

尖晶石 $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ 材料表面 Li_3PO_4 包覆改性及电化学性能

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摘 要: 尖晶石结构 $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) 材料因具备高工作电压、低成本和环境友好等优点, 被认为是最具有发展前景的正极材料之一。然而, LNMO 材料在充放电过程中表现出严重的表面失氧和 Mn 溶出反应, 导致其整体电化学性能较差。采用前驱体 Li_3PO_4 包覆技术, 在 LNMO 材料颗粒表面构建均匀的纳米包覆层, 不仅提高了 LNMO 的循环稳定性和倍率性能, 而且有效抑制了循环过程中阴极材料过渡金属溶出。结合 X 射线衍射仪、扫描电子显微技术、透射电子显微镜和电化学分析等测试手段, 充分对比和分析 Li_3PO_4 包覆 LNMO 材料前后对微观结构和电化学性能的影响。该方法实现了 Li_3PO_4 的均匀包覆, 并且没有改变 LNMO 正极材料的晶体结构。前驱体包覆 3% Li_3PO_4 的 LNMO 材料在 1 C 倍率下循环 300 圈容量保持率从无包覆的 81.82% 提升至包覆后的 90.47%, 2 C 高倍率下的放电容量保持率从 87.72% 提升至 92.39%, 且 EOL 电芯阳极极片中过渡金属 Mn 溶出量明显降低。前驱体 Li_3PO_4 包覆策略是一种有效的材料表面改性策略, 可以有效提升尖晶石型 LNMO 正极材料在循环过程中的结构稳定性和电化学性能。

关键词: 镍锰酸锂; 磷酸锂; 包覆; 电化学性能

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尖晶石型结构 $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ 材料具有 4.7 V (vs. Li/Li^+) 的电压平台^[1]和 $146 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ 的理论克容量, 是一种低成本和高能量型的优良锂离子电池备选材料。且其微观 Li^+ 传输通道是空间三维的, 因此在充放电过程中具有良好的动力学特性^[2-3]。但是, LNMO 在高电压使用过程中溶出的过渡金属离子会催化电解液分解, 产生的 H^+ 会腐蚀镍锰酸锂颗粒表面^[4-8], 加剧导致过渡金属离子大量溶出, 同时溶出的金属离子会沉积到阳极破坏 SEI 膜并造成活性锂的损失^[9-10]。

LNMO 主要的改性策略包括控制热处理工艺优化物相结构、晶粒形貌和晶体取向、提高体相和表面稳定性^[11-15], 表面包覆 Al_2O_3 、 Ta_2O_5 、磷酸盐及氟化物阻隔电解液和 LNMO 的直接接触、降低表面催化活性、提高表面耐酸性^[16-24], 掺杂 F、Ti、Fe 等元素提高尖晶石镍锰酸锂的结构稳定性^[25-29]。在众多的改性方法中, 磷酸盐中的 PO_4^{3-} 具有很强的 P=O 键, 可以有效抑制 LNMO 在制备和使用过程中的释氧, 从而减缓过渡金属离子溶出反应。同时, 碱性的磷酸盐会优先于 LNMO 和电解液中的酸反应, 减少了酸对 LNMO 本体的腐蚀作用^[18-21]。因此,

包覆碱性磷酸盐是突破尖晶石镍锰酸锂高电压体系使用壁垒的良好方案。

在众多的磷酸盐体系中, Li_3PO_4 因具有较强的碱性和较低的熔点 (837°C), 被视为碱性磷酸盐包覆物的优良原材料。采用前驱体预包覆技术, 先在前驱体 $\text{Ni}_{0.25}\text{Mn}_{0.75}(\text{OH})_2$ 表面液相包覆 Li_3PO_4 , 再在 850°C 条件下烧结, 制得均匀致密的 Li_3PO_4 包覆层。上述方法可以实现包覆界面处的 PO_4^{3-} 与尖晶石基体良好的结合, 且还能起到隔绝电解液、捕获 HF、稳定 Ni/Mn 原子的作用。

1 实验

1.1 LNMO 和 Li_3PO_4 包覆材料制备

1.1.1 常规 LNMO 及 Li_3PO_4 包覆材料制备 分别称取 10 g 的 $\text{Ni}_{0.25}\text{Mn}_{0.75}(\text{OH})_2$ 前驱体和 2.06 g 的 Li_2CO_3 , 将两者加入到同一研钵中并研磨均匀, 随后将上述混合物收集并转移至马弗炉中, 在 950°C 保温 10 h, 随炉冷却得到 LNMO 正极材料, 简记为样品 P0。按照 3% 的 Li_3PO_4 包覆量, 称取 0.31 g $\text{NH}_4\text{H}_2\text{PO}_4$ 和 0.33 g $\text{LiOH} \cdot \text{H}_2\text{O}$, 将其依次加入含有 LNMO 颗粒的醇溶液中, 搅拌蒸发后, 将收集的

