Optimizing Current Collector Interfaces for Efficient "Anode-Free" Lithium Metal Batteries

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Current lithium (Li)-metal anodes are not sustainable for the mass production of future energy storage devices because they are inherently unsafe, expensive, and environmentally unfriendly. The anode-free concept, in which a current collector (CC) is directly used as the host to plate Li-metal, by using only the Li content coming from the positive electrode, could unlock the development of highly energy-dense and low-cost rechargeable batteries. Unfortunately, dead Li-metal forms during cycling, leading to a progressive and fast capacity loss. Therefore, the optimization of the CC/electrolyte interface and modifications of CC designs are key to producing highly efficient anode-free batteries with liquid and solid-state electrolytes. Lithiophilicity and electronic conductivity must be tuned to optimize the plating process of Li-metal. This review summarizes the recent progress and key findings in the CC design (e.g. 3D structures) and its interaction with electrolytes.

1. Introduction

Lithium-ion batteries (LIBs) are the most successful energy storage system for portable electronic devices and are massively employed in the transportation sector.[1–3] However, the practical energy density of LIBs must be further increased in order to meet the demand for electric vehicles (EVs).[4,5] Moreover, recycling LIBs is also challenging.[6] Using lithium (Li) metal as the active material for the negative electrode could revolutionize current battery technology, in which graphite (specific capacity 372 mAh g^{-1}, volumetric capacity 841 mAh cm^{-3}) represents almost 100% of the market share for negative electrodes.[7,8]

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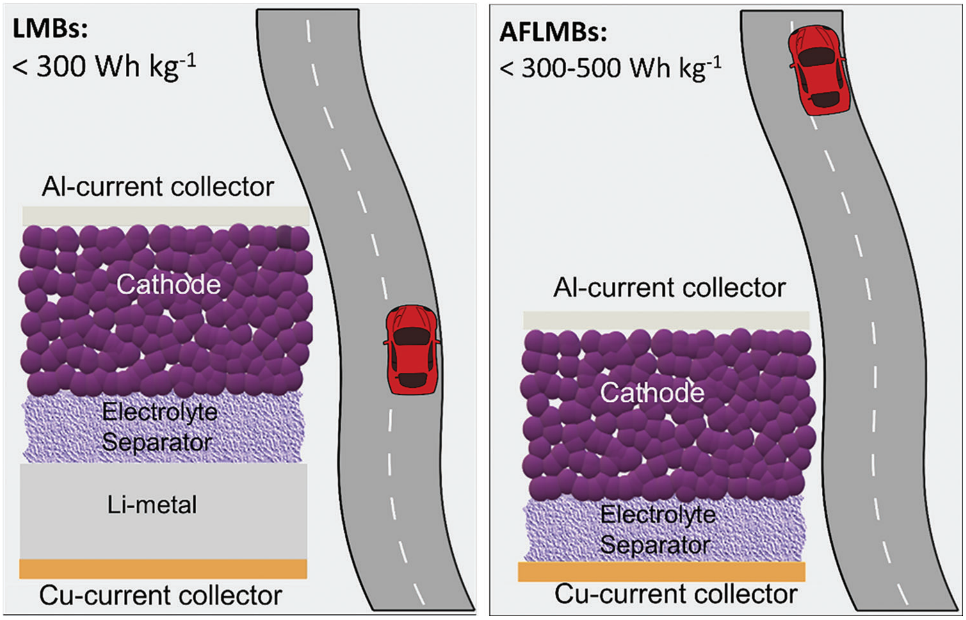

Figure 1. Schematic illustration of Li-metal batteries (LMBs) and anode-free Li-metal batteries (AFLMBs) for EVs applications.

The competitivity of Li is mainly due to its ultrahigh theoretical gravimetric (3860 mAh g_{-1}) and volumetric capacities (2760 mAh cm^{-3}). Thanks to these qualities, beyond-LIB technologies based on Li-metal (Li-metal batteries, or LMBs), would represent a considerable enhancement to the energy density of Li-based batteries.[4,9–15] Despite the theoretical advantages of LMBs, assembling batteries containing foils of metallic Li has many practical disadvantages.[16] Li-metal is expensive and harmful (fire hazard), its shipment is problematic, it needs handling in a moisture-free atmosphere and its production is not environmentally friendly.[17] The abovementioned disadvantages led to the development of a new architecture called “anode-free lithium metal batteries” (AFLMBs), or “anode-less lithium metal batteries” toward high energy density batteries (see **Figure 1**). In such batteries, Li-metal is formed in situ during charge, using only the Li content present at the positive electrode. For this reason, AFLMBs are more correctly described by the name “zero excess Li-metal batteries”.[18,19]

Unfortunately, the real-world application of AFLMBs is mainly hindered by safety and efficiency issues. Upon cycling, Li metal unhomogenuously deposits to form Li dendrites that are known to be the cause of internal short circuits and safety concerns (e.g. fires). Furthermore, the formation of dead Li and the electrolyte decompoistion lead to a quick and progressive loss of capacity. These problems can be solved by optimizing the environment in which Li is plated: the current collector (CC)/electrolyte interface;[20–23] this, if done correctly, leads to the formation of a favorable solid electrolyte interface (SEI), which prevents losses due to electrolyte decomposition, and enable a uniform and dendrite-free plating.[24,25] Beside the electrolyte optimization, which has a fundamental importance and is covered by literature,[26] the other way to optimize the electrode/electrolyte interface is to tune the physicochemical properties of the CC. The scope of this review is to summarize the research efforts in the optimization field of CCs'i'nterface and to elucidate its crucial role in the AFLMB technology.[27–29] In addition, an overview of charge-discharge protocols, characterization methods, and issues associated with different positive electrode chemistries is presented as a guide for researchers entering the field.

1.1. Cycling Protocol in Li-metal batteries (LMBs)

One effective method for enhancing the safety and streamlining the assembly process of AFLMBs is by minimizing the Li-metal content. This approach involves avoiding the usage and handling of Li-metal foils, which ultimately reduces the risk of potential short circuits that may occur before the charging process. Following this approach, the overall safety and efficiency of the AFLMBs are significantly improved compared to LMBs.[15,30–32] However, in AFLMBs, the stable Li-metal deposition/stripping is critical to maintaining cell reversibility for long-time applications, as it is a significant effect on dendrite growth formation and Coulombic efficiency (CE). Therefore, a challenge that currently hinders the advance of AFLMBs is the plating Li non-uniformly on the CC, resulting in the formation of dendrites with needle and whisker morphologies. The dendrite formation and growth leads to a high interface resistance because of low contact area with liquid electrolyte (LE) and current gradient.[33] Despite the interest in commercialization, the development of LMBs has faced regular setbacks due to the Li growth[34] or Li-carbides dendrites,[35] which can lead to short circuits by penetrating separators or solid-state electrolytes (SEs).[13,15,31,33,36] The formation of inactive (dead) Li during cycling dramatically lowers the CE. As a “host-less” electrode, a thick SEI layer is created during every charge step when Li is plated on the surface of the Li-metal electrode. Upon each charge step, a new SEI layer is formed resulting in a volume expansion of the anode, as well as a consumption of electrolyte and increased resistance.[31,37] Additionally, the use of excessively thick Li foil, with a thickness of > 300 µm in full-cells, leads to the

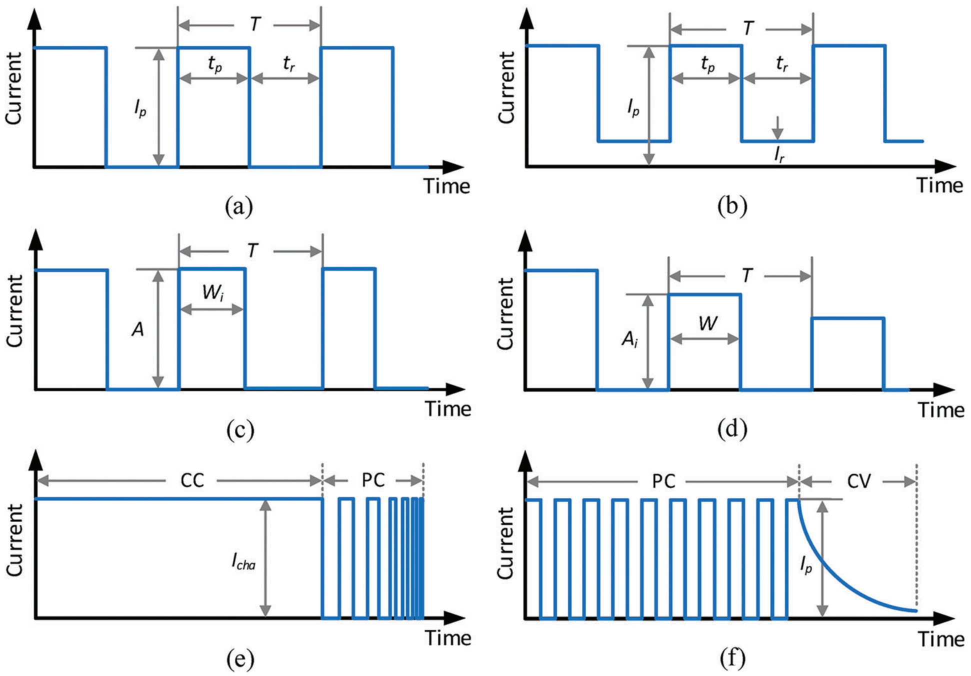

Figure 2. Pulsed current methods for Li plating in LMBs: a) standard, b) constant current, c) width modulation, d) amplitude modulation, e) constant current-pulsed current, and f) pulsed current-constant voltage. Reproduced with permission.[59] Copyright 2020, MDPI.

overuse of Li (> 300%), sacrificing the practical volumetric energy density of LMBs.[11,38,39] Due to its high reactivity, handling of Li-metal during storing and cell fabrication may have challenges with the passivation layer (consisting of mainly Li_2CO_3, LiOH, and Li_2O) on the surface Li-metal for having a high-resistance interface, particularly with SEs.[29,40,41] Hence, the processing costs are elevated due to Li-metal-ingot preparation in an inert atmosphere. Other preparation steps include: a) mechanical processing of Li, and b) surface polishing of Li to make low-resistance interfaces to SEs. Additionally, the cell-manufacturing process of Li metal needs high pressures because of its soft nature, leading to more challenges when employed in solid-state batteries (SSBs).

