Hans Journal of Nanotechnology 纳米技术, 2023, 13(1), 7-28
Published Online February 2023 in Hans. https://www.hanspub.org/journal/nat
https://doi.org/10.12677/nat.2023.131002

Hans汉斯

高锂利用率锂金属负极及其在锂硫电池中的研究进展

沈晓魏[1]，陆豪量[2]，许　娜[2]，朱　鹏[3]，钱　涛[3*]

[1]南通大学电气工程学院，江苏　南通
[2]苏州大学能源学院，江苏省先进碳材料与可穿戴能源技术重点实验室，江苏　苏州
[3]南通大学化学化工学院，江苏　南通

收稿日期：2022年8月15日；录用日期：2023年2月4日；发布日期：2023年2月14日

摘　要

随着社会的进步与环保意识的提高，至2030年，众多老牌汽车厂商都会停止生产内燃机汽车。目前国内外的汽车市场无不对电动汽车或混合动力汽车加大研究投入，高比能量锂离子电池作为新时代汽车储能装置的关键组成部分，一直广受关注。目前锂离子电池负极材料如石墨、硅碳等已经广泛应用于锂离子电池中，但石墨负极低的储锂质量比容量(372 mA·h/g)和硅碳负极巨大的体积膨胀效应一直限制了它们的进一步发展。而正极材料如$LiFePO_4$、$LiMO_2$ (M = Ni、Co、Mn)等虽然也已经投入商用，但低储锂质量比容量(<300 mA·h/g)、安全性、倍率性能等问题也限制着它们的发展。被誉为下一代储能系统最有力候选者的锂硫电池是由有着质量比容量分别为3860 mA·h/g和1675 mA·h/g的锂金属负极和硫正极组成的。然而由于锂金属负极存在着枝晶生长的问题，并且硫正极产生的多硫化物会在电解液中溶解引起穿梭效应，这些都严重影响着锂金属电池锂的利用率及锂硫电池的硫利用率。本综述详细介绍了锂金属电池面临的问题以及锂硫电池目前的研究进展。

关键词

锂金属电池，均匀锂沉积，锂硫电池，穿梭效应，高利用率

Construction of Lithium Metal Anode with High Lithium Utilization and its Application in Lithium-Sulfur Batteries

Xiaowei Shen[1], Haoliang Lu[2], Na Xu[2], Peng Zhu[3], Tao Qian[3*]

[1]School of Electrical Engineering, Nantong University, Nantong Jiangsu
[2]College of Energy, Key Laboratory of Advanced Carbon Materials and Wearable Energy Technologies of Jiangsu Province, Soochow University, Suzhou Jiangsu

[*]通讯作者。

文章引用: 沈晓魏, 陆豪量, 许娜, 朱鹏, 钱涛. 高锂利用率锂金属负极及其在锂硫电池中的研究进展[J]. 纳米技术, 2023, 13(1): 7-28. DOI: 10.12677/nat.2023.131002

[3]School of Chemistry and Chemical Engineering, Nantong University, Nantong Jiangsu

Received: Aug. 15th, 2022; accepted: Feb. 4th, 2023; published: Feb. 14th, 2023

Abstract

By 2030, with the progress of society and the improvement of environmental protection awareness, many established car manufacturers will stop producing internal combustion engine vehicles. At present, the domestic and foreign automotive markets have all increased their research investment in electric vehicles or hybrid vehicles. As a key component of the new era of automotive energy storage devices, high-specific energy lithium-ion batteries have received wide attention. At present, lithium ion battery anode materials such as graphite and silicon carbon have been widely used in lithium ion batteries, but the low lithium storage mass specific capacity (372 mA·h/g) of graphite anode and the huge volume expansion effect of silicon carbon anode have limited their further development. Although cathode materials such as $LiFePO_4$ and $LiMO_2$ (M = Ni, Co, Mn) have also been put into commercial use, the low lithium storage mass specific capacity (<300 mA·h/g), safety, rate performance and other issues still exist. The lithium-sulfur battery, known as the most powerful candidate for the next-generation energy storage system, is composed of a lithium metal anode with a specific capacity of 3860 mA·h/g and a sulfur cathode with a specific capacity of 1675 mA·h/g. However, the lithium metal anode has the problem of dendrite growth, and the polysulfide will dissolve in the electrolyte to cause a shuttle effect, which all seriously affects the effective utilization of lithium anode and sulfur cathode in lithium-sulfur batteries. This review details the problems faced by lithium metal batteries and the research progress of lithium-sulfur batteries.

Keywords

Lithium Metal Battery, Uniform Lithium Deposition, Lithium-Sulfur Battery, Shuttle Effect, High Utilization

1. 引言

随着电动汽车(EV)市场与智能手机的蓬勃发展，人们对具有高能量密度和低成本的电池的需求愈发强烈。在现有的可充电电池中，锂离子电池(LIB)的容量最高，比能量约为 250 Wh/kg，能量密度约为 650 Wh/L [1]。因此，当今的电动汽车和手机仅使用 LIB 作为能源动力[2]。根据 2019 年彭博新能源财经的电池价格调研显示，电池组的价格约为 150 美元。但是，要实现大众市场普及，对于 EV 而言，以较低的成本达到 400 公里以上的行驶里程这至关重要，这相当于要求具有 330 Wh/kg 的电池能量的电池组的成本低于 120 $/kWh [3] [4] [5]。而在智能手机市场上，目前主流手机的一块锂聚合物电池板的售价为 10~30 美元，这价格并不昂贵，但是相较于旗舰手机的用电量情况而言，一块 3000~5000 mA h 的电池板仅够使用 3~5 小时，在旗舰手机满功率运行的情况下，只能运行 2~3 小时，这就对现代锂离子电池的容量提出了很高的要求。

不幸的是，采用石墨负极和锂过渡金属氧化物(LMO)正极的 LIB 几乎无法达到如此高的能量密度。如今最先进的富镍层状氧化物正极，例如镍含量约为 80%的锰钴氧化物(NMC811)或锂镍钴铝氧化物(NCA)的可逆容量约为 200 mA·h/g (锂的脱嵌比例只有 72%)。在智能手机中广泛使用的锂聚合物电池中的聚合物因为导电性等原因，最后也只能提供最多约 500 mA·h/g 的容量。所以正极材料方面仍需要较多的研究投入，另外，锂电池负极方面还有很多的改进之处，锂电池中石墨负极的实际容量(372 mA·h/g)确实可以接近理论容量，但是却远远不够与高负载正极匹配，而且石墨负极虽然有着较为稳定的电化学性能，但是实际应用中容量与性能的矛盾依旧存在。因此，全球新一轮科技革命和产业变革蓬勃发展，汽车与能源、交通、信息通信等领域有关技术加速融合，以及航空航天、尖端国防装备、人工智能等高新技术领域的飞速发展给新能源产业迎来了前所未有的发展空间和技术挑战，对新一代储能器件的能量密度、循环寿命和安全性提出更高的需求，发展更加高效的储能技术具有十分重要的意义。锂金属作为二十世纪以来最有希望的锂电池负极，我们应将更多精力投入到适合社会经济发展需求的锂金属负极上，通过锂金属负极的高效构筑，我们可以开发出高能量密度、高循环稳定性及高安全性的锂金属电池。本综述从锂金属电池中负极面临的挑战、能与之匹配的硫正极材料存在的问题和已发表的相关研究工作等方面详细介绍了锂金属电池面临的问题以及锂硫电池目前的研究进展[6]。

2. 锂金属电池简介

2.1. 锂金属电池概述

金属锂由于具有超高的容量(3860 mA·h/g 或 2046 mA·h/L，是石墨的 10 倍和 2.6 倍)，以及最低的电化学电势(−3.040 V vs SHE)被认为是最有希望替代石墨的负极材料。对于 Li-LMO 电池体系，原则上可以使用无锂(纯铜集流体)负极构建电池，即所有锂均来自 LMO 正极。石墨约占电池质量的 1/4 和电池厚度的 1/25，通过不使用石墨(以及填充孔所需要的电解液)，这种电池结构将至少增加 30%以上的比能量和两倍的能量密度。但是，从性能的角度来看，我们可能需要一些过量的锂来补偿其循环反应中的损失。因此，Li-LMO 电池在能量含量和成本降低方面的总体收益将强烈地受到锂含量的影响。需要注意地是，世界上许多研究组正在对 LMB 进行深入的研究。其中，以太平洋西北国家实验室为首的能源部认为，通过将设计合理的锂金属作为电池负极，可以完全替代市场主流的石墨或硅碳负极[7]。最近，位于波士顿的一家公司已经展示了中试规模的 3.4 Ah 袋电池，它可以提供约 450 Wh/kg 和 1200 Wh/L 的能量密度[8]，但是锂金属在实际应用中还有很多问题。

除 Li-LMO 体系外，使用锂金属作为负极的电池中，正极的选择还可以扩展到不含锂的材料，例如高容量正极硫(S)，Li-S 电池的比能量可以达到 600 Wh/kg [9]。由于硫的成本比 LMO 正极材料低得多，因此可以进一步降低锂金属电池的成本。因此，包括 Li-LMO 和 Li-S 在内的锂金属电池(LMB)在能量密度和成本方面都比 LIB 具有压倒性的优势，这为将来的高续航的电动汽车和智能手机带来了巨大的机遇。但如何实现锂金属的高效利用仍是个突出难题，锂负极的构筑可以为此提供解决之法。

2.2. 高锂利用率金属电池潜在的挑战

要使高能量，低成本的锂金属负极实用化，还需要有高效的负极构筑手段。目前锂金属负极的主要障碍是极短的循环寿命和锂金属负极的安全问题。此外，汽车行业和智能手机还存在许多其他的关键要求。由于电动汽车电池的尺寸差异和工作期间所经历的环境等因素的影响，例如，物理机械性的冲撞振动，极高或极低的温度以及超高的充放电频率，所以电动汽车和智能手机的电池和为其他器件开发的电池在根本上有所不同。如今，尽管人们在提高锂金属负极的循环性和抑制锂枝晶形成方面进行了越来越多的研究，但是在实际的全电池模组和软包电池中，仍然缺乏对高锂利用率 LMB 的系统研究。下面，是

LMB 所面临的问题和挑战。

1) 循环寿命：为了锂电池能够成功的代替其他的能源，电池寿命、价格成为了最令人关心的两个问题[10]。以目前情况来看，电池或电池组在整个用电器件的制造成本中占比并不低。当前在最佳运行条件下的 LMB 至少可以循环 1000 圈，对于 EV，假设每次充满电可以行驶 250~300 英里，则其总行驶里程为 250,000~300,000 英里，如果每年行驶 12,000 英里，则使用时间超过 20 年。考虑到汽车的平均寿命为 150,000 英里，这已经可以与传统汽车媲美甚至超过其使用寿命。随着 LMB 正极能量密度的提高，相同大小或者质量的电池/电池组中可以储存/释放更多的能量，而且由于每次充电的行驶时间更长，LMB 的循环寿命的要求可能会变得不那么苛刻。我们有理由相信，对于 EV，LMB 电池需要 500 圈循环寿命，具体取决于电池的能量密度水平[11] [12]。

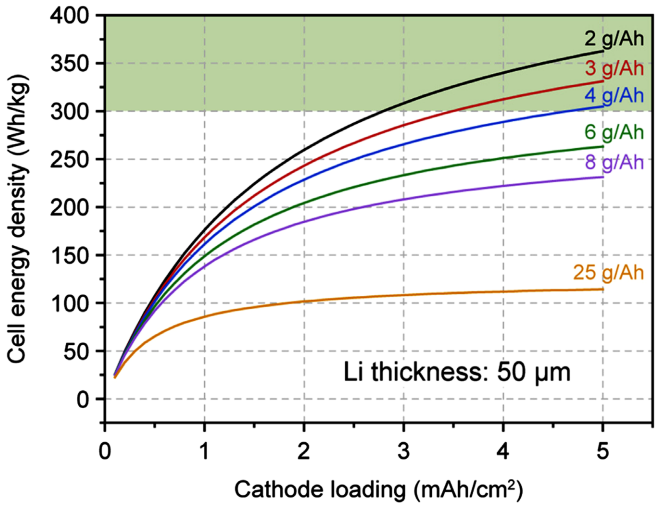

Figure 1. The energy density of batteries under different negative load and electrolyte content [11]
图 1. 不同负极负载和电解液含量下的电池的能量密度[11]

普通的 LIB 拥有长循环稳定性的最大一个原因是石墨负极上会形成稳定的固体电解质层(SEI)，SEI 可有效抑制循环过程中电解液的分解与脱落。然而，与石墨不同，锂金属负极在循环过程中会表现出大的体积变化，由于刚刚沉积的锂和电解液组分具有超高的反应活泼性，坚硬、致密与稳定的 SEI 层很难在锂金属电池中形成，锂和电解液的连续消耗(库仑效率低)会形成新的脆弱的 SEI，并且逐渐增加电池的过电势，导致循环过程中容量快速衰减。这就是为什么锂金属电池如果存在极过量的锂和充足的电解液，有时可以完成数百个循环，但它们并不能保证高能量密度。例如，对于 NMC622，薄锂片(<50 um)和稀电解液(<3 g/Ah)，如图 1 所示。锂和电解液的快速耗尽会大大缩短电池的寿命[13] [14] [15] [16]。

2) 倍率性能：目前的电子产品电池的高倍率性能至关重要。更具体地说，对于电动汽车而言，在车辆起步和加速过程中需要快速放电(>2 C 的速率，相比之下，普通行驶过程需要 0.2~0.5 C 的速率就足够了，而对于任何一种电动汽车，都需要结合快速脉冲放电和连续充电能量存储系统[16] [17] [18] [19]。最近，高效的快速充电能力(5~20 分钟内充电至 80%的充电状态，或> 3 C 的速率)这一因素对于消费者是否接受 EV 至关重要，因此也引起了很多关注[20]-[25]。而对于智能手机而言，快充更为重要。一方面，热失控是锂金属电池高速运行的重要问题，锂沉积溶解过程产生的热量会提高电池温度，加速电池的老化[25] [26] [27] [28]。另一方面，锂负极的形貌和可循环性取决于电镀/剥离的有效面电流密度。而无论是热失控还是锂负极巨大的形貌变化等问题在高倍率充放电时会变得更加严重。所以，快速充电对于 LMB 来说是个大问题。当锂沉积电流密度超过临界值时，锂金属的表面会从光滑变为长满枝晶，并且锂循环

