



氧化物系锂离子固态电解质研究进展

王雅秋, 陈俊超, 朱彦者, 张果泰, 王建辉, 张翔宇, 汤卫平*

上海交通大学化学化工学院, 上海 200240

* 联系人, E-mail: tangweiping@sjtu.edu.cn

2024-06-01 收稿, 2024-07-12 修回, 2024-07-15 接受, 2024-07-15 网络版发表

国家自然科学基金(92372103)资助

摘要 固态锂电池因有望解决化学储能电池的安全隐患、提升能量密度而成为研究热点. 其中固态电解质是固态锂电池的核心材料. 我国在基于氧化物固态电解质的固态电池的研发和产业化上发展迅速, 这对推动我国固态电池行业发展起着不可或缺的作用. 本文对典型氧化物固态电解质包括钠超快离子导体(NASICON)、石榴石(LLZO)型、无机钙钛矿(LLTO)型和LiPON薄膜进行综述, 着重介绍了结晶结构与离子传输机理、提高电导率的方法以及改善电极与电解质界面相容性的措施, 并对它们的优缺点进行了综合对比. 最后, 为未来发展方向提供建议, 以期对氧化物系固态电解质的相关研究提供更加全面的参考.

关键词 固态电池, 氧化物系固态电解质, 电导率, 界面相容性

固态锂电池因具有高能量密度、高安全性等特点而成为目前研发和产业的热点. 固态电解质是固态锂电池不可或缺的关键材料, 左右着固态电池的充放电性能^[1~5]. 目前研发的固态电解质有无机固态电解质和聚合物固态电解质, 无机固态电解质又包括氧化物系、硫化物系、卤化物系、氢化物系^[6~12]. 关于无机固态电解质及固态电池的研究论文很多, 据不完全统计, 目前已被报道的无机固态电解质多达200多种^[13,14].

固态电解质是一类离子导体. 如图1所示, 氧化物系离子导体是最早被开发和研究的材料之一, 早在1884年就有Na⁺/glass离子导体的报道. 1976年Goodenough等人^[15,16]、1978年Alpen等人^[17]报道了钠超快离子导体(sodium super ionic conductor, NASICON) Na₃Zr₂Si₂PO₁₂和LISICON型Li₁₄Zn(GeO₄)₄后, 离子导体被广泛关注. 特别是近年来, 随着我国固态电池产业的迅速发展, 氧化物系锂离子导体以其高物理化学、电化学稳定性而被广泛地用于固态电解质材料, 对推动

我国固态锂电池产业发展起到越来越重要的作用. 据行业统计, NASICON结构Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃(LATP)、石榴石结构Li₇La₃Zr₂O₁₂(LLZO)已经有一定规模的生产, 开始用于固态电池产业中. 我国在氧化物系固态电解质的研发上也非常活跃. 最近, Zhu等人^[18]发明了新型、综合性能优异的NASICON结构Li₃Zr₂Si₂PO₁₂(LZSP).

氧化物系固态电解质按结构分类可分为NASICON结构、石榴石结构、钙钛矿结构、非晶态结构等^[19~21].

1 NASICON型固态电解质

1.1 Li₃Zr₂Si₂PO₁₂

Li₃Zr₂Si₂PO₁₂是最近报道的一种新材料, 由NASICON经过Li⁺/Na⁺离子交换而得到. NASICON于1976年被Goodenough和Hong^[15,16]报道, 其化学通式为Na_xM₂-

引用格式: 王雅秋, 陈俊超, 朱彦者, 等. 氧化物系锂离子固态电解质研究进展. 科学通报, 2025, 70: 1177–1190

Wang Y Q, Chen J C, Zhu Y Z, et al. Research progress in lithium-ion solid electrolytes of oxides (in Chinese). Chin Sci Bull, 2025, 70: 1177–1190, doi: 10.1360/TB-2024-0586

(AO_4)₃, 其中M为过渡族或主族金属, AO_4 为聚阴离子, 用Li取代Na后可得到具有高离子电导率的导体. NASICON结构中 MO_6 八面体和 AO_4 四面体通过共享角氧原子形成了有利于离子快速扩散的三维传输通道, 如图2所示^[22], 这种结构也使得NASICON固态电解质具有良好的导电性能. NASICON固态电解质在空气和水中具有良好的化学稳定性, 并因具有简单的制备工艺而成为炙手可热的氧化物系固态电解质之一^[22-24].

NASICON结构中一个典型的离子导体是 $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$.

PO_{12} (NZSP). 通过骨架保留的阳离子交换方法, 将NZSP中的 Na^+ 替换成 Li^+ , 形成新型NASICON结构LZSP高性能固态电解质. LZSP基本保持了图3(a)所示的框架结构, 但是 Li^+ 占据在 Na^+ 邻位的低配位中, 这让 Li^+ 继承了NZSP前驱体结构中相对较大的离子传导路径(图3(b)~(d))^[18]. LZSP在室温下实现了0.21 eV的低活化能和 $3.59 \times 10^{-3} \text{ S/cm}$ 的高离子电导率. LZSP不但继承了NZSP的空气稳定性, 而且在应用于固态电池时表现出优异的循环稳定性和倍率能力. 该研究为调节阳离

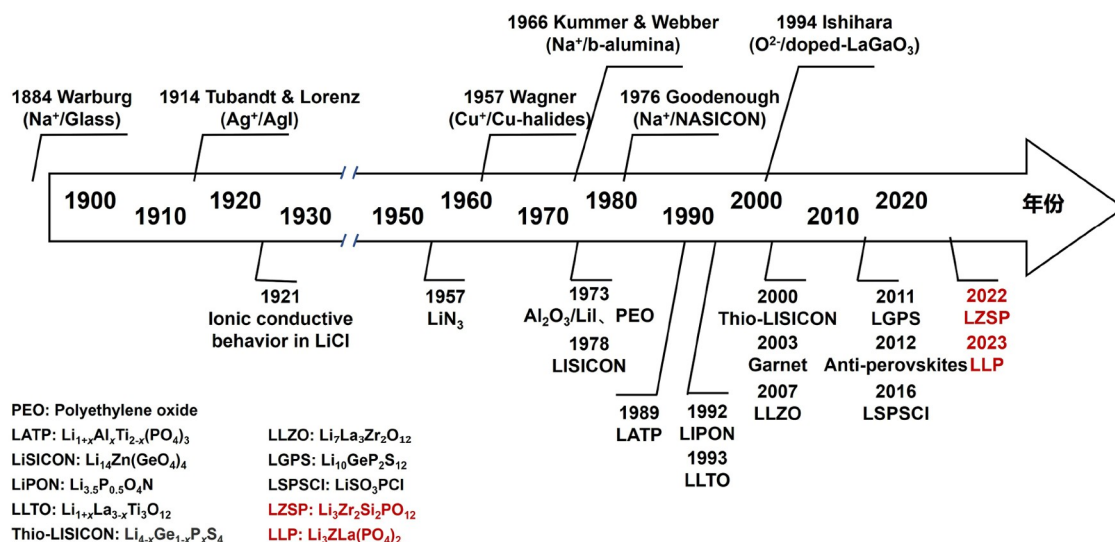


图1 典型离子导体和发现年代

Figure 1 Typical ionic conductors and discovery time

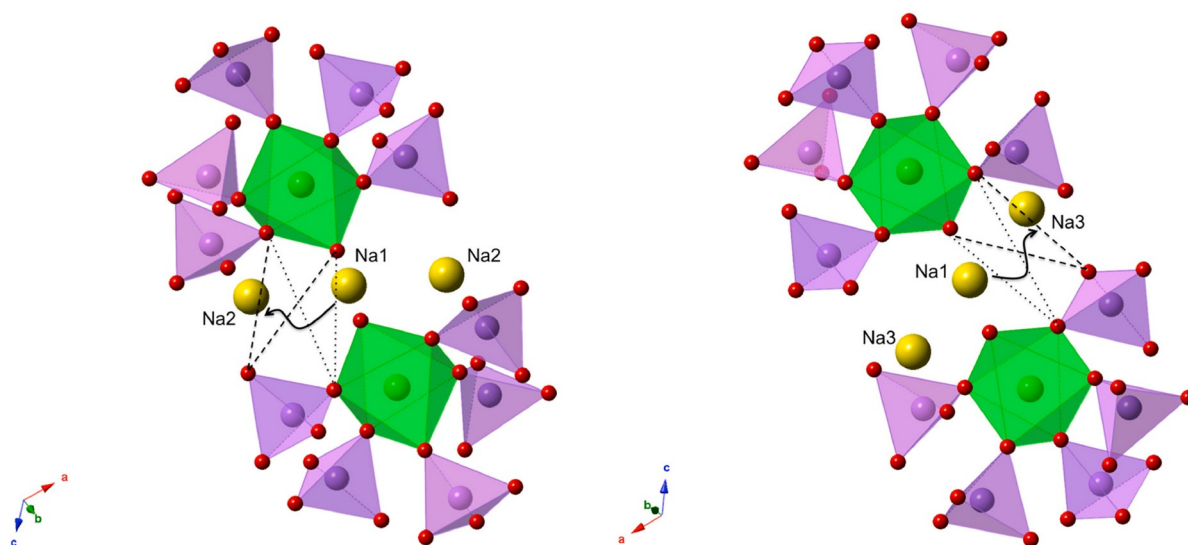


图2 NASICON晶体中的离子传导路径^[22]