Several strategies have been put in place to address the abovementioned issues, like optimizing the composition of the electrolyte by adding additives into it ($LiNO_3$, halogenated Li salts, or gas-phase dopants)[42–44] in order to suppress the formation of Li dendrites and create a robust SEI layer on Li metal.[24,45,46] Coating the surface of Li metal with an artificial SEI (polymers, oxide nanoparticles (NPs), and carbon-based materials) has been demonstrated as new method to enhance the performance of LMBs and control the formation of dendrites.[31,47–52] In particular, several polymer-based coatings like poly(dimethylsiloxane) films, and self-healing polymers[53–55] have been employed as an artificial SEI protective layer because of their chemical/mechanical properties and low-cost fabrication methods.[24,56] An effective artificial SEI should a) have a high mechanical/chemical stability, b) conduct Li-ions uniformly, c) enhance the charge-transfer kinetics, and d) decrease the interfacial resistance. Furthermore, it was reported that the morphology of plated Li (during the charging process) depends strongly on the chemistry of the coated layer.[47]

High-CE cells can be obtained only with an efficient Li plating and stripping protocol, when a suitable CC is used. These processes are not thermodynamically controlled; kinetic parameters instead govern the occurring reactions. Therefore, many attempts have been made to suppress Li dendrite formation by employing optimized deposition protocols like pulsed[57,58] or more complex current profiles (**Figure 2**)[59]. A pulsed current protocol using galvanostatic square-wave pulses and $T_{\mathrm{on}}/T_{\mathrm{off}}$ ratios of 1:5 (in seconds) showed superior cycling performance compared to conventional cycling using continuous currents.[57] By using this protocol, cells withstand more than ≥ 40 cycles, compared to 20 cycles achieved by cells with conventional continuous current profiles. Furthermore, scanning electron microscopy (SEM) analysis showed inhibited dendrite formation and reduced volume expansion of the Li metal electrodes when a pulsed deposition was used. When a pulsed electric field is used, an increased Li^+ diffusion is calculated by Molecular Dynamics (MD) due to their reduced coordination with the anionic species in the electrolyte. This is assumed to be responsible for the improved cycling performance.[58] have promoted the interest in developing advanced current profiles for enabling the safe cycling of Li metal electrodes. However, the complexity of the system is often disregarded, and many important aspects are neglected in the interpretation of the results. When comparing pulsed plating with continuous plating, the mean current of the pulsed method needs to be comparable to the current applied in continuous methods. For the pulsed method using a $T_{\mathrm{on}}/T_{\mathrm{off}}$ ratio of 1:5, the deposition time for the same amount of charge is five times more than for continuous plating, meaning that the charging rate is only 1/5th (1/6th) concerning the control.[57] When similar mean charging rates are employed for pulsed and continuous plating, though, no improvement or even a worsened performance during cycling is observed.[60]

In addition, the impact of the SEI layer on the cycling performance of Li-metal electrodes is often neglected as its composition is not well understood yet and cannot be easily modeled by using theoretical approaches.[60] A good example of the complex nature of SEI formation and its involvement in stabilizing Li-metal plating/stripping was presented by He et al.:[61] in contrast to the literature,[62] the authors showed that lithium fluoride (LiF) yields no intrinsic benefits for Li plating/stripping processes, whereas the reaction kinetics involved in the formation of the LiF plays a crucial role. The high reaction rate of the decomposition of fluorine-rich electrolyte additives (e.g.fluoroethylene carbonate, FEC) on the Li-metal surface was shown to be the stabilizing mechanism, rather than the chemistries of the decomposition products.

Recent findings showed that Li stripping is equally or even more important for stable electrochemical cycling[63,64] and can be regarded as the main limitation for the maximum applicable current without dendrite formation. It could be shown that rather than Li^+ ion diffusion, Li^+ creep is the main mechanism for Li^+ transport to the electrode surface. External pressure is another important parameter that has attracted the attention of researchers in the field of LMBs.[65] For SEs[66] and LEs[67]the application of pressure can significantly reduce Li dendrite formation as well as pore formation during stripping and, thus, lead to more stable electrochemical performance of the Li-metal electrode. On the other hand, for electrolyte or separator layers with low mechanical rigidity, increased pressure during cycling can enhance Li^+ creep and induce internal shorts due to Li-metal penetration through the pores and cracks of the SEI layer.[68] The complex electrochemomechanical interactions of the Li metal electrode with the SE render a complete understanding of the occurring phenomena during cycling a demanding endeavor. Often, only a small number of parameters at a time are investigated during cycling, which leads to misleading conclusions. A more holistic view of the matter is required to advance this field of research further. Although Li-metal plating has been a major research topic for many years now, the latter, i.e., the mechanism of Li-metal stripping has become a major focal point recently.

2. New Challenges for Anode-Free Li-Metal Batteries (AFLMBs) and Solid-State Batteries (AFSSBs)

AFLMBs, better known as "zero excess Li-metal batteries", contain no Li metal when they are assembled. The anode-free architecture is composed of a positive electrode with an active material containing Li, a separator (liquid or solid), and a CC (typically copper (Cu)) with no active material on it. In this architecture, Li^+ ions are released from the Li-rich cathode during charge: a thin layer of Li metal is plated on the CC (in-situ formation) and it can be reversibly stripped from the CC during discharge.[30,69,70] The research interest is so high because, thanks to the lack of excess Li and Li hosts (like graphite), AFLMBs can provide significant improvement in energy density (15% reduction in cell stack volume)[13] and specific energy.[71] Furthermore, this eliminates the issues related to the cost, safety, and handling of metallic Li. Despite their potential benefits, AFLMBs present significant safety and efficiency challenges that must be addressed before they can be utilized in practical applications. These challenges include the formation of Li dendrites that can lead to short circuits, as well as dead Li formation, low CE, and poor cycle life. Resolving these issues will be critical to the successful implementation of this architecture. The following sections address recent approaches for solving certain issues.

2.1. Li-Rich Positive Electrodes for Long Cycling AFLMBs

Li-rich cathodes (LRCs) have been developed for LIBs due to their outstanding capacity of 250–370 mAh g^{-1} for 1-1.2 Li^+ extraction from $Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$, which is provided by the cumulative cationic and anionic redox reactions (involving both positive and negative ions in electrochemical reactions.).[72] Other advantages of LRCs are their high average discharge potential (>3.5 V vs Li/Li^+), leading to higher cell energy, and, in the case of high-Mn-content materials, a decreased cost, environmental friendliness, and high thermal stability.[73–76] The amount of Li in these cathodes is high: $Li_2[Ni_{0.8}Co_{0.1}Mn_{0.1}]O_2$ (Li_2NCM811), has twice the amount of Li than conventional $Li[Ni_{0.8}Co_{0.1}Mn_{0.1}]O_2$ (NCM811). Lin et al.[77] demonstrated how the Li_2NCM811 can be reversibly converted into a stable conventional NCM811 cathode in AFLMBs (**Figure 3**a), during the initial charging process, excess Li resources will be stored in the CC to compensate for the Li loss in the anode, enabling long cycle life AFLMB with high mass loading of 25 mg cm^{-2} and a low electrolyte to cathode ratio of 2 g Ah^{-1} in anode-free Li_{1+x}NCM811 pouch cells (Figure 3b).

2.2. Additives for AFLMBs

Some strategies have been developed by several research groups to enhance the AFLMB performance. For instance, Yu et al.[78] developed Mg^{2+}-blocking thin layers as an effective SEI layer by adding $Mg(N(CF_3SO_2)_2)_2$ co-salt in Li^+-containing carbonate-based electrolytes, which is permeable for Li^+ ions, but showing impermeability for Mg^{2+} ions. AFLMB cells were improved in terms of cycling stability and CE with the help of this SEI layer, which enhanced Li deposition on Cu-CCs and reduced Li dendrite growth significantly. The use of fluorine-rich electrolytes is an effective way to improve the Li-plating and CE of AFLMBs. As for example Bing Joe Hwang's group[79–81] used fluorinated carbonate (FEC) and fluorinated ether (1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE)) solvents with ethyl methyl carbonate (EMC), so-called (FTE 352) which provides higher ionic conductivity and oxidation potential of 5.3 V vs Li/Li^+, as well as higher electrochemical performance than electrolytes free of fluorinated compounds in Cu||$LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NCM111) cells.[79] They also investigated the reducing FEC (costly solvent) amount by replacing it with a linear ester methyl acetate (MA) in 1 M $LiPF_6$ (Lithium hexafluorophosphate) in FEC/TTE/EMC. With the new electrolyte combination (1 M $LiPF_6$ in FEC/TTE/EMC/MA (1/5/2/2 vol ratio) + 1 wt% $LiPO_2F_2$), they were able to increase thermal stability, delivered an average CE of 97.5% at room temperature and 96% at 0°C, however, the Cu||NCM111 with FTE 352 showed only 94.4% at

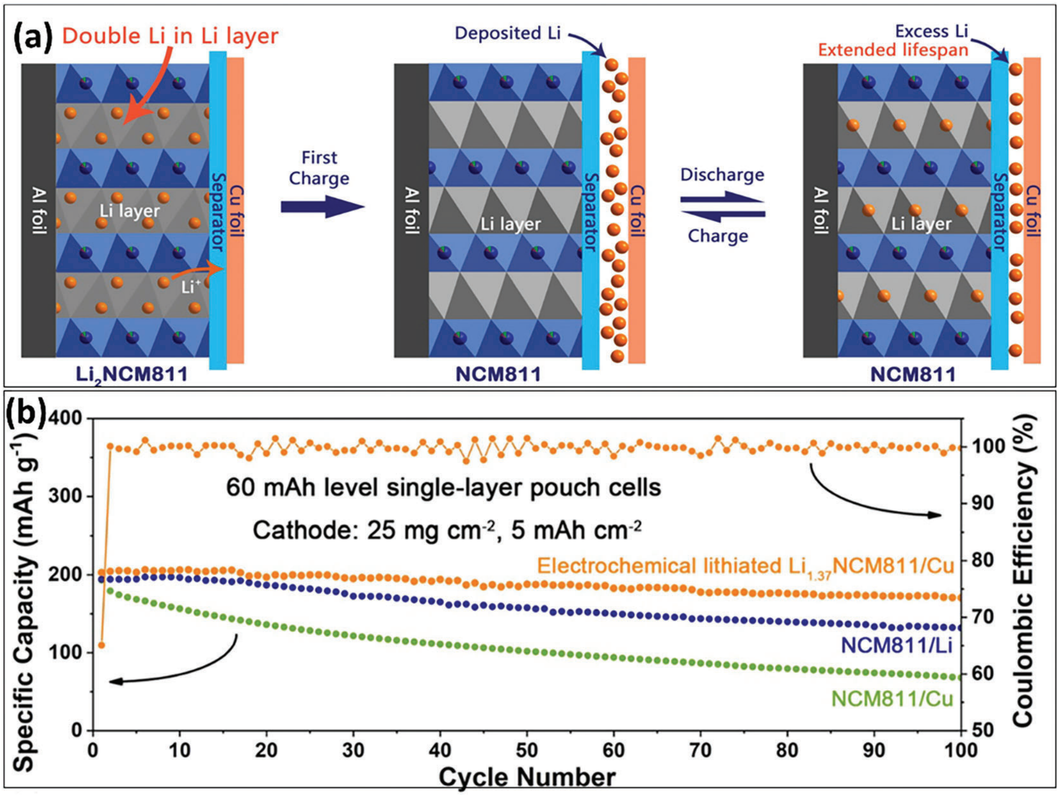

Figure 3. a) Schematic illustration of the advantage of using $Li_2NCM811$ over NCM811 in an AFLMB. b) cycling stability of NCM811||Cu, NCM811||Li, and $Li_{1.37}NCM811$||Cu pouch cells. Reproduced with permission.[77] Copyright 2021, Wiley-VCH.