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间产物置于马弗炉中 2 次低温烧结, 得到常规包覆的 $\text{LNMO}@\text{Li}_3\text{PO}_4$ 材料, 简记为样品 P1。

1.1.2 Li_3PO_4 前驱体包覆 LNMO 材料制备 LNMO 和前驱体磷酸锂包覆工艺流程如图 1 所示。取 10 g 的 $\text{Ni}_{0.25}\text{Mn}_{0.75}(\text{OH})_2$ 前驱体, 将其与去离子水按质量比 1:5 混合并搅拌 0.5 h, 然后加入 0.33 g $\text{LiOH}\cdot\text{H}_2\text{O}$ 并持续搅拌直至充分溶解, 得到悬浊液 A。按照 3% (质量分数) Li_3PO_4 的包覆比称取 0.31 g $\text{NH}_4\text{H}_2\text{PO}_4$, 将其与去离子水按照 1:20 的比例混合, 搅拌至充

分溶解, 得到溶液 B。将溶液 B 匀速滴加到持续搅拌的悬浊液 A 中, 滴加完毕后继续搅拌 1 h, 然后用过滤漏斗将混合液过滤, 将过滤产物在 90 °C 鼓风干燥箱中烘干 24 h 得到 Li_3PO_4 预包覆的 $\text{Ni}_{0.25}\text{Mn}_{0.75}(\text{OH})_2$ 前驱体。按照 Li 和 (Ni+Mn) 摩尔比为 1:2 称取 2.06 g Li_2CO_3 , 将其与上述预包覆的前驱体均匀混合, 随后在 950 °C 保温 10 h, 随炉冷却即得到 Li_3PO_4 湿法包覆的 LNMO 正极材, 简记为样品 P2。

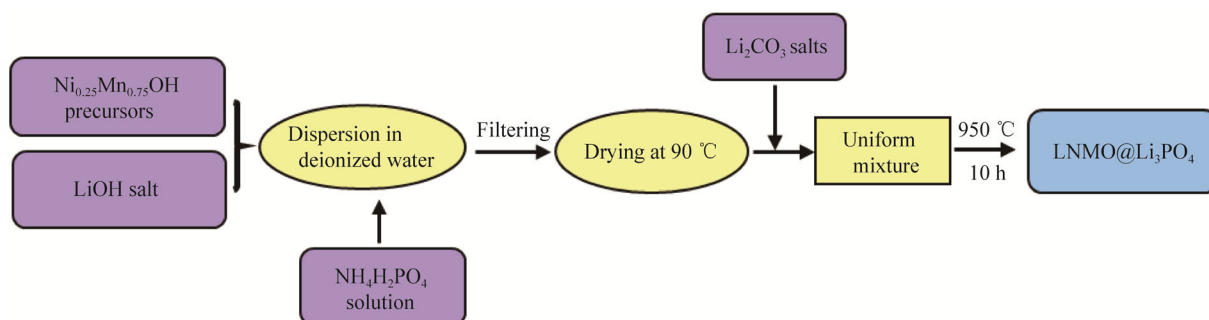


图 1 Li_3PO_4 包覆的 $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ 材料合成工艺图

Fig. 1 Synthesis process diagram of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material coated with Li_3PO_4

1.2 软包电池的制备

将合成的 LNMO 正极材料、黏结剂 PVDF、导电炭黑按照质量比 90:5:5 进行混合, 以 NMP 为溶剂进行正极浆料调制。将调好的浆料双面涂覆在铝箔上, 经过烘干、冷压、分切、裁片等工艺获得正极片。将石墨、导电炭黑、CMC 以 97:2:1 比例混合, 以水为溶剂进行分散。将负极浆料双面涂覆于铜箔上, 烘干、冷压、分切、裁片后获得负极片。将正极片和负极片用隔离膜隔开, 然后经卷绕、热冷压、极耳焊接和封装到铝塑袋中等工序。经过彻底烘干后, 向电芯中注入 1 mol/L LiPF_6 的 EC/EMC/DEC (体积比 3:5:2) 电解液, 真空封装。经过化成-容量步骤后的电芯可用于各种性能测试, 电池额定容量 2.0 A·h。

1.3 样品表征

用荷兰 Philips 公司生产的 Panalytical X'Pert X 射线衍射仪分析材料的物相, 测试条件: Cu 靶, 管电压 40 kV, 管电流 40 mA, 扫描角度为 10°~75°, 扫描速率为 4(°)/min。用日本 Hitachi 公司生产的 S-4800 型扫描电子显微镜分析材料微观形貌, 测试条件: 工作电压 10~30 kV。用美国 Thermo Electron 公司生产的 IRIS IntrepidII XSP 型电感耦合等离子体原子发射光谱仪分析样品中 Li、Mn、Ni、P 等金属元素的相对含量, 测试条件: 光学分辨率为 0.007 nm,