效率和寿命显着降低[29]。然而，有趣的是，最近的一些研究表明快速放电(将脉冲电流用于锂剥离和沉积)有利于提高锂循环效率和抑制锂枝晶的形成[30] [31]。

3) 锂负极体积变化：锂金属电池的体积变化是阻碍其在电动汽车与智能手机中的应用的另一大障碍。首先，锂电镀/剥离的无规律成核极有可能造成锂负极以及整个电池在充电和放电期间的局部膨胀和收缩。从理论上讲，当以 3 mA·h/cm^2 的电流密度循环时，锂的厚度变化预计为 15 μm [32] [33]。再参考其他电池部件，例如，假设 Cu 和 Al 集流体，隔膜和正极的厚度分别为 10 um，10 um，5 um 和 60 um，并且在电池循环中不会改变，如果使用不含锂金属的负极，则负极的变化可导致整个电池 12%~15%左右的体积变化。但是这种情况随着正极厚度增加与负极锂的增多，整个电池的体积变化会适当减小。而且从实际角度出发，假设提供 2 倍过量的锂(30 um)来补偿循环时的锂损失，通过理论计算，相对体积变化可以减少 2%~5%左右。所以为将 LMB 应用于电动汽车或手机，需要提高锂的利用率以适应这种周期性的电池体积变化。另一个问题是长期循环后不可逆的电池体积膨胀。这是由于不均匀的 SEI 和被 SEI 阻隔的“死”锂颗粒积聚而形成的松散粉末状锂结构的增长造成的，这其实也是锂和电解液不可逆及连续反应的结果。如图 2 所示，根据最近的报告，经 200 次循环后，袋式电池的膨胀率也会达到 70% (从 2.7 mm 到 4.5 mm) [34]。这种巨大的膨胀既引起了安全问题，也给电池带来了新的挑战。由于会发生不可逆体积变化的锂负极是循环时积累的“死”锂量引起的，因此可以通过各种策略(例如高锂利用率锂负极构筑)将其最小化至接近零。

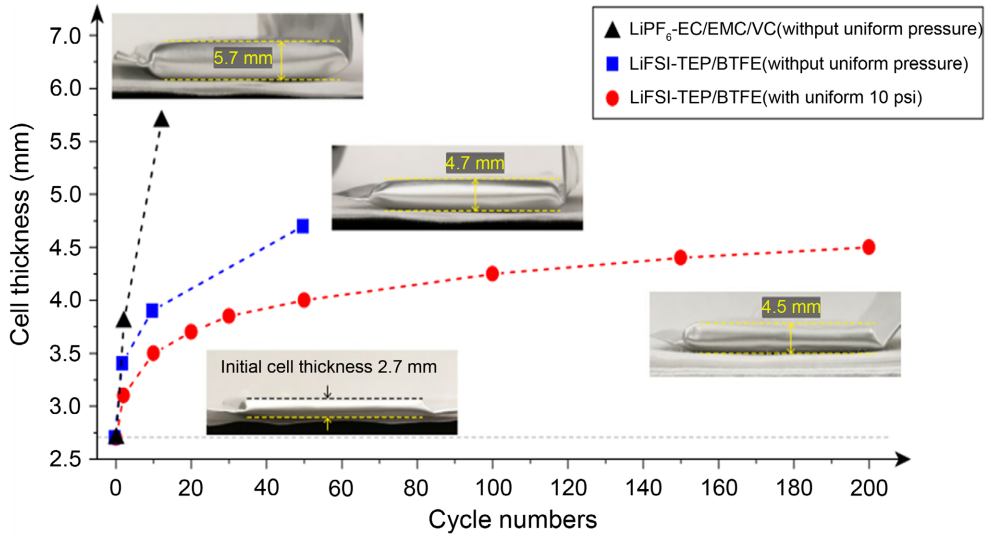

Figure 2. The volume expansion of 350 Wh/kg^{-1} Li||$LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (Li||NMC622) pouch cells (1 Ah) after different electrolyte and uneven external pressure cycles [34]
图 2. 300 Wh/kg 1 Ah Li||NMC622 软包在不同的电解液和不均匀的外部压力循环后的电池胀气情况[34]

4) 安全性问题：锂电池的安全性也是电动汽车与智能手机的考虑因素之一。具有高能量密度和高易燃性的锂电池对外部环境极其敏感，包括机械，电气和热失效，例如振动，碰撞，过度充电/过度放电[35]，恶劣的环境条件会破坏稳定的结构并导致内部短路，引发连锁反应，最终导致热失控，带来严重的安全问题，例如烟，气体喷射，燃烧甚至爆炸[36]。除了外力影响外，制造缺陷，自身电池故障和内部短路也可能导致热失控[37]。电动汽车与手机电池的模组化应用会使热量从一个失效电池传递到相邻电池而带来了额外的热安全问题[38]。与传统的 LIB 相比，LMB 在反复电镀/剥离锂金属负极时因枝晶锂引起的内部短路而导致的内部故障率要高得多[39] [40] [41]。锂金属电池的频繁起火事故使众多厂商停止了商业化试

验[42]。除了锂枝晶外，反复循环后，“死”锂和破碎的 SEI 又是另一个安全问题。在机械振动下，较小的 SEI 和锂颗粒可能容易从负极集流体上脱落并使电池短路。另外，它们由于具有高的表面积和强烈的反应性，当暴露于潮湿的空气或水中或车辆因挤压而破裂时，可能会引起火灾甚至爆炸[43]。

3. 锂金属电池研究进展

从根本上讲，LMB 的挑战主要来自锂的结构变化和循环过程中不稳定的锂电解液界面。在过去的十年中，研究者通过增强锂金属与电解液相间的稳定性并抑制枝晶的生长，在提高库仑效率，循环稳定性和安全性方面已取得了重大成果。这些策略主要集中在电池的电解液改性和负极构筑上，这在最近的一些综述中得到了系统总结[44] [45]。最近，低温透射电子显微镜等一些新的先进表征方法的开发和应用[46] [47] [48]，也极大地加深了对锂电镀/剥离行为的理解。下面重点说明各个方向上的一些最新进展。

3.1. 电解液工程

不同的电解液具有不同的稳定性，并极大地影响 SEI 性能和锂沉积物的形态，从而导致不同的循环库仑效率和锂金属负极膨胀(图 3) [49]。此外，不同的电解液的工作温度范围，倍率性能，可靠性等级都是不一样的。电化学稳定性高，高电导率，高锂离子扩散系数，低流动粘度，低熔点和良好的热稳定性与化学稳定性的电解液对于 LMB 在电动汽车与智能手机中的应用至关重要。迄今为止，电解液添加剂一直是提高锂电镀/剥离效率，减轻枝晶效应和延长电池寿命的最具有可行性的策略[50] [51]。Jeff Dahn 的小组报道了一种可以循环 90 圈的无锂软包电池，该电池使用了双盐电解液和氟代碳酸乙烯酯(FEC)作为助溶剂[52] [53]，并通过不断优化盐浓度进一步提高到 200 个循环。除了使用常规溶剂外，研究者还特别开发了用于锂金属负极电池的电解液[54] [55] [56]。这种新的电解液系统即使在非常宽的温度范围(−60至+55℃)中也显示出高电导率和良好的循环稳定性。引入阻燃助溶剂以制成阻燃型电解液系统也是进一步改善 LMB 安全性的有效方法[57] [58] [59]。

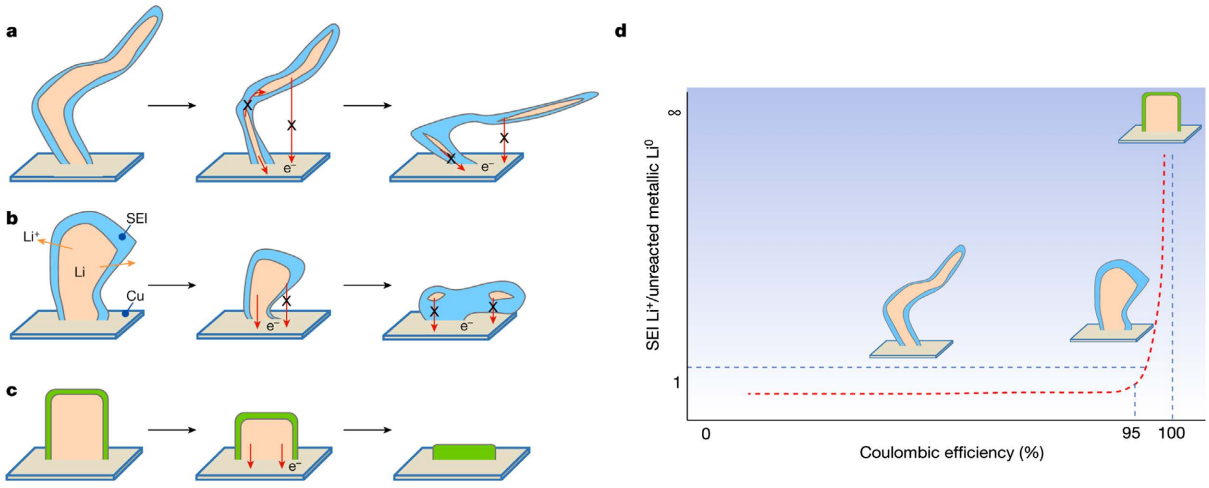

Figure 3. (a) Schematic of different SEI and Li deposition morphologies in different electrolytes; (b) Morphology of lithium deposition, CE and the ratio of Li^+ to the unreacted metal Li in the composition of SEI [49]
图 3. (a) 不同电解液中不同 SEI 和 Li 沉积物形态的示意图；(b) 锂沉积物的形态，库仑效率和 SEI 中 Li^+与未反应金属 Li 的比例的关系[49]

高盐浓度的电解液[60]和进一步优化的局部高浓度电解液[61]也可以使电池达到超高的库仑效率。重要的是，对于典型的 300 Wh/kg 的 1 Ah Li-NMC622 软包电池，添加了阻燃添加剂的局部高浓度电解液可实现 200 圈稳定循环。据我们所知，到目前为止，尽管循环寿命仍然远远不足以满足电动汽车的要求，

这已经是大型袋式电池(扣式电池除外)文献中最好的结果，并且这已经可以用于智能手机中。另外，值得注意的是，在这个 1 Ah 的软包电池中，电解液的量仍然很高(占电池的 24.1 wt%)。为了进一步提高比能量，需要降低电解液的量，但是这可能会缩短循环寿命。除新型液体电解液外，包括固体聚合物电解液和无机固体电解液在内的固态电解液(SSE)，也因其更好的热稳定性和抑制枝晶能力而被认为是可充电 LMB 的关键[62]。但是，大多数 SSE 要么表现出较低的室温电导率、要么降低了电池能量和功率密度、要么表现出较小的电化学稳定性窗口。此外，所有固态电池(SSB)的制造成本(包括 SSE 的材料加工和电池制造)都可能比液态电解液 LMB 更高。

3.2. 锂界面工程

界面工程是应对锂金属负极挑战的重要方法。理想情况下，锂的 SEI 应该薄而致密，均匀且具有高弹性，更重要的是离子导电率高但电子导电性低。这样的话，它可以容忍大的体积变化，并允许 Li^+快速自由地通过，同时防止电解液(或 Li-S 中的可溶性多硫化物)分解，从而实现锂负极的高效无枝晶循环。但是普通电池循环过程中电解液分解而形成的 SEI 不具备如此优秀的功能性。因此，锂负极表面保护层或者人工 SEI 是公认的极简单有效的方法。除了金属的氧化物、固态电解液、碳材料类、卤素类外，一种非人工 SEI，如利用锂与涂层之间的反应生成的 SEI 最近被证明是非常有效的[63] [64] [65] [66] [67]。据报道，衍生自反应性聚合物复合材料(RPC)的聚合物－无机 SEI，可以稳定 Li/电解液界面并防止电解液在循环时分解。使用 RPC 衍生的 SEI 可以在贫电解液(7 uL/mA·h)，过量 Li (1.9 倍)和大容量(3.4 mA·h/cm^2)的条件下，可以循环 200 圈。通过在集流体上自组装单分子层可以调节 SEI 的有效组成成分及方式和锂金属负极的沉积形貌，该方法即使在极端温度和速率充电条件下也获得了高性能的 LMB，有效抑制了电池的自放电和枝晶的产生。然而，为有效起见，通过与锂或铜集流体直接化学反应形成人工 SEI 通常需要精确控制反应条件。从实践的角度来看，大范围放大可能具有挑战性，潜在的成本可能很高。另一种有效的减轻/控制锂枝晶生长的策略是在隔膜表面上构建坚固的界面涂层[68] [69] [70]。微米或纳米改性的结构显示了更好的抑制锂枝晶的性能[71] [72] [73]。通过在隔膜上原位构建纳米结构界面层，有望能够在稳定锂/电解液界面的同时，抑制锂枝晶的生长，在防止热失控过程中内部短路方面起着重要的作用[74]-[82]。

4. 锂硫电池简介

4.1. 锂硫电池概述

锂离子电池，广泛运用于电动汽车和固定式蓄电设备中[83]-[88]。尽管磷酸铁锂，锰酸锂等传统正极材料在锂离子电池中有着出色的表现，人们依旧探索着具有更高质量/体积能量密度的锂电池技术。锂空气电池被认为是有前途的锂电池技术，其理论能量密度最高为 5200 Wh/kg (包括氧气)，重量轻，并且便宜[89] [90]。不幸的是，锂空气电池的性能受到正极中不可控制的放电产物，负极中锂枝晶的形成及电解质不稳定的影响，其大规模运用依旧不能实现[91]。硫由于其高理论容量(1675 mA·h/g)，高能量密度(2600 Wh/kg)，低廉的价格，丰富的储量，较轻的密度等特性，被认为是能够满足未来高能量密度新型锂电池的最有前途的继任者之一[92] [93]。2009 年继 Nazar 等人的研究之后，Li-S 电池在下一代储能应用研究中获得了高度的关注[94] [95]。尽管研究公司，例如 Oxis Energy 即将将该体系商业化，研究者们依旧继续开发具有长循环稳定性和自放电小的 Li-S 电池。这种发展有望提高电池工业的整体水平[96] [97]。

传统的 Li-S 电池包括一个复合的硫碳正极和一个金属锂负极，如图 4 所示，它们通过由有机电解质(通常是醚溶剂)浸润的隔膜隔开。锂和硫的容量分别为 3861 和 1672 mA·h/g，单质硫分子为八个原子组成的环状分子，即 S_8 [98]。而且，这种元素硫可以轻松升华，具有相对较低的熔化温度(115℃) [99]。由于硫本质上是绝缘的，因此向电极中添加导电剂炭黑，可以促进整个正极的电子运输[100]，而聚合物粘

