科学通报
评 述
《中国科学》杂志社
SCIENCE CHINA PRESS

水系锌金属电池: 失效机制、材料调控与实用化路径

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2025-09-19 收稿, 2025-11-23 修回, 2025-11-25 接受, 2025-11-26 网络版发表
国家自然科学基金(92372207)资助

摘要 在“双碳”目标推动新型储能系统发展的背景下, 水系锌金属电池(aqueous zinc metal batteries, AZMBs)因其本征安全、成本低廉和环境友好而备受关注. 但其规模化应用受限于界面主导的失效机制, 包括枝晶生长、析氢腐蚀级正极溶解等耦合问题. 本文以“界面调控”为核心逻辑主线, 系统综述了AZMBs在负极、电解液与正极三个关键环节的研究进展与挑战, 指出其失效根源在于界面反应的非均匀性与动力学失配. 针对这一关键科学问题, 目前的研究重点已从材料筛选逐步发展为以“分子/离子工程”为核心、以“实用化约束”为目标的体系化协同调控策略. 在负极侧, 通过构建人工界面层、三维集流体及优化锌离子沉积动力学,锌沉积可逆性和循环稳定性得到显著改善; 电解液设计则着眼于调控溶剂化结构、去溶剂化能垒与界面成膜行为, 借助高浓度电解质、共溶剂及功能添加剂抑制副反应、拓宽电化学窗口; 正极方面, 围绕多类正极材料, 揭示了多离子嵌入、转化-溶解等复杂反应机制, 并通过结构修饰与电极工程提升其实际面容量与稳定性. 在此基础上, 本文进一步强调了在有限锌源、低电解液用量及高面容量约束下进行性能评价与机制研究的必要性, 倡导建立统一、可复现的评价标准与多尺度表征方法. 未来研究需重点将“界面失效机理—分子/离子调控—实用化约束”三者系统关联, 为AZMBs从基础研究向工程应用的转化提供新的认知框架与研究范式.

关键词 水系锌金属电池, 负极界面, 枝晶抑制, 电解液, 正极材料, 新型评价标准

在“双碳”目标引领与高比例可再生能源并网的背景下, 适用于电网侧及分布式储能的电化学储能技术需兼顾本征安全、低成本、长寿命及环境友好等多维度要求. 水系锌金属电池(aqueous zinc metal batteries, AZMBs)采用水作为电解液的溶剂, 凭借锌金属资源储量丰富、成本低廉、产业链成熟、正极材料选择多样以及水系电解液本征不可燃等优势, 近年来再度成为学术研究与产业开发的热点[1~3]. 然而, 以界面问题为主导的失效机制仍是制约其规模化应用的关键瓶颈: 负极侧, 锌在水系环境中易发生析氢反应(hydrogen evolution reaction, HER)与腐蚀, 致使副反应产物积累、库仑效率衰退; 电沉积过程中, 局域场分布与传质不均匀性易诱发锌枝晶成核与生长, 甚至刺穿隔膜、发生短路; 正极侧则涉及活性物质溶解-再沉积、界面副产物堆积、材料体相结构水迁移及相变等一系列复杂可逆或不可逆过程[4,5]. 这些多场耦合的失效行为与溶剂化/去溶剂化过程动力学、电解液组成与pH缓冲能力、界面电荷转移及固态电解质界面膜(solid elec-

引用格式: 方明哲, 田欣雨, 王玉聪, 等. 水系锌金属电池: 失效机制、材料调控与实用化路径. 科学通报
Fang M, Tian X, Wang Y, et al. Aqueous zinc metal batteries: failure mechanisms, material control, and pathways to practical applications (in Chinese). Chin Sci Bull, doi: 10.1360/CSB-2025-5561

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trolyte interface, SEI)形成机制密切相关. 因此, 从“材料-界面-体相”多尺度视角出发, 开展系统性协同优化, 已成为当前的研究前沿与核心任务[6].

围绕“负极-电解液-正极”协同调控策略, 近五年来AZMBs领域涌现出一系列标志性的研究进展: 在负极侧, 研究从早期依赖“锌过量+低浓度电解液”的被动策略, 逐渐发展为采用人工/原位SEI、晶面调控与合金化改性、三维集流体构建等界面与结构工程手段, 以实现锌离子均匀沉积并有效抑制界面副反应[7]; 在电解液设计中, 体系从传统低浓度电解液扩展至高浓度电解质、水/有机共溶剂、复盐体系及离子液体(ionic liquids, ILs)介入等多种新型系统, 通过分子设计与离子工程策略调控溶剂化结构和去溶剂化能垒, 从而降低界面传输阻抗、抑制活性水, 并引导形成富氟等稳态无机界面膜; 正极材料方面, 在锰基、钒基、卤素基、普鲁士蓝类似物(Prussian blue analogues, PBAs)及有机/聚阴离子等体系研究中, 逐步整合出涵盖“插层-转化-溶解/沉积-质子协同”等反应机制的机理框架; 面向高负载电极的结构优化与离子/电子导电网络设计也逐步进入工程化验证阶段.

因此, 本文以界面化学行为为主线, 以实用化评价体系为约束, 综述了AZMBs领域近年来的重要研究进展与关键科学问题. 具体内容包括: (i) 从锌负极界面过程出发, 梳理了从溶剂化、去溶剂化、成核、生长到溶解的协同失效机制与相应稳定策略, 对比分析无机/有机/杂化SEI构建、晶面调控与织构诱导、三维集流体设计以及合金化分流等策略的作用机制与适用范围; (ii) 在电解液方面, 围绕盐类、溶剂类型、添加剂、ILs、凝胶电解质设计, 阐释了分子与离子工程如何通过调控Zn^{2+}溶剂化结构、局部pH与界面能垒, 实现抑制腐蚀、促进均匀沉积、稳定界面成膜及拓宽温度适应性的协同效果; (iii) 针对正极材料, 剖析了锰基正极的溶解与相变、钒基正极中结构水与离子迁移的耦合行为、PBAs的空位与结晶水稳定性以及有机电极材料的溶解特性等关键问题, 并提出面向高面容量厚电极的极化抑制与传质优化策略.

此外, 在实用化应用中, AZMBs的性能不仅依赖于材料本身的特性, 更受限于负极正极容量比(negative-to-positive capacity ratio, N/P比)、电解液/电池容量比(electrolyte-to-capacity ratio, E/C比)及面容量等严格工况条件. 因此, 在这些约束条件下, 进行系统化的性能评估和机制研究尤为重要, 建议采用统一且可复现的标准进行多尺度表征与评价. 总之, AZMBs的研究已从单纯材料筛选迈入了以“界面化学为核心、多尺度协同为路径、工程实用化为约束”的新阶段, 为后续负极、电解液与正极的分述提供了清晰的研究基础.

1 水系锌金属电池发展历程

AZMBs的发展历程可归纳为三次关键的跃迁: 从早期一次电池及强碱性体系面临的“可逆性困境”, 演变至弱酸/中性电解液环境下的可充电AZMBs体系, 再发展到当前以界面化学与分子/离子工程为核心、以实际工程工况为约束的系统性优化阶段. 这一发展体现为: 通过调控溶剂化-去溶剂化过程及界面成膜机制, 重构锌负极的沉积/剥离行为, 并实现与正极反应路径及电解液电化学稳定窗口的协同匹配. 早期研究可追溯至勒克朗谢(Leclanché)电池和碱性锌锰一次电池体系[8]. 当尝试在KOH等强碱性电解液中实现电化学可逆性(如锌-镍、锌-锰电池体系)时, 锌负极普遍面临腐蚀、枝晶生长以及形变等多类问题, 致使循环效率与安全性难以兼顾, 其发展历程如图1所示. 该阶段的核心在于: 锌负极问题的本质是热力学不稳定性与动力学失控的共同结果, 任何试图只解决其中一个问题的单一策略都会在其他方面引发更严重的失效[9~11].

