Hans 汉斯

稳定锂金属阳极的研究进展

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摘　要

锂金属电池由于具有高的理论比容量(3860 mAh·g⁻¹)，被认为是下一代高能量密度存储设备的最佳选择之一。然而，锂枝晶生长导致固态电解质界面层不稳定，以及锂金属阳极在循环过程中发生的体积膨胀，由此带来了严重的安全风险和循环性差等问题，阻碍了锂金属电池的进一步商业化应用。通过对锂的不均匀沉积的生长机制进行研究，许多研究者们提出了各式各样的方案，比如设计电解液添加剂、开发固态电解质和设计三维集流体等，在这些方面取得了显著进展。最后，对这些方案的不足和优化进行了讨论。

关键词

Research Progress of Stable Lithium Metal Anodes

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Abstract

Lithium metal batteries are considered to be one of the best choices for next-generation high-energy density storage devices due to their extremely high theoretical specific capacity (3860 mAh·g⁻¹). However, dendrite growth of lithium leads to instability of solid electrolyte interfacial layer and volume expansion of lithium during cycling. As a result, serious safety risks and poor circularity have been brought, which to a large extent hinder the further commercial application of lithium metal batteries. Through the study of the growth mechanism of uneven deposition of lithium, many researchers have proposed various schemes. For example, significant progress has been made in the design of electrolyte additives, the development of solid electrolytes and the design of 3D current collectors, etc. Finally, the shortcomings and optimization of these schemes are discussed.

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Keywords

Lithium Metal Anodes, Lithium Dendrites, Electrolyte Additives, Solid State Electrolyte, 3D Current Collectors

1. 引言

煤炭和石油等化石燃料的过度使用让地球环境遭到了严重破坏[1]，迫使人们去开发可替代的、对环境友好的、可持续的新能源，比如风能、水能和太阳能[2]。为了充分利用这些可再生能源，需要设计高效、经济的储能系统[3] [4] [5] [6] [7]。可充电电池可以高效地储存和释放能量，被认为是有效的解决方法[8]。其中，锂离子电池因其可再生性、环境友好性和高效益，被认为是最有潜力的可充电电池，用于满足当前的能源需求[9] [10]。锂离子电池的成功商业化加速了便携式电子产品、电动汽车和智能电网的快速工业化[11] [12] [13]。然而，随着电化学储能系统的迅猛发展，锂离子电池的低能量输出与高能量密度电池系统的需求不匹配[14] [15]，迫切需要开发具有高能量密度的电池系统[16] [17]。

在众多阳极材料中，锂金属阳极因具有超高的理论比容量(3860 mAh·g⁻¹)以及超低的氧化还原电位(−3.04 V vs.标准氢电极)，被认为是下一代可充电电池的优良选择[18] [19] [20] [21]，用来取代石墨来提高电池的能量密度。迄今为止，根据阴极的不同，锂金属电池可以分为三类：插层类阴极锂金属电池、锂–硫电池和锂–空气电池[22]。这些锂金属电池表现出较高的能量密度，容量优于传统的锂离子电池[23] [24] [25] [26] [27]。
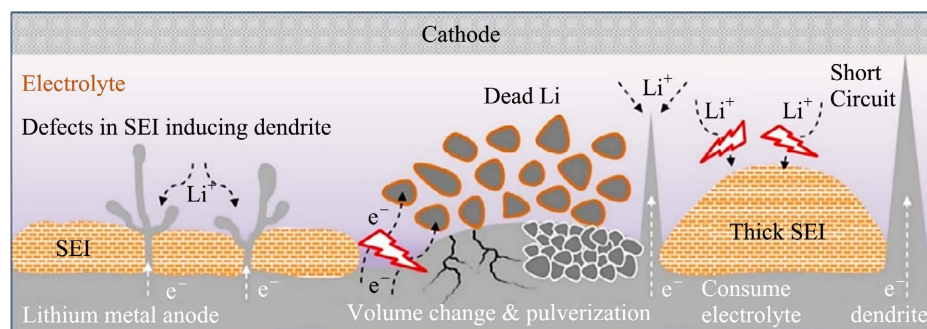

Figure 1. The challenge of lithium metal anode [28]
图 1. 锂金属阳极的挑战[28]

尽管锂金属电池有许多优势，但锂枝晶问题极大地限制了其发展。当锂金属阳极与电解液接触时，在锂金属表面形成了固态电解质界面层(SEI) [28]，该 SEI 层具有电子绝缘性和离子导电性，可以阻止锂金属和电解液进一步的不可逆反应，以避免活性物质的损失。SEI 层有利于离子的可逆运输，但在后续镀锂/剥锂的过程中，锂阳极由于无限体积膨胀和收缩时导致 SEI 层破裂，加剧锂对电解液的消耗、产生"死锂"和表面粉化(图 1)。同时，开裂的 SEI 层会暴露出许多缺陷，进而加速锂原子在缺陷上沉积，形成锂枝晶(图 1)。因此，锂枝晶、"死锂"、SEI 层反复破裂以及厚的 SEI 层会极大地降低锂金属电池的电化学性能，如库伦效率低、循环寿命短、存在安全隐患等。为了克服这些挑战，人们提出了一些重要

的策略。因此，本文综述了其中一些策略，如设计电解液添加剂[29] [30] [31]、开发固态电解质[32] [33] [34]、设计并使用三维集流体[35] [36] [37] [38]，通过抑制锂枝晶的形核和生长，显著提高了锂金属阳极的电化学性能。