波长范围为 165~900 cm^{-1} , 检出限为 0.001%。用美国 FEI 公司生产的 TECNAI F20 高分辨透射电子显微镜分析材料的微观晶体, 测试条件: 加速电压为 50~300 kV, 点和线分辨率分别为 0.205 nm 和 0.102 nm。用美国 Maccor S4000 电池测试系统分析材料的软包电池电性能。将电芯转入 25 °C 恒温箱进行循环测试实验, 按照以下程序进行充放电测试: ① 0.5 C 恒流放电至 3.5 V; ② 0.5 C 恒流充电至 4.9 V; ③ 恒压 4.9 V 充电至 0.05 C; ④ 0.5 C 倍率恒流放电至 3.5 V, 其中: ④ 的测试容量为可逆容量。采用相同的设备进行倍率测试, 具体的充放流程如下: ① 0.5 C 恒流放电至 3.5 V; ② 以 0.2 C 的倍率恒流充电至 4.9 V; ③ 在 4.9 V 下恒压充电至 0.05 C; ④ 以 0.2 C 的倍率恒流放电至 3.5 V; ⑤ 恒流充电电流倍率保持在 0.2 C, 依次调整放电倍率为 0.33、0.50、1.00 C 和 2.00 C, 重复步骤①~步骤④。为保证数据可靠性, 同时对 3 个电池进行并行循环测试。

1.4 理论计算

通过模拟计算的方法, 能够预先筛选出具有结合力强和离子导电性高的包覆材料^[30-31]。在本工作第一性原理计算: 利用维也纳大学 Hafner 小组开发的从头计算软件(VASP)平面波截断能设置为 520 eV^[32-33]。用投影增强波赝势对核电子进行了模拟, 采用 Perdew-Burke-Ernzerhof (PBE) 的广义梯度近似(GGA)

作为交换关联函数^[34]。增加了 Hubbard 型 U 参数来增加 d 电子的局域化, 设置 $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ 中的 Ni 和 Mn 离子分别具有 6.0 和 5.0 的有效 U 值。体相 LNMO 计算采用 $4 \times 4 \times 4$ 的 k 点网格。计算中结构弛豫的力收敛标准为小于 $0.01 \text{ eV}/(\text{\AA} \cdot \text{atom}^{-1})$ 。

2 结果与讨论

2.1 材料 DFT 计算

通过第一性原理计算验证 PO_4^{3-} 在 LNMO 材料表面的吸附效果, 计算模型如图 2 所示。其中, 图 2a~图 2d 所示为 LNMO 结构中(110)晶面对应的吸附位点模型, 相应的吸附能如图 2i 所示; 图 2e~图 2h

所示为 LNMO 结构中(100)晶面对应的吸附位点模型, 相应的吸附能如图 2j 所示。结果表明, LNMO(100)表面吸附能最大的最佳吸附位是 PO_4^{3-} 中的 2 个氧原子吸附到 Mn/Mn 上(-3.57 eV), 其次是吸附到 Mn/Ni 上(-3.26 eV), 最后是单独吸附在 Mn 或者 Ni 上(-2.36 eV); LNMO(110)表面吸附能最大的最佳吸附位点是 PO_4^{3-} 中的 2 个氧原子吸附到 Mn 上(-3.55 eV), 其次是吸附到 Ni 上(-3.19 eV), 最后是单独吸附在 Mn 或者 Ni 上(-1.34 eV)。由此可见 PO_4^{3-} 与 LNMO 材料表面作用非常强, 对低配位 Mn 的吸附能最大, 吸附效果最佳, 在一定程度上抑制低配位 Mn 的溶解。