0 °C.[81] In another work, they studied lithium difluoro (oxalate) borate (LiDFOB) in FEC/TTE/diethyl carbonate (DEC) electrolyte demonstrated higher electrochemical performance for both Cu||NCM523 and Cu||Li cells than FEC/TTE electrolyte. FEC Polymeric species were formed as a result of FEC polymerization, which bound to the inorganic compounds and adhered firmly to the Li metal surface, resulting in enhanced CE and cycling stability of cells.[82–84] Furthermore, FEC and TTE, as fluorinated compounds, were utilized to boost the operating voltage.[79–81,85] The electrolytes with DEC enhanced ionic conductivity, building lithium fluoride (LiF)-rich SEI and plating more Li on the Cu CC, resulting in much better cycling stability and CE, 98.1%.[80] Ye et al.[86] fabricated an artificial LiF-rich SEI layer, which is mixed with highly concentrated lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) mixing in an FEC and/or solid plastic succinonitrile (SN) on the Cu CC to enable uniform Li plating/stripping by removing the uneven electric charges produced from the surface undulation of the Cu CC. The artificial SEI also effectively hindered Li dendrite growth in Cu||NCM811 AFLMBs and provided extra Li resources to compensate for Li loss during the cycling, resulting in increased cycling ability with an average CE of 99%.

The anode-free technology's development requires the solution of the main scientific keys to improve the degradation of the capacity and the stabilization of the cycle life thanks to the structure, morphologies, formation, and properties of the SEI, the morphological evolution of the Li-plate and the understanding of the formation of the dead Li.[87,88] One of the promising strategies to extend the cycle life of anode-less is to understand the capacity loss mechanism and find a key to the CE of anode-less in order to provide clear strategies for improving long-term cycle stability.[89] To develop promising electrolytes, especially regarding functional salts,[90] which facilitate the formation of a protective SEI and uniform Li electrodeposition. Among the various Li salts such as LiTFSI and lithium bis(trifluoromethanesulfonyl)imide (LiFSI) and additives of lithium nitrate ($LiNO_3$) are representative. For example, LiFSI undergoes decomposition, resulting in the formation of an inorganic LiF layer on the surface of Li into various LE or dual-electrolyte systems leading to the improvement of the CE.[91,92] Li plating can be stabilized by using high-concentration dual salt electrolytes consisting of LiFSI or LiTFSI and $LiNO_3$. Recent studies[92,93] have shown that electrolytes with a high concentration of $LiNO_3$ (up to 2 м) can suppress $LiNO_3$ and Li dendrite agglomeration by forming a protective SEI layer and electrolyte oxidation of Al corrosion, leading to good cycling performance by reversible Li operation. Highly concentrated ether-based electrolytes (above 4 м), further diluted by non-solvating and low-viscosity solvents, enable highly reversible Li plating with the highest CE (> 99%) and show great promise for improving the cycle life of Li metal anodes.[92,93] J. Dahn's group tested 65 different electrolyte mixtures consisting of various additives or co-solvents that are added to a base electrolyte with a double salt content.[92] For example, one of these electrolytes using a practical anode-free cathode with a high nickel content and bare Cu, tested at 0.2C/0.5C in the potential range of 3.55–4.40 V vs Li/Li^+, maintains the total energy delivered for

140 cycles. To increase the CE of the anode-free battery, a new cell configuration was used to properly measure and interpret cycling data. For example, a cell consisting of an NCM523 cathode and a Cu anode-free Li-metal anode in a pouch cell configuration was subjected to an ultra-high precision charger at both low and high applied pressures. Results show a significant increase in specific capacity and CE (< 99%) even in carbonate electrolyte 1 м $LiPF_6$ FEC:DEC.[93] The positive effect of pressure on the electrochemical performance of cells operated at low temperatures should be noted. In another work[29], the effect of temperature on the performance of NCM523 cathode and Cu anode-less Li-metal in pouch cell configuration with another type of LE of lithium difluoro(oxalate)borate (LiDFOB) and lithium tetrafluoroborate ($LiBF_4$) double salt electrolyte at applied pressure conditions for cycling is investigated. The cycling protocol is another way to improve the electrochemical performance of anode-less cells. It was shown that rational optimization of the cycling protocol has an impact on improving the electrochemical performance of anode-less cells.[94] For AFLMBs, for example, the intermittent high-depth discharge cycling protocol is an appropriate step.

The high reactivity of Li-metal with most organic-based electrolytes, and the continuously increasing surface area by SEI formation during cycling make limitations for the practical application of AFLMBs by LEs.[25] Replacing them with SEs could provide unique opportunities to overcome these issues, and enable high-performance AFLMBs.[30,95] In addition, SEs make a battery with excellent safety, because many SEs are nonflammable or have higher ignition temperatures than LEs.[96–100]

Generally, in AFLMB with either LEs or SEs, the Li plated morphology depends on the external parameters such as applied stack pressure, temperature, and current density.[101–103] Also it is influence by other properties such as: a) CC nature, b) electrolyte functional groups, and c) surface modifications on the cathode active materials. Optimizing CCs as one key parameter could be a critical challenge to enhancing the electrochemical performance of the AFLMBs. In the following section, we will discuss the modification of CCs for AFLMB with either LEs or SEs.

3. The Importance of Current Collectors (CCs) in AFLMBs and AFSSBs

3.1. Types of CC and their modifications

In a battery the CCs represent the components that collect the electrical current produced during the electrochemical reactions by the electrodes and connect with external circuits. In commercial LIBs, aluminium (Al) and Cu foils are used as CCs for positive and negative electrodes, respectively.[104–106] The chemical modification of the CC is considered a technique to overcome the lithiophobicity of Cu metal and thus improve the cyclability of AFLMBs. In 2019, by computational screening Pande et al.[107] explored new current collectors to nucleate lithium effectively and allow uniform growth. Subsequently, the scientific community aimed to control the possible parasitic reactions at the interface between CC and electrolyte as reported by Tong et al.[108]

Most commonly used CCs for rechargeable batteries, such as stainless steel, Cu, Ti, Al, and Ni due to their high electrical conductivity and good contact with the electrodes. These CCs can be found in different forms, like foils, foams, meshes, and sheets, which could be widely adopted from lab-scale to industrial-scale applications (**Figure 4**a). These CCs have drawbacks with different chemistry of materials and properties (weight and thickness), detachment, and interruption of contact of the active material with the metallic foil, which affects the performances of batteries. Metal-based CCs can be stable only in certain voltage windows: Cu-based metal CCs as anodes and can be operated up to 2.0 V (vs Li/Li^+), on the other hand, Cu cannot be employed for positive electrodes due to its electrochemical dissolution at high operating voltages (3.5–4.5 V vs Li/Li^+).[104] The surface modification of metal CCs allows the coating of a protective layer on the surface, which can retain their high electrical conductivity (Figure 4b). Traditionally, graphite or cathode active materials are used to coat Al foil, Cu foil, and stainless-steel (SS) mesh to produce cheaper, corrosion-resistant, and provide good adhesion and capacity retention.

Generally, Cu-based CCs have been used for both AFLMBs and AFSSBs.The modified Cu-based CCs were explored to obtain efficient and stable cycling, better chemical stability of Li metal, and the adhesion of Li plating during the cycling. Modified Cu-based CC is widely utilized to raise CE and capacity retention of AFLMBs, including surface coating with carbon materials and promoting grain uniform distribution and refinement for Cu-based CC, etc.[104,109,110] As demonstrated by Liu et al.[111] the structure of lithiophilic centers is related to the first lithium metal nuclei and the subsequent deposition. Zhan et al.[112] showed that the advantage of lithiophilic sites gradually disappears under practical conditions due to a rapid accumulation of dead Li. A distribution of lithiophilic sites around a 3D structure is able to accommodate a higher amount of lithium than a planar structure as demonstrated by Zhao et al.[113]

Many CCs use protective layer coatings such as multilayer graphene (MLG), reduced graphene oxide (r-GO), and multiwalled carbon nanotubes (CNTs), alloy compounds, to guide uniform and compact Li nucleation due to their lithiophilicity and good electrical conductivity.[114,115] Modification of CCs, including suitable host structures in combination with lithiophilic coatings shows great promise to be an enable option for increasing reversibility and achieving higher CE close to 100%. In brief, the following sections will discuss more CC modifications of different materials used for AFLMBs and AFSSBs applications. Other materials have been tested as CC. Ren et al.[41] have tested Nickel (Ni) metal as a CC with Li_2S cathode in a pouch cell using SnI_2-I_2 mixture additive: the final anode-free cell could deliver a capacity of 1.8 mAh cm^{-2} after 100 cycles at C/5 (59% of capacity retention) through the formation of SnI_4-Li_2S complex. Ni has a lithiophobic feature like Cu: a plasma treatment can induce the formation of Ni_3N that helps the Li-metal plating through the formation of stable SEI composed by Li_3N.[116] The final cell can deliver a capacity of 120 mAh g^{-1} after 400 cycles with a capacity retention of 85.6%. A sputtering of gold (Au) metal can improve the lithiophilicity of nickel metal forming Au_3Li on the Ni surface during the charging process. GaInSn can stabilize Li-metal plating: a NCM811-based full-cell, showed a capacity of 150 mAh g^{-1} after 50 cycles with a capacity retention of 84%.[117] Kim et al.[118] have prepared a self-standing anode based on silicon (Si)-carbon nanofibers by annealing an electrospun membrane composed of polyacrylonitrile and Si NPs at 800°C in an N_2 atmosphere. The final Si-CNF||$LiMn_2O_4$ full-cell could deliver

