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锂离子电池富锂锰基正极材料的研究进展

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摘要: 随着新能源如电动汽车、储能电站的蓬勃发展, 人们对下一代高性能锂离子电池的能量密度、功率密度和循环寿命提出了更高的要求. 而富锂锰基正极材料 $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($0 < x < 1$, $M = \text{Mn}, \text{Co}, \text{Ni} \cdots$) 具有可逆比容量高 ($240 \sim 280 \text{ mAh} \cdot \text{g}^{-1}$, $2.0 \sim 4.8 \text{ V}$)、电化学性能较佳、成本较低等优点, 已吸引了研究者的关注, 有望成为下一代锂离子电池用正极材料. 本实验室采用固相法和溶胶-凝胶法制备不同的富锂锰基正极材料, 其中, 溶胶-凝胶法制得的 $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ 电极首周期放电比容量 $277.3 \text{ mAh} \cdot \text{g}^{-1}$, 50 周期循环后容量 $272.8 \text{ mAh} \cdot \text{g}^{-1}$, 容量保持率 98.4%. 本文重点结合本实验室的研究工作, 对新型富锂锰基正极材料 $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ 的结构、合成、电化学性能改性和充放电机理等进行总结与评述.

关键词: 锂离子电池; 富锂正极材料; 共沉淀法; $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$

中图分类号: O646

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近年, 研究者都将锂离子电池视为发展电动汽车、储能电站等的关键. 相对而言, 锂离子电池正极材料更多地限制锂离子电池后续发展. 1990 年, 曾报道层状锂离子电池 LiCoO_2 正极材料可商业化^[1]以及 Goodenough 研究小组提出新型橄榄石型锂离子电池 LiFePO_4 正极材料^[2], 上述两种正极材料均已应用于锂离子电池纯电动汽车和混合动力汽车. 然而, LiCoO_2 及其他改进型层状正极材料, 如 $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$, 实际放电容量仅 $140 \sim 170 \text{ mAh} \cdot \text{g}^{-1}$ ^[3-5], 橄榄石结构的 LiFePO_4 的理论放电容量也只有 $170 \text{ mAh} \cdot \text{g}^{-1}$ ^[2,6].

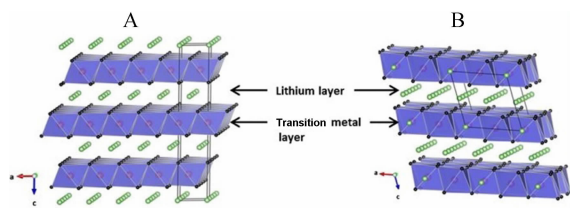
与其他正极材料相比, 富锂锰基正极材料 $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($0 < x < 1$, $M = \text{Mn}, \text{Co}, \text{Ni} \cdots$)^[7-11]的可逆比容量高 ($240 \sim 280 \text{ mAh} \cdot \text{g}^{-1}$, $2.0 \sim 4.8 \text{ V}$)、成本低, 有望成为下一代锂离子电池正极材料. 本文着重结合本实验室的研究工作, 对新型富锂锰基正极材料 $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ 的结构、合成、电化学性能改性和充放电机理等进行总结与评述.

1 富锂锰基正极材料的结构

从结构组成上看, 富锂锰基正极材料 $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($M = \text{Mn}, \text{Co}, \text{Ni} \cdots$) 含有层状

Li_2MnO_3 与 LiMO_2 两种组分 (图 1). Li_2MnO_3 层状岩盐晶体结构, 单斜 $C2/m$ 空间群, 与 $\alpha\text{-NaFeO}_2$ 型层状结构类似^[11-14]. Li_2MnO_3 的化学式 $\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$, 可视为含有特殊 TM 层的 LiTMO_2 氧化物, TM 层两元素 Li^+ 和 Mn^{4+} 的离子比为 1:2, M 层中每个 Li^+ 被 6 个 Mn^{4+} 所包围, 形成六方晶格有序排列的 LiMn_6 超晶格结构. LiMO_2 结构类似于 LiCoO_2 , 属空间群 $R3m$ 型的 $\alpha\text{-NaFeO}_2$ 型层状结构, Li 占据 $3a$, 过渡金属占据 $3b$ 位, 其中过渡金属 Ni、Co、Mn 的价态分别为 +2、+3 和 +4, 有着高能量密度、高容量和高循环寿命特性.

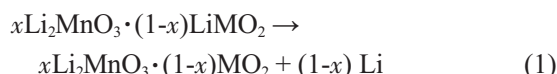
由于单斜晶系 $C2/m$ (Li_2MnO_3) 的 (001) 晶面和六方晶系 $R3m$ (LiMO_2) 的 (003) 晶面点位重合, 晶面距离均接近 0.47 nm 左右, Li_2MnO_3 的 Mn^{4+} 与 LiMO_2 的过渡金属离子可实现某种程度的混排, 使两种组分原子级相溶^[11,15], 导致研究者们对富锂锰基正极材料的具体结构 (纳米复合结构和固溶体结构) 持不同观点. Thackeray 等^[11]认为富锂材料是 Li_2MnO_3 和 LiMO_2 两相组成的纳米复合材料, Li^+ 与周围 6 个 Mn^{4+} 形成六方晶格有序排列, 三维空间展开后形成 Li_2MnO_3 纳米微区, 过渡金属 Ni、

