Challenges, Strategies, and Prospects of the Anode-Free Lithium Metal Batteries

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The anode-free lithium metal batteries (AF-LMB), eliminating the use of host anode, can exploit the full potential of the lithium-containing cathode system in terms of the highest retrievable gravimetric/volumetric energy densities, simplified processing of the anode coating, as well as the reduced cost of cell production and maintenance. However, the issues of interfacial contact resistance, curtailed ion pathway, as well as the dead lithium formation coherently lead to the unsatisfactory cation utilization upon repetitive cycling, which impairs the performance endurance of the practical relevance. Hitherto, a plethora of optimization strategies for the electrolyte and deposition substrate are proposed to extend the cell lifespan. Most of the methods, however, are still based on empirical attempts and lack of systematic diagnosis tools to elucidate the interplay between the structural evolution of the cathode and Li deposition behavior. Herein, the recent research process is summarized and the current development dilemma from multiple perspectives is probed, aiming to highlight the key features of the system that dedicate the cycling endurance. In addition, prospects of the operando characterizations that can be used to accelerate the mechanism elucidation of the AF-LMB configuration are systematically commented.

1. Introduction

Emerging among the most evolutionary technologies in the past few decades, the Li-ion battery (LIB) has successfully prevailed in the market of miniaturized electronics and electrical vehicles.[11] The fundamental understanding of solid-state physics and electrochemistry further led to the configuration innovation and practical deployment of the LIBs for the unmanned aerial vehicles (UAV) and grid-scale energy-storage applications.[2]

Despite the performance progress achieved in the LIB model construction, the commercially available electroactive materials still restrict the exploitation of the realistic energy density (less than 250 Wh kg\(^{-1}\) in the cylinder cells and less than 300 Wh kg\(^{-1}\) in the pouch cell models).[3] As the conventional LIB gradually approaches its extreme limit, in particular, the mature production technologies of the graphitic anodes and lithium-containing oxide cathodes, the innovations of the alternative electrode formats are considered as the indispensable route in the pursuit of the enhanced levels of the overall performance metrics. Due to the merits of ultrahigh theoretical capacity (3860 mAh g\(^{-1}\)) and lowest redox potential (~3.04 V vs standard hydrogen electrode (SHE)), the renaissance of research interest in Li metallic anodes has revived passionate exploration toward energy-dense batteries.[4] However, the practical implementation of Li metal anodes has been hindered by a series of safety concerns and cycling inefficiencies that originate from the metallic dendrite growth.[5]

So far, researchers have established several models to elucidate the origin of the lithium deposition process, such as the diffusion-reaction competition mechanism,[6] self-healing electrostatic shield mechanism,[7] phase-field model, and so forth. [8] The pros and cons of these mechanisms have been discussed in the recent review published by Zhang and co-workers.[9] From the perspective of solid chemistry, the interfacial behavior of the deposition substrate plays a crucial role in dedicating the cycling reversibility of the Li plating/stripping process. Specifically, the thermodynamic energy gap between the metallic lithium and organic solvents would lead to the parasitic reaction and irreversible cycling of the cell.[10] In other words, as the lowest unoccupied molecular orbital (LUMO) of the electrolyte is lower than the Fermi energy level of Li, the electrolyte would spontaneously decompose by electron tunneling until the dense and intact solid-electrolyte interphase (SEI) layer, which is ion conductive yet electrically insulating and could completely passivate the surface reactivity of the Li foil.[11] However, the Li deposit propagation would damage the fragile SEI upon the plating process.[66] The catastrophic separator penetration, short circuit, and even thermal runaway consequences thus threaten the reliable safe operation of the cell.[12]

To optimize the electrochemical performance, excessive lithium dosage is used to compensate for the irreversible...
Li⁺ depletion from the cathode. However, the abuse of the lithium-ion inventory would significantly reduce the actual achievable gravimetric/volumetric energy densities of the battery model.[13] Theoretically, as the lithium source originates from the cathode, minimizing the usage of the lithium foil would maximize the possible energy density of the format till the ultimate milestone configuration of the anode-free lithium metal batteries (AF-LMBs).[14] In this ideal model, the design completely eliminates the host anode by merely adopting a bare copper foil as the deposition substrate.[15] In addition, the AF-LMB also features several merits. 1) Metallic lithium exists in the form of complexes; its extraction from minerals and scalable purification inevitably raise the prime cost of the raw materials. In this regard, the AF-LMB production translates to the reduced cost per kWh by avoiding the Li foil consumption. 2) Manufacturing of the anode-free model can be well integrated into the existing LIB production procedures, avoiding the troublesome equipment calibration and recustomization. 3) The unnecessary slurry-coating, drying, and maintenance procedures of the anode electrodes would reduce the energy consumption and personnel costs. 4) As compared with the LIB with high negative to positive electrode capacity (N/P) ratios, the absence of anode materials would utilize the maximized equilibrium voltage output of the cathode. Unfortunately, the intrinsic irreversible lithium plating/stripping process on the lattice-mismatched Cu substrate would lead to rapid lithium inventory loss upon cycling.[16] The sacrificed cell lifespan thus can hardly satisfy the requirements for commercial applications.[17] In this regard, optimization of the Li-ion utilization degree is the key enabler to the advancement of the AF-LMB configuration.[18] Obviously, the interfacial electrochemical behavior between the substrate and the electrolyte plays a decisive role, and corresponding alleviating strategies and mechanism elucidation are highly required for system optimizations.[19]

