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热/机械稳定的锂金属负极的制备方法

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摘　要

以金属锂化学为基础的可充电电池由于其具有超高容量和能量密度，有希望成为下一代的能源储存装置。然而，锂负极热耐受性较差、结构强度较低等原因，严重阻碍了高安全性和高能量密度的锂金属电池在当前和未来的广泛应用。在这篇综述中，我们从热稳定性和对外力的耐受性等方面严谨地讨论了稳固型金属锂负极制造的研究现状，总结了当前制造稳固型金属锂负极的方法，强调了稳固型锂负极制备过程对锂的能量密度产生的副作用。最后，我们提出了热稳定和机械稳定锂负极设计制造的未来趋势和挑战，及其在下一代电池中的广泛应用前景。

关键词

锂金属，热稳定性，机械稳定性

Fabrication Methods of Thermal/Mechanical-Stable Lithium Metal Anodes

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Abstract

Rechargeable batteries based on metallic lithium chemistry are promising for next-generation energy storage due to their ultrahigh capacity and energy densities. However, the poor thermal

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tolerance, and low structure strength of lithium anode seriously hinder the widespread adoption of high-security and energy-dense lithium metal batteries in today and the future. In this review, we critically discuss the current status of research on robust lithium metal anode processing from the perspectives of thermal stability, and the tolerance for external forces; summarize recent strategies to fabricate a robust lithium metal anode; emphasize the side effect on the energy density of lithium during the robust anode preparation process. Finally, we proposed the future trends and challenges of the design and fabrication of thermal/mechanical-stable lithium anode and prospects toward their broad application in next-generation batteries.

Keywords

Lithium Metal, Thermal Stability, Mechanical Stability

1. 引言

第四次工业革命的兴起依赖于一个可充电的世界。电池行业的进步将直接决定科技的发展方向[1] [2] [3]。在过去 30 年里，锂离子电池(LIBs)凭借着普遍性的大容量和高能量输出，成功地超越了多种二次电池技术(铅酸、镍镉、镍氢电池) [4] [5]。随着成本下降和技术发展，锂离子电池已经遍布世界的各个角落，不仅改变我们每一个人的生活，甚至重塑当今世界能源格局。今天，锂离子电池已经在手机和电脑等个人移动设备中得到广泛使用。此外，以锂离子电池为动力的电力发动机也正在取代汽车行业的内燃机[6] [7] [8]。到 2030 年，将有数十亿美元的投资用于锂离子电池的基础设施建造，预计锂离子电池的容量将增加到每年 1500 GWh (图 1(a)) [9]。美国能源部为先进的高性能牵引电池提出的成本和性能目标分别为 US \$100 kWh^{-1} 和 350 Wh·kg^{-1} [10]。然而，当前的锂离子电池已经达到其理论比能量密度的上限，无法满足未来对更高能量密度的需求(图 1(b)) [11] [12] [13]。基于金属锂化学的可充电电池，如锂硫电池和锂空气电池，由于锂的低氧化还原电位(相对于标准氢电极为−3.04 V)和超高的理论比能量(3860 mAh·g^{-1})，被广泛认为是下一代高能量电池系统的理想选择[14] [15] [16]。与 LIBs 相比，锂金属电池(LMBs)的体积和重量能量密度将实现约 50%和 30%的增长[17]。锂元素所固有的高反应性和充放电过程中不可控的枝晶生长问题，一度使得 LMBs 失去了作为二次电池在实际应用中的机会。在逐渐成熟的表征技术的推动下，人们对枝晶的生长过程进行了深入的研究，现在人们对枝晶形成机制的了解比以前要深入得多[18]。在抑制枝晶生长和稳定电极/电解质界面这两个方面，进行了大量的研究工作，包括采用界面设计工程技术[19] [20] [21] [22]、构建亲锂位点[23] [24] [25]和使用三维(3D)集流体等技术[26] [27] [28]，在循环稳定性和效率方面取得了巨大的进展，金属锂的应用前景十分广阔。

