

高熵无机固态电解质研究进展

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摘 要: 高熵材料通常由复杂的多组元组成, 凭借高构型熵及元素间的协同作用, 展现出较传统非高熵材料更优异的物理和化学特性。针对固态电解质材料, 高熵策略对于其结构的调控作用在优化固态电解质的离子传输特性上具有显著意义。高熵策略通过调节位点能量、优化离子分布状态、引入适度的结构无序以及调控微观形貌, 有效提升了固态电解质的离子电导率及综合性能。本文对高熵型氧化物、硫化物和卤化物固态电解质的特性和性能提升机制进行了回顾和总结, 为高熵固态电解质的开发提供参考, 并对未来研究方向进行了展望。

关键词: 高熵材料; 固态电解质; 离子传输; 局部结构

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在传统合金材料体系中, 通常以 1 种或 2 种元素为主, 仅掺杂少量异质元素以优化材料性能。2004 年, Yeh 等^[1]和 Cantor 等^[2]分别报道了含有多种主要元素的多元合金, 提出了“高熵合金”的概念。随后, 含有多种主要元素或者构型熵大于 $1.5R$ (其中 R 为气体常数) 的材料被称为“高熵材料”。高熵材料中复杂的组成不仅提高了体系的构型熵, 促进了单一结构的形成, 元素之间的差异及相互作用对晶格结构、电子结构和微观形貌的调控赋予了材料优异的性能^[3]。因此, 高熵材料的种类也快速扩张, 目前已从合金、金属间化合物发展至氧化物、碳化物、氮化物和硫化物等, 其应用领域也日益广泛^[4-6]。

在电化学储能领域中, 采用固态电解质的固态锂电池同时具有高能量密度和高安全性的优点^[7-8]。然而, 当前报道的固态电解质材料的性能还存在些许不足, 为了满足实用化需求, 还需进一步提升其离子电导率及综合性能。无机晶态固态电解质材料通常由阴离子、非移动阳离子构成框架结构, 所形成的多面体间隙则为可迁移离子的长程扩散提供通道。为了促进离子的高效迁移, 通过结构调控构建

具有较低迁移能垒的连续迁移路径十分重要^[9]。

材料体系中异质元素间离子半径和电负性的差异对于晶格结构的调控作用使高熵策略在优化和开发高性能固态电解质领域极具潜力。在高熵固态电解质材料中, 复杂组成导致的晶格畸变会使结构偏离原始晶体的对称性, 从而对离子分布、可迁移离子与其他离子之间的库伦作用等产生影响, 而这些因素则与电解质的离子传输特性密切相关。本文介绍了高熵型氧化物、硫化物、卤化物固态电解质材料的研究进展, 总结了高熵策略与电解质性能优化之间的构效关系, 并对高熵固态电解质未来的发展进行了展望。

1 高熵氧化物固态电解质

石榴石型 $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) 具有三维离子传输通道以供离子快速传输^[10-11], 并且 LLZO 的电化学稳定窗口较宽, 使其与金属锂之间的兼容性较好, 有利于提升全固态电池的能量密度^[12-13]。目前, 研究人员已经报道了多种具有更高稳定性和离子电导率的高熵 LLZO 固态电解质材料, 并对其机理进行了深入研究。

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LLZO 具有热力学稳定的四方相(空间群为 $I4_1/acd$)和亚稳态的立方相(空间群为 $Ia\bar{3}d$) 2 种结构。由于这 2 种结构对称性及 Li^+ 排布形式的差异, 立方相 LLZO 的离子电导率比四方相 LLZO 高 2 个数量级 ($10^{-3}\sim 10^{-4}$ S/cm vs. $10^{-5}\sim 10^{-6}$ S/cm)^[14-15]。在以往的研究中, 通常采用高价元素取代造成锂空位来稳定立方相结构^[16-17], 而高熵策略则能够在不改变 Li^+ 含量的情况下提升结构稳定性。如图 1 所示, 向四方相的 $\text{Li}_7\text{La}_3\text{Zr}_{2/3}\text{Hf}_{2/3}\text{Sn}_{2/3}\text{O}_{12}$ 中继续引入 Sc^{3+} , 晶格结构就会从四方相转变为立方相。原位高温 X 射线衍射(XRD)测试结果则进一步表明 $\text{Li}_7\text{La}_3\text{Zr}_{0.5}\text{Hf}_{0.5}\text{Sc}_{0.5}\text{Nb}_{0.5}\text{O}_{12}$ 和 $\text{Li}_7\text{La}_3\text{Zr}_{0.4}\text{Hf}_{0.4}\text{Sn}_{0.4}\text{Sc}_{0.4}\text{Ta}_{0.4}\text{O}_{12}$ 仅在 400 °C 时就开始形成立方相结构, 证实了高构型熵能够有效促进立方相结构的稳定性^[18]。Feng 等^[19]通过逐步增加 LLZO 中组成元素的数量, 也证实了复杂的组成有利于电解质形成立方相结构。快速合成法的应用则能够在数十秒的时间内制备含有 10 种异质元素的高熵 LLZO, 体现了石榴石结构对于复杂元素良好的包容性。然而, 复杂的组成元素不仅能够提高构型熵, 也会对反应的焓变产生影响。 $\text{Li}_{5.75}\text{Ga}_{0.25}\text{La}_3\text{Zr}_{0.5}\text{Ti}_{0.5}\text{Sn}_{0.5}\text{Nb}_{0.5}\text{O}_{12}$ 的吸热焓仅是非掺杂 LLZO 的一半, 有利于电解质材料的合成^[20]。在高熵 LLZO 这一复杂的体系中, 异质元素并非完全随机分布, 本课题组^[21]结合中子对分布函数(NPDF)测试和超胞模型拟合分析了 $\text{Li}_6\text{La}_3\text{Zr}_{0.5}\text{Hf}_{0.5}\text{Ta}_{0.5}\text{Nb}_{0.5}\text{O}_{12}$ 的局部结构。 Zr^{4+} 、 Hf^{4+} 、 Ta^{5+} 和 Nb^{5+} 依据价态形成五价离子优先被四价离子包围的