2. 锂枝晶生长机理

锂金属在充放电过程中是反复电镀/剥离的，在每个循环中都有锂成核过程。在锂沉积过程中，初始成核位置对后续的锂沉积行为起着重要作用。锂倾向于以枝晶的形式沉积在阳极上。当枝晶一直生长会刺穿隔膜，正负极通过枝晶连接，将会迅速短路并可能造成火灾和爆炸[39]。有研究揭示了锂枝晶的生长过程(图 2(a)~(c))：锂沉积不均匀，且不均匀程度随循环增加，在 SEI 层下产生较大应力，压力释放时 SEI 层被刺穿。锂在裂缝中生长，形成初始枝晶，并逐渐生长，直到电池发生短路[40]。如图 2(d)所示，枝晶根部易断裂，断裂部分形成了"死锂"；而新暴露的锂表面迅速与电解液反应，形成电子绝缘性的 SEI 层。断裂的锂失去了与阳极的电子连接，不再参与后续的反应，所以称为"死锂"。此外，堆积的"死锂"使阳极厚度增加(图 2(e))。枝晶的形成是锂沉积不均匀的结果，其成因既有热力学因素，也有动力学因素。
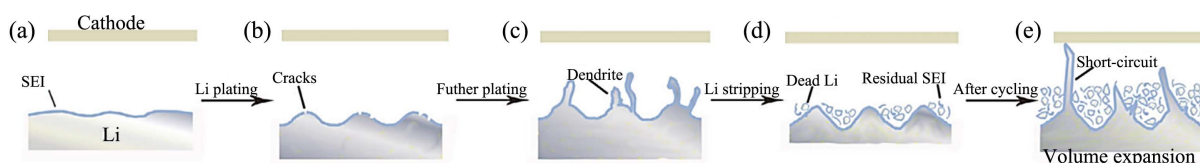

Figure 2. Schematic diagram of the failure process of lithium anode [40]
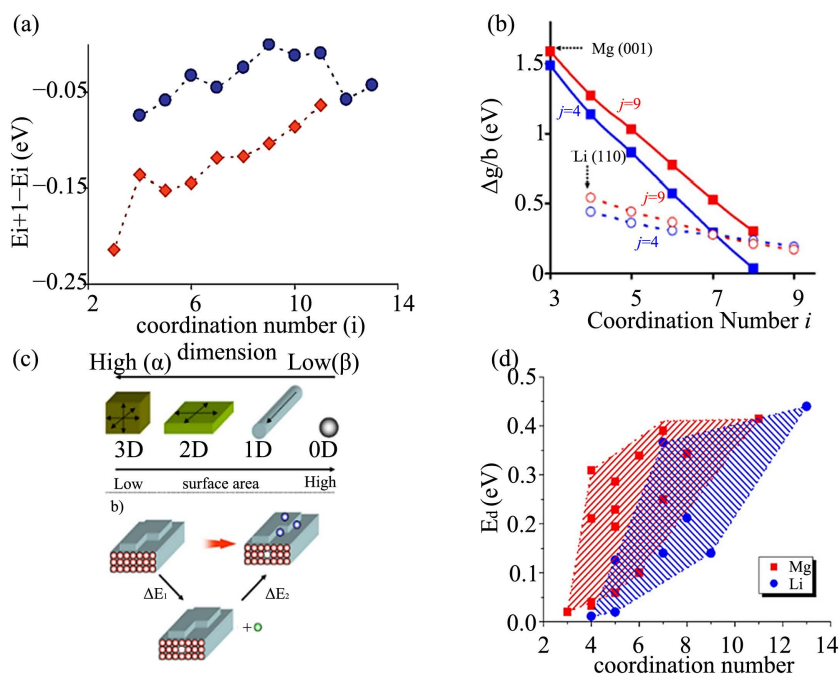**图 2.** 锂阳极失效过程示意图[40]

Figure 3. (a) Contribution of adsorbed atoms to bond strength in an embedded atom model for magnesium (red) and lithium (blue); (b) Free energy changes of adsorbed atom (i) and surface atom (j) with different coordination numbers; (c) Schematic diagram of high-dimensional phase and low-dimensional phase; (d) Relationship between the surface migration barrier of magnesium and lithium and the coordination number of migrating atoms [44]
图 3. (a) 在镁(红色)和锂(蓝色)的嵌入原子模型中，吸附原子对键强的贡献；(b) 吸附原子(i)和表面原子(j)在不同配位数时的自由能变化；(c) 高维相和低维相示意图；(d) 镁和锂的表面迁移势垒和迁移原子的配位数的关系[44]

在电化学沉积过程中，热力学和动力学都会影响沉积物的形态。从热力学角度看，锂金属易于在电极表面生长出树突状形貌，而镁金属则更容易在电极表面生长出无树突状形貌[41] [42] [43]。DFT 计算预测的 Mg-Mg 键的结合能更高(图 3(a))，镁沉积时形成高维相和低维相之间的自由能差值比锂更高(图 3(b)) [44]。这表明，镁沉积比锂沉积更容易形成高维结构(如三维或二维结构，而不是一维的晶须) (图 3(c))。另一方面，沉积的镁和锂的迁移动力学差异不显著。如图 3(d)中阴影区域所示，镁的迁移势垒与锂的迁移势垒在一定的范围内相同。这个结果表明，镁的迁移动力学与锂的迁移动力学接近，即在相同的电化学条件下，迁移动力学对镁和锂的影响相似。镁的沉积更容易受其热力学性质的影响，而动力学则改变了生长方向的倾向。因此，锂金属阳极具有较低的表面能和较高的迁移能是锂枝晶生长的热力学原因。

3. 抑制锂枝晶的方法

3.1. 设计电解液添加剂

为了提高锂金属阳极的性能，人们在过去的几十年里提出了许多策略。其中，在电解液体系中引入功能性添加剂，具有成本效益高、操作简单等优点，被认为是最有前途的应用策略之一。在充放电过程中，电解质添加剂可以通过多种机制抑制锂枝晶的生长，并控制锂离子沉积的形态。然而，电解液添加剂想要得到广泛的应用还很遥远：1) 关于锂枝晶生长、锂沉积行为和 SEI 形成的机制已经被提出，但这些机制缺乏通用性，甚至相互矛盾[45]。此外，功能添加剂对电池性能的影响机理还有待研究。2) 现有的表征技术难以揭示相应的机理[29]。3) 尽管大量的研究都是针对牺牲型添加剂，但是牺牲型添加剂在长循环过程中会不断被消耗，对电池性能的有益作用难以持续[46]。大多数研究集中在单一添加剂，不同添加剂之间的协同效应或添加剂与其他策略(如集流体的设计)之间的协同效应仍需要深入研究。目前，许多 SEI 形成添加剂都致力于通过改变组成成分来形成理想的 SEI 层。根据 SEI 层的主要成分，可将 SEI 成膜添加剂分为形成无机化合物 SEI 层添加剂和形成有机化合物 SEI 层添加剂。