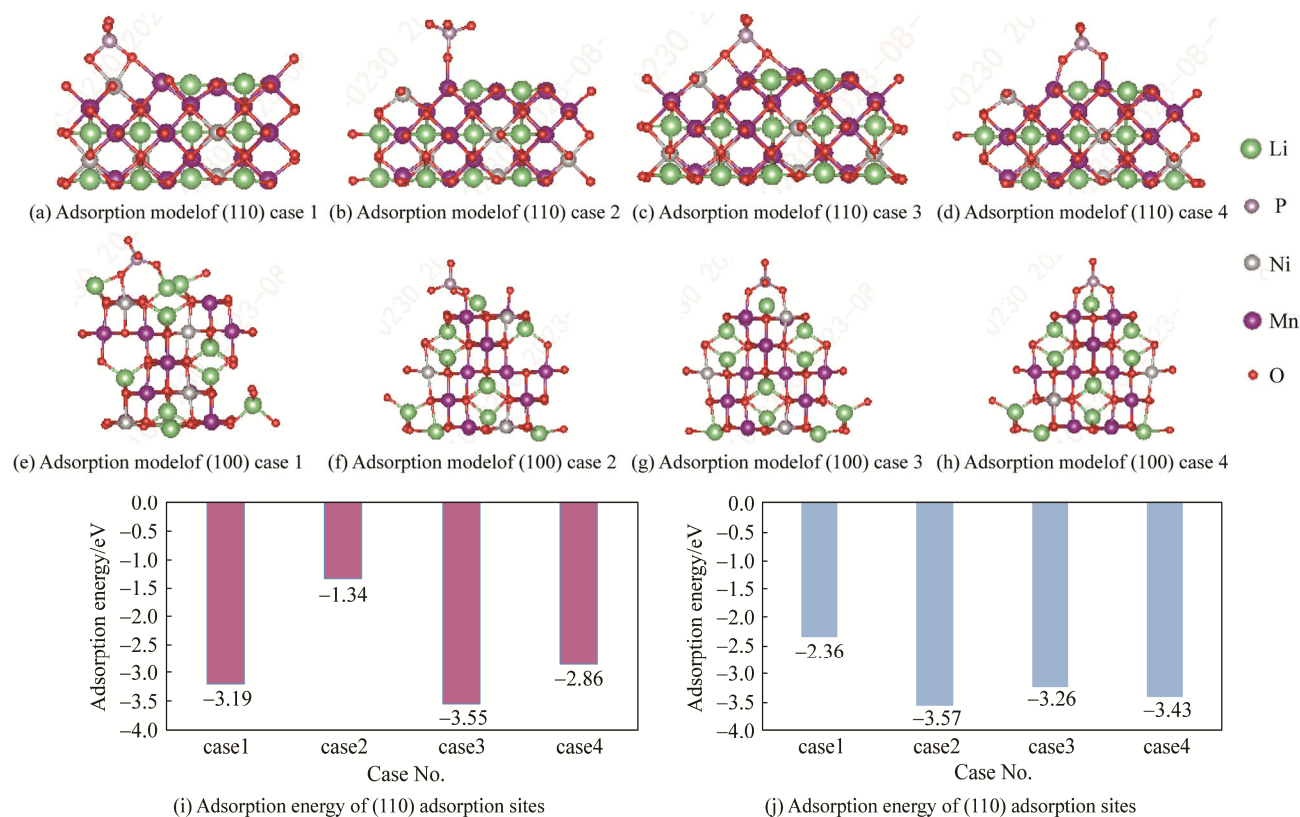


图 2 (110)和(100)晶面对应的吸附模型及吸附位点对应的吸附能

Fig. 2 Adsorption model and adsorption energy corresponding to the adsorption sites of crystal plane (110) and (100)

2.2 材料结构表征

图 3a 为 LNMO 材料在包覆前后对应的 XRD 衍射曲线。由图 3a 可见, 所有合成的 LNMO 材料均具有典型的 $Fd\bar{3}m$ 尖晶石结构特征峰, 且衍射峰尖锐而狭窄, 说明所合成的 LNMO 正极材料具有良好的晶型, Li_3PO_4 包覆不会影响 LNMO 的晶型结构。此外, 通过图 3b 可以观察到 Li_3PO_4 对应的特征峰信号, 说明 Li_3PO_4 对 LNMO 实现了包覆。

2.3 材料形貌及表面成分表征

样品 P0、样品 P1 和样品 P2 对应的微观形貌

进行 SEM 表征, 结果如图 4a~图 4c 所示。由图 4a~图 4c 可见, 3 个样品均呈现出相似的不规则八面体结构, 呈现出典型的尖晶石镍锰酸锂材料特征。所有材料的晶粒尺寸范围为 $5 \sim 10 \mu\text{m}$, 说明采用前驱体预包覆技术在 LNMO 基体上引入 Li_3PO_4 包覆层对颗粒形态没有明显影响。图 4d 中的 TEM 照片证实在 LNMO 材料表面均匀分布一层包覆层, 图 4f 进一步说明 P 元素在材料表面呈均匀分布。以上结果证实了 Li_3PO_4 已经均匀包覆在颗粒表面。

2.4 材料电化学性能表征

图 5 为 LNMO 材料包覆处理前后在 0.1 C ($1\text{ C}=150\text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$) 下的首圈充放电曲线, 电压范围为: $3.50\sim 4.95\text{ V}$ 。由图 5 可见, 所有充电曲线在 4.7 V 时均有 1 个较长的电压平台, 该平台主要对应 $\text{Ni}^{2+}/\text{Ni}^{4+}$ 的氧化还原反应。而在 4.0 V 处有 1 个短暂

的平台, 对应 $\text{Mn}^{3+}/\text{Mn}^{4+}$ 氧化还原反应, 证明了材料中存在 Mn^{3+} 的氧化还原。样品 P0、样品 P1 和样品 P2 中 3 个样品对应的首圈放电克容量分别为 137.05 、 $136.00\text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ 和 $135.70\text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$, 说明 Li_3PO_4 包覆处理后, 并不会明显影响 LNMO 克容量的发挥。

