富锂锰基正极材料研究进展

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摘　要　目前富锂锰基正极材料以其高比容量（ >250 mAh/ g）、高工作电压、低成本、环境友好等优点受到了学术界的极大关注，是极具潜力的下一代锂离子电池正极材料。然而，循环过程中富锂锰基正极材料存在首次库仑效率低、倍率性能差、容量与电压衰减严重等缺点，使其实际应用受到了极大限制。经过几年来的深入研究，人们对富锂锰基正极材料的理论认识逐步加深，发展了针对富锂锰基正极材料各种缺点的改性方法，取得了一系列重要进展。本文总结了近几年来学术界在富锂锰基正极材料方面的重要研究进展，包括放电比容量、首次库仑效率、循环性能、倍率性能、电压稳定性，总结了针对富锂锰基正极材料的各种实验表征手段。此外，还介绍了富锂锰基正极材料在理论研究方面的重要方法以及在全电池方面的应用。最后，基于目前的实验进展和理论认知，对富锂锰基正极材料今后的发展进行了展望。

关键词： 富锂锰基正极材料；锂离子电池；层状材料；阴离子氧化还原对；表征技术

中图分类号： O614　**文献标识码：** A

文章编号： 1009 -2412（2019）02 -0012 -08

DOI：10.3969/j.issn.1009 -2412.2019.02.002

引　言

随着便携式移动电子设备和纯电动汽车的普及，人们对以锂离子电池为代表的储能装置的需求也在不断提升。目前，商用石墨负极材料的比容量为 372 mAh/g[1]，硅基负极材料的比容量可达 2 000 mAh/g[2]。然而，正极材料在比容量方面的提升则比较缓慢，目前常用的正极材料有：层状结构的 $LiCoO_2$、尖晶石结构的 $LiMn_2O_4$、橄榄石结构的 $LiFePO_4$ 和近几年发展较快的层状三元材料[3~7]。但是上述正极材料的实际比容量普遍在 200 mAh/g 以下，并且已经接近各自的理论极限值。因此，急需研发高比容量的新型正极材料。近年来，富锂锰基正极材料（$xLiMO_2 \cdot (1-x) Li_2MnO_3$，M = Ni、Co、Mn 等）以较高的实际比容量（≥250 mAh/g）、较低的价格、环境友好等优势受到了研究人员的极大关注[8~11]。

目前认为富锂锰基正极材料是由 $LiMO_2$（M = Ni、Co、Mn 等）和 Li_2MnO_3 两相复合而成。充电至 4.5 V 左右时，富锂相 Li_2MnO_3 开始贡献容量。由于该反应不完全可逆，造成电极材料较低的首次库仑效率[12]。循环过程中发生的相转变（层状相-尖晶石相-岩盐相）和四价锰降价引起的层状结构破坏，又会导致容量和电压的迅速衰减[13,14]。另外，$LiMO_2$ 和 Li_2MnO_3 相较低的离子导率进一步限制了材料的倍率性能[15]。针对上述问题，研究人员发展了多种改性方案，包括表面包覆和掺杂。表面包覆能够增强电极材料与电解液的界面稳定性，提高界面处的离子传输速率，并可以防止电解液对电极材料的侵蚀[16,17]；掺杂则能够增强电极材料晶体结构的稳定性，抑制相转变和过渡金属离子的迁移，提升循环稳定性[18,19]。为了深入研究富锂材料的充放电机理，研究人员引入了多种新的实验技术手段（原位 XRD、中子衍射、X 射线吸收谱、球差矫正电子显微镜和电子能量损失谱）和理论研究手段（有限元分析、分子动力学和第一性原理计算）。目前，研究人员在富锂锰基正极材料电化学性能方面取得了一系列重要的研究进展。

1　电化学性能

经过近几年的发展，富锂锰基正极材料在放电

收稿日期： 2019-01-28　**修回日期：** 2019-02-26

研究资助： 国家重点研发计划“纳米科技”重点专项（2016YFA0202600）。

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比容量、首次库仑效率、循环性能、倍率性能以及电压衰减方面都取得了不错进展。

