

固态电池富锂锰基层状氧化物正极材料研究进展

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摘 要: 固态电池是具有高能量密度和高安全性的下一代二次电池。当匹配固态电解质与金属锂负极构筑全电池时, 正极材料的种类显著影响了其能量密度。富锂锰基正极材料具有较高的放电比容量, 是实现更高能量密度固态电池的关键材料。当富锂锰基正极与金属锂负极匹配, 有望进一步构筑能量密度大于 $600 \text{ W} \cdot \text{h} \cdot \text{kg}^{-1}$ 的固态电池。因此, 对富锂锰基正极材料开展体相/表界面结构设计、构筑稳定快速的离子/电子通路、促进稳定阴离子氧化还原反应是实现其在固态电池中应用的重要策略。这些策略的重点在于改善多相界面的不兼容、抑制析氧和增强固|固界面高电压稳定性等问题。本文综述了固态电池富锂锰基正极材料的设计开发策略和提升正极与固态电解质固|固界面高电压稳定性问题的最新研究进展, 并展望了未来富锂锰基正极材料在固态电池应用中的研究重点和重要应用场景。

关键词: 固态电池; 富锂锰基正极材料; 能量密度; 阴离子氧化还原反应; 高电压界面
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当前, 锂离子电池占据了绝大部分动力和储能市场的份额, 已成为能源存储领域的主要技术之一^[1-4]。然而, 随着对电池能量密度需求的逐渐增长, 传统基于有机液态电解液的锂离子电池逐渐呈现出高电压不稳定、易腐蚀、易燃易爆等安全问题。另外, 锂枝晶的生长也会刺穿隔膜, 导致电池短路并引发发热失控^[5-7]。因此, 亟需开发下一代固态电池, 以期从本质上解决锂离子电池的安全问题^[8-11]。以金属锂为负极、固体无机材料或聚合物为固态电解质的固态金属锂电池体系, 比采用同类型正极材料的液态锂离子电池能量密度高 20%~30%。因此, 固态电池成为了二次电池的研究热点和前沿科技^[12-16]。

由于常规正极材料容量的限制, 难以进一步提升固态电池能量密度。研究用于固态电池中的高比能正极材料是突破固态电池能量密度的关键所在^[17-19]。富锂锰基正极材料(LRMO), 其分子式简写为

$x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($0 < x < 1$, $\text{M} = \text{Mn}, \text{Co}, \text{Ni}$), 这类材料的容量贡献来源于过渡金属阳离子氧化还原反应与阴离子氧化还原反应的电荷补偿, 容易具有更大的放电比容量($\geq 250 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$)和更高的能量密度($\geq 1000 \text{ W} \cdot \text{h} \cdot \text{kg}^{-1}$)^[20-23]。富锂锰基正极材料元素组成中钴和镍等元素含量较低, 地壳中丰产的锰元素含量相对较高, 因此, 其成本较低、安全性高^[24-27]。当其用于固态电池, 可以有效避免正极材料中过渡金属阳离子溶解至电解液, 从而提升正极材料在长循环过程中的结构稳定性和容量保持率^[28-29]。因此, 采用富锂锰基正极材料构筑固态电池, 不仅可以提升固态电池的能量密度, 还带来环境友好和可持续性发展的优势^[30-31]。然而, 富锂锰基自身较低的电导率、循环过程中的不可逆相变诱导表界面结构退化, 进一步导致其动力学行为较差。当富锂锰基正极材料用于高能量密度固态

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电池中, 阴离子氧化还原反应难以有效激活, 电化学反应可逆性差, 从而导致富锂锰基正极呈现较低的比容量和较差的循环稳定性^[32]。此外, 高电压下的氧逃逸导致电解质氧化分解, 进一步破坏固|固界面稳定性^[33]。因此, 亟需在高性能固态电池中构建和维持稳定快速的离子/电子传输网络, 从而提升正极材料体相表界面离子/电子传输动力学。

近年来, 作为提升固态电池能量密度的最重要正极材料之一, 富锂锰基正极材料的研究主要集中在体相/表界面结构设计、稳定快速的离子/电子传输网络构筑、高电压固|固界面稳定性的改善、阴离子氧化还原反应可逆性的提升等方面, 并取得了一系列研究成果。本文介绍了固态电池富锂锰基正极材料的结构特征、电化学性质, 进一步综述了其在固态电池应用中的最新研究进展和展望了其未来的研究重点方向。

1 固态电池和富锂锰基正极材料概述

当正极和负极材料之间采用固态电解质进行离子传导, 就得到了固态电池(图 1)。固态电池具有能量密度高、安全性好等优势^[34-38]。富锂锰基正极材料是一种极具潜力的固态电池正极材料, 其由两相结构组成的固溶体, 具有高比容量、高电压和比能量等优势^[39-42]。然而, 富锂锰基正极材料在全固态电池的应用中存在首圈库伦效率(CE)低、倍率性能差、析氧和电压衰减问题, 限制了其广泛实用化^[43-45]。为了推动富锂锰基正极材料在固态电池中的实用化, 需要进行体相/表界面结构设计、构筑稳定快速的离子/电子传输网络, 充分发挥阴离子氧化还原反应参与电荷补偿的巨大比容量优势。