3.1.1. 形成无机化合物 SEI 层添加剂
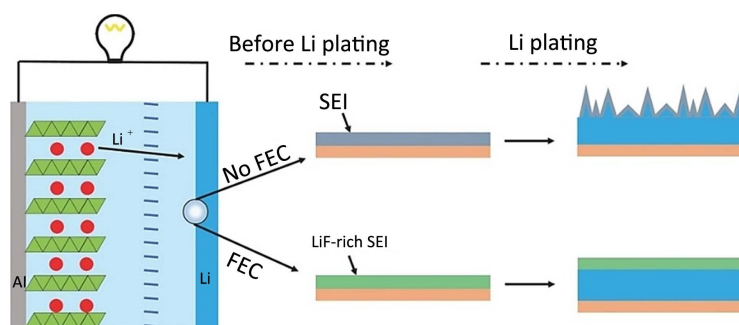
Figure 4. Fluoroethylene Carbonate (FEC) [51]
图 4. 氟代碳酸乙烯酯[51]

一般来说，SEI 的力学性能和离子导电性主要取决于 SEI 层中无机组分的含量。同时，SEI 内部的有机物对 SEI 层的柔韧性和弹性起着至关重要的作用。已经有研究证实，氟化锂(LiF)是 SEI 中的有益成分，可显著增强锂离子在 SEI 表面的扩散速率，并且可以诱导锂离子均匀沉积[47] [48]。氟代碳酸乙烯酯(FEC)是插层锂金属电池中最著名的电解液添加剂之一，它可以在锂阳极上生成含氟化锂的稳定而富有弹性的SEI，从而显著提高电池性能[49] [50]。目前，人们对 FEC 的作用机理进行了广泛的研究。在典型的 $LiPF_6$-EC/DEC 电解液中，通过计算研究了加入 FEC 诱导 SEI 形成的过程。与溶剂分子(EC: −0.38 eV, DEC:0 eV)相比，FEC 添加剂的 LUMO 水平最低(−0.87 eV)，C-F 键在 310 fs 左右断裂，表明在沉锂过程

中 FEC 先进行反应并形成 LiF-SEI 层(图 4) [51]。基于扩散‒控制瞬时过程的 Li-SEI 模型表明，添加 FEC 可以显著降低电解质分解速率常数，其幅度随着过电位和 SEI 断裂程度的增加而增大[52]。此外，FEC 可以显著降低 SEI 的厚度，特别是有机部分的厚度，说明 FEC 的存在显著阻止了溶剂分解[53]。FEC 还可能对锂盐降解具有抑制作用(如 $LiPF_6$) [54]。除 FEC 添加剂外，各种研究表明，电解质中的含氟成分也可能有助于形成稳定而致密的 LiF-SEI 层[50]。此外，LiF 还可以直接用作电解质添加剂，由于界面迁移率的增强，可以大大提高锂沉积的稳定性[55]。但是 LiF 会导致离子导电性差($\sim 10^{-31}$ S·cm^{-1}) [56]。

硝酸锂($LiNO_3$)也是一种典型的添加剂，在锂硫电池中具有显著的应用[57]。人们普遍认为，$LiNO_3$ 通过与锂聚硫化物的协同作用在稳定的锂金属阳极中起着重要作用[58] [59]。有证据表明，硝酸盐离子可以作为氧化剂与锂聚硫化物和金属锂反应，形成富含 Li_xNO_y 和多硫化物氧化产物(如 Li_2SO_4，$Li_2S_2O_3$)的双层 SEI (图 5(a)) [59]。加入 $LiNO_3$ 后，面向隔膜的 SEI 层由 Li_xNO_y 团簇组成，Li_xNO_y 的存在可以作为"网"通过偶极‒偶极相互作用(即锂键)捕获锂聚硫化物[59]。此外，在 2M LiFSI-DME 电解液中，$LiNO_3$ 的存在被证明有利于 FSI$^-$ 的完全分解和致密 SEI 的生成。分子动力学模拟中 Li-O 键(1.7 A)和 Li-N 键(2.9 A)新峰的出现，证明了 NO$_3^-$ 参与了 Li$^+$ 的溶剂化鞘。$LiNO_3$ 的存在可以显着增强锂离子和溶剂分子之间的离子‒偶极相互作用，从而使 FSI$^-$离子迁移率降低(图 5(b)) [60]。
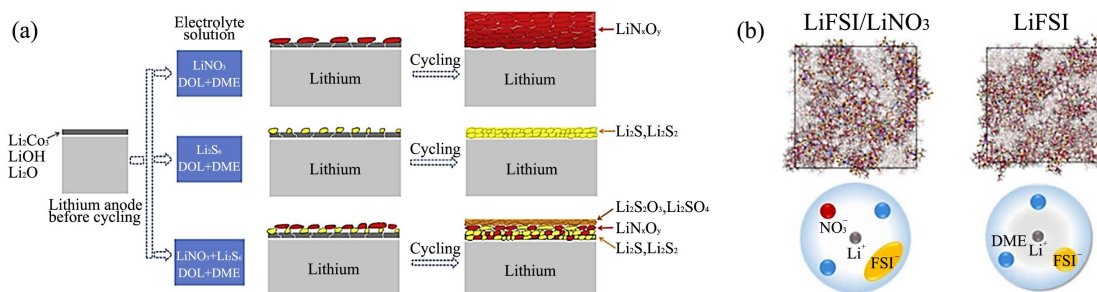