For conventional LIBs, the N/P ratios of the areal capacities are maintained as 1–1.1, as the host anode needs to accommodate the equivalent amount of Li⁺ that migrated from the cathode counterpart.[20] As illustrated in Scheme 1a, a schematic comparison demonstrates the distinct discrepancy among the conventional LIB, LMB, and AF-LMB models. In the exemplar system with a fully lithiated NCA cathode (the preset areal capacity loading of 6.1 mAh cm⁻² for the double-sided electrode) and an N/P ratio of 1.1 (18.6 mg cm⁻² graphite anode, Scheme 1b), the LIB model exhibits the rated gravimetric energy density of 447 Wh kg⁻¹. Here, the calculation of energy density is only based on the electroactive anode and cathode, while the auxiliary weight of other components in the cell is not considered.[21] As the NCA cathode paired with lithium foil (≥30 um, N/P ratio = 1.1) in the LMB model, the theoretical energy density can be increased to 681 Wh kg⁻¹, which is almost 50% higher than the LIB. It is to be noted that the excessive use of lithium metal also endangers the reliable operation of lithium metal batteries. In the AF-LMB model, the lithium ions are extracted from the cathode and directly deposit on the bare current collector, in which the N/P ratio is almost zero and the extreme energy density can approach 720 Wh kg⁻¹.[22] Similarly, the anode-free system achieves more than twice the volumetric energy density of the LIB model, as numerically demonstrated in Scheme 1b.[23]

Based on these obvious energy density merits, therefore, evaluating the hidden information of the substrates and establishing the correlations of their interfacial behavior with the lithium inventory depletion, namely, the capacity decline, become the tasks of paramount importance toward the successful operation of the AF-LMB system.

The fading process of the AF-LBM could be analyzed based on the morphological evolution of the substrate. In the initial stage, the as-deposited metallic Li forms the SEI due to its thermodynamic instability with the electrolyte.[24] At the same time, the SEI layer acts as a physical shield by insulating the electron shuttling yet permitting the Li-ion transfer.[25] The subsequent stripping process subsequently involves the mechanical fracture of the fragile SEI due to localized stress.[26] These cracks induce the preferential Li deposition on the holes and defects, aggravating the formation of wire-wrapped lithium microstructures.[27] At the macrolevel, the mossy morphology would accelerate the parasitic side reactions, resulting in severe electrolyte consumption and electrically isolated lithium.[28] In this regard, the synergy between parasitic reactions and electrically isolated lithium will coherently deplete the lithium source and deteriorate the cell lifespan. In this review, recent research progress for regulating the lithium deposition behavior and enhancing the Li-ion utilization are introduced and evaluated (Figure 1). Here, we would like to describe the development of AF-LMB during the past decade.

1) Optimization of the electrolyte formulation. The traditional electrolyte exhibits serious side reactions with the metallic lithium deposits, which rapidly consume the limited lithium source of the cathode and lean electrolyte in the AF-LMB model. The compositional adjustment of the electrolyte (lithium salt, solvent, and additive) can effectively optimize the SEI species on the substrate interface. For instance, the utilization of the high concentration or dual component of the lithium salts, film-forming additives, or even the solid-state electrolyte could alter the LUMO of the electrolyte, thereby homogenizing the Li-ion influx and enhancing structural stability of the deposits in AF-LMB.

2) Interfacial design of the deposition substrate. Copper foil possesses a face-centered cubic (FCC) structure and thus discourages the epitaxial growth of the body-centered cubic (BCC) structure of the metallic Li. In this regard, the alleviation strategies of the crystalline mismatch, such as the incorporation of the lithiophilic sites, compositional tuning of the substrate, artificial layer coating, and so forth, would thermodynamically regulate the Li nucleation overpotential and the propagation mode.

3) Cycling protocols. Besides the intrinsic configuration design of the cell, external parameters such as stack pressure, storage temperature, cutoff voltage, current density, etc., would largely influence the cycle lifespan of the AF-LMB. Therefore, we probe the thermodynamics of the Li plating process at various environmental conditions based on pioneering studies. The synergistic coupling of the optimal cycling protocols and environmental conditions deserves more in-depth investigations in pursuit of the reversible plating/stripping process.

In the following paragraphs, we would like to elaborate on these design rationale and evaluate the advances and limitations of each category. Afterward, development prospects on AF-LMB are commented from an application point of view. Finally, the emerging characterization techniques that could be used to
Scheme 1. a) Schematic configurations of different cell models. b) Gravimetric energy density (Wh kg\(^{-1}\)) and volumetric energy density (Wh L\(^{-1}\)) of different cell models. The cathode is Li\(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\) (NCA) with an initial capacity of 200 mAh g\(^{-1}\) and loading of 30.5 mg cm\(^{-2}\) (double sided). The calculations of the theoretical energy density are based on the anode capacities of 360 mAh g\(^{-1}\) (Graphite), 2000 mAh g\(^{-1}\) (Si/C-2000), and 3860 mAh g\(^{-1}\) (Li), respectively. The example parameters of the LIB were obtained from a 2018 study by Betz et al.\(^{[21]}\)

Figure 1. Current main research methods on AF-LMB. LiPON electrolyte. Reproduced with permission.\(^{[32]}\) Copyright 2014, The Electrochemical Society. Electrolyte additives. Reproduced with permission.\(^{[41]}\) Copyright 2019, Elsevier. Dual-salt electrolyte. Reproduced with permission.\(^{[46]}\) Copyright 2019, The Electrochemical Society. All-solid-state electrolyte. Reproduced with permission.\(^{[50]}\) Copyright 2020, Nature Publishing Group. Anode sacrificial agent. Reproduced with permission.\(^{[64]}\) Copyright 2021, Wiley-VCH GmbH. Host design. Reproduced with permission.\(^{[76]}\) Copyright 2018, Elsevier. Artificial films. Reproduced with permission.\(^{[109]}\) Copyright 2020, Elsevier.
2. Strategies of Electrolyte–Substrate Interfacial Design

2.1. Liquid Electrolyte Optimization

The electrolyte is one of the most critical elements that affects the morphology of Li nucleation and growth. Depending on the choice of solvent, the electrolyte is simply divided into two categories: 1) carbonate-based solvent, such as ethylene carbonate (EC), propylene carbonate (PC), diethyl carbonate (DEC), dimethyl carbonate (DMC), etc. and 2) ether-based electrolyte, such as dimethyl ether (DME), 1,3-dioxolane (DOL), etc. The different properties of the two electrolytes lead to the varied scope of their applications. Typically, the carbonate-based electrolyte has been widely used in commercial LIBs due to its wide electrochemical stability windows (>4.5 V vs Li/Li⁺) and low cost. The ether-based electrolyte stabilizes the interfacial contact with the Li foil, which thus achieves the reversible redox of the Li–sulfur, Li–O₂ batteries.