Figure 2 Schematic of Na-ion conduction channels in monoclinic NASICON^[22]

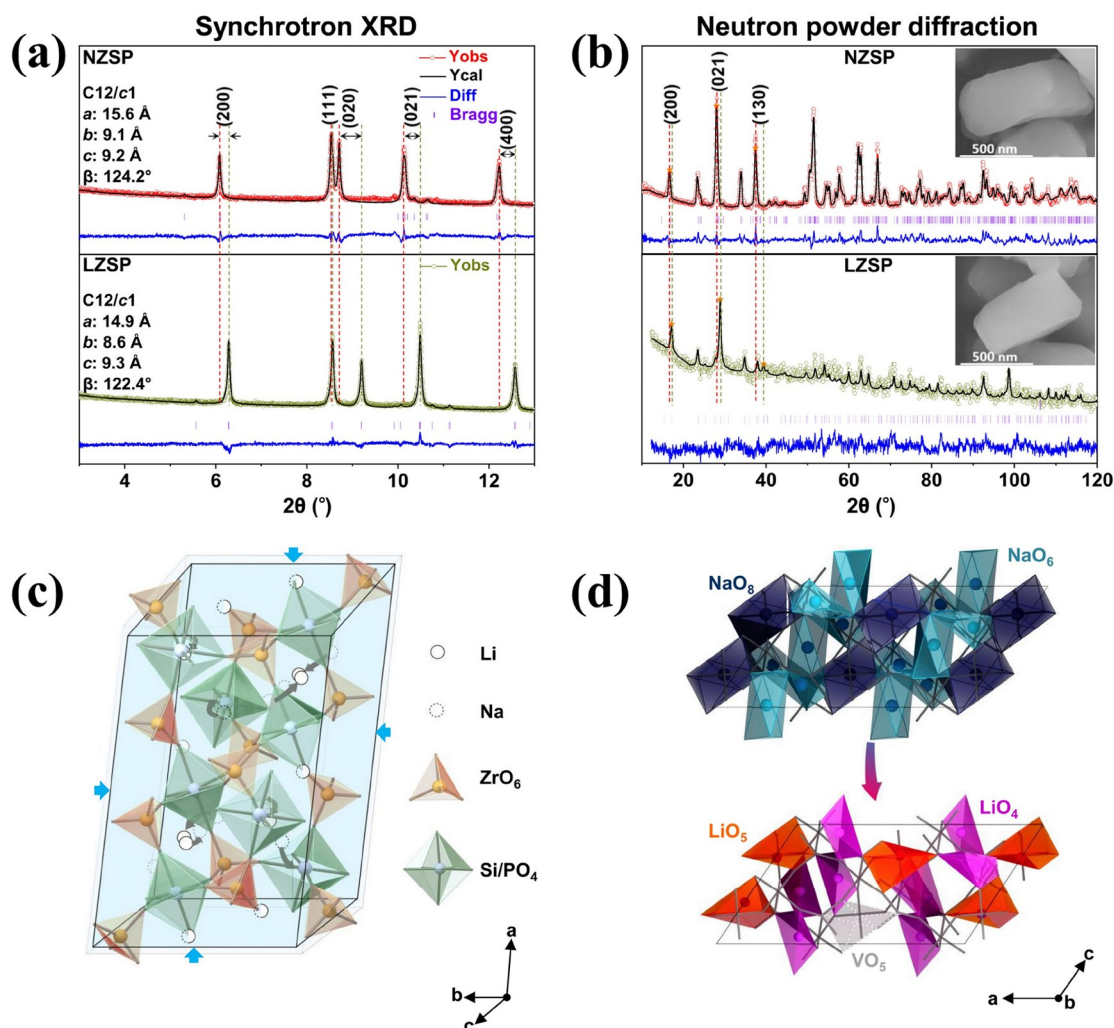


图3 NZSP和LZSP的晶体结构^[18]。使用Rietveld方法对NZSP和LZSP粉末进行精细粉末同步辐射X射线衍射图谱分析(a)和中子粉末衍射图谱分析(b), 将NZSP和LZSP的扫描电子显微镜图像插入(b)中, 图谱均在室温下测量记录; (c) 保留的多面体骨架包含Na⁺到Li⁺的转化路径; (d) 在固定骨架内Na⁺多面体向Li⁺多面体的转化

Figure 3 Crystal structures of NZSP and LZSP^[18]. Refined powder synchrotron X-ray diffraction (XRD) (a) and neutron powder diffraction (NPD) (b) patterns of NZSP and LZSP powders with the Rietveld method. The scanning electron microscope (SEM) images of NZSP and LZSP are inserted in (b). All these patterns are recorded at room temperature. (c) The retained polyhedral skeletons containing the evolution path of Na⁺ ions to Li⁺ ions. (d) The evolution of Na⁺ ions to Li⁺ ions polyhedrons within unchanged skeletons

子占位和制备新型固态电解质材料开辟了一条创新途径^[18]。

1.2 Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃(LATP)/Li_{1.5}Al_{0.5}Ge_{1.5}(PO₄)₃(LAGP)

获得高离子电导率固态电解质的另一种途径是通过异价离子或等效离子的掺杂, 拓宽离子迁移通道, 大幅提高Li⁺迁移速率, 从而进一步提升离子电导率; 同时有助于获得高密度的晶体, 降低晶界电阻^[25]。在传统的NASICON结构Li_xM₂(AO₄)₃中, M通常为Ti或Ge, 当在

晶体中掺杂铝元素以及分别引入钛和锆元素时, 获得的高性能LAGP/LATP型(通式为Li_{1+x}Al_xM_{2-x}(PO₄)₃, 0 ≤ x ≤ 0.5)固态电解质离子电导率进一步上升。研究表明, 当x=0.3时, 材料通常表现出最佳的电导率, 这是由于此时掺杂浓度达到了最优平衡点, 使得晶格中的Li⁺迁移路径最大化^[26~29]。LAGP/LATP的合成方法包括固相合成法、溶剂-凝胶法及热压法等。其中LATP的晶体结构如图4所示^[29], 通过Al掺杂, TiO₆八面体中的部分Ti⁴⁺被Al³⁺替代, 形成了更多的Li⁺迁移通道, 使得LATP具有优异的离子导电性能, 这种优化的结构不仅提升了材

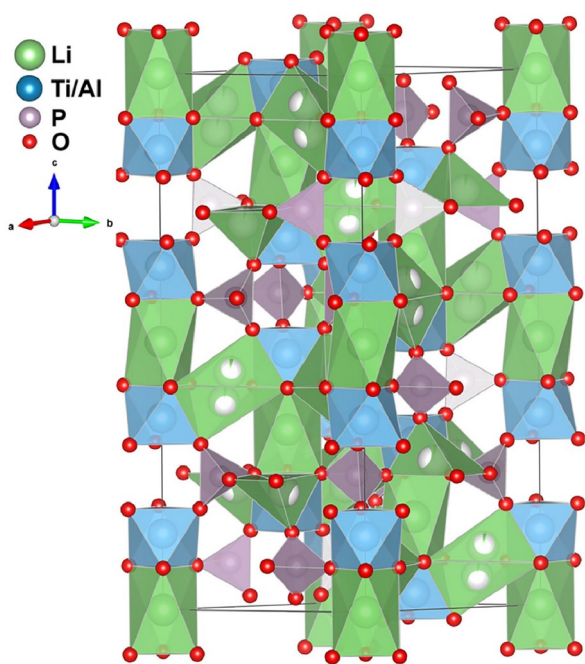


图4 LATP的晶体结构^[29]
Figure 4 Structure of LATP^[29]

料的电导率, 还增强了在实际应用中的稳定性和可靠性。

1.3 提升NASICON型固态电解质电导率措施

为了进一步提升电导率, 常对固态电解质进行掺杂处理。Guo等人^[30]使用固相反应法成功合成了掺杂W的 $\text{Li}_{1.3}\text{Al}_{0.3-2x}\text{W}_x\text{Ti}_{1.7}(\text{PO}_4)_3$ (LAWTP)型电解质。W的掺杂有助于减小晶粒尺寸, 增加晶粒间接触, 从而提高电解质密度, 合成晶体的电导率达到 $1.186 \times 10^{-3} \text{ S/cm}$, 并在 $\text{LiFePO}_4/\text{LAWTP}/\text{Li}$ 结构电池中应用良好。Saffirio等人^[31]使用熔融铸造技术, 在反应过程中添加 B_2O_3 作为烧结助剂, 合成了同时含有Ti和Ge的 $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ge}_{0.4}\text{Ti}_{1.4}(\text{PO}_4)_3 + \text{B}_2\text{O}_3$ 型电解质, 其在 20°C 下的最高电导率为 $3.9 \times 10^{-4} \text{ S/cm}$, 活化能为 0.28 eV , 并在 4.8 V 电压下仍然具有良好稳定性。烧结助剂的添加被证明可以有效促进 Li^+ 的传导。除常见掺杂元素外, Singh等人^[32]创新性地将过渡金属V分别引入LTP和LATP结构中取代 PO_4^{3-} , 通过晶体中 V^{5+} 与 V^{4+} 之间的价态转变有效增强了晶体内部的电子移动, 从而增强晶体电导率。当V掺杂量为40%时, 晶体在常温下的电导率为 $9 \times 10^{-5} \text{ S/cm}$; 当温度升高到 165°C 时, 电导率被进一步增大到 $3 \times 10^{-5} \text{ S/cm}$ 。