局部团簇结构。这一特定的局部团簇有利于降低体系能量, 促进结构稳定性。

高熵策略除了能够稳定立方相结构来提供完整连续的离子传输通道, 所产生的晶格畸变还会对离子迁移的难易程度造成影响。Zeng 等^[22]通过理论计算发现, 由 $\text{Li}_3\text{Nd}_3\text{Te}_3\text{O}_{12}$ 、 $\text{LiTi}_2(\text{PO}_4)_3$ 和 $\text{NaZr}_2(\text{PO}_4)_3$ 结构中的 TM—O 键长偏差引起的晶格畸变, 会扰乱迁移离子位点能量, 使其从独立分布变为区间分布(见图 2a)。当相邻位点的位能分布相互重叠时, 迁移离子在这 2 点间的跳跃活化能将降低, 而当这些位点相互连接时, 迁移离子就能够完成快速的长程扩散(见图 2b)。高熵策略则是实现位点能量调控的有效手段, $\text{Li}_3(\text{La}, \text{Pr}, \text{Nd})_3(\text{Te}, \text{W})_2\text{O}_{12}$ 、 $\text{Li}(\text{Ti}, \text{Zr}, \text{Sn}, \text{Hf})_2(\text{PO}_4)_3$ 和 $\text{Na}(\text{Ti}, \text{Zr}, \text{Sn}, \text{Hf})_2(\text{PO}_4)_3$ 高熵电解质的离子电导率相较于相同原型结构的固态电解质实现了数量级的提升。Wang 等^[23]采用几何相位分析(GPA)来研究 $\text{Li}_7(\text{La}, \text{Nd}, \text{Sr})_3(\text{Zr}, \text{Ta})_2\text{O}_{12}$ (LLNSZTO) 中的应变分布情况。如图 2c 所示, 根据对采集到的高分辨率透射电子显微镜(HRTEM)照片的分析, LLZO 中的应变分布均匀, 而当引入 Nd^{3+} 、 Sr^{2+} 和 Ta^{5+} 后, LLNSZTO 不同区域的应变存在明显差异, 表明晶格发生了严重的收缩和膨胀。晶格畸变的增加显著降低了 Li^+ 迁移活化能, LLNSZTO 的离子电导率达到 6.26×10^{-4} S/cm。

LLZO 的空气稳定性也会对离子传输和电化学性能产生影响, 目前已有一些文献报道了高熵策略能有效提高 LLZO 的空气稳定性^[24-25]。同样在空气

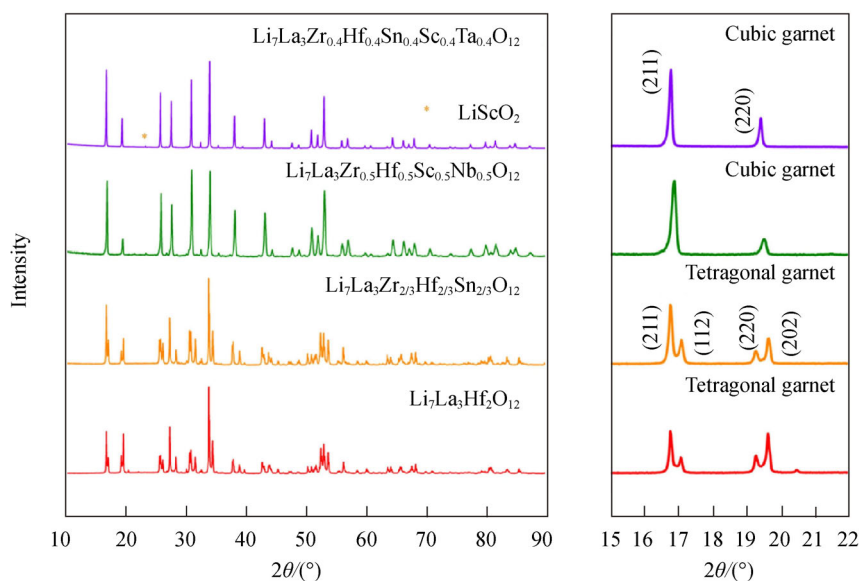


图 1 $\text{Li}_7\text{La}_3\text{Hf}_2\text{O}_{12}$ 、 $\text{Li}_7\text{La}_3\text{Zr}_{2/3}\text{Hf}_{2/3}\text{Sn}_{2/3}\text{O}_{12}$ 、 $\text{Li}_7\text{La}_3\text{Zr}_{0.5}\text{Hf}_{0.5}\text{Sc}_{0.5}\text{Nb}_{0.5}\text{O}_{12}$ 和 $\text{Li}_7\text{La}_3\text{Zr}_{0.4}\text{Hf}_{0.4}\text{Sn}_{0.4}\text{Sc}_{0.4}\text{Ta}_{0.4}\text{O}_{12}$ 的 XRD 谱^[18]