1.1 放电比容量

富锂锰基正极材料的实际比容量可达 250 mAh/g 以上,这得益于其中传统的阳离子氧化还原对(过渡金属)和提供额外容量的阴离子氧化还原对(晶格氧,O^{2-}/O^{-})[19]。但是,高比容量意味着更深程度的脱锂态,这将导致晶格氧的氧化以及氧气的释放,不仅破坏电极材料的结构,同时给电池系统带来安全隐患[20]。一种解决方案为设计新的结构,增强晶格氧在氧化还原反应中的可逆性。例如,Xia 等[21]结合共沉淀法和离子交换法合成了一种具有单层 Li_2MnO_3 超晶格结构的 O_2 型的 $Li_{1.25}Mn_{0.5}Co_{0.25}O_2$,在 10 mA/g 电流密度下首圈比容量可达 400 mAh/g。另一种解决方案为设计新的氧化还原体系。例如,Ceder 等[22]通过高价过渡金属阳离子和低价阴离子共掺杂的方式制备了无钴、镍的富锂锰基正极材料 $Li_2Mn_{2/3}Nb_{1/3}O_2F$ 和 $Li_2Mn_{1/2}Ti_{1/2}O_2F$。该结构能够激活新的氧化还原电对 Mn^{2+}/Mn^{4+},因此在 1.5~5.0 V 电压范围、10 mA/g 电流密度下,材料的比容量高达 317 mAh/g。

1.2 首次库仑效率

富锂锰基正极材料的首次库仑效率与其结构密切相关。目前认为富锂锰基材料中的富锂相 Li_2MnO_3(C2/m)起稳定结构的作用[23,24]。低电压下(<4.5 V),Li_2MnO_3 相没有电化学活性,比容量主要由层状相 $LiMO_2$ 贡献[25]。高电压下(>4.5 V),Li_2MnO_3 相被激活。但由于过渡金属难以继续被氧化,晶格氧开始被氧化,贡献容量。晶格氧氧化容易造成氧释放,破坏晶体结构,导致电化学惰性的 Li_2O 的形成,造成锂源的损失。最终,富锂相会逐步转变为 MnO_2 相[26,27]。另外,在高电压(≈4.7 V)下,有机电解液会被氧化,产生 HF 等酸性物质。酸性物质会侵蚀电极材料和 SEI 膜,加剧锂源损失[28~30]。以上因素造成了富锂锰基材料在首次充放电时较大的不可逆容量损失和较低的库仑效率。

针对上述问题,研究人员发展了一系列的改性措施。例如,Qiu 等[31]研究发现,氧空位能抑制富锂材料晶格氧的释放。基于此,该研究团队通过 CO_2 与材料间的气固界面反应在电极材料表面构筑氧空位。改性后材料的首次库仑效率由初始的 83.8% 提高到了 93.2%。另外,表面包覆也能提高电极材料的首次库仑效率。例如,Qiao 等[32]通过在富锂锰基材料的表面包覆一层 MOF 修饰层来降低极化,同时缓解电解液分解产物对电极材料的腐蚀,并在一定程度上抑制 Li_2O 形式的脱锂和脱氧现象,材料的首次库仑效率从 80.0% 提高到了 91.1%。此外,表面包覆和形貌调控能够促进 Li^+ 的回迁,进而提高材料的首次库仑效率。Ku 等[33]通过在富锂锰基材料表面构造均匀分布的尖晶石纳米颗粒将材料的首次库仑效率由原来的 80.0% 提高到 87.6%。另外,Deng 等[34]通过设计纳米线型的富锂锰基材料,有效地缩短了 Li^+ 的传输路径;并在其中引入适量的尖晶石相,进一步提升 Li^+ 的传输速率,其首次库仑效率达到了 89.4%。

1.3 循环性能

富锂锰基正极材料的容量衰减与循环过程中由表面开始并持续发生的层状到尖晶石的相变密切相关[35]。这种相变过程与以下两个因素有关:其一,在高工作电压下 O^{2-} 的氧化和 Mn^{4+} 变价诱导的离子迁移重排[36,37];其二,循环过程中表面过渡金属离子溶解导致的表面相变[38]。