第二阶段以$ZnSO_4$、$Zn(CF_3SO_3)_2$等中性或弱酸性电解质的应用为代表, 显著缓解了强碱环境下的腐蚀问题[12], 为锰基、钒基化合物、PBAs以及部分有机/聚阴离子正极提供了稳定的可逆反应平台[13~15]. 对其储能机理的认识也从单一的Zn^{2+}嵌入/脱出扩展为H^+协同嵌入、转化及溶解-沉积等多种机制共存的反应机理[16,17], 各路径的相对容量贡献受局域pH环境、结构水含量及Zn^{2+}溶剂化鞘结构的共同调控; 由此, 正极的容量来源与容量衰退机制被统一纳入与“晶体结构/配位化学-电解液溶液化学”相关联的分析框架中.

第三阶段以电解液工程的深入发展为关键特征. 例如, Li等人将研究策略从低浓度水系电解液转向高盐浓度/“盐包水”(water-in-salt electrolytes, WiSEs)体系[18], 降低了自由水活度、拓宽了电化学窗口并改变了Zn^{2+}的溶剂化结构; 此外, 通过引入pH缓冲剂或混合盐可精确调控界面局域pH环境, 抑制副反应的发生[19]; 同时, 利用水/有机共溶剂与功能性分子添加剂, 可在分子尺度调控去溶剂化能垒, 诱导形成富氟等稳定无机界面相; Lu团队进一步将ILs作为添加剂, 通过阴-阳离子协同策略以实现对锌负极腐蚀的深度抑制、锌沉积

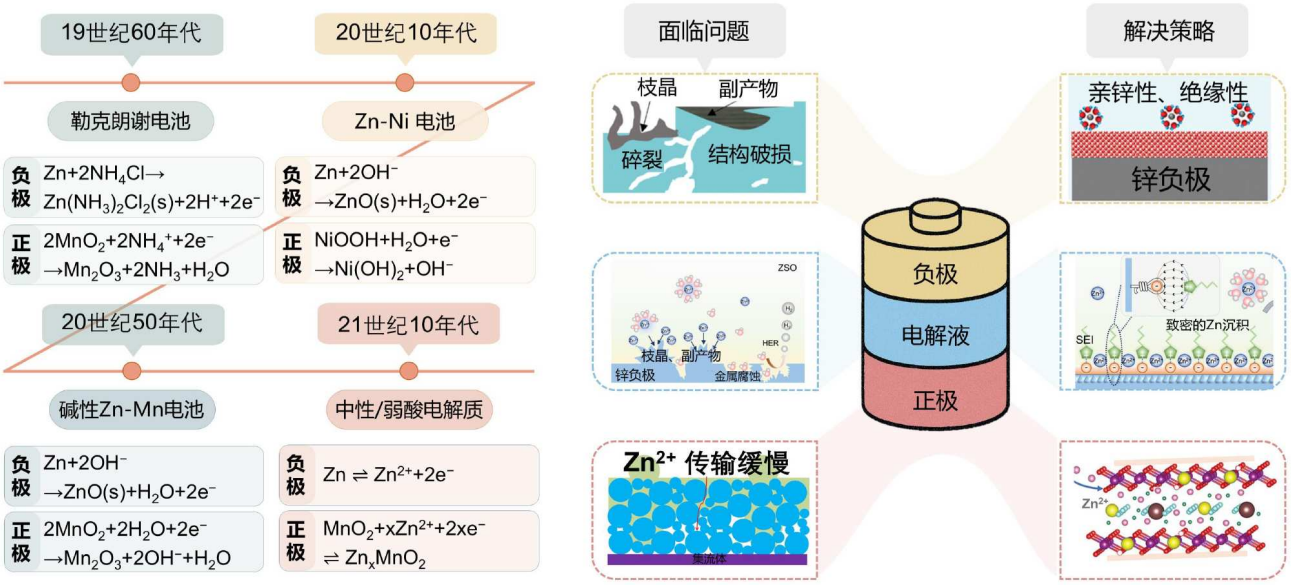


图 1 (网络版彩色)AZMBs的发展历程与技术革新[9~11]
Figure 1 (Color online) The development history and technological innovations of AZMBs[9–11]

形貌优化及电池的宽温域性能提升[10,20,21]; 面向高安全应用场景, 凝胶/固态电解质及功能化隔膜通过“物理限域与离子输运通道”的协同设计, 提升了在高面容量厚电极中的离子传导能力与枝晶抑制效果. 这一系列进展标志着AZMBs的研究从初期的“组分替换”式探索逐步演进为对“溶剂化结构诱导界面成膜、促进离子传输”行为的系统化设计与调控.

值得注意的是, 负极研究从锌源、电解液过量的宽松条件转向了在有限锌源和受限电解液用量的约束下, 追求高平均库仑效率(≥99.5%)及长循环可逆沉积/剥离[22,23]. 主要策略包括: 构建原位/人工SEI(如ZnF_2、磷酸盐、碳酸盐与聚合物杂化层), 赋予了负极/电解液界面电子绝缘、高锌离子导通与阻水的功能[12,24,25]; 采用三维集流体匀化电场并减缓电极形变; 利用晶面诱导与微量合金化降低成核过电位、提高成核密度. 例如Pu等人通过预锌化与脉冲电沉积调节传质与去溶剂化, 引导沉积形貌由枝晶向等轴晶转变, 从而构建了“界面-结构-电解液”协同调控体系[26,27].

正极研究则从材料的筛选与简单拓展迈向了反应机理的深度剖析. Bai等人归纳了锰基正极随电位与电解液呈现Zn^{2+}/H^+共嵌、转化及溶解-沉积等多重反应的内在竞争机理, 并总结了锰基正极现阶段需借助缺陷调控、阳离子预嵌和高导电网络以稳定结构、抑制溶解的优化方案[28]; Luo等人对钒基材料进行了系统性总结, 强调钒基正极需协同优化离子通道与结构水稳定性[29]; PBAs的稳定性依赖于配位环境、结构空位及结晶水; Li等人针对有机/聚阴离子材料, 指出其需在溶解性与离子/电子传输能力之间寻求最佳平衡[30]. 面向工程化应用, 负载量≥10 mg cm^{-2}的厚电极需设计梯度孔隙结构并协同优化黏结剂与集流体以降低极化, 并为软包及叠片电池的验证提供支撑.

2 锌金属负极的失效机制与稳定化策略

水系电解液中, 锌负极失效主要源于枝晶生长、腐蚀/HER及副产物积累三者耦合驱动的复杂过程, 并在工作与空闲状态中持续发生, 其示意图如图2(a)所示[31~33]. 其失效动力学的根源可归结为以下几点: Zn^{2+}第一溶剂化鞘的组成决定其去溶剂化能垒与交换电流密度, 进而调控成核过电位与密度; 沉积过程中局域电场集中与离子浓度极化将放大尖端效应, 加剧枝晶生长; 锌金属负极的自腐蚀与HER致界面附近的pH升高、诱发$Zn(OH)_2$/ZnO/碱式盐等绝缘脆性副产物层, 该钝化层将增加阻抗、引发电子泄漏与二次副反应发生, 这些过程相互加剧, 导致界面持续恶化, 如图2(b)所示. 即便开路静置, 自由水与溶解氧仍然会持续腐蚀导致电池失效, 故仅抑制工作状态下的副反应远无法满足实用要求. 因此, 稳定化策略的核心目标为: 在有限锌源(N/P可控)与低电解液用量(E/C可控)下, 实现高平