尽管如此，锂金属负极也有一些严重的缺陷，影响了当前的商业化进程[17] (图 1(c))。解决 LMBs 的热失控则是电池运行阶段的重中之重。现有的 LMBs 架构中，热失控问题的主要来源是极端条件下的内部放热反应，如枝晶生长和固体电解质相界面(SEI)分解引起短路，热量和压力的不断累积进一步导致有机电解质被点燃从而引发安全问题[29] [30]。因此，除了通过抑制枝晶的生长来实现稳定的锂剥离/镀层外，使用不可燃的电解质被认为是一个可以完全解决电池热失控问题的方法。此外，已经开发了几种方案，包括添加阻燃剂[31]，使用离子液体电解质[32]，热敏电解质[33]。在固态电池的制备中，正常情况下用固体导锂陶瓷电解质取代有机电解质被认为是改善 LMBs 安全性的最有希望的方法之一[34] [35]，而

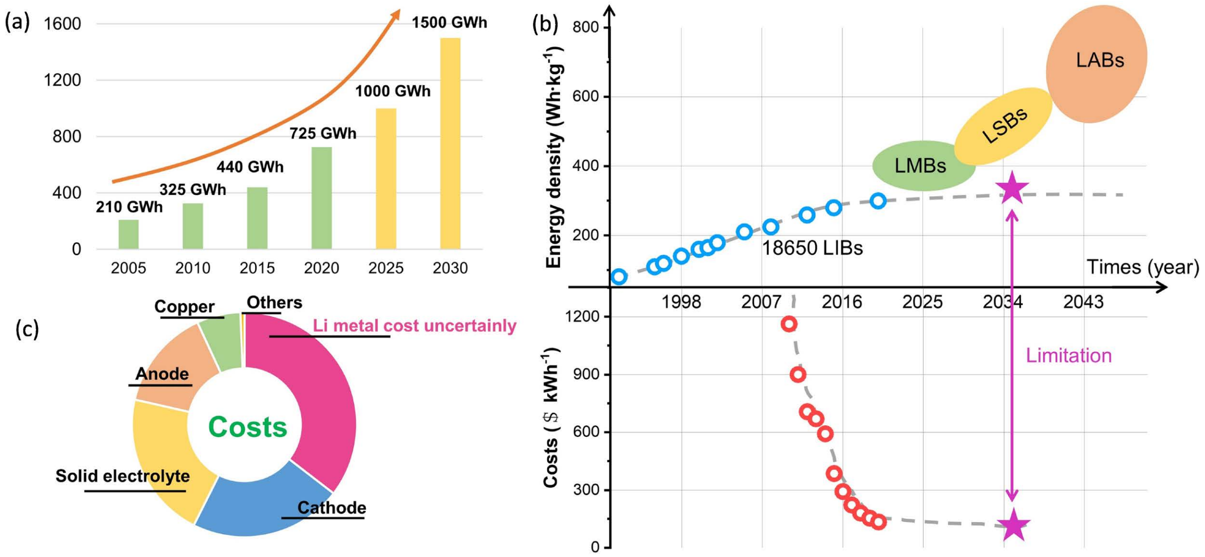

Figure 1. (a) Battery Market Trends Forecast 2005~2030. These data originally came from Avicenna Energy [9]; (b) Energy density and cost roadmap for conventional 18650 LIBs shows that 18650 LIBs are approaching their limits. Rechargeable batteries based on lithium metal negative electrodes will take the energy density of Li-ion batteries to new heights [11] [12] [13]; (c) Cost estimates for solid-state Li-ion batteries with lithium-metal cathodes [17]

图 1. (a) 2005~2030 年电池市场趋势预测[9]。这些数据最初来自阿维森纳能源公司；(b) 传统 18650 LIBs 的能量密度和成本路线图显示，18650 LIBs 正接近其极限。基于锂金属负极的可充电电池将把锂电池的能量密度提升到新的高度[11] [12] [13]；(c) 锂金属负极的固态锂电池的成本估计[17]

且这也使得 LMBs 有可能在高温下工作。然而，金属锂的低熔点(180.5℃)将限制全固态锂金属电池(ASSLMBs)的整体热耐受性。因此，锂负极在面对一些需要高温工作环境的领域，如武器供能和太空探索，难以被直接应用。最后，金属锂的机械稳定性相对较差。当受到外力的反复作用时，金属锂负极会发生不可逆的变形，使电池的内部环境恶化，增加了潜在的安全隐患，限制了 LMBs 在可穿戴领域的广泛应用[36]。这些问题就像“木桶效应”中那最短的一块木板，可能会导致 LMBs 整个蓝图的崩塌。建立一个能够应对上述问题的稳固的锂负极，将大大推动 LMBs 的实际应用进程(图 2)。