图1 LiMO_2 (A) 和 Li_2MnO_3 的晶型结构 (B)Fig. 1 Crystal structure models of LiMO_2 (A) and Li_2MnO_3 (B)

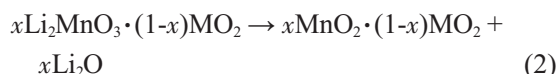
Co 、 Mn 离子同样三维空间展开形成 LiMO_2 纳米微区, 两组分含量比例会影响两微区的无序度和尺寸, 即 $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($\text{M} = \text{Mn}$ 、 Co 、 $\text{Ni} \cdots$) 复合结构. Manthiram 等^[15]则认为富锂锰基正极材料属于单一相的固溶体, 过渡金属层中阳离子无序分布, Li_2MnO_3 中的 Li^+ 、 Mn^{4+} 两种离子被 Ni 、 Co 、 Mn 离子代替, 形成阳离子无序结构, 即 $\text{Li}_{1-y}\text{M}_{1-y}\text{O}_2$ ($\text{M} = \text{Co}$ 、 Ni 、 $\text{Mn} \cdots$) 固溶体结构.

2 富锂锰基正极材料的放电机理

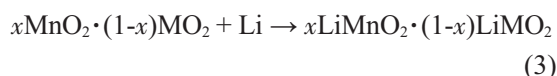
$x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ 电极的首周期充电过程均呈现 1 个 4.5 V 的电压平台, 随之的充放电循环平台消失, 此过程归因于电化学活化, 即其充放电的特征曲线. Johnson 等^[11,14]认为首周期充电过程分为两步, 低于 4.5 V 电压时, Li^+ 的脱嵌伴随着 $\text{Ni}^{2+/4+}$ 以及 $\text{Co}^{3+/4+}$ 之间的氧化还原, 约可贡献 $120 \text{ mAh} \cdot \text{g}^{-1}$; 高于 4.5 V 电压时, 锂层和过渡金属/锂混合层共同脱嵌 Li^+ , 同时锂层两侧的氧也以 Li_2O 的形式脱出, 使晶格原 O 空位被过渡金属离子占据, 致使脱嵌 Li^+ 不能全部回嵌, 从而造成较大的不可逆容量损失. 首周期充电后, 层状富锂锰基电极结构发生不可逆变化^[11,14,16]. 低于 4.5 V 电压时, 随着 Li^+ 脱出, 过渡金属离子发生氧化还原反应:



高于 4.5 V 电压时, 电极锂离子层和过渡金属层共同脱出 Li^+ , 锂离子层两侧的氧也一起脱出:



在充电过程 Li_2O 形式脱出的氧原子不可能再进入材料结构, 其所形成的氧空位也被过渡金属离子占据, 脱出的 Li^+ 不可能再完全嵌入层状材料的体相晶格中, 只有部分 Li^+ 嵌入形成计量比化合物, 造成了首周期不可逆容量损失^[17-18]:



经终止电压的充放电循环, $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$

材料的 Mn^{4+} 部分还原生成具有电化学活性的 Mn^{3+} , 与 LiMO_2 形成更加稳定的结构.

3 富锂锰基正极材料的合成

富锂锰基材料 $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($0 < x < 1$, $\text{M} = \text{Mn}$ 、 Co 、 $\text{Ni} \cdots$) 的结构包含着多种过渡金属离子. 其均匀分布与否, 决定着材料的性能. 作者实验室采用固相、溶胶-凝胶和共沉淀法合成富锂锰基正极材料^[19,21,25].

3.1 固相法

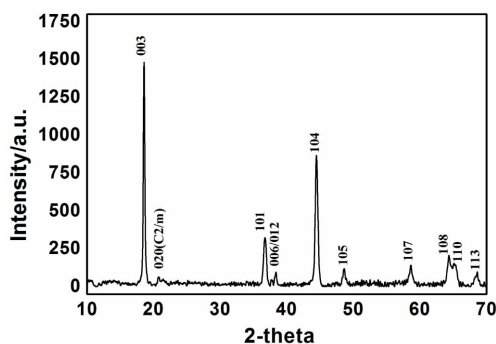
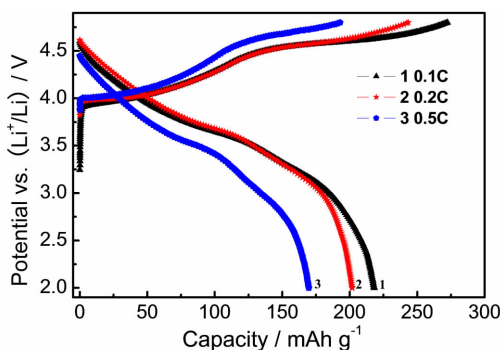
固相法成本低、易控制、产率高、设备简单, 但固相反应影响着反应物比表面积、接触面积、生成物相的成核速率以及物相离子扩散速率等, 故合成材料的均一性较差^[13].

