

锂金属与卤化物电解质界面的失效机制及其抑制策略

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摘 要: 锂金属高理论容量(3860 mA·h/g)和低还原电位(-3.04 V vs. SHE)的优势使其成为最理想的负极材料。然而, 锂金属与电解质之间的界面副反应和枝晶生长导致电池性能快速衰退, 阻碍锂金属电池在实际中的应用和推广。采用基于第一性原理计算的热力学平衡方法对卤化物电解质与锂金属之间的界面副反应的反应能、界面产物以及由界面反应导致的体积变化进行分析。研究表明, 卤化物电解质与锂金属之间的界面反应层为具有电子、Li⁺导通能力的混合导体, 从而导致界面反应在全固态电池循环过程中持续发生。此外, 电解质与锂金属的界面反应会引起体积收缩, 导致锂金属与电解质之间发生界面分离, 增大界面阻抗和加剧负极界面电场的集中分布, 在 Li 沉积过程中诱发锂枝晶的成核和生长。根据界面反应特性, 筛选可有效降低界面层电子电导和缓解界面分离的材料, 有助于提升锂金属全固态电池(ASSBs)的性能。

关键词: 锂金属; 全固态电池; 卤化物电解质; 密度泛函理论; 界面反应

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自 20 世纪 90 年代锂离子电池实现商业化后, 锂离子电池的应用已经从消费类电子产品迅速拓展到动力电池和大规模储能系统等领域。随着社会自动化和智能化的加速发展, 对电池的依赖程度不断加深, 同时对电池的性能, 特别在能量密度和安全性能方面提出了更高的要求。传统锂离子电池的发展已经接近其理论能量密度的瓶颈, 使其在提升电池的能量密度方面变得非常困难。锂金属具有 3860 mA·h/g 的理论容量和 -3.04 V vs. SHE 的低电位, 是最理想的负极材料, 可有效提升电池的能量密度^[1]。然而, 锂金属与液态有机电解液之间的强反应性和沉积过程中的枝晶生长容易造成电池短路, 引发电池安全事故。利用无机且不易燃的固体电解质材料代替传统的液态有机电解质, 可以有效提升锂金属电池的安全性能^[2]。

固体电解质材料作为全固态锂金属电池的关键材料之一, 在近年来的研究中取得快速的发展, 其离子电导率(~25 mS/cm)接近甚至超过液态电解液体系的导锂水平(~10 mS/cm)。^[3-4]按材料体系分

类, 固体电解质材料包含卤化物、硫化物、氧化物和聚合物 4 大类, 其中卤化物电解质材料具有较高的氧化极限(~4 V), 与高压正极材料具有较好的界面兼容性^[5-9]。此外, 卤化物电解质还具有较好的塑性, 在冷压制备的工艺条件下可与正极保持较好的物理接触, 有利于容量发挥。然而, 卤化物电解质 Li-MX(X: F, Cl, Br, I)与锂金属接触时, 电解质中的金属阳离子 M(Zr、Al、In、Y 等)容易被还原生成金属或合金相, 导致电解质在电池循环过程中持续分解增加界面阻抗, 最终导致电池完全失效^[10]。对电解质材料进行掺杂改性、在卤化物电解质与锂金属间引入界面缓冲层或者卤化物电解质与硫化物电解质制作双层固体电解质层, 可以有效提升电池中的界面稳定性和电池的循环性能^[11-16]。

然而, 缓冲层材料的选择仍然局限于几种常用材料, 对卤化物电解质与锂金属之间界面恶化的机制缺乏在原子尺度的理解。本工作通过理论计算分析卤化物电解质与锂金属之间的界面反应特性、界面产物的性质以及由界面反应引起的体积变化效

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应, 加深对界面衰退机制的理解, 为实验中制定可有效提升界面稳定的策略提供依据和指导。