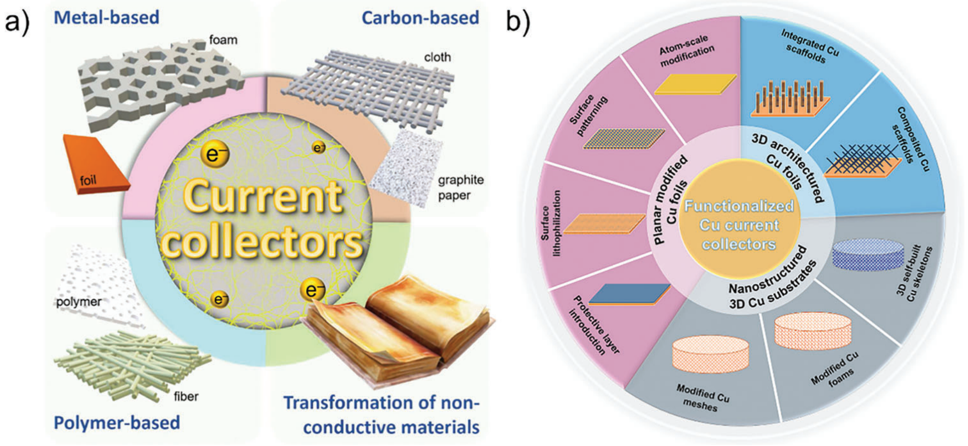

Figure 4. Various kinds of CCs for rechargeable battery applications. Reproduced with permission.[104] Copyright 2023, Elsevier. Cu-based CCs modifications strategy for LMBs. Reproduced with permission.[105] Copyright 2023, Science open.

a capacity of 121 mAh g^{-1} after 50 cycles at a current density of 0.4 A g^{-1}. Despite the high cost, silver (Ag) metal can stabilize the Li-metal plating. Yang et al.[119] anchored Ag NPs over carbon nanofibers (CNFs) as CC: the presence of Ag NPs strongly facilitates the deposition of Li-metal showing a low overpotential (25 mV) in asymmetrical cells at 0.5 mA. By using an Ag-graphite composite, Spencer Jolly et al.[120] observed the existence of Li-Ag alloy formation during charge ($\text{Li}_{10}\text{Ag}_3$) whereas in the absence of Ag, the authors observed a dendrite growth as a consequence of a heterogeneous Li plating over graphite.

3.2. Modifications of Copper CCs for AFLMBs

The biggest obstacles to the commercialization of practical LMBs are still the safety issues due to a potentially infinite volume change at the negative electrode and uncontrolled Li dendrite growth.[121] To overcome these challenges, Shan et al. recently reported a composite formed by a Cu matrix reinforced with multi-walled carbon nanotubes (Cu-CNTs).[122] The Cu-2% vol. CNTs composite CC paired with LiFePO_4 improves cycling stability with CE of 97.8% after 500 cycles (1 mA cm^{-2}) and the capacity retention of 69.4% (100 cycles) at 0.5 C (**Figure 5**a). The lithiophilicity of modified CC is improved by adding CNTs with grain size reduction and distribution to increase the Li nucleation sites. Liu et al. recently reported that replenishable Li is shown the mitigate the formation of "dead" Li and results from more homogenous stripping behavior.[123] For the cells, Li|Cu||LFP specific capacity initially dropped to 96.8 mAh g^{-1} for 10 cycles. Using ether-based electrolyte, Cu|Li||LFP cells showed a specific capacity of 117.5 mAh g^{-1}, which is 75% capacity retention (90th cycle) and suggesting that the SEI layer on the isolated Li particles was not able fully to insulate and only partially accessed during the cycling. Additionally, modifications of carbonate-based electrolytes for these AFLMBs provide a higher CE and good cycling performance.

Strategies for mitigating volumetric changes[124,125] have been proposed via modification of CCs through the introduction of polymeric coating as buffer layer to achieve an even physical and electrochemical interface between electrolyte and CCs, which may open new perspectives for polymers in advanced LIBs.[126] Hwang et al. have developed a series of polymer coatings on bare Cu foil with different processing methods to enhance the Li cycling efficiency, suppressing the growth of Li dendrites and guiding the Li-ion flux during charging.[127–129] A smooth thin film of poly-ethylene oxide (PEO) with a thickness of 200 nm has been spin-coated on Cu foil to enhance CE of ≈100% after 200 cycles and with a low voltage hysteresis of ≈30 mV.[127] Aiming at large-scale production, the electrospinning process was developed to prepare 1 µm ß-poly(vinylidene difluoride) (PVDF) conformal coating on Cu. This thermally and electrochemically activated (TEA) ß-PVDF fiber helps to guide the homogeneous Li flux during the charging process, and an average CE of ≈99.04% was achieved after 30 cycles in a full-cell with NCM111 as cathode and coated Cu as an anode.[128] To further guide the Li$^+$-ion flux for avoiding short circuits and extending the cycle life of AFLMBs, an electronic insulating perforated polyimide film (PI, 70 µm in thickness, hole diameter of 400 µm) was sputtered with lithiophilic Au (≈340 nm) on one side which was used as the back side of Li-free anode, a compact and dendrite-free and horizontally grown Li morphology was observed under SEM as direct evidence of facilitated nucleation of Li during charging on the anode.[129]

To build uniform conditions for Li deposition in AFLMBs, a naturally inspired product of functional polydopamine (PDA) was coated on to Cu foil, whose hydroxyl groups could react with Li ions firstly during charging, resulting in uniformly distributed Li complex carbonyl groups to serve as favorable nucleation sites for Li ion during deposition on CCs. With such PDA-coated Cu foil, a Cu||LiFePO_4 cell could survive till 150 cycles.[130] Compared to the previous strategy of using one single polymer for modification of CCs in AFLMBs, a complex polymer with a copolymer structure has been performed to affect or control the migration of Li$^+$ by electron delocalization and electron cloud density of the polymer,[131] another strategy was carried out through including dielectric NPs to modify the crystallinity of PVDF as well as its dielectric properties, where uniform Li deposition and stripping could be achieved.[31] An active strategy to include Si NPs associated with PAN (polyacrylonitrile) as a coating was performed onto

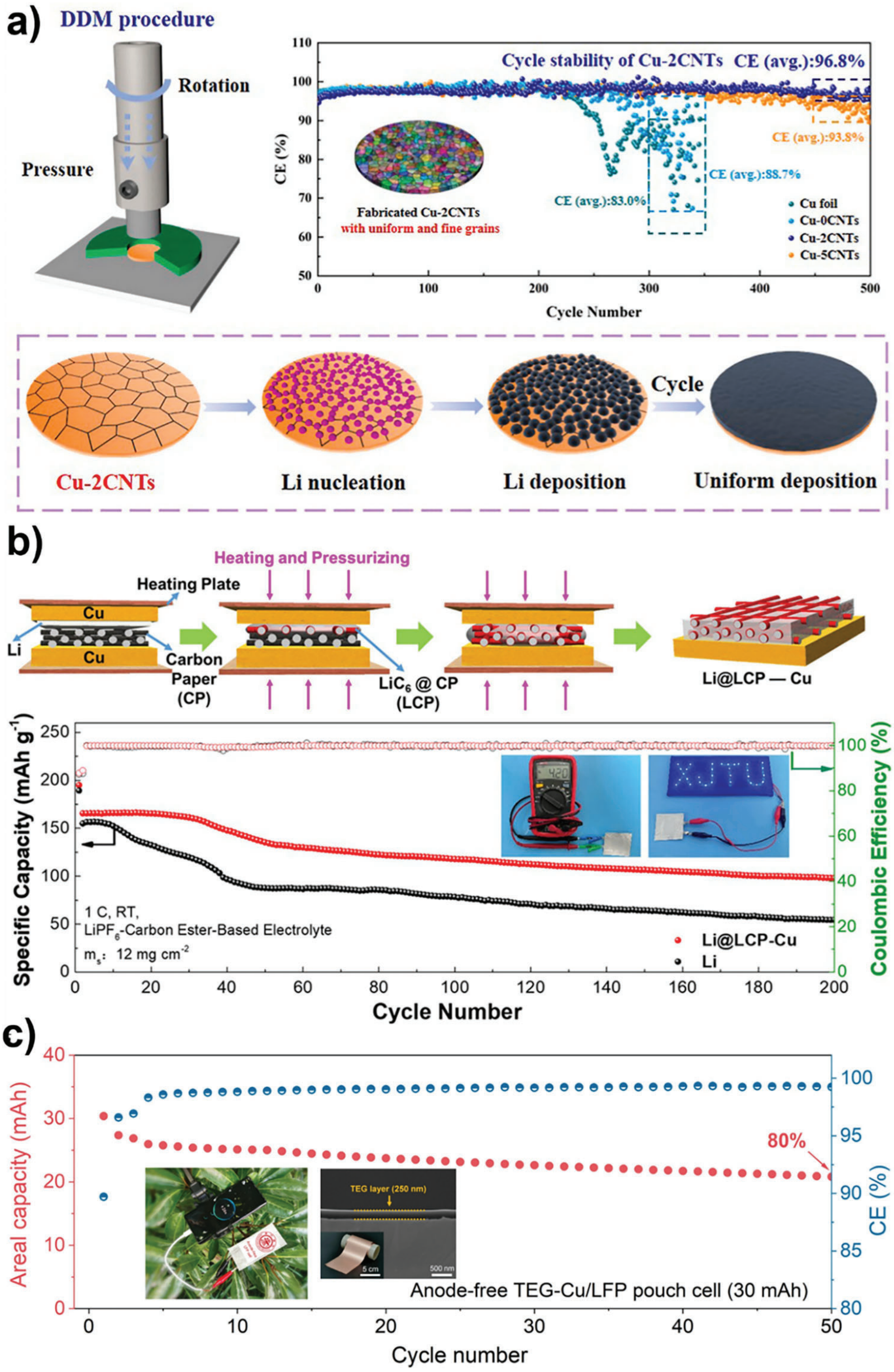

Figure 5. a) The modified Cu-CNTs CC is synthesized by deformation-driven metallurgy (DDM) technology. The CE of AFLMBs, Li||Cu with 1 м LITFSI in DME/DOL (1:1 v/v) with 3.0 wt% $LiNO_3$ as electrolyte, and Li||Cu-0CNTs, Li||Cu-2CNTs and Li||Cu-5CNTs at 1.0 mA·cm^{-2}. The schematic of Li deposition and morphology of Cu foil and Cu-CNTs CCs. Reproduced with permission.[122] Copyright 2022, Elsevier. b) A 3D lithophilic carbon paper/CC integrated with Li metal (Li@LCP-Cu) via a hot-pressing method. The electrochemical performances of unmodified and modified CCs for Li||NCM811 and Li@LCP-Cu||NCM811 pouch cells. Reproduced with permission.[134] Copyright 2023, Elsevier. c) Cycling performance of a 30 mAh anode-free TEG-Cu/LFP pouch cell at 0.3 C charge/0.5 C discharge rates. Reproduced with permission.[135] Copyright 2023, Wiley-VCH.

