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空气/水稳定的锂金属负极研究进展

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摘要

锂金属作为最理想的二次电池负极材料，以锂金属为负极的锂金属电池是应对未来高能量密度储能器件需求挑战的有效解决方案之一。但是，锂金属电池的实际应用受到锂金属固有缺点的限制，例如在循环过程中锂枝晶的过度生长，生产过程中对潮湿空气的敏感性，都存在潜在的安全性问题，本文总结了生产制造阶段设计空气/水稳定的锂金属负极的研究进展。

关键词

锂金属，空气稳定，水稳定，低成本

Research Progress on Producing Air/Water Stabilized Lithium Metal Anode

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Abstract

Lithium metal, as the most ideal anode material for rechargeable batteries, is an effective solution for the challenges of future high-energy density storage demand. Nevertheless, the practical application of lithium metal batteries suffers from the inherent limitations of pure lithium such as excessive dendrites growth and sensitivity to the humid atmosphere in cycling and handling which involves potential security concerns. This paper summarizes the research progress in designing

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air/water stabilized lithium metal cathodes at the manufacturing stage.

Keywords

Lithium Metal, Air Stability, Water Stability, Low Cost

1. 引言

近年来，由于传统锂离子电池(LIBs)越来越接近理论能量密度极限，导致其实际能量密度提高变得缓慢，难以满足未来对高能量密度存储不断增长的需求。锂(Li)金属被认为是锂电池系统中的理想负极，以锂金属为负极的锂金属电池是应对未来高能量密度储能器件需求挑战的有效解决方案之一[1] [2] [3] [4] [5]。锂具有 2060 mAh·mL^{-1} 或 3860 mAh·g^{-1} 的高理论比容量，最低负电化学电位(与标准氢电极相比为 –3.040 V)和低密度(0.534 g·cm^{-3}) [6] [7] [8] [9] [10]。但是，锂金属电池的实际应用仍处于初级研究阶段。所面临的最主要的挑战是锂金属负极反应过程中体积变化过大和循环过程中锂枝晶连续生长所带来的安全问题。这些问题可能导致短路、热失控和爆炸等。另外，在电池循环过程中因为锂枝晶的生长、锂的产生导致的电解液分解的问题会进一步带来电池电解液“干涸”、库伦效率变低、循环寿命缩短等问题[11] [12] [13] [14]。所以，为了实现锂金属电池的实际应用，解决以上问题，设计出高安全性锂金属负极，研究人员付出了大量的努力。方法主要分为以下四点：1) 锂金属表面设计构建稳定界面保护层改善锂负极/有机电解液界面层[15]；2) 使用固态电解质代替有机电解液，可以从根本上解决锂离子沉积行为，提高锂金属电池安全性[16]；3) 设计新型结构的锂金属负极，改善锂离子沉积[17]；4) 制备合金锂负极，用离子态锂代替金属态锂解决枝晶生长问题[18]。

另外，锂金属的易腐蚀问题还没有得到很好的解决。一般认为，锂金属在干的氧气和二氧化碳中，或者空气温度达 250℃以上，干燥的氮气达 160℃以上才是惰性的。因为锂金属对水非常敏感(蒸汽或者液体)，能迅速与水反应生成氢气($2Li (s) + 2H_2O (g/l) = 2LiOH (s) + H_2 (g)$) [19] [20]，在生产制造阶段和一些特殊情况下也会产生巨大的安全问题，这也是阻碍锂金属实际应用的因素之一。例如，在锂金属生产和电池组装过程中需要在相对湿度小于 1%的干燥房中进行，负极的制造过程和之后的电池包装过程需要更加严格的操作环境(惰性气体环境)，这意味着现有的 LIBs 生产基础设施无法满足 LMBs 生产制造，而且复杂的制造工艺和严格的储存条件也大大增加了锂金属负极的不确定性成本。