Zhou 等^[19]将化学计量比为 1.13:0.20:0.20:0.47 的乙酸锂 ($\text{C}_2\text{H}_3\text{O}_2\text{Li} \cdot 2\text{H}_2\text{O}$)、乙酸钴 ($\text{C}_4\text{H}_6\text{CoO}_4 \cdot 4\text{H}_2\text{O}$)、乙酸镍 ($\text{C}_4\text{H}_6\text{NiO}_4 \cdot 4\text{H}_2\text{O}$)、乙酸锰 ($\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$) 完全溶解于乙醇溶液后, 在 120 °C 烘干, 充分球磨, 经 400 °C 预烧结 4 h 和 800 °C 烧结 6 h 的分步固相法煅烧, 得到不同配比的富锂锰基正极材料. 其中, $\text{Li}_{1.13}[\text{Ni}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.47}]\text{O}_2$ 正极材料的 XRD 图谱如图 2 所示. 该电极在 2.0 ~ 4.8 V (vs. Li^+/Li) 区间的放电比容量达 $218.2 \text{ mAh} \cdot \text{g}^{-1}$ (见图 3), 50 周期循环后容量为 $193.7 \text{ mAh} \cdot \text{g}^{-1}$. 另一 $\text{Li}_{1.17}[\text{Ni}_{0.17}\text{Co}_{0.17}\text{Mn}_{0.50}]\text{O}_2$ 电极在 0.1C 时首周期放电比容量高达 $240.1 \text{ mAh} \cdot \text{g}^{-1}$. Xiang 等^[20]采用固相法合成 $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.17}\text{Co}_{0.16}\text{Mn}_{0.47}]\text{O}_2$ 纳米材料, $15 \text{ mA} \cdot \text{g}^{-1}$ 充放电条件下的首周期放电容量为 $195.1 \text{ mAh} \cdot \text{g}^{-1}$, 40 周期循环后容量为 $179.5 \text{ mAh} \cdot \text{g}^{-1}$.

3.2 溶胶-凝胶法

将过渡金属离子和有机络合物混合, 其凝胶前躯体水解缩合反应生成螯合物, 经溶液、溶胶、凝胶等过程使螯合物固化, 经热处理后可得到固体氧化物的固溶体. 溶胶-凝胶法制备的材料高纯、均匀、超细, 系纳米级颗粒, 但反应时间长, 产率较低^[13,18,21].

Jin 等^[21]以化学计量比为 1.20:0.13:0.13:0.54 的乙酸锂 ($\text{C}_2\text{H}_3\text{O}_2\text{Li} \cdot 2\text{H}_2\text{O}$)、乙酸钴 ($\text{C}_4\text{H}_6\text{CoO}_4 \cdot 4\text{H}_2\text{O}$)、乙酸镍 ($\text{C}_4\text{H}_6\text{NiO}_4 \cdot 4\text{H}_2\text{O}$)、乙酸锰 ($\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$) 的原材料, 改进工艺, 以草酸替代柠檬酸螯合剂, 制备了 $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ 正极材料. 该电极在 2.0 ~ 4.8 V 电压范围室温 0.1C 下, 首周期放电比容量为 $277.3 \text{ mAh} \cdot \text{g}^{-1}$, 50 周期循环后容量为 $272.8 \text{ mAh} \cdot \text{g}^{-1}$, 容量保持率 98.4% (见图 4). Toprakci 等^[18]制得 $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ($x = 0.1, 0.2, 0.3, 0.4, 0.5$) 系列正极材料, 其中 $0.3\text{Li}_2\text{MnO}_3 \cdot$

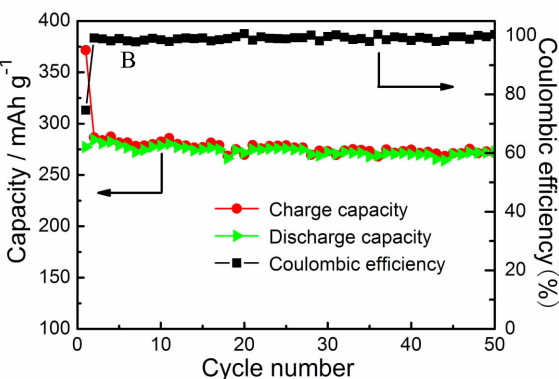
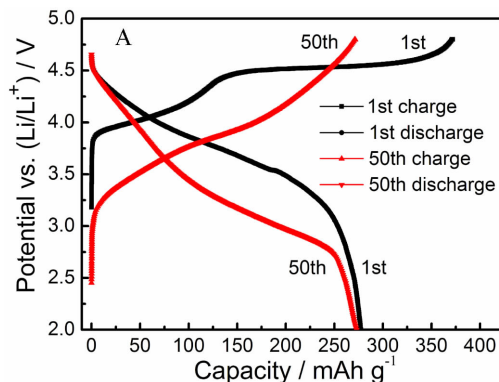
图 2 $\text{Li}_{1.13}[\text{Ni}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.47}]\text{O}_2$ 正极材料的 XRD 图^[19]Fig. 2 XRD pattern of the $\text{Li}_{1.13}[\text{Ni}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.47}]\text{O}_2$ powder sample^[19]图 3 $\text{Li}_{1.13}[\text{Ni}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.47}]\text{O}_2$ 电极 0.1C、0.2C 和 0.5C 下首周期充放电曲线^[19]Fig. 3 Initial charge-discharge curves of the electrode of $\text{Li}_{1.13}[\text{Ni}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.47}]\text{O}_2$ at 0.1C, 0.2C and 0.5C^[19]

$0.7\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ 电极性能最佳,首周期放电容量为 $184 \text{ mAh} \cdot \text{g}^{-1}$,50 周期循环后容量保持率 98%.

