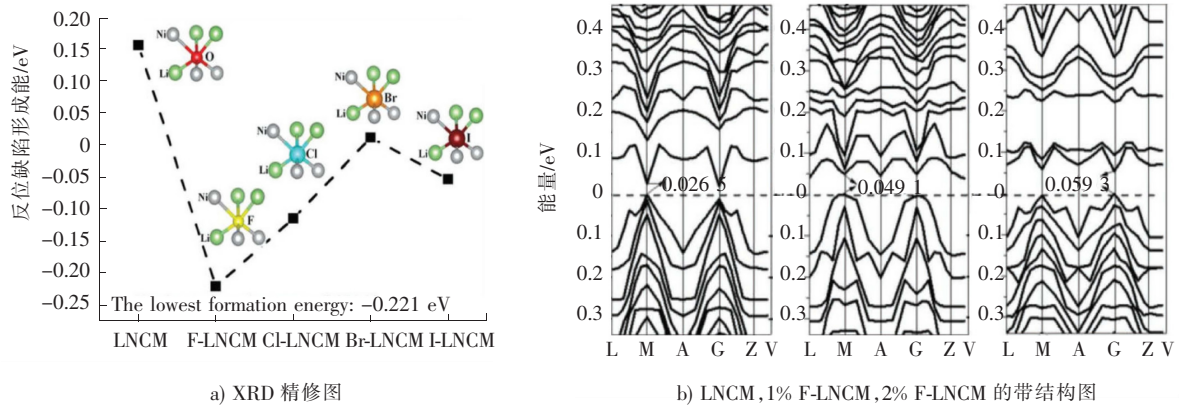


图5 XRD精修图和带结构图

Fig.5 Graphs of XRD rietveld refinement and band structure

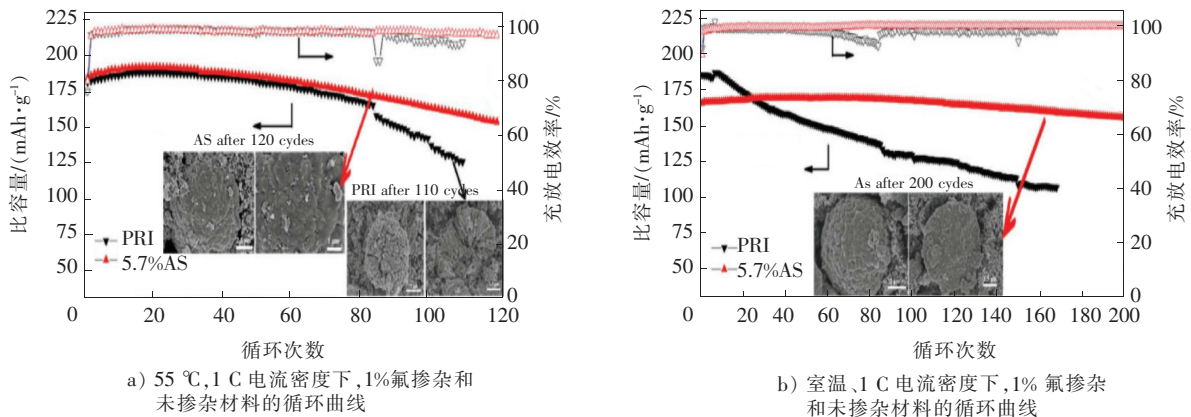


图6 不同温度条件下的1%氟掺杂和未掺杂材料的循环曲线

Fig.6 Cycle curves of 1% F doped and undoped materials at different temperatures

显微裂纹。综上可知,掺杂氟元素能够有效改善材料的高、低温性能。可作为掺杂体的材料还包括 Ga^[62], V^[63], La^[64] 以及碱金属^[65] 等。这些掺杂材料能够有效改变材料的晶格参数,稳定材料层状骨架,改善离子、电子导电性。