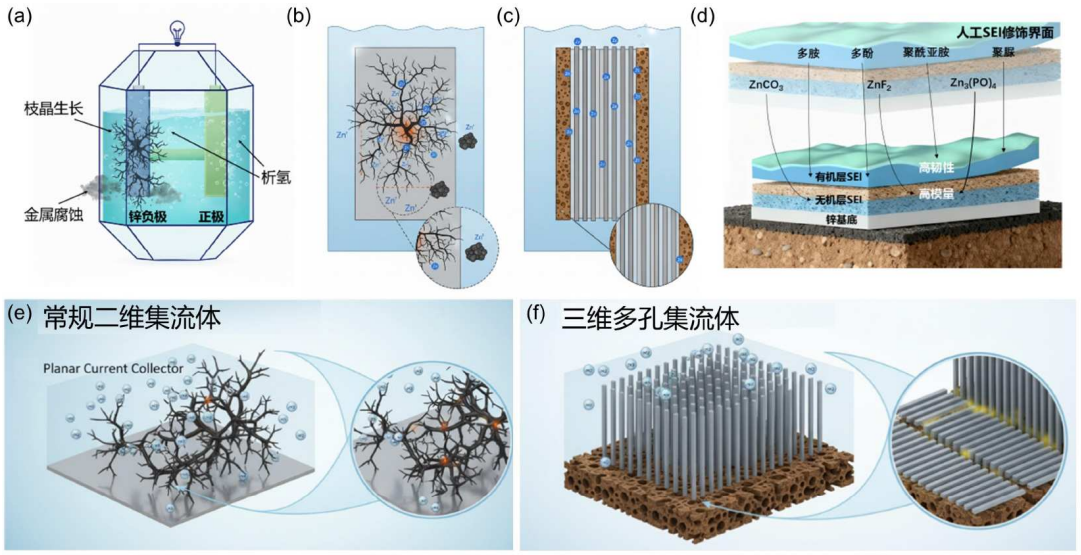


图 2 (网络版彩色)锌金属负极的失效机制与稳定化策略. (a) AZMBs中常见的枝晶生长、金属腐蚀、HER三大问题示意图. 三大问题耦合驱动的界面恶化示意图(b)及界面处理想的形貌示意图(c). (d) 同时具有高韧性、高模量的有机-无机人工SEI修饰界面示意图. 二维集流体(e)与三维多孔集流体(f)对锌沉积的影响示意图

Figure 2 (Color online) Failure mechanisms and stabilization strategies of zinc metal anodes. (a) Schematic diagram illustrating the three major issues commonly encountered in AZMBs: dendrite growth, metal corrosion, and the hydrogen evolution reaction. Schematic illustration of interface degradation driven by the coupling of three major issues (b) and the ideal interfacial morphology (c). (d) Schematic of an organic-inorganic hybrid artificial SEI modification interface with both high toughness and high modulus. Schematic of the influence of two-dimensional current collectors (e) and three-dimensional porous current collectors (f) on zinc deposition

均库仑效率(≥99.5%, 有效抑制工作与空闲状态的腐蚀反应)、长循环可沉积/剥离及可控形貌, 理想的界面形貌如图2(c)所示. 研究者主要从界面修饰、结构工程及工况与电解液协同调控三个方面提出了多种稳定化策略, 以实现均匀沉积与长期循环稳定性.

在界面修饰方面, 通过在锌负极表面构建人工或原位界面层(类SEI/ASEI), 凭借电子绝缘、离子选择性导通及阻水特性, 实现长期腐蚀抑制与锌离子均匀沉积. He等人发现以无机成分为主导的SEI(如ZnF_2、$Zn_3(PO_4)_2$、$ZnCO_3$及含硼氧化物)具备高致密性与稳定性, 但普遍缺乏韧性[34,35]; Wang等人提出的高极性聚合物/有机层SEI(如多胺、多酚、聚酰亚胺、聚脲等)具有良好的柔韧性, 其分子链上含有的配位基团或氢键位点可有效降低界面水活度、促进Zn^{2+}传输, 但其热/化学稳定性与离子电导率仍有待提升[36]; Lu等人原位构筑的无机-有机杂化层则可兼顾二者优势, 具有较好的离子传输动力学和热力学稳定性, 保护新鲜沉积锌金属避免腐蚀, 实现长时间的单晶锌成核[37]. 界面层的构筑方法包括化学转化、原位诱导、溶胶-凝胶层及低电流预成形等[38]; 为平衡电子阻挡与离子传输, 保护层的理想厚度通常控制在数十至一百纳米之间. 理想的具有高韧性、高模量的有机-无机人工SEI界面如图2(d)所示.

锌金属负极的结构工程旨在通过均匀化电场与传质抑制尖端效应. Zeng等人开发的三维多孔集流体(如金属泡沫、碳气凝胶、纳米纤维)可有效降低局部电流密度、提供锌离子横向的扩散路径, 但其孔径、孔隙率与连通性需与面容量匹配, 以防锌离子在孔道内部发生局部沉积堆积和堵塞(图2(e, f))[39]; Miller等人设计的晶面/织构诱导与“亲锌”层(如Cu、Ag、In合金)有助于降低成核过电位[40]、提高锌离子成核密度, 但需避免形成导电微短路通路; 微量合金化(如In、Bi、Sn)可调节成核热力学、改变HER路径并增强锌负极耐腐蚀性, 但需防止合金相脆化和循环后粉化失效.

工况与工艺调控可用于动态优化沉积形貌并抑制副反应. Zhi等人提出的低电流预沉积和电化学成形方法, 可制备均匀的初始沉积层, 为后续循环奠定良好的基础[41]; 脉冲调制通过沉积-弛豫交替缓解电极表面锌离子离子浓度极化、降低去溶剂化能垒, 必要时可采用轻微反向电流以缓解枝晶效应; 温度与微对流调控需在抑制副反应与优化电解液黏度-离子扩散间权衡; 锌负极在空闲状态下的稳定性依赖于界面层抗溶胀/溶

解性及电解液的pH缓冲能力，以减少开路状态下腐蚀和pH波动. 锌负极稳定性与电解液化学稳定性紧密耦合，需协同推进分子/离子工程[42]: Lu团队采用弱配位阴离子、共溶剂或少量ILs重构Zn^{2+}第一溶剂化鞘，以降低去溶剂化能垒、提高交换电流密度[43]; Zhang等人利用具有定向吸附与成膜能力的阴离子(如$DFOB^-$、F^-、PO_4^{3-}、有机磺酸根)，在循环初期诱导形成致密无机界面层[44]; 通过缓冲/复盐与水活度调控抑制析氢与静置腐蚀. 负极界面的结构工程需在宽温域、阻燃性与离子传输性能之间进行系统权衡.

3 电解液优化

电解液在AZMBs中具有多重关键作用: 它不仅决定了Zn^{2+}的溶剂化结构、去溶剂化能垒与界面电荷转移过程，还主导负极腐蚀、析氢行为、界面SEI的形成与演化, 以及正极活性物质溶解-再沉积行为, 并直接影响电导率、黏度及安全性等多重工程指标[45]. 因此, 电解液优化的核心在于对“溶剂化-去溶剂化-传输”全过程进行分子/离子尺度精细调控，以实现高初始成核密度与致密沉积，并在长循环和静置中持续抑制副反应、维持界面稳定. 在锌盐选择上，需结合实际应用在$ZnSO_4$、$Zn(CF_3SO_3)_2$间权衡, 如图3所示. Wu团队的综述指出, 前者成本低、稳定性高, 而后者更易调控溶剂化结构、降低去溶剂化能垒并促进早期无机界面层形成[46,47]. 引入混合盐或pH缓冲剂可有效抑制局部pH波动，减少$Zn(OH)_2$/碱式盐生成，但应避免过度缓冲引发盐沉淀或干扰正极固有的氧化还原机制. 浓度策略上, 准高浓或WiSE电解液可降低水活性、拓宽电化学稳定窗口并抑制析氢, 然而, 这通常会以牺牲离子传输和经济性为代价，电解液效能平衡示意图如图4(a)所示[48]. 因此, 在实际应用中需在电化学窗口拓展、腐蚀抑制、离子传输、经济成本间寻求工程实用化的最优平衡区间[49], 图4(b)进一步总结了锌盐与共溶剂的筛选标准.