合剂则用于固定活性物质[101]-[106]。

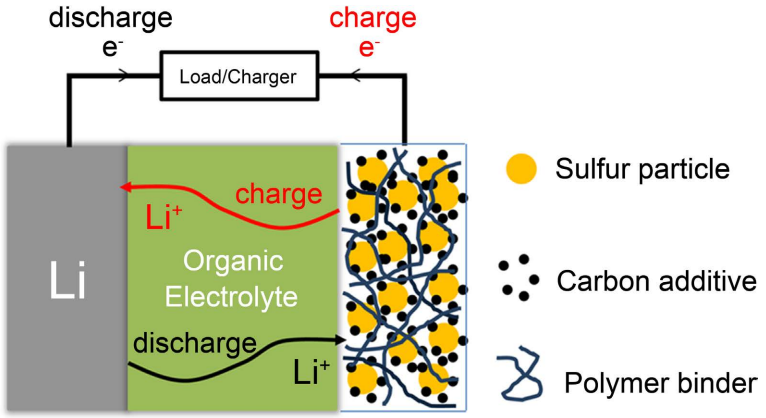

Figure 4. Schematic illustration of Li-S battery
图 4. 锂硫电池工作示意图[92]

Li-S 电池反应过程中硫正极伴随多重相变，其初始还原反应产物能够溶于电解液。因此，选择用于 Li-S 电池系统的电解液对于实现高能量密度，长循环寿命和低自放电起着重要作用[107]。溶剂必须与溶质和多硫化物化学相容，考虑溶剂的性质(例如粘度和介电常数)也很重要，因为这些性质决定了电解质的性质(溶解度，离解度和迁移率) [108]。迄今为止，大多数电解质是基于不同醚的二元混合物，即体积比相等的 1,3-二氧戊环(DIOX)和 1,2-二甲氧基乙烷(DME)。高分子量醚，例如二甘醇二甲醚(DEGDME)，四甘醇二甲醚(TEGDME)和聚乙二醇二甲醚(PEGDME)也已被广泛研究[109]。电解质中还加入了各种添加剂，以改善界面性能以及电池的循环性能[110] [111] [112]。通常使用市售的包含聚乙烯(PE)或聚丙烯(PP)的聚烯烃膜或 PP/PE Celgard 膜的组合作为隔膜[113]。

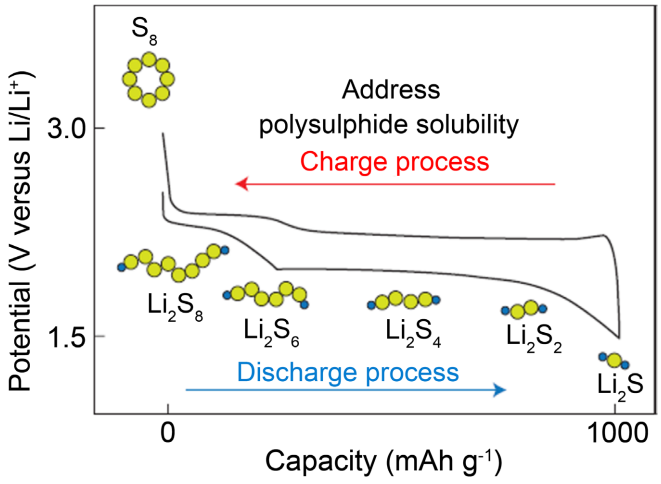

Figure 5. The charge-discharge curves of Li-S battery
图 5. 锂硫电池工作电压曲线[92]

图 5 显示了锂电池的典型电压曲线。在放电过程中，硫还原为低级多硫化物 Li_2S，充电过程发生逆反应[114]。整个反应如式 1 所示：

$$S_8 + 16Li^+ + 16e^- \leftrightharpoons 8Li_2S \quad (式\ 1)$$

放电过程大致分为三个区域，如 Yan 及其同事所述[115]，贡献理论容量的约 25%的第一个区域是固态硫被初步还原为可溶于电解液的S_8^{2-}与S_6^{2-}，然后进一步被还原为S_4^{2-}的区域[116]。方程式 2 显示了相应的能斯特方程式：

$$E_u = E_u^{\theta} + \frac{RT}{n_H F}\ln\left\{\frac{\left[S_8^0(l)\right]}{\left[S_4^{2-}\right]^2}\right\} \quad (式\ 2)$$

可溶性S_4^{2-}的浓度随放电深度(DOD)的增加而增加，而 S_8 则保持几乎恒定的饱和浓度。结果，该区域中的电压主要受S_4^{2-}的浓度影响并一直降低，直到电解液的粘度增加并达到阻碍锂离子迁移的一定水平为止。因此，可以看到小的反向峰(在图 5 中用圈 1 表示)。之后在区域 I 中看到的急剧的电压降表明S_4^{2-}浓度减少。此外，在区域 II 中，可溶性物种S_4^{2-}被还原为不溶性Li_2S_2或Li_2S。报道表明，从高放电电压平稳期过渡到低放电电压平稳期的过程与固体Li_2S_2和Li_2S的形成同时发生[117] [118]。电池容量的主要部分是在固定电势下从该反应中获得的。公式 3 显示了相应的能斯特方程。

$$E_u = E_u^{\theta} + \frac{RT}{n_L F}\ln\left\{\frac{\left[S_4^{2-}\right]}{\left[S_2^{2-}/S^{2-}\right]^4}\right\} \quad (式\ 3)$$

由于Li_2S_2或Li_2S在液体电解液中的溶解度非常低，因此S_4^{2-}和S^{2-}-的浓度恒定。相反，由于从可溶性S_4^{2-}到非导电性和不溶性的 Li_2S/Li_2S_2 的缓慢动力学反应，S_4^{2-}的浓度逐渐降低。因此，放电曲线趋于保持在 2.1 至 2 V 之间，并持续相对较长的时间。这一直持续到硫正极大部分被非导电Li_2S/Li_2S_2覆盖为止，这会严重阻塞电荷转移路径，如电池电阻的增加。随后，电压显示出快速下降并且反应终止。最后一个斜坡对应于固态Li_2S_2还原为固态Li_2S，这是最困难的过程，因为固态扩散到主体中的速度很慢。进行充电反应时，我们观察到一个平坦而长的平台，该平台代表不溶性Li_2S/Li_2S_2氧化成可溶于电解液的长链多硫化物，这代表着由固态Li_2S/Li_2S_2溶解引起的充电过程中极化的进一步降低(在图 5 中用圈 2 起来)。Wang 等人报道的密度泛函理论(DFT)得出可以从吉布斯自由能分析预测反应的趋势，即较低的吉布斯能量有利于该反应。总之，在放电过程中主要包含了三步反应路线，即约 2.30 V 的$S_8 \rightarrow Li_2S_4$，约 2.22 V 的$Li_2S_4 \rightarrow Li_2S_2$和 2.18 V 的$Li_2S_2 \rightarrow Li_2S$，这是公认的锂硫电池复杂放电机理的理论。还须注意，电解液，硫与电解液的比例以及硫的面负载在影响放电曲线方面也起着至关重要的作用[119]。

4.2. Li-S 电池潜在的挑战

对于锂硫电池而言，普遍的负极是纯金属锂箔，所以锂金属负极存在的问题在锂硫电池中也存在。如上文所言：循环寿命、体积变化、SEI 表面电阻增大及安全性等问题依旧突出。在 Li-S 电池中，正极是活性物质硫，硫作为介于金属与气体物质之前的固态非金属，其导电性差强人意。在 Li-S 电池中，往往需要添加导电剂如乙炔黑、碳纳米管、科琴黑等碳材料都具备高的比表面积，电解液浸润正极就需要更多的液体，这就导致了能量密度的下降。另外随着正极在充放电过程中活性物质的转化，电池的内阻并不能保持一致，影响整个 Li-S 电池在电子产品中的应用。

在 Li-S 电池中，负极(Li/Li^+)和正极(S_8/S_x^{2-}，$x \in [1,8]$)的电活性不同。多硫化物由于浓度梯度而从正极迁移到负极(普通隔膜不具备阻止溶解在电解液里的多硫化物通过的能力)，并与 Li 发生化学反应，从而导致活性物质的损失，降低了电化学容量。相反，到达正极的Li^+已经处于最高氧化态，并且只能参与其自身的非氧化还原相互作用，例如Li_2S沉淀，这种现象被称为多硫化物穿梭效应，这些都被证明是与 Li-S 系统相关的不可逆性的来源。值得一提的是，还原机理纯属化学过程，是通过锂的失去电子(氧化)而发生的，而硫接受电子并进一步还原[120]。这过程即使在开路条件下也会发生，导致 Li-S 电池自放电。

虽然多硫化物穿梭是由于正极产物引起的，但是合适的电解液改性、隔膜修饰及负极改性都可以构建高锂利用率的锂硫电池。

5. 锂硫电池研究进展

5.1. 正极导电性提升

硫由于其固有的电导率较小而不适合直接用作电化学活性材料。因此，它经常与各种碳材料和衍生的碳材料结合，例如多孔碳[121] [122]，石墨烯[123] [124]和碳纳米管。近年来，随着金属有机骨架(MOF)的发展，基于 MOF 的衍生碳材料在锂硫电池中的应用正在增加[125] [126]。使用碳材料的主要目的是为非导电的硫提供足够的电子传输通道和离子反应位点。锂硫电池硫正极中使用的碳材料应具有合理设计的电子/离子传输路径，并具有足够的体积以适应电化学反应中硫的体积变化。

2009 年，Nazar 及其团队制备了一种有序介孔多孔碳材料 CMK-3，该材料由 6.5 nm 厚的中空碳棒组成，并具有 3~4 nm 宽的孔作为硫的载体。在 155℃下，通过将 CMK-3 与硫混合将硫填充到材料的孔中。该材料可使硫与导电基质充分接触。这项研究为锂硫电池的研究打开了新的大门。在早期研究中，硫主要与不同类型的碳材料结合[127]-[141]。石墨烯通常与碳纳米管结合以构建长程和短程的电子/离子传输通道[142]。许多源自生物质材料的碳衍生材料因为具有这种特性，所以在随后的研究中受到了广泛关注[143] [144] [145] [146] [147]。使用简单的碳材料可以提高电导率，但这不是最佳的解决方案。进一步的研究应集中在精心设计的导电通道，使电子可以准确地传输到导电基质表面上的硫附着点，从而促进电化学反应。值得注意的是，导电碳有利于提高电极的电导率，但同时也会降低电极的能量密度[148]。与锂离子电池的正极类似，理想的情况是将碳含量降低到 5%以下。此外，使碳含量最小可能有助于形成合适的孔隙率，提高电解液润湿性以及与多硫化物的相互作用。除直接添加碳材料外，Cai [149]使用 $Ni_3(HITP)_2$ 这种高导电性的石墨烯状 MOF 材料作为锂硫电池的正极硫载体，是一种具有平面配位金属离子和 π-π 共轭的二维分层 MOF。与传统的 MOF 材料相比，配体具有很高的电导率。在 $Ni_3(HITP)_2$ 中，Ni 原子与 dsp^2 杂化，形成二维共轭结构。粉末的电导率可以达到 200 S/m，甚至比某些活性炭材料还高。$S@Ni_3(HITP)_2$ 正极具有良好的可逆性，0.2 C 下的初始容量达到 1022 mA·h/g，在 100 个循环后仍可以保持在 703.2 mA·h/g，在 0.5 C 的 150 个循环后仍可以保持在 524.3 mA·h/g。与 MOF 材料(ZIF-67 等)相比，$Ni_3(HITP)_2$ 对多硫化物的吸附能力更强。导电 MOF 材料是一个有前途的方向，它可以避免过多添加碳材料，并且由于其金属存在，还可以改善锂硫电池的其他缺陷。例如 Co-HAB [150]，一些 MOF 已用于其他电池系统或其他领域。同时，MOF 的金属核被部分还原，并且插入其他一些离子以平衡电荷可以实现电荷离域。事实证明，该方法能够将非导电 MOF 转换为导电 MOF [151]。

5.2. 抑制穿梭效应

通过极性分子强吸附电子的特性吸附多硫化物是抑制穿梭效应的最有前途的策略之一[152] [153]。迄今为止，已开发出多种具有极性表面的主体材料，包括改性的含碳材料及其他材料[154] [155]。对于极性主体材料，必须有足够的电子导电性，以确保高负载硫电极中高效的获取电子[156]。如果强吸附剂不导电，则被吸收的多硫化锂(LiPS)将无法有效地接收电子，从而阻止了电化学氧化还原过程。在这种情况下，吸附的 LiPS 必须行进到导电基质的表面反应，这会减慢反应速度。

具有掺杂杂原子(如 N，O 或 S)的多孔碳质材料可以为 LiPSs 吸收提供出色的电导率和足够的结合位点[157]。例如，通过生物可持续性纤维素纳米晶体的自组装，合成了双重掺杂有 N 和 S 的有序纳米多孔碳[158]。N 和 S 杂原子的协同作用改变了基质的电子密度分布，从而导致更强的多硫键结合。在另一项研究中，研究者开发了硼掺杂的碳－硫(BCS)气凝胶，其中硫球为“核”，硼掺杂的石墨烯片为“壳”[159]。

硼掺杂的碳片可以通过化学相互作用和物理约束来限制 LiPS 的穿梭。硫负载量为 13.5 mg/cm^2 时，基于 BCS 气凝胶的正极在 1 C 时的初始容量可以达到 1120 mA·h/g (14.6 mA·h/cm^2)，500 个循环后最终容量为 836 mA·h/g。