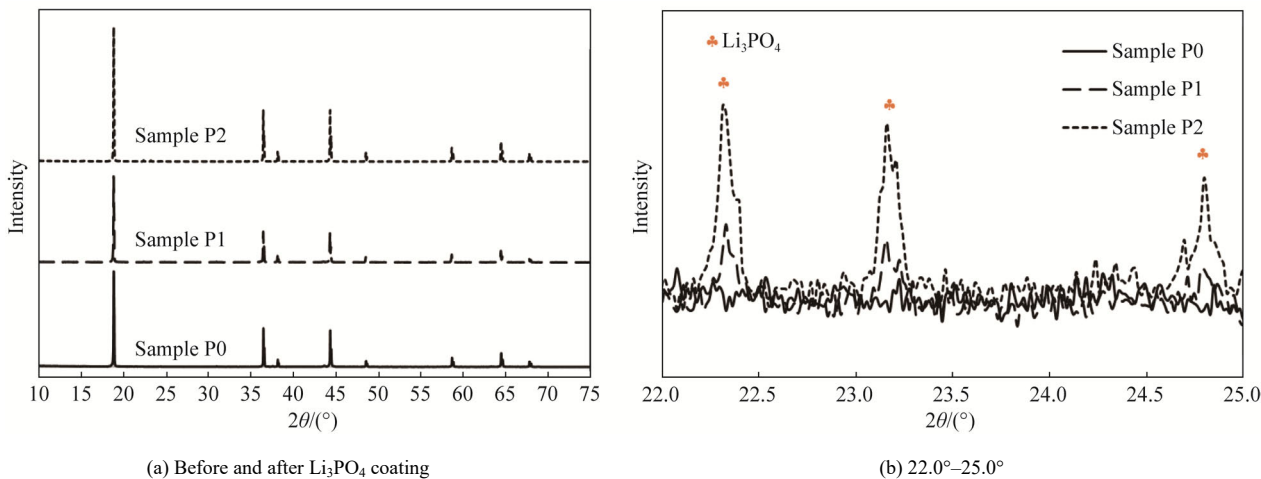


图 3 Li_3PO_4 包覆前后的 $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ 材料的 XRD 谱
Fig. 3 XRD patterns of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material before and after Li_3PO_4 coating

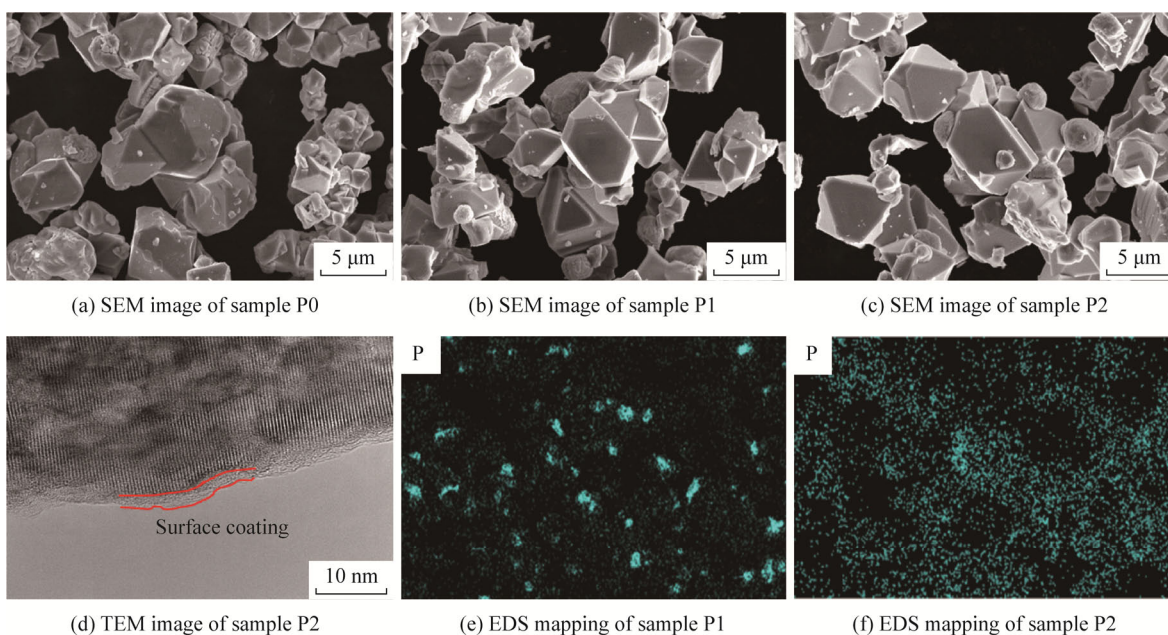


图 4 样品 P0、样品 P1、样品 P2 的 SEM 和 TEM 照片
Fig. 4 SEM and TEM images of samples P0, P1 and P2

图 6 为 Li_3PO_4 包覆前后样品在 0.5 C 电流密度下的循环性能曲线, 样品 P0、样品 P1 和样品 P2 的首圈放电克容量值分别为 129.22 、 $129.03\text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ 和 $129.06\text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$, 经过 300 圈循环后, 对应的放电克容量分别衰减至 105.68 、 $113.65\text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ 和