the Cu surface, and the embedded Si NPs were fully lithiated during charging and then served as nucleation sites for subsequent Li deposition. With this treatment, a high voltage of up to 4.7 V vs Li/Li$^+$ has been realized in AFLMBs, and the mechanical robust property of PAN coating helped to reversibly expand/shrink during Li deposition/striping, thus accommodating the volumetric variation of cells and resulted in stable cycling performance (80% capacity retention after 120 cycles).[132]

Zhang et al. tested a Cu CC modified with a thin layer of tin (Sn) to help the plating process of Li.[133] In this way, Li metal reacts first with Sn to form a Li—Sn alloy, the alloy then electrically connects the Li plating and Cu. This approach improves lithiophilicity, the uniformity of Li nucleation forming large Li granules, and helps to increase CE and stability. Following by, Wang et al. proposed a hybrid anode-free approach to 3D lithophilic carbon paper/Cu CC with ultra-low Li metal prepared by a hot-pressing method (Figure 5b).[134] They assembled the pouch cells based on Li@LCP-Cu||NCM811 and Li||NCM811 delivering the specific capacity of 166 and 155 mAh g^{-1} (1st cycle) and 100 and 55 mAh g^{-1} at 2 C (200 cycles), respectively. These results show the improvement of CP in limiting Li metal deposition volume change and suppressing Li dendrite growth. The presence of a lithiophilic material is crucial for both the CE and the charging overvoltage, while the 3D has generally less beneficial effects on the AFLMBs.

With the requirement of high energy density and high safety on LIBs, the development of solid-state anode-free batteries depicts a new scenario. Recently work showed that a gelling polymer consisting of copolymer poly(vinylidene fluoride-co-hexafluoro propylene) (PVDF-co-HFP) blended with poly(2-hydroxyethyl methacrylate (PHEMA) and lithiated with LiTFSI and LiPF$_6$ could induce uniform Li plating and minimize the formation of dead Li on untreated Cu foil.[136] The in-situ transition of a dense protective barrier formed from graphene oxide (GO) interlinked poly-1,3-dioxolane (DOL) (GPD) under the existence of a certain amount of LE to a multifunctional gel polymer electrolyte (GPE) could stabilize Li$_2$S cathode in air and prolong the cycle life of an anode-free Li—S battery to 2000 times.[71] More recently, an ultrathin composite layer composed of triethylamine (organics) and germanate (inorganic) (TEG) was prepared onto Cu foil via a drop casting process, Figure 5c showed the thickness was controlled to ≈250 nm, and confirmed the enhanced rate capability of TEG-Cu/LFP cell in comparison with that of bare Cu: the improvement was due to the cooperative effect of triethylamine and germanate facilitating the Li-ion absorption and nucleation.[135] He-yi Xia et al.[137] reported that cuprite NPs (HCu) modified CC via a heat treatment method. The modified CC used in the half-cell (Li||HCu) and full-cell (HCu||NCM523) shows a CE of 99.24% for >300 cycles and a CE of 99.11% for 100 cycles, respectively. Interestingly, using Cu-Zn alloy through an electrochemical etching method to form 3D Cu/ZnO/F helps the Li dendrite and prevents the significant volume change of Li metal anode during the electrochemical process with a CE of 98% over 300 cycles.[138] Wang et al.[139] studied Cu CC with coated BaTiO$_3$ porous scaffold to mitigate the morphological inhomogeneities during Li metal stripping/plating and provided the full-cells can reach the CE of 99.37%. Apart from that, commercial Cu foils can be modified as 3D hosting CC, which improves surface's lithiophilicity.[140] The 3D Cu$_2$S nanosheet arrays provide better interfacial contact and structural design for AFLMBs, which helps to reduce local current density.[141][142] Huang et al.[143] reported that a free-standing 3D host of lithiophilic Mo$_2$C clusters-embedded carbon nanofibers (Mo$_2$C@CNF) tested with LFP full-cells resulted in an energy density of 378 Wh kg^{-1}.

Recently, Pyo et al.[144] employed Ag NPs combined with a p-doped conjugated polymer (Ag-PCP) for having a uniform Li plating and rapid formation LiF-rich SEI layer at an early stage. Ag NPs serve as Li nucleation seeds and polymer chain modifiers, resulting in a stable LiF-rich SEI that enables fast Li-ion diffusion and suppresses Li dendritic growth and resource reduction. The Ag-PCP/Cu|LiFePO$_4$ full-cells demonstrated a capacity retention of 72% over 200 cycles at 1C with a first CE of 88% and an outstanding average CE of 99.95%. **Figure 6** displays the Li plating behavior and SEI development on bare Cu, PCP/Cu, and Ag-PCP/Cu over cycling, and their electrochemical beahviour. The phase LiAg is totally reversible as reported by Qian et al.:[145] a thin Ag can be used to improve the cyclability of a graphite anode with a complete dealloying voltage of 0.2–0.4 V vs Li/Li$^+$. On the contrary Bach et al.[146] have observed the existence of irreversible reactions during lithiathion–delithathion process of Au.

3.3. Modifications of Copper CCs for AFSSBs

The choice of SEs has an impact on the modifications of CCs in full-cell configuration. Mostly Cu-based CCs have been modified by coating with metals or other protective layers to avoid detrimental side reactions, interface degradation, capacity fading, etc. In this section, we discuss the recent development of sulfide-based SEs as well as other types of SEs for AFSSB applications.

3.3.1. Sulfide-based SEs for AFSSBs

Sulfide-based SEs have been extensively explored due to their superior ionic conductivities. It is possible to synthesize three different sulfide-based electrolytes, such as a) glass-ceramics Li$_7$P$_3$S$_{11}$ (LPS), b) argyrodites type Li$_6$PS$_5$X (LPSX, X = Cl, Br, I), and c) glassy type Li$_{10}$GeP$_2$S$_{12}$ (LGPS), as reported for SSB applications. Many researchers have made diverse efforts to mitigate these drawbacks, of which the integration of a thin protective layer on the CC has had the most remarkable effect. In anode-less configuration the current collector material needs to be selected and modified to i) avoid side reactions with the sulfide-based SE, ii) enable efficient lithium plating/ stripping cycles, and iii) ensure tight contact between the electrode and electrolyte layers. Regarding the first point, Cu current collectors, which are used for conventional anodes and cannot be used as reactions with sulfide electrolytes have been reported to lead to Cu corrosion and thus poor cell performance.[147] Thus, alternative CCs need to be applied. In recent studies, mainly stainless-steel foils have been adopted as CCs for anode-less approaches,[148–151] whereas Ni foil was used for graphite coatings.[152] Several strategies have been developed for addressing point ii) efficient Li plating/stripping. Oh et al.[148] investigated the use of thin metallic layers on an SS current collector for improved cycling efficiency. They tested four different lithiophilic coatings, i.e., Au, Ag, Zn, and Mg, which are known to have high lithium solubility. Mg was found to stabilize

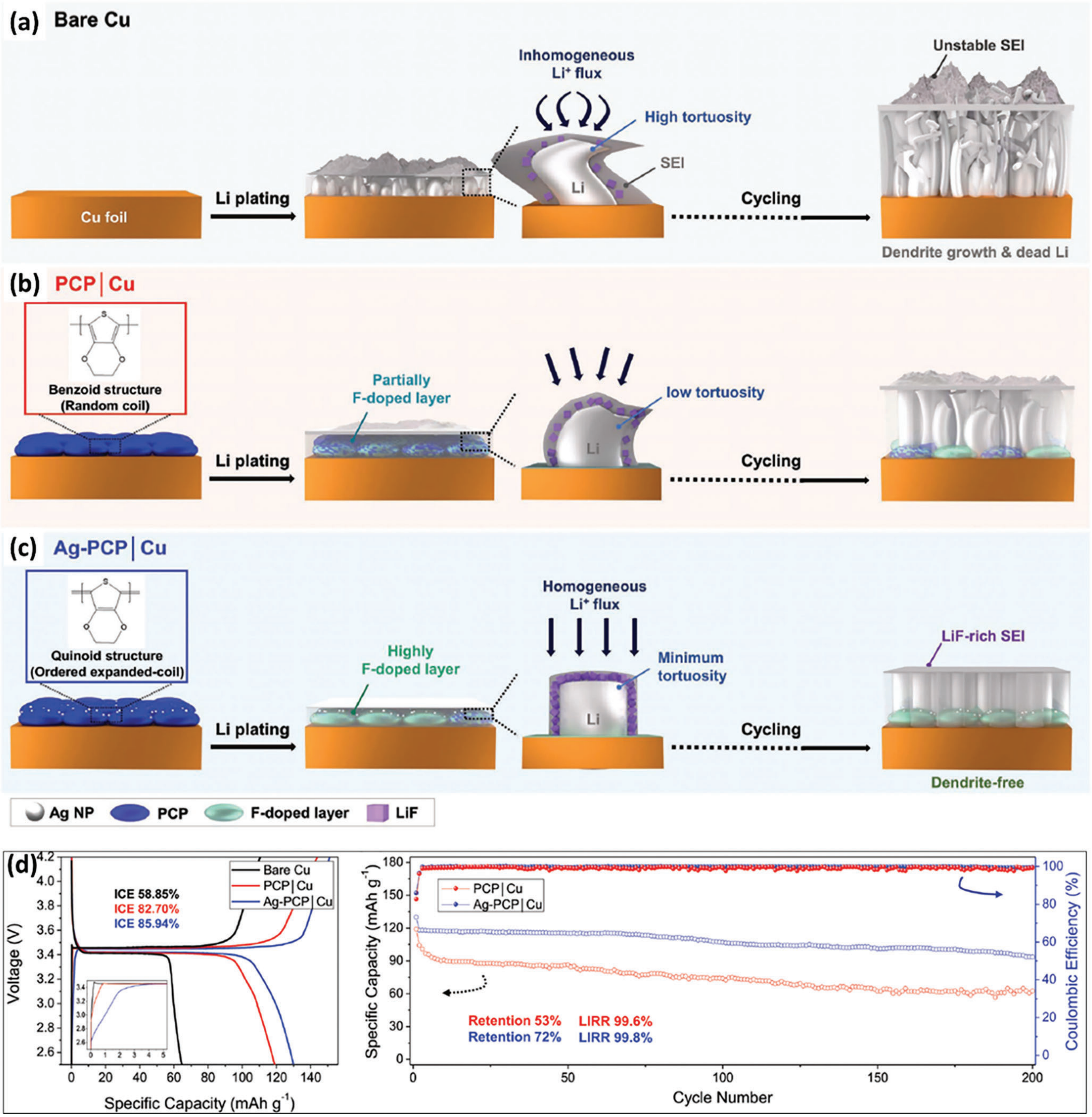

Figure 6. Schematic illustration of Li plating behavior and the SEI formation mechanism. a) Bare Cu, b) PCP|Cu, and c) Ag-PCP|Cu. (d) their electrochemical performance. Reproduced with permission.[144] Copyright 2022, Wiley-VCH.