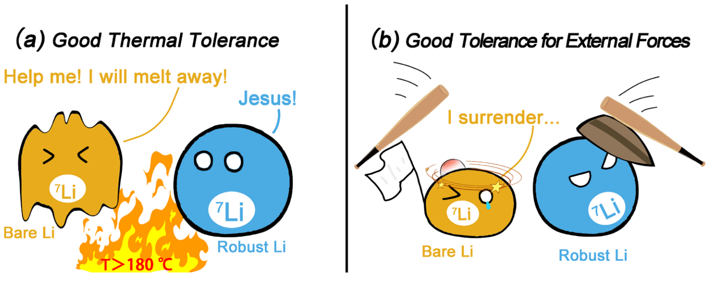

Figure 2. Robust lithium metal cathode should have the following properties: (a) good thermal tolerance; (b) good mechanical stability

图 2. 稳固型金属锂负极应具备的性能：(a) 良好的热耐受性；(b) 良好的机械稳定性

本文针对上述问题，概括了目前最先进的制造热稳定和机械稳定的稳固锂负极的技术，并讨论其特点、机遇和挑战。我们希望这些简洁而深刻的讨论能够启迪思想，提供合理的设计稳固锂金属负极的方案，并且能够促进锂金属负极的发展。在不久的将来，这些合理的稳固锂金属负极的设计，能够促进 LMBs

更好的实用化和商业化。

2. 热稳定的锂负极

锂电池在高温环境下安全地运行一直是科学家们追求的目标[37] [38]。不久的将来，ASSLMBs 可以使二次电池的安全性和稳定性更上一层楼[39]。然而，到那时，金属锂的低熔点(MT) (180.5˚C)将注定成为限制 ASSLMBs 在更高温度下工作的短板(>200℃)。在锂表面形成的 SEI 会在锂熔化时由于基底的流动性而被破坏。高温下，熔融金属巨大的表面张力使得常见的堆叠电池无法束缚住它。熔融的锂将从电池边缘流出，导致电池失效[40]。此外，熔融的锂是具有高度反应性的，可能直接与固体电解质发生剧烈反应，导致过热和烧毁[41] [42]。目前，特殊原电池的特别应用也迫切需要金属锂的热耐受性。例如，为导弹的制导和通信系统提供动力的原电池。由于火箭需要超高的运行稳定性，因此热耐受性是一个重要的前提条件[43]。所以设计一种具有优良热耐受性的稳固锂金属负极对于提高电池的安全性和稳定性至关重要。到目前为止，提高金属锂负极热耐受性的两个主要策略是合金化和空间限制。

合金化是改良金属熔化问题的有效方法[44]。由于锂合金可以降低电解液的还原性，同时能够使锂离子迁移到电极中，所以在很长一段时间内，锂合金作为金属锂的替代品受到了广泛的关注[45] [46] [47]。从本质上讲，充满电的 LIBs 的负极，LiC_6，是一种具有高热耐受性的锂碳合金。然而，LiC_6 中的锂含量不足，注定了它的比容量和能量密度会很低。因此，在设计热容性锂合金负极时，应注意不要牺牲过多的理论容量。科学家们已经确定了大多数锂合金的相图，从中我们很有可能可以找到热稳定的锂合金负极。图 3(a)总结了元素周期表中可以与金属锂形成合金的各种元素以及被开发的合金的熔点。一些二元系统，如 Li-B [48]、Li-Si [49]、Li-Sn [50]、Li-In [51]、Li-Sb [52]、Li-Bi [53] [54]和 Li-Ca [55]，已经在 400℃左右的温度下进行了研究，并表现出了良好的热稳定性。相比之下，Na、Y、Hg 等可以与金属锂形成共晶点。因此我们可以得出一个一般的结论，亲锂元素通常可以与更多的锂形成合金。这一特性也对 LMBs 的稳定运行起着至关重要的作用。合金负极中的亲锂相可以均匀电极表面的局部电流密度，减少 Li^+成核过程中的障碍[56]。研究还发现，亲锂合金负极可以作为一个高度电子化和离子化的管道，使 Li^+在电极材料内部转移，作为一个优秀的集流体和后续稳定镀锂的主体[57] [58]。此外，在锂金属负极中添加合金可以调节 SEI 的形成过程，从而减少与电解质反应的副作用，提高负极的稳定性[59]。图 3(b)总结了一些已报道的锂合金负极，并计算了它们相应的理论容量，可以指导我们改良锂合金负极[60]。