共溶剂策略通过引入有机分子重构电解液氢键网络并影响Zn^{2+}配位，可有效降低去溶剂化能垒[14,45,50]; 低聚醚、多元醇及部分酰胺类共溶剂有助于改善界面动力学并提高锌离子的成核密度[51~54]; 其用量需通过拉曼/红外光谱、黏度-离子导电性分析及界面谱学表征共同确定, 以避免过度稀释Zn^{2+}或引发宏观上的相分离. 少量ILs作为多功能添加剂, 可在不明显增加黏度的同时增强腐蚀抑制与宽温性能. Mai等人的工作指出,

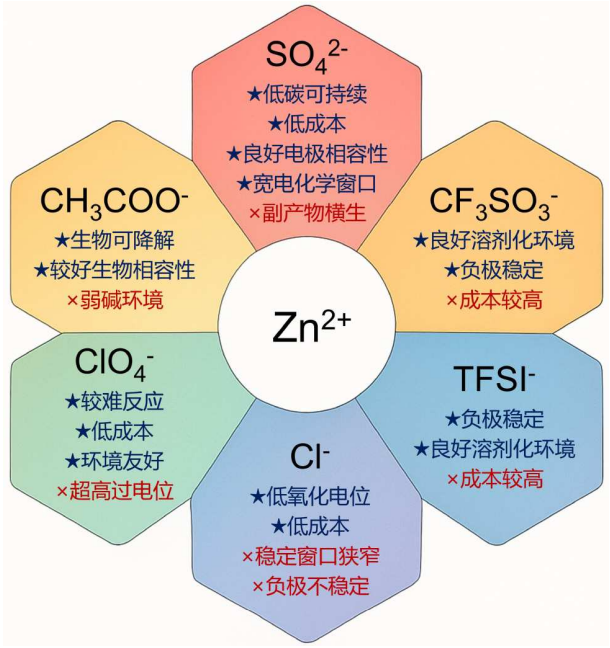


图 3 (网络版彩色)用于AZMBs电解液的不同锌盐优缺点
Figure 3 (Color online) Advantages and drawbacks of different zinc salts used in AZMBs electrolyte

ILs含氟、磷或硼官能团的离子可作为界面吸附剂或成膜前驱体[10,20,55,56]; 但其阴离子有与正极高价金属离子(Mn^{3+}、V^{4+}/V^{5+})形成稳定可溶络合物、加剧正极材料溶解的风险, 因此需注意ILs与正极匹配问题. 近年来提出的局部高浓(localized high-concentration electrolytes, LHCEs)策略通过在高浓度电解液中引入惰性稀释剂，以保持局部高离子配位结构、有效降低整体黏度与成本，从而在电化学稳定性与传输性能之间实现更优平衡. Lu团队的工作揭示了共溶剂策略下的常规LHCEs、离子解耦型LHCEs体相的状况(图4(c))[43]. 此外, Guo团队也证明了醚醇类共溶剂策略对Zn^{2+}脱溶剂化的积极影响(图4(d))[14]. 经验表明, “适中配位强度阴离子-低黏度共溶剂-微量功能性成膜组分”的三元协同体系，通常比单纯采用极高浓度或极强配位策略更易实现综合性能优化.

添加剂的设计旨在构建“吸附-成核-成膜-缓冲”的闭环调控机制(图4(e)). Lu等人引入卤素阴离子动力学增强策略，以四甲基卤化铵(TMAX, X=F, Cl, Br)为研究对象, 诱导稳定的固相卤素间化合物形成, 提升了电化学性能[57]; Hu等人探讨了含氟磺酸盐在构筑复杂保护层、诱导锌均匀沉积、微调电解液物化性质方面的贡献[58]; Wang团队提出含磷酸根/硼酸根等阴离子的添

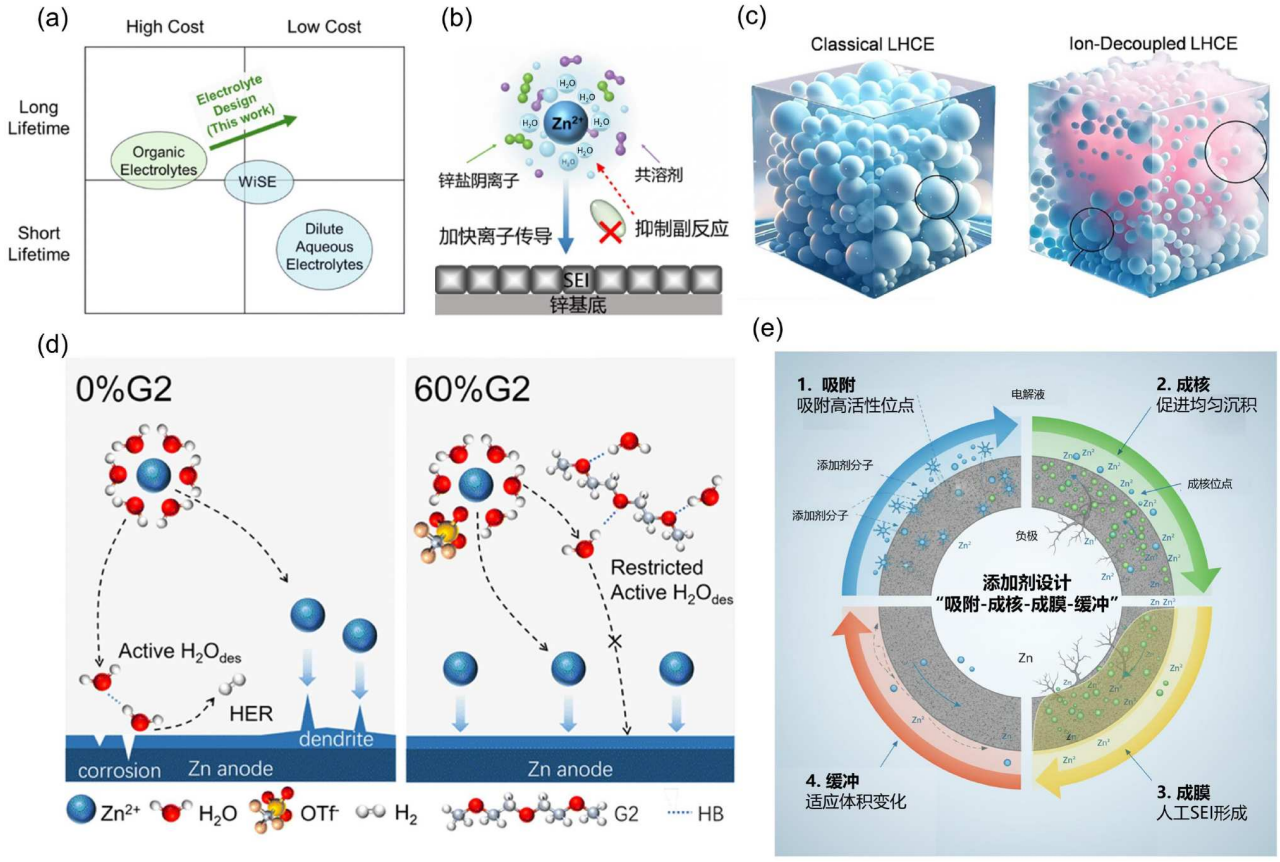


图 4 (网络版彩色)用于AZMBs的电解液优化策略. (a) 用于AZMBs的电解液效能平衡定性示意图[48]. (b) 电解液策略中锌盐与有机共溶剂的选择示意图. (c) LHCE策略与离子解耦型LHCE的设计策略对比[43]. (d) 共溶剂策略中(以60% G2为例)中弱溶剂化环境Zn^{2+}脱溶过程示意图[14]. (e) 锌负极添加剂设计的"吸附-成核-成膜-缓冲"闭环调控机制示意图