Figure 5. (a) Schematic illustration of the synergy between $LiNO_3$ and lithium polysulfides [59]; (b) Schematic illustration of the effect of $LiNO_3$ on alerting Li$^+$ solvation sheath. Top panel: Snapshots from MD simulation of 2 M LiFSI-DME electrolytes with and without $LiNO_3$ addition, respectively. Bottom panel: Schematic illustration of the Li$^+$ salvation sheath in corresponding electrolyte, respectively [60]
图 5. (a) $LiNO_3$ 与锂聚硫化物的协同作用示意图[59]；(b) $LiNO_3$ 对 Li$^+$溶剂化鞘的协同作用示意图。上部分：在 2 M LiFSI-DME 电解质中是否添加 $LiNO_3$ 的分子动力学模拟图。下部分：对应电解质中 Li$^+$溶剂化鞘[60]

3.1.2. 形成有机化合物 SEI 层添加剂

SEI 层中的常规有机化合物表现出不稳定的物理化学性质，如低杨氏模量(例如 ROCO$_2$Li/ROLi < 1Gpa)以及在电解质中的较高溶解度，说明这并不能有效地阻止锂进一步发生反应[61] [62]。目前，关于 SEI 中新型有机化合物的作用的报导越来越多，它们具有高弹性和柔韧性，可以承受锂阳极的体积变化[63]。将碘化锂作为电解质添加剂，可以引发乙二醇二甲醚(DME)聚合，并进一步在锂金属阳极表面形成富含低聚物的 SEI [31] [64]。根据量子化学计算结果，首先生成 I 自由基，然后与 DME 反应形成 DME (-H)·自由基。最后，通过 DME (-H)·自由基聚合得到梳形支化聚醚(图 6(a)) [64]。金属离子(如 Al^{3+}) [65] 和含硅有机化合物[66]也可作为 DOL 聚合的理想引发剂。除了诱导溶剂聚合外，还可以引入一系列有机分子作为单体生成有弹性的 SEI [67] [68] [69]。含硫聚合物作为高性能 SEI 形成添加剂也被广泛应用，以提高锂离子电池的性能 [63] [70]；例如，硫和三烯丙胺共聚物(PST)与锂金属阳极接触后电化学分解为锂有机硫化物(RS$_6$Li$_6$)、锂有机多硫化物(RS$_x$Li$_6$)、Li$_2$S$_x$ 和 Li$_2$S/Li$_2$S$_2$ (图 6(b))。有机物 RS$_6$Li$_6$ 和 RS$_x$Li$_6$ 在无机相 Li$_2$S/Li$_2$S$_2$ 中具有良好的弹性和柔软性，增强了 SEI 的稳定性。在电流密度为 2 mA·cm^{-2}，容量为 1 mAh·cm^{-2} 的条件下，400 个循环的平均库仑效率可达 99% [63]。
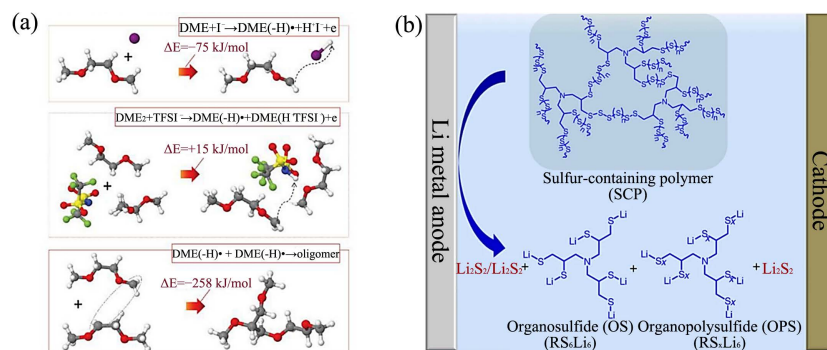
Figure 6. (a) Schematic depicting the catalysis of I⁻ for DME polymerization [64]; (b) Schematic depicting the decomposition of PST to sulfides and polysulfides [63]

图 6. (a) I⁻引发 DME 聚合的示意图[64]；(b) PST 分解成硫化物和多硫化物的示意图[63]

3.2. 使用固态电解质

锂枝晶可以穿透多孔隔膜与阴极接触，引起锂金属电池内部短路。解决这一难题的直接方法是用高机械强度和致密的固态电解质取代多孔隔膜和液态电解质。Monroe 指出，具有高剪切模量(> 6.8 GPa)的固态电解质有助于抑制锂枝晶[71]，提高电池长期循环的安全性。但进一步的研究表明，固态电解质的其他性质，如 Li⁺电导率，也会影响抑制锂枝晶的效果[72]。此外，使用固态电解质，避免了商用液态电解质的缺点，如泄漏和易燃性。固态电解质的设计应符合以下特点：1) 环境温度下 Li⁺电导率高；2) 具有合理的机械强度以抑制枝晶的生长；3) 与两电极接口处兼容性好；4) 具有良好的化学和电化学稳定性。目前的研究出现了多种类型的固态电解质，包括无机固态电解质、聚合物固态电解质和无机/聚合物混合固态电解质。

无机固态电解质是 Li⁺的良好导体(> 10^{-3} S·cm⁻¹) [73]，具有较高的弹性模量。一些氧化物[74] [75] [76]和硫化物[77] [78]可作为锂金属电池的电解质。然而，由于无机固态电解质本身的脆性、刚性以及无机固态电解质与锂的界面相容性差，所以在实际应用中面临着严峻的挑战。在固态电解质和锂之间建立夹层可以解决上述问题[79]。由高氯酸锂、聚环氧乙烷和石榴石型材料组成的复合膜(图 7(a))被用作石榴石无机电解质和金属锂之间的中间层[80]。聚环氧乙烷的柔韧性改善了石榴石型材料与锂阳极的接触，同时锂盐的存在增强了锂离子在界面处的运输。基于复合膜的对称电池在界面处的电荷转移电阻(≈ 413 Ω·cm²)是无复合膜对称电池(1638 Ω·cm²，图 7(b))的四分之一，在 0.1 mA·cm⁻² 电流密度下能稳定循环(图 7(c))，而只有石榴石的固态电解质制备的电池在仅工作 32 小时后显示出较大的极化(> 2000 mV)。然而这些研究中的界面电阻仍然太高，因此应用在电池上的电流密度相对较低。
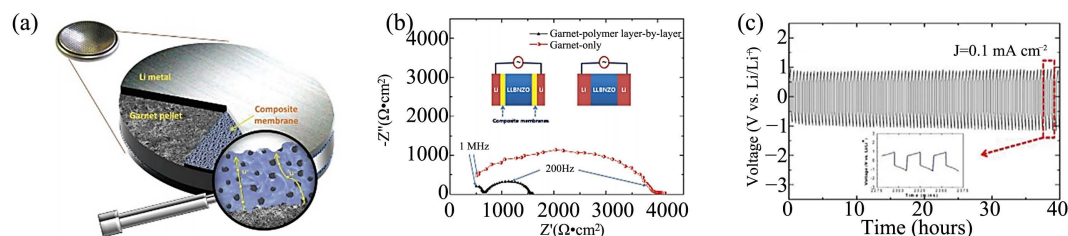
Figure 7. (a) Schematic illustration of the layer-by-layer design where the polymer membrane acts as an adhesive layer between lithium anode and garnet electrolyte; (b) Comparison of Nyquist plots for symmetric batteries with garnet-polymer layer-by-layer and garnet-only structures, respectively; (c) Electrochemical lithium deposition/dissolution cyclic performance of the garnet-polymer layer-by-layer symmetrical batteries at 0.1 mA·cm⁻² [80]