极性金属氧化物，硫化物，氮化物等由于具有化学吸附多硫化物的能力而被用作载硫宿主材料[160] [161]。对于金属氧化物，研究者构建了具有卵壳结构的碳包覆的 Fe_3O_4 纳米盒[162]，碳壳提供物理阻挡，而 Fe_3O_4 核则显示出与多硫化物的强相互作用。硫载量为 5.5 mg/cm^2 时，掺入硫作为正极的卵壳纳米盒的初始容量为 6.07 mA·h/cm^2，并在在 0.1 C 下进行 200 次循环之后保持 77.4%的容量。据报道，对于氮化物，由氮化钛纳米线和掺氮石墨烯组成的复合材料可作为 Li-S 电池的独立硫宿主[163]。在 8 mA/cm^2 的电流密度和 9.6 mg/cm^2 的负载下，正极可实现 12 mA·h/cm^2 的面积容量，并在 60 个循环后保持在 9.96 mA·h/cm^2，这归因于 TiN 对多硫化物的强化学锚定作用。金属硫化物由于与 LiPS 的牢固的化学结合，也已被证明是有希望的硫主体。但是，这些金属硫化物往往会形成大颗粒和团聚，这导致 LiPS 表面积和吸附位点的减少。因此，研究者在 Li-S 电池的正极中可以引入了一种小颗粒硫化镍(NiS_2) [164]。NiS_2 化学固定在导电 RGO 上用来改善电荷转移，并形成海绵状结构以容纳大量活性物质。在硫负载为 21 mg/cm^2 的情况下，电池在 50 个循环后，正极在 0.2 C 和 13 mA·h/cm^2 的电流密度下可达到 16 mA·h/cm^2。对于金属硼化物，研究者通过化学处理生长在 CNT 上的 ZIF-67 制备了 Co_2B@CNT 的复合材料[165]。CNT 穿透 Co_2B，从而充当电子路径，使用修饰有 Co_2B@CNT 的隔膜，由于 Li_2S_4 与 Co 和 B 的强化学键合，电池在 0.5 C 时的面积容量为 5.5 mA·h/cm^2。

其他极性材料，例如共价有机骨架(COF) [166]，MOF [167]，沸石咪唑酸酯骨架(ZIF) [168]，MXene [169]，和无机－有机复合物[170]也用于防止多硫化物穿梭。例如，导电 MOF 膜在液－固界面处生长到商用隔膜上。MOF 层对 LiPS 具有高结合能。硫负载为 8 mg/cm^2 时，使用 MOF 功能化隔膜的 Li-S 电池 0.5 C 下在 200 个循环后，面积容量仍可达到 7.24 mA·h/cm^2 [170]。

加快多硫化物转化，在高负载 Li-S 电池中不可避免的多硫化物的穿梭效应还可归因于对硫的亲和力差以及氧化还原引起的在电解液中的缓慢积累的多硫化物的产生。积累的 LiPS 可能扩散到负极形成不溶的 Li_2S_2/Li_2S，无法再利用，这将进一步加剧电池的容量衰减[171] [172]。因此，据报道，基于各种极性材料提供的吸附和加速机理，研究者构建了多种能够催化多硫化物转化的材料。这些极性材料充当在吸附多硫化物的同时也能够提供充足的催化活性位点，降低了电荷转移电阻与反应极化，从而促进了多硫化物向最终反应产物硫化锂的转化。

常见的能够催化硫正极转化的材料有硫族化物[173] [174] [175]，氧化物[176] [177]，和氮化物[178]等。过渡金属化合物因其与多硫化物的强相互作用而在 Li-S 电池的催化过程中代表了一个重要的研究方向。例如，3D 石墨烯/1T MoS_2(3DG/TM)气凝胶作为 Li-S 电池的正极材料。硫负载为 10 mg/cm^2 时，该电池在 0.1 C 电流密度下可逆容量为 1181 mA·h/g，在 500 C 的高倍率下每圈仅显示了 0.08%的低容量衰减。通过比较结果表明，1T MoS_2 比 2H MoS_2(HM)表现出更好的催化能力。在循环伏安法(CV)研究中，与 3DG/HM 电极相比，3DG/TM 显示更负的负极峰值电压，更正的正极峰电压和更高的峰电流密度。此外，与 3DG/HM 相比，3DG/TM 降低了 LiPS 氧化的起始电位。而 Tafel 斜率值的降低，证明了该结构加速了多硫化物的转化[179]。Co_3S_4 纳米颗粒还用作高硫负载电池的催化剂，通过碳化到 CNTs 网络上的金属有机骨架(MOF)，将分散的 Co_3S_4 纳米颗粒(≈10 nm)嵌入到分层多孔 CNT 中。随后，将硫渗透到分层结构中，以确保与 Co_3S_4 催化位点紧密接触。在硫载量为 7.4 mg/cm^2 的情况下，优化的电极可保持≈850 mA h/g 的容量和在 5 C 下 1000 次循环后保持 85%的保留率而表现出非凡的倍率性能。

使用固态电解液(SSE)替代液态电解液是构建高性能 Li-S 电池(ASSLSBs)的一个有前途的方向，并且可能是安全可靠的便携式设备中 Li-S 电池的最终解决方案[180] [181]。除了可以避免易燃液体电解液带

来的风险外，SSE 还可以防止可溶性 LiPSs 穿梭。然而，活性材料的低电子电导率和 SSE 的低离子电导率仍然是高性能 ASSLSB 所需要解决的问题。除了导电性问题外，还应考虑 ASSLSB 中电极的机械强度[182]。与使用液体电解液的 Li-S 电池的正极不同，该电解液包含可容纳体积变化的孔，ASSLSB 的正极主要由活性材料，导电添加剂和 SSE 的致密混合物组成[183]。因此，在硫发生反应期间，刚性正极结构中会产生很大的应力，导致正极内出现裂纹，这将破坏活性材料与 SSE/导电添加剂之间的接触，从而导致容量衰减[184]。ASSLSB 的正极复合材料主要是机械混合的 S/Li_2S，两相之间的界面接触不良会导致容量降低低和速率性能变差。因此，除了对 SSE 的研究以外，还需要集中力量在正极复合材料的制造上[185]。由于活性材料(S 或 Li_2S)的导电性较差，最好减小活性材料的尺寸，以增强电子和离子的传输。因此，研究者提出了一种自下而上的方法，发明了一种嵌入碳基质中的纳米级 Li_2S 和 Li_6PS_5Cl 作为固态 Li-S 电池正极材料的复合材料[186]。制造过程包括将 Li_2S，聚乙烯吡咯烷酮(PVP，碳前体)和 Li_6PS_5Cl SSE 混合，然后共沉淀和碳化，从而使 Li_2S 纳米晶体和 Li_6PS_5Cl 纳米颗粒在碳基质中均匀分布，从而提供足够的三相接触用来改善电荷转移反应。

6. 总结与展望

随着历史的车轮滚滚向前与环保意识的与时俱进，在不久的将来，汽油车将成为历史。目前国内外的汽车市场已经将自己的研究重点放到了电动汽车上，高比能量锂离子电池作为新时代汽车储能装置的关键组成部分，目前正极材料如磷酸铁锂，锰酸锂等虽然也已经投入商用，但是层出不穷的问题，如安全性、容量保持率、倍率性能等都表明了 LMO 等正极材料还需要长足的发展才能实现全民化应用。而负极材料如石墨或硅负极等，首次库伦效率差或体积膨胀效应等问题也限制着其进一步发展。锂金属负极作为理论容量最高的负极材料，虽然也存在着诸如安全性、体积效应等问题，但是广大研究者都相信通过高效的锂负极构筑可以解决这些缺点。虽然锂硫电池正极导电性与多硫化物穿梭效应等问题一直困扰着研究者，但因硫正极令人遐想连篇的理论容量，人们采用的用于解决锂硫电池存在的问题的技术手段也走在锂电技术的时代前沿。

本文从锂金属电池研究现状出发，详细地介绍了目前锂金属电池面临着循环寿命，倍率性能以及最重要的安全性能这些问题，同时我们也从电解质和界面改性方面研究改进。目前的热门锂硫电池也亟需解决穿梭效应这个问题。但我们坚信通过研究者们前仆后继的不断努力研究，终将获得安全稳定的高锂利用率的锂硫电池。

参考文献

[1] Chen, S., Dai, F. and Cai, M. (2020) Opportunities and Challenges of High-Energy Lithium Metal Batteries for Electric Vehicle Applications. *ACS Energy Letters*, **5**, 3140. https://doi.org/10.1021/acsenergylett.0c01545

[2] Cha, C. and Yang, H.X. (1993) Recent Advances in Experimental Methods Applied to Lithium Battery Researches. *Journal of Power Sources*, **43**-**44**, 145. https://doi.org/10.1016/0378-7753(93)80111-2

[3] Andre, D., Hain, H., Lamp, P., Maglia, F. and Stiaszny, B. (2017) Future High-Energy Density Anode Materials from an Automotive Application Perspective. *Journal of Materials Chemistry A*, **5**, 17174. https://doi.org/10.1039/C7TA03108D

[4] Schmuch, R., Wagner, R., Hörpel, G., Placke, T. and Winter, M. (2018) Performance and Cost of Materials for Lithium-Based Rechargeable Automotive Batteries. *Nature Energy*, **3**, 267. https://doi.org/10.1038/s41560-018-0107-2

[5] Betz, J., Bieker, G., Meister, P., Placke, T., Winter, M. and Schmuch, R. (2019) Theoretical versus Practical Energy: A Plea for More Transparency in the Energy Calculation of Different Rechargeable Battery Systems. *Advanced Energy Materials*, **9**, Article ID: 1803170. https://doi.org/10.1002/aenm.201803170

[6] Louli, A.J., Eldesoky, A., Weber, R., Genovese, M., Coon, M., deGooyer, J., Deng, Z., White, R.T., Lee, J., Rodgers, T., Petibon, R., Hy, S., Cheng, S.J.H. and Dahn, J.R. (2020) Diagnosing and Correcting Anode-Free Cell Failure via Electrolyte and Morphological Analysis. *Nature Energy*, **5**, 693. https://doi.org/10.1038/s41560-020-0668-8

[7] Liu, J., Bao, Z., Cui, Y., Dufek, E.J., Goodenough, J.B., Khalifah, P., Li, Q., Liaw, B.Y., Liu, P., Manthiram, A., Meng, Y.S., Subramanian, V.R., Toney, M.F., Viswanathan, V.V., Whittingham, M.S., Xiao, J., Xu, W., Yang, J., Yang, X.-Q. and Zhang, J.-G. (2019) Pathways for Practical High-Energy Long-Cycling Lithium Metal Batteries. *Nature Energy*, **4**, 180. https://doi.org/10.1038/s41560-019-0338-x

[8] Zhan, X., Bonnett, J.F., Engelhard, M.H., Reed, D.M., Sprenkle, V.L. and Li, G. (2020) A High-Performance Na-Al Battery Based on Reversible $NaAlCl_4$ Catholyte. *Advanced Energy Materials*, **10**, Article ID: 2001378. https://doi.org/10.1002/aenm.202001378

[9] Hagen, M., Hanselmann, D., Ahlbrecht, K., Maça, R., Gerber, D. and Tübke, J. (2015) Lithium-Sulfur Cells: The Gap between the State-of-the-Art and the Requirements for High Energy Battery Cells. *Advanced Energy Materials*, **5**, Article ID: 1401986. https://doi.org/10.1002/aenm.201401986

[10] Cano, Z.P., Banham, D., Ye, S., Hintennach, A., Lu, J., Fowler, M. and Chen, Z. (2018) Batteries and Fuel Cells for Emerging Electric Vehicle Markets. *Nature Energy*, **3**, 279. https://doi.org/10.1038/s41560-018-0108-1

[11] Chen, S., Niu, C., Lee, H., Li, Q., Yu, L., Xu, W., Zhang, J.-G., Dufek, E.J., Whittingham, M.S., Meng, S., Xiao, J. and Liu, J. (2019) Critical Parameters for Evaluating Coin Cells and Pouch Cells of Rechargeable Li-Metal Batteries. *Joule*, **3**, 1094. https://doi.org/10.1016/j.joule.2019.02.004

[12] Zhu, K., Wang, C., Chi, Z., Ke, F., Yang, Y., Wang, A., Wang, W. and Miao, L. (2019) How Far Away Are Lithium-Sulfur Batteries from Commercialization? *Frontiers in Energy Research*, **7**, 123. https://doi.org/10.3389/fenrg.2019.00123

[13] Jaguemont, J., Boulon, L. and Dubé, Y. (2016) A Comprehensive Review of Lithium-Ion Batteries Used in Hybrid and Electric Vehicles at Cold Temperatures. *Applied Energy*, **164**, 99. https://doi.org/10.1016/j.apenergy.2015.11.034

[14] Raj, H., Rani, S. and Sil, A. (2018) Antisite Defects in Sol-Gel-Synthesized $LiFePO_4$ at Higher Temperature: Effect on Lithium-Ion Diffusion. *ChemElectroChem*, **5**, 3525. https://doi.org/10.1002/celc.201800889

[15] Ouyang, D., Chen, M., Huang, Q., Weng, J., Wang, Z. and Wang, J. (2019) A Review on the Thermal Hazards of the Lithium-Ion Battery and the Corresponding Countermeasures. *Applied Sciences*, **9**, 2483. https://doi.org/10.3390/app9122483

[16] Huang, J., Qin, D. and Peng, Z. (2015) Effect of Energy-Regenerative Braking on Electric Vehicle Battery Thermal Management and Control Method Based on Simulation Investigation. *Energy Conversion and Management*, **105**, 1157. https://doi.org/10.1016/j.enconman.2015.08.080

[17] Zhang, Y., Shang, Y., Cui, N. and Zhang, C. (2018) Parameters Identification and Sensitive Characteristics Analysis for Lithium-Ion Batteries of Electric Vehicles. *Energies*, **11**, 19. https://doi.org/10.3390/en11010019

[18] Xu, K. (2004) Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries. *Chemical Reviews*, **104**, 4303. https://doi.org/10.1021/cr030203g

[19] Waldmann, T., Hogg, B.-I. and Wohlfahrt-Mehrens, M. (2018) Li Plating as Unwanted Side Reaction in Commercial Li-Ion Cells: A Review. *Journal of Power Sources*, **384**, 107. https://doi.org/10.1016/j.jpowsour.2018.02.063

[20] Li, Z., Huang, J., Yann Liaw, B., Metzler, V. and Zhang, J. (2014) A Review of Lithium Deposition in Lithium-Ion and Lithium Metal Secondary Batteries. *Journal of Power Sources*, **254**, 168. https://doi.org/10.1016/j.jpowsour.2013.12.099

[21] Akolkar, R. (2014) Modeling Dendrite Growth during Lithium Electrodeposition at Sub-Ambient Temperature. *Journal of Power Sources*, **246**, 84. https://doi.org/10.1016/j.jpowsour.2013.07.056

[22] Gabrisch, H., Ozawa, Y. and Yazami, R. (2006) Crystal Structure Studies of Thermally Aged $LiCoO_2$ and $LiMn_2O_4$ Cathodes. *Electrochimica Acta*, **52**, 1499. https://doi.org/10.1016/j.electacta.2006.02.050

[23] Ecker, M., Nieto, N., Käbitz, S., Schmalstieg, J., Blanke, H., Warnecke, A. and Sauer, D.U. (2014) Calendar and Cycle Life Study of $Li(NiMnCo)O_2$-Based 18650 Lithium-Ion Batteries. *Journal of Power Sources*, **248**, 839. https://doi.org/10.1016/j.jpowsour.2013.09.143