Figure 4 (Color online) Electrolyte optimization strategies for AZMBs. (a) Qualitative schematic illustrating the efficiency balance of electrolytes for AZMBs[48]. (b) Schematic showing the selection criteria for zinc salts and organic co-solvents in electrolyte strategies. (c) Comparison of LHCE strategy and the design strategy of ion-decoupled LHCE[43]. (d) Schematic of the Zn^{2+} desolvation process in a weakly solvated environment within a co-solvent system, using 60% G2 as an example[14]. (e) Schematic diagram of the closed-loop regulation mechanism of "adsorption - nucleation - film formation - buffering" for zinc anode additive design

加剂可通过界面定向吸附，诱导ZnF_2、$Zn_3(PO_4)_2$等致密无机界面层的原位形成[44,59]；多胺、多酚、咪唑/苯并三唑、脲/多元醇等分子抑制剂可降低水活度与去溶剂化能垒，提升成核密度；Pan等人提出的过硫酸铵添加剂作为pH缓冲剂或牺牲剂，可在界面碱化时消耗OH^-或清除自由基[60]；针对锰基正极的补锰/溶出抑制策略有助于缓解溶解-再沉积与价态变化引发的容量衰减. 设计复合添加剂体系应避免组分间的竞争配位与非功能性吸附，并遵循"正负极兼容、低用量高效"的核心原则. 为兼顾安全性与厚电极中的离子传输，可采用薄层聚合物凝胶与功能化隔膜一体化策略. 总体而言，精细化的添加剂设计已成为调控电极/电解液界面反应动力学与构建稳定界面的关键途径.

凝胶电解质通过构建三维网络结构，能够有效引导锌离子均匀沉积、抑制枝晶生长，同时显著降低水活度与抑制副反应(如HER)，从而大幅提升水系锌离子电池的循环稳定性与安全性. Chen等人制备了一种乙酸根整合的聚丙烯酰胺(polyacrylamide，PAM)凝胶电解质，可锚定水分子并诱导均匀的Zn^{2+}沉积，赋予其温度适应性和循环稳定性[61]. Zhi团队设计了一种基于聚乙二醇甲基醚甲基丙烯酸酯(polyethylene glycol methyl ether methacrylate, PMEM)和N-羟乙基丙烯酰胺(N-hydroxyethyl acrylamide, HEAA)的凝胶电解质，可促进离子传输、降低水的活性，在宽温域(−10~90°C)下实现长期稳定循环. 因此，凝胶电解质的分子结构设计与离子调控能力在实现高安全性与宽温域可操作性的水系

电池中具有重要意义.

通过对隔膜进行功能化改性，可引导锌离子均匀流动以抑制枝晶生长，同时有效阻隔电解液中的水分子及副反应产物，从而显著提升水系锌离子电池的循环稳定性与可逆性. Li团队设计并制备了HTO@GF功能隔膜，其亲锌/负电荷特性可匀化电场、缩短锌离子传输路径、选择性阻隔阴离子[62]. 此外, 高机械模量隔膜也是抑制负极枝晶穿刺的有效物理屏障. Chen等人设计的V-NFC-CS高模量隔膜通过排列规整的垂直离子通道实现了Zn^{2+}的快速离子传输, 极大提升了循环性能[63]. 这类隔膜的厚度与孔结构应与电极的面容量、倍率及E/C比协同设计，以避免引入额外的极化、降低电池的体积能量密度. 综上, 功能化高模量隔膜在实现离子选择性传输与结构稳定性平衡方面，为水系锌离子电池的长寿命与高能量密度提供了新的设计思路.

4 正极材料的失效机制与优化策略

正极材料的现存问题如图5(a)所示[64], 水系锌电池的正极材料既是容量与电压平台的提供者，也是与电解液紧密耦合、动态演变的反应中心. 一般来说, 嵌入型正极的长期循环衰退通常源于三类机制的叠加: (i) 正极材料的结构退化; (ii) 正极材料的溶解流失; (iii) 界面副反应与不可逆产物生成. 这三者并非孤立存在, 而是相互关联、彼此加剧. 例如, 结构退化会暴露出更多新鲜表面，加剧溶解流失；而溶解出的金属离子(如Mn^{2+})在电解液中迁移，可能又在锌负极表面沉积，或与溶解的锌离子反应生成惰性产物，进一步加剧界面副反应和整体失效[68,69]. 对于转化型正极而言, 除上述结构退化、溶解流失与界面副反应外，其循环衰退还常源于反应过程中价态与相结构的不可逆转化. 反复的转化/逆转化反应会导致活性物质团聚、电荷传输通道中断及部分中间产物难以重新氧化还原，从而进一步加速容量衰退与界面失稳. 此外，在高负载厚电极中，离子/电子传输路径的受限会显著加剧极化，使材料本征优势难以转化为实际电极性能. 因而, 任何有效的优化策略都需在材料、电极和体系三个层面协同开展，并在有限锌源与低电解液用量等工程约束下对其可行性与实用性加以验证.

Gan团队已经研究并证明, 以锰基氧化物为代表的正极材料在中性或弱酸性电解液中通常不限于单一的Zn^{2+}嵌入，还涉及H^+共嵌，甚至伴随转化/溶解-沉积过程[70]. 在酸性电解液(pH<4)中，Mn^{2+}首先被电氧化为Mn^{3+}，Mn^{3+}会由于其不稳定的电子排布而发生Jahn-Teller畸变，导致不规则的晶格形变并导致电压平台的衰退(图5(b))[65,71]；同时，这种不稳定的结构促进了Mn^{3+}的歧化反应，然而由于电极界面MnO_2形核动力学缓慢, 形成了大量电化学惰性的“死MnO_2”颗粒, 造成活性物质的损失[72]. 常见的有效抑制策略包括: 预嵌K^+、Na^+、Zn^{2+}或NH_4^+等“支柱”离子以扩大层间距，结合氧空位或异价掺杂调节电子结构与应力；采用碳包覆或构建正极电解质界面膜(cathode electrolyte interphase, CEI)等方式物理隔绝活性材料与电解液的直接接触[73~76]. Ma等人使用多功能乳酸钠(SCNa)添加剂，在充电过程中吸附于MnO_2正极表面形成CEI层，有效阻止了Mn^{2+}溶出，并使Jahn-Teller畸变转为可逆过程[77]. 体系优化上，电解液中补充适量Mn^{2+}并添加pH缓冲剂可稳定局部pH、抑制溶解-再沉积循环，但需避免过酸/碱或强配位阴离子改变H^+/Zn^{2+}反应路径.

层状和隧道型钒氧化物具备更高比容量，但其循环可逆性与结构水的稳定性密切相关: 层间距收缩或晶格水的不可逆流失易导致Zn^{2+}扩散受阻与偏钒酸根溶出[78]. Chen等人研究并提出, 稳定该体系的关键在于通过有序预嵌入阳离子(如Na^+、K^+、Zn^{2+}、NH_4^+、Mg^{2+})或小分子插层以维持层间支撑并保障离子传输通道的畅通，利用氧空位或异质原子掺杂缩短离子迁移路径，并借助柔性碳网络缓解应力变化(图5(c))[66,79,80]；在电解液选择上，宜选用配位能力适中的阴离子和低黏度共溶剂，兼顾降低去溶剂化能垒与避免过度抽取晶格水，从而在电压窗口、离子传输与结构稳定性之间实现工程化的平衡.

PBAs的循环稳定性主要受$[Fe(CN)_6]$空位、结晶水含量及金属活性位点价态协同演变的制约，阴离子、阳离子络合制备PBAs正极的示意图如图5(d)所示[67]. Zhao等人在合成PBAs过程中通过调控pH与配位环境, 降低了空位密度，并引入金属阳离子以调节晶格应力, 合成了Na^+、K^+掺杂的Na-PB、K-PB正极材料, 显著提升了材料的结构稳定性[81]；纳米碳包覆或导电聚合物复合可弥补本征电子电导不足并阻隔电解液侵蚀. 电解液体系应避免使用强配位或强氧化性组分，以防止金属位点价态的不可逆变化. 结晶水含量是另一关键因素: 结晶水过多会软化骨架并加剧体积形变, 过少则增加离子扩散能垒. 因此, 需通过精确控制结晶水含量及离子交换等方法，在“适度水合”区间内实现动态平衡.