在较低的电势窗口下, LATP/LAGP中的M位点离子容易被锂金属电极还原, 从而改变晶体结构, 严重降低了晶界电导率, 这种电解质与电极的界面相容问题引起了诸多关注^[33]。Huang等人^[34]通过旋涂方法将 $\text{MoS}_2 + \text{PVDF} + \text{NMP}$ 混合溶液涂布在LATP表面形成缓冲层, 极大改善了由于LATP与锂金属电极接触产生微裂纹导致界面传输不良的问题。与未涂覆的LATP相比, 当被应用于 $\text{Li}/\text{LATP}/\text{LFP}$ 电池系统中时, 其界面极化电阻由 1077Ω 大幅减小到 65.07Ω , 相同容量时电池的可循环次数由50次提升到300次, 共同证明了缓冲涂层的积极作用。

Zhang等人^[35]使用物理气相沉积(physical vapor deposition, PVD)方法在LATP上沉积60 nm的Al涂层, 其中Al不仅作为延展性金属保护层稳定晶面连接, 还在电池系统中充当阳极和集流体, 具有多重作用。X射线光电子能谱测试结果显示, 包覆Al涂层的晶体在参与循环后, $\text{Ti}^{4+} 2p_{3/2}$ 峰和 $\text{Ti}^{4+} 2p_{1/2}$ 峰位置不变, 证明没有发生 Ti^{4+} 的还原反应; 循环后也没有监测到 $\text{Li} 1s$ 峰, 证明Al涂层未被锂化为 LiAl 。Al涂层促进了界面处的离子转移、保持了LATP晶型稳定、增强了与锂电极的界面连接, 使得LATP对称电池在 0.1 mA/cm^2 的电流密度下循环100周期后仍能表现出稳定的电化学性能。

Li等人^[36]使用低成本的干法制备了EMIM离子液体电解质膜覆盖在LAGP上, 通过在LAGP界面与离子液体界面建立新的 Li^+ 传输路径来促进锂的快速运输, 提高电导率。当EMIM的添加量为20wt%时, 离子电导率高达 $1.05 \times 10^{-3} \text{ S/cm}$, 是目前报道的最高值之一。

2 石榴石型固态电解质

2.1 $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO)

石榴石是一种硅酸盐, 其通式为 $\text{A}_3\text{B}_2(\text{SiO}_4)_3$ 。用与硅原子具有相同结构的各种金属原子替代石榴石中的硅原子后则形成石榴石型电解质。最初使用的石榴石型电解质为 $\text{Y}_3\text{Al}_5\text{O}_{12}$, 后逐渐演化出其他结构。目前常用石榴石型固态电解质的通式为 $\text{Li}_{3+x}\text{A}_3\text{B}_2\text{O}_{12}$, 其中A原子为八配位的金属元素, 常用La等镧系元素; B原子为六配位的金属元素, 常用Zr等4价金属或Ta等5价金属。最典型的晶体分子式为 $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, 晶体中 ZrO_6 八面体与 LaO_8 十二面体相连形成三维骨架, Li^+ 填充在四面体空隙或八面体空隙中, 共同构成了复杂的石榴石型固态电解质结构^[37,38]。

LLZO包括两种晶体结构：四方晶型和立方晶型。前者晶体中，Li占据四面体8a位点、正八面体16f位点和偏心八面体32g位点，但在后者晶体中，Li仅占据四面体24d位点和偏心八面体96h位点，因此立方晶体存在更多空位，这更有利于Li⁺的运输，直接导致了立方型LLZO电导率较四方型晶体高出一个数量级^[39,40]。除此之外，LLZO还有电化学稳定窗口宽、对锂金属稳定的优点^[41]。立方相LLZO晶体结构如图5(a)所示^[38]。

2.2 LLZO的改性

目前对LLZO晶体的研究主要聚焦于以下几方面：维持高电导率的立方相结构、改善电极与电解质接触不佳的情况、避免晶体在空气中产生Li₂CO₃钝化层。

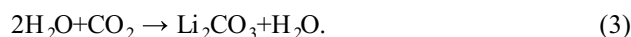
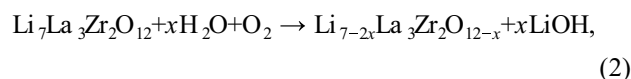
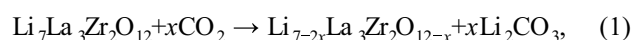
通过掺杂降低Li含量或增加Li空位浓度来稳定立方相结构，是一种提高离子电导率的有效方法，可分为对Li、Zr、La位点的掺杂^[42]。Mahnaz等人^[43]将Al成功掺杂到Li位点上，使用0.25 mol铝掺杂剂在1100°C下采用溶剂凝胶燃烧法制得的晶体致密度高达94%，25°C下的电导率为5.89×10⁻⁴ S/cm，较未掺杂时提高了半个数量级。Song等人^[44]使用Gd³⁺代替LLZO中的Zr⁴⁺以改善其性能，掺杂粉末XRD谱图如图5(b)所示，得到的Li_{7.2}La₃Zr_{1.8}Gd_{0.2}O₁₂晶体总电导率在各掺杂比例中最高，达到2.3×10⁻⁴ S/cm，并能在15天内保持稳定。关于La位点掺杂的报道相对较少，目前较为常见的La位点掺杂元素包括Y、Ce等^[45,46]。

在单个位点掺杂的基础上，目前已实现在多个位点上共同掺杂，从而进一步提升晶体稳定性。Alizadeh等人^[47]采用溶剂凝胶法同时将Ga与Y成功掺杂到LLZO晶体中，探究了不同比例掺杂元素对晶体性能的影响，发现当掺杂晶体化学式为Li_{6.4}Ga_{0.2}La₃Zr_{1.925}Y_{0.1}O₁₂时，在25°C下的电导率高达1.04×10⁻³ S/cm(晶体断裂表面SEM图如图5(c)所示)，并且Y的加入有效降低了晶体传导活化能。

LLZO固态电解质与电极之间的固-固界面接触产生了较高的界面阻抗，因此需要通过界面修饰措施来提高界面相容性和稳定性。Shao等人^[48]使用ZnO作为LLZO与锂电极之间的夹层来增强LLZO表面的润湿性，进而增强两者接触，实验结果证明采用该材料组装的电池具有良好的性能和较低的电阻。其他先进的沉积技术，如化学气相沉积、脉冲激光沉积、原子层沉积和磁控溅射沉积，也被应用于制备界面修饰层^[49-51]。

LLZO在空气氛围中极度敏感，容易与CO₂和H₂O

反应形成不导电的Li₂CO₃钝化层覆盖在LLZO表面，严重影响其导电性。反应方程式如下：



目前，各国学者关于如何避免Li₂CO₃钝化层的产生已展开研究。Zhao等人^[52]在LLZO煅烧过程中加入煅烧添加剂六方氮化硼(BN)，通过BN与Li₂CO₃发生反应来消除晶体表面的Li₂CO₃钝化层，同时产物Li₃BO₃具有一定的离子电导率，从而达到提高晶体电导率和消除钝化层的双重目的(图5(d))。Cuevas等人^[53]使用无毒无污染的硼酸(H₃BO₃)作为改性剂，将LLZO晶体浸泡在H₃BO₃与乙醇的混合溶液中，当浸泡过的晶体与空气接触时，优先生成LiBO₂导电缓冲层，这极大降低了界面电阻、增强了Li⁺传导，同时促进了固态电解质与锂金属电极的紧密接触。Xu等人^[54]使用草酸预先对LLZO进行处理，通过H⁺与LLZO反应消除表面的Li₂CO₃钝化层，发现浓度为5%的草酸可以完全去除钝化层；检测了酸处理前后PVDF+LLZO复合电解质膜的电导率，发现酸处理后的膜电导率由1.4×10⁻⁴ S/cm上升至9.0×10⁻⁴ S/cm，证明了该化学方法易于操作且切实可行。

最近，Chen等人^[55]通过引入高熵概念有效提升了电解质的性能。研究团队在LLZO晶体的Zr位点(16a位点)引入4种等摩尔比的元素，从而获得中等熵石榴石(Li₆La₃Zr_{0.5}Hf_{0.5}Ta_{0.5}Nb_{0.5}O₁₂, ME-LLZO)。中子衍射、中子对分布函数测量和计算结果证明引入的离子有效调节了ME-LLZO的瓶颈尺寸和Li-O键长，使得其室温下离子电导率达到3.3×10⁻⁴ S/cm，活化能为0.44 eV；组装的Li-C|ME-LLZO|Li-C对称电池可稳定循环超过3600 h，50次循环后容量保持率高达98.83%。

3 钙钛矿型固态电解质

3.1 Li_{0.33}La_{0.56}TiO₃ (LLTO)

钙钛矿型固态电解质(LLTO)属于ABO₃型钙钛矿家族(A一般为稀土或碱土元素阳离子，B一般为过渡金属离子)^[56]，其通式为Li_{3x}La_{(2/3)-x}□_{(1/3)-2x}TiO₃ (0.04 < x < 0.16，其中□代表A位点空隙)，最早于1993年被Yoshiyuki Inaguma报道，是目前已知的拥有最高晶体