图 7. (a) 将石榴石材料夹在复合膜和锂阳极之间的示意图；(b) 分别用石榴石复合膜和石榴石材料制备的对称电池 Nyquist 图比较；(c) 在 0.1 mA·cm⁻² 下，石榴石复合膜对称电池的锂电镀/剥离循环性能[80]

聚合物固态电解质由混合的锂盐和聚合物部分组成[78]。由于其柔软的结构和良好的弹性，聚合物固态电解质与锂金属阳极具有良好的界面接触，而且制造简便、成本低，有利于大规模生产。但是聚合物固态电解质存在离子导电性和机械强度不如无机固态电解质的问题[81]。为了应对这些挑战，Zhang 等[82]研究了几种聚偏氟乙烯(PVDF)基固态电解质在锂金属电池中的电化学性能。对 PVDF-LiX (X = FSI⁻，TFSI⁻和ClO₄⁻)电解质进行了测试和分析，比较了它们的电化学行为。其中，PVDF-LiFSI 的综合性能最好，在室温下具有 1.18×10^{-4} S·cm⁻¹ 的高锂离子电导率，其稳定性远远优于其他两种聚合物电解质(图 8(a))。PVDF-LiFSI 电解质与锂阳极的界面上形成一个界面层，抑制了锂枝晶的生长。Zhou 等[83]提出了一种用于锂金属电池的双层聚合物固态电解质(图 8(b))，以抑制锂枝晶生长并扩大聚合物固态电解质的氧化还原电位窗口。如图所示，低电压的聚合物电解质与锂金属阳极接触，可实现无枝晶沉积，高电压聚合物电解质与阴极接触，可从中获取锂离子，避免电解质氧化。选用 PEO 作为低压聚合物，选用聚(N‐甲基‐丙二酰胺) (PMA) (图 8(c))作为高压聚合物。由于有效地抑制了锂枝晶的生长，双层聚合物固态电解质表现出非常稳定的循环性能，在 65℃时的锂离子电导率为 2.05×10^{-4} S·cm⁻¹。

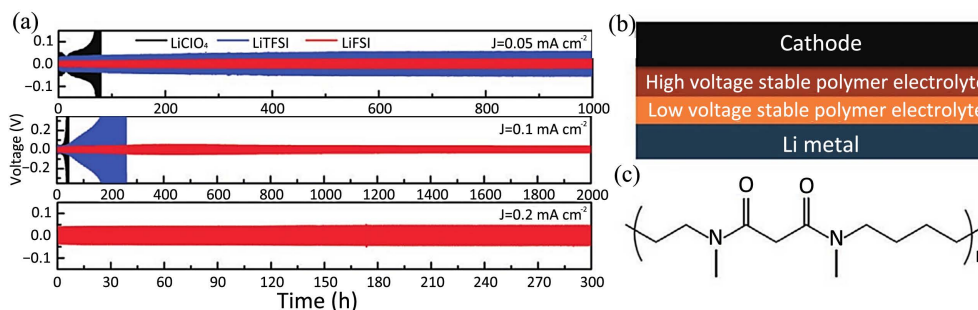**Figure 8.** (a) Galvanostatic cycling profiles of the cells with PVDF-LiX at current rates of 0.05, 0.1, and 0.2 mA·cm⁻² [82]; (b) Structure diagram of Double-Layer Polymer Solid Electrolyte (DLPSE) [83]; (c) Molecular structure of PMA [83]
图 8. (a) PVDF-LiX 在 0.05、0.1 和 0.2 mA·cm⁻² 电流密度下的恒流循环曲线[82]；(b) 双层聚合物固体电解质示意图[83]；(c) PMA 的分子结构[83]
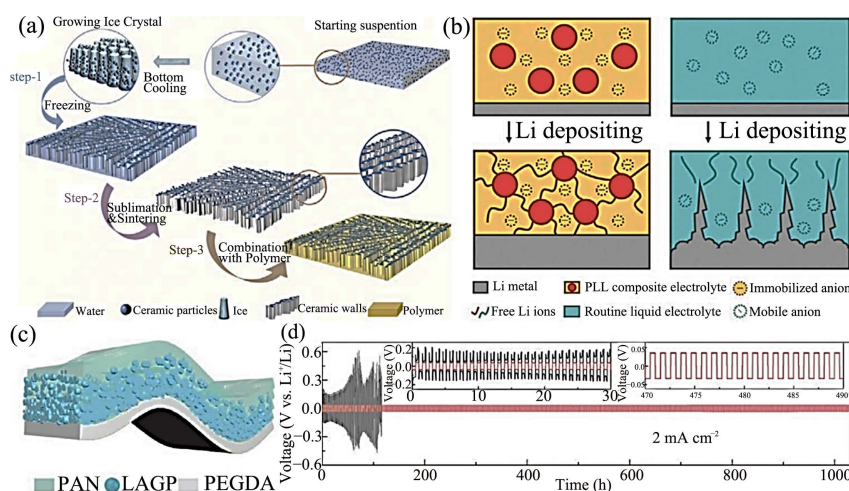
Figure 9. (a) Fabrication of vertical aligned LAGP/PEO composite [84]; (b) Comparison of Li dendrite inhibition of PLL electrolyte and normal liquid electrolyte [85]; (c) Structure diagram of HMSE [86]; (d) Voltage profiles of the Li/HMSE/Li and Li/liquid electrolyte/Li symmetric batteries at a current density of 2 mA·cm⁻². The red curve represents the performance for HMSE and the black curve represents the performance for liquid electrolyte [86]
图 9. (a) 垂直排列 LAGP/PEO 复合材料的制备[84]；(b) PLL 电解质与正常液态电解质对锂枝晶抑制作用的比较[85]；(c) HMSE 结构图[86]；(d) Li/HMSE/Li 和 Li/液态电解质/Li 对称电池在电流密度为 2 mA·cm⁻²时的电压分布。红色曲线表示 HMSE 的性能，黑色曲线表示液态电解质的性能[86]