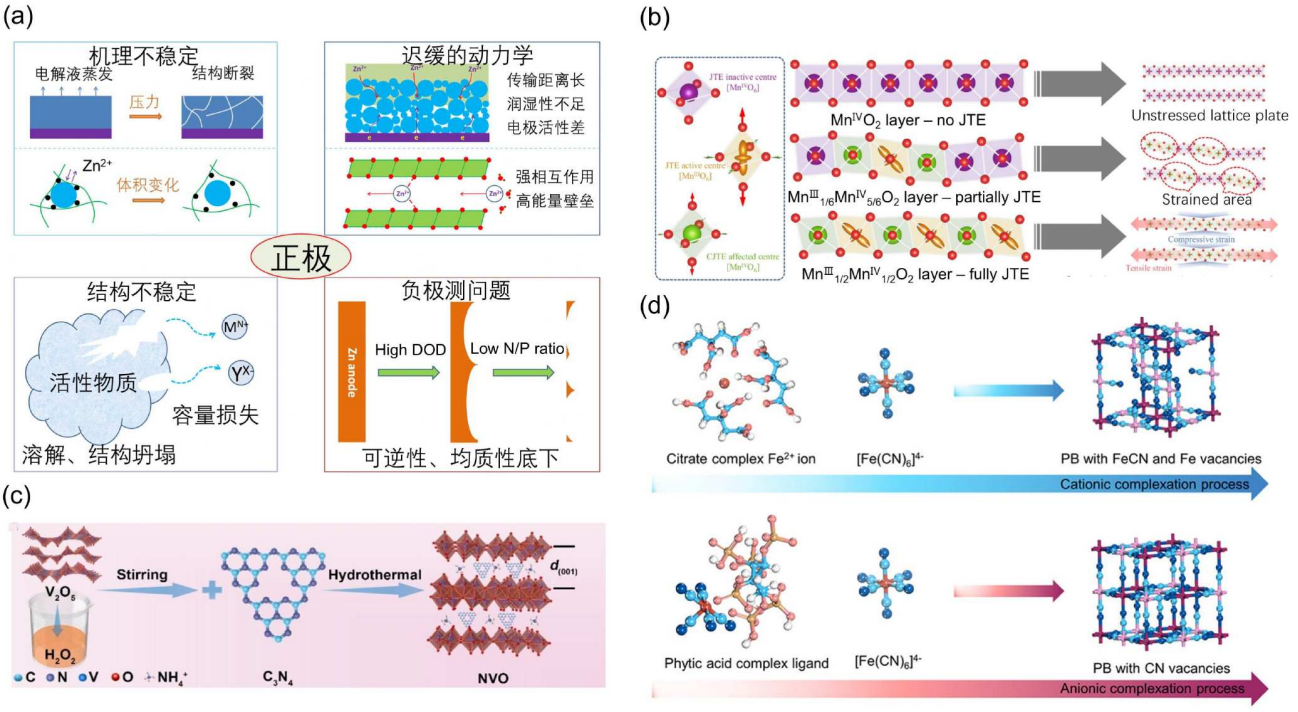


图 5 (网络版彩色)AZMBs正极材料的现存问题与优化策略. (a) 研制高性能高负载AZMBs正极的关键问题[64]. (b) 层状MnO_2中三种不同结果情形: 无协同Jahn-Teller效应(JTE)、部分协同Jahn-Teller效应(p-CJTE)和完全协同Jahn-Teller效应(f-CJTE)的示意图[65]. (c) 由氮化碳(C_3N_4)支撑的缺氧钒酸盐正极的合成路径[66]. (d) 阳离子络合、阴离子络合制备PBAs正极的合成路径[67]

Figure 5 (Color online) Existing challenges and optimization strategies for cathode materials in AZMBs. (a) Key issues in the development of high-performance and high-loading AZMBs cathodes[64]. (b) Three distinct structural evolution scenarios in layered MnO_2: schematic illustrations of the non-cooperative Jahn-Teller effect (JTE), partially cooperative Jahn-Teller effect (p-CJTE), and fully cooperative Jahn-Teller effect (f-CJTE)[65]. (c) Synthesis pathway for an anoxic vanadate cathode supported by carbon nitride (C_3N_4)[66]. (d) Synthetic routes for preparing PBAs cathodes via cation complexation and anion complexation strategies[67]

有机与聚阴离子正极具有结构可调控和环境友好等优势, 但面临活性组分溶解/穿梭效应及本征的电子/离子传导受限等挑战[85,86]. Zhang团队设计了一种具有丰富电活性基团和稳定扩展π-共轭结构的新型有机主体材料BNDTH, 作为AZMBs的正极时, 展现出高达296 mAh g^{-1}的比容量[87,88]. Jin等人通过聚合、交联或构筑共价有机框架(COF)可将活性单元锚定于不溶性载体(图6(a))[82]. 通过分子层面位点工程引入可协同适配Zn^{2+}与H^+的配位位点, 提升活性位点利用率. 通过纳米化并与导电碳复合构建电子传导网络, 再结合亲水离子型黏结剂与定向孔道设计, 可在厚电极中维持有效的离子供给. 该类材料对电解液组分极为敏感, 通常宜采用弱配位阴离子锌盐与低黏度共溶剂体系, 以兼顾结构稳定性与去溶剂化动力学.

卤素/硫等转化型正极虽具有高理论能量密度, 但其活性物质的严重溶出所引发的穿梭效应与副反应较为严重, 是工程化应用的核心障碍[84,89,90]. 可行的解决方案必须协同利用化学络合与物理限域策略. 例如, Liang等人通过向锌-溴电池中引入络合剂四丙基溴化铵(TPABr)以降低活性物种溶解度, 同时采用多孔碳主体材料封装活性物质, 并结合功能化隔膜或黏附层构建“双重阻隔”机制, 从而在低电解液用量下保持快速传质和可控反应界面(图6(b))[83]. 新型的KBr正极制备的软包电池能够在3 C大电流下循环超过750圈, 展现出惊人的应用前景(图6(c))[84].

规模化应用的挑战不仅源于材料的本征稳定性, 更体现在厚电极技术的关键瓶颈上. 当活性物质负载量超过10 mg cm^{-2}时, 离子传输路径的延长与电解液浸润孔道的减少会显著加剧界面处的浓差极化. 解决途径在于构建连续电子-离子双传导网络与梯度孔隙结构: 采用碳纳米管/石墨烯/导电聚合物建立电子传输骨架[91~93], 利用亲离子孔道和离子型黏结剂(如PAA/CMC/海藻酸钠)保持电解液的深度渗透与界面润湿[94~96]; 通过温和的辊压工艺平衡压实密度与孔道连