Fig. 1 XRD patterns of $\text{Li}_7\text{La}_3\text{Hf}_2\text{O}_{12}$, $\text{Li}_7\text{La}_3\text{Zr}_{2/3}\text{Hf}_{2/3}\text{Sn}_{2/3}\text{O}_{12}$, $\text{Li}_7\text{La}_3\text{Zr}_{0.5}\text{Hf}_{0.5}\text{Sc}_{0.5}\text{Nb}_{0.5}\text{O}_{12}$, and $\text{Li}_7\text{La}_3\text{Zr}_{0.4}\text{Hf}_{0.4}\text{Sn}_{0.4}\text{Sc}_{0.4}\text{Ta}_{0.4}\text{O}_{12}$ ^[18]

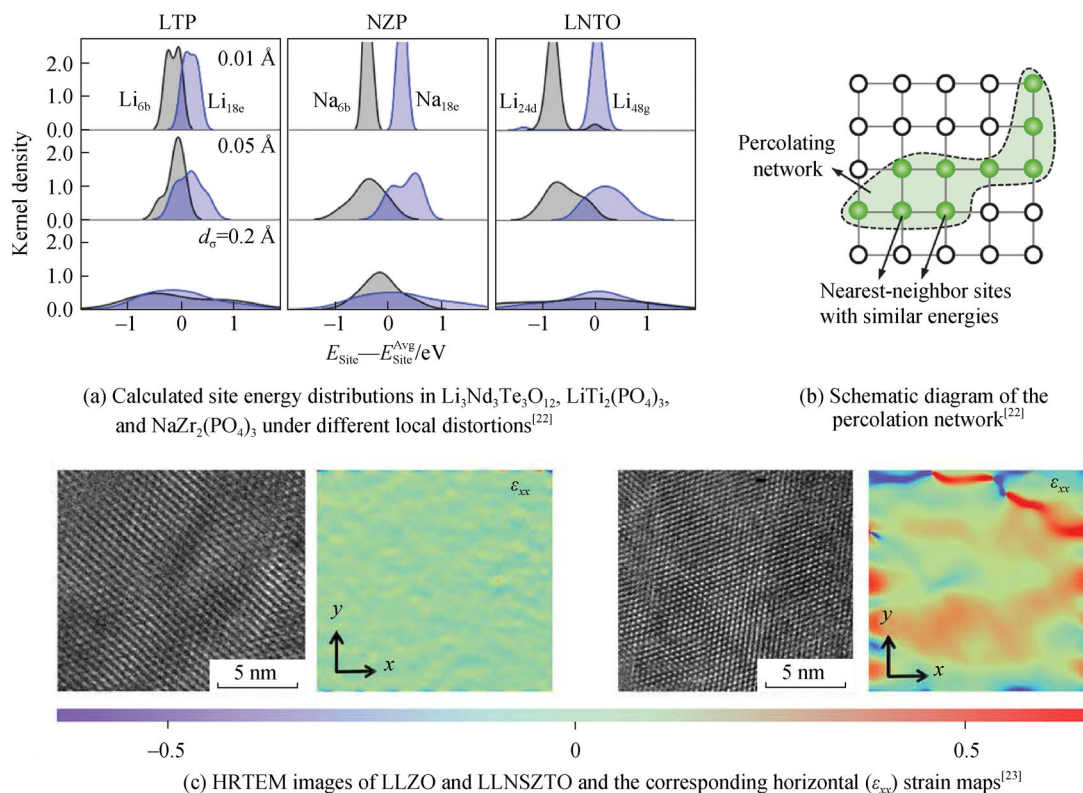


图2 高熵氧化物电解质的位点能量分布及应变分析^[22–23]

Fig. 2 Site energy distributions and strain analysis of high-entropy oxide electrolytes^[22–23]

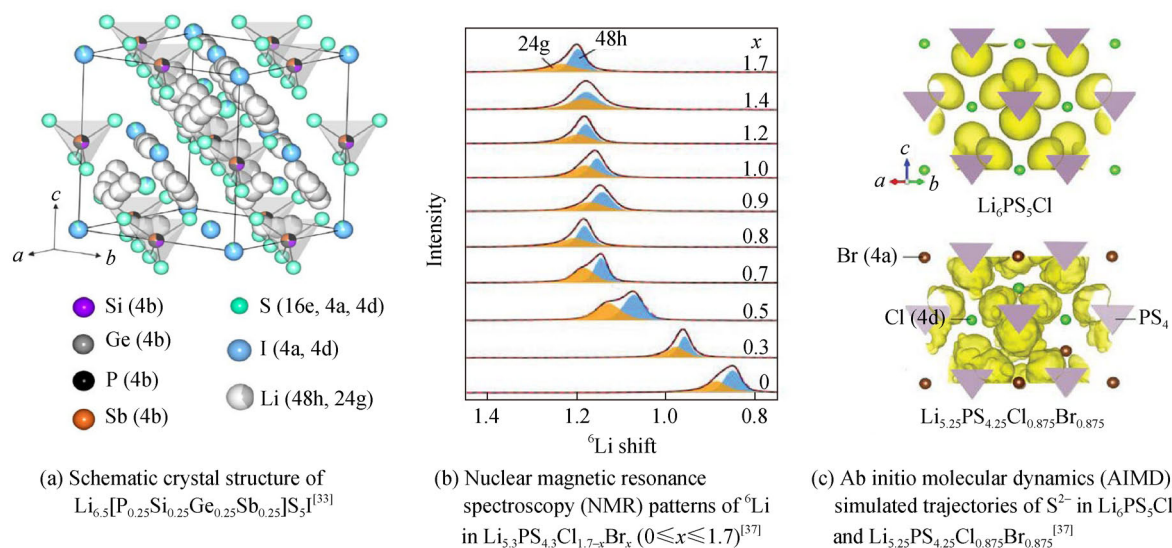
中放置 10 d, $\text{Li}_{5.75}\text{Ga}_{0.25}\text{La}_3\text{Zr}_{0.5}\text{Ti}_{0.5}\text{Sn}_{0.5}\text{Nb}_{0.5}\text{O}_{12}$ 表面的 Li_2CO_3 杂质仅有 2 μm 厚, LLZO 表面的 Li_2CO_3 杂质层的厚度则超过 20 μm , 表明高熵策略能够降低 LLZO 与空气中的 H_2O 和 CO_2 的反应程度^[20]。 $\text{Li}_{6.2}\text{La}_3(\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Ti}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2})_2\text{O}_{12}$ 高熵电解质在空气中放置 2 个月后离子电导率仍达到 10^{-4} S/cm^[25], 良好的空气稳定性也为其商业化应用提供基础。此外, 高熵策略还能够调控 LLZO 的带隙, 相较于 LLZO (3.96 eV), $\text{Li}_{5.75}\text{Ga}_{0.25}\text{La}_3\text{Zr}_{0.5}\text{Ti}_{0.5}\text{Sn}_{0.5}\text{Nb}_{0.5}\text{O}_{12}$ 的带隙提升至 4.64 eV, 有利于抑制电化学过程中锂枝晶的形成和生长^[20]。