$116.76\text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$, 相应的容量保持率分别为 81.82% 、 88.11% 和 90.47% 。显然, Li_3PO_4 包覆能够有效提升 LNMO 在高电压下的循环稳定性。其中, 采用前驱体包覆的 LNMO 电极材料样品 P2 展现出最好的稳定性, 说明在长循环过程中, 样品 P2 中的包覆层能

够稳定正极材料表面的过渡金属离子、捕获电解液中的酸、抑制过渡金属离子溶出,同时阻隔电解液。

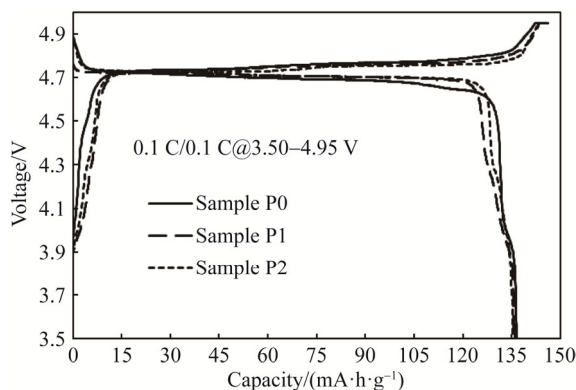


图 5 Li_3PO_4 包覆前后的 $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ 材料的首次充放电曲线

Fig. 5 First charge-discharge curve of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material before and after Li_3PO_4 coating

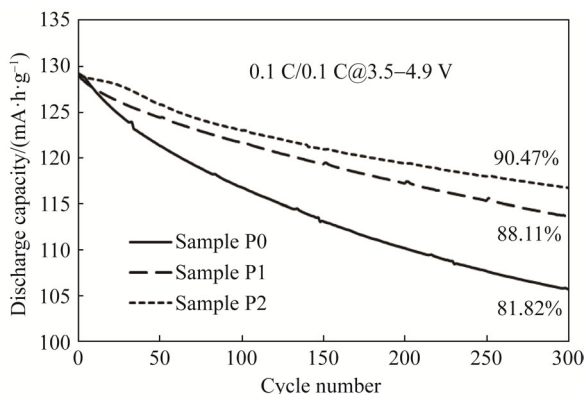


图 6 Li_3PO_4 包覆前后的 $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ 材料在 0.5 C 下循环性能图

Fig. 6 Cyclic performance diagram of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material before and after Li_3PO_4 coating at 0.5 C

0.5 C 电流倍率下循环 300 圈后的 EOL 电芯对应阳极的过渡金属含量如图 7 所示。由图 7 可以看出,采用 Li_3PO_4 对 LNMO 正极材料进行表层包覆处理,能够显著抑制阴极在充放电过程中过渡金属 Ni 和 Mn 的溶出速率。样品 P2 的过渡金属溶出量最小,说明对应阴极材料最稳定,这和实际的循环结果也是相一致的,说明前驱体预包覆 Li_3PO_4 技术能够提高尖晶石型 LNMO 材料长循环过程中表面稳定性,减缓过渡金属离子溶出。

图 8 为样品 P0、样品 P1 和样品 P2 3 个样品分别在 0.20、0.33、0.50、1.00 C 和 2.00 C 的倍率下放电容量保持率曲线,所有倍率测试的电压范围为 3.5~4.9 V。由图 8 可见,随着放电电流倍率的提升,放电容量逐渐降低,这和大电流放电下电极极化作

用增大有关。当放电倍率增大到 2.0 C 时,样品 P0、样品 P1 和样品 P2 对应的容量保持率分别为 90.41%、87.72%和 92.45%,说明采用前驱体包覆 Li_3PO_4 能够有效提升 LNMO 材料的倍率放电性能。相比之下,样品 P1 的倍率性能最差,这是因为样品 P1 中包覆的 Li_3PO_4 偏聚严重,增大了 Li^+ 固相扩散的距离,从而恶化了电极动力学。

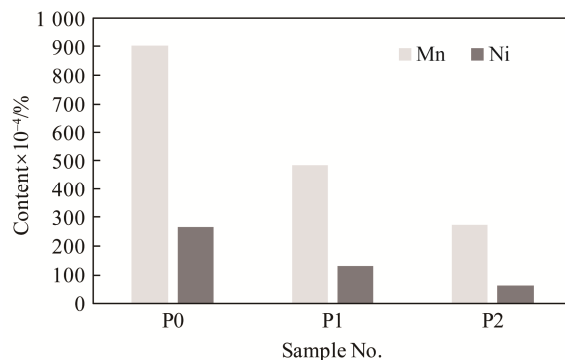


图 7 Li_3PO_4 包覆前后的 $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ 材料的循环后负极石墨中的过渡金属含量

Fig. 7 Transition metal content in negative electrode graphite after cycling of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material before and after Li_3PO_4 coating