1 方法

Materials Project(MP)数据库中整合了大量无机材料的第一性原理计算结果, 包括焓、电子结构和力学常数等^[17]。Pymatgen(Python Materials Genomics)模块可以对 MP 数据库中材料的信息进行访问和检索, 利用这些数据可以构建 2 种固体材料的反应相平衡并计算反应能, 预测不同材料之间的热力学稳定性。这种方法已经被广泛应用于研究电池中电解质和电极之间界面的稳定性, 并可以此为条件对 MP 数据库中的材料进行筛选, 筛选出可提升全固态电池界面稳定性包覆材料^[18–21]。其基本原理是将 2 种接触的材料 A 和 B 假想为一个伪二元体系:

$$C_{\text{interface}}(c_A, c_B) = xc_A + (1-x)c_B \quad (1)$$

式中: x 为组分 A 的摩尔分数, 伪二元界面体系的能量可描述为组分 A 和组分 B 的能量分别乘其摩尔分数并加和:

$$\Delta E_{\text{interface}}(c_A, c_B, x) = xE(c_A) + (1-x)E(c_B) \quad (2)$$

界面反应能为伪二元界面体系的反应能减去组分 A 和 B 自身的分解能, 并对反应能做归一化处理, N 为参与反应的所有原子数:

$$\Delta E_{\text{D,mutual}}(c_A, c_B, x) = \min_{x \in [0,1]} \frac{1}{N} [E_{\text{eq, interface}}(xc_A + (1-x)c_B) - xE_D(c_A) - (1-x)E_D(c_B)] \quad (3)$$

式中: $E_{\text{eq, interface}}$ 为界面反应能; $E_D(c_A)$ 和 $E_D(c_B)$ 分别为组分 A 和 B 的分解能; E_D 为通过搜索组分所

有元素化学空间内的化合物, 构建相图获取其分解能。构建 A 与 B 的反应相平衡后, 统计界面产物中电子导电相在所有界面产物中的摩尔分数作为界面层的电子导电性的描述子, 摩尔分数越高, 界面层的电子导电能力越强^[22]。

对于反应相平衡: $x_A A + x_B B \rightarrow x_C C + x_D D + x_E E + \dots$

由界面反应引起的体积变化率 V_c 可由式(4)计算:

$$V_c = \frac{(x_C v_C + x_D v_D + x_E v_E + \dots) - (x_A v_A + x_B v_B)}{x_A v_A + x_B v_B} \times 100\% \quad (4)$$

式中: x 为相平衡中不同组分的化学计量数; v 为反应物和产物单位分子的体积。

2 结果与讨论

2.1 全固态电池中的界面反应和体积效应

全固态锂金属电池复杂的制备工艺导致在电池内部存在正极/电解质、电解质/电解质、电解质/锂金属等诸多界面, 如图 1 所示。固体电解质与 Li 金属发生界面反应生成一系列的界面产物, 这些产物的体积相比参与反应的 Li 金属与电解质的体积会发生不同程度变化, 并对全固态电池的性能产生不同影响。 $V_c < 0$ 表示 Li 金属与质反应后界面层的体积收缩, 会导致 Li 金属与电解质之间物理接触失效并形成空隙, 锂离子在界面处的传输阻力增加。 $V_c > 0$ 表示界面反应层的体积膨胀, 此类界面反应有利于提升 Li 金属与电解质的物理接触, 但是如果体积变化过大, 会导致局部应力堆积过大, 进一步导致电解质颗粒破裂。界面层的性质对全固态锂金属电池的循环影响重大, 如果界面层是 Li