因此，本文将主要针对生产制造阶段锂金属所面临的关键问题，概述了目前主流的解决策略，主要包括：1) 在金属锂负极表面构造一层低表面能的界面层；2) 构造致密的绝缘层来密封金属锂负极。提供设计空气/水环境下锂金属负极的研究方案，促进锂金属电池实际应用和商业化进程。

2. 生产制造阶段空气/水环境下稳定的锂金属负极

目前，LIBs 中所使用的石墨和硅/碳复合负极，其生产过程一般可以在开放环境下进行。此外，目前 LIBs 所使用的正极材料和电解质，基本也都可以在干燥的开放环境中稳定进行，这就使得锂离子电池整个生产过程，包括堆叠、密封和填充，只需要一个干燥的环境即可[21] [22] [23]。对于锂金属负极(电池级)，一个非常棘手的问题就是金属锂与环境空气中几乎所有的主要成分(N_2、O_2、CO_2、水分)都具有高

度反应性。因此，所有与锂负极有关的制造操作(包括生产、储存、运输和最后的电池组装步骤)都必须在惰性环境中进行。这样使得锂电极LMBs与现有的LIBs的工业生产体系不相容，增加了复杂的生产步骤，提高了LMBs的整体成本[24] [25] [26]。因此，构造一个稳固的、在空气环境中稳定的甚至是具有防水性锂负极，将推动LMBs的实用化和商业化进程。

2.1. 空气环境下稳定的锂金属负极

为了实现金属锂负极在空气环境下稳定，已经研究出了两种主要的方法。一般情况下来说，流体对材料的表面亲和力取决于表面能。高表面能产生的极强的表面亲和力可以将水份吸附过来，形成高度润湿的表面环境[27] [28]。因此，可以在金属锂负极表面构建一个低表面能的界面层，可以排斥空气中的气体分子，将有效地提高金属锂的环境适应性。近年来，构建这种功能界面层来使得锂负极在空气环境下稳定的方向取得了突破性进展[29]。Yan 的团队报道了一种操作简单并且成本很低的技术来制造锂/氟石墨复合负极并使其在空气中保持稳定。在金属锂负极的表面制造了一个由氟化碳和氟化锂组成的保护层(图1(a))。氟化物的低表面能可以使其在空气环境中长期稳定，并且可以防止锂负极在循环过程中直接接触电解质。即使暴露在潮湿的环境中24小时以上，这种稳固的锂负极依旧表现出优异的性能。Li等人选择富勒烯来构建保护层，因为它比大多数碳材料疏水性更强。总的来说，即便把改良的锂负极暴露在潮湿的空气中(相对湿度 > 30%) 12小时以上，电池依然具有优异的稳定性和出色的容量性能(图1(b)) [30]。Cui等人开发了一系列由大型石墨烯纳米片包裹的锂合金纳米颗粒。石墨烯片的气密性可以防止气体的渗透，包括氧气、氮气、二氧化碳和水分子[31]。这种稳固的锂负极在相对湿度高达60%时仍能保持稳定。

另一种保持锂负极在空气环境中稳定的有效方法是构造致密的绝缘层来密封金属锂。因为这种保护层足够致密，甚至连电解质也无法穿透，并且这种绝缘层具有优秀的锂离子传导能力，可以使电池能够良好运行[32] [33]。Yang等人通过简单的磁溅射法在锂负极上沉积了一层铝(Al)薄膜，作为保护层来抑制金属锂腐蚀。铝在锂负极的表面形成了一个致密的氧化层，可以效地防止环境空气的进一步渗透(图1(c)) [34]。这个金属保护层在循环过程中会转变为稳定的锂铝合金层，而且不会对电池运行产生不利影响。黄等人报道了一种空气环境下稳定的核壳型锂球结构，金属锂作为内核，Li_2CO_3薄膜是外壳[35]。Li_2CO_3外壳是在CO_2环境下锂还原时形成的，成功地钝化了锂核和空气之间的反应。实验表明，Li_2CO_3薄膜是一个良好的Li离子导体。因为保护层必须足够严密并且能够传导锂离子，所以固态电解质(SSEs)层由于其良好的锂离子传导性和在空气环境下良好的稳定性，在钝化锂负极方面会更有优势，除了一些在水分子环境下不稳定的电解质，如硫化物和氢化物电解质。Yang等人通过简单的浸涂技术将金属锂包裹在蜡和聚氧化乙烯(PEO)的混合涂层中。由于蜡具有良好的密闭性，这种涂层可以有效地延缓锂负极的腐蚀，而且PEO具有良好的离子传导性，可以使电池能够正常充放电[36]。Yan等人展示了一种设计优良的人工双层膜，可以使金属锂负极在空气环境下保持稳定。顶部致密且具有高度活性的聚磷酸酯层和底部的刚性无机层都能使金属锂抵抗环境空气的腐蚀，表现出与在惰性气体中的金属锂几乎相同的性能(图1(d)) [37]。