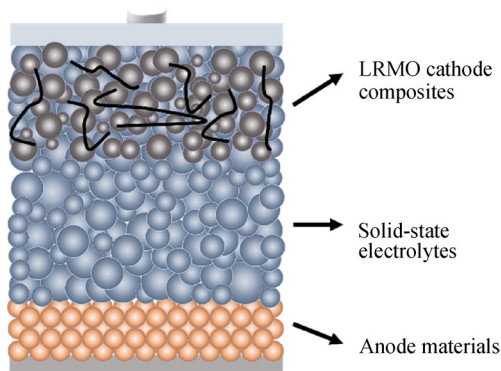


图 1 固态电池示意图

Fig. 1 Schematics of solid-state battery

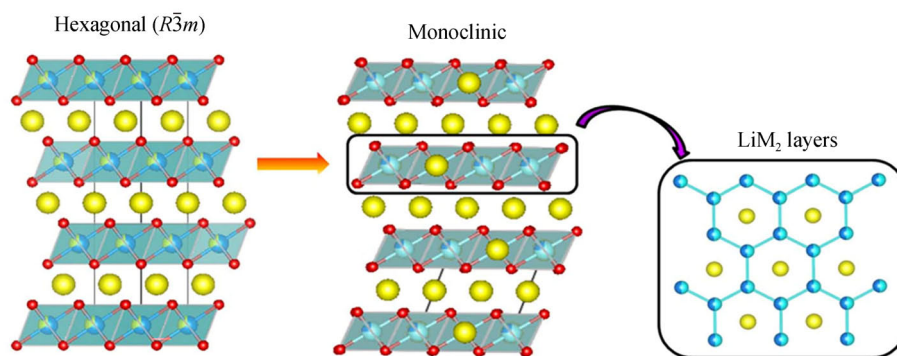
1.1 富锂锰基正极材料的结构

富锂锰基正极材料晶体结构主要有 Li_2MnO_3 和

LiMO_2 ($M=\text{Mn}, \text{Ni}, \text{Co}$) 2 种组分构成。 Li_2MnO_3 组分的晶体结构也可以使用类似于 LiMO_2 成分的结构分子式 $\text{Li}[\text{Li}_x\text{Mn}_{1-x}]\text{O}_2$ 来表示。因此, 可将 Li_2MnO_3 组分也看成是具有特殊结构的 LiMO_2 成分, 其中过渡金属层的部分 Mn 原子被 Li 原子取代(图 2), 形成 Li 原子被 6 个 Mn 原子包围的蜂窝状结构^[46-47]。这 2 种组分是层状相的 $\alpha\text{-NaFeO}_2$ 类型的岩盐结构, 氧原子在其中形成立方密排阵列结构, 其中, 过渡金属离子和锂离子占据八面体位置^[48-49]。在富锂锰基正极材料中, 如果过渡金属中含有镍原子, 由于镍离子和锂离子的离子半径相近, 会出现锂/镍混排现象, 即过渡金属层中的镍离子进入到层间锂离子的位置上^[50-51]。锂/镍混排现象虽然会增加电解液与电极表面的副反应, 导致倍率性能和循环性能变差。但是, 进入到层间锂离子位置的镍离子作为“支柱”可以有效缓解在充放电过程中正负离子之间的静电相互作用, 还可以减少晶格参数的变化, 抑制应力应变的发生^[52]。近年来, 针对零应变的富锂材料结构研发逐渐得到重视, 其特点一般是在锂脱出与嵌入的过程中, 结构变化较小, 体积变化率 $<1\%$ 。应用到固态电池体系中, 可以有效避免晶胞体积膨胀与收缩带来的应力应变, 导致晶粒破碎, 从而稳定长循环性能。另外, 人工智能(AI)的快速发展可以加速富锂材料的结构设计, 替代传统试错的方式高效发现新的材料结构, 进一步扩大富锂材料结构的基因库。

1.2 富锂锰基正极材料的电化学性能

富锂锰基正极材料首次充放电过程的充电曲线可以分成 2 部分: 一是为倾斜的区域, 锂离子主要是从 LiMO_2 结构中脱出, 伴随着过渡金属离子的氧化过程; 二是为一段较长的阴离子氧化还原反应平台区域, 当首次充电电压超过 4.45 V 时, 富锂锰基正极材料中的 Li_2MnO_3 组分被激活, 此时锂离子主要从 Li_2MnO_3 结构中脱出, 伴随着 O^{2-} 的氧化过程, 最终形成 O_2 析出^[53-54]。首次充电结束后脱出的 Li 和 O 的原子数之比为 2:1, 可将净脱出的物质看作 Li_2O , Li_2MnO_3 也转变为具有电化学活性的 MnO_2 。这个新形成的层状结构存在大量空位, 可供 Li^+ 在随后放电过程中可逆嵌入与脱出, 从而使该材料的实际容量高于传统层状氧化物正极材料^[55-56]。然而, 净脱出的 Li_2O 是不能可逆回到富锂锰基正极材料晶格当中的, 导致首圈不可逆容量损失较大, 即表现出富锂锰基正极材料首圈库伦效率较低。此外, 由于部分氧离子以氧气的形式析出, 进一步造成不

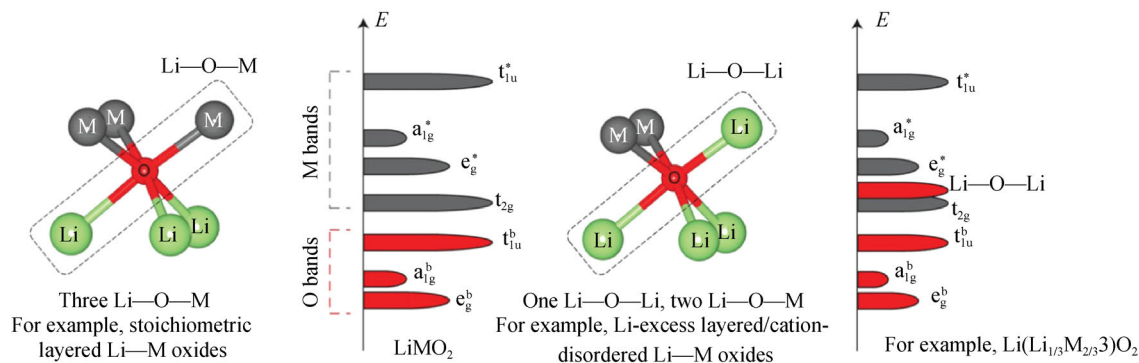
图2 层状结构的 LiMO_2 组分和 Li_2MnO_3 组分不同晶面的晶体结构示意图^[46]Fig. 2 Schematic diagram of different crystal planes of LiMO_2 and Li_2MnO_3 component of layered structures^[46]

可逆的转变,也使得首圈容量损失。因此,这也是富锂锰基正极材料的首圈库伦效率比较低的原因之一^[57–58]。在充电首圈损失的 Li^+ 有部分迁移至负极表面,与电解液和负极材料反应形成 SEI 膜,所得 SEI 膜有利于负极材料的结构稳定性^[59–61]。因此,随着充放电循环次数的增加,富锂锰基正极材料的库伦效率逐渐趋于正常的水平。

在固态电池应用中,富锂锰基正极材料在高电压下进行的阴离子氧化还原反应,其不可逆导致的氧析出使得表界面结构衰退影响电池性能。因此,为了提升固态电池电化学稳定性,需要进一步理解富锂锰基正极材料反应机制,发展表面结构调控策略,提高阴离子氧化还原反应可逆性。富锂锰基正极材料的高容量主要来源于过渡金属阳离子和氧阴离子共同参与电荷补偿进行的容量贡献,由于富锂锰基正极材料中特有的未杂化的 $\text{O}2\text{p}$ 态(Li—O—Li 态),所以氧离子能够参与电荷补偿。常规锂含量的层状氧化物正极材料(LiMO_2)并不存在这种氧孤对电子^[62–63],因此,阴离子氧

化还原反应发生在超晶格结构中(图 3)。由于 $\text{Li}2\text{s}$ 和 $\text{O}2\text{p}$ 轨道的巨大能量差, Li—O—Li 构型中的 $\text{O}2\text{p}$ 轨道几乎不会受到 Li 的影响,所以阴离子氧化还原反应的活性起源于 Li_2MnO_3 相中特殊的“ Li—O—Li ”构型,从而呈现出非键轨道特性和可逆的电子得失能力^[64–65]。