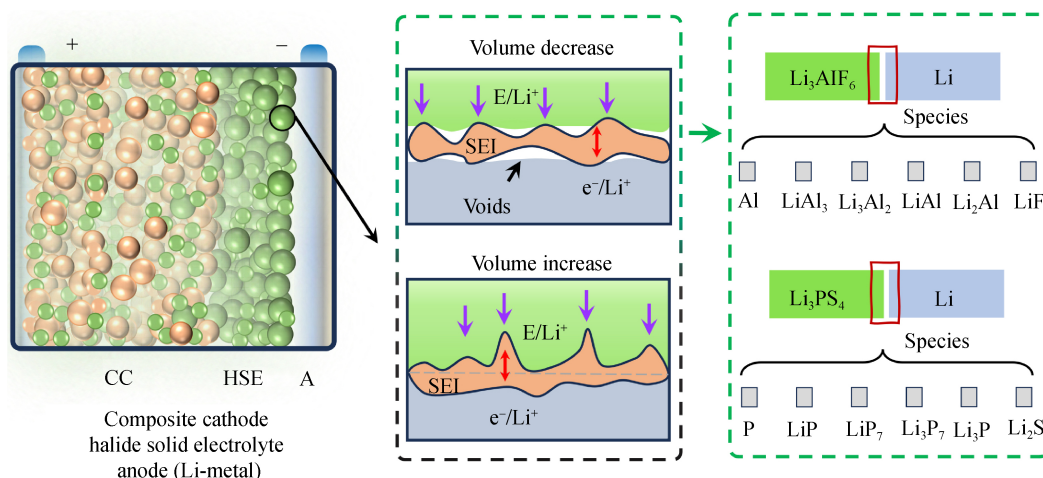


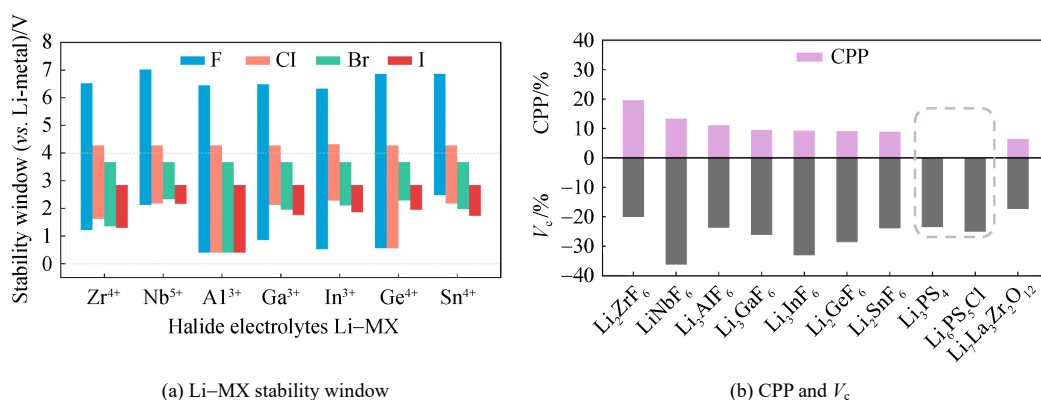
图 1 全固态电池中的锂金属负极与电解质界面反应和体积效应示意图

Fig. 1 Schematic diagram of interface reaction and volume effects between Li-metal and electrolyte in all-solid-state batteries

离子导通电子绝缘, 该界面层可有效钝化界面。例如, Li_3PS_4 和锂金属接触后生成的界面产物均为电子绝缘相(Li_2S 、 Li_3P 、 Li_3P_7 等), 可以钝化 Li_3PS_4 表面, 阻止其进一步被还原。如果界面层是电子和离子的混合导体, 会导致电解质在电池循环过程中持续被还原, 导致界面阻抗持续增大。例如, Li_3AlF_6 与锂金属接触后生成 LiF 和 Al 金属相以及 Li-Al (LiAl_3 , Li_3Al_2 , LiAl , Li_2Al)合金相, 如图 1 所示, 这类现象同样存在于部分氧化物和硫化物电解质体系(LLZO、LGPS 等)^[9]。此外, 需要强调的是如果界面层为混合离子导体, 界面层的体积不论增大或者收缩, 都会导致电场在界面处集中分布, 诱导 Li 金属和枝晶在尖端处优先沉积和生长^[23-26]。如果界面层为电子绝缘体, 界面体积收缩导致界面分离迫使锂离子在界面接触的位置由电解质扩散过 SEI 层至锂金属表面发生沉积。因此, 界面层的电子导电性以及由界面反应引发的体积效应对锂金属负极的性能影响很大, 在选择材料体系和界面缓冲层材料时, 需要加以考虑。