为了充分利用无机和有机两种材料的优势，设计和合成了一种新型的聚合物电解质和无机固态电解质复合结构的全固态锂金属电池。Wang 等[84]用无机纳米颗粒和聚合物合成了固态电解质。用 $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ (LAGP)无机纳米颗粒制备了无机垂直排列模板，然后将其与乙二醇二甲醚、聚环氧乙烷和 LiTFSI 反应(图 9(a))。LAGP 膜通过提供连续的通道促进了锂离子的传输，PEO 基质使电解质变得柔韧，改善了界面接触。该复合材料在室温下的离子导电性为 1.67×10^{-4} S·cm^{-1}。Zhao 等[85]制备了另一种由无机–聚合物组成的复合电解质。该组合物由 $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$ (LLZTO)、聚环氧乙烷和 LiTFSI (简称 PLL)组成。PLL 可以束缚 TFSI$^-$，实现均匀的离子分布，从而减缓锂枝晶生长。在 25°C 下，该复合固态电解质的离子电导率为 1.12×10^{-5} S·cm^{-1} (图 9(b))。Duan 等[86]提出了一种非均相多层固体电解质(HMSE)，将电化学窗口扩大到 0~5 V，以克服界面不稳定问题。在 HMSE 中，聚丙烯腈(PAN)与阴极连接，因为 PAN 抗氧化。聚乙二醇二丙烯酸酯与锂金属阳极接触，中间层为 PAN@$Li_{1.4}Al_{0.4}Ge_{1.6}(PO_4)_3$ (LAGP, 80 wt%)复合材料。这种复合固态电解质的高机械强度阻止了锂枝晶的生长，其离子电导率为 3.7×10^{-4} S·cm^{-1} (图 9(c))，这使Li/HMSE/Li 对称电池在电流密度为 2 mA·cm^{-2} 时具有超过 1000 h 的良好的循环稳定性(图 9(d))。

3.3. 设计和使用三维集流体

3.3.1. 金属纳米材料

在锂金属电池中，集流体是在活性材料和外部电路之间传递电子的关键组件。但传统的抛光铜集流体在锂金属阳极上使用时，存在着锂体积变化大、锂枝晶生长不受控制、SEI 不稳定等问题。三维集流体可以降低局部电流密度以及拥有足够的内部空间储存锂金属，实现了无枝晶和稳定的锂金属阳极。可采用多种材料构建三维多孔集流体，其最终的电化学性能在很大程度上取决于所使用的材料和相应的三维结构。
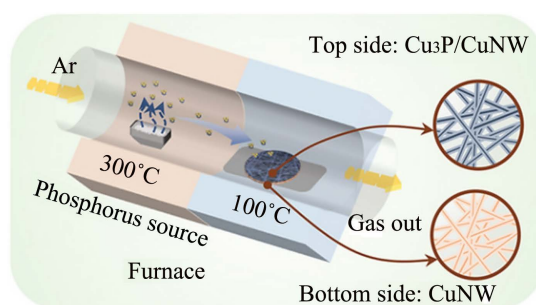
Figure 10. Schematic diagram of the phosphidation reaction of Cu nanowires [87]
图 10. 铜纳米线的磷化反应示意图[87]

金属纳米材料进一步增加了锂金属阳极的表面积，从而显著降低了局域电流密度，有效抑制了锂枝晶的形成。为获得高性能锂金属阳极，采用了两种典型的基于金属纳米材料的集流体中构建方法，包括构建三维框架和进行表面修饰以形成更多亲锂位点。金属骨架具有高导电性和大的比表面积，是制备高性能锂金属阳极的新型集流体的重要候选材料。比如 Kang 等[87]通过化学气相沉积制备了含 Cu_3P 粒子的 3D 铜纳米线网络(图 10)。利用亲锂性和离子导电性实现了锂的均匀沉积。结果表明，基于铜纳米线网络的集流体在 1 mA·cm^{-2}、1 mAh·cm^{-2} 的 150 个循环中，具有 97.3%的高 CE。一般来说，大部分用作集流体的材料，如铜[88]-[93]、镍[94] [95] [96]、钛[97]、碳[98] [99]和石墨烯[100] [101]等都是疏锂性的或对锂金属的润湿性较低，锂的成核势垒较高，容易由于锂与各种集流体之间存在较大的晶格不匹配而引起锂的不均匀沉积。即使在已有的锂金属上沉积了额外的锂，初始表面形貌仍然决定了后续的锂沉积行为。因此，利用不同的金属纳米材料对集流体表面进行亲锂改性是必要的。