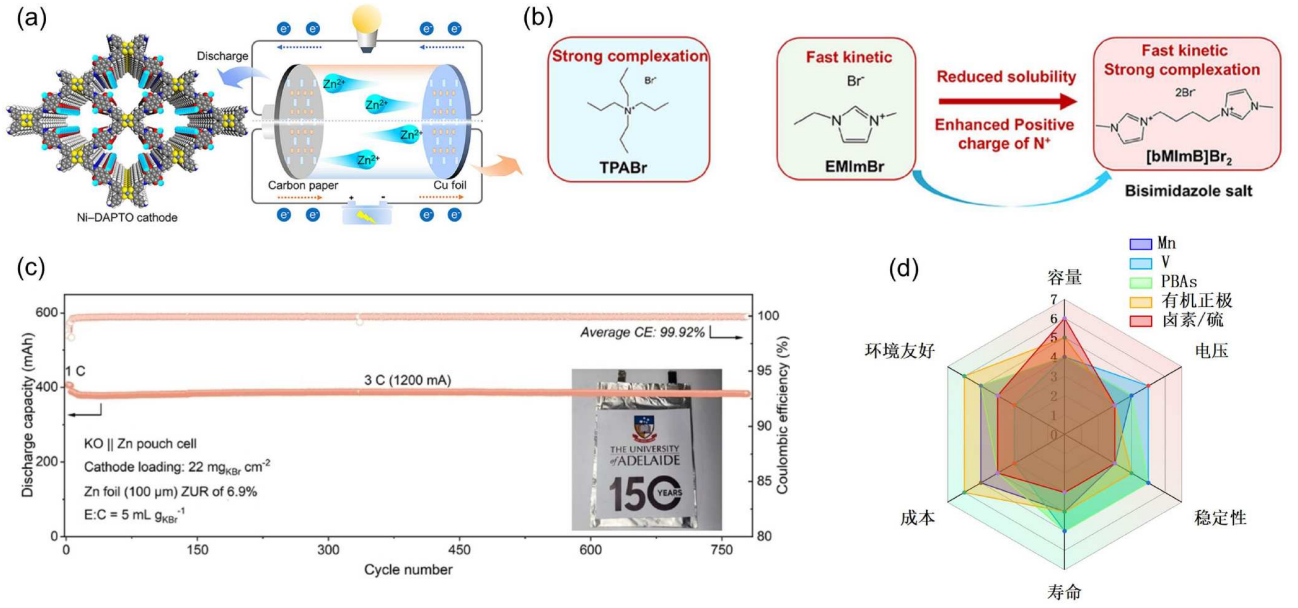


图 6 (网络版彩色)正极材料的现存问题与优化策略. (a) Ni-DAPTO作为COF材料对AZMBs的Zn^{2+}储存和Zn沉积控制的工作机理图[82]. (b) 用于AZMBs的卤素正极1,4-二(甲基咪唑)丁烷二溴盐([bMImB]Br_2)的合成路径及功能机理[83]. (c) 自制KO正极(将OC_4N^+引入KBr正极)的软包电池循环性能[84]. (d) 用于AZMBs的不同正极材料综合性能雷达图

Figure 6 (Color online) Current challenges and optimization strategies for cathode materials. (a) Working mechanism of Ni-DAPTO as a COF material for regulating Zn^{2+} storage and zinc deposition behavior in AZMBs[82]. (b) Synthesis pathway and functional mechanism of 1,4-bis(3-methylimidazolium-1-yl) butane dibromide ([bMImB]Br_2) for AZMBs[83]. (c) Cycling performance of pouch cells employing self-synthesized KO cathodes (with OC_4N^+ introduced into KBr-based cathodes)[84]. (d) Radar chart of the comprehensive performance of different cathode materials for AZMBs

通性, 并可结合选择性涂层隔膜缩短电极表面的离子扩散距离.

在评估用于AZMBs的正极材料时, 必须采用多维度的指标体系进行综合性能考量. 如图6(d)所示的雷达图作为一种高效的可视化工具, 清晰地揭示了不同正极材料在各项关键性能参数上的现有优势与短板. 通过对图谱的直观分析可知, 锰基正极面临电压窗口狭窄的限制, 钒基正极则存在环境友好性不佳的问题, 而PBAs的容量密度相对偏低, 有机正极和卤素正极则普遍缺乏循环稳定性. 这种可视化的性能分布评估, 为深入理解和针对性地优化AZMBs正极材料的综合电化学性能提供了关键的参考依据.

综上所述, 水系锌电池正极在长期循环过程中普遍面临结构演变、界面失稳与反应动力学失衡等多重挑战. 针对这些问题, 研究者正通过多层级协同策略进行优化——包括结构调控(离子预嵌、异质掺杂、氧空位工程)、界面稳化(碳包覆、聚合物复合、功能隔膜)以及体系设计(电解液配位环境与pH缓冲调控)等. 在“结构稳定—传输通畅—界面可控”的主线指导下, 实现正极反应可逆性与体系整体稳定性的协同提升, 已成为推动高比能、高可靠性水系锌电池走向实用化的关键.

5 走向实用化: 从表征到工程化设计

实现AZMBs的实用化, 其关键并非追求单一性能指标的极致, 而是在实用化工况约束下, 将分子及界面层面的改进方案, 稳健地转化为器件整体的可靠性能. 针对电解液和电极材料的性能表征, 应在实用化工况条件下, 通过多维度表征构建溶剂化与界面反应的证据链, 从而支撑优化策略的科学性与可重复性. 具体而言, 塔菲尔曲线测试(Tafel plot)应进行iR补偿, 并区分动力学与扩散控制区间; 电化学阻抗谱(electrochemical impedance spectroscopy, EIS)可用于解析去溶剂化、电荷转移与传质过程的耦合关系; 借助电泳-核磁共振(electrophoretic nuclear magnetic resonance, e-NMR)评估离子的扩散/迁移行为. 此外, 原位拉曼光谱(*in-situ* Raman spectroscopy)、X射线衍射(X-ray diffraction, XRD)、X射线吸收光谱(X-ray absorption spectroscopy,

XAS)、飞行时间二次离子质谱(time-of-flight secondary ion mass spectrometry, ToF-SIMS)及X射线光电子能谱(X-ray photoelectron spectroscopy, XPS)等可用于追踪溶剂化结构、成核、界面成膜/溶解的动态演变; 结合扫描电子显微镜(scanning electron microscopy, SEM)、电子背散射衍射(electron backscatter diffraction, EBSD)与力学测试分析形貌与界面完整性. 同时高低温性能的分析应与电导率/黏度/阻抗的阿伦尼乌斯模型相结合. 静置腐蚀行为需作为独立指标进行评估, 通过监测开路状态下的自放电程度、pH变化与气体析出,清晰区分工作状态与空闲状态下的体系稳定性. 此外, 性能评价应始终基于受限锌源与低电解液用量条件, 避免过量锌源对副反应的掩盖效应, 并须同时报告极片厚度与孔隙率等关键参数[97]. 锌对称电池的评估应报告电流密度、单半周期面容量及静置时间等组合参数, 而非单一的电流密度, 以清晰揭示极化转折与短路倾向; 全电池也应报告N/P比(≈1.1~1.5)、E/C比(≤5~8 g Ah^{-1})、面容量(≥3~5 mAh cm^{-2})、平均库仑效率与能量密度, 并注明温度与倍率条件, 如图7所示; 厚电极验证需在载量≥10 mg cm^{-2}下进行, 对比面容量、极化和能量效率随循环的演变, 并与薄电极基线数据进行比较, 以量化孔道设计、黏结剂选择及压延工艺的实际贡献[98]. 总体而言, 所有优化策略的提出, 都必须有坚实的溶剂化与界面证据链作为支撑, 并最终在实用化的N/P比、E/C比及面容量等约束条件下验证其有效性. 通过上述“界面-结构-电解液”的多层级协同策略, 有望在严苛的实用化工况约束下, 使锌负极达到工业应用所需的能量密度与循环寿命, 从而为开发高比能、高安全性的全电池提供关键支撑.