构建三维主体框架也被证实可以有效限制挤压的熔融锂。锂负极在高温下面临的一个重要问题就是，层状结构的电极无法保持熔融锂在电解质和集流体之间的均匀堆积。熔融的锂在高表面能的作用下，其表面积往往会发生减少。在整个制造过程中，三维结构上的亲锂点可以减少熔融锂的表面能。熔融锂将会被吸入框架并被毛细管所限制，因此这种类型的锂负极可以在高温环境下保持稳定[61] [62] [63]。此外，独特的三维结构和亲锂点可以均匀电极表面电流密度，促进了锂的均匀沉积。常见的亲锂性结构(如碳纤维、石墨烯和硅纤维)已经证实了这一特性。例如，孙等人报导了一种 Li-B 合金/锂复合负极，其特点是金属锂中布满了三维 Li_5B_4 纤维状框架。即使在高温条件下(325℃)，这种纤维状框架也能保持其初始结构，并通过毛细管力和亲锂表面能限制熔融锂的泄漏(图 3(c)) [64]。需要注意的是，在各种锂负极保护方法中，复合金属锂负极中的主体框架通常会导致 LMBs 的体积和重量能量密度发生明显的衰减。此外，用于结合熔融锂的三维主框架的作用力是二级键(锂键)或弱相互作用的范德瓦尔斯力[65]。主体框架像是一块海绵，当面临外部压力时，熔融的锂可能会被挤压出来。因此，这种方法对电池模组的结构强度有较高要求。

与基本的锂负极相比，具有良好热耐受性的稳固锂金属负极对电极结构的稳定性有更高的要求。除了热稳定性外，还必须能够稳定地进行锂镀层/剥离，使 LMBs 能够在高温环境下运行。在上述方法中，锂

合金负极可能有更广阔的发展前景。少量的合金元素可以增加电极的熔点，这相比在锂中嵌入非活性框架来说，对整体能量密度的负面影响要小的多。需要注意的一个方面是，锂合金的氧化还原电位一般比锂要高，这点也很重要，因为它决定了整个电池的运行电位。锂金属负极的热耐受性受到的关注相对较少，应鼓励多多努力研发热稳定的锂负极，以便更好地将其应用于热电池、ASSLMBs 和更多的特殊环境下。