[24] Handel, P., Fauler, G., Kapper, K., Schmuck, M., Stangl, C., Fischer, R., Uhlig, F. and Koller, S. (2014) Thermal Aging of Electrolytes Used in Lithium-Ion Batteries: An Investigation of the Impact of Protic Impurities and Different Housing Materials. *Journal of Power Sources*, **267**, 255. https://doi.org/10.1016/j.jpowsour.2014.05.080

[25] Bodenes, L., Naturel, R., Martinez, H., Dedryvère, R., Menetrier, M., Croguennec, L., Pérès, J.-P., Tessier, C. and Fischer, F. (2013) Lithium Secondary Batteries Working at Very High Temperature: Capacity Fade and Understanding of Aging Mechanisms. *Journal of Power Sources*, **236**, 265. https://doi.org/10.1016/j.jpowsour.2013.02.067

[26] Park, H.E., Hong, C.H. and Yoon, W.Y. (2008) The Effect of Internal Resistance on Dendritic Growth on Lithium Metal Electrodes in the Lithium Secondary Batteries. *Journal of Power Sources*, **178**, 765. https://doi.org/10.1016/j.jpowsour.2007.12.081

[27] Mogi, R., Inaba, M., Abe, T. and Ogumi, Z. (2001) *In Situ* Atomic Force Microscopy Observation of Lithium Deposi-

tion at an Elevated Temperature. *Journal of Power Sources*, **97-98**, 265. https://doi.org/10.1016/S0378-7753(01)00511-0

[28] Yan, K., Wang, J., Zhao, S., Zhou, D., Sun, B., Cui, Y. and Wang, G. (2019) Temperature-Dependent Nucleation and Growth of Dendrite-Free Lithium Metal Anodes. *Angewandte Chemie International Edition*, **58**, 11364. https://doi.org/10.1002/anie.201905251

[29] Dolle, M., Sannier, L., Beaudion, B. and Trentin, M. (2002) Live Scanning Electron Microscope Observations of Dendritic Growth in Lithium-Polymer Cells. *Electrochemical and Solid-State Letters*, **5**, A286-A289. https://doi.org/10.1149/1.1519970

[30] Crakawa, M., Tobishima, S., Nemoto, Y. and Ichimura, M. (1996) Lithium Electrode Cycleability and Morphology Dependence on Current Density. *Journal of Power Sources*, **43-44**, 27. https://doi.org/10.1016/0378-7753(93)80099-B

[31] Chandrasekar, M.S. and Pushpavanam, M. (2008) Pulse and Pulse Reverse Plating-Conceptual, Advantages and Applications. *Electrochimica Acta*, **53**, 3313. https://doi.org/10.1016/j.electacta.2007.11.054

[32] Lin, D., Liu, Y. and Cui, Y. (2017) Reviving the Lithium Metal Anode for High-Energy Batteries. *Nature Nanotechnology*, **12**, 194. https://doi.org/10.1038/nnano.2017.16

[33] Niu, C., Lee, H., Chen, S., Li, Q., Du, J., Xu, W., Zhang, J.-G., Whittingham, M.S., Xiao, J. and Liu, J. (2019) High-Energy Lithium Metal Pouch Cells with Limited Anode Swelling and Long Stable Cycles. *Nature Energy*, **4**, 551. https://doi.org/10.1038/s41560-019-0390-6

[34] Louli, A.J., Genovese, M., Weber, R., Hames, S.G., Logan, E.R. and Dahn, J.R. (2019) Exploring the Impact of Mechanical Pressure on the Performance of Anode-Free Lithium Metal Cells. *Journal of the Electrochemical Society*, **166**, A1291-A1299. https://doi.org/10.1149/2.0091908jes

[35] Guida, P. and Vazquez, M.E. (2007) Cytotoxic and Cell Cycle Effects in Human Neuronal Progenitor Cells Exposed to 1GeV/n Fe Ions. *Advances in Space Research*, **39**, 1004. https://doi.org/10.1016/j.asr.2006.12.009

[36] Feng, X., Ouyang, M., Liu, X., Lu, L., Xia, Y. and He, X. (2018) Thermal Runaway Mechanism of Lithium-Ion Battery for Electric Vehicles: A Review. *Energy Storage Materials*, **10**, 246. https://doi.org/10.1016/j.ensm.2017.05.013

[37] Mohanty, D., Hockaday, E., Li, J., Hensley, D.K., Daniel, C. and Wood, D.L. (2016) Effect of Electrode Manufacturing Defects on Electrochemical Performance of Lithium-Ion Batteries: Cognizance of the Battery Failure Sources. *Journal of Power Sources*, **312**, 70. https://doi.org/10.1016/j.jpowsour.2016.02.007

[38] Ruiz, V., Pfrang, A., Kriston, A., Omar, N., van den Bossche, P. and Boon-Brett, L. (2018) A Review of International Abuse Testing Standards and Regulations for Lithium-Ion Batteries in Electric and Hybrid Electric Vehicles. *Renewable and Sustainable Energy Reviews*, **81**, 1427. https://doi.org/10.1016/j.rser.2017.05.195

[39] Zheng, J., Kim, M.S., Tu, Z., Choudhury, S., Tang, T. and Archer, L.A. (2020) Regulating Electrodeposition Morphology of Lithium: Towards Commercially Relevant Secondary Li Metal Batteries. *Chemical Society Reviews*, **49**, 2701. https://doi.org/10.1039/C9CS00883G

[40] Cheng, X.-B., Zhang, R., Zhao, C.-Z. and Zhang, Q. (2017) Toward Safe Lithium Metal Anode in Rechargeable Batteries: A Review. *Chemical Reviews*, **117**, 10403. https://doi.org/10.1021/acs.chemrev.7b00115

[41] Li, S., Jiang, M., Xie, Y., Xu, H., Jia, J. and Li, J. (2018) Developing High-Performance Lithium Metal Anode in Liquid Electrolytes: Challenges and Progress. *Advanced Materials*, **30**, e1706375. https://doi.org/10.1002/adma.201706375

[42] Brandt, K. (1994) Historical Development of Secondary Lithium Batteries. *Solid State Ionics*, **69**, 173. https://doi.org/10.1016/0167-2738(94)90408-1

[43] Schiemann, M., Bergthorson, J., Fischer, P., Scherer, V., Taroata, D. and Schmid, G. (2016) A Review on Lithium Combustion. *Applied Energy*, **162**, 948. https://doi.org/10.1016/j.apenergy.2015.10.172

[44] Fang, C., Wang, X. and Meng, Y.S. (2019) Key Issues Hindering a Practical Lithium-Metal Anode. *Trends in Chemistry*, **1**, 152. https://doi.org/10.1016/j.trechm.2019.02.015

[45] Guo, Y., Li, H. and Zhai, T. (2017) Reviving Lithium-Metal Anodes for Next-Generation High-Energy Batteries. *Advanced Materials*, **29**, Article ID: 1702165. https://doi.org/10.1002/adma.201700007

[46] Wang, X., Zhang, M., Alvarado, J., Wang, S., Sina, M., Lu, B., Bouwer, J., Xu, W., Xiao, J., Zhang, J.-G., Liu, J. and Meng, Y.S. (2017) New Insights on the Structure of Electrochemically Deposited Lithium Metal and Its Solid Electrolyte Interphases via Cryogenic TEM. *Nano Letters*, **17**, 7606. https://doi.org/10.1021/acs.nanolett.7b03606

[47] Li, Y., Li, Y., Pei, A., Yan, K., Sun, Y., Wu, C.-L., Joubert, L.-M., Chin, R., Koh, A.L., Yu, Y., Perrino, J., Butz, B., Chu, S. and Cui, Y. (2017) Atomic Structure of Sensitive Battery Materials and Interfaces Revealed by Cryo-Electron Microscopy. *Science*, **358**, 506. https://doi.org/10.1126/science.aam6014

[48] Zachman, M.J., Tu, Z., Choudhury, S., Archer, L.A. and Kourkoutis, L.F. (2018) Cryo-STEM Mapping of Solid-Liquid Interfaces and Dendrites in Lithium-Metal Batteries. *Nature*, **560**, 345.

https://doi.org/10.1038/s41586-018-0397-3

[49] Fang, C., Li, J., Zhang, M., Zhang, Y., Yang, F., Lee, J.Z., Lee, M.-H., Alvarado, J., Schroeder, M.A., Yang, Y., Lu, B., Williams, N., Ceja, M., Li Yang., Cai, M., Gu, J., Xu, K., Wang, X. and Meng, Y.S. (2019) Quantifying Inactive Lithium in Lithium Metal Batteries. *Nature*, **572**, 511. https://doi.org/10.1038/s41586-019-1481-z

[50] Lu, Y., Tu, Z. and Archer, L.A. (2014) Stable Lithium Electrodeposition in Liquid and Nanoporous Solid Electrolytes. *Nature Materials*, **13**, 961. https://doi.org/10.1038/nmat4041

[51] Zhang, Y., Qian, J., Xu, W., Russell, S.M., Chen, X., Nasybulin, E., Bhattacharya, P., Engelhard, M.H., Mei, D., Cao, R., Ding, F., Cresce, A.V., Xu, K. and Zhang, J.-G. (2014) Dendrite-Free Lithium Deposition with Self-Aligned Nanorod Structure. *Nano Letters*, **14**, 6889. https://doi.org/10.1021/nl5039117

[52] Yu, Z., Wang, H., Kong, X., Huang, W., Tsao, Y., Mackanic, D.G., Wang, K., Wang, X., Huang, W., Choudhury, S., Zheng, Y., Amanchukwu, C.V., Hung, S.T., Ma, Y., Lomeli, E.G., Qin, J., Cui, Y. and Bao, Z. (2020) Molecular Design for Electrolyte Solvents Enabling Energy-Dense and Long-Cycling Lithium Metal Batteries. *Nature Energy*, **5**, 526. https://doi.org/10.1038/s41560-020-0634-5

[53] Weber, R., Genovese, M., Louli, A.J., Hames, S., Martin, C., Hill, I.G. and Dahn, J.R. (2019) Long Cycle Life and Dendrite-Free Lithium Morphology in Anode-Free Lithium Pouch Cells Enabled by a Dual-Salt Liquid Electrolyte. *Nature Energy*, **4**, 683. https://doi.org/10.1038/s41560-019-0428-9

[54] Rustomji, C.S., Yang, Y., Kim, T.K., Mac, J., Kim, Y.J., Caldwell, E., Chung, H. and Meng, Y.S. (2017) Liquefied Gas Electrolytes for Electrochemical Energy Storage Devices. *Science*, **356**, 1351. https://doi.org/10.1126/science.aal4263

[55] Yang, Y., Davies, D.M., Yin, Y., Borodin, O., Lee, J.Z., Fang, C., Olguin, M., Zhang, Y., Sablina, E.S., Wang, X., Rustomji, C.S. and Meng, Y.S. (2019) High-Efficiency Lithium-Metal Anode Enabled by Liquefied Gas Electrolytes. *Joule*, **3**, 1986. https://doi.org/10.1016/j.joule.2019.06.008

[56] Yang, Y., Yin, Y., Davies, D.M., Zhang, M., Mayer, M., Zhang, Y., Sablina, E.S., Wang, S., Lee, J.Z., Borodin, O., Rustomji, C.S. and Meng, Y.S. (2020) Liquefied Gas Electrolytes for Wide-Temperature Lithium Metal Batteries. *Energy & Environmental Science*, **13**, 2209. https://doi.org/10.1039/D0EE01446J

[57] Chawla, N., Bharti, N. and Singh, S. (2019) Recent Advances in Non-Flammable Electrolytes for Safer Lithium-Ion Batteries. *Batteries*, **5**, 19. https://doi.org/10.3390/batteries5010019

[58] Chen, S., Zheng, J., Yu, L., Ren, X., Engelhard, M.H., Niu, C., Lee, H., Xu, W., Xiao, J., Liu, J. and Zhang, J.-G. (2018) High-Efficiency Lithium Metal Batteries with Fire-Retardant Electrolytes. *Joule*, **2**, 1548. https://doi.org/10.1016/j.joule.2018.05.002

[59] Fan, X., Chen, L., Borodin, O., Ji, X., Chen, J., Hou, S., Deng, T., Zheng, J., Yang, C., Liou, S.-C., Amine, K., Xu, K. and Wang, C. (2018) Non-Flammable Electrolyte Enables Li-Metal Batteries with Aggressive Cathode Chemistries. *Nature Nanotechnology*, **13**, 715. https://doi.org/10.1038/s41565-018-0183-2

[60] Qian, J., Henderson, W.A., Xu, W., Bhattacharya, P., Engelhard, M., Borodin, O. and Zhang, J.-G. (2015) High Rate and Stable Cycling of Lithium Metal Anode. *Nature Communications*, **6**, 6362. https://doi.org/10.1038/ncomms7362

[61] Janek, J. and Zeier, W.G. (2016) A Solid Future for Battery Development. *Nature Energy*, **1**, 16141. https://doi.org/10.1038/nenergy.2016.141

[62] Chen, S., Zheng, J., Mei, D., Han, K.S., Engelhard, M.H., Zhao, W., Xu, W., Liu, J. and Zhang, J.-G. (2018) High-Voltage Lithium-Metal Batteries Enabled by Localized High-Concentration Electrolytes. *Advanced Materials*, **30**, e1706102. https://doi.org/10.1002/adma.201706102

[63] Park, K. and Goodenough, J.B. (2017) Dendrite-Suppressed Lithium Plating from a Liquid Electrolyte via Wetting of Li_3N. *Advanced Energy Materials*, **7**, Article ID: 1700732. https://doi.org/10.1002/aenm.201700732

[64] Li, N.-W., Yin, Y.-X., Yang, C.-P. and Guo, Y.-G. (2016) An Artificial Solid Electrolyte Interphase Layer for Stable Lithium Metal Anodes. *Advanced Materials*, **28**, 1853. https://doi.org/10.1002/adma.201504526

[65] Gao, Y., Zhao, Y., Li, Y.C., Huang, Q., Mallouk, T.E. and Wang, D. (2017) Interfacial Chemistry Regulation via a Skin-Grafting Strategy Enables High-Performance Lithium-Metal Batteries. *Journal of the American Chemical Society*, **139**, 15288. https://doi.org/10.1021/jacs.7b06437