富锂锰基正极材料首圈充电过程中的阴离子容易发生不可逆氧化还原反应,从而引起库伦效率低、析氧、电压衰减、循环稳定性差等问题。当前,电压衰减问题是制约富锂锰基正极材料实际应用的瓶颈。循环过程中,富锂锰基电极的放电电压平台会持续降低,导致能量密度不断下降^[66]。在首圈充电过程中,由于析氧产生大量的氧空位,从而使氧空位邻近的锰离子可以通过空位迁移到锂层并占据四面体间隙位。在随后的电化学过程,锰离子会继续迁移到周围八面体间隙位置形成稳定的 MnO_6 八面体结构,在后续锂离子嵌入则会占据邻近的四面体间隙位置,最后形成一种类尖晶石结构。这种类尖晶石结构会随着循环的进行进一步转化为无序的岩

图3 富锂锰基正极材料局域结构中的原子配位信息和相应能带结构示意图^[64]Fig. 3 Structural and chemical origin of preferred oxygen oxidation along Li—O—Li configuration^[64]

盐结构^[67-68]。随着循环次数的持续增加,这种结构的变化会从材料表面逐渐渗透到材料的内部,正是这种随着循环逐渐发生的相变,使得整个材料的电压持续衰减^[69-70]。但是,这种类尖晶石相和岩盐相结构的形成并不会减少锂离子能够可逆脱/嵌的位置,所以,富锂锰基正极材料随循环容量下降的原因并不是相的转变,而更多的是来自表面锰的化合价降低造成的锰溶解。固态电池可以有效的避免这一过渡金属离子溶解现象。因此,富锂锰基正极材料在固态电池中的应用前景广阔^[71-72]。

2 固态电池富锂锰基正极材料研究进展

由于受到能量密度的限制,传统正极材料无法满足当下对于高能量密度、高安全储能器件的需求。基于富锂锰基正极材料的固态电池逐渐成为当下的

研究热点领域,表 1 为最近基于富锂锰基正极材料的固态电池电化学性能,包括硫化物、卤化物、聚合物和氧化物固态电解质体系都取得了一些研究进展,展现出其在固态电池领域应用的巨大潜力。另外,使用固态电解质可以防止富锂锰基正极材料由于氧析出引起的化学串扰,高强度的固体电解质可以防止明显的内部短路行为,提高极端机械滥用稳定性,从而提升基于富锂锰基正极材料的固态电池安全性^[73-76]。固态电解质高熔点的特性,也赋予了全电池显著的高温稳定性。因此,基于富锂锰基正极材料的固态电池热稳定性也大大提升,从而进一步减轻热管理系统的负载,促进更大电池系统的集成和优化。虽然富锂锰基正极材料在全固态电池中的应用面临着较大的挑战,但是其商业化的前景使得其备受关注。

表 1 基于富锂锰基正极材料的固态电池性能参数对比

Table 1 Comparison of electrochemical performance of LRMO cathode SSBs

LRMO cathodes	Electrolyte types	Initial discharge capacity/CE	Cycling performance	Testing temperature/°C
$\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$	Sulfide solid electrolytes	About 225 $\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$ /About 70%	0.5 C/1000cycle/83%	27 ^[77]
$\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$		About 220 $\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$ /About 67.7%	0.5 C/1000cycle/87%	27 ^[78]
$\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$		204 $\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$ /67.8%	1 C/2022cycle/72%	55 ^[79]
$\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$		248 $\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$ /94%	1 C/300cycle/81.2%	25 ^[80]
$\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$		230 $\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$ /83%	0.5 C/431cycle/60%	25 ^[33]
$\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$	Halide solid electrolytes	231 $\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$ /90%	1 C/2000cycle/80.4%	25 ^[81]
$\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$		244 $\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$ /73%	1 C/750cycle/88.6%	45 ^[82]
$\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$		235.4 $\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$ /74.83%	1 C/1200cycle/84.1%	25 ^[83]
$\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$		About 245 $\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$ /84%	1 C/200cycle/82.7%	25 ^[84]
$\text{Li}_{1.2}\text{Ni}_{0.16}\text{Co}_{0.08}\text{Mn}_{0.56}\text{O}_2$	Polymer solid electrolytes	N.A.	1 C/400cycle/84.8%	25 ^[30]
$\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$		N.A.	0.2 C/200cycle/91%	30 ^[85]
$\text{Li}_{1.2}\text{Ni}_{0.167}\text{Co}_{0.067}\text{Mn}_{0.567}\text{O}_2$	Oxide solid electrolytes	226 $\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$ /N.A.	N.A./30cycle/N.A.	80 ^[86]
$\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$		245 $\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$ /N.A.	0.2 C/200cycle/100%	25 ^[87]

N.A. is not available.

2.1 富锂锰基正极材料在固态电池中的应用挑战

为了解决复杂的界面机械和化学稳定性,需要明晰富锂锰基正极材料的结构特征、氧析出和正极电解质高电压界面稳定性来源^[88]。图 4 为富锂锰基正极材料在固态电池中的应用挑战。由图 4 可见,富锂锰基正极材料在固态电池中的应用面临着诸多挑战。首先,富锂锰基正极材料具有独特的两相结构,在固态电池中富锂锰基正极材料中的 Li_2MnO_3 相与电解质界面不兼容;由于正极材料电解质界面的高阻抗值和富锂锰基正极材料的低离子/电子电导率,反应动力学缓慢导致其活化受到严重限制,以至于无法发挥阴离子氧化还原反应

带来的容量贡献^[73];其次,固态电解质与富锂锰基正极材料的化学势不匹配,在复合正极中会出现自发的化学反应,容易形成即导离子又导电子的正极电解质界面层(CEI)。随着循环过程中持续增长,固态电池的电化学性能迅速衰减^[32];最后,在高电压下,阴离子氧化还原反应不可逆导致氧逃逸,进一步氧化固态电解质界面形成钝化层,增加界面阻抗,影响界面处离子传输^[80]。为了解决这些难题,通过表面改性稳定材料微观结构,引入元素掺杂以及新颖的体相/表界面结构设计策略稳定重复脱/嵌锂过程中的晶体结构,提升复合正极材料中活性物质的利用率。