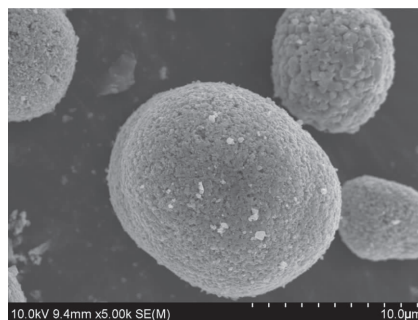
3.3 共沉淀法

共沉淀法是将过渡金属盐混合,加入沉淀剂,调控 pH 值使过渡金属离子与沉淀剂反应生成不溶性沉淀,经过滤、洗涤、干燥后续处理得目标产物.其制得的粉末材料粒径小、形貌清晰,但合成设备复杂、反应物浓度、反应温度、pH 难以调控.常见的主要有氢氧化物、碳酸盐和草酸盐共沉淀法^[16,22-23].

Tang 等^[24]采用碳酸钠作沉淀剂,与化学计量比的硫酸锰、硫酸镍、硫酸钴溶液共沉淀.由碳酸盐前驱体预氧化,与碳酸锂共混进行烧结可得 $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$.该材料由一次纳米单晶聚合成二次球状粒子(见图 5),电极样品的首周期放电比容量 $252.6 \text{ mAh} \cdot \text{g}^{-1}$ (0.1C, $2.0 \sim 4.8 \text{ V}$),200 周期循环容量保持率 85%.

图 4 $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ 电极首周期和 50 周期循环的充放电曲线(A)及寿命曲线(B)^[21]Fig. 4 Initial and 50th charge-discharge profiles (A) and cycling performances (B) of $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ ^[21]

此外,还以化学计量比 1.20:0.13:0.13:0.54 的乙酸锂($\text{C}_2\text{H}_3\text{O}_2\text{Li} \cdot 2\text{H}_2\text{O}$)、乙酸钴($\text{C}_4\text{H}_6\text{CoO}_4 \cdot 4\text{H}_2\text{O}$)、乙酸镍($\text{C}_4\text{H}_6\text{NiO}_4 \cdot 4\text{H}_2\text{O}$)、乙酸锰($\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$)为原材料,8-羟基喹啉为沉淀剂,制得 $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]\text{O}_2$ 材料^[25].该电极 $2.0 \sim 4.8 \text{ V}$ 电压范围,0.2C 首周期放电比容量为 $287.2 \text{ mAh} \cdot \text{g}^{-1}$,100 周期循环放电比容量为 $261.4 \text{ mAh} \cdot \text{g}^{-1}$,容量保持率 91%(见图 6).共沉淀溶液过渡金属离子 Ni^{2+} 、 Co^{2+} 、 Mn^{2+} 的 3d 空

图 5 $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ 的 SEM 图^[24]Fig. 5 SEM image of $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ ^[24]

轨道与 8-羟基喹啉的杂原子 N、O 孤电子对极易结合,使过渡金属离子 Ni^{2+} 、 Co^{2+} 、 Mn^{2+} 在有机沉淀剂 8-羟基喹啉作用下实现共沉淀,所得正极材料其颗粒均一,结晶度较高。Wei 等^[26]以草酸作为沉淀剂制得 $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]\text{O}_2$ 正极材料,所得电极 1C 和 10C 的首周期放电容量分别为 $251.9 \text{ mAh} \cdot \text{g}^{-1}$ 和 $107.5 \text{ mAh} \cdot \text{g}^{-1}$ 。

3.4 其他合成法

富锂锰基正极材料制备还有水热法、喷雾干燥法、乳液合成法、电解法、控制结晶法等^[27-31]。其中,喷雾干燥法可合成粉体团聚少、颗粒分散性好的正极材料,其性能较好,然而所需设备昂贵、工艺复杂,不适宜规模化生产。Son 等^[32]采用喷雾热解法制得 $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ($x = 0, 0.2, 0.4, 0.5, 0.8, 1$) 系列材料,其中 $x = 0.5$ 时所得电极的首周期放电容量为 $291 \text{ mAh} \cdot \text{g}^{-1}$ 。

4 富锂锰基正极材料的改性

体相掺杂和表面包覆可改善锂离子电池正极材料性能。

4.1 掺杂

据报道^[33-37], Al、Ti、Cr、Mo、Fe、Ru 等元素均可掺杂在正极材料的晶型结构中。作者实验室在 $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]\text{O}_2$ 材料的基础上,掺杂 Mg、Mo 等微量元素,可有效地改善其倍率性能和循环性能。 Mg^{2+} 和 Li^+ 的粒径相似,微量掺杂 Mg^{2+} 可有效地减少材料充放电过程的阳离子混排度。Jin 等^[38]采用溶胶-凝胶法将 Mg 元素掺杂 $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]\text{O}_2$ 材料,即得不同 Mg 元素配比材料(XRD 图谱如图 7 所示)。图 8 示出 $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]_{1-x}\text{Mg}_x\text{O}_2$ ($x = 0.02, 0.03, 0.04$)

电极在 $2.0 \sim 4.8 \text{ V}$ 电压范围室温 0.2C 下的首周期和 50 周期循环的充放电曲线和寿命曲线。由图可知, $x = 0.02$ 时电极首周期充放电比容量均高于其他材料。 $x = 0$ 时电极首周期放电容量为 $223.0 \text{ mAh} \cdot \text{g}^{-1}$, $x = 0.02$ 时电极首周期放电容量达到 $275.8 \text{ mAh} \cdot \text{g}^{-1}$,较无掺杂电极高 $52.8 \text{ mAh} \cdot \text{g}^{-1}$ 。这归因于 Mg 元素使材料层间距增大,更利于充放电过程锂离子扩散。此外,还采用溶胶-凝胶法制得掺杂微量 Mo 元素的 $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]_{1-x}\text{Mo}_x\text{O}_2$ ($x = 0.01, 0.02, 0.03, 0.04$) 材料,其 Mo 掺杂量 $x = 0.03$ 的电极材料性能最佳^[39]。