[66] Gao, Y., Yan, Z., Gray, J.L., He, X., Wang, D., Chen, T., Huang, Q., Li, Y.C., Wang, H., Kim, S.H., Mallouk, T.E. and Wang, D. (2019) Polymer-Inorganic Solid-Electrolyte Interphase for Stable Lithium Metal Batteries under Lean Electrolyte Conditions. *Nature Materials*, **18**, 384. https://doi.org/10.1038/s41563-019-0305-8

[67] Gao, Y., Rojas, T., Wang, K., Liu, S., Wang, D., Chen, T., Wang, H., Ngo, A.T. and Wang, D. (2020) Low-Temperature and High-Rate-Charging Lithium Metal Batteries Enabled by an Electrochemically Active Monolayer-Regulated Interface. *Nature Energy*, **5**, 534. https://doi.org/10.1038/s41560-020-0640-7

[68] Liu, K., Zhuo, D., Lee, H.-W., Liu, W., Lin, D., Lu, Y. and Cui, Y. (2017) Extending the Life of Lithium-Based Re-

chargeable Batteries by Reaction of Lithium Dendrites with a Novel Silica Nanoparticle Sandwiched Separator. *Advanced Materials*, **29**, Article ID: 1603987. https://doi.org/10.1002/adma.201603987

[69] Liu, Y., Liu, Q., Le, X., Liu, Y., Yang, F., Stach, E.A. and Xie, J. (2017) Making Li-Metal Electrodes Rechargeable by Controlling the Dendrite Growth Direction. *Nature Energy*, **2**, 17083. https://doi.org/10.1038/nenergy.2017.83

[70] Lin, D., Zhuo, D., Liu, Y. and Cui, Y. (2016) All-Integrated Bifunctional Separator for Li Dendrite Detection via Novel Solution Synthesis of a Thermostable Polyimide Separator. *Journal of the American Chemical Society*, **138**, 11044. https://doi.org/10.1021/jacs.6b06324

[71] Pan, R., Sun, R., Wang, Z., Lindh, J., Edström, K., Strømme, M. and Nyholm, L. (2019) Sandwich-Structured Nano/Micro Fiber-Based Separators for Lithium Metal Batteries. *Nano Energy*, **55**, 316. https://doi.org/10.1016/j.nanoen.2018.11.005

[72] Liang, J., Chen, Q., Liao, X., Yao, P., Zhu, B., Lv, G., Wang, X., Chen, X. and Zhu, J. (2020) A Nano-Shield Design for Separators to Resist Dendrite Formation in Lithium-Metal Batteries. *Angewandte Chemie International Edition*, **59**, 6561. https://doi.org/10.1002/anie.201915440

[73] Tang, Z., Li, S., Li, Y., Xu, H., Yu, Y., Huang, Y. and Li, J. (2020) Lithium Metal Electrode Protected by Stiff and Tough Self-Compacting Separator. *Nano Energy*, **69**, Article ID: 104399. https://doi.org/10.1016/j.nanoen.2019.104399

[74] Kim, P.J. and Pol, V.G. (2018) High Performance Lithium Metal Batteries Enabled by Surface Tailoring of Polypropylene Separator with a Polydopamine/Graphene Layer. *Advanced Energy Materials*, **8**, Article ID: 1802665. https://doi.org/10.1002/aenm.201802665

[75] Lee, H., Yanilmaz, M., Toprakci, O., Fu, K. and Zhang, X. (2014) A Review of Recent Developments in Membrane Separators for Rechargeable Lithium-Ion Batteries. *Energy & Environmental Science*, **7**, 3857. https://doi.org/10.1039/C4EE01432D

[76] Feng, X., Fang, M., He, X., Ouyang, M., Lu, L., Wang, H. and Zhang, M. (2014) Thermal Runaway Features of Large Format Prismatic Lithium Ion Battery Using Extended Volume Accelerating Rate Calorimetry. *Journal of Power Sources*, **255**, 294. https://doi.org/10.1016/j.jpowsour.2014.01.005

[77] Jeong, H.-S., Kim, D.-W., Jeong, Y. U. and Lee, S.-Y. (2010) Effect of Phase Inversion on Microporous Structure Development of Al_2O_3/Poly(vinylidene fluoride-hexafluoropropylene) Based Ceramic Composite Separators for Lithium-Ion Batteries. *Journal of Power Sources*, **195**, 6116. https://doi.org/10.1016/j.jpowsour.2009.10.085

[78] Shi, C., Zhang, P., Huang, S., He, X., Yang, P., Wu, D., Sun, D. and Zhao, J. (2015) Functional Separator Consisted of Polyimide Nonwoven Fabrics and Polyethylene Coating Layer for Lithium-Ion Batteries. *Journal of Power Sources*, **298**, 158. https://doi.org/10.1016/j.jpowsour.2015.08.008

[79] Lee, J., Lee, C.-L., Park, K. and Kim, I.-D. (2014) Synthesis of an Al_2O_3-Coated Polyimide Nanofiber Mat and Its Electrochemical Characteristics as a Separator for Lithium Ion Batteries. *Journal of Power Sources*, **248**, 1211. https://doi.org/10.1016/j.jpowsour.2013.10.056

[80] Zhang, Y., Luo, W., Wang, C., Li, Y., Chen, C., Song, J., Dai, J., Hitz, E.M., Xu, S., Yang, C., Wang, Y. and Hu, L. (2017) High-Capacity, Low-Tortuosity, and Channel-Guided Lithium Metal Anode. *Proceedings of the National Academy of Sciences of the United States of America*, **114**, 3584. https://doi.org/10.1073/pnas.1618871114

[81] Ye, H., Xin, S., Yin, Y.-X., Li, J.-Y., Guo, Y.-G. and Wan, L.-J. (2017) Stable Li Plating/Stripping Electrochemistry Realized by a Hybrid Li Reservoir in Spherical Carbon Granules with 3d Conducting Skeletons. *Journal of the American Chemical Society*, **139**, 5916. https://doi.org/10.1021/jacs.7b01763

[82] Yang, C., Zhang, L., Liu, B., Xu, S., Hamann, T., McOwen, D., Dai, J., Luo, W., Gong, Y., Wachsman, E.D. and Hu, L. (2018) Continuous Plating/Stripping Behavior of Solid-State Lithium Metal Anode in a 3D Ion-Conductive Framework. *Proceedings of the National Academy of Sciences of the United States of America*, **115**, 3770. https://doi.org/10.1073/pnas.1719758115

[83] Liang, Z., Lin, D., Zhao, J., Lu, Z., Liu, Y., Liu, C., Lu, Y., Wang, H., Yan, K., Tao, X. and Cui, Y. (2016) Composite Lithium Metal Anode by Melt Infusion of Lithium into a 3D Conducting Scaffold with Lithiophilic Coating. *Proceedings of the National Academy of Sciences of the United States of America*, **113**, 2862. https://doi.org/10.1073/pnas.1518188113

[84] Suriyakumar, S. and Stephan, A.M. (2020) Mitigation of Polysulfide Shuttling by Interlayer/Permselective Separators in Lithium-Sulfur Batteries. *ACS Applied Energy Materials*, **3**, 8095. https://doi.org/10.1021/acsaem.0c01354

[85] Goodenough, J.B. and Kim, Y. (2010) Challenges for Rechargeable Li Batteries. *Chemistry of Materials*, **22**, 587. https://doi.org/10.1021/cm901452z

[86] Whittingham, M.S. (2004) Lithium Batteries and Cathode Materials. *Chemical Reviews*, **104**, 4271. https://doi.org/10.1021/cr020731c

[87] Dunn, B., Kamath, H. and Tarascon, J.-M. (2011) Electrical Energy Storage for the Grid: A Battery of Choices.

Science, **334**, 928. https://doi.org/10.1126/science.1212741

[88] Yoo, H.D., Markevich, E., Salitra, G., Sharon, D. and Aurbach, D. (2014) On the Challenge of Developing Advanced Technologies for Electrochemical Energy Storage and Conversion. *Materials Today*, **17**, 110. https://doi.org/10.1016/j.mattod.2014.02.014

[89] Wang, F., Liang, C.-S., Pang, Y., Xu, Y.-H. and Luo, Z.-K. (2013) Electrochemical Performance of a Nonaqueous Rechargeable Lithium-Air Battery. *Ionics*, **19**, 1791. https://doi.org/10.1007/s11581-013-0932-z

[90] Christensen, J., Albertus, P., Sanchez-Carrera, R.S., Lohmann, T., Kozinsky, B., Liedtke, R., Ahmed, J. and Kojic, A. (2011) A Critical Review of Li/Air Batteries. *Journal of the Electrochemical Society*, **159**, R1-R30. https://doi.org/10.1149/2.086202jes

[91] Li, F., Zhang, T. and Zhou, H. (2013) Challenges of Non-Aqueous Li-O_2 Batteries: Electrolytes, Catalysts, and Anodes. *Energy & Environmental Science*, **6**, 1125. https://doi.org/10.1039/c3ee00053b

[92] Manthiram, A., Fu, Y., Chung, S.-H., Zu, C. and Su, Y.-S. (2014) Rechargeable Lithium-Sulfur Batteries. *Chemical Reviews*, **114**, 11751. https://doi.org/10.1021/cr500062v

[93] Ji, X. and Nazar, L.F. (2010) Advances in Li-S Batteries. *Journal of Materials Chemistry*, **20**, 9821. https://doi.org/10.1039/b925751a

[94] Ji, X., Lee, K.T. and Nazar, L.F. (2009) A Highly Ordered Nanostructured Carbon-Sulfur Cathode for Lithium-Sulphur Batteries. *Nature Materials*, **8**, 500. https://doi.org/10.1038/nmat2460

[95] Pang, Q., Liang, X., Kwok, C.Y. and Nazar, L.F. (2015) Review—The Importance of Chemical Interactions between Sulfur Host Materials and Lithium Polysulfides for Advanced Lithium-Sulfur Batteries. *Journal of the Electrochemical Society*, **162**, A2567-A2576. https://doi.org/10.1149/2.0171514jes

[96] Cleaver, T., Kovacik, P., Marinescu, M., Zhang, T. and Offer, G. (2018) Perspective Commercializing Lithium Sulfur Batteries: Are We Doing the Right Research? *Journal of the Electrochemical Society*, **165**, A6029-A6033. https://doi.org/10.1149/2.0071801jes

[97] Rosenman, A., Markevich, E., Salitra, G., Aurbach, D., Garsuch, A. and Chesneau, F.F. (2015) Review on Li-thium-Sulfur Battery Systems: An Integral Perspective. *Advanced Energy Materials*, **5**, Article ID: 1500212. https://doi.org/10.1002/aenm.201500212

[98] Yang, Y., Zheng, G. and Cui, Y. (2013) Nanostructured Sulfur Cathodes. *Chemical Society Reviews*, **42**, 3018. https://doi.org/10.1039/c2cs35256g

[99] Xin, S., Gu, L., Zhao, N.-H., Yin, Y.-X., Zhou, L.-J., Guo, Y.-G. and Wan, L.-J. (2012) Smaller Sulfur Molecules Promise Better Lithium-Sulfur Batteries. *Journal of the American Chemical Society*, **134**, 18510. https://doi.org/10.1021/ja308170k

[100] Liang, C., Dudney, N.J. and Howe, J.Y. (2009) Hierarchically Structured Sulfur/Carbon Nanocomposite Material for High-Energy Lithium Battery. *Chemistry of Materials*, **21**, 4724. https://doi.org/10.1021/cm902050j

[101] Suriyakumar, S., Angulakshmi, N. and Stephan, A.M. (2017) Better Performing Composite Cathode Encompassing Graphene and Magnesium Aluminate for Li-S Batteries. *Nano-Structures & Nano-Objects*, **11**, 46. https://doi.org/10.1016/j.nanoso.2017.06.001

[102] Wang, Z., Wang, B., Yang, Y., Cui, Y., Wang, Z., Chen, B. and Qian, G. (2015) Mixed-Metal-Organic Framework with Effective Lewis Acidic Sites for Sulfur Confinement in High-Performance Lithium-Sulfur Batteries. *ACS Applied Materials & Interfaces*, **7**, 20999. https://doi.org/10.1021/acsami.5b07024

[103] Yuan, L.-X., Wang, Z.-H., Zhang, W.-X., Hu, X.-L., Chen, J.-T., Huang, Y.-H. and Goodenough, J.B. (2011) Devel-opment and Challenges of $LiFePO_4$ Cathode Material for Lithium-Ion Batteries. *Energy & Environmental Science*, **4**, 269. https://doi.org/10.1039/C0EE00029A

[104] Ji, L., Rao, M., Zheng, H., Zhang, L., Li, Y., Duan, W., Guo, J., Cairns, E.. and Zhang, Y. (2011) Graphene Oxide as a Sulfur Immobilizer in High Performance Lithium-Sulfur Cells. *Journal of the American Chemical Society*, **133**, 18522. https://doi.org/10.1021/ja206955k

[105] Park, H. and Siegel, D.J. (2017) Tuning the Adsorption of Polysulfides in Lithium-Sulfur Batteries with Metal-Organic Frameworks. *Chemistry of Materials*, **29**, 4932. https://doi.org/10.1021/acs.chemmater.7b01166

[106] Suriyakumar, S., Madasamy, K., Kathiresan, M., Alkordi, M.H. and Stephan, A.M. (2018) Improved Cycling Perfor-mance of Lithium-Sulfur Cell through Supramolecular Interactions. *The Journal of Physical Chemistry C*, **122**, 27843. https://doi.org/10.1021/acs.jpcc.8b08785

[107] Chang, D.-R., Lee, S.-H., Kim, S.-W. and Kim, H.-T. (2002) Binary Electrolyte Based on Tetra(ethylene glycol) Di-methyl Ether and 1,3-Dioxolane for Lithium-Sulfur Battery. *Journal of Power Sources*, **112**, 452. https://doi.org/10.1016/S0378-7753(02)00418-4

[108] Pan, Q., Smith, D.M., Qi, H., Wang, S. and Li, C.Y. (2015) Hybrid Electrolytes with Controlled Network Structures for

Lithium Metal Batteries. *Advanced Materials*, **27**, 5995. https://doi.org/10.1002/adma.201502059

[109] Scheers, J., Fantini, S. and Johansson, P. (2014) A Review of Electrolytes for Lithium-Sulphur Batteries. *Journal of Power Sources*, **255**, 204. https://doi.org/10.1016/j.jpowsour.2014.01.023

[110] Suriyakumar, S., Kathiresan, M. and Stephan, A.M. (2019) Charge-Discharge and Interfacial Properties of Ionic Liquid-Added Hybrid Electrolytes for Lithium-Sulfur Batteries. *ACS Omega*, **4**, 3894. https://doi.org/10.1021/acsomega.8b03544