2 高熵硫化物固态电解质

以 $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS)^[26] 和 $\text{Li}_6\text{PS}_5\text{X}$ (X=Cl, Br, I)^[27–30] 为代表的硫化物固态电解质材料不仅具有适合离子快速迁移的框架结构, 极化更强的 S^{2-} 还有利于晶格软化以进一步降低离子迁移活化能, 因而此类电解质的室温离子电导率普遍都高于 10^{-3} S/cm。硫化物固态电解质不仅能够容纳多种阳离子, 对于阴离子也具有高兼容性, 因此, 采用高熵策略优化性能时, 可以对硫化物固态电解质中的阳离子和阴离子位点单独或同时进行调控^[31–32]。

在 $\text{Li}_6\text{PS}_5\text{I}$ 中, Li^+ 分布于 24g 和 48h 2 种晶格位

点中, 而这 2 个位点中 Li^+ 占有率与电解质的离子电导率密切相关。在 P 位点含有多种阳离子的 $\text{Li}_{6.5}[\text{P}_{0.25}\text{Si}_{0.25}\text{Ge}_{0.25}\text{Sb}_{0.25}]\text{S}_5\text{I}$ 中 (见图 3a), 元素之间的相互作用使 Li^+ 发生重排, 24g 位点的占有率上升。这一现象增强了相邻 48h 位点中 Li^+ 之间的库伦斥力, 从而扩大了 48h–48h 双跃迁距离、缩短了晶间跃迁距离, 有效促进了 Li^+ 的长程扩散。得益于这一结构优势, $\text{Li}_{6.5}[\text{P}_{0.25}\text{Si}_{0.25}\text{Ge}_{0.25}\text{Sb}_{0.25}]\text{S}_5\text{I}$ 的活化能降低至 0.20 eV, 离子电导率高达 1.30×10^{-2} S/cm^[33]。硫化物固态电解质中, 阴离子的变化会直接影响相邻 Li^+ 的排布, 从而对其动力学产生显著影响^[34–36]。Wang 等^[37] 借助构型熵调控的思路, 对 $\text{Li}_{5.3}\text{PS}_{4.3}\text{Cl}_{1.7-x}\text{Br}_x$ ($0 \leq x \leq 1.7$) 中的 Cl 和 Br 比例进行系统调整以探究对电导率的影响。随着体系构型熵的增加, 阴离子在 4a 和 4d 位点的混排增加了体系的无序度, Li^+ 在 24g 位点的占有率也随之变化。如图 3b 所示, 随着 Cl 和 Br 的比例逐渐相近, Li^+ 在 24g 位点的占率先增加后降低, 与电导率的变化一致。此外, 硫化物固态电解质的阴离子基团通常具有可移动性, 从模拟的 S^{2-} 运动轨迹中也可以看出, PS_4^{3-} 阴离子基团的旋转运动随着构型熵的增加得到增强 (见图 3c), 有利于进一步加速 Li^+ 的迁移。当 $x=1.0$ 时, $\text{Li}_{5.3}\text{PS}_{4.3}\text{Cl}_{0.7}\text{Br}$ 离子电导

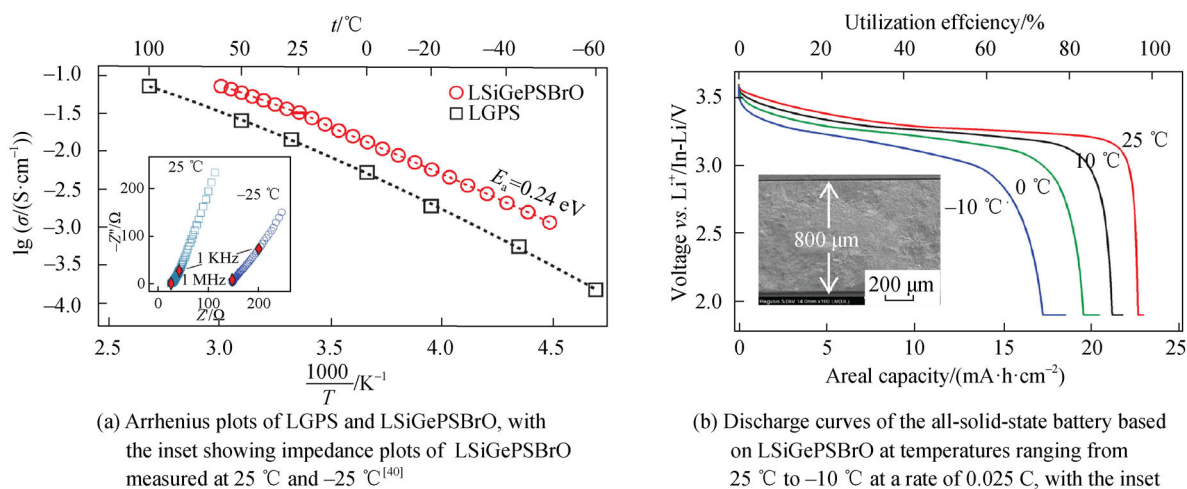
图 3 高熵硫化物电解质的晶体结构示意图和化学环境分析^[33, 37]Fig. 3 Schematic crystal structure and chemical environment analysis of high-entropy sulfide electrolytes^[33, 37]