2.2. 水环境下稳定的锂金属负极

当前的LIBs对水分子含量具严格的要求(≤10 ppm) [38]。当电池中的水分子高于一定量时，电池中的化学平衡将会被打破，电极上形成的SEI将会被破坏，导致电池性能的非线性老化[39]。因此电解质必须是非常干燥的，电解质的注入和封装过程必须在干燥的室内进行。对于LMBs，水分子含量的影响将会更加严重。水分子可以与金属锂快速反应，产生LiOH，释放出H_2和大量热量，这会导致严重的安全问题，并损坏电池。由于电解质的强吸湿特性会导致金属锂的快速腐蚀，这对研发一些开放系统的LMBs (如

Li-O_2 电池)构成了巨大的挑战[40] [41]。因此，在保证空气环境稳定性的前提下，实现水环境稳定的锂电负极可以简化 LMBs 的装配过程，并且降低对电解质水分含量要求。此外，它还可以进一步提高电池的循环稳定性，特别是对于那些具有超高能量密度的开放式 LMBs。

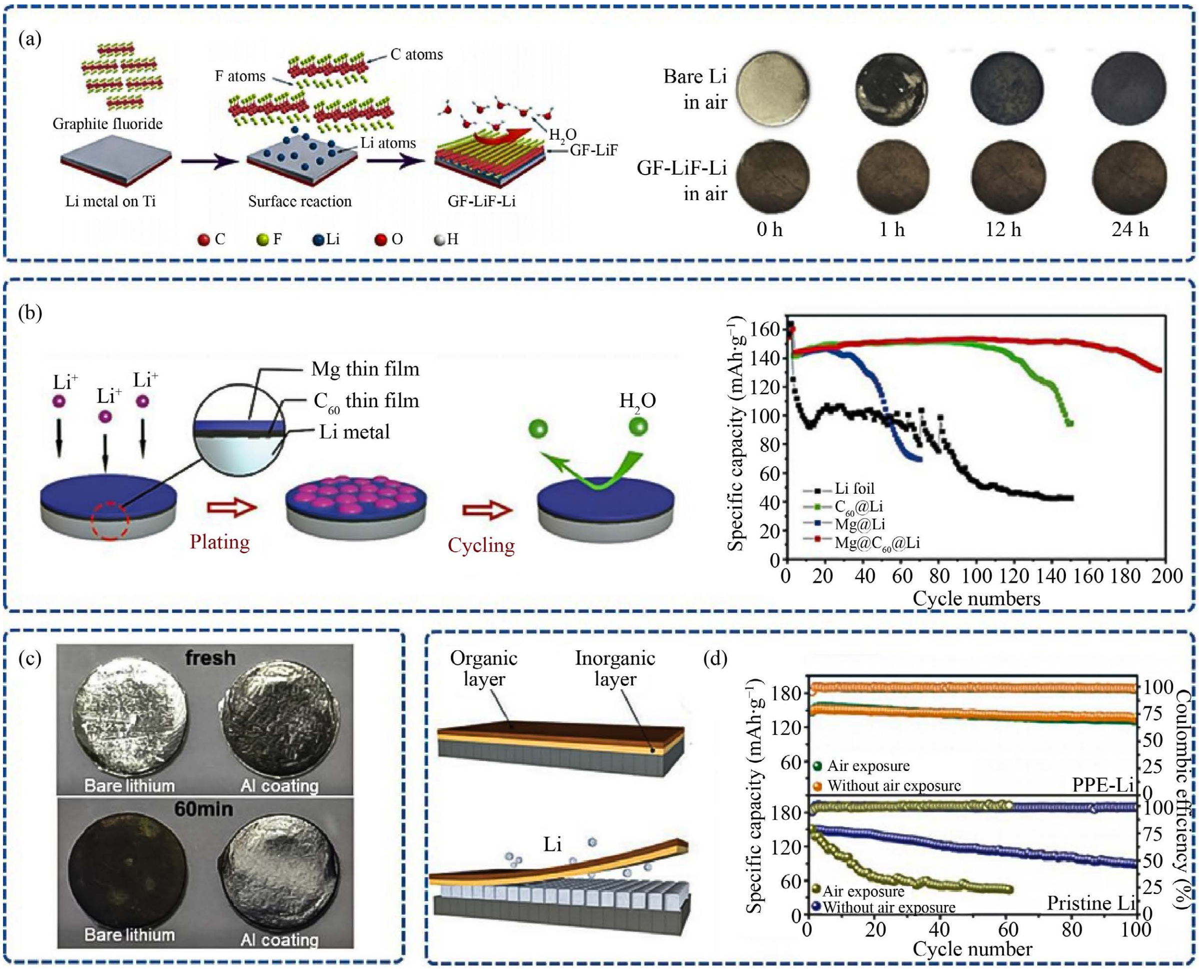

Figure 1. (a) Lithium/graphite fluoride composites for the protection of lithium metal (left), and photographs of bare Li and GF-LiF-Li exposed to air at 20%~35% relative humidity for different times (right) [29]; (b) Schematic of the fabrication of Mg@C_{60}@Li and the contribution of the hybrid interface to improve the wetting resistance and cycling stability of the Li -metal negative electrode [30]; (c) Digital photographs showing the stability of pristine Li (left) and Li/Al-10 (right) sheets in ambient air (humidity: ~37%) for different times (0 min and 60 min) [34]; (d) Schematic diagram of air ambient stabilized Li anode achieved by a stable bilayer film on a shaped and mechanically strong stabilized Li metal surface [37]

图 1. (a) 锂/氟化石墨复合材料对金属锂的保护效果(左)，以及裸露的 Li 和 GF-LiF-Li 在相对湿度为 20%~35%的空气中暴露不同时间的照片(右) [29]；(b) Mg@C60@Li 的制作示意图，以及混合界面对改善 Li-金属负极的湿润电阻和循环稳定性的贡献[30]；(c) 显示原始 Li (左)和 Li/Al-10 (右)片在环境空气(湿度：~37%)中不同时间(0 分钟和 60 分钟)的稳定性的数码照片[34]；(d) 空气环境稳定的 Li 负极由定形和机械强度稳定 Li 金属表面的稳定的双层膜示意图[37]

理想的情况下，一个疏水的、保形的、稳定的、致密的、具有超强耐水性的封装层对于保护金属锂在运行和应用中不受水的腐蚀是必不可少的[42] [43] [44]。与空气环境稳定型锂电负极相比，水环境稳定型锂负极对保护层提出了更高的要求。该保护层需要隔绝水分子并且可以传导 Li^+。它还需要在充/放电过程中防止被锂枝晶刺穿，导致保护层失效[45] [46]。在这方面，最近已经研发了许多稳固的保护层，可以使金属锂在电池组装和循环过程中不受水分子的侵蚀。周等人创造了一个稳固的，致密的薄保护层。