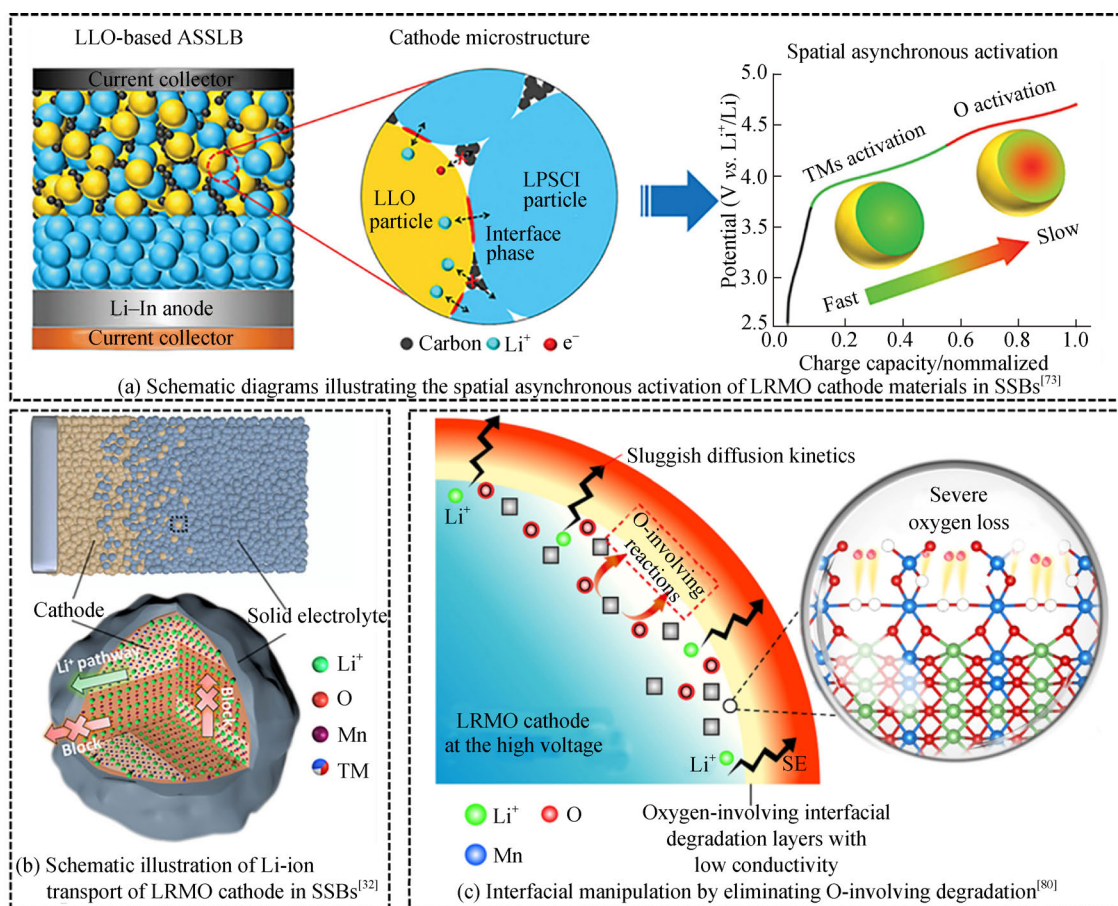


图4 富锂锰基正极材料在固态电池中的应用挑战

Fig. 4 Challenges in application of LRMO cathode materials in SSBs

2.2 固态电池富锂锰基正极材料改性策略

富锂锰基正极材料的种类按照结构特征可以分为多晶和单晶富锂材料。多晶型富锂锰基正极材料是由纳米尺寸的一次晶粒堆积而成的微米级二次颗粒^[89–90]。由于多晶材料中的一次颗粒之间不可避免会有一些空隙和晶界,且固态电解质具有不流动性,导致锂离子传输路径曲折,电极材料机械稳定性和活性物质利用率普遍较低^[91]。由于各向异性体积的变化致使晶界处产生较强应力,晶间裂纹和晶内裂纹的形成造成颗粒的物理结构明显损伤。随着电化学循环的进行,累积的应力沿着晶界释放,使得多晶颗粒产生大量裂纹。这是其在固态电池中性能快速衰减的重要原因之一^[92]。

2.3 多晶富锂锰基正极材料改性策略

2.3.1 多晶材料体相/表面改性 图5为多晶富锂锰基正极材料改性策略。由图5a~图5c可见,为了解决锂离子和电子的传输动力学问题, Sun 等在富锂锰基电极材料中引入适量的碳纳米管添加剂建立连续的电子传输网络,然后通过原子层沉积

(ALD)和退火技术在富锂锰基正极材料颗粒表面构建了1层具有抗氧化性和优异离子导率的 Li_3PO_4 界面层,促进了在卤化物固态电解质体系的固态电池中界面锂离子的传输、扩散动力学,稳定了正极材料中的晶格氧,最大限度的减少了局部结构的变化,抑制了正极材料|固态电解质界面降解。因此,所得材料在室温下呈现出 $230.7 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ 的高初始放电比容量和100圈的长循环稳定性,即使在2 C的高倍率下依然具有 $62.4 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ 的放电比容量。这项工作也为固态电池富锂锰基正极材料设计提供了新的策略和深入见解^[33]。

Wu 等提出了一种体相掺杂和表面硫化的双功能改性策略,这是硫化物固态电池中超高比容量的富锂锰基正极材料稳定运行的前提。在富锂锰基正极材料晶体结构中引入微量的钨元素,促进Li在 Li_2MnO_3 组分中的扩散,促进了 Li_2MnO_3 相部分活化。由于钨元素强共价键的参与,增强了晶格氧的稳定性^[93–94],抑制氧析出,防止硫化物固态电解质氧化,形成界面副反应的产物。此外,采用一种时

间/成本效益高的硫化过程,可在富锂锰基正极材料表面形成超薄且均匀的表面层,不仅可以构建一个稳定的界面层来促进正极材料|电解质界面处的锂离子传输,还可以有效缓解由于界面处的低电子电导引起的空间电荷层效应^[95]。改性后的富锂锰基正极材料在硫化物基固态电池中表现出优异的电化学

性能,即在高温 55℃,具有优异的倍率性能(0.5 C, 140.6 mA·h·g⁻¹)和超长循环稳定性(2022 次循环容量保持率>70%) (图 5d~图 5e),这揭示了影响硫化物基固态电池中富锂锰基正极材料的界面稳定性和锂扩散动力学的根本原因,从而通过结构设计改进并抑制高电压下氧析出引起的界面降解^[79]。