3 核壳结构材料的开发

锰材料显示优良的循环稳定性,高镍材料具有高的容量,因此富含镍元素和富含锰元素的壳结构被设计合成来提高富镍材料的循环稳定性。WU 等^[66] 采用在硫酸镍、硫酸钴、硫酸锰的水溶液中加入不同量的丁二酮二脲(C₄H₈N₂O₂)的乙醇溶液,再进行后续过滤、干燥、煅烧等处理得到核壳结构材料。该结构的内核是 LiNiO₂,物质外壳是二价镍离子和四价锰离子居多的 NCM 材料。在 5 C 的电流密度下测试材料的循环性能发现,3% C₄H₈N₂O₂ 条件下的核壳结构具有最佳的循环性能,如图 7 a) 所示,经过 500 次循环后,材料保持 86% 的容量,而 NCM811 材料经过 500 次循环后容量仅为 57%。图 7 b) 和图 7 c) 为 NCM811 材料和 3% C₄H₈N₂O₂ 条件下 NCM811 核壳材料电压-容量曲线,结果表明,NCM811 材料前期容量衰减比较明显,而 NCM811 核壳结构材料前期容量衰减缓慢,后期衰减才增加。NCM811 核壳结构放电电压降仅为 4.18%,而 NCM811 材料放电电压降达到 9.62%,2 倍于核壳结构。测试结果表明,壳层富锰结构能有效降低材料的锂镍混排程度和副反应的发生,核壳结构能够稳定 NCM811 材料的整体结构,进而有利于循环性能的提升。

LONGO 等^[67] 采用理论计算进一步确定了核壳结构具有稳定材料结构的特点。SHIN 等^[68]、DONG 等^[69]、MAENG 等^[70] 也对富镍核壳正极材料进行了合成测试表征,表明核壳结构在缓解正极材料锂镍混排、稳定材料结构、抑制副反应、隔离酸性物质对材料的溶解等方面能够起到有效的改善作用。

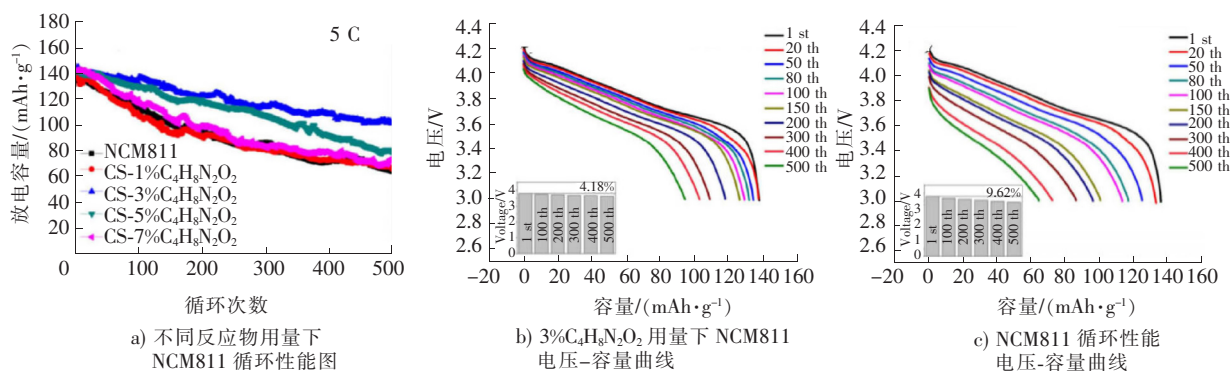


图 7 循环性能图和电压-容量图

Fig.7 Cycle performance graph and voltage-capacity graph

4 浓度梯度材料的设计

设计浓度梯度富镍材料是解决正极过快衰减的另一种有效方法。DUAN 等^[71]设计出 Al 掺杂浓度梯度 $\text{LiNi}_{0.815}\text{Co}_{0.15}\text{Al}_{0.035}\text{O}_2$ 材料(LGNCAO),该材料的特点是从材料的内核到外壳铝元素分布逐渐增加,而材料的镍和钴元素分布逐渐降低。如表 2 所示, $I(003)/I(104)$ 比值是用来确定材料的锂镍混排程度,比值越大,材料的锂镍混排程度越低。非浓度梯度材料(LNCAO)的比值明显小于 LGNCAO 材料,说明 LGNCAO 材料的锂镍混排程度更低。表 2 中的镍在锂位的占比也表明,LGNCAO 材料的锂镍混排程度(0.29)要小于 LNCAO 材料(0.36)。对 LGNCAO 材料进行电子探针微量分析的结果如图 8 a)所示。从中心区域到外层 Co 的原子占比少量降低,而 Ni 的原子占比却下降比较明显,特别是在外层区域更加显著。相反,Al 原子占比从内到外逐渐升高,最外层升高更加明显。这表明材料从内到外 Al 浓度逐渐升高,Ni 浓度梯度逐渐降低。对两种材料的循环测试比较如图 8 b)所示,发现 LGNCAO 材料容量逐渐衰减,而 LNCAO 材料容量衰减特别显著。浓度梯度策略能够有效改善正极富镍材料的容量衰减问题。图 8 c)的阻抗结果表明,LGNCAO 材料较 LNCAO 材料能够更好地在空气条件下稳定存在。SU 等^[72]设计了 NCM811 浓度梯度材料来改善材料的循环性能、倍率性能和热稳定性。其他科研人员也设计合成了不同浓度梯度的正极材料来改善材料的各项性能^[73-75]。相信在不远的将来,随着科技的发展和进步,更多方法会被发现,用来改善富镍正极材料的各项性能。