通过涂覆因纳米颗粒层，Quan 等[88]通过化学电镀将铜集流体的表面改为亲锂性(图 11(a))。利用银

纳米粒子与锂的合金化反应，制备的锂金属阳极表现出均匀的锂沉积行为，这是由于改性后的铜集流体的锂成核过电位低于裸铜集流体的锂成核过电位(图 11(b))。结果表明，锂金属阳极在 1 mA·cm^{-2}、1 mAh·cm^{-2} 的条件条件下表现出了 360 小时的稳定循环(图 11(c))。除了银纳米颗粒，Hong 等[102]还使用银纳米晶体修饰二氧化钛纳米管。二氧化钛纳米管所具有的亲锂性促进了锂金属在其表面的均匀沉积。在容量为 2 mAh·cm^{-2} 时经过 300 次循环后，得到的锂金属阳极的库仑效率高达 99.4%。利用高导电性、大表面积的金属纳米材料构建高性能的三维集流体可以有效抑制锂枝晶，但材料成本高、可扩展性差、亲锂性差等问题，在进一步的商业化应用中需要得到充分解决。
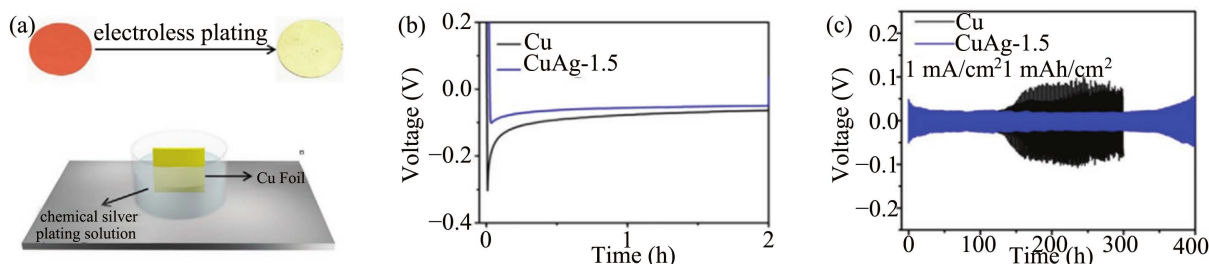
Figure 11. (a) Schematic of the Ag nanoparticle-decorated Cu foil; (b) Voltage curves of Li nucleation on the bare Cu foil and Ag nanoparticle-decorated Cu foil; (c) Cycling stability of the Li metal anodes based on the bare Cu foil and Ag nano-particle-decorated Cu foil at 1 mA·cm^{-2} at 1 mAh·cm^{-2} [88]
图 11. (a) 银纳米粒子修饰铜箔的原理图；(b) 裸铜箔和镀银铜箔上锂成核的电压曲线；(c) 基于裸铜箔和镀银铜箔的锂金属阳极在 1 mA·cm^{-2}、1 mAh·cm^{-2} 下的循环稳定性[88]

3.3.2. 碳材料

碳材料因其比表面积大、质量轻、导电性好等优点被广泛应用于锂金属电池中。碳纳米管(CNTs)用作集流体时，由于具有三维多孔特性，可以提供均匀的电场。Wang 等[103]使用碳纳米管海绵作为集流体，实现了无枝晶锂金属阳极，由于结构稳定，提高了 CE 和循环稳定性。碳纳米管的大表面积降低了集流体的局部电流密度，从而使锂在其表面沉积更加均匀。即使在 10 mAh·cm^{-2} 的高容量下，三维碳纳米管仍能以无枝晶的方式进行锂沉积。

三维碳纳米纤维(CNFs)作为铜集流器上方的修饰材料，可以有效降低局部电流密度，从而诱导均匀的锂沉积[104]。此外，多孔结构可以缓解锂金属在循环过程中的体积膨胀，维持锂金属阳极的稳定性。在 2 mA·cm^{-2}、1 mAh·cm^{-2} 条件下，300 次循环可达到 99.9% 的高库仑效率。Cheng 等[105]通过在平面铜箔上构建垂直排列的 CNF 阵列，利用高导电性和丰富的亲锂性石墨边缘位点，得到一个三维多孔主体，以诱导均匀的镀锂/剥锂过程。制备的阳极的对称电池在 1 mA·cm^{-2}、2 mAh·cm^{-2} 条件下显示出 35 mV 的低电压，稳定循环超过 500 h。
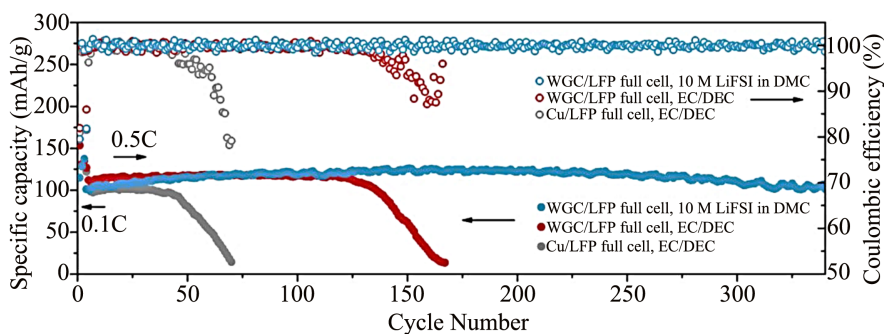
Figure 12. Full battery cycle stability based on graphene cage and bare copper [106]
图 12. 基于石墨烯笼和裸铜的全电池循环稳定性[106]

空心碳具有独特的结构，具有较大的内部空间，可以缓解电池循环过程中锂的巨大体积变化。Wang 等[106]以商用镍粉为生长模板，制备了含有金纳米颗粒的褶皱石墨烯笼。由于锂金属在金基底上的成核势垒较低，制备的锂金属阳极在石墨烯笼内优先沉积。在电流密度为 0.5 mA·cm^{-2}，容量为 1~10 mAh·cm^{-2} 的条件下，基于石墨烯笼的锂金属阳极具有高达 98% 的高库仑效率。基于石墨烯笼的锂金属阳极和 LiFePO$_4$ 阴极的全电池显示出，在 0.5 C 下超过 120 次循环时 120 mAh·g^{-1} 的高比容量(图 12)。