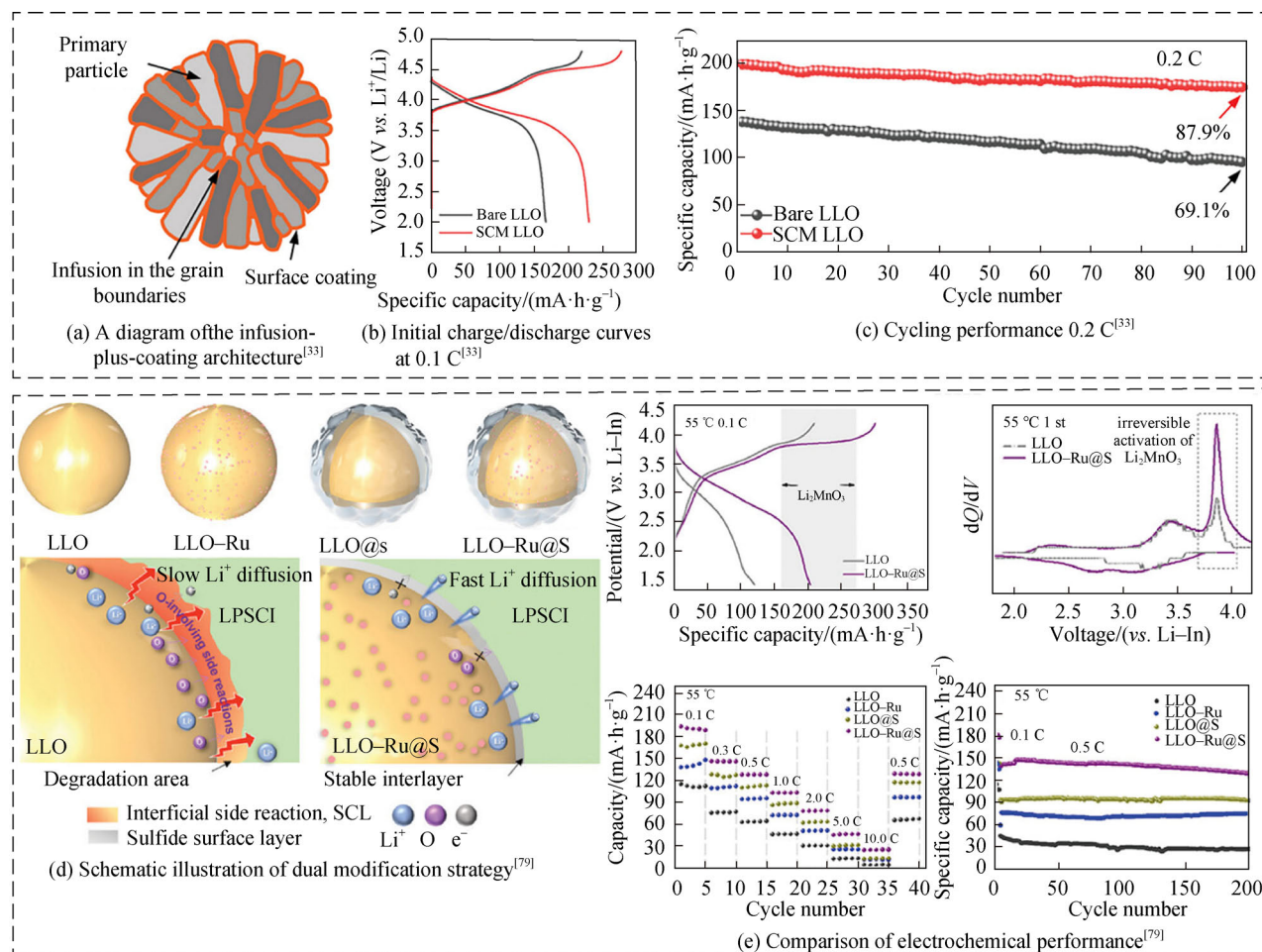


图 5 多晶富锂锰基正极材料改性策略

Fig. 5 Modification strategy of polycrystalline LRMO cathode materials in SSBs applications

2.3.2 机械化学法制备固态电池富锂锰基正极材料 多晶颗粒在高能球磨下,将二次多晶颗粒破碎成一次颗粒,同时,在一次颗粒表界面引入一些快离子导体形成三维离子传输网络,进一步增强锂离子传输动力学和氧结构的热力学稳定性,使得阴离子氧化还原活性和可逆性大幅提升(图 6a)。富锂锰基正极材料的表面氧不稳定性是界面电荷转移动力学快速降低的关键因素,最终引发固态电池电化学性能的快速衰减。针对该问题,通过简单的机械化学球磨方法,将富锂锰基正极材料应用到全固态电池体系,发挥出较高的电化学性能(图 6b)。富锂锰基正极材料表面阴离子电荷补偿中心从氧离子转移

至表面键合的亚硫酸根离子位置,构筑了高效的富锂锰基正极|电解质界面离子传输网络,最终在卤化物基全固态电池体系下,实现室温超高首圈库伦效率(94%)、高首圈放电比容量(约 248 mA·h·g⁻¹)、优异的倍率性能和循环稳定性(图 6c),这证实了富锂锰基正极材料表面稳定的氧离子以及高效的界面离子传输网络对电池性能发挥起到了关键作用^[84];进一步通过固态机械化学的方法和随后的退火处理,成功的将硼元素引入到富锂锰基正极材料晶体结构中,并将非晶态的 Li₂B₄O₇ 在正极材料表面形成了三维的锂离子传输网络,这一过程实现了富锂锰基正极材料与非晶态的 Li₂B₄O₇ 无缝连接,在整个晶

体结构中生成了强的 B—O 键(图 6d), 提高了晶格氧化还原反应的可逆性^[96–97]。得益于富锂锰基正极材料|电解质界面稳定性的改善, 基于改性后富锂锰基正极材料的固态电池展现出了优异的室温长循

环稳定性, 在 1 C 的倍率下经过 2000 个循环容量保持率为 80.6%。为实现基于固态电池富锂锰基正极材料 Li_2MnO_3 相组分的高度活化和阴离子氧化还原反应可逆性提供了一种有效的途径^[81]。

