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Hans汉斯

锂硫电池硫还原反应金属催化剂的研究进展

钱思逸，钱　涛*

南通大学，化学化工学院，江苏　南通

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摘　要

一直以来，储能技术着重在能量密度、功率密度、寿命、安全性和成本方面不断改进。近年来不断扩大的电子设备市场，包括电动汽车和便携式电子产品，促使电池逐渐向高能量密度方向发展。尽管锂离子电池已被广泛应用于电动工具、电子通讯设备甚至电动汽车等应用领域，但是锂离子电池的能量密度已接近其理论极限，仅能驱动一辆电动汽车行驶约300公里，或为全功能智能手机供电不到一天。锂硫电池因其较高的理论容量(1675 mAh g^{-1})和丰富的硫储量而受到了广泛的关注。但是，S_8和Li_2S的导电性差、循环时巨大的体积膨胀(80%)、多硫化物溶解引起的“穿梭效应”等，会导致活性物质利用率低，电池容量衰减迅速，进而限制了其高功率输出。此外，充放电过程中的非均相氧化还原反应通常伴随着缓慢的反应动力学，这导致了电池的倍率性能不理想。考虑到这些阻碍因素，除了可以通过引入中间层或设计合适的隔膜来捕获和限制锂离子外，寻找合适的正极主体材料也是提高锂硫电池电化学性能的有效途径。具体来说，利用极性材料作为高效的多硫化物介质来加速多硫化锂的反应已经成为近年来的研究热点。一些研究人员发现在硫正极材料中引入电催化剂可以加快硫的氧化还原过程，抑制多硫化锂的穿梭。本综述详细总结了加速硫还原反应的金属催化剂材料的最新进展，包括金属单原子材料、金属纳米材料、金属化合物材料，并为进一步优化锂硫电池的电化学性能指明了方向。

关键词

锂硫电池，硫还原反应，金属催化剂

Research Progr ess of Metal Catalysts for Sulfur Reduction of Lithium Sulfur Batteries

Siyi Qian, Tao Qian*

School of Chemistry and Chemical Engineering, Nantong University, Nantong Jiangsu

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*通讯作者。

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Abstract

Energy storage technology has always focused on improvements in energy density, power density, longevity, safety and cost. The expanding market for electronic devices in recent years, including electric cars and portable electronics, has led to the gradual development of batteries in the direction of higher energy density. Although lithium-ion batteries are already widely used in applications such as power tools, electronic communications devices and even electric cars, their energy density is approaching its theoretical limit, allowing them to drive only about 300 km in an electric car or power a fully functional smartphone for less than a day. Lithium-sulfur batteries due to its high theoretical capacity (1675 mAh g^{-1}) and abundant sulfur reserves and has received the widespread attention. However, the high power output of S_8 and Li_2S is limited by the low utilization of active materials and the rapid decline of battery capacity due to the poor conductivity of S_8 and Li_2S, the huge volume expansion (80%) during the cycle, and the shuttle effect caused by the dissolution of polysulfides. Worse still, the heterogeneous redox reaction during charge and discharge is usually accompanied by sluggish reaction kinetics, which leads to the unsatisfactory rate performance of the battery. Considering these hindering factors, in addition to the introduction of an intermediate layer or the design of a proper separator to trap and confine lithium ions, finding a suitable anode main material is also an effective way to improve the electrochemical performance of lithium-sulfur batteries. Specifically, the use of polar materials as efficient polysulfide medium to accelerate the reaction of polysulfide lithium has become a research hotspot in recent years. Some researchers have found that the introduction of electrocatalysts in sulfur cathode materials can accelerate the sulfur redox process and inhibit the shuttle of polylithium sulfide. This review summarizes in detail the latest progress of metal catalysts materials for accelerating sulfur reduction reactions, including metal monatomic materials, metal nanomaterials, metal compound materials, and points out the direction for further optimization of the electrochemical performance of Li-sulfur batteries.

Keywords

Lithium-Sulfur Batteries, Sulfur Reduction, Metal Catalysts

1. 引言

电动汽车的复兴以及风能和太阳能的实施增加了对高性能储能系统的需求[1] [2] [3] [4]。目前，商用锂离子电池采用 $LiCoO_2$ 或 $LiFePO_4$ 作为正极，能量密度相对较低(200~300 Wh kg^{-1})并且存在安全隐患，严重阻碍了锂离子电池的大规模实际应用[5] [6] [7]。因此，开发具有高能量密度和高安全性的可充电电池将是当务之急，其中，最有希望的候选者之一是锂硫电池(LSB)，它在解决这些问题方面具有很大的潜力[8] [9] [10]。基于硫还原成硫化锂的转化反应产生了 1675 mAh g^{-1} 的高理论容量，这一容量明显高于嵌入式正极材料，如 $LiCoO_2$ 和 $LiFePO_4$，其容量低于 200 mAh g^{-1}。在工作电压约为 2.2 V 的电化学电荷转移反应下，锂硫电池的比能量密度可达 2600 Wh kg^{-1}。考虑到额外的电池组件，最佳配置下的锂硫电池的实际能量密度可以达到 500~600 Wh kg^{-1} [11]。此外，硫还具有资源丰富、安全、环保等优点。锂硫电池的优化将促进可再生能源的发展和应用。

尽管锂硫电池具有巨大的取代锂离子电池的潜力，但也仍然面临着几个关键问题[12] [13] [14]。主要问题是放电过程中硫还原反应的转化动力学缓慢，这是由硫的低电导率和 16 个电子的复杂转换过程所导致的。硫还原反应涉及一系列相变过程，即从固体硫还原为各种可溶中间体，然后再还原为最终的不溶性 Li_2S/Li_2S 产物。动力学迟缓导致放电过程中硫不能充分被还原，从而降低了锂硫电池的比容量和倍率性能。另一个挑战是多硫化锂中间体(Li_2S_x, $3 \le x \le 8$)在正极和电解液之间的溶解和扩散。硫与锂的转化反应生成各种可溶于一般有机电解质的多硫化锂。由于电场和浓度梯度的作用，长链 $Li_2S_x(6 \le x \le 8)$可以穿透隔膜并迁移到负极上，在负极上被金属锂还原形成短链 $Li_2S_x(2 < x < 6)$和不溶的 Li_2S_2/Li_2S。这种麻烦的现象会造成两个不利的影响：1) 非活性的 Li_2S_2/Li_2S 层的沉积导致锂负极的钝化；2) 短链多硫化锂在锂负极的积累。这些短链多硫化物可以扩散回正极，然后与长链多硫化锂反应。这种重复的过程形成了一种穿梭效应，导致锂硫电池的容量快速衰减和库仑效率降低。此外，锂金属负极也面临严峻的挑战，如严重的副反应和有害的锂枝晶生长。由于本综述的重点是正极的硫还原反应，锂金属负极已在其他地方发表，因此不包括在这里[15] [16] [17] [18]。