The characteristic SEI could be simplified as a multilayered mosaic structure, which is composed of an inner inorganic layer and outer organic layer. The inner layer near the electrode contains a large amount of inorganic-ion conductors (LiF, Li₂O), and the polymeric outer layer involves dilithium ethylene glycol decarbonate (Li₂EDC) and ROLi, which can be permeable for both the Li⁺ and solvation molecules. The electrolyte formulations that enable a stable SEI layer by regulating different components are critical to achieving the excellent electrochemical performance of AF-LMB. Recently, Woo et al. assembled the anode-free batteries with LiNi₀.₃Mn₀.₃Co₀.₄O₂ (NCM111) as the cathode and copper foil as the anode. In conventional carbonate-based electrolytes (1 M LiPF₆-EC/DMC), the cell showed a poor reversible capacity of only 23% and a poor cycle life was significantly increased from 15 cycles to 50 cycles (Figure 2b). Hagos et al. reported a dual-electrolyte strategy consisting of KPF₆ and tris (trimethylsilyl) phosphite (TMSP). The self-healing electrostatic shielding (SHES) of KPF₆ could prevent the formation of dendrites, and the TMSP could remove the byproduct of hydrofluoric acid (HF). Brown et al. investigated the effect of vinylene carbonate (VC) on the plating/stripping behavior of lithium metal. The electrolyte was 1.2 M LiPF₆ in EC: ethyl methyl carbonate (EMC) (3:7, vol) containing 5% of added VC. The enhanced CE of cells was ascribed to the formation of polymeric species on the anode surface, which effectively alleviated the volume expansion. Nilsson et al. demonstrated robust lithium deposition behavior using highly concentrated electrolytes containing 1.86 M lithium bis(trifluoromethane sulfonyl) imide ([LiTFSI] in EC solvent. Anode-free full cells pairing a LiFePO₄ cathode with a copper foil current collector in this electrolyte displayed 50% capacity retention after 30 cycles. The initial capacity was up to 3.5 mAh cm⁻² under the high current density of 1 mAh cm⁻².

Besides electrolyte salt and solvent molecules, functional electrolyte additives also play a crucial role in normalizing lithium metal deposition. Sahalie et al. studied the effect of KNO₃ additives in carbonate-based electrolytes using an anode-free Cu||NMC111 full cell (Figure 2g). Under the effect of KNO₃, the cycle life was significantly increased from 15 cycles to 50 cycles (Figure 2h). Hagos et al. reported a dual-electrolyte strategy consisting of KPF₆ and trimethylsilyl) phosphite (TMSP). The high concentration of LiNO₃ in the electrolyte can effectively stabilize the Li plating process by the formation of an SEI in nitrogenated species.
Beyene et al. first investigated the performance of the dual-salt electrolyte system (2 M LiFSI + 1 M LiTFSI) in the anode-free lithium full configuration (Cu||LFP). Upon the interfacial analysis of the copper foil, a large amount of lithium-containing inorganic compounds appeared after cycling (Figure 3a). The anions (FSI\(^{-}\)/C\(_0\)) in the electrolyte could decompose to form abundant inorganic ion conductor species on the surface of the lithium metal, such as LiF and Li\(_2\)O, which serve as a sturdy fortress to avoid the corrosion of electrolytes. Also, the dual-salt electrolyte is superior to the single-salt electrolyte in prolonging the cycling life of anode-free models. Recently, Weber et al. designed a novel dual-salt liquid electrolyte to construct anode-free pouch cells. The optimized electrolyte was composed of 1 M LiDFOB and 0.2 M LiBF\(_4\) in the mixture of FEC/DEC. As shown in Figure 3b, the cell with optimized dual-salt electrolyte manifested higher capacity retention of 80% after 90 cycles. The initial discharge capacity was 2.4 mAh cm\(^{-2}\), when the charge and discharge current density were 0.48 and 1.2 mAh cm\(^{-2}\), respectively. The superior performance was obtained in strict accordance with the commercial lean electrolyte conditions of \(\approx 2\) g Ah\(^{-1}\). These cells were evaluated at 40 °C with low external stack pressure (\(\approx 75\) kPa). The LiDFOB/LiBF\(_4\) blend electrolyte could operate at a high voltage of 4.5 V (Figure 3c). The pouch cell was disassembled to observe the morphological change of the Li deposition under different conditions. The morphology of lithium metal with dual-salt electrolytes showed a dense and flat structure (Figure 3d). The role of pressure will be discussed in detail in the latter part. By analyzing the interfacial composition by the X-ray photoelectron spectroscopy (XPS) technique (Figure 3e), the as-formed SEI with LiDFOB contained a higher content of organic boronated and fluorinated species, whereas the SEI formed with LiPF\(_6\) contained more organic species relative to LiF. Through the double-salt strategy, the obtained hybrid SEI layer was composed of organic and inorganic species. The synergy of these unique hybrid compositions leads to enhanced cycle performance of AF-LMB.