率高达 $2.60 \times 10^{-2} \text{ S/cm}$ 。

对 $\text{Li}_6\text{PS}_5\text{Br}$ (LPSBr) 固态电解质同时进行阳离子和阴离子取代时, 同样会造成结构无序和 Li^+ 排布情况的改变。随着构型熵的增加, $\text{Li}_6\text{P}_{0.85}\text{Si}_{0.05}\text{Ge}_{0.05}\text{Sn}_{0.05}\text{S}_5\text{Br}$ (HE-LPSBr) 和 $\text{Li}_6\text{P}_{0.85}\text{Si}_{0.05}\text{Ge}_{0.05}\text{Sn}_{0.05}\text{S}_{4.5}\text{BrCl}_{0.5}$ (HE-LPSBrCl) 中 4a 和 4d 位点上的离子反位也愈发显著, 体系无序度的提升促进了 Li^+ 的长程扩散, 使 HE-LPSBrCl 的离子电导率相较于 LPSBr 提升了一个数量级。由 HE-LPSBrCl 与 LiNbO_3 包覆的 $\text{LiNi}_{0.7}\text{Co}_{0.1}\text{Mn}_{0.2}\text{O}_2$ (NCM712@ LiNbO_3) 正极和 Li-In 合金负极构成的全电池, 在 5 C 的倍率条件下, 经过 1400 次循环后的容量保持率高

达 85.6%, 展现了良好的电化学稳定性^[38]。虽然高熵策略能够调控电解质的结构以提升电导率, 但是电导率并不随构型熵线性变化, 阴离子和阳离子的同步取代可能会导致过度的晶格软化, 反而使得离子电导率降低。例如, 构型熵更高的 $\text{Li}_{6.5}[\text{Ge}_{0.5}\text{P}_{0.5}][\text{S}_{2.5}\text{Se}_{2.5}][\text{Cl}_{0.33}\text{Br}_{0.33}\text{I}_{0.33}]$ 的离子电导率低于 $\text{Li}_6\text{P}[\text{S}_{2.5}\text{Se}_{2.5}][\text{Cl}_{0.33}\text{Br}_{0.33}\text{I}_{0.33}]$ ($1.10 \times 10^{-3} \text{ S/cm}$ vs. $1.30 \times 10^{-3} \text{ S/cm}$)^[39]。因此, 在构建高熵固态电解质时, 合适的元素选择与组成十分重要。

Li 等^[40]分析了硫化物固态电解质的晶体结构与阴离子和阳离子的体积比以及构型熵之间的关系, 设计了 LGPS 型 $\text{Li}_{9.54}[\text{Si}_{0.6}\text{Ge}_{0.4}]_{1.74}\text{P}_{1.44}\text{S}_{11.1}\text{Br}_{0.3}\text{O}_{0.6}$

图 4 LSiGePSBrO 的电化学性能^[40]Fig. 4 Electrochemical performance of LSiGePSBrO^[40]

(LSiGePSBrO)固态电解质。高度无序化的结构有效降低了离子迁移活化能,使得 LSiGePSBrO 的离子电导率达到 3.20×10^{-2} S/cm(见图 4a),是 LGPS 离子电导率的 3 倍,并且高于当前报道的所有锂离子固态电解质材料。在 -10°C 的低温环境下,LSiGePSBrO 的离子电导率仍可达到 9.00×10^{-3} S/cm,展现了出色的离子传导特性。得益于超高的离子电导率,该电解质搭配理论容量高达 $23.5 \text{ mA} \cdot \text{h} \cdot \text{cm}^{-2}$ 的 LiCoO_2 正极组装的全固态电池,在 4.25 V 的截止电压和 0.025 C 的电流倍率条件下,实际容量达到 $22.7 \text{ mA} \cdot \text{h} \cdot \text{cm}^{-2}$ (见图 4b),经过 100 d 的循环后容量保持率为 92.0%。