该保护层由 Ge、GeO_x、LiOH、$LiCO_3$、Li_2O 组成，实现了锂负极稳固性，即使在水含量高达 10,000 ppm 的电解质中也能保持稳定(图 2(a))。这个稳固的保护层的高杨氏模量可以抑制枝晶的生长，使锂金属负极在 Li-O_2 体系和对称电池中都能正常循环。聚合物是另一种使锂负极在水环境下稳定的优秀材料，因为它们具有非常好的密闭性。然而，它们中的大多数离子传导性较差，因此，电池必须在相对较高的温度下运行(>50℃)。此外，聚合物材料的低杨氏模量性使它们容易被锂枝晶刺穿。张等人设计了一种稳定的疏水性聚合物电解质膜来保护锂负极。这种防水层大大减少了对锂的腐蚀，提高了 Li-O_2 电池的循环稳定性、倍率性和比容量(图 2(b)) [47]。黄等人结合液体离子聚合物和液体电解质的优点，通过简便的流延法在金属负极表面制造了一个具有很高锂离子电导率的疏水和聚阳离子保护层。改良后的负极与水直接接触时可以保持稳定 120 秒时间[48]。该保护层在电池循环过程中也可以稳定锂离子的流量，促进形成均匀的锂镀层(图 2(c))。