the lithium plating with a stable cycling up to 1100 h for symmetrical Li||Li cells and the lowest overpotential among the tested samples. Increasing the layer thickness from 50 to 500 nm further increased the cycling stability and decreased the first cycle capacity loss. Nevertheless, mechanical stress during cell operation is expected in anode-less configuration, due to the high volumetric changes stemming from the lithium plating (1 mAh cm^{-2} corresponds to ≈5 µm Li layers). Thus, one of the main challenges identified for feasible AFSSB operation is the maintenance of tight contact between the electrode and electrolyte layers. During alloying reactions of lithiophilic layers, e.g., Mg and Li[148], high volumetric changes are observed, which lead to mechanical stress causing cracks and delamination. Thus, high pressures are usually required for feasible cell operation (10–20 MPa). To enable proper electrochemical performance also under ambient pressures, additional layers need to be provided which improve the mechanical stability. A buffer zone composed of MXene compounds ($Ti_3C_2T_x$) was combined with the lithiophilic Mg layer to

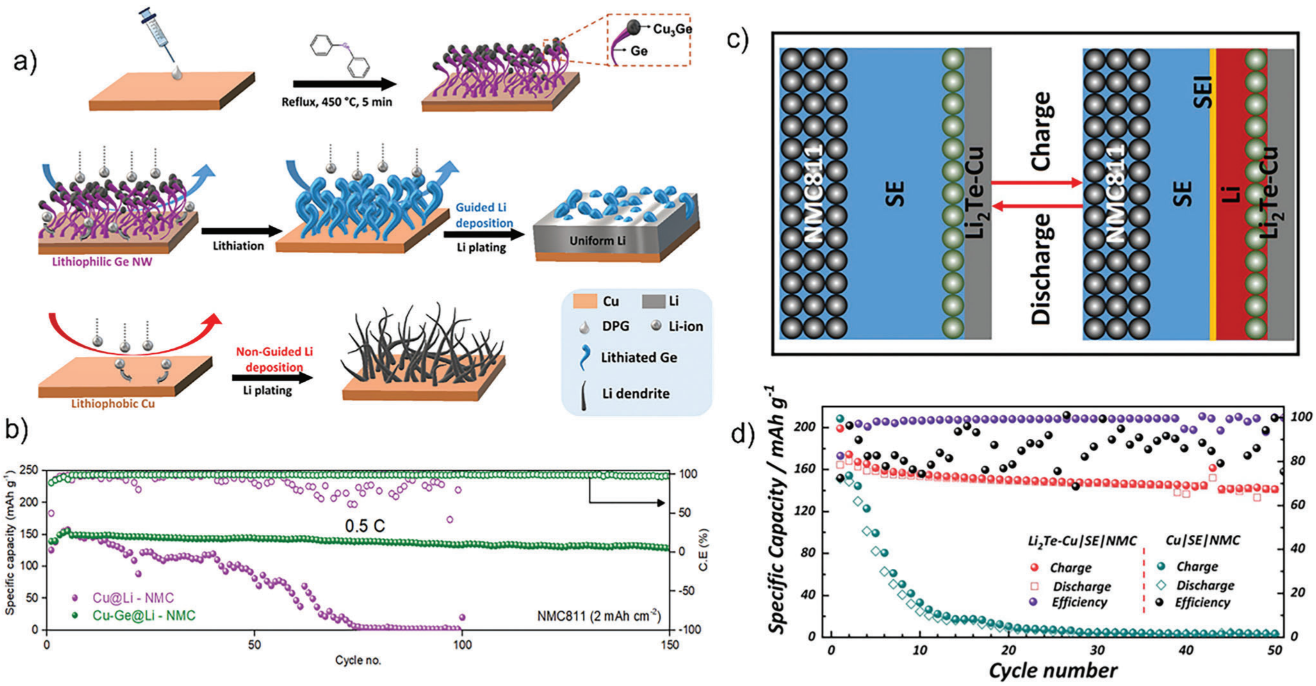

Figure 7. a) Schematic illustration of Ge NWs synthesis on Cu foil. b) The electrochemical performances of Cu||Li-NCM811 and Cu-Ge||Li-NCM811 for AFSSBs at 0.5 C. Reproduced with permission.[154] Copyright 2023, Wiley-VCH. A working principle for AFSSBs I and two different CCs full-cell testing of Li_2Te–Cu|SE|NCM and d) Cu|SE|NCM. Reproduced with permission.[155] Copyright 2023, Wiley-VCH.

compensate for volume changes.[148] This two-layer approach was shown to yield superior electrochemical performance in half cells using NMC811 as cathode active material. A similar approach was shown by Lee et al.,[150] using metal fluorides: AgF produced a mixture of protective LiF and lithiophilic AgLi . Stable cycling of half cells could be thus achieved for 500 h with a high CE value (99.7%) . Therefore, it can be concluded that multilayer approaches seem to be the most promising option for practical cell operation. In another attempt, thin Li film was evaporated onto SS substrate to eliminate initial sites for heterogeneous lithium nucleation in AFSSBs, and for practical and up-scalable consideration, the Ag-C layer was coated onto SS, both confirmed the improvement of interfacial stability between chlorine-rich solid electrolyte and bared CCs.[153]

The anode-free concept has been studied for SSBs by Lee and Han et al., which insert a 10 µm thick Ag-C composite layer between an argyrodite type Li_6PS_5Cl (LPSCl) SE and an SS-CC and delivers the cell capacity of a 0.6 Ah and 99.8% of capacity retention after 1000 cycles.[15] Cu foil reacted with LPSCl and SS-CC was electrochemically inactive for Li deposition from the LPSCl. This means that the promoting Li plating and Ag NPs provided Li nucleation sites onto the CC. Recently, Ahad et al. studied germanium (Ge) nanowires (NWs) directly grown on Cu foil (Cu-Ge) via a physical vapor deposition approach[154] : Ge-NW forms $Li_{15}Ge_4$ phase that creates the pathway of Li^+-ion flux and fast charge, and higher CE during Li plating/stripping (**Figure 7**a). In comparison to planar Cu substrates, the Cu-Ge substrates provide lithiophilic anchoring points, enabling the Cu-Ge to function as high-performance CCs for AFSSBs (Figure 7b). The Ge NWs grown on Cu foil (Cu-Ge) that are generally directly grown on Cu surface contain no “dead” weight from a binder or conductive materials and improve the ED of the AFLMBs. On the other hand, Ge is a highly lithiophilic material with high Li-ion diffusivity and helps to regulate Li plating/stripping processes with Li^+-ion flux.

During the plating process, CC’s surface forms Li dendrites, resulting in low CE and safety issues. A lithiophilic 3D Cu-based magnetic CC (CNZ) is designed by introducing ferromagnetic nickel–cobalt alloy and lithiophilic zinc oxide onto the Cu foam reported by Zhang et al.[156] The use of CNZ as CC allows to plate Li-metal to have a capacity of 1 mAh cm^{-2} (current density of 1 mA cm^{-2}) the CE is ≈95% (590 cycles) as well and the CNZ symmetric cells deliver a stable cycle of 560 h at 2 mA cm^{-2} (capacity of 1 mA h cm^{-2}). This implies that CNZ CCs possess significant improvement in promoting deep Li deposition for AFLMBs. Wang et al. reported tellurium-coated Cu-CC (Te–Cu) via a one-step tellurization process using 1 µm Li_2Te lithophilic by exposing the CC to tellurium vapor, followed by in situ Li activation during the first charge (Figure 7c).[155] The modified and unmodified CCs coupled with NCM811 cathodes and argyrodite LPSCl SEs for AFSSBs (13 MPa external pressure) and resulted from stable cycling with a capacity retention of 80% after 50 cycles (CE 99%) for Li_2Te–Cu||SE||NCM and 33 mAh g^{-1} for Cu||SE||NCM (0.2 C), respectively (Figure 7d). The unmodified Cu CC integrated the inhomogeneous Li electrodeposition and electro-dissolution to inactive “dead metal,” dendrites that extend into SE, and thick non-uniform SEI interspersed with pores. They introduced a new coating toward the Cu CC with ultrathin Li-activated tellurium to control how Li metal spread across or “wetted” the Cu and provide a uniform layer. Without this new coating, Cu foil is covered with irregular microscopic structures forming dead Li during recharging and discharging. With AFSSBs, the role of metal wetting on the CC is also distinct from the thick metal anode and SE compatibility effects for garnet-based SEs. Therefore, elucidating the role of CC lithiophilicity in the electrochemical stability of AFSSBs represents a new advance that should significantly influence next-generation materials and system design.