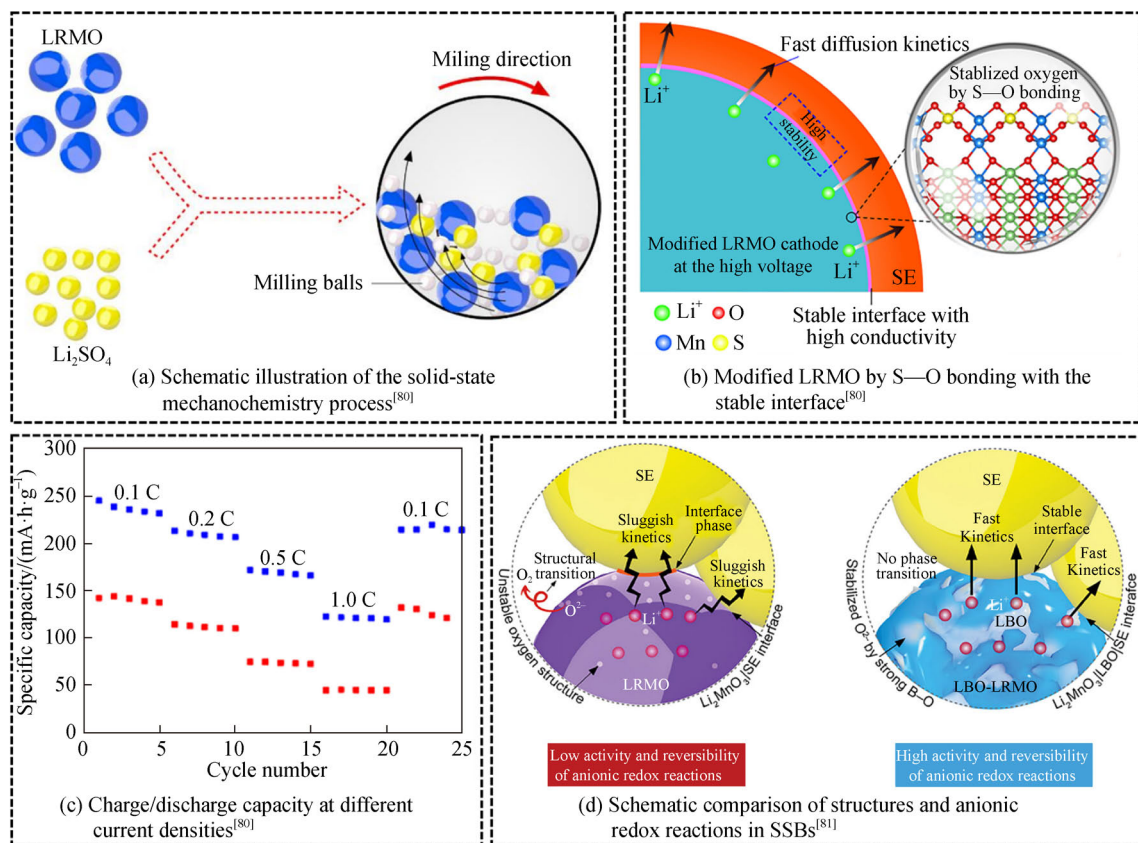


图 6 机械化学法制备固态电池富锂锰基正极材料

Fig. 6 Preparation of LRMO cathode materials for SSBs by mechanochemical method

2.4 固态电池单晶富锂锰基正极材料研究进展

与多晶材料相比, 单晶型的富锂锰基正极材料颗粒尺寸小, 几乎没有明显的晶界, 得益于其形貌的优势, 单晶型富锂锰基正极材料具有更高的结构强度和抑制晶间裂纹形成的能力^[98–100]。得益于与固态电解质电化学—机械兼容的微观结构, 单晶材料更容易在表面构筑一些离子/电子通路, 且单个颗粒间的离子传输路径较短, 扩散动力学行为也优于多晶的大颗粒正极材料。因此, 单晶富锂锰基正极材料在固态电池应用中的潜力突出^[101–102]。

亚微米富锂锰基正极材料与固态电池的结合有助于发挥其高容量和高能量密度特性。由于富锂锰基正极材料自身的导电性差和独特的两相结构使得其与固态电解质界面不兼容, 从而阻碍了固态电池的进一步发展。图 7 为微米—亚微米级单晶富锂锰基正极材料在固态电池中的应用。由图 7a 可见, 通过

一步法合成得到体相具有立方隧道结构的 Li_2WO_4 相的富锂锰基正极材料^[103], 实现了体相嵌入高离子导率相结构, 改善固态电池富锂锰基正极材料体相/表面界面的 Li^+/e^- 传输动力学, 提升复合正极材料中活性物质的利用率。原位引入 Li_2WO_4 相, 不可避免的会引起掺杂效应, W 元素的掺杂增强了富锂锰基正极材料的结构稳定性, 提高了过渡金属阳离子和阴离子氧的氧化还原活性, 有效抑制了过渡金属离子的迁移^[104–105]。此外, Li_2WO_4 相的表面包覆提升了阴离子氧化还原反应可逆性, 有效防止长循环过程中卤化物固态电解质的氧化, 稳定了高电压固|固界面, 最终实现了室温高面容量($\geq 3.15 \text{ mA} \cdot \text{h} \cdot \text{cm}^{-2}$)和长循环稳定性, 在 1 C 高倍率下循环 1200 圈容量保持率为 84.1%(图 7b~图 7c)^[83]。

对于单晶富锂锰基正极材料, 急需解决的问题依然是改善锂离子和电子的传输动力学行为以及单

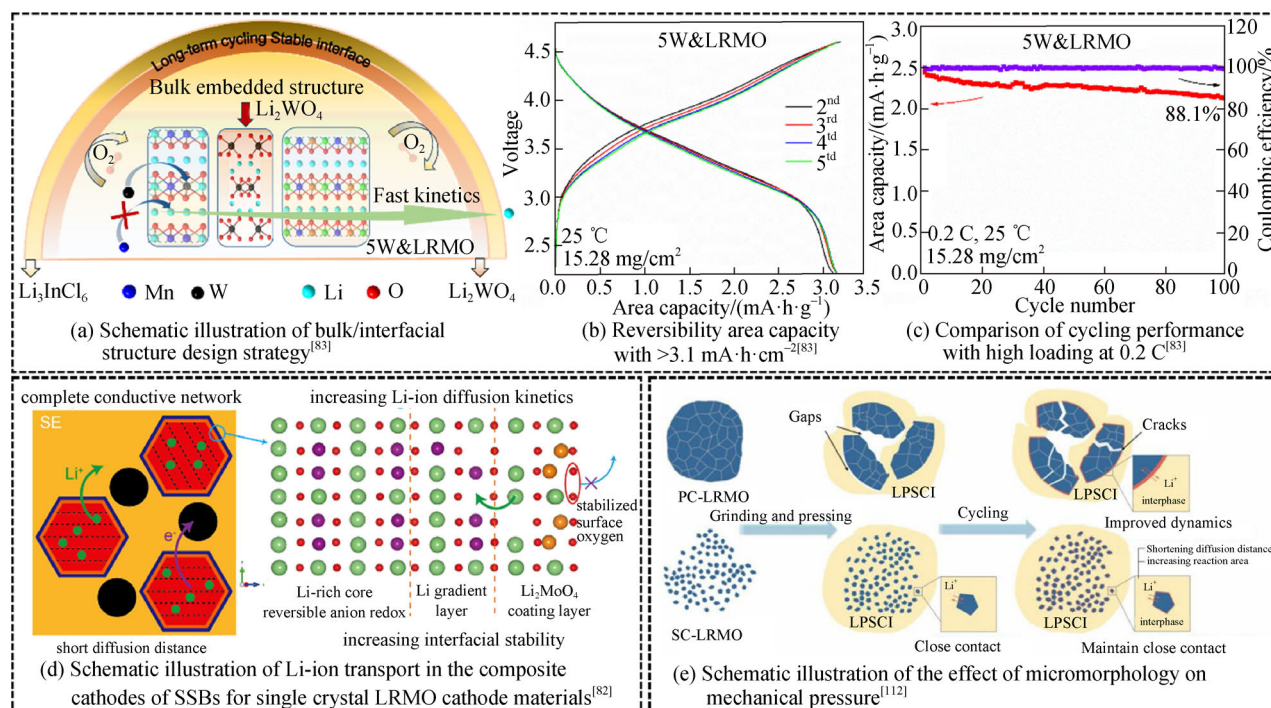


图 7 微米-亚微米级单晶富锂锰基正极材料在固态电池中的应用

Fig. 7 Application of micro and sub-micro single crystal LRMO cathode materials in SSBs