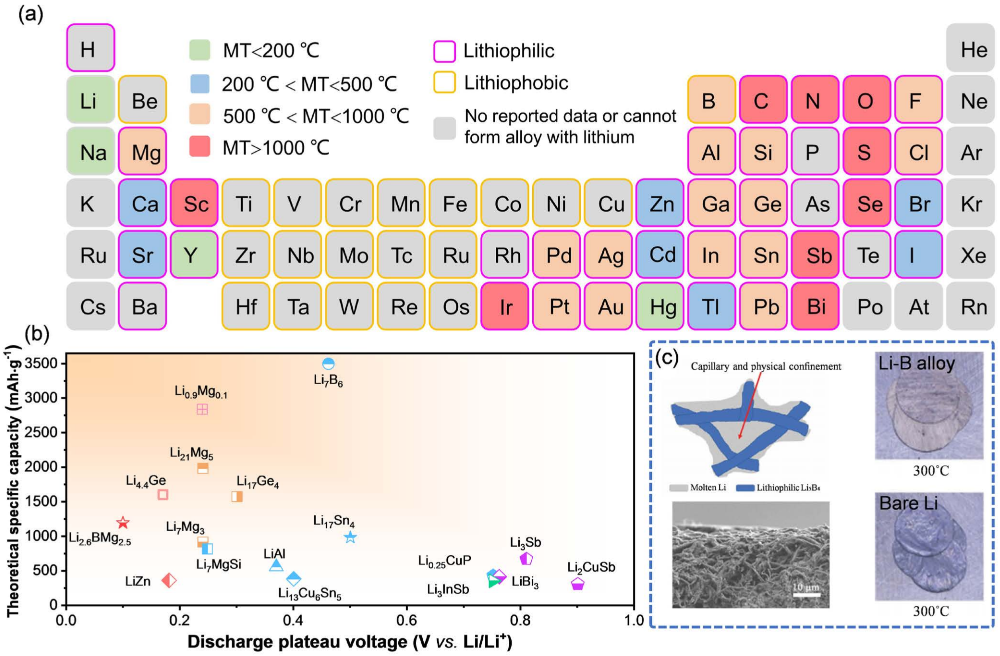

Figure 3. (a) The various elements in the periodic table that can form alloys with lithium metal and the melting points of the developed alloys [48]-[55]; (b) Comparison of the theoretical capacity and discharge plateau voltage of different lithium-containing alloy anodes [60]; (c) The attachment of liquid lithium in the Li_5B_4 framework at high temperatures above the melting point of lithium metal [64]

图 3. (a) 元素周期表中的各种元素可以与金属锂形成合金，以及所研制合金的熔点[48]-[55]；(b) 不同含锂合金阳极的理论容量和放电平台电压的比较[60]；(c) 在高于金属锂熔点的高温下，液态锂在 Li_5B_4 框架中的附着[64]

3. 机械稳定的锂负极

灵活的电子设备，如可穿戴的智能电子产品和可拉伸/弯曲的手机，在最近几年引起了广泛的关注[66] [67]。毋庸置疑，使用金属锂负极的电池为这些设备供电可以提供比其他电池更强的续航能力。虽然金属锂在受到轻微的机械变形时表现出一定程度的柔韧性，但传统的层状金属锂负极由于其适应重大弹性变形的能力较差，当电子设备进行动态运动时很难保持良好的电化学性能。金属锂会在 25%以上的不可逆的塑性伸长率下出现颈缩，随后形成折痕，甚至发生延展性断裂[36] [68]。产生的折痕和断裂将破坏 Li^+ 沉积的电场，并促进局部锂枝晶的形成，从而导致电池的循环性能恶化和安全风险提高[69] [70] [71]。因此，迫切需要研发一种稳固的锂金属负极，既能够承受机械变形，同时又不影响电池的循环性能。

到目前为止，大多数关于柔性金属锂负极的研究是将金属锂附着在柔性支架上。为了制造这种柔性复合锂负极，开发了主要三种方法，包括电沉积法[72]、热灌注法[73]和物理混合法[74]。一般来说，柔性支架具有的大面积和多孔结构可以使锂离子均匀沉积，同时使得体积变化可忽略不计，局部电流密度也较低。更重要的是，支架的亲锂性对热灌注法等方法来说至关重要，对电池的循环稳定性起着重要作用。碳支架是理想的柔性锂主体，因为其重量轻，制备简单，并且可以进行表面改性。李等人通过将熔融的

锂注入由亲锂的氧化锌阵列修饰的软碳纳米管中，制造了一种柔性锂负极[75]。这种锂/碳纳米管/氧化锌复合材料表现出令人震惊的延展性，并在反复的锂镀层/剥离循环中表现出优异的循环稳定性(图 4(a))。崔等人制造了一种超薄的独立锂金属箔，锂分布在还原氧化石墨烯(rGO)的内部通道中[76]。这种独特的锂负极表现出更高的机械强度、独立能力和灵活性，并在循环过程中表现出十分出色的性能。此外，一些类似石墨烯的材料，如 Mxene，也显示出类似的性能。郭等人通过简单的旋蒸技术设计了一种独立、质轻、灵活的 $Ti_3C_2T_x$ MXene/纳米纤维素复合薄膜(图 4(b)) [77]。这种具有大量极性官能团的功能性薄膜表现出与锂的良好亲和力，可以使锂的电化学沉积更加均匀。在沉积了一定量的锂之后，会形成一种柔性锂复合负极，该负极可以在承受较大的柔性弯曲后恢复到原来的状态而不会断裂。