一般来说，由于硫还原反应动力学缓慢会导致硫的利用不足进而加剧多硫化物的穿梭。在过去的几十年里，研究人员为克服这些挑战作出了巨大的努力[19] [20] [21] [22]。Nazar 等人的开创性研究为解决硫正极问题提供了新的见解[23]。在硫阴极上引入介孔碳(CMK-3)作为宿主材料，有效地限制了硫的扩散，并为锂离子与硫的高反应性提供了通道。这种约束保证了氧化还原反应能充分进行，提高了硫的利用率。从那时起，具有高硫约束的材料被开发为高性能 LSB 的宿主[24] [25] [26]。然而电解质中的浓度梯度会不可避免地导致多硫化物向正极侧扩散，受约束的多硫化物仍然会在正极区域积聚，因而约束策略并没有从根本上解决氧化还原反应的迟滞性和穿梭效应。

因此，加速硫还原反应的转化动力学被认为是实现硫正极充分利用的一个有前途的策略。催化剂材料能促进硫正极的电荷转移，降低硫正极的反应能垒，在改善硫还原反应动力学方面显示出很大的优势[27] [28]。因此，本综述系统地总结了金属催化剂的设计策略，为进一步改善锂硫电池的电化学性能指明了方向。

2. 金属单原子催化剂

向锂硫电池中引入催化剂材料虽然可以提高硫的利用率，但是非活性成分的引入也导致了能量密度的降低。因此，单原子(SA)作为原子间分散的金属原子，由于其最大限度的原子利用效率而备受关注。就 LSB 的正极而言，单原子含量占正极总质量的比例可以降低到 10%以下。此外，不饱和的配位环境和独特的电子结构使得单原子在催化方面具有明显的优势。由于单个原子具有极高的自由能，因此它们通常与其他原子(例如 N 和 O)配位以保持结构稳定性。考虑到碳材料的结构灵活性，将单原子锚定在各种碳基底上可以有效地催化硫的氧化还原反应[29]。表 1 总结了提高 LSB 电化学性能的各种单原子催化剂。

2.1. 金属单原子 Fe

金属单原子 Fe 分散在氮掺杂碳上催化硫正极的氧化还原反应已经被广泛报道[48] [49] [50]。密度泛函理论(DFT)算表明，单原子位点可以降低多硫化物转化的能垒，从而提升电池的倍率性能[40]。此外，单个原子的催化活性很大程度上取决于配位环境。$M-N_4$ (M 指金属)的四配位结构具有较高的结构稳定性，是硫还原反应的典型活性位点。尽管结构稳定，但单原子的四配位构型可能不会表现出最佳的催化性能，而控制配位环境可进一步增强单个原子的催化活性。例如，与 $Fe-N_4-C$ 相比，$Fe-N_5-C$ 的更多的 N 配位数有望表现出更强的多硫化物吸附能力[28]。锂离子在 $Fe-N_5-C$ 表面的迁移能垒明显低于 $Fe-N_4-C$，这意味着由于 N 配数位的增加，离子迁移也得以增强。除了过饱和配位之外，$Fe-N_4$ 配位的不足也能够为 LSB

产生不同的活性位点[35]。例如，和 Fe-N_4 相比，Fe-N_2 配位中的 Fe 具有更高的 d 带中心(ε_d) (图 1)。而较高的 ε_d 导致反键轨道能增加，从而增强对多硫化物的亲和力和催化转化[29]。

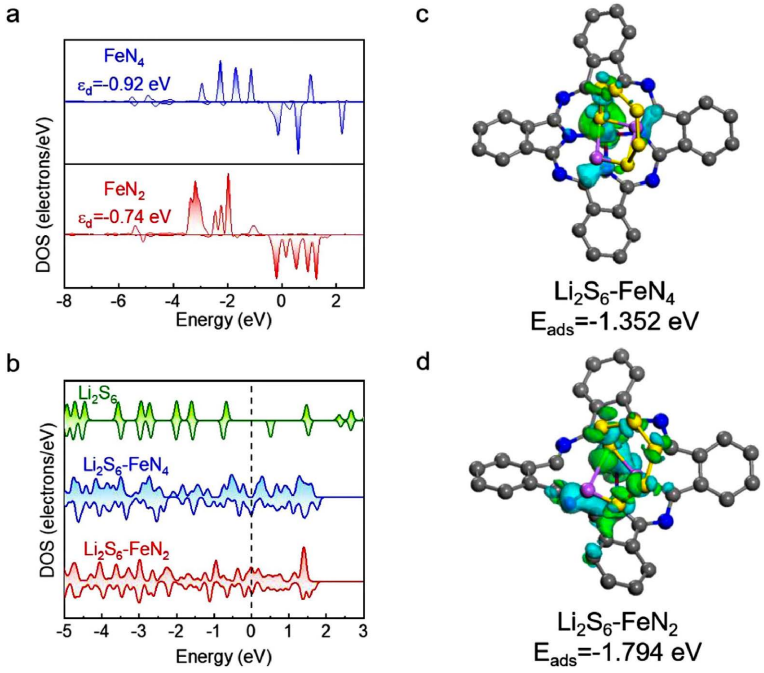

Figure 1. Optimization model of (a) (b) state density (c) (d) before and after adsorption of Li_2S_6 by FeN_4 and FeN_2 [45]
图 1. FeN_4 和 FeN_2 吸附 Li_2S_6 前后的(a) (b) 态密度(c) (d) 优化模型[45]

2.2. 金属单原子 Co

与金属单原子 Fe 一样，金属单原子 Co 也被用于 LSB 中以增强电化学转化。Co-N_x 位点的整合使得疏锂纤维碳骨架变得亲锂，有效缓解了锂负极的枝晶生长。同时，Co-N_x 位点还加快了电化学转化，有效地抑制了多硫化物穿梭。和金属单原子 Fe 相似，金属单原子 Co 的配位数也是催化活性的关键。Co-N_4 是一种常见且稳定的结构，可以增强硫正极的催化转化率。而在 Co-N_2 中，金属单原子 Co 的配位数的减少会导致电荷分布不对称，d 带中心上移，有利于 Co-N_2 和多硫化物之间的化学相互作用，从而有效加快硫的氧化还原[31]。此外，还可以通过增加负载单原子催化剂的含量和暴露更多的活性位点，以获得最大化的催化活性。