2.2. The Solid Electrolyte

The use of solid electrolytes in the cell will improve the operation safety, which could avoid the leakage and flammability...
issues of the organic liquid electrolytes. In addition, solid electrolytes potentially enable the stabilized interfacial contact with metallic deposits.\textsuperscript{[52]} The solid-state ion conductors involve the sulfide-type electrolytes, garnet-type oxide electrolyte Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} (LLZO),\textsuperscript{[53]} polymer-based electrolytes (PEO/LiF\textsubscript{SI}),\textsuperscript{[54]} NASION-based Li\textsubscript{1+x}Al\textsubscript{0.4}Ti\textsubscript{1.6}(PO\textsubscript{4})\textsubscript{3} (LATP), and so forth.\textsuperscript{[55]} However, the technological barriers in producing the thin-layer solid electrolytes restrict the cell assembly according to the industrial manufacturing techniques; the inactive mass of the thick solid electrolyte would adversely sacrifice the practical energy density of the battery model.

According to the designed pouch cell model in the literature, for various types of solid electrolytes with different relative densities, the gravimetric energy density varies as a function of the solid electrolyte thickness.\textsuperscript{[52c]} As shown in Figure 4a, it is assumed that all solid electrolytes occupy the same volume as the pore electrolyte and separator in the liquid electrolyte-based cell, so switching from the liquid electrolyte to a solid-state electrolyte will have no impact on the volume energy density. The sulfides electrolyte (LPSCI) can only reach a target gravimetric energy density of 412 Wh kg\textsuperscript{-1} at the thickness of \(\approx 15 \mu\text{m}\). The energy density of cells would be inevitably sacrificed with the thickness increase in the solid electrolytes; thus, it is necessary, yet quite challenging, to realize the thin-layer production of the inorganic solid electrolytes. Meanwhile, the tap density of solid electrolytes also dramatically affects the practical energy density. For instance, the replacement of the solid electrolyte LPSCI (1.64 g cm\textsuperscript{-3}) with LLZO (5.07 g cm\textsuperscript{-3}) at the same thickness would reduce the energy density from 412 to 373 Wh kg\textsuperscript{-1}. The polymer electrolytes possess relative lower density as compared with other solid electrolytes; however, their ionic conductivities at the room temperature are difficult to meet the requirements of the practical relevance. Moreover, the loose contact between solid electrolytes and the deposition substrates would induce a high interfacial resistance, which leads to the pile-up of the dendrite deposits.

In 2020, the Samsung company demonstrated a high-performance solid-state battery in the anode-free full cell with Ni-rich LiNi\textsubscript{0.9}Co\textsubscript{0.05}Mn\textsubscript{0.05}O\textsubscript{2} (NMC) cathode and an argyrodite Li\textsubscript{6}PS\textsubscript{5}Cl sulfide electrolyte (Figure 4b).\textsuperscript{[56]} Ag nanoparticles were introduced to minimize the overpotential of metal deposition and interface resistance. In the microstructure of the Ag–C
nanocomposite layer, the Ag nanoparticles were uniformly distributed in the carbon layer, and the thickness of the layer was controlled as 5 μm. In the early stage of the charging process, the Ag−Li alloy first formed, and then the uniform Li deposition was realized by the normalization of Ag−Li solution. Ingeniously, due to the Ag−Li solution reaction, silver particles gradually migrate to the stainless steel (SUS), and upper carbon can prevent side reactions between the sulfide electrolyte and the Li deposit. Benefitting from lower interface resistance, a high initial areal capacity of 6.8 mAh cm⁻² and 89% capacity retention for 1000 cycles at the current density of 0.5 C (Figure 4c) were achieved. The high average CE value (>99.8%) is close to the CE of current commercial LIBs with graphite anodes. Traditional graphite anode affords reversible Li insertion and extraction as the structural host. However, in anode-free batteries, the consumption of SEI formation and the incomplete stripping process would seriously deteriorate the Li-ion utilization efficiency. Based on the earlier model from Samsung company,
the 5 μm Ag–C nanocomposite layer could partially act as the anode host, in which the formation of the Li–Ag alloy intermediate could significantly reduce the Li nucleation overpotential.

In the solid-state battery prototype, the CE upon cycling is largely degraded by the thermodynamic instability of solid electrolytes and the high interface resistance. The lowest chemical potential of metallic deposits evoked the reduction of electrolyte, resulting in higher interfacial impedance and cell polarization.[57] Both the processes would deplete the lithium reservoir and cause severe capacity fading. At present, various prelithiation strategies were utilized to compensate for lithium losses upon cycling.[58] Because of the higher chemical activity at the oxidized state, it is difficult to directly utilize the lithiated cathodes in the battery assembly. Instead, the sacrificial cathode materials such as Co/LiF,[59] Li₃N,[60] and Li₂S,[61] are more compatible with the slurry preparation procedures. Inspired by the concept of prelithiation strategies, Park et al first reported lithium nitride (Li₃N) as the sacrificial cathode material to assemble all-solid-state batteries with Li-free In layer (Figure 4d).[62] In this study, Li₃PS₅Cl was used as solid electrolyte due to its high room-temperature ionic conductivity (10⁻²–10⁻¹ S cm⁻¹). It can be observed from the charging curve that a voltage plateau appeared at 2.4 V (≈3.0 V vs Li/Li⁺), which was ascribed to the decomposition of Li₃N (Figure 4e).[64] In addition, the capacity retention of the cell without Li₃N was only 37.9% after 80 cycles; in contrast, the cell with 5% Li₃N enabled 75.8% capacity retention after 200 cycles (Figure 4f). According to the analysis of the earlier results, the lithium consumption by the interfacial side reaction can be supplemented by Li₃N decomposition, which can improve the cycle life of the battery. For the anode side, the substrate without excess Li still maintains a stabilized interface as compared with the Li foil after 50 cycles (Figure 4g–j). Despite the performance improvement, these sacrificial agents also have several drawbacks in terms of capacity penalty, poor electrical conductivity, and high price. In addition, the moisture sensitivity of some lithium-containing compounds (e.g., LiS and Li₃N) would increase the overall storage cost. Most seriously, some prelithiation agents are thermally unstable, the decomposition of which will generate the gas or undesired inactive species in the electrode. This process deteriorates the interfacial contact among the active particles, which also hinders the ionic migration path and electron transport.