抑制相转变的方法主要包括表面修饰、离子掺杂和体相复合等。目前,表面修饰主要是在电极材料表面构筑导 Li^+ 的保护层[39~42]或者改变其表面成分(贫 Ni[43]、氧空位[44]、NiCo 量子点修饰[45]),从而抑制固液界面处副反应的发生,减少电极材料中过渡金属离子的溶解和电解液的消耗。离子掺杂具体包括表面掺杂[46]、体相掺杂[47]以及梯度掺杂[48]等方式。这种方法不仅可以阻止过渡金属离子向锂层迁移,还可以束缚晶格氧,避免晶格氧的不可逆释放。体相复合主要是通过在层状富锂锰基正极材料的内部引入一定量的尖晶石相,以稳定体相晶体结构,抑制层状向尖晶石的转变[49]。例如,Wang 等人[50]通过添加碳纳米管(CNT)的方式,获得了包含电子导体 CNT 和离子导体异质外延尖晶石结构的富锂正极材料。该材料表面极化小,结构转变被抑制,离子/电子的扩散快,因此循环稳定性能优异。在 1 C 下经过 200 圈循环后,电极材料仍保留了 227 mA h /g 的放电比容量,容量保持率为 92.3%。Wang 等人[51]在富锂锰基正极材料表面 4~5 个原子层厚度中引入了 Nb^{5+} 等重金属离子,通过抑制 O^{2-} 和 Mn^{4+} 的活性,阻止相变的发生,维持结构的稳定性。该材料在 0.1 C 下循环 100 圈后,容量保持率由原始材料的 76% 提升至 95%。此外,Yue 等人[49]报道了一种通过梯次锂盐调控对富锂锰基正极材料进行体相尖晶

石修饰的简便方法，有效地提高了材料的晶体结构稳定性，在 2C 下循环 300 圈后容量保持率高达91.5%。

1.4 倍率性能

富锂锰基正极材料的倍率性能与其动力学特性密切相关，包括材料本身的 Li^+ 离子扩散速率和电极/电解液界面处的转移速率。富锂锰基正极材料中的 Li_2MnO_3 相较低的锂离子本征扩散系数严重制约了其倍率性能[52]。另外，电极/电解液界面副反应产生的表面惰性层会增加界面电荷转移阻抗[53]。所以，改善材料内部和表面的动力学性能是提高富锂锰基正极材料倍率性能的关键。

研究表明，离子掺杂不但可以增强材料的导电性，而且能增大(003)晶面的间距，降低锂离子扩散阻力。富锂锰基正极材料中适量的钴元素能够提高材料的电导率，缓解不同电流密度下放电比容量的差异，同时提高其低温性能[54]。Ru[55]、Sn[56,57]和 Mo[58]等金属元素也能够有效扩大晶面间距，提升材料的倍率性能。此外，得益于尖晶石相中存在的三维 Li^+ 扩散通道，层状-尖晶石相复合电极材料展现了优异的倍率性能[59~61]。Sun 等人发现 AlF_3 包覆层能有效抑制材料表面电解液的分解和惰性层的形成，维持表面结构的稳定性，从而保证高倍率下锂离子的快速嵌入/脱出[62]。多种包覆材料都有显著的作用，例如 Al_2O_3[63]、$FePO_4$[64]、$AlPO_4$[65]和 MnO_2[66]等。此外，通过表面修饰导电层，例如 Al[67]和 C[68]等，也能够提高电极材料的倍率性能。

通过纳米化来缩短锂离子的扩散路径也是提升富锂锰基正极材料倍率性能的有效途径[69,70]。但材料的微纳米化设计不利于结构的稳定性和振实密度的提升。因此需要优化材料设计来平衡倍率性能和结构稳定性之间的关系。研究表明，在二次颗粒的直径大于 10 μm 的情况下有利于在提升倍率性能的同时保持电极材料的结构稳定性[71]。

1.5 电压衰减

目前认为高电压状态下 Mn^{4+} 转变为 Mn^{3+} 造成的相转变(层状结构-尖晶石结构-岩盐结构)是富锂正极材料电压衰减的重要原因之一[72]。解决该问题常用的改性方法为包覆和掺杂。例如，Guo 等[42]通过 $KMnO_4$ 溶液在富锂材料表面诱导产生尖晶石相。尖晶石结构稳定，能够提升电解液-电极材料的固液界面稳定性，防止电解液对电极材料的侵蚀，显著改善了电压衰减。另外，Liu 等[73]通过溶胶-凝胶法对富锂材料表面进行 $LiFePO_4$ 包覆。除维持电极/电解液界面稳定外，部分铁离子会进入到体相内部，与晶格氧形成了更强的 Fe-O 键从而起到掺杂作用，既能够抑制过渡金属迁移引起的相转变又可以提升 Li^+ 的传输速率。Huang 等[74]通过表面 WO_3 处理来调节表面 Ni/Mn 比例，从而在电极材料表面构建新的相结构，实现抑制电压衰减的目的。Meng 等[75]通过构造一种富锂@SiO_2 的核壳结构，显著地抑制了电压衰减。此外，Na^+ 离子的梯度掺杂[18,76]、Zr^{4+} 在过渡金属层的掺杂[35,77]都对电压衰减有明显的抑制作用。另外，设计特殊的结构也能够改善电极材料的电压稳定性。例如，Yang 等[78]设计了外部富 Mn 内部富 Co 的梯度分布的富锂正极材料，有效抑制了其电压衰减。在其他抑制电压衰减策略方面：Anh 等[79]则证实 25~55 ℃的温度范围有利于维持电压的稳定；Yang 等[80]证实最佳的电压稳定性范围为 2.8~4.4 V；新型粘结剂羧基纤维素钠、海藻酸钠等也能够提高电压稳定性[81,82]。