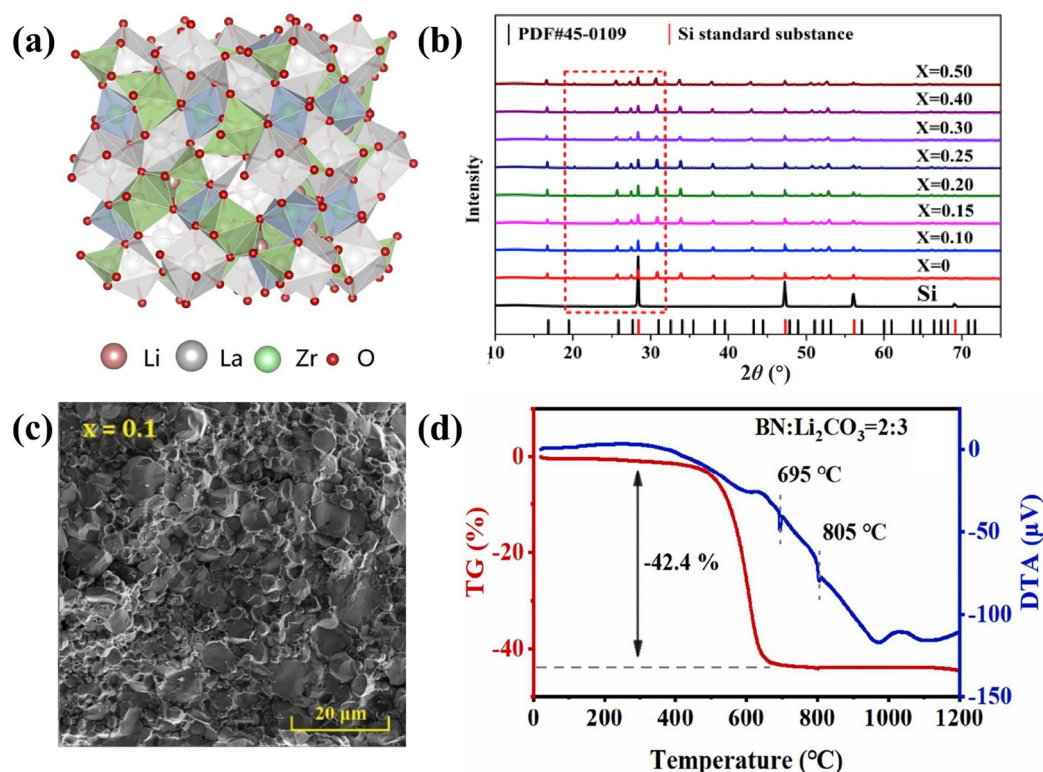


图5 立方相LLZO材料的结构和表征. (a) 立方相 $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ 的晶体结构^[38]; (b) 硅标准物质存在下掺杂Gd的LLZO粉末XRD图谱^[44]; (c) $\text{Li}_{6.4}\text{Ga}_{0.2}\text{La}_3\text{Zr}_{1.925}\text{Y}_{0.1}\text{O}_{12}$ 断裂表面的SEM图^[47]; (d) 摩尔比 $\text{BN}:\text{Li}_2\text{CO}_3 = 2:3$ 混合物的热重-差热分析曲线^[52]

Figure 5 Structure and characterization of cubic phase LLZO. (a) Crystal structure of cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ ^[38]; (b) XRD pattern of Gd-doped LLZO powders with Si standard substance^[44]; (c) SEM images from the fracture surface of $\text{Li}_{6.4}\text{Ga}_{0.2}\text{La}_3\text{Zr}_{1.925}\text{Y}_{0.1}\text{O}_{12}$ samples^[47]; (d) thermogravimetry-differential thermal analysis (TG-DTA) curves of mixed raw materials with a ratio of $\text{BN}:\text{Li}_2\text{CO}_3 = 2:3$ mol^[52]

电导率的晶态电解质之一, 晶体结构如图6(a)所示, 电导率在室温下高达 10^{-3} 数量级($x=0.11$ 时), 同时具有结构稳定、循环性强的优点^[57~59]. 其高电导率归因于 Li^+ 的空位跃迁机制, 由于晶体中 Li^+ 和 La^{3+} 的无序排列产生了大量的A位点空隙, 使得 Li^+ 既可以传输到同层A位点空隙产生二维电导率, 又可以向其他层A位点空隙移动产生三维电导率, 两者共同导致了电导率的提高^[60~62].

然而, 在1.7~1.8 V的电势下, LLTO中的 Ti^{4+} 容易被锂金属负极还原, 进而引起LLTO晶格结构畸变, 影响其性能. 目前解决这个问题的有效策略之一是在LLTO表面镀缓冲层以避免两者的直接接触^[63]. 此外, LLTO因存在显著的晶界电阻, 导致其晶界电导率较离子电导率降低了两个数量级. Yang等人^[64]基于扫描透射电子显微镜并结合其他手段详细研究了LLTO的晶界结构, 揭示了LLTO低晶界电导率的内在来源, 发现由于空间电荷的诱导, 晶体表层Ti-O结构下方产生了La偏

析层, 这直接阻止了 Li^+ 通过A位点空隙的传输, 导致了A位点的局部耗竭, 对 Li^+ 传导产生有害影响.

3.2 LLTO的改性

目前, 改善电导率的方法主要是掺杂, 即通过加入其他物质来取代LLTO结构中A位点或B位点上的离子, 从而提高晶体电导率. Luo等人^[65]将不同量的 Bi_2O_3 掺杂到LLTO基体中, 着重探究了掺杂量对晶体电导率的影响. XRD和拉曼光谱证明Bi成功掺杂到LLTO晶格中的A位点取代部分La(图6(b)); 实验结果显示, 当 Bi_2O_3 掺杂量为1 wt%时, 材料电导率最高可达 $2.71 \times 10^{-5} \text{ S/cm}$, 组装的LLTO+1wt% Bi_2O_3 固态电池具有良好循环稳定性和高循环容量, 电池的临界电流密度可达到0.16 mA, 循环工作时间超过300 h, 在40次充放电循环后显示出133.1 mAh/g的放电容量和98.0%的容量保持率. Zhang等人^[66]将Sr作为掺杂剂引入LLTO晶胞的A位点中, 通过溶胶-凝胶法成功合成了具有高

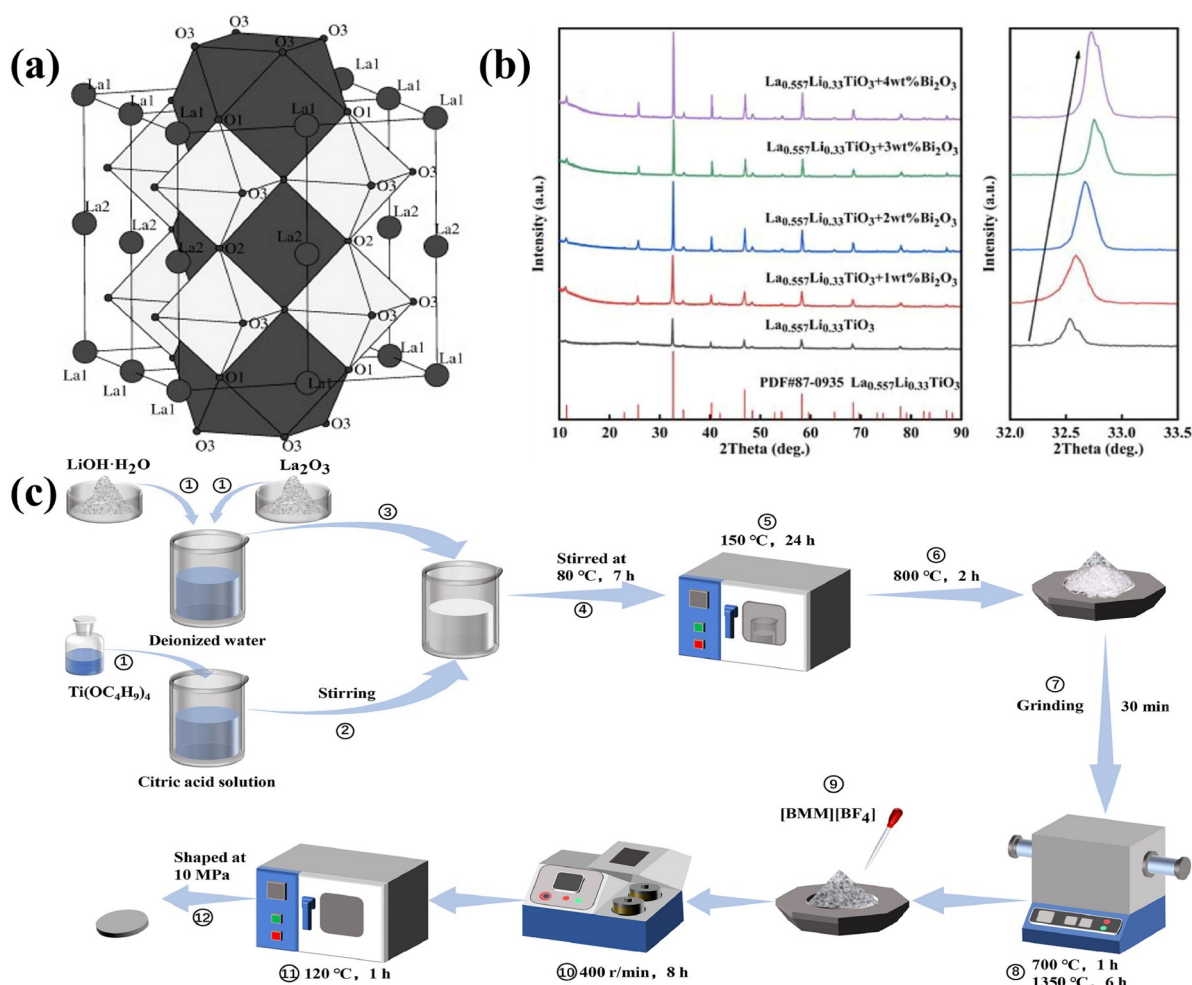


图6 LLTO材料的结构、掺杂及制备过程。(a) $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ 的晶体结构；(b) 不同 Bi_2O_3 掺杂量 $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ 晶体的拉曼光谱^[65]；(c) 掺杂 $[\text{BMIM}][\text{BF}_4]$ 离子液体的样品制备过程^[68]