Song 等^[36]采用共沉淀法制得金属钌掺杂的 $\text{Li}[\text{Li}_{0.2-x}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13-x}\text{Ru}_x]\text{O}_2$ 材料。当 $x = 0.01$ 时,该电极性能最好, $\text{Li}[\text{Li}_{0.19}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.12}\text{Ru}_{0.01}]\text{O}_2$ 电极 2C 放电容量高达 $182 \text{ mA} \cdot \text{g}^{-1}$ 。He 等^[35]通过聚合物热解法在 $\text{Li}_{1.2}[\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]\text{O}_2$ 的 Li 层引入 Na 离子,制备所得 $\text{Li}_{1.2-x}\text{Na}_x[\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]\text{O}_2$ 材料结构更加规则,立方晶系特征更明显。该电极首周期放电比容量可达 $307.0 \text{ mAh} \cdot \text{g}^{-1}$,充放电效率达 87%。Zheng 等^[37]采用溶胶-凝胶法合成了 $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_{2-x}\text{F}_x$, F 元素掺杂量为 0.05 时, $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_{1.95}\text{F}_{0.05}$ 电极 0.2C 充放电条件下 50 周期循环容量保持率为 88.1%。

4.2 包覆

正极材料表面可包覆惰性氧化物、磷酸盐乃至氟化物等,当正极材料表面形成保护层,减少其溶解,可有效改善正极材料的电化学性能。常用的包覆剂有 Al_2O_3 、 TiO_2 、 AlPO_4 、 CoPO_4 、 AlF_3 等^[40-46]。

Zhao 等^[44]采用共沉淀法制得材料 $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]\text{O}_2$,并在表面包覆不同量

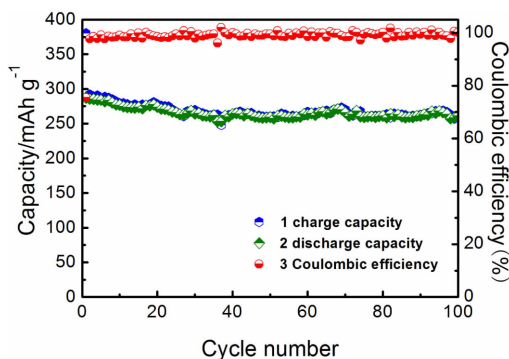


图 6 $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]\text{O}_2$ 电极 0.2C 下的循环寿命曲线^[25]

Fig. 6 Cycling performances of $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]\text{O}_2$ electrode at 0.2C ^[25]

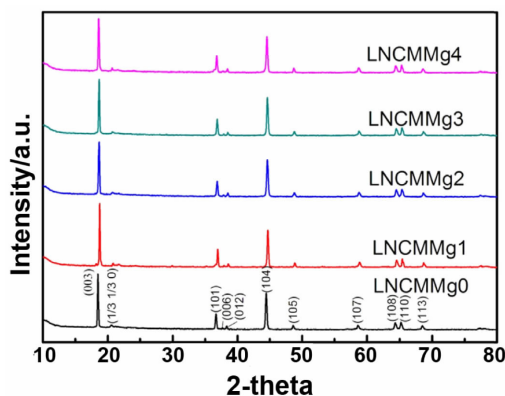


图 7 $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]_{1-x}\text{Mg}_x\text{O}_2$ 正极材料的 XRD 图^[38]

Fig. 7 XRD patterns of $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]_{1-x}\text{Mg}_x\text{O}_2$ powder samples^[38]

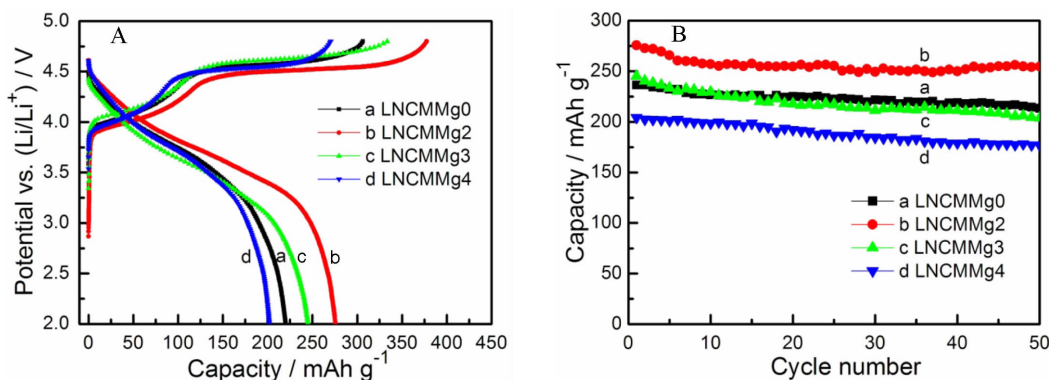


图 8 $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]_{1-x}\text{Mg}_x\text{O}_2$ 电极 0.2C 首周期充放电曲线(A)和寿命曲线(B)^[38]