1.6 全电池

目前对于富锂锰基正极材料性能评估大都是基于半电池体系。这些评估数据虽有一定的意义，但并不完全适用于全电池体系。因此，迫切需要对基于富锂锰基正极的全电池体系展开系统的研究[83]。在消费电子领域，全电池的体积能量密度和质量能量密度一样重要[84]。虽然富锂材料的质量能量密度较高，但是它的振实密度较低，导致其体积能量密度低于其他正极材料[85]。半电池体系通常选用 AM∶BM∶CM = 8∶1∶1(AM：活性物质；BM：粘结剂；CM：导电剂)的浆料配比[86]，并且忽略了电极片的压实程度。对全电池体系，这会导致粘结剂和导电剂过量，压实密度过低。商用电池为了提升能量密度，通常将电极材料的密度提高到 2.5 g/cc，浆料的配比一般为 AM∶CM∶BM = 94∶3∶3，这对于富锂材料而言是个巨大的挑战[87]。

此外，首次库仑效率也是全电池的关键指标，其依赖于正极和负极之间的最小值。目前主流商用正极材料首次库仑效率普遍高于石墨(92%)[88]。但是富锂锰基正极材料的首次库仑效率较低(≤83%)[89]，低于商用石墨负极。因此，提高富锂材料的首次库仑效率非常重要。此外，富锂材料严重的电压和容量衰减会对全电池的循环寿命造成极大影响[90,91]。Jing 等人利用球形的 $Li[Li_{0.2}Ni_{0.16}Co_{0.1}Mn_{0.54}]O_2$(LNCM)为正极材料，以预锂化后的纳米硅

为负极材料，制备了 LNCM/Si 体系的扣式全电池，其能量密度高达 590 Wh kg^{-1}，远高于当前的商用锂离子电池[92]。这种全电池在 0.1 C 下循环 50 次之后，LNCM 正极能够维持 215 mAh g^{-1}的比容量，容量维持率为 95%。但是浆料中活性物质含量较少，且极片的负载较低，实际参考意义不大。Qiu 等人以 $Li_{1.144}Ni_{0.136}Co_{0.136}Mn_{0.544}O_2$（LNCMO）为正极材料、中间相碳微球（MCMB）为负极材料制备了 18650 型商用圆柱全电池进行测试，在 0.2 C 下循环 300 次的容量保持率为 85%[93]。其中 18650 型圆柱全电池的设计容量为 1 800 mA h，制备的工艺参数接近商用锂离子电池，对富锂锰基正极材料进一步商业化应用具有参考价值。

2 表征技术

在富锂锰基正极材料表征方面，除了常用的 X 射线衍射仪（XRD）、扫瞄电子显微镜（SEM）、透射电子电子显微镜（TEM）和 X 射线光电子能谱（XPS）外，研究人员还引入了多种新的表征技术，包括原位 X 射线衍射（In-situ XRD）[45]、中子衍射（ND）[94]、原位拉曼[95]、电子能量损失谱（EELS）、球差矫正电子显微镜和 X 射线吸收谱（XAS）[36]等。例如，Xiao 等人通过原位 XRD 证实了 MOF 诱导表面碳包覆的 NiCo 纳米点能够抑制富锂正极材料在高度脱锂态下晶格氧的氧化程度，从而提升材料结构稳定性[45]。Qiu 等人则通过中子衍射精修的方法确认了气固界面反应改性材料中氧空位的存在，揭示了表面氧空位构筑提升富锂锰基正极材料储锂性能的相关机理[94]。Li 等人将原位 XRD 技术和原位拉曼光谱相结合，直接观测到了 c 轴方向上的 $O^-—O^-$（过氧根）键，证实了富锂锰基正极材料中可逆的 O^{2-}/O^- 氧化还原过程[93]。Hu 等人结合 EELS、球差矫正电子显微镜和 XAS 等先进技术，观测到了富锂锰基正极材料在充放电过程中的过渡金属离子价态持续降低的现象[36]。