2.3. 其他金属单原子

除了金属单原子 Fe 和 Co，其他金属单原子催化剂已被尝试用于 LSB，例如 Ni [42] [51]、Zn [43] [52] [53]、Mo [34]、V [35]、W [36]和 Ru [37]。当与掺杂的 N 配位时，金属单原子 Ni 具有相似的物理化学特性。例如，Ni-N_4 结构中氧化的 Ni 位点通过形成 S_n^{2-}–Ni–N 键可逆地催化多硫化物转化[51]。此外，由于具有不对称的电子分布，过饱和的 Ni-N_5 结构是催化多硫化物转化的最佳候选者。基于 DFT 计算，Ni-N_5/C 具有最低的硫还原反应动力学能垒和适中的硫物质吸附强度。基于电子结构计算，发现单原子催化剂和硫物质之间的 d-p 轨道杂化可以作为描述符来指导 LSB 单原子催化剂的设计[54]。具有低原子序数的过渡金属(例如 Ti)表现出较少的填充反键态和有效的 d-p 轨道杂化，可以增加与硫物质的结合并降低硫氧化还原反应的能垒。

Table 1. Metallic monatom catalysts improve the performance of lithium Sulfur batteries
表 1. 金属单原子催化剂提升锂硫电池性能

催化剂	含硫量/%	载硫量/mg cm^{-2}	倍率/C	循环圈数	初始容量/mAh g^{-1}	剩余容量/mAh g^{-1}	参考文献
单原子 Fe	–	2.3	0.2	200	1255	1129	[30]
			2.0	1000	915	624	
单原子 Fe	52	1.0	1.0	1000	905	477	[31]
单原子 Fe	70	1.5	0.2	200	1242	999	[32]
			1.0	500	951	800	
单原子 Fe	59	1.0	0.2	100	1124	920	[33]
			1.0	500	907	662	
单原子 Fe	56	1.3~1.5	0.2	100	1227	1104	[34]
			2.0	2000	795	620	
单原子 Fe	60	1.5	0.2	100	1397	1176	[35]
			1.0	500	899	800	
单原子 Co	68	2.0	1.0	500	927	681	[36]
单原子 Co	56	1.0	0.5	700	871	571	[37]
单原子 Co	54	–	0.1	150	1417	1182	[38]
			1.0	500	1113	1003	
单原子 Co	–	3.5	0.2	600	1000	500	[39]
单原子 Co	56	1.2	1.0	1000	1038	675	[40]
		4.9	0.2	120	1062	871	
单原子 Co	–	2.8	0.5	200	850	682	[41]
		1.0	1.0	500	950	700	
单原子 Ni	–	1.3~1.6	0.5	500	1086	798	[42]
单原子 Zn	–	1.0	0.2	100	1230	1079	[43]
			1.0	800	932	680	
单原子 Mo	65	2.0	1.0	200	912	900	[44]
			2.0	550	831	817	
单原子 V	68	2.0	0.2	100	1200	770	[45]
			0.5	400	780	551	
单原子 W	75	1.1	1.0	500	1063	691	[46]
单原子 Ru	64	1.2	0.2	100	1200	992	[47]
			1.0	800	800	500	

3. 金属纳米催化剂

金属对许多反应都表现出优异的催化活性，最初被研究用于加速多硫化物的转化的金属是贵金属 Pt [55]。自此之后，其他贵金属或过渡金属，如 Ir [56]、Co [57]和 Fe [58]，都被证明能够有效地改善硫转化。表 2 总结了不同种金属纳米催化剂对 LSB 性能的改善。

3.1. 金属 Co

Co 是锂硫电池催化剂中研究的最多的金属，而硫还原反应涉及多步反应过程，单个催化剂可能无法实现全部的催化转化。通常，Co 与 N 结合掺杂在碳材料中可以增加活性位点的数量，增强与多硫化物的相互作用并加速反应，从而改善电化学性能。可以通过将两种不同的碳掺杂材料结合使用，协同加速硫还原反应。金属有机框架(MOF)是制备 Co，N 掺杂碳纳米结构的优良前驱体。Fang 等人利用 Co-MOF 制备了 Co，N 掺杂的碳基复合材料(图 2) [71]。Co 和 N 杂原子的协同作用有效增强了与多硫化物的相互作用，加快了反应速率。

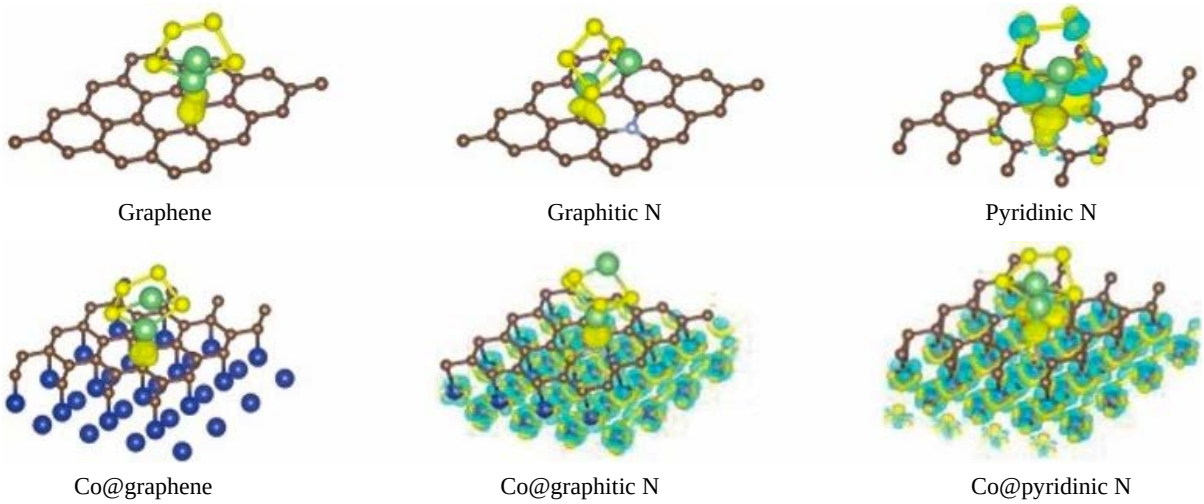

Figure 2. Differential charge density diagram of Li_2S_4 adsorbed on different substrates [90]
图 2. Li_2S_4 吸附在不同底物上的差分电荷密度图[71]