2.2 卤化物电解质热力学稳定性和界面反层的性质

图 2a 为不同卤化物电解质材料 Li-MX (M : Zr , Al , In , Y , Sc 等; X : F , Cl , Br , I)热力学稳定的电化学窗口, 其中 Cl 和 F 阴离子材料体系的氧化电位均超过 4.0 V , F 体系电解质材料具有高的氧化电位($\sim 7.0\text{ V}$)。此外, 在电解质氧化过程中需要克服动力学的限制, 例如, LLZO 的热力学氧化电位为 2.9 V , 实验测得 LLZO 氧化极限接近 4.0 V , 说明阴离子氧化过程中的动力学限制使电解质材料的抗氧化能力得到进一步提升^[20, 27-28]。 Cl 和 F 2 种阴离子化学的电解质材料可以满足不同正极材料的工作电压范围需求。用卤化物电解质 $\text{Li}_2\text{In}_{1/3}\text{Sc}_{1/3}\text{Cl}_4$ 与 NCM 制备复合正极组装的全固态电池在 $2.8\sim 4.8\text{ V}$ 电压范围内循环 3000 圈, 容量保持率仍高于 80%, 优异的电化学性能得益于电解质与正极之间稳定的界面层和电解质具有较高的抗氧化性^[29]。 Br 和 I 的氧化电位均在 4.0 V 以下, 电解质材料在电池充电过程中容易被氧化, 在正极与电解质之间形成界面反应层增加界面阻抗。



V_c is volume change rate. CPP is conductive product percentage.

图 2 Li-MX 的稳定电化学窗口和电解质与锂金属之间界面层中电子电导产物的占比以及由界面反应引起的体积变化率
Fig. 2 Stable electrochemical window of Li-MX (vs. $\text{Li}^+/\text{Li-metal}$) and the molar percentage of electronically conductive products in the interfacial layer between the electrolyte and lithium metal, as well as the volume change rate induced by interfacial reactions

相比于硫化物电解质($\sim 1.7\text{ V}$), 卤化物电解质的还原下限有明显改善^[9]。然而, 这些卤化物电解质对锂金属热力学不稳定, 导致电解质在循环过程中仍然被还原生成界面中间相。由于卤化物电解质的化学属性(Li-MX , M : Zr , In , Ge , Al 等), 材料中的金属阳离子在锂金属沉积过程中被还原形成金属相(Zr 和 Nb)或者合金相(Li-Al , Li-In , Li-Ge), 如表 1 所列。这些金属和合金相存在于界面层导致其为混合离子导体, 电解质在循环过程中持续被还原, 界面阻抗和极化持续增大, 最终导致电池失效。

这些还原产物在实验中得到了充分的证实, 证明了热力学相平衡分析方法在研究界面反应和界面产物预测方面的准确性^[9, 16, 30-36]。 Li-MF 相比于其他卤化物体系具有更高的氧化电位, 因此这里以氟化物电解质为例, 对其界面反应产物中电子电导产物的摩尔分数(CPP)、由界面反应引入的体积变化进行分析。图 2b 总结了界面产物中金属和合金相在所有界面产物中的 CPP, Li-MF (M : Zr , Nb , Al , Ga , In , Ge , Sn)电解质与锂金属反应后界面层中的 CPP 值在 9%~20%, 氧化物电解质 LLZO 的

CPP(6.4%)值略低于卤化物电解质。与卤化物和氧化物电解质不同的是硫化物电解质 Li_3PS_4 和 $\text{Li}_6\text{PS}_5\text{Cl}$ 的 CPP 值均为 0, 说明这一类界面层可以有效地钝

化电解质界面。 $\text{Li}_6\text{PS}_5\text{Cl}$ 经常被用来与卤化物电解质制备双层电解质, 解决卤化物电解质被持续还原的问题^[16, 37–39]。

表 1 不同卤化物、氧化物、硫化物电解质的还原电位和还原相

Table 1 Reduction potential of Li–MF, oxide and sulfide electrolytes, and the phase equilibria at the reduction