3 高熵卤化物固态电解质

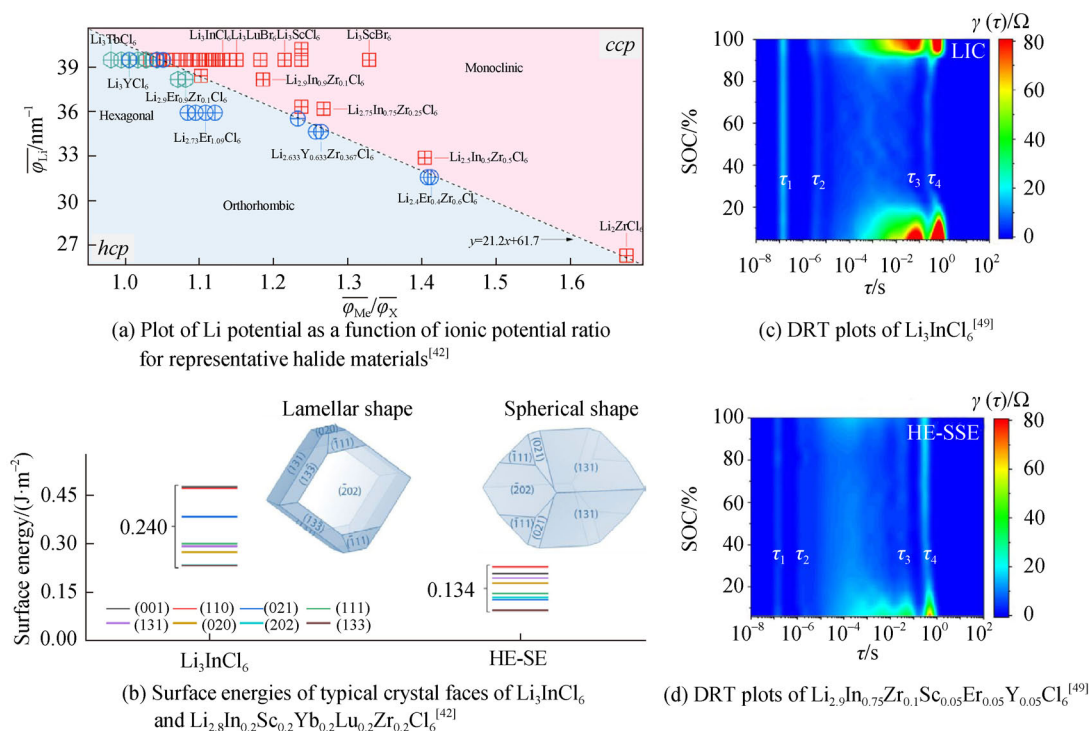
卤化物固态电解质由于室温离子电导率相对较高,且与高比容量氧化物正极材料兼容性较好而被认为极具应用前景^[7, 41]。在以往对卤化物电解质的研究中,研究人员通常聚焦于阴离子半径与相稳定性之间的关联,而较少关注金属离子价态通过离子间相互作用对结构稳定性产生的潜在影响。Wang 等^[42]则根据离子电荷数(n)和离子半径(R)提出了离子势($\Phi = n/R$)的概念,而阳离子和阴离子之间的离子势比即可有效描述这 2 种离子间的相互作用。结合锂离子势和离子势比就可以分析 $\text{Li}_{3+m}\text{Me}_{1+n}\text{X}_6$ 中 $[\text{LiX}_6]$ 和 $[\text{MeX}_6]$ 八面体之间的静电排斥作用,从而判断其倾向于形成的晶体结构(见图 5a)。基于这一标准,研究人员合成了阴离子为立方紧密堆积(ccp)构型的 $\text{Li}_{2.8}\text{In}_{0.2}\text{Sc}_{0.2}\text{Yb}_{0.2}\text{Lu}_{0.2}\text{Zr}_{0.2}\text{Cl}_6$ 固态电解质。在卤化物固态电解质中,阴离子和阳离子的排布对 Li^+ 的传输有重要作用,其中阴离子亚晶格决定了间隙位点的连通性以及 Li^+ 迁移过程中的配位环境,而阳离子的排列则通过调控结构中的 Li^+ 空位数量及静电作用而影响迁移能垒^[43–45]。因此,在 $\text{Li}_{2.8}\text{In}_{0.2}\text{Sc}_{0.2}\text{Yb}_{0.2}\text{Lu}_{0.2}\text{Zr}_{0.2}\text{Cl}_6$ 中,更大的层间距比以及 Li^+ 与 Me 的部分无序分布增加了 LiX_2 层中的空位,从而显著增强了 Li^+ 在结构内的三维扩散能力,使 $\text{Li}_{2.8}\text{In}_{0.2}\text{Sc}_{0.2}\text{Yb}_{0.2}\text{Lu}_{0.2}\text{Zr}_{0.2}\text{Cl}_6$ 的离子电导率达到 2.20×10^{-3} S/cm^[42]。

对于阴离子非紧密排布的 UCl_3 型卤化物电解质而言^[46],高熵策略同样能够在保证结构的同时改善其离子传输性能。用 Al^{3+} 、 Zr^{4+} 、 Hf^{4+} 和 Ta^{5+} 部分取代 LaCl_3 和 CeCl_3 中的 La^{3+} 和 Ce^{3+} ,能够显著提升电解质的离子电导率。当体系中含有 5 种及以上非 Li^+ 阳离子时, UCl_3 型电解质的离子电导率能够

超过 10^{-3} S/cm。 UCl_3 型电解质较大的骨架尺寸还能够容纳离子半径更大的 Na^+ 、 K^+ 、 Cu^{2+} 和 Ag^+ 等离子,向这些电解质中引入多种异质元素时,同样能够获得高离子电导率。采用相同的取代元素, Cu-LaCeZrHfTa-Cl 的离子电导率为 7.13×10^{-3} S/cm,而 Ag-LaCeZrHfTa-Cl 的离子电导率更高,达到 7.75×10^{-3} S/cm^[47]。

高熵策略不仅能够提升卤化物固态电解质的离子电导率,对其微观形貌也会产生影响。在 Li_3InCl_6 电解质中,高熵策略会改变晶面的表面能,从而影响晶粒的生长。尽管 Li_3InCl_6 与 $\text{Li}_{2.8}\text{In}_{0.2}\text{Sc}_{0.2}\text{Yb}_{0.2}\text{Lu}_{0.2}\text{Zr}_{0.2}\text{Cl}_6$ (HE-SE)都为层状晶体结构,但是不同于 Li_3InCl_6 的片状形貌,则呈现为球形颗粒(见图 5b),有利于提升其压实致密度^[42]。在 UCl_3 型电解质中,元素的增加会导致电解质晶粒发生细化, $1.5\text{LiCl} \cdot (\text{LaCl}_3 \cdot \text{CeCl}_3 \cdot \text{ZrCl}_4 \cdot \text{HfCl}_4 \cdot \text{TaCl}_5)_{0.2}$ 电解质粉末的粒径约为几百纳米,且其中非晶含量超过 50%。细小以及非晶化的颗粒可能引发 Li^+ 的界面传导,从而有利于离子实现快速迁移^[47]。