Figure 6 Structure, doping, and preparation process of LLTO. (a) Crystal structure of $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$; (b) Raman spectra of Bi_2O_3 -doped $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ crystals^[65]; (c) preparation procedure of samples doped with $[\text{BMIM}][\text{BF}_4]$ ^[68]

稳定性的LLTO薄膜，当Sr掺杂率为5%时， 30°C 下的离子电导率达到 $8.38 \times 10^{-5} \text{ S/cm}$ ，较未掺杂时高出一个数量级，且该材料具有良好的稳定性，与锂直接接触时的稳定性窗口高达10 V. Lin等人^[67]通过在LLTO的B位点掺杂与Ti同主族的IV族元素Zr来增强LLTO的电导率，其中通过溶胶-凝胶法制备的掺Zr的 $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ 晶体总电导率约是未掺杂的1.9倍。

在LLTO中掺杂离子液体也被认为是提高电导率的有效方法之一。Lu等人^[68]在LLTO晶体成型之前加入不同重量百分比的离子液体 $[\text{BMIM}][\text{BF}_4]$ ，操作流程见图6(c)。实验结果显示，随着离子液体加入量的增大，掺杂晶体的总离子电导率呈现先增大后减小的趋势，在添加量为12.5wt%时达到极大值 $4.71 \times 10^{-4} \text{ S/cm}$ ；同时

监测了样品放置18个月前后的Li转移数，发现基本没有变化，证明了这种掺杂晶体在大气中的稳定性良好。

除此之外，受固-固界面的限制，针对LLTO电解质与电极之间的界面改进问题也有一系列进展，例如利用锂离子玻璃作为界面改性剂。Zhang等人^[69]将锂硼氧化物($50\text{Li}_2\text{O}-50\text{B}_2\text{O}_3$, LIB)玻璃引入LLTO基体中以改变LLTO晶界的微观结构和组成。结果显示，LLTO+1.5wt% LIB复合电解质在室温下的电导率为 $1.06 \times 10^{-4} \text{ S/cm}$ ，较未掺杂晶体有巨大提升，这是因为LLTO/LIB复合材料中产生了局部晶格畸变，有效地促进了 Li^+ 沿LLTO电解质颗粒和电解质/电极界面的迁移，同时降低了传导势垒。

目前，也有研究表明晶体制备原料的选择对LLTO

电导率有影响。Lu等人^[70]对比了多种锂源 Li_2CO_3 、 LiNO_3 、 $\text{LiOH}\cdot\text{H}_2\text{O}$ 、 Li_2O 、 CH_3COOLi 和 Li_3PO_4 制得的 $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$ 电解质的性能,发现不同的锂源对晶体的晶相、晶粒尺寸、相对密度均会产生影响,这些变化共同决定了 Li^+ 在LLTO晶体中的迁移速率.为了获得具有高电导率的LLTO,应以合成大晶粒、立方相和高相对密度的晶体为优化目标.由于立方相LLTO需要在较高温度下合成,如何控制在降温时立方晶体不发生相变,以及室温下立方晶型如何保持也成为研究的热点^[71].

4 LiPON固态电解质

LiPON固态电解质的发现始于20世纪90年代.1993年,美国橡树岭国家实验室(ORNL)研究团队发现,通过锂磷酸盐中O被N取代,可形成具有交联结构的锂磷氮氧化物LiPON,其在室温下的离子电导率达到 $3.3\times 10^{-6}\text{ S/cm}$,满足作为电解质材料的条件^[72].

LiPON固态电解质薄膜通常通过反应射频磁控溅射沉积法(简称反应溅射法)制备,该方法因具有诸多优点而在薄膜制备工艺中脱颖而出^[73~75].在此基础上,Qian等人^[76]开发了一种合成独立LiPON薄膜的方法:使用旋涂法在玻璃基板涂覆光致抗蚀剂,通过反应溅射法将LiPON薄膜沉积到玻璃基板上,最后将LiPON膜从玻璃基板上剥离,从而得到独立形式的LiPON薄膜.杨氏模量测量证明制得的独立薄膜具有高柔韧性;在膜表面镀金后将其应用于Li-Cu电池,发现在不施加外部压力的情况下即可实现均匀、全致密的锂金属沉积,同时在锂剥离过程中锂金属矿床内不会形成空隙,证明合成的LiPON薄膜具有灵活性和实用性.

LiPON固态电解质薄膜通常具有以下优点:电压窗

口宽(高达5.5 V)、电子电导率低($<8.0\times 10^{-13}\text{ S/cm}$)、与锂金属电极不发生反应且界面相容性强,被广泛应用于全固态薄膜锂电池中.但与晶体型氧化物系固态电解质相比,LiPON固态电解质薄膜的离子电导率不高,开发出提高电导率的有效手段势在必行^[77~80].

Feng等人^[81]采用分子动力学和第一性原理计算评估了在LiPON中分别掺杂B、Al、As对 $\text{LiCoO}_2(\text{LCO})$ 电极-LiXPON($X=0, \text{B}, \text{Al}, \text{As}$)电解质界面性能的影响.对体系进行结构优化和能量计算,发现掺杂体系的黏附能和界面形成能较未掺杂体系有所上升(LCO/LiB-PON体系界面结合能高达 $1.703\text{ eV/\AA}$),表明掺杂有助于增强界面稳定性;态密度计算显示掺杂使得界面的能带间隙减小、电导率提高;通过模拟反应过渡态计算了体系中锂迁移的扩散势垒,结果显示掺杂体系界面的 Li^+ 扩散势垒降低(LCO/LiBPON界面扩散势垒仅为 0.76 eV ,见图7(a)),证明掺杂可有效增强电极界面的 Li^+ 扩散性能.这些基于不同角度的分子模拟研究共同证实了掺杂对于高性能全固态电池的积极作用.

此外,LiPON也已被成功用作固态电池结构中锂负极与LLZTO界面的夹层.Zhang等人^[82]构建了Li/LLZTO界面的LiPON夹层,其SEM形貌如图7(b)所示.夹层的存在使得LLZTO电子电导率由 $1.40\times 10^{-7}\text{ S/cm}$ 降低至 $5.18\times 10^{-10}\text{ S/cm}$,同时锂对称电池的内阻由 $3400\ \Omega$ 显著降低到 $700\ \Omega$,在 1.2 mA/cm^2 下循环1000 h后在LLZTO内未观察到锂枝晶.综上,LiPON具有一定的离子电导率和极低的电子电导率,当用作LLZTO与锂电极之间的夹层时,有效阻止了电子向LLZTO的传导而促进了 Li^+ 向LLZTO的运输,从而避免锂枝晶的生成,同时极大改善了电极-电解质的界面相容性,增强了界面电化学稳定性^[83,84].

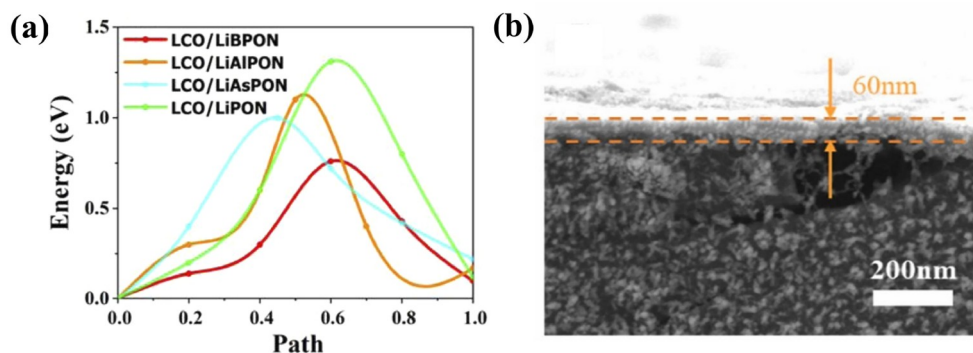


图7 LiPON的锂迁移及夹层结构. (a) 不同体系中锂迁移的扩散势垒^[81]; (b) LiPON夹层截面的SEM形貌^[82]

Figure 7 Lithium migration and interlayer structure of LiPON. (a) Activation energy barriers in different systems^[81]; (b) cross-section SEM morphology of LiPON interlayer^[82]

表 1 氧化物系固态电解质分类和性能

Table 1 Classification and performance of oxide solid-state electrolytes

结构分类	典型材料	离子电导率(S/cm)	优点	缺点	文献
NASICON 结构	$\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP)	1.40×10^{-4}	热稳定性好、对空气不敏感	低电势下 Ti^{4+} 易被锂电极还原、与电极接触的固-固界面阻抗大、生产成本高难以量产	[18,85~90]
	$\text{Li}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ (LZSP)	3.59×10^{-3}			
	$\text{Li}_{1-x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$ (LAGP)	2.3×10^{-4}			
石榴石结构	$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO)	2.20×10^{-4}	高温下稳定、电化学窗口宽、对锂电极稳定	易在空气中产生钝化层、与电极接触的固-固界面阻抗大	[91~94]
钙钛矿结构	$\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$ (LLTO)	1.31×10^{-4}	离子电导率高、对空气不敏感、电化学稳定窗口宽、断裂韧性高、易于加工	晶界电导率低、低电势下 Ti^{4+} 易被锂电极还原、与电极接触的固-固界面阻抗大	[95,96]
非晶态结构	$\text{Li}_{3x}(\text{PO}_4)_y\text{N}_z$	4.91×10^{-6}	良好电化学窗口和热稳定性、对电极材料不敏感、界面相容性强、电子电导率极低	离子电导率有限、材料易碎裂、制备工艺复杂成本高	[72,97,98]

5 总结与展望

表1总结了氧化物系固态电解质的分类和性能,虽然它们都具有相当的离子电导率,但也都分别存在着晶界电导率有限、对 H_2O 和 CO_2 敏感、与电极之间固-固界面相容性差等问题,这严重制约了发展与工业化应用.若要进行大规模的长期使用,则需要对氧化物系固态电解质进行更加深入的研究,并结合实际应用的需要扬长避短.