Halide electrolyte	Reduction potential (vs. Li-metal)/V	Phase equilibria at reduction potential
Li_2ZrF_6	1.21	Zr, Li_4ZrF_8 , LiF
LiNbF_6	2.13	Nb, Nb_2F_5 , LiF
Li_3AlF_6	0.40	Al, Li_3Al_2 , LiAl_3 , LiAl, LiF, Li_2Al
Li_3GaF_6	0.85	Ga, Li_2Ga_7 , Li_2Ga , Li_3Ga_2 , LiGa, Li_5Ga_4 , LiF
Li_3InF_6	0.53	In, LiIn_3 , LiIn, Li_2In , Li_5In_4 , Li_3In_2 , $\text{Li}_{13}\text{In}_3$, LiF
Li_2GeF_4	0.56	Ge, LiGe, Li_9Ge_4 , $\text{Li}_{15}\text{Ge}_4$, LiF
Li_2SnF_4	2.48	Sn, SnF_2 , LiSn, Li_5Sn_2 , Li_3Sn , Li_7Sn_2 , $\text{Li}_{17}\text{Sn}_4$, LiF
$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$	0.05	Zr_3O , Li_2O , La_2O_3 , Zr_4O
$\text{Li}_6\text{PS}_5\text{Cl}$	1.71	LiP, Li_3P , LiP_7 , Li_2S , P, Li_3P_7

不同电解质体系下, 界面产物的体积相比于参与反应的电解质和锂金属的体积变化不同, 从而导致界面不同的微观结构对锂金属的沉积和枝晶生长有重大影响^[40]。图 2b 为不同电解质与锂金属之间由界面反应而引入的体积变化率(V_c), 结果显示常见的电解质体系的体积变化率均为负值, 范围为 $-36.2\%\sim-17.4\%$, 表明二者之间界面反应层体积收缩, 会引发界面分离和在局部形成空隙。由界面反应引入的界面分离和空隙会进一步加剧电场在界面分布不均性, 诱发锂枝晶的生长。在实验中, 利用聚焦离子束(Focused Ion Beam)切割和截面扫描电子显微镜(Cross-Sectional SEM)的表征方法在不同的硫化物/卤化物电解质与锂金属界面均观测到了界面分离和空隙的现象^[30, 41–43]。Mandal 等^[32]组装了 $\text{Li}|\text{HSE}|\text{Li}$ 对称电池(HSE: Li_2ZrCl_6 , Li_3InCl_6 和 Li_3YCl_6), 并施加了 5 MPa 的堆积压力, 在静置 20 h 后, 压力有明显的衰减, 并在界面处观测到了界面分离和局部空隙。虽然 $\text{Li}_6\text{PS}_5\text{Cl}$ 可以有效钝化电解质界面, 但是界面层的体积收缩仍然较大, 容易导致微观下的界面分离和诱发枝晶生长。因此, 为提升卤化物电解质与锂金属的稳定性、电池的循环性能和极限电流密度(CCD), 应该同时考虑缓冲材料与锂金属的反应性、界面钝化效果以及界面反应引起的体积变化率。

2.3 界面缓冲层材料筛选

利用候选材料与锂金属反应引入的体积变化率 V_c 、界面产物中电子导电产物的摩尔分数和反应能作为筛选条件分别对二元 M-X ($\text{X}=\text{N}$ 、P、S)和三

元含锂的 Li-M-X ($\text{X}=\text{N}$ 、P、S)化合物进行筛选, 目标是筛选出能够有效钝化界面(电子导电产物摩尔分数小于 1%)、体积变化率小($V_c<1\%$)且反应驱动力较小的候选材料, 改善卤化物电解质与锂金属负极的界面兼容性, 筛选结果如图 3 所示。图 3a~图 3c、图 3d、图 3e 分别为 M-N/P/S 二元和 Li-M-N/P/S 三元化合物的分布, 95%以上的化合物与锂金属负极发生反应, 其界面层的体积收缩, 体积变化率集中分布在 -40% 以内, 其中 P 的二元和三元化合物具有较小的 V_c 。体积变化率在 1%以内的部分化合物由于还原产物包含大量的电子导电相而被排除, 因为这一部分材料不能形成有效的钝化层。类似地, 部分可以钝化界面的材料, 由于界面反应的体积变化率过大而被排除, 这类材料可能由于反应层体积收缩过大而导致界面分离。例如, Li_3PS_4 (-23.55%)、 $\text{Li}_7\text{P}_3\text{S}_{11}$ (-14.73%)、 Li_7PS_6 (-17.36%)等一系列硫化物电解质材料均出现在 Li-M-S 中, 但由于体积变化率过大而被排除。在二元材料中, Li_3N 和 Li_3P 出现在筛选结果中。 Li_3P 作为对锂金属稳定的二元 P 化物, 在实验中经常被用作缓冲层, 提升锂金属负极界面稳定性^[14–15]。Li 等^[13]通过调控 $\beta\text{-Li}_3\text{N}$ 中 Li/N 的空位浓度可以有效改善其离子电导率, 并以此为电解质材料组装 $\text{Li}|\text{vacancy-rich-}\beta\text{-Li}_3\text{N}|\text{Li}$ 对称电池, 具有在 7.5 mA/cm^2 的电流密度下稳定循环 4000 h 的优异性能。在三元化合物中, Li_9NS_3 化合物出现在筛选结果中。Yu 等^[12]通过向 Li_2S 结构中引入 N 元素, 有效改善了材料的离子电导率, 并使其对锂金属负极表