3. The Substrate Design

3.1. Metallic Host Design for the Homogenous Lithium Plating

Apart from the electrolyte, the current collector also plays a crucial role in affecting anode-free cell cycling performance.[65] The host substrates of Li deposition have paramount influence on plating behaviors. Inherently, the lattice mismatch between the traditional current collectors and lithium metals causes a huge interfacial energy barrier for lithium-ion transmission, resulting in excessive deposition overpotential, which is harmful to plating metallic lithium.[66] In addition, the higher nucleation barrier will lead to forming massive dead lithium. Stabilizing lithium metal deposition by regulating the interface properties on the current collector is considered another feasible option.[67]

Cui and co-workers adopted the classical nucleation theory as a manual to explain the initial nucleation growth behavior of lithium metal.[68] This study established a clear code of conduct for the regulation of the lithium deposition behavior in batteries. Starting from classical nucleation theory, lithium metal was obtained from the electrolyte and reduced to the electrode surface by electroplating, which could be associated with the free energy barrier. As illustrated in the free-energy schematic diagram (Figure 5a,b), the driving force for the electrodeposition process can be divided into the reaction overpotential, charge transfer overpotential, and crystalization overpotential, which was too complex to accurately analyze the rate steps. The complex electrode polarization process was further simplified, and the electrode polarization during galvanostatic Li electrodeposition was evaluated by two quantitative characteristics of overpotential. Finally, it was found that the nuclei size was proportional to the inverse of overpotential, and the number density of nuclei was proportional to the cubic power of overpotential (Figure 5c). Therefore, lower nucleation overpotential and plateau overpotential is an effective strategy to achieve the uniform of electrodeposited metallic lithium on the electrode surface.

Recently, Pande et al. combined with theoretical knowledge electrocatalytic perspective and density functional theory calculations to explain the lithium nucleation and growth mechanisms on current collectors by computational screening (Figure 5d–f).[69] These were determined by the free energy of lithium adsorption and surface diffusion barrier on various candidate transition metal-based collectors. Lithium alloy phase materials displayed much better Li nucleation and surface diffusion than that of candidate transition metals as hosts. The correlation between adsorption energy and Li-diffusion activation energy was established. Achieving the balance between nucleation and diffusion was critical. Hence, Li alloys such as Li–Zn,[70] Li–Al,[71] Li–B,[72] Li–Sn,[73] Li–Ag,[74] etc. were selected as hosts to reduce overpotentials and regulate the morphology of lithium deposition.

The construction of lithophilic functional materials on the surface of the current collector is considered to be a reliable method by the pretreatment method.[75] Liu et al. induced atomically distributed Zn artificial defects on the commercial Cu foils by magnetic sputtering of Cu₉₉Zn alloy. Thanks to the lithophilic properties of Cu₉₉Zn substrate, the Cu₉₉Zn substrate exhibited a better wetting effect for molten lithium. Solid Cu₉₉Zn can dissolve with lithium metal to form solid-solution material before Li deposition, which reduced the deposition interface energy of atomically distributed seeds. As illustrated in Figure 6b, Cu₉₉Zn foil exhibited lower nucleation overpotential in voltage profiles during the plating process. The Li–Li symmetric cell with planar Cu₉₉Zn electrode can be stably cycled for more than 1000 h, which significantly enhanced the plating/striping performance of Li metal anodes (Figure 6c,d). The Cu₉₉Zn electrode could maintain CE over 98% at a Li plating capacity of 10 mAh cm⁻². Zhang et al. used an electroless tin plating technique to prelate an ultrathin layer onto the surface of Cu substrate (Figure 6e,f). Subsequently, Li metal was reacted with tin to form Sn–Li alloy. Thanks to the chemical similarity between Li metal and Sn alloy, the Li–Sn alloy function acted as a tontic glue that electrically connects the Li deposits and the Cu substrate, which improved the
adhesion of Li plating to the electrode foil and enhanced the Li cycling efficiency of the Sn–Cu/LiNi0.85Co0.10Al0.05O2 (NCA) cells. Various alloys (e.g., SnOx, Ag, Sb, and SiOx) were also attempted as the intermediate interphases, however, the deep lithiation process of which accompanied with the substantial volume expansion and Li source consumption. Subsequently, the cracking and pulverization of the alloy particles will cause their detachment from the current collector. Therefore, the thin-layer construction of the alloy intermediate interphase, with minimum dose, should be balanced with the facile ionic pathway design.

Graphene oxide has promising application prospects because of its electrically insulating properties and facile processability. Assegie et al. utilized ultrathin multilayer graphene to modify Cu current collector by chemical vapor deposition.[77] Paired with commercial LiFePO4 cathode, the initial discharge capacity was 151 mAh g−1, and the capacity retention was 50% after 100 round-trip cycles, which effectively alleviated the capacity loss compared with bare cells. In addition, Wondimkun et al. also reported the lipophilicity properties of the hybrid electrode (Cu|Ag@PDA-GO) by the two-step spin-coated methods (Figure 6g).[78] The functional material was designed on the current collector surface to reduce the Li nucleation barrier, which enables higher 55.7% capacity retention after 60 cycles within the FEC in the carbonate-based electrolyte at 0.5 mA cm−2 (Figure 6h,i). Lithiophilic silver nanoparticles with polydopamine (Ag@PDA) were crucial as nucleation seeds to facilitate the uniformity of the initial lithium nucleation by forming an alloy LiAg phase, which could maximize the utilization of the limited lithium inventory for plating and stripping. Meanwhile, the outermost layer of graphene oxide (GO) on top of Ag@PDA was used to buffer the Li-ion flux in the AF-LMB. The synergistic effect of Ag@PDA-GO achieved uniform deposition and dendrite-free morphology during repeated cycling. Moreover, various methods and strategies, such as inorganic materials,[79] liquid metal,[80] and 3D structure,[81] are applied to the current collector substrate for modification and optimization, which effectively extend the cycle life of lithium metal batteries.