此外，钴金属还可以和其他半导体结合形成莫特－肖特基异质结，作为催化剂使用时具有优化界面电子相互作用的特点。这种莫特－肖特基效应会导致异质结构界面处的自驱动电荷密度分布，有利于与多硫化物的化学结合，增强电荷传输，并减少硫还原反应的能垒[61]。

3.2. 其他金属纳米催化剂

Fe 是另一种有前景的催化硫还原反应的金属。Ye 等人报道了一种具有丰富 Fe 和 N 位点的高度石墨化碳管，用于催化 LSB 中的电化学反应[59]。Fe 的引入促进了石墨化碳管的形成，并作为硫还原反应的催化位点，增强 Li_2S 的沉积。Ru 也被证实是一种有效的催化剂，可以加速 Li_2S_2 到 Li_2S 的转化过程。而且尺寸小于 3 nm 的 Ru 纳米粒子嵌入多孔空心碳球时可降低硫正极的界面电阻[56]。在多孔 N 掺杂碳纳米棒中嵌入超细 Bi 纳米颗粒会导致材料发生局部电荷重排，优化电子结构，提升多硫化物的转化率[64]。

3.3. 纳米合金

合金纳米粒子可以整合单独金属组分的优点，进一步增强催化活性。CoFe 合金优异的催化活性引起了极大的关注。研究发现，CoFe 合金纳米粒子可以通过路易斯酸碱相互作用化学限制多硫化物，催化硫物质的氧化还原过程，并提供快速电子转移途径以获得良好的倍率性能[67]。除了 CoFe 合金，CoSn [72]、FeNi [68]、ZnPd [69]合金和高熵合金[70]也被应用于 LSB 中以催化硫的转化。而所有这些合金都是由碳基底作为支撑材料以获得增强的催化效果。

Table 2. Metallic nanocatalysts improve the performance of lithium sulfur batteries
表 2. 金属纳米催化剂提升锂硫电池性能

催化剂	含硫量/%	载硫量/mg cm^{-2}	倍率/C	循环圈数	初始容量/mAh g^{-1}	剩余容量/mAh g^{-1}	参考文献
Co 团簇	61	1.8	0.1	100	1380	1150	[13]
			1.0	500	912	780	
Co 纳米颗粒	–	2.0	0.2	200	1093	986	[60]
			3.0	500	627	508	
Co 纳米颗粒	60	1.5	1.0	500	909	657	[61]
Co 纳米颗粒	60	1.0	0.2	100	1172	980	[62]
			1.0	500	1100	660	
Co 纳米颗粒	70	1.0	0.2	100	1393	1035	[63]
			1.0	1000	1261	625	
Fe 纳米颗粒	64	–	0.5	300	1050	827	[59]
			2.0	500	750	526	
Bi 纳米颗粒	56	1.2~1.6	0.5	100	1157	970	[64]
			1.0	500	1010	811	
Ag 纳米颗粒	53	1.3	0.5	200	1294 (0.1C)	849	[65]
			2.0	550	918	652	
CoFe 合金	53	1.0	0.1	100	1226	1158	[66]
			1.0	300	890	770	
CoFe 合金	–	1.0	0.2	100	1300	1170	[67]
			5.0	300	1034	870	
CoFe 合金	70	1.0	0.2	100	1264	986	[16]
			1.0	1000	914	457	
NiFe 合金	73	4.1	0.2	200	1000	800	[68]
			1.0	800	950	600	
ZnPd 合金	60	1.2	1.0	500	916	627	[69]
高熵合金	80	1.0~2.0	2.0	500	816	680	[70]

4. 金属化合物催化剂

综合考虑了元素周期表中各元素的价格、丰度等因素，认为在 LSB 中使用金属化合物作为硫氧化还原反应的催化剂具有较大优势(图 3) [73] [74]。极性含氧化合物的 O 原子上含有孤对电子，这导致金属氧化物与多硫化物之间具有较高的结合能[75] [76]。金属硫化物[77] [78]、金属硒化物[79] [80]、金属氮化物[81] [82]、金属磷化物[83] [84]、和金属碳化物[85] [86]可以有效地催化多硫化物的转化过程。金属硼化物的密度较小，有助于 LSB 保持较高的能量密度[87] [88]。由两个或多个金属化合物组成的异质结构具有更为明显的催化作用[89] [90]。此外，催化剂的电子结构和表面性质对金属化合物的催化活性有很大影响[91] [92]。内部和表面缺陷[93] [94]、微观形貌[95] [96]、元素掺杂[97] [98]等改性策略不仅可以产生更多的锚定/催化多硫化物的活性位点，还能提高催化剂的活性，从而实现多硫化物的快速转化[99]。

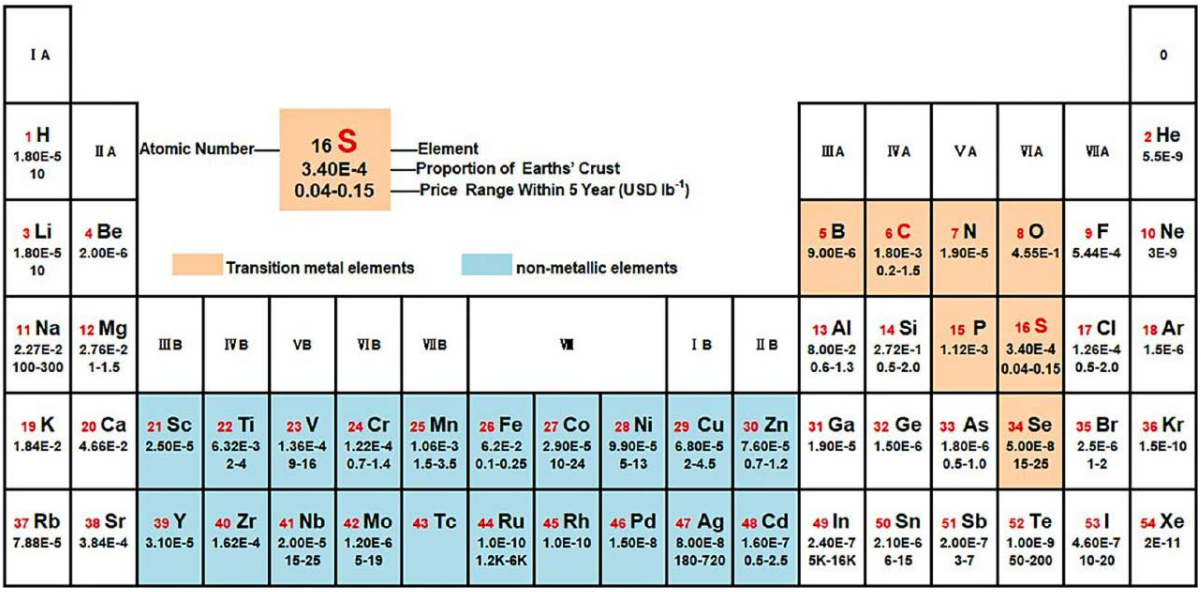

Figure 3. Price and abundance of elements associated with lithium battery catalysts [28]
图 3. 与锂电池催化剂相关的元素的价格及丰度[28]