[111] Barchasz, C., Leprêtre, J.-C., Alloin, F. and Patoux, S. (2012) New Insights into the Limiting Parameters of the Li-S Rechargeable Cell. *Journal of Power Sources*, **199**, 322. https://doi.org/10.1016/j.jpowsour.2011.07.021

[112] Rezqita, A., Sauer, M., Foelske, A., Kronberger, H. and Trifonova, A. (2017) The Effect of Electrolyte Additives on Electrochemical Performance of Silicon/Mesoporous Carbon (Si/MC) for Anode Materials for Lithium-Ion Batteries. *Electrochimica Acta*, **247**, 600. https://doi.org/10.1016/j.electacta.2017.06.128

[113] Raja, M., Angulakshmi, N. and Stephan, A.M. (2016) Sisal-Derived Activated Carbons for Cost-Effective Lithium-Sulfur Batteries. *RSC Advances*, **6**, 13772. https://doi.org/10.1039/C5RA25850B

[114] Mikhaylik, Y.V. and Akridge, J.R. (2004) Polysulfide Shuttle Study in the Liõs Battery System. *Journal of the Electrochemical Society*, **151**, A1969-A1976. https://doi.org/10.1149/1.1806394

[115] Yan, J., Liu, X. and Li, B. (2016) Capacity Fade Analysis of Sulfur Cathodes in Lithium-Sulfur Batteries. *Advanced Science*, **3**, Article ID: 1600101. https://doi.org/10.1002/advs.201600101

[116] Yan, J., Liu, X., Wang, X. and Li, B. (2015) Long-Life, High-Efficiency Lithium/Sulfur Batteries from Sulfurized Carbon Nanotube Cathodes. *Journal of Materials Chemistry A*, **3**, 10127. https://doi.org/10.1039/C5TA00286A

[117] Barchasz, C., Molton, F., Duboc, C., Leprêtre, J.-C., Patoux, S. and Alloin, F. (2012) Lithium/Sulfur Cell Discharge mechanism: An Original Approach for Intermediate Species Identification. *Analytical Chemistry*, **84**, 3973. https://doi.org/10.1021/ac2032244

[118] Nelson, J., Misra, S., Yang, Y., Jackson, A., Liu, Y., Wang, H., Dai, H. andrews, J.C., Cui, Y. and Toney, M.F. (2012) In Operando X-Ray Diffraction and Transmission X-Ray Microscopy of Lithium Sulfur Batteries. *Journal of the American Chemical Society*, **134**, 6337. https://doi.org/10.1021/ja2121926

[119] Wang, L., Zhang, T., Yang, S., Cheng, F., Liang, J. and Chen, J. (2013) A Quantum-Chemical Study on the Discharge Reaction Mechanism of Lithium-Sulfur Batteries. *Journal of Energy Chemistry*, **22**, 72. https://doi.org/10.1016/S2095-4956(13)60009-1

[120] Mistry, A.N. and Mukherjee, P.P. (2018) “Shuttle” in Polysulfide Shuttle: Friend or Foe? *The Journal of Physical Chemistry C*, **122**, 23845. https://doi.org/10.1021/acs.jpcc.8b06077

[121] Yang, L., Li, Q., Wang, Y., Chen, Y., Guo, X., Wu, Z., Chen, G., Zhong, B., Xiang, W. and Zhong, Y. (2020) A Review of Cathode Materials in Lithium-Sulfur Batteries. *Ionics*, **26**, 5299. https://doi.org/10.1007/s11581-020-03767-3

[122] Yu, Z., Liu, M., Guo, D., Wang, J., Chen, X., Li, J., Jin, H., Yang, Z., Chen, X. and Wang, S. (2020) Radially Inwardly Aligned Hierarchical Porous Carbon for Ultra-Long-Life Lithium-Sulfur Batteries. *Angewandte Chemie International Edition*, **59**, 6406. https://doi.org/10.1002/anie.201914972

[123] Ren, M., Lu, X., Chai, Y., Zhou, X., Ren, J., Zheng, Q. and Lin, D. (2019) A Three-Dimensional Conductive Cross-Linked All-Carbon Network Hybrid as a Sulfur Host for High Performance Lithium-Sulfur Batteries. *Journal of Colloid and Interface Science*, **552**, 91. https://doi.org/10.1016/j.jcis.2019.05.042

[124] Cao, J., Chen, C., Zhao, Q., Zhang, N., Lu, Q., Wang, X., Niu, Z. and Chen, J. (2016) A Flexible Nanostructured Paper of a Reduced Graphene Oxide-Sulfur Composite for High-Performance Lithium-Sulfur Batteries with Unconventional Configurations. *Advanced Materials*, **28**, 9629. https://doi.org/10.1002/adma.201602262

[125] Wang, R., Yang, J., Chen, X., Zhao, Y., Zhao, W., Qian, G., Li, S., Xiao, Y., Chen, H., Ye, Y., Zhou, G. and Pan, F. (2020) Highly Dispersed Cobalt Clusters in Nitrogen-Doped Porous Carbon Enable Multiple Effects for High-Performance Li-S Battery. *Advanced Energy Materials*, **10**, Article ID: 1903550. https://doi.org/10.1002/aenm.201903550

[126] Jin, J., Cai, W., Cai, J., Shao, Y., Song, Y., Xia, Z., Zhang, Q. and Sun, J. (2020) MOF-Derived Hierarchical CoP Nanoflakes Anchored on Vertically Erected Graphene Scaffolds as Self-Supported and Flexible Hosts for Lithium-Sulfur Batteries. *Journal of Materials Chemistry A*, **8**, 3027. https://doi.org/10.1039/C9TA13046B

[127] Chen, M., Zheng, J., Sheng, O., Jin, C., Yuan, H., Liu, T., Liu, Y., Wang, Y., Nai, J. and Tao, X. (2019) Sulfur-Nitrogen Co-Doped Porous Carbon Nanosheets to Control Lithium Growth for A Stable Lithium Metal Anode. *Journal of Materials Chemistry A*, **7**, 18267. https://doi.org/10.1039/C9TA05684J

[128] Xu, G., Ding, B., Nie, P., Shen, L., Wang, J. and Zhang, X. (2013) Porous Nitrogen-Doped Carbon Nanotubes Derived from Tubular Polypyrrole for Energy-Storage Applications. *Chemistry—A European Journal*, **19**, 12306. https://doi.org/10.1002/chem.201301352

[129] Ai, W., Zhou, W., Du, Z., Chen, Y., Sun, Z., Wu, C., Zou, C., Li, C., Huang, W. and Yu, T. (2017) Nitrogen and Phosphorus Codoped Hierarchically Porous Carbon as an Efficient Sulfur Host for Li-S Batteries. *Energy Storage Materials*, **6**, 112. https://doi.org/10.1016/j.ensm.2016.10.008

[130] Wang, Y., Li, M., Xu, L., Tang, T., Ali, Z., Huang, X., Hou, Y. and Zhang, S. (2019) Polar and Conductive Iron Carbide@N-Doped Porous Carbon Nanosheets as a Sulfur Host for High Performance Lithium Sulfur Batteries. *Chemical Engineering Journal*, **358**, 962. https://doi.org/10.1016/j.cej.2018.10.086

[131] Deng, W., Zhou, X., Fang, Q. and Liu, Z. (2017) A Bifunctional Hierarchical Porous Carbon Network Integrated with an *in Situ* Formed Ultrathin Graphene Shell for Stable Lithium-Sulfur Batteries. *Journal of Materials Chemistry A*, **5**, 13674. https://doi.org/10.1039/C7TA01291H

[132] Wang, H., Yang, Y., Liang, Y., Robinson, J.T., Li, Y., Jackson, A., Cui, Y. and Dai, H. (2011) Graphene-Wrapped Sulfur Particles as a Rechargeable Lithium-Sulfur Battery Cathode Material with High Capacity and Cycling Stability. *Nano Letters*, **11**, 2644. https://doi.org/10.1021/nl200658a

[133] Yin, L.-C., Liang, J., Zhou, G.-M., Li, F., Saito, R. and Cheng, H.-M. (2016) Understanding the Interactions between Lithium Polysulfides and N-Doped Graphene Using Density Functional Theory Calculations. *Nano Energy*, **25**, 203. https://doi.org/10.1016/j.nanoen.2016.04.053

[134] Zhang, L., Liu, D., Muhammad, Z., Wan, F., Xie, W., Wang, Y., Li, S., Niu, Z. and Chen, J. (2019) Single Nickel Atoms on Nitrogen-Doped Graphene Enabling Enhanced Kinetics of Lithium-Sulfur Batteries. *Advanced Materials*, **31**, e1903955. https://doi.org/10.1002/adma.201903955

[135] Wan, P., Yang, W., Wang, X., Hu, J. and Zhang, H. (2015) Reduced Graphene Oxide Modified with Hierarchical Flower-Like $In(OH)_3$ for NO_2 Room-Temperature Sensing. *Sensors and Actuators B*, **214**, 36. https://doi.org/10.1016/j.snb.2015.02.100

[136] Zhang, Y., Ge, X., Kang, Q., Kong, Z., Wang, Y. and Zhan, L. (2020) Vanadium Oxide Nanorods Embed in Porous Graphene Aerogel as High-Efficiency Polysulfide-Trapping-Conversion Mediator for High Performance Lithium-Sulfur Batteries. *Chemical Engineering Journal*, **393**, Article ID: 124570. https://doi.org/10.1016/j.cej.2020.124570

[137] Zhao, Y., Wu, W., Li, J., Xu, Z. and Guan, L. (2014) Encapsulating MWNTs into Hollow Porous Carbon Nanotubes: A Tube-in-Tube Carbon Nanostructure for High-Performance Lithium-Sulfur Batteries. *Advanced Materials*, **26**, 5113. https://doi.org/10.1002/adma.201401191

[138] Ummethala, R., Fritzsche, M., Jaumann, T., Balach, J., Oswald, S., Nowak, R., Sobczak, N., Kaban, I., Rümmeli, M. H. and Giebeler, L. (2018) Lightweight, Free-Standing 3D Interconnected Carbon Nanotube Foam as a Flexible Sulfur Host for High Performance Lithium-Sulfur Battery Cathodes. *Energy Storage Materials*, **10**, 206. https://doi.org/10.1016/j.ensm.2017.04.004

[139] Fang, R., Li, G., Zhao, S., Yin, L., Du, K., Hou, P., Wang, S., Cheng, H.-M., Liu, C. and Li, F. (2017) Single-Wall Carbon Nanotube Network Enabled Ultrahigh Sulfur-Content Electrodes for High-Performance Lithium-Sulfur Batteries. *Nano Energy*, **42**, 205. https://doi.org/10.1016/j.nanoen.2017.10.053

[140] Zhou, G., Wang, D.-W., Li, F., Hou, P.-X., Yin, L., Liu, C., Lu, G.Q., Gentle, I.R. and Cheng, H.-M. (2012) A Flexible Nanostructured Sulphur-Carbon Nanotube Cathode with High Rate Performance for Li-S Batteries. *Energy & Environmental Science*, **5**, 8901. https://doi.org/10.1039/c2ee22294a

[141] Zhang, C., Wu, H.B., Yuan, C., Guo, Z. and Lou, X.W. (2012) Confining Sulfur in Double-Shelled Hollow Carbon Spheres for Lithium-Sulfur Batteries. *Angewandte Chemie International Edition*, **51**, 9592. https://doi.org/10.1002/anie.201205292

[142] Zhu, L., Peng, H.-J., Liang, J., Huang, J.-Q., Chen, C.-M., Guo, X., Zhu, W., Li, P. and Zhang, Q. (2015) Interconnected Carbon Nanotube/Graphene Nanosphere Scaffolds as Free-Standing Paper Electrode for High-Rate And Ultra-Stable Lithium-Sulfur Batteries. *Nano Energy*, **11**, 746. https://doi.org/10.1016/j.nanoen.2014.11.062

[143] Wang, T., Zhu, J., Wei, Z., Yang, H., Ma, Z., Ma, R., Zhou, J., Yang, Y., Peng, L., Fei, H., Lu, B. and Duan, X. (2019) Bacteria-Derived Biological Carbon Building Robust Li-S Batteries. *Nano Letters*, **19**, 4384. https://doi.org/10.1021/acs.nanolett.9b00996

[144] Yu, M., Li, R., Tong, Y., Li, Y., Li, C., Hong, J.-D. and Shi, G. (2015) A Graphene Wrapped Hair-Derived Carbon/Sulfur Composite for Lithium-Sulfur Batteries. *Journal of Materials Chemistry A*, **3**, 9609. https://doi.org/10.1039/C5TA00651A

[145] Wu, W., Pu, J., Wang, J., Shen, Z., Tang, H., Deng, Z., Tao, X., Pan, F. and Zhang, H. (2018) Biomimetic Bipolar Microcapsules Derived from *Staphylococcus aureus* for Enhanced Properties of Lithium-Sulfur Battery Cathodes. *Advanced Energy Materials*, **8**, Article ID: 1702373. https://doi.org/10.1002/aenm.201702373

[146] Luo, C., Zhu, H., Luo, W., Shen, F., Fan, X., Dai, J., Liang, Y., Wang, C. and Hu, L. (2017) Atomic-Layer-Deposition Functionalized Carbonized Mesoporous Wood Fiber for High Sulfur Loading Lithium Sulfur Batteries. *ACS Applied Materials & Interfaces*, **9**, 14801. https://doi.org/10.1021/acsami.7b01205

[147] Bhargav, A., He, J., Gupta, A. and Manthiram, A. (2020) lithium-Sulfur Batteries: Attaining the Critical Metrics. *Joule*, **4**, 285. https://doi.org/10.1016/j.joule.2020.01.001

[148] Li, Q., Liu, Y., Wang, Y., Chen, Y., Guo, X., Wu, Z. and Zhong, B. (2020) Review of the Application of Biomass-Derived Porous Carbon in Lithium-Sulfur Batteries. *Ionics*, **26**, 4765. https://doi.org/10.1007/s11581-020-03694-3

[149] Cai, D., Lu, M., La Li., Cao, J., Chen, D., Tu, H., Li, J. and Han, W. (2019) A Highly Conductive MOF of Graphene Analogue $Ni_3(HITP)_2$ as a Sulfur Host for High-Performance Lithium-Sulfur Batteries. *Small*, **15**, e1902605. https://doi.org/10.1002/smll.201902605