表 2 非浓度梯度和浓度梯度材料 XRD 精修结果

Tab.2 XRD refinement results of non-concentration gradient and concentration gradient materials

材料	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$I(003)/I(104)$	$d(003)/\text{\AA}$	$d(104)/\text{\AA}$	Ni 在 Li 位的占比/%	$R_{wp}/\%$	$R/\%$
LNCAO	2.867 98	2.867 98	14.185 62	1.735 9	4.728 5	2.034 4	0.36	12.49	8.98
LGNCAO	2.865 68	2.865 68	14.186 02	1.758 3	4.728 7	2.033 4	0.29	11.65	8.58

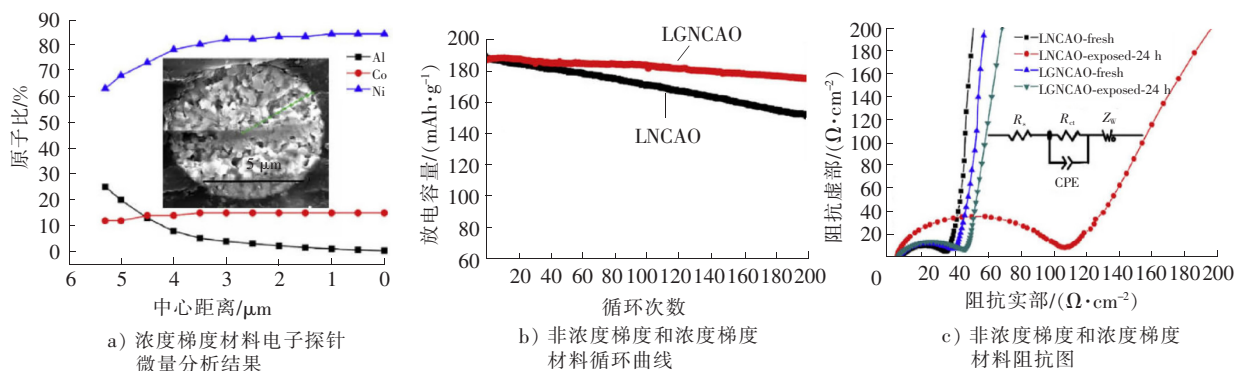


图 8 电子探针微量分析结果、循环曲线和阻抗图

Fig.8 Microprobe analysis results, cycle curves and impedance plots

5 结 语

开发具有高比容量的正极材料是增加电动汽车续航里程最为有效的方法。当前富镍三元层状过渡金属氧化物正极材料 $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ (NCM), $\text{LiNi}_{1-x-y}\text{Co}_x\text{Al}_y\text{O}_2$ (NCA) ($1-x-y \geq 0.6$) 表现出比容量高、价格低廉、毒性小等特点,是最具潜力的正极材料体系。

富镍三元层状过渡金属氧化物正极材料能够满足提升电池能量密度的需求,但需要改善材料本身存在的容量衰减严重的状况,解决锂镍混排、相变反应、产气、微裂纹、过渡金属溶出、表面结构变化等问题,这些问题并非孤立存在而是互为影响的。解决这些问题可从以下几方面入手;一是制备表面包覆材料,降低材料与电解液的接触,进而抑制副反应的发生;二是制备过程中掺杂少量元素,稳定材料层状骨架,改善离子、电子的导电性;三是合成核壳结构材料,缓解正极材料锂镍混排程度,提高材料结构的稳定性,抑制副反应的发生,隔离酸性物质对材料的溶解;四是合成浓度梯度材料,改善材料的循环性能、倍率性能和热稳定性能等。当然还要综合考虑电池的正极、负极材料和电解液的匹配,以及与电池电压的匹配。总之,高镍层状过渡金属氧化物正极材料的广泛应用需要从不断完善材料制备方法、改变材料性状、降低材料成本等方面入手,开发高能量密度的锂离子电池,才能使富镍三元层状过渡金属氧化物正极材料在动力电池领域尽早得到广泛应用。

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