Fig. 8 The initial charge and discharge profiles vs. voltage (A) and cycling performances (B) of $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]_{1-x}\text{Mg}_x\text{O}_2$ electrodes at 0.2C^[38]

的无定形 FePO_4 . 该电极材料的可逆容量 $271.7 \text{ mAh} \cdot \text{g}^{-1}$, 首周期充放电效率 85.1%. Li 等^[45]在 $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]\text{O}_2$ 的表面包覆纯相 $(\text{NH}_4)_3\text{AlF}_6$, 5% $(\text{NH}_4)_3\text{AlF}_6$ 包覆电极首周期充放电效率最高, 而 1% 和 3% $(\text{NH}_4)_3\text{AlF}_6$ 包覆电极呈现出优异的寿命性能. 1% $(\text{NH}_4)_3\text{AlF}_6$ 包覆 $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]\text{O}_2$ 电极 5C 可逆容量达 $143.4 \text{ mAh} \cdot \text{g}^{-1}$. Manthiram 等^[46]采用 Al_2O_3 和 RuO_2 混合包覆 $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]\text{O}_2$, 包覆 1% Al_2O_3 +1% RuO_2 的 $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]\text{O}_2$ 电极的可逆容量达 $280 \text{ mAh} \cdot \text{g}^{-1}$, 30 周期循环后容量保持率仍达 94.3%, 5C 可逆容量 $160 \text{ mAh} \cdot \text{g}^{-1}$.

5 结论与展望

近年研究者已大力研发电动汽车和储能电站, 而目前电动汽车的续航能力不足 300 公里, 亟待开发更高能量密度、功率密度和循环寿命的下一代高性能动力锂离子电池. 富锂锰基正极材料 $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ 有较佳的电化学安全性、较低成本和低毒性等, 已引发关注.

富锂锰基正极材料 $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ 的复杂结构和独特电化学性能需深入研究. 目前, 已经有学者针对首周期循环不可逆容量损失问题进行深入研究, 有望降低不可逆容量、减少析氧, 这为提高该材料的安全性能奠定了良好的基础^[47]. 除了富锂锰基正极材料的结构设计、制备方法和电化学改性, 还需探讨该材料电极表面在电解液体系中生成的固态电解质膜和锂离子在电极表面充放电机理. 同时, 还需开发此类高压正极材料体系的电解液、粘结剂以及其他添加剂等, 以期有效改善和提高该类材料电化学安全性, 大力促进其实用化.

参考文献(References):

- [1] Nagaura T, Tozawa K. Lithium ion rechargeable battery [J]. Progress in Batteries and Solar Cells, 1990, 9 (2): 209-217.
- [2] Padhi A K, Nanjundaswamy K S, Goodenough J B. Phospho-olivines as positive-electrode materials for rechargeable lithium batteries[J]. Journal of the Electrochemical Society, 1997, 144(4): 1188-1194.
- [3] Scott I D, Jung Y S, Cavanagh A S, et al. Ultrathin coatings on nano- LiCoO_2 for Li-ion vehicular applications[J]. Nano Letters, 2011, 11(2): 414-418.
- [4] Ohzuku T, Makimura Y. Layered lithium insertion material of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ for lithium-ion batteries[J]. Chemistry Letters, 2001, 7: 642-643.
- [5] Jiang K C, Xin S, Lee J S, et al. Improved kinetics of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material through reduced graphene oxide networks[J]. Physical Chemistry Chemical Physics, 2012, 14(8): 2934-2939.
- [6] Yuan L X, Wang Z H, Zhang W X, et al. Development and challenges of LiFePO_4 cathode material for lithium-ion batteries[J]. Energy & Environmental Science, 2011, 4(2): 269-284.
- [7] Li J, Klopsch R, Stan M C, et al. Synthesis and electrochemical performance of the high voltage cathode material $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}]\text{O}_2$ with improved rate capability[J]. Journal of Power Sources, 2011, 196(10): 4821-4825.
- [8] Yabuuchi N, Yoshii K, Myung S T, et al. Detailed studies of a high-capacity electrode material for rechargeable batteries, Li_2MnO_3 - $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ [J]. Journal of the American Chemical Society, 2011, 133(12): 4404-4419.
- [9] Park K S, Cho M H, Jin S J, et al. Structural and electrochemical properties of nanosize layered $\text{Li}(\text{Li}_{1/5}\text{Ni}_{1/10}\text{Co}_{1/5}\text{Mn}_{1/2})\text{O}_2$ [J]. Electrochemical and Solid-State Letters, 2004, 7(8): 209-217.