晶富锂锰基正极材料与固态电解质颗粒的粒径比等、进一步提升阴离子氧化还原反应动力学和界面稳定性。表界面改性大多数是作为单一的界面保护层,如果能采用多功能界面改性,就有望减轻发生界面副反应,长期循环过程中稳定单晶富锂锰基正极材料的表界面结构^[106–107]。基于此,Guo 等通过原位高温反应将亚微米单晶结构设计和多功能表面改性策略相结合,在固态电池中实现了富锂锰基正极材料优异的电化学性能(图 7d)。通过亚微米单晶颗粒尺寸匹配优化,可以改善正极颗粒与固态电解质之间的界面接触,缩短颗粒内锂离子和电子的扩散距离,在复合正极中形成更加完美的导电网络,从而增强传输过程动力学。在单晶富锂锰基正极材料表面构建的锂梯度层和钨酸锂包覆层可以促进界面锂离子传输,增强界面稳定性,而不会影响富锂锰基正极材料中的阴离子氧化还原活性。因此,实现了基于富锂锰基正极材料与卤化物固态电解质匹配组装的固态电池,展现出相对较高的比容量发挥,在 0.05 C 时为 $244 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$,即使是在 45°C 的高温下循环 750 次依然具有优异的电化学稳定性^[82]。

减小单晶富锂锰基正极材料的粒径,可以提高低电导率活性材料的氧化还原活性,从而改善电化学性能的可行策略。除了粒径外,富锂锰基正

极材料的微观结构对固态电池的循环性能也起着至关重要的作用。在多晶的正极材料中,纳米级初级粒子的聚集显著增加了晶界处的电阻,从而导致较差的倍率性能^[108]。电极压实和循环脱/嵌锂的过程中的不均匀应力分布会导致结构的坍塌和容量迅速衰减^[109]。相比之下,单晶富锂锰基正极材料主要是由单个或者少数初级颗粒组成^[110],这减轻了沿晶界的单向各向异性,抑制了裂纹的形成,在循环过程中结构完整性得到了保持和坚韧的正极材料|电解质界面接触^[111]。Yang 等获得了一种单晶富锂锰基正极材料,作为硫化物基固态电池的正极材料,旨在通过调整粒径大小来提高电化学性能,证实了亚微米级别小单晶富锂锰基正极材料颗粒在硫化物基固态电池中的优异的离子迁移和增强的机械性能(如图 7e)。在 60°C 、0.05 C 的倍率下,可逆比容量从多晶的 $243 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ 增加至 $316 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$,且在高倍率 1 C 时也有所提升,从 $105 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ 提高至 $210 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$,循环 300 次后容量保持率为 86%,即使在 $20 \text{ mg} \cdot \text{cm}^{-2}$ 的高负载下,固态电池也能展现出 $296 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ 的比容量,循环 50 次后容量保持率为 90%。进一步揭示了颗粒形貌和粒径控制在提升固态电池中富锂锰基正极材料循环稳定性的重要性,也为发展高比能固态电池提供了可借鉴的意见^[112–114]。

3 结论与展望

富锂锰基正极材料由于较高的放电比容量和能量密度,引起了固态电池领域的强烈关注,并在硫化物、卤化物和聚合物电解质体系下取得了显著进展。有望攻克液态电池体系中存在的产气、过渡金属溶解以及电压衰减等阻碍富锂锰基正极材料产业化进程的关键难题,从而推动高能量密度固态电池的快速且高质量的发展。采用体相/表界面结构设计、固态机械化学方法、颗粒单晶化策略能够有效改善锂离子/电子传输网络、增强阴离子氧化还原反应可逆性、并增强高电压正极|电解质界面稳定性,从而赋予了富锂锰基正极材料的固态电池优异的电化学性能。

然而,富锂锰基正极材料在固态电池中的产业化之路依然面临两相结构导致电子导电性差、界面电荷转移动力学缓慢、晶格氧损失、高电压界面不稳定和电化学-机械力学失效等挑战。因此,亟待对富锂锰基正极材料在固态电池应用中的失效机制及改性策略需展开深入细致的研究与探讨。因此,针对基于富锂锰基正极材料的固态电池研究工作还需要考虑以下几个方面:

1)鉴于单晶富锂锰基正极材料的制备流程相对复杂,有必要进一步优化其合成路线,旨在确保主体结构的稳定性,提升单晶富锂锰基正极材料的产量和质量。在此基础上,深入探究单晶富锂锰基正极材料在固态电池应用中的失效机制,明晰固态电池内部力-电-化学耦合机制。同时,研究单晶材料颗粒尺寸与固态电池长循环稳定性之间的关联,为有针对性的指导开发高性能固态电池所需的富锂锰基正极材料奠定坚实可靠的理论与实践基础。

2)零应变富锂材料的开发,在充放电循环中能维持其晶体结构的高度稳定,几乎不发生体积变化,这一独特性质对于固态电池至关重要。能有效减轻电池在循环过程中产生的机械应力,防止晶间裂纹和晶内裂纹的产生,显著提升固态电池的长循环稳定性。深入研究零应变富锂材料的制备工艺、性能优化策略及其与其他材料的复合应用,有望全面提升固态电池的综合性能表现。通过优化富锂锰基正极材料的组分和结构,可以提升固态电池的能量密度,更好的满足当前市场对更高能量密度固态电池的迫切需求。

3)借助机器学习驱动的多尺度大模型开发^[115–119],将成为筛选和设计固态电池富锂锰基正极材料晶体

结构,并指导界面包覆层设计的宝贵工具。其应用范围广泛,涵盖了零应变材料的结构优化设计以及具有高离子电导率、电化学和热力学稳定的表界面包覆材料的筛选等多个方面。通过这一工具,科学指导富锂锰基正极材料体相/表界面结构优化设计,以实现与固态电解质固|固界面优异的相容性,提升固|固界面的高电压稳定性。