此外,固态电解质的电化学窗口对于其实际应用时的电池性能有较大影响,而高熵策略则有望进一步改善其抗氧化性。在 $\text{Li}_{2.75}\text{Y}_{0.16}\text{Er}_{0.16}\text{Yb}_{0.16}\text{In}_{0.25}\text{Zr}_{0.25}\text{Cl}_6$ 中,由阳离子无序分布引发的晶格畸变会导致 Cl^- 位点能量分布不均匀,使其容易陷于低能量位点,从而产生迟滞扩散效应。这一迟滞扩散效应能够有效减缓 Li_3InCl_6 型固态电解质的氧化动力学,使其氧化电位从 4.25 V 提升至 4.40 V^[48]。Li 等^[49]报道的 $\text{Li}_{2.9}\text{In}_{0.75}\text{Zr}_{0.1}\text{Sc}_{0.05}\text{Er}_{0.05}\text{Y}_{0.05}\text{Cl}_6$ 电解质具有高达 4.80 V 的高压稳定性。对 $\text{Li}_{2.9}\text{In}_{0.75}\text{Zr}_{0.1}\text{Sc}_{0.05}\text{Er}_{0.05}\text{Y}_{0.05}\text{Cl}_6$ 与未包覆的 $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ (NMC532)正极组装的电池进行电化学阻抗谱测试并进行弛豫时间分布分析来探究界面 Li^+ 动力学的演变情况。如图 5c 和图 5d 所示,电解质与正极之间界面所对应的 $\gamma(\tau_3)$ 和 $\gamma(\tau_4)$ 的强度会随着电池充电状态(SOC)的变化而变化。当充电至 4.30 V 后(SOC 约为 90%), Li_3InCl_6 和 NMC532 所对应的 $\gamma(\tau_3)$ 和 $\gamma(\tau_4)$ 强度急剧上升,表明 Li_3InCl_6 与 NMC532 在高电压下不稳定。对高熵电解质而言,直到充电至 4.80 V, $\gamma(\tau_3)$ 和 $\gamma(\tau_4)$ 的强度也没有发生明显上升,体现了 $\text{Li}_{2.9}\text{In}_{0.75}\text{Zr}_{0.1}\text{Sc}_{0.05}\text{Er}_{0.05}\text{Y}_{0.05}\text{Cl}_6$ 在充电过程中出色的界面稳定性。因此,由该高熵电解质与 Li-In 负极和 $\text{LiNi}_{0.9}\text{Mn}_{0.05}\text{Co}_{0.05}\text{O}_2$ (Ni90)正极组装的全电池,在充电截止电压为 4.80 V 的条件下,经过 250 次循环后的容量保持率可达 81.4%。

图 5 高熵卤化物电解质的结构特征和电化学性能^[42, 49]Fig. 5 Structural characterization and electrochemical performance of high-entropy halide electrolytes^[42, 49]

4 总结与展望

高熵策略是开发新型无机固态电解质的有利手段, 不仅能够调整固态电解质材料的构型熵来提升结构稳定性, 还能够通过调节位点能量、结构无序度、可迁移离子的分布状态等来提升固态电解质的离子电导率。在氧化物固态电解质中, 主要通过阳离子取代调控位点能量和局部结构来改善其离子传输性能。在硫化物和卤化物体系中, 阴离子具有较大的选择性和特殊性, 因此, 除了阳离子位点调控以外, 阴离子亚晶格的调控对离子电导率的提升产生更显著的影响。同时, 高熵策略还能够对固态电解质材料的微观形貌、空气稳定性、抗氧化还原性能产生调节作用, 为构建高能量密度、高安全性的固态电池提供基础。然而, 高熵固态电解质材料的发展仍处于起步阶段, 其发展面临着一系列关键问题和挑战:

1) 在构建高熵固态电解质材料时, 元素的选择对其性能具有重要影响, 而复杂的组成增加了建立普适性设计准则的难度。同时, 在设计高熵固态电解质时还需对其综合性能进行权衡, 如何选择恰当的元素在调控结构以提升离子电导率的同时还能兼顾空气稳定性、电化学稳定性等综合性能的提升, 这是发展高熵固态电解质的一大难点。此外, 目前

的研究也较少涉及元素成本与安全性问题, 这对于材料的实际应用潜力有较大影响。后续研究应优先选用低成本、高安全性的原材料, 以提高其实际应用价值。

2) 当前高熵固态电解质材料的研究多集中于离子传输特性, 要实现其实际应用还需深入探讨其与高压正极和锂金属负极之间的界面兼容性与稳定性, 这对于全电池的性能有重要影响。

3) 未来研究应引入机器学习方法, 针对元素选择和结构设计进行预测与筛选, 以加速高性能固态电解质的开发。然而, 高熵固态电解质仍处于早期探索阶段, 实验数据有限且构效关系尚不清晰, 这制约了数据模型的准确性。因此, 可结合传统元素掺杂策略, 量化不同元素对材料性能的影响, 并借助理论计算生成虚拟数据集, 以补充实验数据的不足。此外, 通过实验验证优化预测模型, 实现“计算-数据-实验”协同迭代, 提高模型的可靠性和适用性, 从而加速高熵固态电解质的开发。