3.3.2. Other Inorganic SEs for AFSSBs

The oxide-based SEs have good electrochemical stability, relatively high ionic conductivity, and air stability focused on to apply for SSB. Over the years, plenty of oxide-based SEs have been investigated related to the perovskite-type $Li_x La_{(2-x)/3}TiO_3$, $Li_{1+x}Al_x Ti_{2-x}(PO_4)_3$, and garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO). Hsueh et al. recently used the DC sputtering method to deposit a protective layer of 100 nm-thick Ag thin film onto 1 µm-thick thin conductive carbon black (CCB) coated Al CC.[157] They designed AFSSBs based on the NCM111/gel polymer electrolyte (GPE)/(Ag)/ CCB coated Al CC and reported a discharge capacity of 0.935 mAh cm^{-2} and capacity retention of 86.1% (30 cycles). This approach provides an open gateway for modification CCs to achieve higher energy density and longer cycle life. Inspired by these pioneering works, Donghee Gu et al. systematically investigate the effect of the surface roughness of the CCs on the Li plating/stripping behavior in AFSSBs.[158] The SS foil was weakly etched with an etchant solution containing 10% HCl for 2 min to form weakly etched SS (WESS) foil. The results provide that the moderately roughened CC improved the CE and cycle stability of AFSSBs due to the increased contact between the SE and the roughened CC. By using electrospinning method, Abrha et al. formed a composite ceramic film based on $Li_7La_{2.75}Ca_{0.25}Zr_{1.75}Nb_{0.25}O_{12}$ (LLCZN), $LiClO_4$, and polyvinylidene fluoride PVDF which was deposited directly onto Cu CC.[159] The modified CC tested with full-cells like Cu@LLCZN||PVDF||NCM showed a CE of 97.6% (30th cycle). Wu et al. recently reported a 3D host Li with Ag and $LiNO_3$ modified CC for AFSSBs.[160] The modified CC (ALCP@Li) paired with sulfide SEs delivers the specific capacities of 140.6 mAh g^{-1} (0.1 C) and 105.4 mAh g^{-1} (0.5 C) (**Figure 8**a).

M. McDowell's group investigated the short circuit of AFSSBs and their void formations for the sulfide-based Li_6PS_5Cl SEs with Li (>5 mAh cm^{-2}) could plating of current density range of 1 mA cm^{-2}.[161] They found that filament growth and short-circuiting during different stages of void formation and interface reactions were limiting the capacity. Especially, the continued plating steps near the voids significantly grow the filament nucleation (Figure 8b). Building a buffer layer between the Li anode and SE to manipulate the Li plating/stripping in AFSSBs has been investigated intensively recently. An innovative strategy of mixing zinc salt into a hybrid solid electrolyte film could build a lithophilic layer between CC and SE through the intrinsic high potential Zn element against Li versus standard hydrogen electrode (SHE) during the first charging cycle, which forms an inherent buffer layer for the following Li plating/stripping with stable performance.[162] Although the sputtered Au thin layer on CC couldn't resist the lithium dendrite growth leading to internal short, thermal treatment of the sputtered Au thin layer at 400 °C helped to transfer the Au thin layer into separately distributed Au clusters, which forms electrical contact between SE/CC and could prevent localized current concentration during cycling.[163] An outstanding achievement has been reported, where a 3D interconnected ionic-electronic composite of carbon paper filled with SE was prepared and served as CC, a high areal capacity (>8 mAh cm^{-2}) and long cycle life (>5000 cycles) could be realized in AFSSBs.[164] Thus, the modification of the different CCs and the Li formation mechanism must be understood very well and essential for AFSSBs and AFLMBs.

4. Interfaces Challenges and Approach

Interface stability plays a critical role in the electrochemical performance of all LIBs and SSBs.[165] Ku et al. recently reported an excellent overview of interface and interphase on conventional LIBs and next-generation SSBs.[166] The conceptual difference between interface and interphase has not been clearly stated in battery research. Interface is where the electrode is in cotact with the electrolyte which ideally should have zero thickness whereas, interphase is the result of irreversible reactions between electrode and electrolyte.[167,168] The impurities produced by reactions deposit on the surface and form an independent phase. There has been an extensive effort to comprehend the interphase between SEI and cathode-electrolyte interface (CEI). In this section, our focus is on SEI formation. The SEI acts as a passivating layer that hinders further electrolyte disintegration which is crucial for CE and battery performance.[169] Forming stable SEI is key for conventional anode-graphite as well as Li metal anodes for long-term cycling performance.

Recently there has been an extensive effort to comprehend the dendrite formation and SEI reactions.[170] An inhomogeneous SEI can destabilize the LMBs since, at any current density, it can easily crack and expose fresh Li to electrolyte, which is therefore depleted. Recharging a LMB requires electrodeposition on Li itself which is a fundamentally unstable reaction. Thus, indipendently from thecurrent density value, the deposition of Li^+ on Li results in a rough and dendritic surface. The formed Li dendrites lead to cell short circuits, the evolution of dead Li from dendrites, and increased polarization. Most of the strategies target the protection of the Li metal anode and stabilization of the anode architecture. Archer et al. summarized the principles to design the interphase between the anode and the electrolyte.[171] An unstable ion deposition, mechanical strength of the electrolyte, and unregulated surface reactions are stated as the main control points to have a stable Li deposition.[171] Creating an artificial SEI on the Li-metal is one of the approaches to achieving a stable interface.[51,172–174]

The current state-of-the-art electrolyte for LIBs is Li salt dissolved in a carbonate-based organic solvent, and the computability with Li metal is not promising due to safety-related issues. SEs are drawn to the attention to replacing the LE. Monreo and Newman's theory suggested that the dendrite growth might be prevented by introducing a mechanically strong separator.[178] Later, Viswanathan et al. reported that solid ion conductors can be designed with either pressure-driven dendrite blocking or density-driven dendrite-suppressing properties.[179] Besides the mechanical stability, the ion transport properties of the electrolyte play an important role in both dendrite propagation and interface

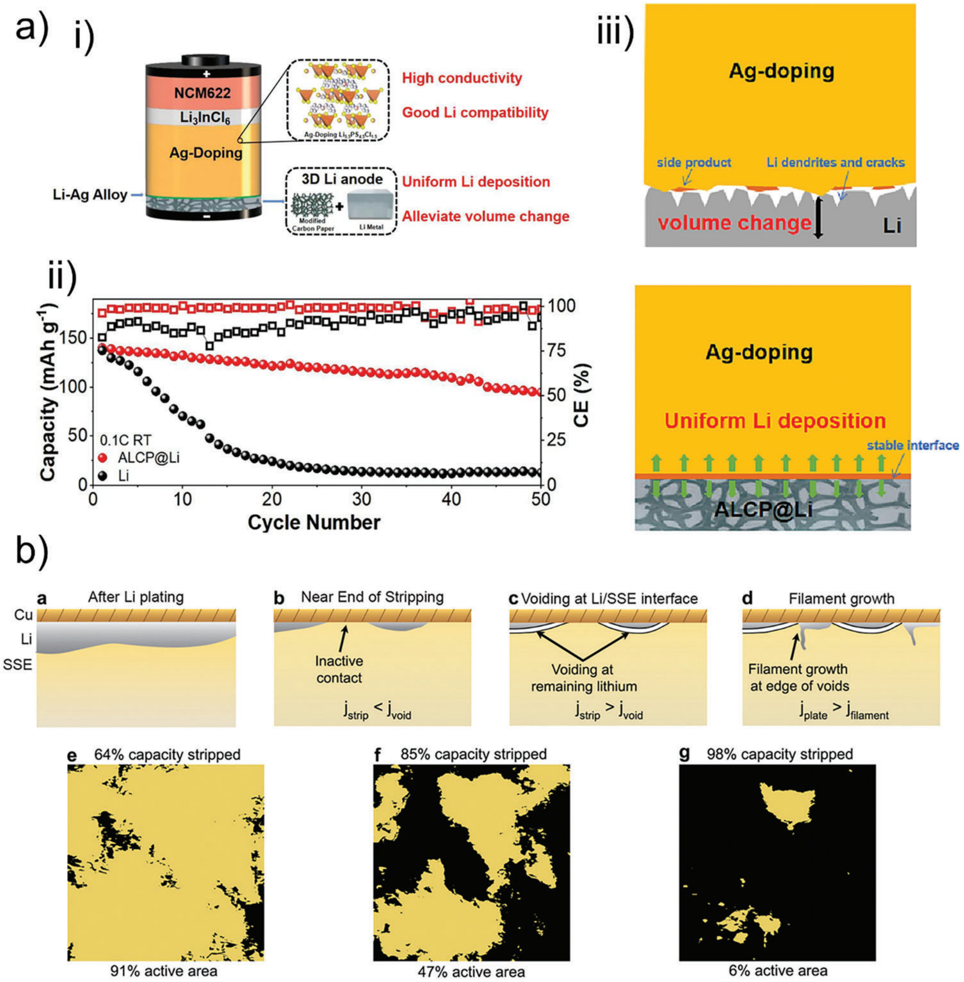

Figure 8. a) A schematic of i) 3D Li metal host for AFSSBs. ii) The electrochemical performances of modified and unmodified CCs with Li with a rate of 0.5 C after 50 cycles at room temperature. iii) Schematic illustration of the interface of the assembled batteries during the charging/discharging processes. Reproduced with permission.[160] Copyright 2023, Elsevier. b). The stripping and plating mechanism of AFSSB interfaces. The deposited Li metal onto CC, the initial stage of Li plating, end of stripping, void formations, filament growth (a–d), and the simulated capacity stripping data e–g). Reproduced with permission.[161] Copyright 2023, Wiley-VCH.

stability. Regarding the space-charge theory, when the ions are close to the anode, the transport is mainly driven by an electric field which leads to ramified Li-metal growth.[180] Thus, controlling the anion distribution and concentration resulted in anion-immobilized electrolytes.[181–183]

The abovementioned issues with the application of Li-metal as an anode inspire researchers to design AFLMBs. Within the implementation of AFLMBs, the energy density of the battery can be maximized whilst, the pack level of cost can be decreased in comparison to the graphite or Li metal anode. In **Figure 9**a deposition of Li on CC is shown. Li et al. observed the Li deposition dynamics by using in situ micro-nano electrochemical scanning electron microscopy (SEM) manipulation platform on ten different substrates (Cu, Ti, Ni, Bi, Cr, In, Ag, Au, Pd, and Al).[184] The results concluded that the affinity for Li and good lattice compatibility with Li play important roles in homogeneous and in-plane Li plating, facilitating uniform and lateral Li deposition. Viswanathan and Pande performed an extensive computational screen on CCs to obtain the most suitable one for Li^+ deposition.[107] Additionally, Hwang's group demonstrated the effect of the applied current on forming SEI and deposition on the CC (Figure 9b).[176] The CC for the AFLMB application is highly critical. Researchers aimed for a detailed understanding of Li nucleation and growth on a variety of candidate CC (Cu, Fe, Ti, Ni, Cr, V, Mo, W, Zr, Mn, LiZn, Li_9A_{14}, Li_2Ga, LiB, $Li_{22}Si_5$, $Li_{17}Sn_4$, $Li_{22}Pb_5$, Li_3Cd and Li_3Ag) using density functional theory calculations (DFTs). The nucleation overpotentials and surface diffusion activation energies for Li on above mentioned CC were calculated by DFTs. It was found that Li alloys as CCs were able to reach 400 Wh kg^{-1} due to better Li nucleation and Li surface diffusion. This study shows the importance of the selection of the CC to build a stable SEI. In addition to the various CCs, the 3D electrode hosts such CCs with micro/nano special structures that are promising to improve the interfacial reactions with the electrolyte.[185,186] Especially, in the case of LE, there are four strategies such as a) nonconductive 3D framework,[142,187] b) metallic 3D framework,[188,189] c) gradient 3D framework,[190] and d) carbon-based framework.[191,192]