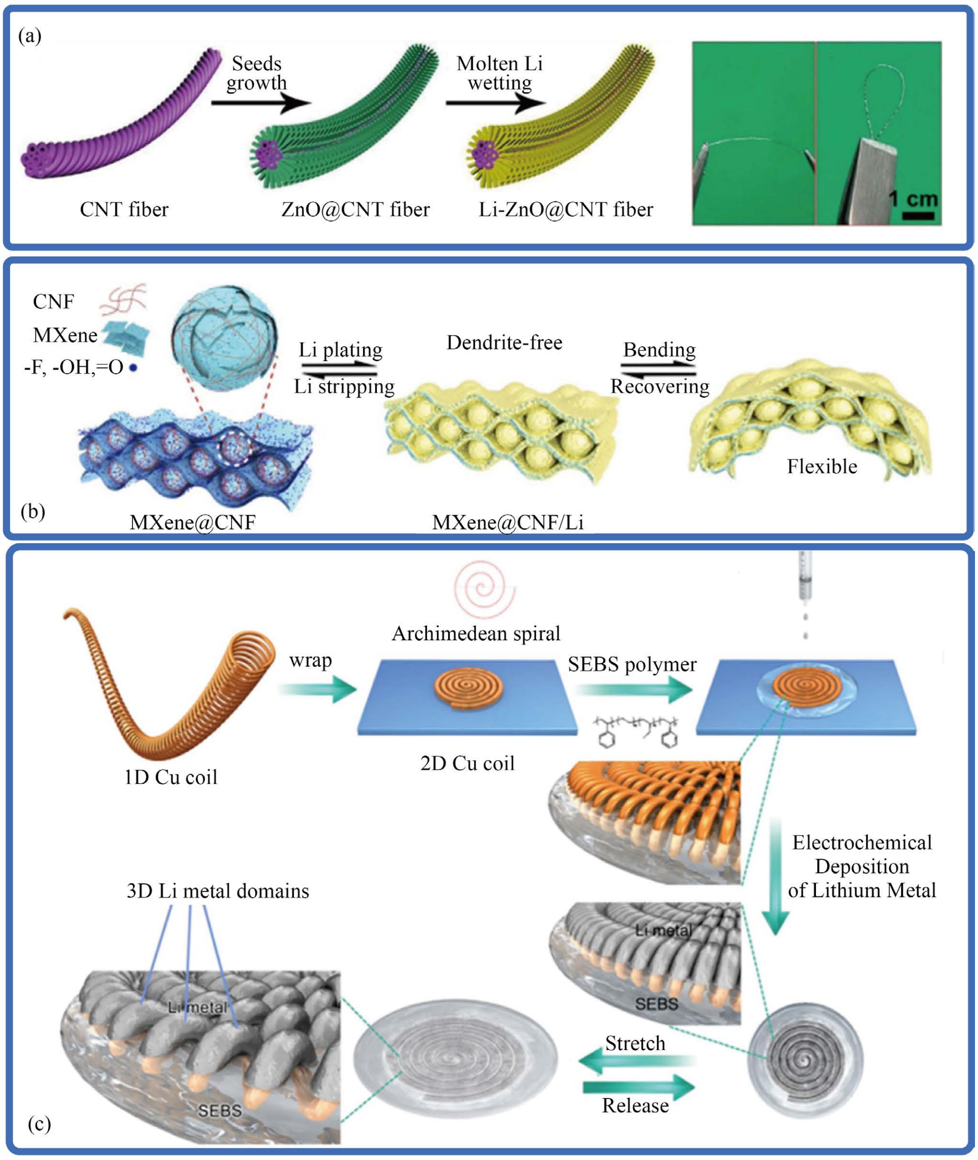

Figure 4. (a) Schematic showing the fabrication process of fibrous lithium metal anode and digital pictures of the flexible lithium anode under straightening and bending conditions [75]; (b) Schematic diagram of the flexible MXene@CNF@Li anode [77]; (c) Schematic diagram of the synthesis of stretchable Li/Cu electrode [78]

图 4. (a) 示意性地展示了纤维状锂金属负极的制作过程和柔性锂阳极在矫直和弯曲条件下的数字图片[75]；(b) 柔性 MXene@CNF@Li 负极示意图[77]；(c) 可拉伸 Li/Cu 电极的合成示意图[78]