4.1. 金属氧化物

与非极性碳相比，极性金属氧化物与多硫化物有更强的化学相互作用和更高的催化活性。它们具有

Table 3. Metallic oxide catalysts improve the performance of lithium sulfur batteries
表 3. 金属氧化物催化剂提升锂硫电池性能

催化剂	含硫量/mg cm^{-2}	载硫量/mg cm^{-2}	倍率/C	循环圈数	初始容量/mAh g^{-1}	剩余容量/mAh g^{-1}	参考文献
$STMn_{0.3}$	–	1.5	2.0	1500	780	406	[104]
Janus 颗粒	–	1.0	2.0	250	841	801	[105]
NC@Nb-TiO_{2-x}	–	2.0	1.0	1000	920	696	[106]
Zr_2N_2O/NC-6	–	2.0	1.0	300	857	702	[76]
Fe_2O_3/N-MC	–	5.1	1.0	500	19.4 mAh cm^{-2}	3.7 mAh cm^{-2}	[96]
Ti_4O_7	–	–	0.5	500	1490	819	[107]
CoO	–	2.0	1.0	500	1248	1037	[108]
$NiMoO_4$@NSCC	–	2.0	1.0	500	682	654	[109]
$NiFe_2O_4$	–	–	0.2	500	921	55	[110]
$CoFe_2O_4$	–	–	2.0	500	816	557	[77]
NFB$CoFe_2O_{4-x}$ @MWCNTs	0.3	2.0	1.0	1000	1035	870	[111]
FVO/CNT	0.24	2.0	1.0	850	1183	751	[112]
$ZnCo_2O_4$	0.28	0.6	2.0	450	–	557	[113]
$MnCo_2O_{4.5}$	40%	1.3~1.4	2.0	500	657	553	[114]
V_2O_5	0.2	1.2	1.0	1000	930	586	[100]
OVs-TiO_2	0.12	1.0	2.0	500	802	631	[115]

缓解多硫化物的消耗和提高硫的利用率等优势[100]。由于金属阳离子和氧阴离子之间的极性键可以提供足够的极性活性位点来锚定多硫化物，许多价格低廉的金属氧化物已应用于 LSB [101] [102] [103]。表 3 总结了金属氧化物作为催化剂在 LSB 中的电化学性能。

通过调节原子结构可以进一步提高金属氧化物的活性。值得一提的是，缺陷工程可以通过局部电子的重新分布调节表面电子结构，从而使缺陷电极材料暴露出富集的不饱和配位位点[116]。氧空位(OVs)是典型的缺陷之一，在锚定多硫化物和促进硫氧化还原反应方面具有良好的应用前景[113]。

此外，双金属氧化物也可用于 LSB，抑制穿梭效应，加速硫的氧化还原反应。和 Fe_2O_3 相比，$FeVO_4$ 中的 Fe 3d 能带向费米能级偏移了 0.12 eV；和 V_2O_5 相比，$FeVO_4$ 中的 V 3d 能带更大，更接近费米能级[111]。三维能带的重构增强了双金属氧化物对多硫化物的催化活性(图 4)。

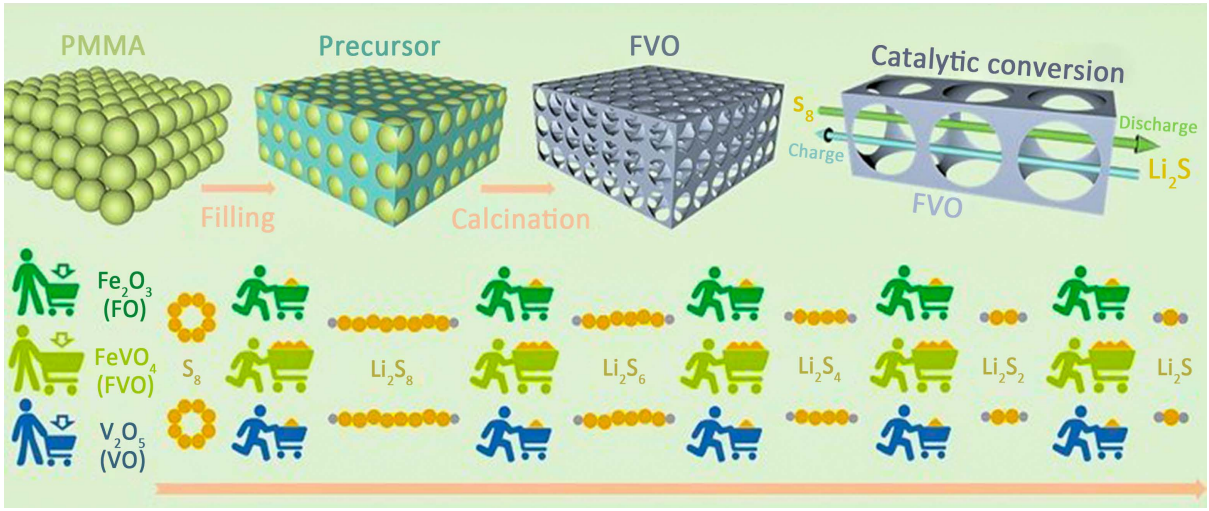

Figure 4. Catalytic processes of $FeVO_4$, Fe_2O_3 and V_2O_5 on sulfur substances [111]
图 4. $FeVO_4$，Fe_2O_3 和 V_2O_5 对硫物质的催化过程[111]

由于金属氧化物能与多硫化物反应生成硫代硫酸盐和多硫酸盐，因此对多硫化物具有很强的吸附能力。然而，典型金属氧化物的导电性不足严重影响了多硫化物的转化和反应速率。因此，未来金属氧化物的设计应侧重于通过与导电聚合物或碳材料耦合来提高电导率，从而提高 LSB 的性能[117]。

4.2. 金属硫化物

金属硫化物中的硫原子具有较高的电负性，有助于从过渡金属中捕获电子，并作为活性位点稳定反应中间体。此外，金属硫化物通常比金属氧化物表现出更好的导电性，这有利于硫化物电极中的电化学转换。