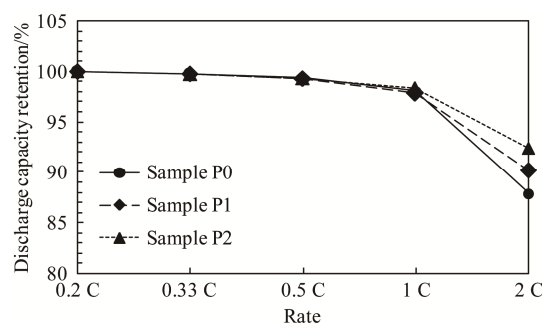
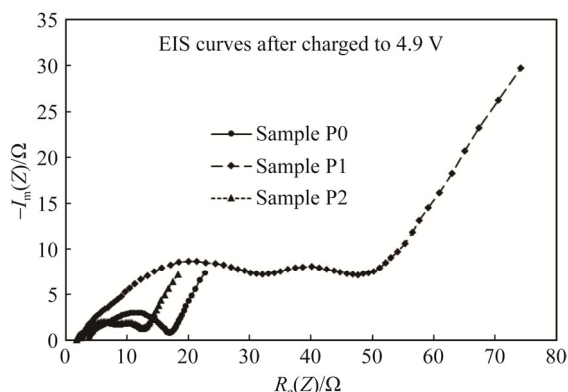


图 8 Li_3PO_4 包覆前后的 $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ 材料的倍率放电容量保持率曲线

Fig. 8 Rate discharge capacity retention curve of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material before and after Li_3PO_4 coating

电化学阻抗谱法(EIS)可测试 Li_3PO_4 包覆 LNMO 前后的阻抗值,测试频率范围:0.1 Hz~100.0 kHz。图 9 为电池首圈充电至 4.9 V 后测得的电化学阻抗谱。由图 9 可以看出,所有 EIS 曲线由中高频段的半圆和在低频频段的斜线组成。其中, R_s 为电解质电阻的值; R_{sei} 为 Li^+ 在固体电解质界面(SEI)层上的扩散阻抗; R_{ct} 为电荷转移电阻。样品 P2 对应的 R_{sei} 和 R_{ct} 均低于未包覆的样品 P0,这是由于活性电极材料与电解质之间的紧密相互作用以及稳定的 SEI 膜的形成,能够显著提升 LNMO 材料中离子传输和电荷转移速率。另外,样品 P1 对应的

阻抗值最大, 这可能是因为样品 P1 中的 Li_3PO_4 偏聚严重, 造成 Li^+ 固相扩散的距离增大, 电极动力学恶化。



$R_e(Z)$ is real part and $-Z_m(Z)$ is imaginary part.

图 9 Li_3PO_4 包覆前后的 $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ 材料的电化学阻抗谱
Fig. 9 Electrochemical impedance spectroscopy (EIS) diagram of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material before and after Li_3PO_4 coating

3 结论

采用前驱体预包覆技术对 LNMO 材料进行包覆改性, XRD 和 SEM 结果证实 LNMO 正极材料表面生成 Li_3PO_4 包覆层, 且包覆层的引入不会改变 LNMO 材料的基本物相结构和微观形貌。TEM 照片进一步证明了前驱体预包覆技术能在材料颗粒表面构建均匀致密的 Li_3PO_4 包覆层。电性能数据显示, 经过 Li_3PO_4 表面改性的样品 P2 与未包覆样品 P0 相比, 1 C 倍率下循环 300 次后的容量保持最高可从 81.82% 提升至 90.47%, 2 C 放电倍率下, 样品 P2 的容量保持率高达 92.45%。此外, EIS 曲线结果表明, Li_3PO_4 包覆材料电荷转移电阻明显降低。综上所述, 前驱体预包覆 Li_3PO_4 技术可以作为一种简单易行的材料改性策略, 可以用于阻止锂离子电池在充放电过程中正极活性材质与电解质的不良副反应的有效方法, 为 LNMO 材料的电性能提升提供了一条新的改性路径。

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Surface Modification and Electrochemical Performance of Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Cathode Material with Li_3PO_4 Coating

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Extended Abstract

Introduction As a positive material with a low cost, a high energy density and a good power performance, spinel lithium manganese nickel oxide ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$) has attracted much attention in the industry of lithium ion battery. Reducing the surface oxygen release behavior and the resolution of Ni or Mn during charging and discharging is a main method to improve the electrochemical performance. The conventional coating technique is to construct a coating layer on the surface of the material particles, which can isolate the electrolyte and reduce side reactions at the interface. Since the solid-phase coating method cannot form the uniform and compact coating layer, the improvement of the electrochemical performance is limited. In this paper, a precursor with Li_3PO_4 layer that was produced by a wet coating method was sintered at 850 °C. In addition, the impact of coating method was also analyzed by the first-principles calculation and characterizations.

Methods According to a molar ratio of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, a certain amount of $\text{Ni}_{0.25}\text{Mn}_{0.75}(\text{OH})_2$ precursor and Li_2CO_3 were weighed and mixed. The mixed material was ground in a mortar evenly. Afterwards, the ground material was sintered in a muffle furnace at 950 °C for 10 h, finally obtaining a LNMO positive electrode material (*i.e.*, sample P0) after cooling in the furnace.