对于固态电解质,未来的研究仍将围绕两个核心进行:提高电解质材料的电导率和对电极-电解质界面性能的调控与优化.目前已有不少研究通过在聚合物固态电解质中加入氧化物系固态电解质等无机填料成功合成了复合固态电解质,具有高机械强度、良好柔韧性、低界面电阻的优点,可有效提高离子电导率并抑制电极-电解质界面上锂枝晶的生长,增强电池的化学稳定性,为组装高密度固态锂金属电池提供条件.

电极与固态电解质界面性能的改善可考虑围绕以

下方面进行: (1) 设计电极与电解质之间的界面缓冲层,将电极与电解质的接触由直接刚性接触转化为柔性接触; (2) 在固态电解质表面覆盖具有自适应性的人工保护膜以改善接触; (3) 在电池结构中引入3D集流体,诱导锂在集流体内部进行沉积; (4) 通过光、电等引发剂催化原位固化,形成离子传输通道.这些方法均能在一定程度上实现电极与电解质的有效接触,降低界面阻抗,促进 Li^+ 传递,提高界面的电化学性能和稳定性,同时调控锂沉积行为,抑制锂枝晶的产生.

随着经济社会的快速发展,对锂金属电池的需求也日益迫切.全固态锂离子电池具有诸多优点,其发展已成为大势所趋.伴随着固态电解质核心技术的日益蓬勃,未来全固态电池有望超越液态电池、半固态电池、准固态电池,成为锂电行业中占据绝对地位的龙头产业.期待在未来全固态锂离子电池技术拥有更具创新性的突破,为科技发展和社会进步作出巨大贡献.

参考文献

- Jain A, Saroha R, Kumar A, et al. Advancements and challenges in solid-state lithium-ion batteries: From ion conductors to industrialization. *Mater Today-Proc*, 2024, <http://doi.org/10.1016/j.matpr.2024.05.070>
- He P, Tang Y, Tan Z, et al. Solid-state batteries encounter challenges regarding the interface involving lithium metal. *Nano Energy*, 2024, 124: 109502
- Li W X, Li X P, Chen Y W, et al. Understanding and modifying strategies for lithium metal anode solid electrolyte interphase (in Chinese). *Chin Sci Bull*, 2024, 69: 1298–1314 [李宛峡, 李新鹏, 陈亚威, 等. 锂金属负极固体电解质界面膜的理解与改性策略. 科学通报, 2024, 69: 1298–1314]
- Qi S H, Wang Z S, Guo K L, et al. Progress on wide-ranging temperature electrolytes for lithium batteries (in Chinese). *Chin Sci Bull*, 2022, 67: 2937–2949 [戚世翰, 王中升, 郭康隆, 等. 宽温域锂电池电解液研究进展. 科学通报, 2022, 67: 2937–2949]
- Hu Y, Li W, Zhu J, et al. Multi-layered electrolytes for solid-state lithium batteries. *Next Energy*, 2023, 1: 100042
- Zhou X Y, Fu J L, Li Z, et al. Research progress on solid polymer electrolytes (in Chinese). *Chin Sci Bull*, 2022, 8: 832–859 [周晓燕, 付佳龙, 李卓, 等. 聚合物基固体电解质研究进展. 科学通报, 2022, 8: 832–859]

- 7 Zhao N, Guo X. A new family of halide electrolytes for all-solid-state lithium batteries. *Sci Bull*, 2023, 68: 1598–1599
- 8 Chen W, Li Y, Feng D, et al. Recent progress of theoretical research on inorganic solid state electrolytes for Li metal batteries. *J Power Sources*, 2023, 561: 232720
- 9 Yang Y N, Cui C H, Hou Z Q, et al. Interface reconstruction via lithium thermal reduction to realize a long life all-solid-state battery. *Energy Storage Mater*, 2022, 52: 1–9
- 10 Hatzell K B. Opportunities for halide solid electrolytes in solid-state batteries. *Matter*, 2022, 5: 2533–2535
- 11 Tao B, Zhong D, Li H, et al. Halide solid-state electrolytes for all-solid-state batteries: Structural design, synthesis, environmental stability, interface optimization and challenges. *Chem Sci*, 2023, 14: 8693–8722
- 12 Choi Y S, Lee Y S, Oh K H, et al. Interface-enhanced Li ion conduction in a $\text{LiBH}_4\text{-SiO}_2$ solid electrolyte. *Phys Chem Chem Phys*, 2016, 18: 22540–22547
- 13 Le T T, Abbas M, Dreistadt D M, et al. Ionic conductivity in complex hydrides for energy storage applications: A comprehensive review. *Chem Eng J*, 2023, 473: 145315
- 14 Kharton V, Marques F, Atkinson A. Transport properties of solid oxide electrolyte ceramics: A brief review. *Solid State Ion*, 2004, 174: 135–149
- 15 Goodenough J B, Hong H Y P, Kafalas J A. Fast Na^+ -ion transport in skeleton structures. *Mater Res Bull*, 1976, 11: 203–220
- 16 Hong H Y P. Crystal structures and crystal chemistry in the system $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$. *Mater Res Bull*, 1976, 11: 173–182
- 17 Alpen U, Bell M F, Wichelhaus W, et al. Ionic conductivity of $\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$ (Lisicon). *Electrochim Acta*, 1978, 23: 1395–1397
- 18 Zhu L, Wang Y, Chen J, et al. Enhancing ionic conductivity in solid electrolyte by relocating diffusion ions to under-coordination sites. *Sci Adv*, 2022, 8: abj7698
- 19 Nikodimos Y, Ihrig M, Taklu B W, et al. Solvent-free fabrication of freestanding inorganic solid electrolyte membranes: Challenges, progress, and perspectives. *Energy Storage Mater*, 2023, 63: 103030
- 20 Ouelidna N, Sabi N, Ben youcef H. Correlation between physical properties and the electrochemical behavior in inorganic solid-state electrolytes for lithium and sodium batteries: A comprehensive review. *J Energy Storage*, 2024, 86: 111254
- 21 Ke X, Wang Y, Dai L, et al. Cell failures of all-solid-state lithium metal batteries with inorganic solid electrolytes: Lithium dendrites. *Energy Storage Mater*, 2020, 33: 309–328
- 22 Chiang S J, Kaduk J A, Shaw L L. High ionic conducting NASICON enabled by mechanical activation enhanced reaction. *Mater Chem Phys*, 2024, 312: 128656
- 23 Thirupathi R, Kumari V, Chakrabarty S, et al. Recent progress and prospects of NASICON framework electrodes for Na-ion batteries. *Prog Mater Sci*, 2023, 137: 101128
- 24 Singh M D, Kumar Gorai D, Brajesh K, et al. Ruthenium doping of NASICON electrolyte augments the performance of solid-state sodium-ion batteries. *Chem Eng J*, 2024, 489: 151330
- 25 Xiang L, Li X, Xiao J, et al. Interface issues and challenges for NASICON-based solid-state sodium-metal batteries. *Adv Powder Mater*, 2024, 3: 100181
- 26 Xiao W, Wang J, Fan L, et al. Recent advances in $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ solid-state electrolyte for safe lithium batteries. *Energy Storage Mater*, 2019, 19: 379–400
- 27 Courbaron G, Nuernberg R B, Sevillano J S, et al. Multi-scale characterization of submicronic NASICON-type solid electrolyte $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ degraded by spark plasma sintering. *J Alloys Compd*, 2024, 985: 174062
- 28 Zallocco V M, Freitas J M, Bocchi N, et al. Electrochemical stability of a NASICON solid electrolyte from the lithium aluminum germanium phosphate (LAGP) series. *Solid State Ion*, 2022, 378: 115888
- 29 Zhu J, Xiang Y, Zhao J, et al. Insights into the local structure, microstructure and ionic conductivity of silicon doped NASICON-type solid electrolyte $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}\text{P}_3\text{O}_{12}$. *Energy Storage Mater*, 2022, 44: 190–196
- 30 Guo Y, Zhao E, Li J. Superior ionic conductivity of W-doped NASICON-type $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ solid electrolyte. *J Eur Ceramic Soc*, 2024, 44: 7081–7091
- 31 Saffirio S, Falco M, Appetecchi G B, et al. $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ge}_{0.4}\text{Ti}_{1.4}(\text{PO}_4)_3$ promising NASICON-structured glass-ceramic electrolyte for all-solid-state Li-based batteries: Unravelling the effect of diboron trioxide. *J Eur Ceramic Soc*, 2022, 42: 1023–1032
- 32 Sharma N, Dalvi A. Vanadium substituted Li^+ -NASICON systems: Tailoring electronic conductivity for electrode applications. *J Alloys Compd*, 2021, 861: 157954
- 33 Zhu L, Wang Y, Wu Y, et al. Boron nitride-based release agent coating stabilizes $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3/\text{Li}$ interface with superior lean-lithium electrochemical performance and thermal stability. *Adv Funct Mater*, 2022, 32: 2201136
- 34 Huang C, Li Z, Duan S, et al. Improving the stability of NASICON-type electrolyte with Li metal anode by interfacial modification. *J Power Sources*, 2022, 536: 231491
- 35 Zhang Q, Jiang M, Kungl H, et al. Stabilization the interface of NASICON-type solid electrolyte and Li metal by Al interlayer. *Electrochim Acta*,