现出良好的稳定性。通过分析界面反应特性制定筛选条件, 其筛选结果与材料在实验中的应用一致性非常好, 证实了筛选条件的合理性。除这几

种已经被广泛应用的材料, 还筛选出一些其他的二元材料和三元材料, 如 Sr_2N 、 Sc_7P_3 、 LaS 、 Li_7TaN_4 、 Li_5SiN_3 和 Li_4SrP_2 等。

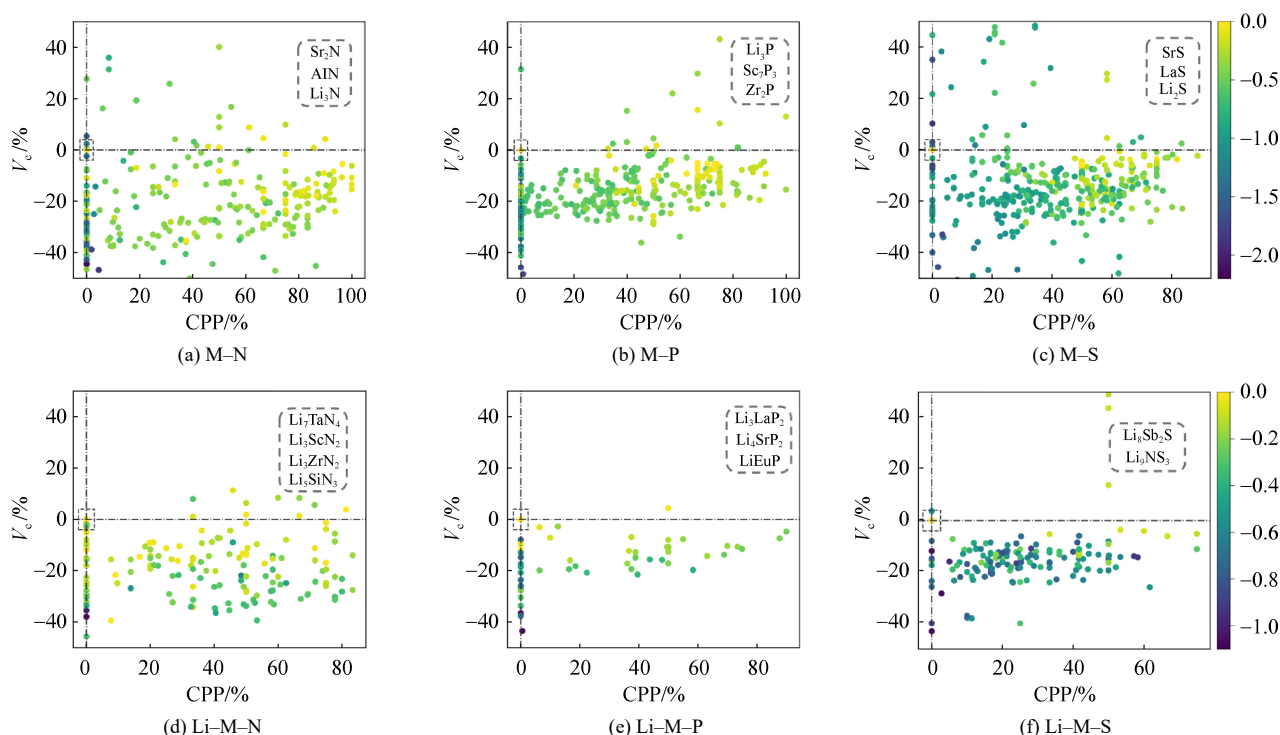


图 3 高通量筛选二元和三元化合物与锂金属反应界产物的 CPP 和 V_c

Fig. 3 High-throughput screening the CPP and V_c of the interphases formed by interfacial between binary/ternary compounds and lithium metal