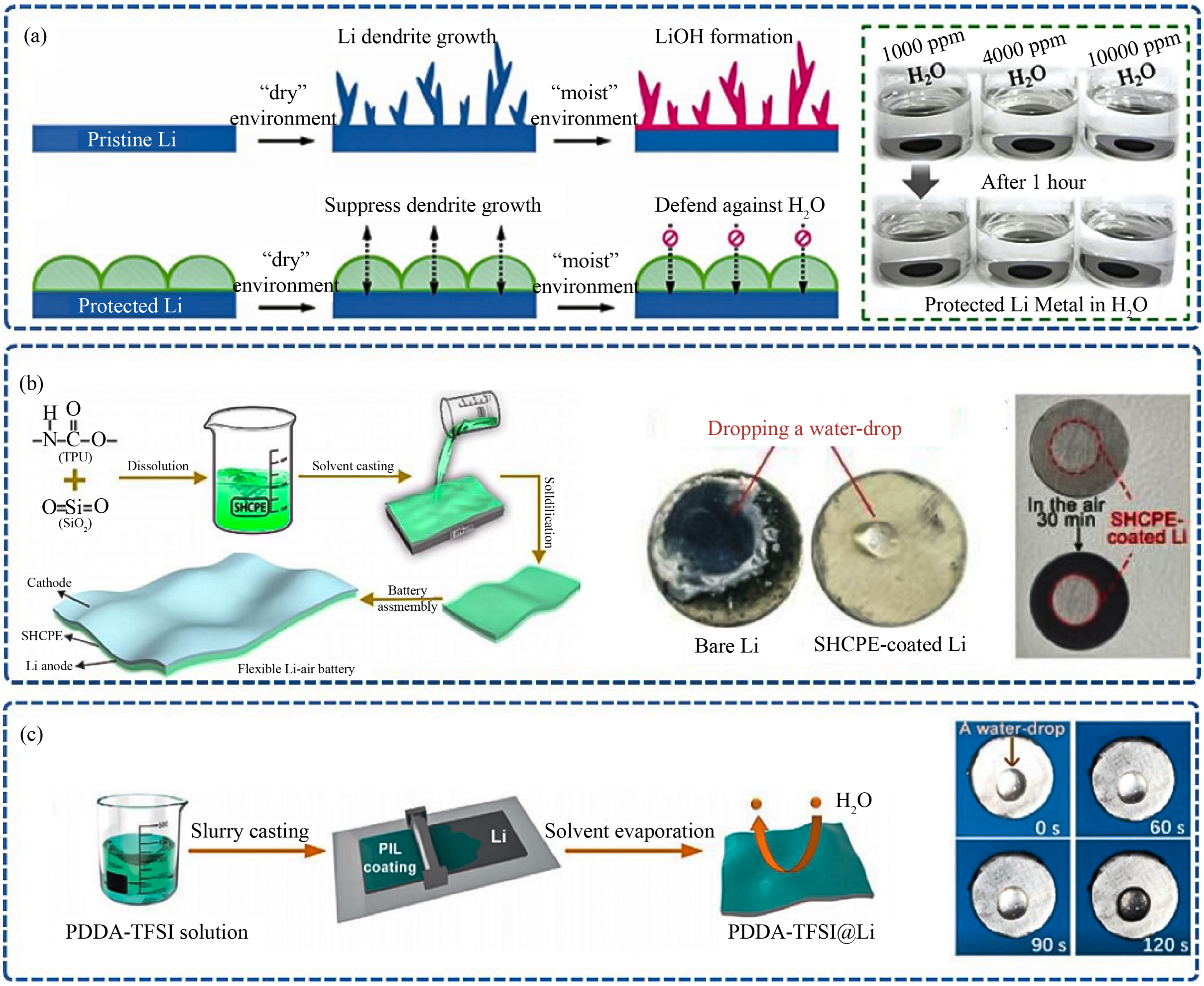

Figure 2. (a) Schematic diagram of plated/stripped lithium in different environments without and with a protective layer, and sealed vials of lithium protected immediately after exposure to solutions containing different amounts of H_2O and after 1 h of exposure [45] [46]; (b) Scheme of waterproof lithium cathode fabrication process, photos of exposed lithium and waterproof lithium flakes after exposure to a drop of water [47]; (c) Schematic diagram of PDDA-TFSI@Li fabrication process, photos of PDDA-TFSI@Li after dropping water drops at different times [48]

图 2. (a) 在没有保护层和有保护层的不同环境下的电镀/剥离锂示意图，以及在接触到含有不同量 H_2O 的溶液后立即和暴露 1 小时后被保护的锂的密封小瓶[45] [46]；(b) 防水锂负极制作工艺方案，滴一滴水暴露在户外后裸露的锂片和防水锂片的照片[47]；(c) PDDA-TFSI@Li 制作过程示意图，PDDA-TFSI@Li 在不同时间滴下水滴后的照片[48]

可以发现，使得锂金属负极可以在开放环境中使用的简便方法就是人工制造一个保护层。然而，我们不能忽视的是，在电池系统中加入额外的保护层，会使得整个电池的能量密度和成本方面出现一些弊端[49]。因此，这些报导的通过构建保护层来保护锂负极却导致 LMBs 高能量密度优势减少的方法就是本末倒置。通过可以完全忽略副作用的原位转换反应或相互稳定的材料制作而成的保护层似乎更加合适[50] [51]。固体电解质保护层可能是保护锂负极免受空气腐蚀、抑制循环过程中枝晶的刺穿问题、并且也不会减少电池的能量密度的最有希望的方法[52]。当然，固体电解质层的厚度应限制在 25 μm 以内(与典型的 celgard 隔膜相比)，这对生产技术提出了更高的要求。因此，固体电解质加工技术的进步将极大地促进的锂负极的发展。ASSLMBs 将成为未来锂电池的主要形式。

3. 总结与展望

综上所述，我们从空气环境和水环境两方面系统阐述了目前稳固锂负极的研究进程。对于具有良好环境适应性的金属锂负极，我们发现，在金属锂表面构造一个具有低表面能的功能性界面，可以有效地排斥空气中的气体分子对锂的腐蚀。此外，对锂进行封装处理是实现空气环境下稳定甚至防水的锂负极的另一个有效途径。封装层必须满足三个基本条件：1) 致密、疏水和定形，使其对空气或水具有良好的耐受性；2) 具有足够的 Li^+电导率，使电池能够正常运行；3) 在电池循环过程中防止枝晶穿透。由于固体电解质具有高能量密度、良好的 Li^+电导率和优良的机械性能，可能是最有希望的封装材料。

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