3.2. Artificial Coating Layers

The in situ-formed SEI film is uncontrollable and varies in structure and composition, which might possess ion diffusion resistance and large activation energy.[82] Thus, various ex situ-formed artificial layers with high ionic conductivity were designed to mitigate the interfacial resistance. The artificial coating layers on the surface of Cu could avoid the direct contact between the reactive Li deposits and the electrolyte.[83] Glassy lithium phosphorous oxynitride (LiPON) was used as overlayers for lithium-free film batteries. It achieved 80% capacity retention over 10 000 cycles with the aid of overlayers.[84]

The application of polymer electrolytes is considered as the ideal choice due to their merits such as flexible processability, a broad electrochemical window, and better electrode/electrolyte interfacial properties.[85] Polymer electrolytes using PEO polymer have received widespread attention due to promising stability against Li metal. Assegie et al. modified Cu foil with a nanosized PEO porous polymer membrane by spin-coating approach (Figure 7a).[86] The cathode LiFePO4 with Cu@PEO electrode was assembled into full-cell configuration (Cu@PEO||LiFePO4), and the electrolyte was composed of 1M LiTFSI,

![Graph](https://www.advancedsciencenews.com/figs/advenergysustres_2100197_f5.png)

Figure 5. a,b) Fundamentals of lithium nucleation and growth. c) The mathematical model. Reproduced with permission.[68] Copyright 2019, American Chemical Society. d) Cell-specific density of anode-free batteries using different current collector materials. e) Classical adsorption model. f) The adsorption energy on different current collectors. Reproduced with permission.[69] Copyright 2019, American Chemical Society.
DME/DOL(1/1, v/v) with 2% LiNO$_3$. As shown in Figure 7b, the integrated cell device demonstrated capacity retention of 50% after 100 cycles at 0.2 C. Comparison with the nonuniform and thicker PEO coating, uniform lithium deposition was observed with the appropriate thickness PEO coating. Nevertheless, the ion conductivity of the traditional PEO-based polymer electrolytes is poor due to huge grain boundary resistance. Using computational and experimental studies, it was found that a complex interplay between the fillers and film PEO polymer was responsible for conductivity and mechanical strength, with unique chemistry suited for expediting ion migration. The fillers could be metal oxides, such as SiO$_2$, Al$_2$O$_3$, and TiO$_2$, and fast Li$^+$ conductors, such as LLZO, LGPS, and Li$_{1+x}$Al$_{0.5}$Ti$_{1.5}$(PO$_4$)$_3$. These materials could realize the enhanced performance of the PEO-based electrolyte by undermining the crystallinity of polymer and providing additional ion transport channels. To better accommodate the volume change during the Li plating and stripping process,
the coating layer generally needs to be mechanically flexible. The insufficient mechanical strength of thin coating layers cannot effectively inhibit the substantial volume expansion of the high-capacity deposit loadings, while thicker coatings might hinder the ion migration pathway. Thus, the intrinsic parameters of the mechanical strength, ionic conductivity, and interfacial resistance should be taken into consideration for exquisite coating engineering.

Zegeye et al. used the garnet–polymer composite electrolyte (LLZTO/PEO–CPE) laminated on both the anode and cathode surface by a spin-coating method (Figure 7c).

This composite polymer electrolyte (CPE) was composed of the polyethylene oxide (PEO) polymer, lithium bis(trifluoromethanesulphonil) imide (LiTFSI) salt, and Li6.75La3Zr1.75Ta0.25O12 (LLZTO) filler. To enhance interface compatibilities, a well-designed LLZTO/PEO–CPE was laminated onto the anode and cathode surface, which minimized the boundary resistance. The lithium-ion conductivity of LLZTO/PEO–CPE composite films was investigated with electrochemical impedance spectroscopy (EIS) with laminated two copper-blocking electrodes in the temperature range of 25–70 °C. The Nyquist plot of PEO–SPE and LLZTO/PEO–CPE film is characterized in Figure 7d,e. Compared with the PEO–SPE film, LLZTO/PEO–CPE film showed much lower bulk resistance at the lower temperature of 25 °C, suggesting that the incorporation of LLZTO significantly improved the lithium transference number. According to the Arrhenius formula, the ionic conductivity of LLZTO/PEO–CPE film was $4.76 \times 10^{-4} \text{ S cm}^{-1}$ at room condition. In addition, the corresponding activation energy can also be calculated according to the formula. The energy ($E_a = 0.16 \text{ eV}$) for the LLZTO/PEO–CPE film was lower than that of the PEO–SPE film ($E_a = 0.26 \text{ eV}$). The electrochemical performance of the laminated LLZTO/PEO–CPEs on both cathode (NCM111) and Cu foil in the anode-free cell was tested at 55 °C. The full cell exhibited the initial discharge capacity of 2.20 mAh cm$^{-2}$, and the capacity retention was 41.2% after 65 cycles at 0.2 mA cm$^{-2}$ (Figure 7f). In such systems, the rigid one via acid–base coupling between PEO segments and LLZTO particles could lead to faster Li$^+$-migration path than in the single isolated electrolyte-based LiB.