3 结论

卤化物电解质与锂金属之间具有本征的热力学不稳定, 其来源是电解质中的金属阳离子被还原成金属相和合金相, 其摩尔百分比范围为 9%~20%。这些电子导电相的存在使得界面中间相为电子和锂离子的混合导体, 导致电解质在电池循环过程中持续被还原。此外, Li-MF (M: Zr、Nb、Al、Ga、In、Ge、Sn) 界面反应生成的界面中间相体积发生收缩, 体积变化率范围为 -36.2%~-17.4%, 这会导致界面分离和在界面处形成局部空隙, 这些现象在实验中已经得到证实。界面分离和局部空隙会显著影响对锂金属的沉积和枝晶生长, 从而进一步降低锂金属固态电池的性能。根据锂金属与卤化物电解质之间的界面反应特性 ($V_c < -17.4\%$, $\text{CPP} > 9\%$), 筛选出能够有效钝化界面并减小因反应导致的体积变化的材料, 从而提升全固态电池的性能。筛选结果中的二元材料 Li_3N 、 Li_3P 和三元材料 Li_9NS_3 在实验中得到了验证, 证明了筛选条件的科学性和有效性。

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Interface Degradation Mechanisms between Lithium Metal and Halide Electrolytes and Their Suppression Strategies

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Extended Abstract

Introduction Conventional liquid electrolyte-based lithium-ion batteries have achieved a great commercial success. However, their energy density has theoretical limits, and safety concerns such as electrolyte leakage and thermal runaway remain. Replacing liquid electrolytes with inorganic, nonflammable solid electrolytes can significantly enhance battery safety and potentially enable the application of lithium metal anode in all-solid-state batteries (ASSBs), thereby further improving the energy density. Recent development on solid electrolyte materials has advanced rapidly, with significant improvements in ionic conductivity. Among them, halide electrolytes exhibit a high oxidative stability (*i.e.*, ~4 V) and an excellent compatibility with high-voltage cathodes. However, cations (*e.g.*, Zr^{4+} , Al^{3+} , In^{3+} , Y^{3+}) in the electrolyte reduce when halide electrolytes come into contact with lithium metal, forming metallic or alloy phases. These electronically conductive phases could cause continuous electrolyte decomposition, ultimately leading to battery failure. To improve interfacial stability, some strategies such as electrolyte doping, introducing interfacial buffer layers, and employing bilayer solid electrolyte structures are implemented to suppress interfacial reactions. However, the selection of buffer layer materials remains limited to a few commonly used compounds, and the degradation mechanisms at the lithium metal/halide electrolyte interface are still unclear in the atomic scale. This study was to employ theoretical calculations to systematically analyze the interfacial reaction between halide electrolytes and lithium metal, including the electronic conductivity of interfacial reaction products and the effects of volume changes.

Methodes The reaction phase equilibria between two contacting solid materials could be constructed by the Pymatgen (Python Materials Genomics) module. Based on enthalpy data retrieved from the Materials Project (MP) database, the interfacial reaction energy was calculated to predict the thermodynamic stability of different materials. This approach is widely used to study the interfacial stability between electrolytes and electrodes in batteries. The fundamental principle is to conceptualize two contacting materials, A and B, as a pseudo-binary system:

$$C_{\text{interface}}(c_A, c_B) = xc_A + (1-x)c_B \quad (1)$$

where x is the mole fraction of component A. The total energy of the pseudo-binary interfacial system can be described as the sum of the energies of components A and B, each weighted by their respective mole fractions:

$$\Delta E_{\text{interface}}(c_A, c_B, x) = xE(c_A) + (1-x)E(c_B) \quad (2)$$

The interfacial reaction energy is described as the reaction energy of the pseudo-binary interfacial system minus the decomposition energies of components A and B:

$$\Delta E_{\text{D,mutual}}(c_A, c_B, x) = \min_{x \in [0,1]} \frac{1}{N} [E_{\text{eq, interface}}(xc_A + (1-x)c_B) - xE_{\text{D}}(c_A) - (1-x)E_{\text{D}}(c_B)] \quad (3)$$

where $E_{\text{eq, interface}}$ is the interfacial reaction energy of the pseudo-binary interfacial system; $E_{\text{D}}(c_A)$ and $E_{\text{D}}(c_B)$ are the decomposition energies of components A and B, respectively; E_{D} can be obtained by searching the chemical space of all elements of the components and constructing the phase diagram. N is the total number of atoms involved in the reaction. The molar percentage of the electronically conductive phase in the interfacial products is calculated and used as a descriptor for the electronic conductivity of the interphase layer after constructing the reaction phase equilibrium between A and B. The higher the molar percentage is, the stronger the electronic conductivity of the interface layer will be.

For interface reaction phase equilibrium: $x_A A + x_B B \rightarrow x_C C + x_D D + x_E E + \dots$. The volume change rate V_c induced by the interfacial reaction can be calculated by

$$V_c = \frac{(x_C v_C + x_D v_D + x_E v_E + \dots) - (x_A v_A + x_B v_B)}{x_A v_A + x_B v_B} \times 100\% \quad (4)$$

where x is the stoichiometric number of different components in the phase equilibrium; v is the volume of the reactant and product per unit molecule.

Results and discussion The properties of interphases formed between Li-metal and solid electrolyte play a crucial role in the performance of all-solid-state batteries (ASSBs). If the interphase layer exhibits a mixed electronic and ionic conductivity (MIEC), continuous electrolyte decomposition will occur during battery cycling, thus leading to an increased interfacial resistance and an accelerated performance degradation. The complex interfacial reactions generate various interphases, whose volumes may change relative to the reactants (lithium metal and electrolyte). If the interphase layer undergoes volume shrinkage, interfacial separation

may occur, exacerbating the inhomogeneous distribution of the interfacial electric field and current. It promotes lithium dendrite nucleation and growth at the interface. The calculation results indicate that the CPP of the interphase layer between halide electrolytes and Li-metal exceeds 9%, leading to the formation of MIEC, which can accelerate electrolyte decomposition during cycling. In addition, the volume shrinkage of interfacial interphase layer ($V_c < -17.4\%$) can also further intensify interfacial separation and dendrite growth. Therefore, optimizing electrolyte composition to reduce interfacial reactivity as well as minimizing CPP and V_c are critical for improving ASSB performance. Based on these interfacial reaction characteristics, selecting coating materials that effectively suppress interfacial reactivity, form a passivating interphase, and exhibit minimal volume changes can significantly enhance the interfacial stability between the Li-metal anode and the electrolyte.

Conclusions Halide electrolytes exhibited an intrinsic thermodynamic instability with Li-metal, originating from the reduction of metal cations in the electrolyte into metallic and alloy phases, with a CPP ranging from 9% to 20%. The presence of these electronically conductive phases rendered the interphases layer a MEIC, leading to continuous reduction of the electrolyte during battery cycling. Also, the interfacial reaction between Li-metal and Li-MF ($M = \text{Zr, Nb, Al, Ga, In, Ge, Sn}$) resulted in interphase layer that underwent volume contraction, with a volume change rate ranging from -36.2% to -17.4% . This could lead to interface separation and the formation of local voids at the interface, which was experimentally confirmed. These phenomena significantly impacted Li-metal deposition and dendrite growth, further deteriorating the performance of Li-metal ASSBs. Based on the interfacial reaction characteristics between Li-metal and halide electrolytes ($V_c < -17.4\%$, $\text{CPP} > 9\%$), high-throughput screening was performed to identify materials that could effectively passivate the interface and mitigate reaction-induced volume changes, thereby enhancing the performance of ASSBs. The screening identified binary materials like Li_3N and Li_3P , along with the ternary material Li_3NS . These materials were validated to enhance the stability of the Li-metal/electrolyte interface, confirming the scientific validity and effectiveness of the screening criteria.

Keywords lithium metal; all-solid-state-battery; halide electrolyte; density functional theory; interfacial reaction