当研究进一步拓展至软包或叠片电池尺度时, 器件的可靠性已不仅取决于材料的本征性能, 更与结构设计及工艺控制的细节密切相关[99~102]. 在系统集成层面, 锌负极侧宜采用亲锌三维基底与纳米复合界面层(如无机致密外壳与高极性聚合物韧核复合结构), 其厚度控制在数十至百纳米, 以平衡电子绝缘与Zn^{2+}传导; 功能化隔膜(如带负电涂层或定向润湿层)可缩短电极表面的离子扩散距离并抑制气泡滞留. 正极侧需利用导电碳或导电聚合物构建连续电子网络并设计孔隙梯度, 以维持厚电极内部的离子渗透性. 在工艺控制层面, 注液宜采用真空-压力分步工艺, 在满足E/C比的前提下, 结合称重与红外热成像技术检验润湿均匀性. 对于难以完全避免的HER, 可通过内置微孔垫片、吸氢剂或单向安全阀等结构进行疏导与吸收, 并实时监测电池厚度与内部压力变化. 热管理方面, 应结合稳态/瞬态仿真优化极耳与汇流排的电阻分布及导热路径, 确保电流密度与温度分布均匀; 红外热成像及内嵌热敏传感可用于闭环验证与标定, 实现结构热安全的动态调控. 因此, 在软包及叠片电池研究中, 性能评价指标应从材料层面的比容量转向电极与电池层面的面容量、能量效率、极化电压及功率密度等综合参数, 并明确报告极片厚度、N/P比、E/C比、载量、内阻与软包电池的实测能量密度与循环寿命数据. 只有在接近实际工程化约束的测试条件下, 才能避免因采用薄电极或过量电解液而对体系潜在应用价值产生过度外推. 总体而言, 软包及叠片电池的开发应遵循“结构-工艺-性能”一体化优化思路, 通过结构设计提升界面稳定性, 通过工艺精控实现参数一致性, 并以系统级验证评估其在实际使用场景下的能量输出与安全特性, 从而推动锌基电池从实验室向工程化应用的可持续转化.

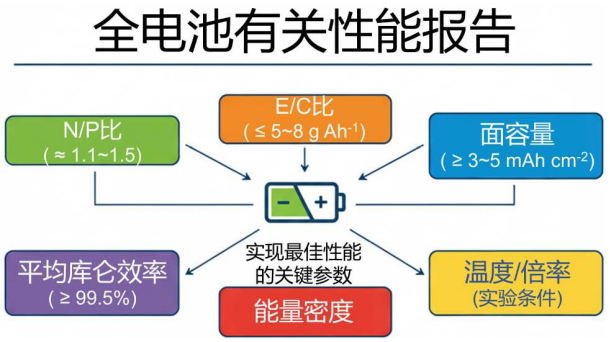


图 7 (网络版彩色)影响全电池性能和实现最佳性能所需要关注的关键参数

Figure 7 (Color online) Key parameters to pay attention that affect full battery performance and achieve optimal performance

6 总结与展望

本文从负极-电解液-正极协同体系出发, 系统综述了AZMBs领域的重要研究进展, 核心观点在于: AZMBs的失效机制本质上由界面行为主导, 其关键在于分子/离子工程的协同调控, 最终目标需遵循实用化工况约束. 以“溶剂化-去溶剂化-界面成膜-离子传输”全过程为主线, 在有限锌源、低电解液用量、高面载量电极及软包电池等实用化条件下, 系统评估面容量、库仑效率与能量效率, 并统一规范N/P比、E/C比、极片厚度及适合温域-倍率性能等关键参数的报告, 是确保研究结果具备可靠工程推演价值的必要前提.

当前，领域内的研究已取得显著成果. 负极借助“无机致密层-有机韧层”复合界面、三维亲锌结构及电沉积成核/脉冲工艺, 在面容量≥3~5 mAh cm^{-2}、锌源受限条件下将平均库仑效率提升至约99.5%[103]; 电解液通过“准超浓盐-低黏度共溶剂-微量成膜/缓冲剂”策略，实现了腐蚀抑制与离子传输之间的精妙平衡; 正极针对Mn/V/PBAs/有机体系提出了“插层-H^+协同-转化/溶解-沉积”的统一反应机制框架[16,104], 并在双导电网络与梯度孔隙结构支撑下实现了高载量厚电极的初步适用. 尽管如此, 基础科学和工程技术方面仍面临若干挑战. 基础科学方面, 需通过原位表征与计算模拟深入解析界面反应与电化学动力学，揭示多电子正极中H^+/Zn^{2+}的作用机制，发展类SEI膜的自修复动力学，优化高浓度电解液的结构-性能平衡，并构建跨尺度的多物理场耦合模型，探索厚电极和低电解液条件下的极化与副反应. 工程技术难题方面，需通过导电网络优化和黏结剂工程实现高载量厚电极的离子输运和机械稳定性，开发软包电池集成工艺以提高循环稳定性，设计高效电解液体系实现低E/C比条件下的离子均衡. 综上所述，未来的研究应在基础科学问题和工程技术难题上同步突破，通过“界面-结构-电解液”的多层级协同优化，推动AZMBs从实验室研究向实际应用转化，为大规模储能领域的商业化应用提供坚实基础.

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Summary for “水系锌金属电池: 失效机制、材料调控与实用化路径”

Aqueous zinc metal batteries: failure mechanisms, material control, and pathways to practical applications

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Aqueous zinc metal batteries (AZMBs) have emerged as a promising candidate for large-scale energy storage systems, particularly in the context of achieving the “dual carbon” goals. AZMBs are highly regarded due to their intrinsic safety, low cost, and environmental friendliness. This paper provides an in-depth overview of the research progress and highlights the challenges in the three key components of AZMBs—anode, electrolyte, and cathode. While AZMBs show significant potential, their large-scale application faces critical challenges primarily stemming from interfacial-dominated failure behaviors, such as zinc dendrite growth, hydrogen evolution and corrosion, and cathode dissolution/phase transformation. This paper systematically reviews the research progress and challenges in the three key components of AZMBs—anode, electrolyte, and cathode—focusing on the core theme of “interface regulation”. The paper identifies that the root cause of failure lies in the non-uniformity and kinetic mismatch of interface reactions. In addressing this critical scientific issue, current research has shifted from material selection to a more systematic, synergistic approach centered on “molecular/ion engineering” with the goal of “practical constraints”. On the anode side, improvements in reversibility and cycling stability of zinc deposition have been achieved through the development of artificial interface layers, three-dimensional current collectors, and optimized deposition kinetics. These innovations help mitigate the growth of zinc dendrites and improve the overall performance of the anode. Electrolyte design has also seen significant advancements. Research focuses on regulating the solvation structure, lowering the desolvation energy barrier, and enhancing interfacial film formation. The use of high-concentration electrolytes, co-solvents, and functional additives has proven effective in suppressing undesirable side reactions and broadening the electrochemical window. These strategies not only improve the efficiency of the electrochemical reactions but also enhance the overall stability of the electrolyte under prolonged cycling. Regarding the cathode, AZMBs have seen progress in understanding complex reaction mechanisms, such as multi-ion intercalation and transformation-dissolution processes. These mechanisms have been studied in a variety of cathode materials, including manganese-based, vanadium-based, Prussian blue, and organic/polyanion compounds. Through structural modifications and electrode engineering, researchers have managed to enhance the areal capacity and stability of these cathode materials. The improved performance of the cathode is crucial for achieving higher energy density and cycle life in AZMBs. However, despite these advances, significant challenges remain in optimizing the overall performance of AZMBs. A key issue is to evaluate battery performance under strict operational constraints, such as a limited zinc source, low electrolyte dosage, and high areal capacity. These constraints more accurately reflect real-world usage and provide a more reliable basis for evaluating the practical applicability of AZMBs. The establishment of unified and reproducible evaluation standards, alongside multi-scale characterization techniques, is essential for advancing research and ensuring consistent performance metrics. Looking forward, the paper emphasizes the importance of addressing critical challenges such as interfacial film formation kinetics, the development of multi-field coupled failure models, and the integration of thick electrode devices. These issues are pivotal for the transition of AZMBs from laboratory-scale research to commercial-scale application. Overcoming these challenges will facilitate the broader adoption of AZMBs in large-scale energy storage systems, helping to meet the growing demand for efficient, sustainable, and cost-effective energy storage solutions. In conclusion, overcoming these challenges will be pivotal for the practical implementation of AZMBs in large-scale energy storage systems, ultimately meeting the growing demand for efficient, sustainable, and cost-effective solutions.

aqueous zinc metal battery, anode interface, dendrite suppression, electrolyte, cathode material, new evaluation standard

doi: 10.1360/CSB-2025-5561