3 理论研究

富锂锰基正极材料一般要在高温下进行较长时间的热处理（>8 h，>600 ℃），以获得好的结晶性[35,96,97]。因此，引入物理和化学的研究方法非常必要。得益于计算机技术水平的提高，计算研究已经逐步成为独立于实验研究和理论研究之外的第 3 种研究方法。从研究对象的尺度上划分，计算研究包括电子结构层次的第一性原理计算（DFT）、原子层次的分子动力学计算（MD）和微观层次的有限元模拟[98]。在目前的富锂锰基正极材料的计算研究中，运用最广泛的是为以 Vienna Ab initio simulation package（VASP）为代表的第一性原理计算。计算内容包括晶格常数、电荷密度、结合能、态密度和过渡态搜索等。例如，Lee 等人设计了一种具有可逆 Mn^{2+}/Mn^{4+} 双氧化还原对的富锂正极材料。该材料在 Li_2MnO_3 中引入高价阳离子（Ti、Nb）和氟离子，在舍弃了昂贵、环境友好性差、安全性低的 Co、Ni 元素的同时，保持了其高比容量和高工作电压的优点[99]。研究人员通过第一性原理计算研究了该材料在充放电过程中 Mn 和 O 的价态变化，给出了应力和离子环境变化对其性能的影响，阐明了该新型材料的充放电机理。另外，结合差分电荷密度图，本课题组对设计的双壳层中空微球富锂锰基正极材料的良好倍率性能给予了理论解释[100]。结果表明充放电过程中氧空位引起的局域电荷的不平衡分布够提高锂离子的传输速率。此外，Li 等人证实在富锂锰基正极材料中引入聚阴离子（BO_4 和 BO_3）能够显著增强电极材料的循环性能[101]。态密度图表明聚阴离子的引入能够降低高度脱锂态下晶格氧的活性，稳定了材料的晶体结构。这种基于电子结构层次的调控有利于加深对富锂锰基正极材料的理解以及该方案在类似材料中的拓展应用。

4 总结与展望

富锂锰基正极材料以其超高的放电比容量、较高的工作电压、较低的成本和良好的环境友好性成为目前锂离子电池正极材料的研究热点。但是该电极材料也存在首次库仑效率低、倍率性能差、电压和循环稳定性差等一系列问题。经过近年来的发展，研究人员结合先进的表征技术和理论计算，通过大量的实验，在电极材料的各个性能指标上取得了一系列重要进展。但是由于富锂锰基正极材料的研究牵涉到物理、化学等多个学科，电极材料的性能仍需要继续改善，并且对其中的阴离子氧化还原对的认识仍需要进一步加深。综上所述，富锂锰基正极材料仍然是最有潜力的下一代高性能锂离子电池正极材料之一。

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Research Progresses on Li- and Mn- Rich Cathodes

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Li-rich layered oxide cathodes have attracted great attention, and are among the most promising cathodes in the next generation lithium ion batteries because of their high specific capacity (>250 mAh /g) , high operation voltage, low cost and environment-friendly. However, they suffer from severe disadvantages during cycling, such as low initial Coulombic efficiency, poor rate capability, rapid capacity fading and voltage decay, prohibiting their practical application. After exploiting and lucubrating on Li-rich layered oxide cathodes for years, our theoretical understanding have been deepened greatly, a variety of modifying methods have been developed to conquer the above-mentioned shortcomings and great improvements have been achieved. In this article, we summarize the most important processes in academia on Li-rich layered oxide cathodes in recent years including discharge capacity, initial Coulombic efficiency, cycling performance, rate capability and voltage stability. In addition, various characterization techniques for Li-rich layered oxide cathodes are also included. Furthermore, we also introduce some important theoretical methods on Li-rich layered oxide cathodes especially a few representative accomplishments. Meanwhile, the applications of Li-rich layered oxide cathodes in full cells are also briefly introduced. At last, a perspective for the further development on Li-rich layered oxide cathodes is also given on the base of the current theoretical and experimental understanding.

Keywords: Li- and Mn-rich cathode materials, lithium ion batteries, layered oxides, anionic redox, characterization techniques