- 2024, 477: 143791
- 36 Li H, Zhang X, Huang H, et al. Ionic liquid reinforced NaSICON-type oxide electrolyte films enabling solid state conversion metal fluoride-lithium batteries. *Energy Storage Mater*, 2024, 70: 103452
 - 37 Thangadurai V, Narayanan S, Pinzaru D. Garnet-type solid-state fast Li ion conductors for Li batteries: Critical review. *Chem Soc Rev*, 2014, 43: 4714–4727
 - 38 Liu X, Zhong M, Chen X, et al. Enriching lithium and separating lithium to magnesium from sulfate type salt lake brine. *Hydrometallurgy*, 2022, 192: 105247
 - 39 Xu L, Li J, Deng W, et al. Garnet solid electrolyte for advanced all-solid-state Li batteries. *Adv Energy Mater*, 2021, 11: 2000648
 - 40 Samson A J, Hofstetter K, Bag S, et al. A bird's-eye view of Li-stuffed garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ ceramic electrolytes for advanced all-solid-state Li batteries. *Energy Environ Sci*, 2019, 12: 2957–2975
 - 41 Kalita G, Endo T, Nishi T. Recent development on low temperature synthesis of cubic-phase LLZO electrolyte particles for application in all-solid-state batteries. *J Alloys Compd*, 2023, 969: 172282
 - 42 Sun H, Kang S, Cui L. Prospects of LLZO type solid electrolyte: From material design to battery application. *Chem Eng J*, 2023, 454: 140375
 - 43 Ashuri M, Golmohammad M, Soleimany Mehranjani A, et al. Al-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ garnet-type solid electrolytes for solid-state Li-Ion batteries. *J Mater Sci-Mater Electron*, 2021, 32: 6369–6378
 - 44 Song S, Chen B, Ruan Y, et al. Gd-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ garnet-type solid electrolytes for all-solid-state Li-ion batteries. *Electrochim Acta*, 2018, 270: 501–508
 - 45 Deviannapoorani C, Shankar L S, Ramakumar S, et al. Investigation on lithium ion conductivity and structural stability of yttrium-substituted $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$. *Ionics*, 2016, 22: 1281–1289
 - 46 Rangasamy E, Wolfenstine J, Allen J, et al. The effect of 24c-site (A) cation substitution on the tetragonal–cubic phase transition in $\text{Li}_7\text{—La}_3\text{—AZr}_2\text{O}_{12}$ garnet-based ceramic electrolyte. *J Power Sources*, 2013, 230: 261–266
 - 47 Alizadeh S M, Moghim I, Golmohammad M. Synthesis and characterization of highly conductive Ga/Y co-doped LLZO by facile combustion sol-gel method. *Solid State Ion*, 2023, 397: 116260
 - 48 Shao Y, Wang H, Gong Z, et al. Drawing a soft interface: An effective interfacial modification strategy for garnet-type solid-state Li batteries. *ACS Energy Lett*, 2018, 3: 1212–1218
 - 49 Han Y, Chen Y, Huang Y, et al. Recent progress on garnet-type oxide electrolytes for all-solid-state lithium-ion batteries. *Ceramics Int*, 2023, 49: 29375–29390
 - 50 Dadkhah Tehrani A, Efafi B, Majles Ara M H. Preparing a new class of ultrathin graphene nanostructure by chemical vapor deposition and its lasing ability. *ACS Appl Mater Interfaces*, 2020, 12: 46429–46438
 - 51 Ma Y, Li L, Qian J, et al. Materials and structure engineering by magnetron sputtering for advanced lithium batteries. *Energy Storage Mater*, 2021, 39: 203–224
 - 52 Zhao G, Luo C, Hua Q. Enhanced comprehensive performance of the LLZO series solid electrolyte via multifunctional additive. *J Eur Ceramic Soc*, 2024, 44: 2251–2260
 - 53 Cuevas I, Nkosi F, Edström K, et al. $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ interface functionalization via boric acid treatment: A step to contact improvement. *Appl Surf Sci*, 2024, 656: 159611
 - 54 Xu J, Tian W, Lu K, et al. Effect of acid treatment of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ on ionic conductivity of composite solid electrolytes. *IOP Conf Ser-Earth Environ Sci*, 2020, 512: 012110
 - 55 Chen Y, Wang T, Chen H, et al. Local structural features of medium-entropy garnet with ultra-long cycle life. *Matter*, 2023, 6: 1530–1541
 - 56 Parameswaran A K, Pazhaniswamy S, Dekanovsky L, et al. An integrated study on the ionic migration across the nano lithium lanthanum titanate (LLTO) and lithium iron phosphate-carbon (LFP-C) interface in all-solid-state Li-ion batteries. *J Power Sources*, 2023, 565: 232907
 - 57 Inaguma Y, Liqun C, Itoh M, et al. High ionic conductivity in lithium lanthanum titanate. *Solid State Commun*, 1993, 86: 689–693
 - 58 Lu X, Duan M, Xiang J, et al. Enhancement of ionic conductivity and fracture toughness by infiltrating porous $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$ pellets. *J Rare Earths*, 2024, 42: 392–398
 - 59 Chen C. Ionic conductivity, lithium insertion and extraction of lanthanum lithium titanate. *Solid State Ion*, 2001, 144: 51–57
 - 60 Mazza D. Modeling Li-ion conductivity in fast ionic conductor $\text{La}_{2/3-x}\text{Li}_{1/3}\text{TiO}_3$. *Solid State Ion*, 2002, 149: 81–88
 - 61 Chandra S, Kim Y, Vivona D, et al. Thermally-driven reactivity of $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ solid electrolyte with LiCoO_2 cathode. *J Mater Chem A*, 2022, 10: 3485–3494
 - 62 Ruiz A. Electrical properties of $\text{La}_{1.33-x}\text{Li}_{0.3x}\text{Ti}_2\text{O}_6$ ($0.1 < x < 0.3$). *Solid State Ion*, 1998, 112: 291–297
 - 63 Yao Z R, Sun Q, Gu X Y, et al. Recent progress of oxide solid-state electrolytes for lithium-ion batteries (in Chinese). *Adv New Renewable En*, 2023, 11: 76–84 [姚忠冉, 孙强, 顾骁勇, 等. 锂离子电池氧化物固态电解质研究进展. *新能源进展*, 2023, 11: 76–84]
 - 64 Peng S, Chen Y, Zhou X, et al. Atomistic origin of high grain boundary resistance in solid electrolyte lanthanum lithium titanate. *J Materiomics*,