Abrha et al. prepared lithium-ion-conducting
composite film (LLCZN/PVDF) by electrospinning. The abundant inorganic lithium salt (LiF and LiCl) in the composite film can enhance the mechanical strength of the SEI and effectively suppress the dendrite problem. Herein, the anode-free cell configuration (Cu@LLCZN/PVDF)[NMC] showed excellent capacity retention of 58.66% and average CE of 97.6% after 30 cycles. Generally, to ensure rapid ion diffusion of the hybrid polymer coating that needs to work at high temperatures. Therefore, promising hybrid polymer coatings used at room temperature should be identified. The earlier paragraph briefly introduced research efforts of electrolyte formulation and substrate modification to regulate the Li deposition process in the anode-free batteries. To obtain a comprehensive understanding of the relationship between various strategies and cycle life, we have summarized the electrochemical results, as presented in Table 1.

### 4. Testing Protocol

Lithium metal anode is considered to be the “holy grail” of LIBs, which is the key enabler to achieving high-energy-dense rechargeable batteries. Researchers have made tremendous progress in constructing a realistic LMB prototype. Nevertheless, several insurmountable barriers, including dendrite growth and low CE during Li deposition/striping processes, have prevented their large-scale applications. In the case of solid-state batteries, the stacked pressure and temperature range must be accurately managed to ensure reliable battery operation. The electrode stack should be pressurized to guarantee that the solid—solid interface between particles is in close contact to reduce interface impedance. It is noteworthy that the elevated temperature can accelerate the mass transport of the lithium ion, thereby increasing the electrode kinetics of the battery. Louli et al. thoroughly investigated the trade-offs between several different electrolytes versus the condition of the stacked pressure. Therefore, it deserves further exploration of the causal relationship between the testing protocol and cycle stability of the AF-LBM.

Fan et al. revealed the dynamic behavior evolution of lithium metal deposition under pressure. Here, a customized split cell equipped with pressure sensors (Figure 8a) was used to precisely apply the uniaxial stack stress on the battery. As shown in Figure 8b, with the increase in stack pressure, the initial CE of the Li–Cu symmetrical battery was significantly boosted, which was more obvious at the high current density of 2 mA cm⁻², using an ether-based basil electrolyte 4.6 M LiFSI and 2.3 M LiTFSI in DME. In contrast, the initial efficiency gradually decreased from 92.5% to 82% at current densities of 1–2 mA cm⁻² without stack pressure. When the stack pressure started from 0 to 35 kPa, its efficiency increased exponentially. The porosity of Li deposition layer was measured to be 43.57% and 0.51% at 70 and 350 kPa, respectively (Figure 8c), which was close to its theoretical value. Ideally, the deposited lithium metal should have dense-packed columnar morphology, which can effectively reduce the exposed area and alleviate extra side reactions with the liquid electrolyte. Such distinct Li growth behaviors and mechanisms are depicted in Figure 8d. Without external factors, the defect site of the copper foil surface will reduce the diffusion barrier, giving priority to lithium deposition, resulting in the production of porous and isolated lithium metal. Through molecular dynamics simulation, the surface energy of the Li metal growing in the vertical orientation was restricted under external critical pressure. Thus, the Li metal tends to be deposited horizontally that achieves columnar morphology. Lithium–copper soft-pack batteries were assembled to further verify the effects of pressure on the long cycle. Under the pressure of 350 kPa, its lifespan was almost doubled compared with 70 kPa. Importantly, when the pressure is from 70 to 350 kPa, the average CE increases from ≈98% to above 99% at a high current density of 4 mA cm⁻² under room temperature. Therefore, the influence of pressure must also be considered in the lithium metal battery. Genovese et al. investigated the effect

### Table 1

Summary of published work on AF-LMBs discussed in this article.

| Category               | Anode          | Cathode | Electrolyte | Current [mA cm⁻²] | Capacity retention | Cycles | Ref.       |
|------------------------|----------------|---------|-------------|-------------------|-------------------|--------|------------|
| Interfacial design     | Cu–Sn          | NCA     | LiPF₆ in FEC:EMC | 0.5              | 12%               | 80     | [73a]      |
|                        | Cu₉ₓZn         | TiS₂     | LiTFSI in DOL:DME | 0.12             | 55%               | 120    | [76]       |
|                        | Cu@Cu₃N        | LiFePO₄  | LiTFSI in DOL:DME + 0.4 M LiNO₃ | 0.5          | 30%               | 50     | [110]      |
|                        | Cu@PEO         | LiFePO₄  | LiTFSI in DOL:DME + 2% LiNO₃ | 0.153         | 30%               | 200    | [86]       |
|                        | Cu@GO          | NCM111   | LiPF₆ in EC:DEC + 5% FEC | 0.2          | 44%               | 50     | [109]      |
|                        | Cu@MLG         | LiFePO₄  | LiTFSI in DOL:DME + 2% LiNO₃ | 0.2          | 61.3%             | 100    | [77]       |
|                        | Cu@Pi          | LiFePO₄  | LiTFSI in DOL:DME + 2% LiNO₃ | 0.5          | 20%               | 340    | [111]      |
|                        | Cu@SiO₂        | LiFePO₄  | LiTFSI in DME | 0.9              | 45.6%             | 100    | [112]      |
| Electrolyte optimization | Cu             | LiCoO₂   | LiPON       | 1                 | 80%               | 1000   | [84a]      |
|                        | Cu@Ag-C        | NCM      | Li₄PS₄Cl    | 1.36              | 89%               | 1000   | [56]       |
|                        | Cu             | NCM532   | LiDFOB + 0.2 M LiPF₆ in FEC:DEC | 1.2          | 80%               | 90     | [48]       |
|                        | Cu             | NCM111   | LiPF₆ in EC:DEC + 0.5 M KNO₃ | 0.2          | 40%               | 50     | [43]       |
|                        | Cu             | NCM111   | LiPF₆ in EC:DEC + 2% LiNO₃ | 0.5          | 40%               | 50     | [39]       |
|                        | Cu             | LiFePO₄  | LiTFSI in DOL:DME | 0.2          | 40%               | 100    | [113]      |
|                        | Cu             | NCM622   | LiTFSI + 2.3 M LiTFSI in DME | 0.3          | 55%               | 54     | [105]      |
of cutoff voltage on the performance of NMC532||Cu anode-free lithium metal pouch cells (Figure 8e).\[107\] The discharge cutoff from 3.6 to 1.25 V caused a significant change in capacity retention and CE. Due to the protocol of deep discharge, excess lithium was stripped from the anode to enhance capacity retention. In addition, the potential temperature–pressure interaction is shown in Figure 8f. The capacity retention of cells under low pressure (75 kPa) was rapidly decayed as the temperature decreased from 40 to 20°C.\[108\] Once a higher pressure value is applied, the battery life will be doubled. So, the conclusion can be inferred that in the absence of mechanical pressure, the cycle life of the anode-free cell at room temperature is significantly affected. A new “hot formation” protocol was proposed to optimize lower-temperature performance (Figure 8g). The mechanism could be attributed to the formation of CO$_2$ during hot formation, which acted as a beneficial additive. The earlier results unveiled that internal chemical transformation is essential; meanwhile, the external environmental factors could have a drastic effect on the cycle life of AF-LMB. Hitherto, various modification strategies achieved performance improvement with the aid of empirical attempts; nevertheless, the challenges still remain in the technological barriers of scalable processing, reliable system evaluation, as well as the unresolved degradation mechanism on the device level (Figure 9).