[150] Park, J., Lee, M., Feng, D., Huang, Z., Hinckley, A.C., Yakovenko, A., Zou, X., Cui, Y. and Bao, Z. (2018) Stabilization of Hexaaminobenzene in a 2D Conductive Metal-Organic Framework for High Power Sodium Storage. *Journal of the American Chemical Society*, **140**, 10315. https://doi.org/10.1021/jacs.8b06020

[151] Aubrey, M.L., Wiers, B.M. andrews, S.C., Sakurai, T., Reyes-Lillo, S.E., Hamed, S.M., Yu, C.-J., Darago, L.E., Mason, J.A., Baeg, J.-O., Grandjean, F., Long, G.J., Seki, S., Neaton, J.B., Yang, P. and Long, J.R. (2018) Electron Delocalization and Charge Mobility as a Function of Reduction in a Metal-Organic Framework. *Nature Materials*, **17**, 625. https://doi.org/10.1038/s41563-018-0098-1

[152] Hu, Y., Chen, W., Lei, T., Jiao, Y., Huang, J., Hu, A., Gong, C., Yan, C., Wang, X. and Xiong, J. (2020) Strategies toward High-Loading Lithium-Sulfur Battery. *Advanced Energy Materials*, **10**, Article ID: 2000082. https://doi.org/10.1002/aenm.202000082

[153] Liu, X., Huang, J.-Q., Zhang, Q. and Mai, L. (2017) Nanostructured Metal Oxides and Sulfides for Lithium-Sulfur Batteries. *Advanced Materials*, **29**, Article ID: 1601759. https://doi.org/10.1002/adma.201601759

[154] Wang, H., Zhang, W., Xu, J. and Guo, Z. (2018) Advances in Polar Materials for Lithium-Sulfur Batteries. *Advanced Functional Materials*, **28**, Article ID: 1707520. https://doi.org/10.1002/adfm.201707520

[155] Shi, H., Lv, W., Zhang, C., Wang, D.-W., Ling, G., He, Y., Kang, F. and Yang, Q.-H. (2018) Functional Carbons Remedy the Shuttling of Polysulfides in Lithium-Sulfur Batteries: Confining, Trapping, Blocking, and Breaking Up. *Advanced Functional Materials*, **28**, Article ID: 1800508. https://doi.org/10.1002/adfm.201800508

[156] Hang, J.-Y., Kim, H.M., Lee, S.-K., Lee, J.-H., Abouimrane, A., Khaleel, M.A., Belharouak, I., Manthiram, A. and Sun, Y.-K. (2016) High-Energy, High-Rate, Lithium-Sulfur Batteries: Synergetic Effect of Hollow TiO_2-Webbed Carbon Nanotubes and a Dual Functional Carbon-Paper Interlayer. *Advanced Energy Materials*, **6**, Article ID: 1501480. https://doi.org/10.1002/aenm.201501480

[157] Xu, Z.-L., Kim, J.-K. and Kang, K. (2018) Carbon Nanomaterials for Advanced Lithium Sulfur Batteries. *Nano Today*, **19**, 84. https://doi.org/10.1016/j.nantod.2018.02.006

[158] Pang, Q., Tang, J., Huang, H., Liang, X., Hart, C., Tam, K.C. and Nazar, L.F. (2015) A Nitrogen and Sulfur Dual-Doped Carbon Derived from Polyrhodanine@cellulose for Advanced Lithium-Sulfur Batteries. *Advanced Materials*, **27**, 6021. https://doi.org/10.1002/adma.201502467

[159] Sun, K., Li, S.-J., Chen, X.-L., Liu, Y., Huang, X.-Q., Wei, D.-H., Qu, L.-B., Zhao, Y.-F. and Yu, B. (2019) Silver-Catalyzed Decarboxylative Radical Cascade Cyclization toward Benzimidazo2,1-aisoquinolin-6(5H)-ones. *Chemical Communications*, **55**, 2861. https://doi.org/10.1039/C8CC10243K

[160] Li, T., Bai, X., Gulzar, U., Bai, Y.-J., Capiglia, C., Deng, W., Zhou, X., Liu, Z., Feng, Z. and Proietti Zaccaria, R. (2019) A Comprehensive Understanding of Lithium-Sulfur Battery Technology. *Advanced Functional Materials*, **29**, Article ID: 1901730. https://doi.org/10.1002/adfm.201901730

[161] Lv, X., Lei, T., Wang, B., Chen, W., Jiao, Y., Hu, Y., Yan, Y., Huang, J., Chu, J., Yan, C., Wu, C., Wang, J., Niu, X. and Xiong, J. (2019) An Efficient Separator with Low Li-Ion Diffusion Energy Barrier Resolving Feeble Conductivity for Practical Lithium-Sulfur Batteries. *Advanced Energy Materials*, **9**, Article ID: 1901800. https://doi.org/10.1002/aenm.201901800

[162] He, J., Luo, L., Chen, Y. and Manthiram, A. (2017) Yolk-shelled C@Fe_3O_4 Nanoboxes as Efficient Sulfur Hosts for High-Performance Lithium-Sulfur Batteries. *Advanced Materials*, **29**, Article ID: 1702707. https://doi.org/10.1002/adma.201702707

[163] Li, Z., He, Q., Xu, X., Zhao, Y., Liu, X., Zhou, C., Ai, D., Xia, L. and Mai, L. (2018) A 3D Nitrogen-Doped Graphene/TiN Nanowires Composite as a Strong Polysulfide Anchor for Lithium-Sulfur Batteries with Enhanced Rate Performance and High Areal Capacity. *Advanced Materials*, **30**, e1804089. https://doi.org/10.1002/adma.201804089

[164] Luo, L., Chung, S.-H. and Manthiram, A. (2018) Rational Design of a Dual-Function Hybrid Cathode Substrate for Lithium-Sulfur Batteries. *Advanced Energy Materials*, **8**, Article ID: 1801014. https://doi.org/10.1002/aenm.201801014

[165] Guan, B., Zhang, Y., Fan, L., Wu, X., Wang, M., Qiu, Y., Zhang, N. and Sun, K. (2019) Blocking Polysulfide with Co_2B@CNT via "Synergetic Adsorptive Effect" toward Ultrahigh-Rate Capability and Robust Lithium-Sulfur Battery.

ACS Nano, **13**, 6742. https://doi.org/10.1021/acsnano.9b01329

[166] Zang, Y., Pei, F., Huang, J., Fu, Z., Xu, G. and Fang, X. (2018) Large-Area Preparation of Crack-Free Crystalline Microporous Conductive Membrane to Upgrade High Energy Lithium-Sulfur Batteries. *Advanced Energy Materials*, **8**, Article ID: 1802052. https://doi.org/10.1002/aenm.201802052

[167] Chen, X., Xu, Y., Du, F.-H. and Wang, Y. (2019) Covalent Organic Framework Derived Boron/Oxygen Codoped Porous Carbon on CNTs as an Efficient Sulfur Host for Lithium-Sulfur Batteries. *Small Methods*, **3**, Article ID: 1900338. https://doi.org/10.1002/smtd.201900338

[168] Ding, B., Fan, Z., Lin, Q., Wang, J., Chang, Z., Li, T., Henzie, J., Kim, J., Dou, H., Zhang, X. and Yamauchi, Y. (2019) Confined Pyrolysis of ZIF-8 Polyhedrons Wrapped with Graphene Oxide Nanosheets to Prepare 3D Porous Carbon Heterostructures. *Small Methods*, **3**, Article ID: 1900277. https://doi.org/10.1002/smtd.201900277

[169] Bao, W., Liu, L., Wang, C., Choi, S., Wang, D. and Wang, G. (2018) Facile Synthesis of Crumpled Nitrogen-Doped Mxene Nanosheets as a New Sulfur Host for Lithium-Sulfur Batteries. *Advanced Energy Materials*, **8**, Article ID: 1702485. https://doi.org/10.1002/aenm.201702485

[170] Singh, V., Padhan, A.K., Adhikary, S.D., Tiwari, A., Mandal, D. and Nagaiah, T.C. (2019) Poly(ionic liquid)-Zinc Polyoxometalate Composite as a Binder-Free Cathode for High-Performance Lithium-Sulfur Batteries. *Journal of Materials Chemistry A*, **7**, 3018. https://doi.org/10.1039/C8TA12192C

[171] Li, X., Zang, X., Li, Z., Li, X., Li, P., Sun, P., Lee, X., Zhang, R., Huang, Z., Wang, K., Wu, D., Kang, F. and Zhu, H. (2013) Large-Area Flexible Core-Shell Graphene/Porous Carbon Woven Fabric Films for Fiber Supercapacitor Electrodes. *Advanced Functional Materials*, **9**, eea645. https://doi.org/10.1002/adfm.201300464

[172] Chung, S.-H., Chang, C.-H. and Manthiram, A. (2016) Hierarchical Sulfur Electrodes as a Testing Platform for Understanding the High-Loading Capability of Li-S Batteries. *Journal of Power Sources*, **334**, 179. https://doi.org/10.1016/j.jpowsour.2016.10.023

[173] Ma, L., Zhang, W., Wang, L., Hu, Y., Zhu, G., Wang, Y., Chen, R., Chen, T., Tie, Z., Liu, J. and Jin, Z. (2018) Strong Capillarity, Chemisorption, and Electrocatalytic Capability of Crisscrossed Nanostraws Enabled Flexible, High-Rate, and Long-Cycling Lithium-Sulfur Batteries. *ACS Nano*, **12**, 851. https://doi.org/10.1021/acsnano.8b01763

[174] Feng, S., Zhong, H., Song, J., Zhu, C., Dong, P., Shi, Q., Liu, D., Li, J., Chang, Y.-C., Beckman, S.P., Song, M., Du, D. and Lin, Y. (2018) Catalytic Activity of Co-X (X = S, P, O) and Its Dependency on Nanostructure/Chemical Composition in Lithium-Sulfur Batteries. *ACS Applied Energy Materials*, **1**, 7014. https://doi.org/10.1021/acsaem.8b01434

[175] Wu, J., Li, X., Zeng, H., Xue, Y., Chen, F., Xue, Z., Ye, Y. and Xie, X. (2019) Fast Electrochemical Kinetics and Strong Polysulfide Adsorption by a Highly Oriented MoS_2 Nanosheet@N-Doped Carbon Interlayer for Lithium-Sulfur Batteries. *Journal of Materials Chemistry A*, **7**, 7897. https://doi.org/10.1039/C9TA00458K

[176] Liu, Y.-T., Han, D.-D., Wang, L., Li, G.-R., Liu, S. and Gao, X.-P. (2019) $NiCo_2O_4$ Nanofibers as Carbon-Free Sulfur Immobilizer to Fabricate Sulfur-Based Composite with High Volumetric Capacity for Lithium-Sulfur Battery. *Advanced Energy Materials*, **9**, Article ID: 1803477. https://doi.org/10.1002/aenm.201803477

[177] Song, Y., Zhao, W., Kong, L., Li Zhang., Zhu, X., Shao, Y., Ding, F., Zhang, Q., Sun, J. and Liu, Z. (2018) Synchronous Immobilization and Conversion of Polysulfides on a VO_2-VN Binary Host Targeting High Sulfur Load Li-S Batteries. *Energy & Environmental Science*, **11**, 2620. https://doi.org/10.1039/C8EE01402G

[178] Xiang, K., Cai, S., Wang, X., Chen, M. and Jiang, S. (2018) Nitrogen-Doped Activated Microporous Carbon Spheres as a Sulfur Matrix for Advanced Lithium-Sulfur Batteries. *Journal of Alloys and Compounds*, **740**, 687. https://doi.org/10.1016/j.jallcom.2018.01.026

[179] He, J., Hartmann, G., Lee, M., Hwang, G.S., Chen, Y. and Manthiram, A. (2019) Freestanding 1T MoS_2/Graphene Heterostructures as a Highly Efficient Electrocatalyst for Lithium Polysulfides in Li-S Batteries. *Energy & Environmental Science*, **12**, 344. https://doi.org/10.1039/C8EE03252A

[180] Chen, W., Lei, T., Wu, C., Deng, M., Gong, C., Hu, K., Ma, Y., Dai, L., Lv, W., He, W., Liu, X., Xiong, J. and Yan, C. (2018) Designing Safe Electrolyte Systems for a High-Stability Lithium-Sulfur Battery. *Advanced Energy Materials*, **8**, Article ID: 1702348. https://doi.org/10.1002/aenm.201702348

[181] Lei, T., Chen, W., Lv, W., Huang, J., Zhu, J., Chu, J., Yan, C., Wu, C., Yan, Y., He, W., Xiong, J., Li, Y., Yan, C., Goodenough, J.B. and Duan, X. (2019) Inhibiting Polysulfide Shuttling with a Graphene Composite Separator for Highly Robust Lithium-Sulfur Batteries. *Joule*, **3**, 303. https://doi.org/10.1016/j.joule.2018.12.016

[182] Yu, S., Schmidt, R.D., Garcia-Mendez, R., Herbert, E., Dudney, N.J., Wolfenstine, J.B., Sakamoto, J. and Siegel, D.J. (2016) Elastic Properties of the Solid Electrolyte $Li_7La_3Zr_2O_{12}$(LLZO). *Chemistry of Materials*, **28**, 197. https://doi.org/10.1021/acs.chemmater.5b03854

[183] Nagata, H. and Chikusa, Y. (2014) Transformation of P_2S_5 into a Solid Electrolyte with Ionic Conductivity at the Positive Composite Electrode of All-Solid-State Lithium-Sulfur Batteries. *Energy Technology*, **2**, 753. https://doi.org/10.1002/ente.201402040

[184] Xu, R., Yue, J., Liu, S., Tu, J., Han, F., Liu, P. and Wang, C. (2019) Cathode-Supported All-Solid-State Lithium-Sulfur Batteries with High Cell-Level Energy Density. *ACS Energy Letters*, **4**, 1073. https://doi.org/10.1021/acsenergylett.9b00430

[185] Ulissi, U., Ito, S., Hosseini, S.M., Varzi, A., Aihara, Y. and Passerini, S. (2018) High Capacity All-Solid-State Lithium Batteries Enabled by Pyrite-Sulfur Composites. *Advanced Energy Materials*, **8**, Article ID: 1801462. https://doi.org/10.1002/aenm.201801462

[186] Han, F., Yue, J., Fan, X., Gao, T., Luo, C., Ma, Z., Suo, L. and Wang, C. (2016) High-Performance All-Solid-State Lithium-Sulfur Battery Enabled by a Mixed Conductive Li_2S Nanocomposite. *Nano Letters*, **16**, 4521. https://doi.org/10.1021/acs.nanolett.6b01754