- 2024, 10: 1214–1221
- 65 Wu Z, Wu Z, Wang Z, et al. Effect of Bi_2O_3 on the ion migration and interfacial properties of $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ solid electrolytes. *Corrosion Sci*, 2023, 224: 111473
- 66 Zhang Y, Meng Z, Wang Y. Sr doped amorphous LLTO as solid electrolyte material. *J Electrochem Soc*, 2020, 167: 080516
- 67 Ling M, Zhu X, Jiang Y, et al. Comparative study of solid-state reaction and sol-gel process for synthesis of Zr-doped $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ solid electrolytes. *Ionics*, 2016, 22: 2151–2156
- 68 Lu X, Li X, Duan M, et al. Preparation of hybrid perovskite-type $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$ by adding ionic liquids. *J Rare Earths*, 2023, 41: 758–763
- 69 Zhang H, Hao S, Lin J. Influence of $\text{Li}_2\text{O-B}_2\text{O}_3$ glass on ionic migration and interfacial properties of $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ solid electrolyte. *J Alloys Compd*, 2017, 704: 109–116
- 70 Lu X, Zhang F, Li J. The influence of lithium sources on properties of perovskite-type lithium ion conductor. *J Alloys Compd*, 2021, 875: 159887
- 71 Lin C, Ihrig M, Kung K, et al. Low-temperature sintering of $\text{Li}_{0.33}\text{La}_{0.55}\text{TiO}_3$ electrolyte for all-solid-state Li batteries. *J Eur Ceramic Soc*, 2023, 43: 7543–7552
- 72 Bates J. Electrical properties of amorphous lithium electrolyte thin films. *Solid State Ion*, 1992, 53-56: 647–654
- 73 Bayzou R, Trébosc J, Landry A K, et al. Identification of phosphorus sites in amorphous LiPON thin film by observing internuclear proximities. *J Magn Reson*, 2023, 354: 107530
- 74 Huang W, Li J, Wei K, et al. Boosted Li^+ migration in LiPON electrolyte via introducing Ti-based bridge for solid-state thin film batteries. *J Power Sources*, 2023, 587: 233698
- 75 Wang K, Wei L, Wang L, et al. Ab-initio investigation on the interface improvement by doping boron and carbon in $\text{LiMn}_2\text{O}_4/\text{LiPON}$ all solid state battery. *J Solid State Chem*, 2022, 306: 122797
- 76 Cheng D, Wynn T, Lu B, et al. A free-standing lithium phosphorus oxynitride thin film electrolyte promotes uniformly dense lithium metal deposition with no external pressure. *Nat Nanotechnol*, 2023, 18: 1448–1455
- 77 López-Aranguren P, Reynaud M, Gluchowski P, et al. Crystalline LiPON as a bulk-type solid electrolyte. *ACS Energy Lett*, 2021, 6: 445–450
- 78 Le Van-Jodin L, Ducroquet F, Sabary F, et al. Dielectric properties, conductivity and Li^+ ion motion in LiPON thin films. *Solid State Ion*, 2013, 253: 151–156
- 79 Song X, Yu W, Zhou S, et al. Enhancement of Mn-doped LiPON electrolyte for higher performance of all-solid-state thin film lithium battery. *Mater Today Phys*, 2023, 33: 101037
- 80 Wu Y M, Wu X M, Zhu L, et al. The development of studies in all-solid-state thin film lithium batteries (in Chinese). *Energy Storage Sci Technol*, 2016, 5: 678–701 [吴勇民, 吴晓萌, 朱蕾, 等. 全固态薄膜锂电池研究进展. *储能科学与技术*, 2016, 5: 678–701]
- 81 Feng Q, Xie X, Zhang M, et al. Superior interfacial stability and conductivity of B-doped LiPON electrolyte for LiCoO_2 electrode in solid-state lithium batteries. *Colloids Surf A-Physicochem Eng Aspects*, 2022, 648: 129349
- 82 Zhang Y, Mei Y, Gao X, et al. Inhibition of lithium dendrites by a LiPON interlayer with Li^+ conductive and electron non-conductive dynamic properties based on $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ solid electrolyte. *J Alloys Compd*, 2024, 971: 172746
- 83 He Z, Yang S, He P, et al. Unraveling dendrite behavior: Key to overcoming failures in lithium solid-state batteries. *Sci Bull*, 2023, 68: 2503–2506
- 84 Lu G, Dong Z, Liu W, et al. Universal lithiophilic interfacial layers towards dendrite-free lithium anodes for solid-state lithium-metal batteries. *Sci Bull*, 2021, 66: 1746–1753
- 85 Yu C E, Gregory D H, Liu W R. $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) solid electrolytes synthesized by microwave-assisted hydrothermal reactions for Li all-solid-state battery applications. *Surf Coatings Tech*, 2024, 481: 130671
- 86 Shen S P, Tang G, Li H J, et al. Low-temperature fabrication of NASICON-type LATP with superior ionic conductivity. *Ceramics Int*, 2022, 48: 36961–36967
- 87 Han S, Liu S, Gao J, et al. A novel composite polymer electrolyte containing the lithium-ion conductor $\text{Li}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ synthesized by cationic-exchange method for solid lithium metal batteries. *Electrochim Acta*, 2023, 441: 141795
- 88 Gao J, Wu J, Han S, et al. A novel solid electrolyte formed by NASICON-type $\text{Li}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ and poly(vinylidene fluoride) for solid state batteries. *Funct Mater Lett*, 2021, 14: 2140001
- 89 Baek S J, Cha E, Kim D G, et al. Reaction-sintered LAGP solid electrolytes with MoS_2 coating for improved stability with Li metal. *Ceramics Int*, 2022, 48: 34828–34836
- 90 Hayamizu K, Haishi T. Ceramic-glass pellet thickness and Li diffusion in NASICON-type LAGP ($\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$) studied by pulsed field gradient NMR spectroscopy. *Solid State Ion*, 2022, 380: 115924
- 91 Nasir M, Seo J, Park J S, et al. Excellent electrochemical response of Ce stabilized cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$. *J Eur Ceramic Soc*, 2024, 44: 4606–4611
- 92 Li W, Zhang S, Bu X, et al. Preparation and performance of highly-conductive dual-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ solid electrolytes for thermal batteries. *Green Energy Environ*, 2025, 10: 399–409
- 93 Cojocar-Mirédin O, Schmieg J, Müller M, et al. Quantifying lithium enrichment at grain boundaries in $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ solid electrolyte by

- correlative microscopy. *J Power Sources*, 2022, 539: 231417
- 94 Zhang L, Zhuang Q, Zheng R, et al. Recent advances of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ -based solid-state lithium batteries towards high energy density. *Energy Storage Mater*, 2022, 49: 299–338
- 95 Choi H J, Kim S Y, Gong M K, et al. Tailored perovskite $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$ via an adipic acid-assisted solution process: A promising solid electrolyte for lithium batteries. *J Alloys Compd*, 2017, 729: 338–343
- 96 Teranishi T, Ishii Y, Hayashi H, et al. Lithium ion conductivity of oriented $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$ solid electrolyte films prepared by a sol–gel process. *Solid State Ion*, 2016, 284: 1–6
- 97 Hamed Jouybari Y, Berkemeier F. Enhancing silicon performance via LiPON coating: A prospective anode for lithium ion batteries. *Electrochim Acta*, 2016, 217: 171–180
- 98 Schwöbel A, Hausbrand R, Jaegermann W. Interface reactions between LiPON and lithium studied by *in-situ* X-ray photoemission. *Solid State Ion*, 2015, 273: 51–54

Summary for “氧化物系锂离子固态电解质研究进展”

Research progress in lithium-ion solid electrolytes of oxides

Yaqiu Wang, Junchao Chen, Yanzhe Zhu, Guotai Zhang, Jianhui Wang, Xiangyu Zhang & Weiping Tang*

*School of Chemistry and Chemical Engineering, Shanghai Jiaotong University, Shanghai 200240, China** Corresponding author, E-mail: tangweiping@sjtu.edu.cn

In order to deal with the increasingly severe global energy crisis as well as serious environmental pollution, it is urgent to develop new energy resources. Although lithium-ion batteries have only been successfully introduced into the market since 1990s, there is still an exponentially growing demand for lithium-ion batteries all over the world. As a considerable novel energy source, lithium-ion batteries have significant potential, which is widely used in electric vehicles, energy-storage systems, metallurgy, ceramic production, glass manufacturing and aviation fuel industries. Among them, the solid-state lithium-ion batteries (SSLIBs) represent a promising evolution in battery technology, offering superior safety, energy density, and longevity compared to conventional liquid electrolyte batteries. Traditional lithium-ion batteries, which use liquid electrolytes, suffer from safety issues such as leakage, flammability and thermal runaway. SSLIBs replace these liquid electrolytes with solid electrolytes, mitigating these risks and enabling higher energy densities due to the ability to accommodate lithium metal anodes. The SSLIB consists of a positive electrode, a negative electrode and a solid electrolyte. Compared with liquid electrolytes, solid electrolytes avoid the direct contact between positive electrodes and negative electrodes, fundamentally eliminating the risk of lithium dendrites piercing the separator, so as to enhance the safety of lithium batteries greatly. Furthermore, the SSLIBs are expected to be a hot spot in future lithium battery research due to the advantages of high energy density, wide operating voltage range and long cycle life. Advancements in SSLIBs technology are crucial for the next generation of electric vehicles, portable electronics, and large-scale energy storage systems, pushing the boundaries of battery performance, safety and sustainability. Solid electrolytes are regarded as the key component of SSLIBs, serving dual functions as both separators and electrolytes. The currently developed solid electrolytes can be divided into two categories: Polymer solid electrolytes and inorganic solid electrolytes, in which the oxide solid electrolytes, as the earliest developed inorganic solid electrolytes, play an indispensable role in the development of solid-state battery industry. The typical oxide solid electrolytes, including sodium super ionic conductor (NASICON), garnet (LLZO), inorganic perovskite (LLTO), and LiPON films, are reviewed in this paper. NASICON, for example, is known for its high ionic conductivity and structural stability. Garnet-type electrolytes, such as LLZO, possess high ionic conductivity and chemical stability with lithium. Inorganic perovskite (LLTO) provides a good balance between ionic conductivity and mechanical strength. LiPON films, widely used in thin-film batteries, have excellent electrochemical stability and compatibility with lithium metal. In addition, the crystal structures and ion-transport mechanism, the solutions to improve conductivity and measures to improve the compatibility between electrodes and electrolytes are introduced, along with a comparison of oxide solid electrolytes. Finally, several suggestions for future development directions are proposed. These include enhancing the ionic conductivity of solid electrolytes, improving the interface compatibility between the electrolytes and electrodes, and developing cost-effective and scalable manufacturing processes. Additionally, further research is needed to understand the degradation mechanisms and long-term stability of solid-state batteries. These recommendations aim to provide a more comprehensive reference for ongoing and future research on oxide solid electrolytes, supporting the broader goal of advancing solid-state lithium battery technology.

lithium-ion batteries, oxide solid electrolytes, conductivity, interfacial compatibilitydoi: [10.1360/TB-2024-0586](https://doi.org/10.1360/TB-2024-0586)