According to the designed coating amount of 3% Li_3PO_4 , $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{LiOH}\cdot\text{H}_2\text{O}$ were weighed and sequentially added to alcohol solution with LNMO particles. After stirring and evaporation, the collected products were sintered in a muffle furnace to obtain conventional coating LNMO@ Li_3PO_4 material (*i.e.*, sample P1).

Also, $\text{Ni}_{0.25}\text{Mn}_{0.75}(\text{OH})_2$ precursor was mixed with deionized water in a mass ratio of 1:5. $\text{LiOH}\cdot\text{H}_2\text{O}$ was added to the coating at 3% under stirring until fully dissolved. Also, $\text{NH}_4\text{H}_2\text{PO}_4$ was added in another beaker and mixed with deionized water in a mass ratio of 1:20 until fully dissolved. The above two solutions were mixed thoroughly and filtered. The obtained filtered product was dried in a blast drying oven at 90 °C for 24 h to obtain $\text{Ni}_{0.25}\text{Mn}_{0.75}(\text{OH})_2$ precursor pre-coated with Li_3PO_4 . Li_2CO_3 in a ratio of Li:(Ni+Mn) of 1:2 was mixed evenly with the pre-coated precursor, and heated in a furnace at 950 °C for 10 h to obtain a wet coated LNMO cathode material with Li_3PO_4 after cooling (*i.e.*, sample P2).

The morphologies and structures of the cathode materials were examined by a model S-4800 scanning electron microscope (SEM, Hitachi Co., Japan) a model F20 aberration-corrected transmission electron microscope (TEM) with a cold field emission gun

at 200 kV (TECNAI), and a model Panalytical X'Pert X-ray diffractometer (XRD) in the 2θ range of 10° – 75° with $\text{Cu K}\alpha$ radiation ($\lambda=1.5405 \text{ \AA}$). The compositions of TMs in materials were measured by a model IRIS IntrepidII inductively coupled plasma atomic emission spectroscopy (ICP-AES, XSP).

Density functional theory (DFT) calculations were carried out through a named Vienna ab initio package (VASP), in which the cut-off energy was set to 520 eV for an accurate test, and the projector augmented wave (PAW) was used to describe the interaction between ions and electrons. For the optimization of crystal structures, the exchange correlation function was used as the Perdew-Burke-Ernzerhof (PBE) form of generalized gradient approximation (GGA). The lattice vector and the atomic position were sufficiently optimized until the resultant force was less than $0.01 \text{ eV}/(\text{\AA} \cdot \text{atom}^{-1})$. The Brillouin zone was adopted with a $4 \times 4 \times 4$ k-mesh.

Each material was mixed with carbon black and polyvinylidene fluoride binder in N-methyl-2-pyrrolidone with a mass ratio of 90:5:5 to prepare the electrode slurry. Subsequently, the slurry was casted on the Al foil and dried in vacuum at 100°C . Pouch cells were assembled with graphite as an anode, and 1 mol/L LiPF_6 solution in EC/EMC/DEC (3:5:2 by volume) as an electrolyte. Pouch cells were tested at 3.50–4.95 V and 0.1 C (1 C = $150 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$) for the first cycle on a model Maccor S4000 battery testing system. The cycling performance, EIS, and rate capability at 25°C were tested at 3.5–4.9 V.

Results and discussion Based on the powder XRD patterns of samples P0, P1, and P2, all the samples have a typical $Fd\bar{3}m$ spinel structure, since the Li_3PO_4 coating layer has no impact on the LNMO's crystal structure. The SEM images of samples reveal that the coating process has a slight effect on the surface appearance and particle size distribution. Based on the TEM and SEM-EDS analysis, the coating layer of sample P2 has higher homogeneity than that of sample P1, which can provide a better protective effect and reduce the corrosion of the electrolyte. According to the cycling data, the capacity retention is 90.47%, which is obvious improvement from sample P0 after running 300 cycles, and the superior cycling performance indicates an outstanding structural stability of sample P2, which can be proved by the Mn dissolution data. The capacity retention of 92.45% at 2C discharging can verify that sample P2 has a uniform coating layer. As a result, the precursor pre-coating Li_3PO_4 technique affects the phase structure and morphology of spinel LNMO slightly, and improves the electrical properties effectively.

Conclusions The main phase structure and micromorphology of spinel LNMO remained unchanged after Li_3PO_4 coating, and the characteristic peak of Li_3PO_4 appeared. The rate discharging and cycling performance was significantly improved, and the charge transfer impedance was reduced by Li_3PO_4 layer. This study indicated that precursor pre-coating Li_3PO_4 technique could be an effective approach to reduce the dissolution of transition metal and could be thus a potential method to improve the electrochemical performance of lithium manganese nickel oxide.

Keywords lithium nickel manganese oxide; lithium phosphate; coating; electrochemical performance