4)开发能够匹配富锂锰基正极材料的耐高电压固态电解质,改善现有的制备方式,加强固态电解质成膜工艺和超薄固态电解质膜、电极薄膜的规模化制备工艺研发,包括当前干法电极技术中的黏结剂筛选、粘附特性、混合特性以及具体成膜制备技术进行深入探索。进一步理清“正负极材料-固态电解质-固|固界面-电池封装工艺”多方面的影响因素和联系。开发新型 A·h 级大电芯制备技术,实现富锂锰基正极材料在固态电池中的大规模商业化应用。

固态电池正进入一个关键时期,许多科学发现正迅速转变成科技生产力,从实验室的研发阶段逐步过渡到工厂的试制阶段。另外,低空经济的快速兴起也为固态电池产业打开了新的成长空间和增长点。富锂锰基正极材料的发展前景广阔,特别是在追求高能量密度固态电池的领域,其特色鲜明且应用潜力巨大。目前,持续进行的科学研究与跨学科的合作,有望克服富锂锰基正极材料现存的关键挑战,推动这些正极材料真正走向产业化应用。这些技术不仅为能源存储领域提供了更安全、更高效的解决方案,更为固态电池的可持续和高水平发展奠定了坚实的基础。

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Li-Rich Mn-Based Layered Oxide Cathodes for Solid-State Rechargeable Batteries

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Extended Abstract:

Solid-state batteries (SSBs) are a promising next-generation secondary battery due to their potential for high energy density and enhanced safety, offering solutions to the problems inherent in conventional lithium-ion batteries (LIBs) with organic liquid electrolytes (*i.e.*, flammability, corrosion susceptibility, and high-voltage instability). In the construction of SSBs, the selection of the cathode materials is critical to achieving a high energy density, particularly when coupled with lithium metal anodes. However, conventional cathodes often affect the energy density of SSBs due to their constrained specific capacities. It is thus crucial for achieving substantial improvements in the energy density of SSBs to develop high specific capacity cathodes. The Li-rich Mn-based layered oxide (LRMO) is a promising cathode material for SSBs for energy densities of above $600 \text{ W}\cdot\text{h}\cdot\text{kg}^{-1}$ due to their high discharge specific capacities. Furthermore, LRMO cathodes offer some additional advantages, *i.e.*, reduction of Co and Ni content, leverage of the abundance of Mn to achieve lower materials costs and improved safety. Their application in SSBs also mitigates the dissolution of TM-ions into the electrolyte, thereby enhancing the structural stability and capacity retention during long-term cycling progress. In addition, the resource-efficient composition of LRMO cathodes also align with environmentally friendly and sustainable development goals.

This review represents that the LRMO cathode materials are characterized by a composite crystal structure comprising two key components, *i.e.*, Li_2MnO_3 phase and LiMO_2 ($\text{M}=\text{Mn}, \text{Ni}, \text{Co}$) phase. Li_2MnO_3 phase can be considered as a superlattice-structured variant of LiMO_2 , formulated as $\text{Li}[\text{Li}_x\text{Mn}_{1-x}]\text{O}_2$. This superlattice-structured introduces unique unhybridized O 2p states, arising from Li—O—Li configurations. These unique oxygen states enable the participation of oxygen in charge compensation processes. Consequently, the high capacity in LRMO cathodes is attributed to the synergistic contributions of both TM cations and oxygen redox reactions.

LRMO cathodes, while exhibiting a distinctive biphasic structure, encounter significantly some challenges in SSBs. Specifically, the application of LRMO cathodes in SSBs is hindered by two primary issues. Firstly, the inherent incompatibility between Li_2MnO_3 phase and SEs interfaces results in sluggish reaction kinetics, severely restricting the activation of oxygen redox activity and consequently reducing the associated capacity contribution. Secondly, a chemical potential mismatch between SEs and LRMO cathodes drives spontaneous reactions at the composite cathode interfaces. These reactions lead to the formation of mixed ionic/electronic conductive CEI. Furthermore, irreversible oxygen escape further oxidizes the SEs interface, generating the passivation layers. These passivation layers increase interfacial impedance and impeded ion transport, ultimately hindering practical advancements in SSBs technology.

LRMO cathodes hold a significant promise for SSBs, as evidenced by research progress across various SEs, including sulfides, halides, polymers, and oxides. To fully realize this potential, some strategies addressing the inherent incompatibility between LRMO cathodes and SEs are crucial. These strategies encompass bulk/ interfacial structure design, nanostructured particle engineering, and the construction of stable Li^+/e^- transport pathways. These approaches can suppress oxygen escape, enhance the high-voltage stability of solid-solid interfaces, and ultimately stabilize oxygen redox while optimizing interfacial dynamics. Consequently, the implementation of these strategies leads to a significant enhancement in the electrochemical performance of LRMO-based SSBs.

Summary and prospects LRMO cathodes have attracted considerable attention for SSBs due to their high discharge specific capacity and energy density. Advancements in SSBs utilizing sulfide, halide, polymer, and oxide SEs demonstrate a potential of LRMO cathodes to overcome limitations currently hindering their industrial applications in liquid electrolyte systems. These limitations include gas evolution, TM dissolution, and voltage decay. However, the practical application of LRMO cathodes in SSBs faces some challenges stemming from their inherent properties, such as poor electronic conductivity attributed to their biphasic structure, sluggish interfacial charge transfer kinetics, oxygen escape, high-voltage interfacial instability, and electrochemical-mechanical degradation. Consequently, a comprehensive understanding of failure mechanisms and the development of advanced modification strategies for LRMO cathodes in SSBs are urgently needed. This necessitates several key research directions. Firstly, optimizing large-scale synthesis techniques for single-crystal LRMO cathodes is crucial, coupled with systematic investigation into their degradation mechanisms within SSBs. Such studies should elucidate the complex interplay of mechanical, electrical, and chemical coupling within SSBs. Secondly, the development of zero-strain LRMO cathodes, designed to maintain structural integrity with minimal volume changes during cycling, can effectively mitigate mechanical stress, suppress crack formation (both intergranular and intragranular), and significantly improve long-term cycling stability. Furthermore, machine learning-driven multiscale modeling offers an effective tool for the rational design of bulk/interfacial structures, facilitating superior compatibility and high-voltage stability at the solid-solid interfaces. Finally, the exploration of high-voltage-tolerant SEs specifically tailored for LRMO cathodes, alongside innovations in scalable fabrication processes for ultrathin electrolyte membranes and electrode films, is essential. The synergistic convergence of materials innovation, interfacial engineering and scalable manufacturing offers a transformative potential for realizing the full capabilities of LRMO cathodes. This convergence is crucial for advancing SSBs toward unprecedented levels of energy density, reliability and sustainability. Specifically, these combined efforts will facilitate the production of large-format batteries at the A·h-level, ultimately enabling the large-scale commercialization of SSBs incorporating LRMO cathodes.

Keywords solid-state batteries; lithium-rich manganese-based cathode materials; energy density; oxygen redox; high-voltage interface