高分子材料良好的延展性为制备柔性金属锂负极提供了一条新的思路。然而，由于其与生俱来的低电子/离子导电性，在用作集流体时，它们必须与导电材料融合才可以。刘等人报告了这方面的一项重要工作，在弹性(聚苯乙烯–乙烯–丁烯–苯乙烯)橡胶的帮助下，制造了一个可拉伸的阿基米德螺旋状锂/铜复合负极(图 4(c)) [78]。获得了优异的抗疲劳性能(超过 1000 次拉伸)和可拉伸能力(高达 60%的单轴应变) [78]。此外，独特的三维结构可以有效地分散电场，促进锂的均匀沉积。李等人在 2019 年首次报道了一类半液态金属锂负极(SLMA) [79]。SLMA 是锂颗粒均匀分散在聚合物/碳混合基质中形成的胶体，其中聚合物可以传导 Li^+，而碳可以提供优良的导电性(图 5(a))。SLMA 在 25%的剪切应力下表现出优异的流变特性，并且基于这种巧妙的设计，不会产生锂枝晶问题。若是锂能被印在柔性基底上，用金属锂墨水进行书写也是一个巧妙的有前途的柔性金属锂负极的设计思路。罗等人在此基础上进行了初步尝试，制备了可以书写的金属锂墨水。在熔融的锂中加入碳颗粒，大大降低了锂的表面张力，使墨水可以在金属箔和固体电解质等基质上书写(图 5(b)) [80]。胡等人研发出了一种新方法，通过直接冲压熔融合金溶液，可以在不同的基质上制备具有不同形状的柔性、超薄、高性能的锂-锡合金电极(图 5(c))。当与 NMC 正极匹配时，添加的锡不仅可以有效地减少锂枝晶的形成，还改善了循环性能[81] [82]。