金属硫化物对含硫物质具有很强的亲硫性，可以很好地化学锚定多硫化物。同时杂原子掺杂会破坏金属化合物的局部晶格排列，产生更多的缺陷和活性位点，进而改善 LSB 的电化学性能。例如，Zhang 等人制备了 2D 超薄 3% Co-VS_4/rGO，其电子结构受到 Co 掺杂和 S 空位缺陷(SVs)的影响。氧化还原石墨烯优异的导电性和杂化结构大大提升了材料对多硫化物的吸附/催化，改善了 LSB 的电化学性能(图 5)。S@3%Co-VS_4/rGO 正极的 Li^+扩散系数高于 S@VS_4/rGO 正极，这得益于 Co 掺杂引入的大量缺陷和活性位点。此外，从图 5(b)的原位 X 射线衍射图可以看出，α-S_8 转化为 β-S_8 改善了多硫化物的氧化还原反应，提升了反应的可逆性。然而，虽然金属硫化物的导电性普遍优于金属氧化物，但仍有必要引入导电碳材料，进一步降低内阻，提高硫的利用率。

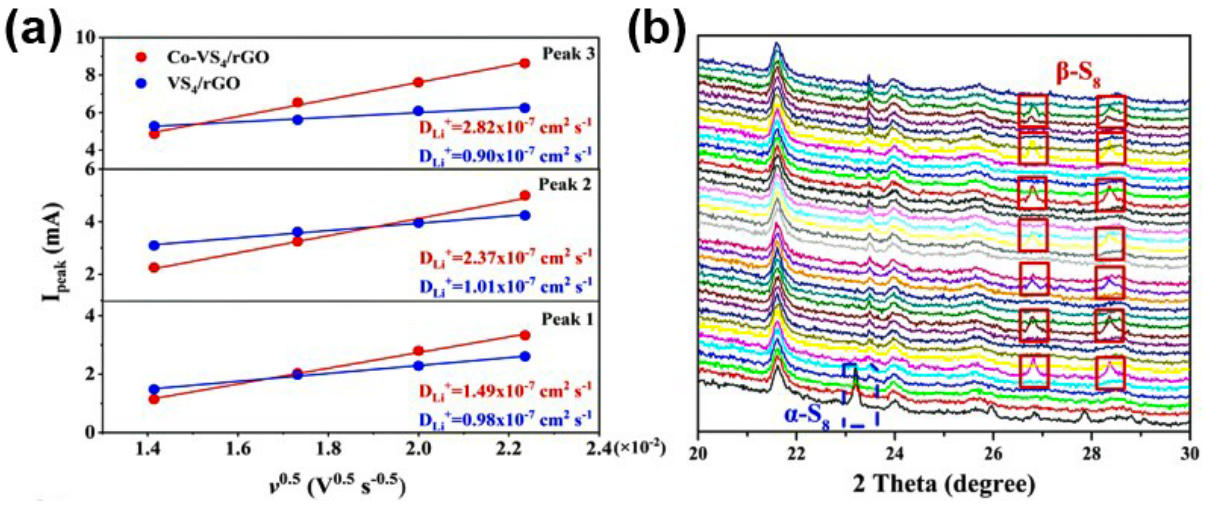

Figure 5. (a) Linear fitting of peak current and Li^+ diffusion coefficient of S@3%Co-VS_4/rGO and S@VS_4/rGO cathode; (b) *In situ* X-ray diffraction pattern

图 5. S@3%Co-VS_4/rGO 和 S@VS_4/rGO 正极(a) 峰值电流和 Li^+扩散系数的线性拟合；(b) 原位 X 射线衍射图

4.3. 金属硒化物

由于 Se 原子和 S 原子具有近似的电负性和离子半径，所以金属硒化物与相应的金属硫化物具有相似的晶体结构、缺陷密度和极性特征[118]。但硒化物的电导率却远远地高于硫化物，这是因为硒的电导率(1×10^{-3} S m^{-1})比硫(5×10^{-28} S m^{-1})高了好几个数量级[119]。因此，金属硒化物(如 $CoSe_2$ [120]、$FeSe_2$ [121]、ZnSe [122])具有合适的 d-电子结构、优异的极性和良好的导电性，对硫转化过程具有催化活性。

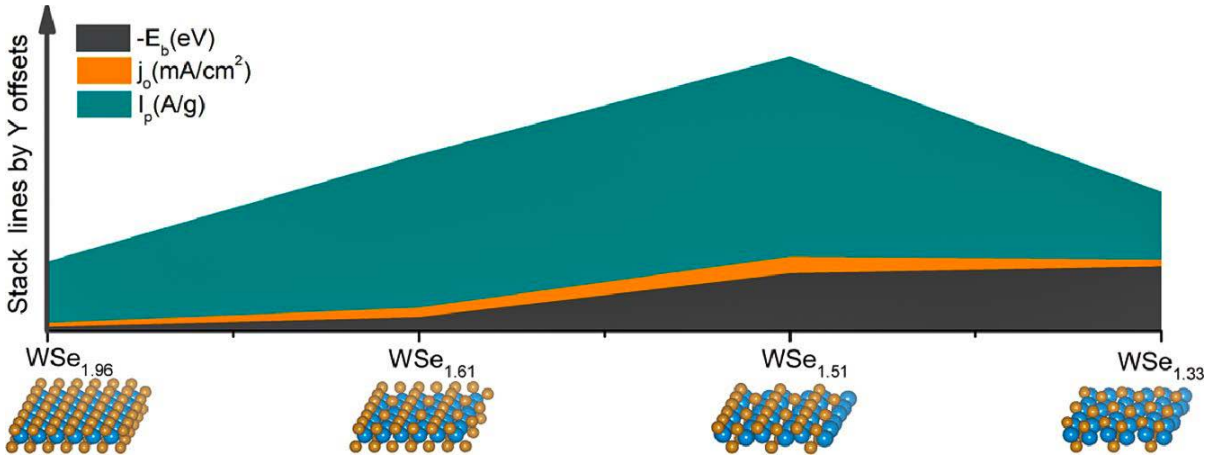

Figure 6. Quantitative comparison of bond energy, exchange current density and peak current intensity at WSe_{2-x}/CNT

图 6. WSe_{2-x}/CNT 的键能、交换电流密度和峰值电流强度的定量比较

Li 等人通过设计 2D WSe_{2-x} 深入探究了硒空位缺陷对多硫化物转化的影响(图 6)。$WSe_{1.51}$ 表现出最合适的硒空位缺陷，对多硫化物具有较强的吸附和催化作用。除阴离子缺陷外，金属阳离子空位的调控也是增强 Li_2S 催化转化的有效途径。硫化物的制备方法和表征方法也同样适用于硒化物，有助于深入理解硒化物和多硒化物之间的作用机理。然而，硒化物在 LSB 中的应用处于起步阶段，仍需适当优化硒化物以进一步适应硫氧化还原过程中的多相反应。