- A239-A241.
- [10] Martha S K, Nanda J, Veith G M, et al. Electrochemical and rate performance study of high-voltage lithium-rich composition: $\text{Li}_{1.2}\text{Mn}_{0.525}\text{Ni}_{0.175}\text{Co}_{0.1}\text{O}_2$ [J]. *Journal of Power Sources*, 2012, 199: 220-226.
 - [11] Thackeray M M, Kang S H, Johnson C S, et al. Li_2MnO_3 -stabilized LiMO_2 ($\text{M} = \text{Mn, Ni, Co}$) electrodes for lithium-ion batteries [J]. *Journal of Material Chemistry*, 2007, 17(30): 3112-3125.
 - [12] Koyama Y, Tanaka I, Nagao M, et al. First-principles study on lithium removal from Li_2MnO_3 [J]. *Journal of Power Sources*, 2009, 189(1): 798-801.
 - [13] Zhang J(张洁), Wang J L(王久林), Yang J(杨军). Progress of lithium rich cathode materials for Li-ion batteries [J]. *Journal of Electrochemistry(电化学)*, 2008, 14(4): 398-401.
 - [14] Johnson C S, Li N, Thackeray M M, et al. Anomalous capacity and cycling stability of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ electrodes ($\text{M} = \text{Mn, Ni, Co}$) in lithium batteries at 50 °C [J]. *Electrochemistry Communication*, 2007, 9(4): 787-795.
 - [15] Arunkumar T A, Wu Y, Manthiram A. Factors influencing the irreversible oxygen loss and reversible capacity in layered $\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2 \cdot \text{LiMO}_2$ ($\text{M} = \text{Mn}_{0.57}\text{Ni}_{0.57}\text{Co}_{0.2}$ and $\text{Ni}_{1.7}\text{Co}_3$) solid solutions [J]. *Chemistry of Materials*, 2007, 19(12): 3067-3073.
 - [16] Yabuuchi N, Yoshii K, Myung S T, et al. Detailed studies of a high-capacity electrode material for rechargeable batteries, $\text{Li}_2\text{MnO}_3\text{-LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ [J]. *Journal of the American Chemical Society*, 2011, 133(12): 4404-4419.
 - [17] Armstrong A R, Holzapfel M, Novak P, et al. Demonstrating oxygen loss and associated structural reorganization in the lithium battery cathode $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$ [J]. *Journal of the American Chemical Society*, 2006, 128(26): 8694-8698.
 - [18] Toprakci O, Li Y, Zhang X W, et al. Synthesis and characterization of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ composite cathode materials for rechargeable lithium-ion batteries [J]. *Journal of Power Sources*, 2013, 241: 522-528.
 - [19] Zhou L Z, Xu Q J, Liu M S, et al. Novel solid-state preparation and electrochemical properties of $\text{Li}_{1.13}[\text{Ni}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.47}]\text{O}_2$ material with a high capacity by acetate precursor for Li-ion batteries [J]. *Solid State Ionics*, 2013, 249: 134-138.
 - [20] Xiang Y H, Yin Z L, Zhang Y H, et al. Effects of synthesis conditions on the structural and electrochemical properties of the Li-rich material $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.17}\text{Co}_{0.16}\text{Mn}_{0.47}]\text{O}_2$ via the solid-state method [J]. *Electrochimica Acta*, 2013, 91: 214-218.
 - [21] Jin X, Xu Q J, Zhou L Z, et al. Synthesis, characterization and electrochemical performance of $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ cathode materials for lithium-ion batteries [J]. *Electrochimica Acta*, 2013, 114: 605-610.
 - [22] Gao J, Manthiram A. Eliminating the irreversible capacity loss of high capacity layered $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ cathode by blending with other lithium insertion hosts [J]. *Journal of Power Sources*, 2009, 191(2): 644-647.
 - [23] Gao J, Kim J, Manthiram A. High capacity $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2\text{-V}_2\text{O}_5$ composite cathodes with low irreversible capacity loss for lithium ion batteries [J]. *Electrochemistry Communications*, 2009, 11(1): 84-86.
 - [24] Song J H, Tang W P, Xie J Y. Surface modification of Mn-based Li-rich cathode material by AlPO_4 for high energy lithium-ion battery [C]//The 16th International Meeting on Lithium Batteries (IMLB), ICC, Jeju, Korea, 2012.
 - [25] Yuan X L, Xu Q J, Wang C, et al. A facile and novel organic coprecipitation strategy to prepare layered cathode material $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ with high capacity and excellent cycling stability [J]. *Journal of Power Sources*, 2015, 279(1): 157-164.
 - [26] Wei X, Zhang S C, Du Z J, et al. Electrochemical performance of high-capacity nanostructured $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ cathode material for lithium ion battery by hydrothermal method [J]. *Electrochimica Acta*, 2013, 107: 549-544.
 - [27] Liu B, Zhang Q, He S, et al. Improved electrochemical properties of $\text{Li}_{1.2}\text{Ni}_{0.18}\text{Mn}_{0.59}\text{Co}_{0.03}\text{O}_2$ by surface modification with LiCoPO_4 [J]. *Electrochimica Acta*, 2011, 56(19): 6748-6751.
 - [28] He W, Qian J, Cao Y, et al. Improved electrochemical performances of nano-crystalline $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ cathode material for Li-ion batteries [J]. *RSC Advances*, 2012, 2(8): 3423-3429.
 - [29] Croy J R, Kang S H, Balasubramanian M, et al. Li_2MnO_3 -based composite cathodes for lithium batteries: A novel synthesis approach and new structures [J]. *Electrochemistry Communications*, 2011, 13(10): 1063-1066.
 - [30] Lee Y J, Kim M G, Cho J. Layered $\text{Li}_{0.88}[\text{Li}_{0.18}\text{Co}_{0.33}\text{Mn}_{0.49}]\text{O}_2$ nanowires for fast and high capacity Li-ion storage material [J]. *Nano Letters*, 2008, 8(3): 957-961.
 - [31] Kim M G, Jo M, Hong Y S, et al. Template-free synthesis of $\text{Li}[\text{Ni}_{0.25}\text{Li}_{0.15}\text{Mn}_{0.6}]\text{O}_2$ nanowires for high performance lithium battery cathode [J]. *Chemical Communications*, 2009, 2: 218-220.
 - [32] Son M Y, Hong Y J, Choi S H, et al. Effects of ratios of Li_2MnO_3 and $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ phases on the properties of composite cathode powders in spray pyrolysis [J]. *Electrochimica Acta*, 2013, 103: 110-118.
 - [33] Park J H, Lim J, Kim J, et al. The effects of Mo doping on $0.3\text{Li}[\text{Li}_{0.33}\text{Mn}_{0.67}]\text{O}_2 \cdot 0.7\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ cathode material [J]. *Dalton Transactions*, 2012, 41(10): 3053-3059.
 - [34] Hwang S Y, Chang W Y, Stach E A, et al. Investigation of changes in the surface structure of $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode materials induced by the initial charge [J]. *Chemistry of Materials*, 2014, 26(2): 1084-1092.
 - [35] He W, Yuan D D, Cao Y L, et al. Enhanced high-rate