5. Prospects of the Future Research Direction

In summary, despite the formidable technological challenges that are encountered for the AF-LMB development, the fundamental study is still in their infant stage and thus leaves huge room for performance improvement. This review systematically covers the research activities that were implemented for both the failure mechanism elucidation and the mitigation strategies
from multiple dimensions. Moreover, R&D prospects of the operando and ex situ characterization methods, surveyed from the literature, are proposed as follows.

1) An SEI layer with improved mechanical strength and flexibility is the key to realize the uniform ion influx and alleviate the volume expansion of the piled-up deposits on the substrate. The commercial electrolyte cannot meet the requirements; thus, the formulations with the novel salts, solvent, and additives were continuously attempted. However, most of the studies are still based on "Edisonian"-type optimization without the thorough consideration of the selection rationales. In addition, high cost of the novel electrolytes would hinder their widespread applications; therefore, the viable choice should rely on the low-cost, readily accessible species for industrial formulation.

2) The lattice mismatch of copper with the Li foil could deplete the Li source and lead to the formation of dead lithium. Even upon substrate modification, it is still difficult to achieve the close-to-unit CE for the plating/stripping process. In this regard, a suitable Li supplementary strategy, with the aid of the prelithiation agent from the cathode or Li-rich solid-solution-treated substrate, would provide extra cyclable cations and enhance the reversibility of the model.

3) The research prospect is to comprehensively analyze the real-time evolution of the cell via multiscale in situ/operando characterizations, involving the dynamic structural and lattice changes of the Li-containing cathode and the physicochemical property variations of the deposition substrate upon the Li nucleation process. For instance, the cathode lattice strain would induce metallic dissolution and ion migration toward the substrate, largely influencing the Li deposit propagation. Note that the interplay of the Li utilization degree between the cathode and anode is of paramount significance, the correlation of which could be investigated from multiple scales, such as the functional groups at the interfacial molecular level, morphological and phasic transition at the electrode scale, as well as the overall performance (electrolyte, cell processing) on the device level.

4) For the characterization technique, the threshold numerical values of the X-ray and electron flux do need to be quantified; thus, the electron microscope (EM) or spectral investigations could avoid the structural damage to the beam-sensitive Li deposits or other metastable phases contained in the AF-LMB system. In addition, there is subtle structural information in the nonequilibrium state of the electrode during the fast lithiation process; it is thus hard to detect these signals with the conventional characterization methods. In this regard, the quick signal collection (temporal resolution) and increased spatial resolution of the characterization are vital to capture the extraordinary findings under the dynamic condition. Different from the ambient conditions in the laboratory, the external environmental parameters, like stacked pressure or temperature gradient, would compromise the cycle life and even the operation reliability of the energy-storage systems. Thus, it is expected to develop the operando characterization method that could be implemented under the coupled multiphysical fields. The simultaneous realization of these demanding requirements relies on the coherent synergy of the instrument development for characterization and configuration design of the AF-LMB.

5) From the perspective of practical application, the AF-LMB suffers from insufficient Li-ion utilization and thus limited cycle life. As a result, the construction of the anode-less LMB models with balanced energy density and cycle endurance would be the practical choice. On the one hand, the presence of the lithium inventory would improve the reversibility of the Li plating/stripping process; on the other hand, the models with N/P ratio < 1 save the mass and space in the anode part, resulting in the enhanced gravimetric/volumetric energy densities.

We expect this introductory review could afford insights for R&D of energy-dense prototypes, including the suitable nanoeengineering strategies, to enhance the cation utilization degree as well as multidimensional prototypes for mechanism investigation. The combination of these efforts is expected to provide a feasible way to establish the systematic configuration designs of the energy-dense, reliable AF-LMB.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (52173229), the Natural Science Foundation of Shaanxi (2019JXX-099), the Fundamental Research Funds for the Central Universities (3102019(C)005), and the Key Research and Development Projects of Shaanxi Province (no. 2019ZDLGCY04-05).

Conflict of Interest

The authors declare no conflict of interest.

Keywords
anode-free batteries, cation utilization degrees, electrolyte optimizations, interfacial designs, operando characterizations
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