4.4. 金属氮化物

和金属氧化物、金属硫化物和金属硒化物相比，金属氮化物具有更优异的导电性。研究表明，TiN 对多硫化物的吸附能力强于 ZnS、CoS 和碳类材料[123]。这是因为 N 原子可增加金属原子的 d 电子密度，缩小金属原子的 d 能带，所以金属氮化物的电子结构与贵金属相似，这使得金属氮化物可有效地催化硫的氧化还原。

氮化钒(VN)具有良好的耐电化学腐蚀性和优异的导电性(1.17×10^6 S m^{-1})，是最有前途的催化剂材料之一。Liu 等人在 VN 中掺杂了 Co 原子(Co-VN/NC)以便进一步优化电子结构，增强吸附活性。Co 的引入富集 VN 的 d 轨道电子，增加 d 带中心，提高 VN 对多硫化物的亲和力，促进反应动力学。

过渡金属氮化物由于其电子结构、高导电性和较强的多硫化物吸附能力等特点，在 LSB 中得到广泛的研究。然而，目前报道的过渡金属氮化物通常是通过在氨气中氮化金属前驱体来制备的，这导致成本的增加和设备的损坏。因此，亟须制定策略以便在可靠的条件下大量制备金属氮化物，从而进一步推动在 LSB 电池中的应用。

4.5. 金属磷化物

与金属氧化物和金属硫化物相比，金属磷化物具有相似的电导率以及较为适中的多硫化物吸附能力。与金属氮化物和金属碳化物相比，金属磷化物的制备过程更为温和、经济。此外，金属磷化物可以通过相互作用与多硫化物形成 Li-P 键和 P-S 键，从而促进化学吸附过程的进行和短链 Li_2S_2/Li_2S 的生成[124] [125]。

Sun 等人制备了含有 P 空位的 CoP (CoP-Vp)作为模型来探索 P 空位缺陷对电池性能的影响。研究发现，CoP-Vp 的电子构型可以有效增强与多硫化物之间的化学吸附能力，加速多硫化物转化的氧化还原反应(图 7)。紫外可见光谱上的弱 Li_2S_6 峰和吸附后的透明液体均表明，高浓度的 P 空位缺陷具有优异的多硫化物吸附能力。

多金属磷化物中不同金属原子之间的协同互补作用有望促进多硫化物的氧化还原反应。金属磷化物材料具有高导电性、极性表面和优异的催化效果。然而，该材料在室温条件下容易被氧化，为进一步了解结构和活性之间关系带来了巨大的挑战。目前，金属磷化物的制备涉及到复杂的多步骤过程和不可控的相结构。因此，迫切需要探索一步法合成结构精细、催化性能优异的金属磷化物。

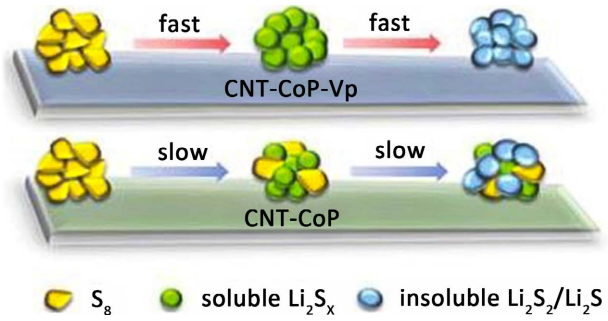

Figure 7. Diagram of continuous reduction process from S_8 to Li_2S_2/Li_2S
图 7. 从 S_8 到 Li_2S_2/Li_2S 的连续还原过程示意图

4.6. 金属碳化物

金属碳化物因其具有优异的导电性而备受关注。与金属氧化物和金属硫化物不同，金属碳化物表现出无带隙的金属性质，改善了导电性并加快了 Li_2S 的沉积速率[126] [127] [128]。

金属活性中心的价态调控工程是调节多硫化物吸附和获得高性能电池的潜在策略。例如，Wang 等人将 Zn^{2+}调控的 Co_3ZnC 锚定在三维介孔氮掺杂碳上制备了 Co_3ZnC@NC。如图 8，首先，NC 作为

导电多孔骨架提供了快速离子/电子传输通道。其次，丰富的 N 原子和 Co 原子活性位点共同作用，吸附并催化多硫化物的可逆转化。最后，部分取代的 Zn^{2+}在优化双金属碳化物的物理结构和增加催化活性位点方面起到协同作用。Co_3ZnC@NC 的最低电荷内阻进一步证实其对多硫化物的强吸附和催化能力(图 8)。

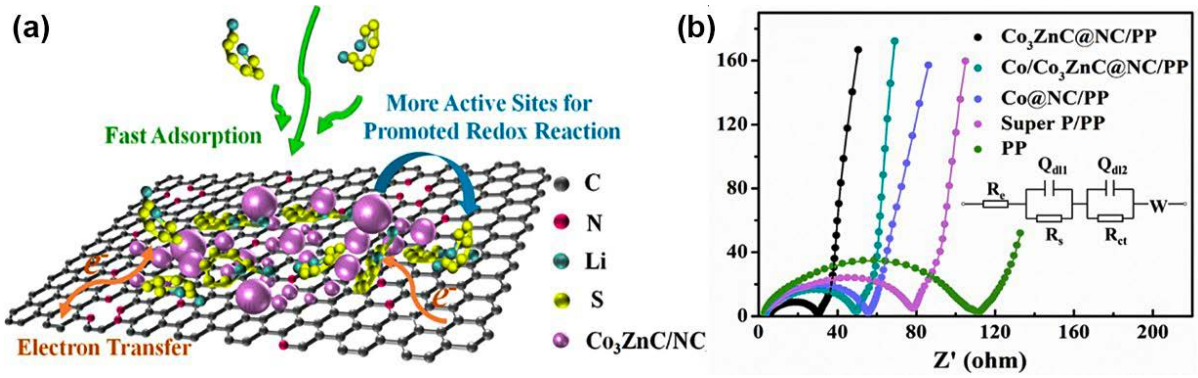

Figure 8. (a) Schematic diagram of the mechanism of Co3ZnC@NC; (b) Impedance diagrams of different cells
图 8. (a) Co_3ZnC@NC 的机理示意图；(b) 不同电池的阻抗图