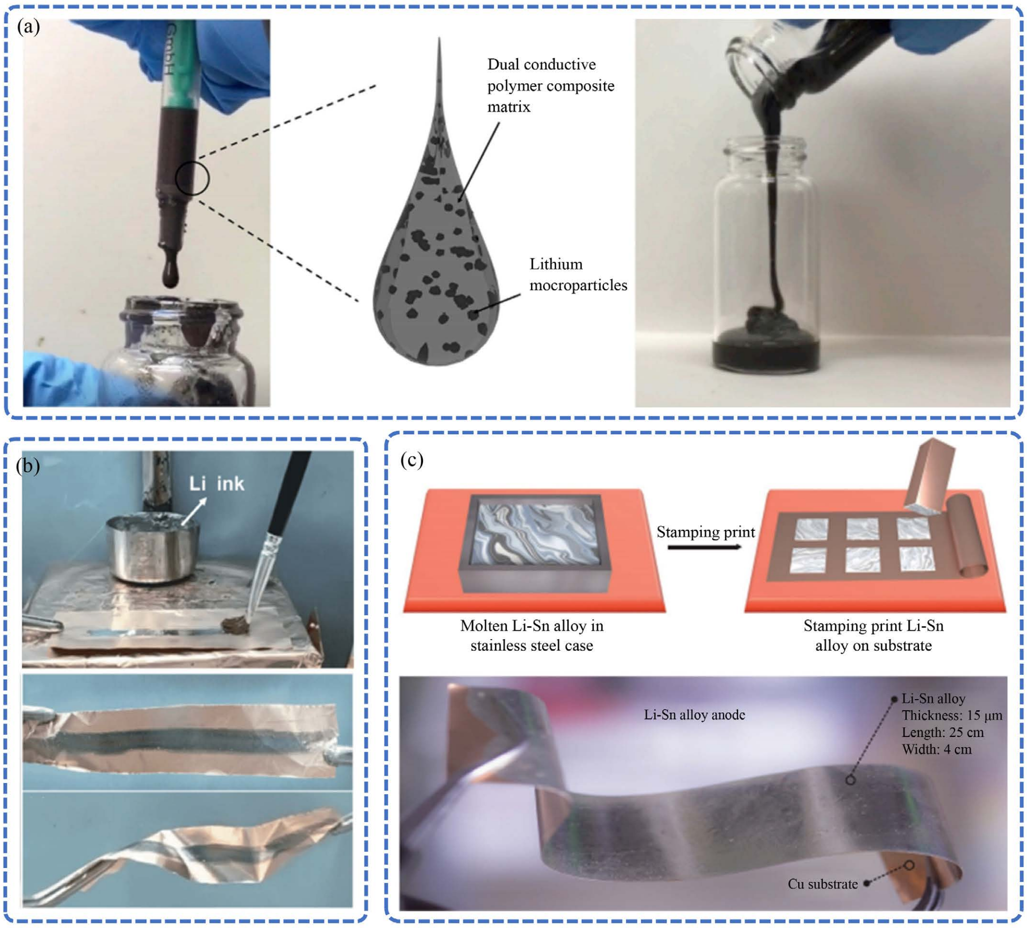

Figure 5. (a) Digital photograph of semi-liquid Li metal ink [79]; (b) Digital photo of handwritten Li metal ink on copper foil and the obtained finished product showing good ductility [80]; (c) Schematic demonstration of stamping Li-Sn alloy on a substrate and a large flexible Li-Sn alloy film printed on a copper foil substrate [81] [82]

图 5. (a) 半液态锂金属墨水的数码照片[79]；(b) 手写 Li 金属墨水在铜箔上的数码照片和得到的成品展现出很好的延展性[80]；(c) 在基板上冲压 Li-Sn 合金的原理图演示，以及在铜箔基板上印制一大块柔性 Li-Sn 合金薄膜的演示[81] [82]

4. 总结与展望

综上所述，我们从热耐受性和对外力承受能力两个方面系统阐述了目前稳固锂负极的研究进程。

对于具有良好热耐受性的稳固锂负极，目前更多地被用于一次热电池领域，以保证高温环境下的稳定供电。其在二次电池中的应用，将主要体现在全固态电池中。我们总结了实现热稳定性锂电负极的两个主要方法。一种是合金化方法，通过共晶熔化锂与其他金属或类金属来制造锂合金负极。这种方法提高了电极的整体熔点，同时保持与金属锂相似的电化学性能。另一种是构建一个三维框架以防止熔融锂的泄漏。一般来说，该功能框架应满足三个要求。1) 三维框架应具有良好的机械和热稳定性；2) 该框架的主体应该是亲锂的；3) 多孔结构在框架中必不可少。

此外，我们还介绍了具有优良外力承受能力的锂金属负极。需要强调的是电极同时需要具有良好的灵活性。实现柔性锂负极的一个方法是将锂附着在柔性基质上，如 Mxene、石墨烯、聚合物等。另一种方法是打破传统观念，将锂负极制成半液态或液态，从而提高锂负极的外力耐受性。在未来的研究中，重要的是要建立一个统一的标准来系统地评估柔性金属锂负极的机械质量。

我们可以发现，所有类型的稳固锂金属负极都面临着一个共同的问题，那就是由于引入了非活性材料，导致了容量和能量密度的损失。一个实用性的锂金属电池需要一个面积容量约为 5 mAh·cm^{-2} 的薄金属锂箔与商业正极材料匹配，这意味着锂负极的厚度应小于 50 微米，才能实现高能量密度。此外，稳固锂负极上的功能性保护层的厚度也会影响充电/放电过程中 Li^+转移的速度。因此，稳固锂负极上的涂层或框架必须足够薄，并且应在 1~20 微米的理想尺寸范围内，这对于构造保护层的技术提出了严格要求。一些能够实现厚度可控的致密涂层的技术，如原子层沉积和化学气相沉积法，有非常好的应用前景。在严格限制负极厚度的条件下，稳固的锂电负极面临的另一个棘手问题是枝晶的生长和锂的不可逆损失。目前报道的大多数稳固锂负极都是基于锂过量的前提下。制造出能够实现稳定的重复电镀/剥离的超薄稳固锂负极将更具有更大的实用价值。除了对负极的进一步改进之外，也应该足够重视对薄而稳固的固态电解质层的研究。固态电解质的一些优良特性，如足够的密度、良好的封装性和高离子传导性，有望在不损害电池整体能量密度的前提下实现稳固的锂负极。在未来，稳固的金属锂负极应该与稳固的固态电解质互相补充，推动更安全的全固态锂金属电池的实际应用进程。最后，值得探讨的是，由于钠和钾等其他碱金属也同样具有很高的反应特性和广阔的潜在应用前景，现有的实现稳固锂负极的方法是否可以应用到其他碱金属上？

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