尽管高熵固态电解质的研究尚处于早期阶段, 但具有显著的发展潜力, 通过持续的基础研究与技术创新, 有望为推动固态电池的实用化进程提供思路。

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Research progress on High-Entropy Inorganic Solid-State Electrolytes

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Extended Abstract

High-entropy materials (HEMs) tend to be composed of five or more elements or have a configurational entropy greater than $1.5R$ (R is gas constant). The high configurational entropy caused by the complex elements can enhance the solubility of elements within the structure and promote the formation of a single-phase structure. The differences in electronegativity and ionic radii among the constituent elements introduce lattice distortion and sluggish-diffusion effect, playing a critical role in regulating the physical and chemical properties and micromorphology of HEMs. Due to these advantages, the high-entropy strategy has emerged as an effective approach for advancing the existing materials and developing novel ones. Thus, the diversity of HEMs has expanded from high-entropy alloys and intermetallic compounds to high-entropy oxides, sulfides, carbides, and so on. Consequently, their application fields are wide and show great potential in electrochemical energy storage fields.

The development of high-performance solid-state electrolytes (SSEs) is essential for advancing solid-state batteries to satisfy the increasing demands for high energy density, enhanced safety, and long-term stability. As key components, SSEs play an indispensable role in providing migration pathways for alkali metal ions, making the facilitation of ion transport to achieve high ionic conductivity a primary objective in their development. Among various SSEs, inorganic ones have emerged as prominent candidates due to their relatively high ionic conductivity and stability. However, current inorganic SSEs require further improvements in ionic conductivity and overall performance to meet practical application requirements. A particularly important factor influencing the performance of inorganic SSEs is their local structural configuration. The arrangement of ions and the degree of structural order directly govern the migration energy barrier, which in turn has a great influence on ionic conductivity. Tailoring the local structure through compositional engineering and structural modulation offers a promising pathway to minimize migration energy barriers, thereby enhancing ion transport efficiency.

Given the advantages of the high-entropy strategy in regulating local structures, this approach has been preliminarily applied to optimize the performance of inorganic SSEs, including oxide, sulfide, and halide SSEs. The mechanisms by which high-entropy strategies improve properties vary depending on the intrinsic characteristics of each prototype structure. For oxide SSEs, the incorporation of multiple elements effectively regulates site energy and refines the local structure of ion migration pathways, facilitating ion transport. In contrast, sulfide and halide SSEs benefit from their high anion tolerance, which enables the introduction of diverse anion species. This diversity disrupts the arrangement of adjacent Li^+ and directly modulates ion migration behavior, contributing to improved ionic conductivity. This work systematically reviews the unique characteristics and performance enhancement mechanisms of high-entropy oxide, sulfide, and halide SSEs. Furthermore, it identifies key challenges and proposes future research directions aimed at advancing the design and improvement of high-entropy SSEs, paving the way for their application into next-generation solid-state batteries.

Summary and prospects The high-entropy strategy is an effective approach for optimizing and developing SSEs. It can not only adjust the configurational entropy to stabilize the structure, but also enhance the ionic conductivity of SSEs by regulating site energy, structural disorder, and the distribution of mobile ions. For high-entropy oxide SSEs, cation substitution is primarily employed to

regulate site energy and local structure, thereby improving ion transport properties. In high-entropy sulfide and halide SSEs, the anionic sublattice offers greater flexibility in composition. Hence, beyond cationic site regulation, modifications to the anionic sublattice result in a more pronounced effect on ionic conductivity. Furthermore, such strategies can regulate micromorphology, air stability, and resistance to oxidation and reduction, laying a solid foundation for high-energy-density and high-safety solid-state batteries.

However, high-entropy solid-state electrolytes remain in their infancy, and their development faces several critical challenges and key issues. First, in the design of high-entropy solid-state electrolyte materials, the selection of elements critically governs the properties, while the compositional complexity poses significant challenges in establishing universal design principles. Besides, the development of high-entropy solid-state electrolyte materials necessitates careful trade-offs among different properties. A key scientific challenge lies in rationally choosing elements that simultaneously modulate structural configurations to enhance ionic conductivity while maintaining air stability and electrochemical stability. Current research has paid insufficient attention to elemental cost-effectiveness and safety implications, both of which substantially impact the practical application potential of these materials. Further investigations should prioritize the adoption of low-cost and high-safety raw materials to enhance the practical application. Second, current research on high-entropy SSEs mainly focused on the ionic transport properties. However, achieving practical applications requires a deeper investigation into their interfacial compatibility and stability with high-voltage cathodes and lithium metal anodes, which are critical for the performance of full battery systems. Third, future research could introduce machine learning methods to predict and screen elemental combinations and structural designs, thus accelerating the development of high-performance solid-state electrolytes. However, high-entropy solid-state electrolytes remain in the early exploratory stage, where limited experimental data and unclear structure-properties relationships constrain the accuracy of the data-driven model. To address this, researchers could combine conventional elemental doping strategies with quantitative analyses of individual element contributions to material performance. Concurrently, theoretical calculations could generate supplementary theoretical datasets. Furthermore, experimental validation should be employed to refine predictive models, establishing a “computation-data-experiment” collaborative framework. This approach will improve the model's reliability and generalizability, ultimately accelerating the rational design of high-entropy solid-state electrolytes.

Although research on high-entropy SSEs is still in its early stages, these materials are expected to provide new avenues for advancing the practical applications of solid-state batteries through ongoing fundamental studies and technological innovations.

Keywords high-entropy materials; solid-state electrolytes; ion transport; local structure