金属碳化物的极性、高电导率和丰富的活性位点可以有效地促进电荷转移，从而进一步延缓多硫化物的溶解。然而，具有高比表面积的金属碳化物很难制备。其制备过程通常涉及到高温退火的步骤，这极大地限制了其在 LSB 中的大规模应用。在不久的将来，仍需要探索开发易于控制碳化物形态的温和合成方法。

4.7. 金属硼化物

大多数金属氧化物导电性较差，但化学稳定性较高，因而主要通过 Li-O 结合与多硫化物发生强烈的相互作用。金属硫化物、金属硒化物、金属碳化物、金属氮化物、金属磷化物的导电性较强，但化学性质不稳定[129]。而具有空 2p 轨道的硼化物中的 B 原子可以通过 B-S 键锚定多硫化物。金属原子和 B 原

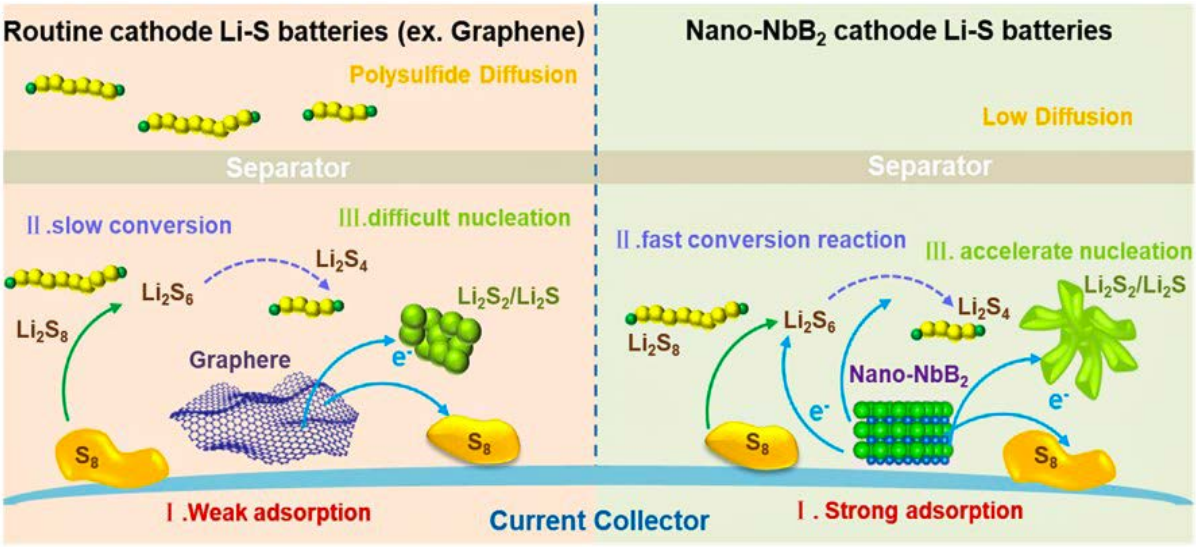

Figure 9. Schematic diagram of catalyst NbB_2 accelerating polysulfide conversion and promoting nucleation of Li_2S
图 9. 催化剂 NbB_2 加速多硫化物转化和促进 Li_2S 成核的原理图

子都能化学吸附多硫化物，有利于化学锚定位点的增加[130]。此外，B 原子 sp 轨道的强杂化改变了金属原子的 d 能带性质，从而增强了金属原子与多硫化物之间的相互作用[131]。

金属硼化物的上述优点已经被应用于研究促进多硫化物的转化过程。Xu 等人合成了 N-P 共掺杂石墨烯(NPG)和二硼化铌(NbB_2)纳米颗粒的复合材料。其中，NPG 具有较大的比表面积和优异的导电性，而 NbB_2 具有丰富且高效的催化位点。NbB_2 纳米颗粒可以调节 Li_2S 的三维成核和生长，从而引导 Li_2S 的径向生长来平衡原子的横向扩散(图 9)。结果表明，NbB_2 可以显著促进 Li_2S 成核，催化 LSB 的液－固反应。

尽管金属硼化物在 LSB 中表现出了巨大的应用潜力，但它们也面临着许多问题，例如苛刻的生产制备条件和不可控的形貌等。金属硼化物在锂硫电池中的进一步应用很大程度上取决于合成方法和结构调控的改进。

5. 总结与展望

在本综述中，我们系统地总结了锂硫电池中硫还原反应金属催化剂材料的最新进展。理想的催化剂应具有良好的导电性、对硫的吸附能力和丰富的催化位点。此外，催化剂的高结构稳定性是延长电池循环寿命的先决条件。目前对硫还原反应金属催化剂的研究主要分为金属单原子、金属纳米和金属化合物三类。尽管在设计更好的硫还原反应催化材料方面已经取得了巨大的进展，但仍需寻求合理的解决方案，以公平地评价和比较催化剂的活性。许多报道表明，各种材料都表现出优异的硫还原反应催化活性。评价催化剂活性的直接标准是锂硫电池的电化学性能，如比容量、倍率和循环稳定性。优良的硫还原反应催化剂可以显著改善电极反应动力学，减轻多硫化物穿梭现象。因此，具有更高的放电容量和更强的倍率性能。此外，基于催化剂材料的固有性质，它们可以降低反应活化能。在等效实验条件下，硫还原反应的反应过电位和塔菲尔斜率等电化学参数可用于评价硫还原反应的催化剂活性。硫各还原步骤的活化能和 Li_2S 沉积容量是反映催化剂性能的重要指标。此外，从光谱分析和理论计算中得到的硫还原反应的途径变化将是催化剂评价的另一个有价值的指导。

然而，由于催化剂的活性是在不同的条件下进行评估的，因此很难对不同的报告进行比较。而氧还原反应和析氢反应都有统一的评价标准，如起始电位、过电位、塔菲尔斜率等，这些参数可以直接与基准进行比较。在锂硫电池中，由于电池结构和电解质成分通常不同，因此很难对不同实验条件下获得的这些值进行直接比较。因此，合理的评价策略有利于设计和筛选高效的硫还原反应催化剂。此外，开发更有效和直接的表征方法对于准确检测各种硫种类和揭示硫还原反应过程中复杂的转化途径至关重要。强烈建议开发更先进的硫还原反应原位表征方法，以反映硫物种的实时演化。总之，最近的研究表明，虽然各种催化剂材料有效加快了硫还原反应动力学，但是仍然需要进行更多的研究来阐明潜在的机制，设计更有效的催化剂，开发先进的表征方法，进而进一步推动高性能锂硫电池的实际应用。

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