3.3.3. 合金

银、锌和金等金属材料在锂金属电池中使用时更倾向于与锂金属形成合金。这一特性促进了合金实现无枝晶锂金属阳极策略的发展。该合金化过程可在电池循环过程中诱导锂均匀沉积，从而在集流体上形成更光滑的锂金属层。市售铜箔是制备多孔 CuZn 合金以获得高性能锂金属阳极的重要原料。由于价格低廉，该合金具有可扩展和批量生产的优势。通过便捷的热灌注方法，Deng 等[107]以多孔 CuZn 合金为基底，制备了无枝晶锂金属阳极(图 13(a))。内部丰富的锌亲锂位点可诱导均匀的锂沉积。当与 LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ (NCM811)阴极配对时，使用 Li/CuZn 复合电极的整个电池在 1 C 下表现出超过 500 个循环的优异性能(图 13(b))。同时，在 1 C 时，放电容量也稳定在 172 mAh·g^{-1} 左右(图 13(c))。
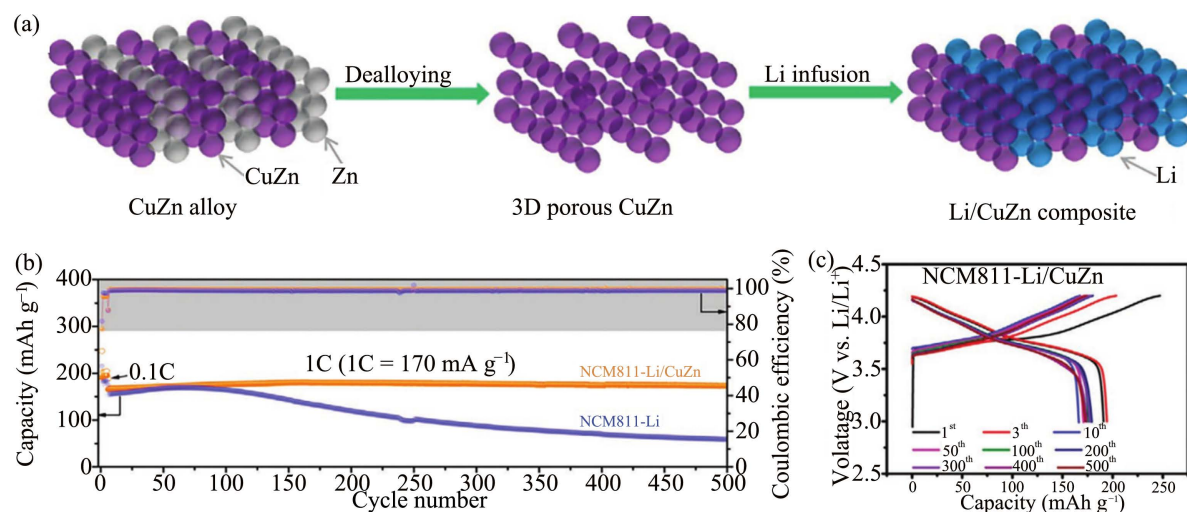
Figure 13. (a) Schematic of the fabrication process of Li/CuZn composite; (b) Cycling stability of the full cells based on the Li/CuZn and bare Lianodes at 1 C; (c) The corresponding galvanostatic discharge/charge profiles of the full cell based on the Li/CuZn anode [107]

图 13. (a) Li/CuZn 复合阳极的制备过程示意图；(b) Li/CuZn 和裸锂阳极的全电池在 1 C 的循环稳定性；(c) 基于 Li/CuZn 阳极的全电池相应的恒流放电/充电分布图[107]

4. 总结与展望

在过去的几十年里，科学家们一直在努力解决锂枝晶的问题。在过去的四十年中，锂枝晶的生长机理(如表面成核与扩散模型)被提出，基于这些机理提出了各种各样的稳定锂阳极的策略，并对与锂阳极相关的各个组成部分(集流体、SEI 层、电解质、隔膜)进行了更为深入的研究。尽管在解决锂枝晶生长、低库仑效率、体积变化大、循环稳定性差和安全性等问题上取得了巨大的进展，但该领域仍存在许多障碍，这限制了锂金属电池在短时间内实现商业化。因此，实现长期稳定循环、高安全无枝晶锂金属阳极是未来的发展方向。

通过对电解液进行修饰，在锂金属阳极上原位形成保护 SEI 是一种有效、且成本低的方法。应进一步发展包括添加剂、锂盐和溶剂在内的新型电解质成分，在初始循环过程中诱导形成致密、薄(10 nm~50

nm)、稳定、均匀和离子导电性好的锂金属阳极表面保护层。但是，不稳定的界面限制了电解液添加剂在循环过程中的作用。

在电解质方面，为了获得高性能的锂金属电池，需要在固态电解质上投入更多的研究。固态电解质在室温下的锂离子电导率仍远低于有机液体电解质，以及在固态锂金属的实际应用中，无机固态电解质的电子电导率也是关键问题，导致了无机固态电解质中锂枝晶的生长。因此，需要开发具有较高锂离子导电性和较低电子导电性的新型固态电解质。由于锂的氧化还原电位最低，由锂金属驱动的还原反应似乎是不可避免的，这增加了界面阻抗。在其他化学反应中，锂金属/固态电解质界面的物理接触是一个需要优先解决的问题。

三维多孔集流体通过降低局部电流密度和具有足够的内部空间储存锂金属，实现了锂金属阳极的无枝晶稳定。另一方面，由于体积变化大，锂阳极在镀/剥离过程中可能会粉碎，可以使用合适的锂宿主材料或改进的集流体来消除体积变化带来的副作用。但三维结构的宿主材料或集流体的比表面积过大，会导致副反应较多、电解液消耗较多，导致电池在运行过程中突然失效。因此，应寻找一个合适的锂的宿主材料或集流体的高孔隙率，否则也会降低锂金属阳极的体积能量密度。

总的来说，在所有碱金属负极中，锂金属是最有可能在商业应用中领先的。科学的快速发展为锂金属阳极的研究提供了多种技术，促进了锂金属电池的实际应用。随着锂金属阳极的发展，各种辅助体系不断向前发展，可能的应用场景也在不断变化。因此，各个领域都迫切需要对锂电镀/剥离行为和抑制锂枝晶生长的策略进行更科学的探索。通过对锂金属阳极进一步研究，可充电锂金属电池将具有广阔的应用前景。

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