- capability and cycling stability of Na-stabilized layered $\text{Li}_{1.2}[\text{Co}_{0.13}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{O}_2]$ cathode material[J]. *Journal of Materials Chemistry A*, 2013, 1(37): 11397-11403.
- [36] Song B H, Lai M O, Lu L. Influence of Ru substitution on Li-rich $0.55\text{Li}_2\text{MnO}_3 \cdot 0.45\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode for Li-ion batteries[J]. *Electrochimica Acta*, 2012, 80: 187-195.
- [37] Zheng J M, Wu X B, Yang Y. Improved electrochemical performance of $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2]$ cathode material by fluorine incorporation[J]. *Electrochimica Acta*, 2013, 105: 200-208.
- [38] Jin X, Xu Q J, Liu H M, et al. Excellent rate capability of Mg doped $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2]$ cathode material for lithium-ion battery[J]. *Electrochimica Acta*, 2014, 136: 19-26.
- [39] Jin X(靳雪), Xu Q J(徐群杰). Synthesis, characterization and electrochemical performance of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ cathode materials for lithium ion batteries[D]. Shanghai: Shanghai University of Electric Power, 2014: 39-45.
- [40] Sun Y K, Yoon C S, Scrosati B, et al. The role of AlF_3 coatings in improving electrochemical cycling of Li-enriched nickel-manganese oxide electrodes for Li-ion batteries[J]. *Advanced Materials*, 2012, 24(9): 1192-1196.
- [41] Wang Q Y, Liu J, Manthiram A, et al. High capacity double-layer surface modified $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2]$ cathode with improved rate capability [J]. *Journal of Materials Chemistry*, 2009, 19: 4965-4972.
- [42] Kang S H, Thackeray M M. Enhancing the rate capability of high capacity $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($\text{M}=\text{Mn, Ni, Co}$) electrodes by LiNiPO_4 treatment[J]. *Electrochemistry Communications*, 2009, 11(4): 748-751.
- [43] West W C, Soler J, Manthiram A, et al. Electrochemical behavior of layered solid solution $\text{Li}_2\text{MnO}_3 \cdot \text{LiMO}_2$ ($\text{M}=\text{Ni, Mn, Co}$) Li-ion cathodes with and without alumina coatings[J]. *Journal of The Electrochemical Society*, 2011, 158(8): A883-A889.
- [44] Wang Z Y, Liu E Z, Zhao N Q, et al. Effect of amorphous FePO_4 coating on structure and electrochemical performance of $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$ as cathode material for Li-ion batteries[J]. *Journal of Power Sources*, 2013, 236: 25-32.
- [45] Xu G F, Li J L, Xue Q R, et al. Elevated electrochemical performance of $(\text{NH}_4)_3\text{AlF}_6$ -coated $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material via a novel wet coating method[J]. *Electrochimica Acta*, 2014, 117: 41-47.
- [46] Liu J, Manthiram A. Functional surface modifications of a high capacity layered $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2]$ cathode [J]. *Journal of Materials Chemistry*, 2010, 20(19): 3961-3967.
- [47] Wang F X, Wu Y P, Holze R, et al. Coaxial $\text{LiCoO}_2@\text{Li}_2\text{MnO}_3$ nanoribbon as a high capacity cathode for lithium ion batteries[J]. *International Journal of Electrochemical Science*, 2014, 9(11): 6182-6190.

Research Progress of Mn-Based Lithium-Rich Cathode Materials for Li-Ion Batteries

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Abstract: With rapid development of new energy industry like electric vehicles and energy storage station, these fields highly demand the next generation of high performance Li-ion battery systems with stronger energy density, higher power density, and longer cycling life. Lithium-rich Mn-based cathode materials, $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($\text{M}=\text{Mn, Co, Ni} \cdots$), have become the hot topic and drawn attentions of scholars worldwide because of their high reversible capacity exceeding $240 \text{ mAh} \cdot \text{g}^{-1}$, excellent electrochemical properties, and low cost, which makes them most promising cathode material candidates for next Li-ion battery system. The cathode material $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2]$ prepared in our laboratory shows high initial discharge capacity of $277.3 \text{ mAh} \cdot \text{g}^{-1}$ with retention of 98.4% after 50 cycles. Based on our previous works, we have introduced and reviewed the structures, preparation methods, and charge/discharge mechanisms of these lithium-rich Mn-based cathode materials $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$.

Key words: Li-ion battery; lithium-rich cathode materials; co-precipitation method; $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$