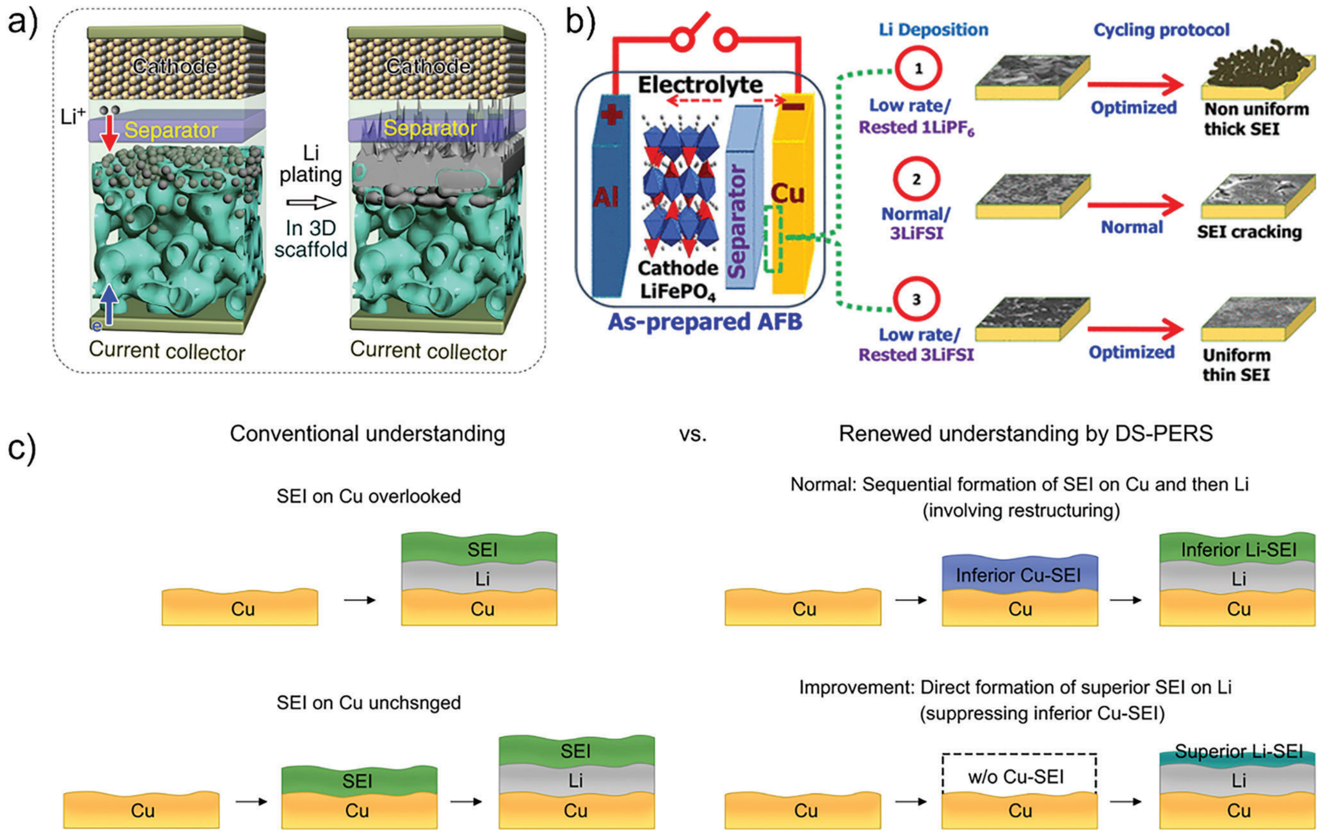

Figure 9. a) A schematic of a 3D Li-metal scaffold as a host for AFSSBs. Reproduced with permission.[175] Copyright 2019, Nature Publishing Group (CC-By). b) The cycling protocol for different electrolyte salts for AFLMBs. Reproduced with permission.[176] Copyright 2023, Wiley-VCH. c) The understanding of SEI formation and evolution of conventional and renewed stages of Cu CC. Reproduced with permission.[177] Copyright 2023, Nature Publishing Group (CC-BY).

Recently, Suo et al. reported the performance of an anode-free couple with high voltage NCM811 on a pouch cell with 100 cycles.[193] The electrolyte was a combination of fluorinated linear carboxylic ester (ethyl 3,3,3-trifluoropropanoate, FEP) with weakly solvating fluoroethylene carbonate and dissociated Li salts ($LiBF_4$ and lithium difluoro(oxalate)borate (LiDFOB)) to create an anion driven interface chemistry. An anion enchainment interface boosts more anion decomposition in the inner Helmholtz plane and higher reduction potential of anions. This unique study is one of the rare examples to show the anode-free concept with LEs. As it is stated previously, the SEs are considered favorable to replace the LE. Thus, there is a tremendous effort within the battery community to overcome the bottlenecks of SEs such as: low ionic conductivity at room temperature and high interfacial resistance. The application of SE on the AFSSBs is currently limited. To control the unstable interface between SEs and the CC, similar approaches as the LE case (artificial interlayer and 3D framework of the anode) are suggested.[194] However, it is noted that the Li plating and stripping mechanisms are quite different due to the Li diffusion pathway. Guo and colleagues reported using a 10 nm interlayer of ($Li_{6.375}La_3Zr_{1.375}$-$Nb_{0.625}O_{12}$, LLZNO) decreased the interfacial resistance from 758 to 46.6 ΩC m^{-2}, which is strong evidence of the effectiveness of the artificial interlayer.[195] Kim et al. investigated Li$^+$ deposition with a conventional $Li_7La_3Zr_2O_{12}$ (LLZO) electrolyte, which revealed that the geometry of the surface of the SE had a significant influence on the deposition morphology of Li.[196] The artificial interface is one of the most promising and applied techniques for both anode-free and LMB applications. The layer can be prepared either by the spin coating technology, physical/chemical vapor deposition, and self-assembly on the substrate or by forming the coordinate bond directly on the substrate.[197,198] Hwang et al.[127] synthesized a nanosized polyethylene oxide (PEO) film as the artificial interface layer via a spin coating method and successfully applied it to AFLMBs with the ether-based LE. The strong interaction between ether oxygen groups of the PEO chains and Li$^+$ promoted a well-distributed ion flux and protection for the CC.

5. Characterization Methods to Analyze Anode-Free Batteries

It is possible to analyze the efficiency of Li-metal plating over CC by using different characterization methods.[199–202] SEM is a useful tool to monitor the Li-metal morphology by following the possible inhomogeneities, as reported by Su et al.[203] Zhu et al.[204] could observe the accumulation of dead Li on a 5 µm Cu-following its 110 facets by using X-ray diffraction (XRD), when NMC811 was used as the cathode.. Liu et al. followed the evolution of plated Li in Li_2S@MX||LE||Cu full-cells via operando XRD, the authors have shown the beneficial influence of a gel

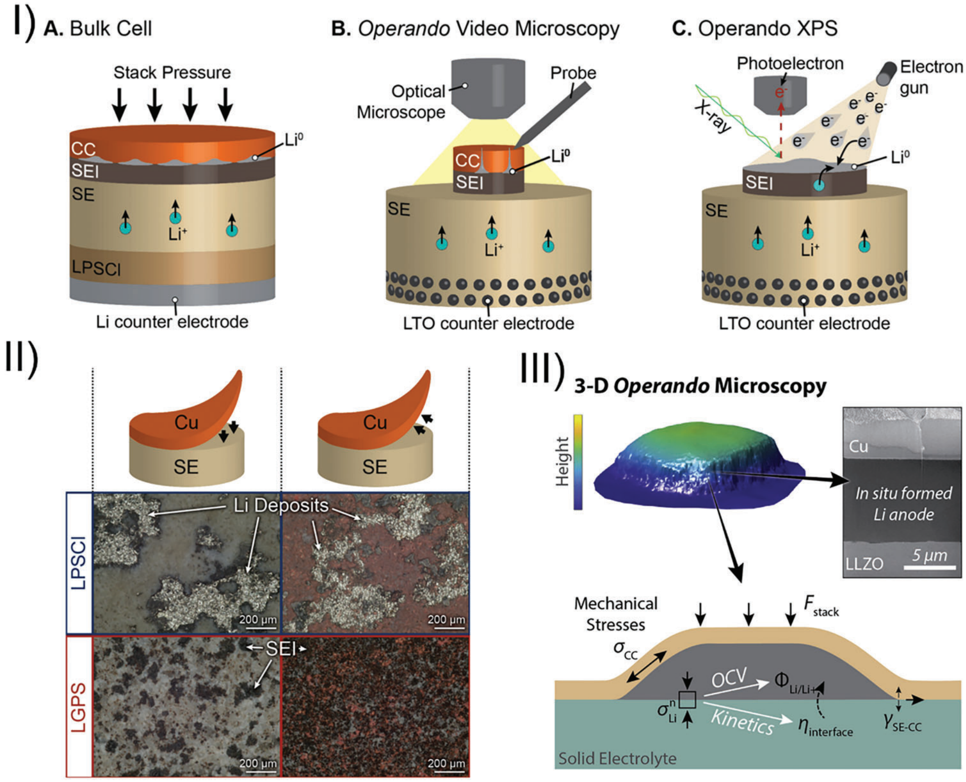

Figure 10. a) A detailed schematic of different cell configurations at the anode-free interface under microscopy studies. Bulk cell with a Cu foil CC. b) Operando video microscopy cell with a sputtered Mo CC. c) Operando XPS cell using an electron gun. ii) Optical microscopy of the SE and Cu surfaces after the 1st cycle. In the LPSCl sample, minimal SEI is observed, and metallic Li deposits are visible on both surfaces. In the LGPS sample, both surfaces exhibit significant SEI byproducts and mechanical degradation. Reproduced under the terms of CC BY license.[211] Copyright 2023, The Authors, published by Nature Publishing Group. III) The Li morphology evolution during Li anode formation via operando microscopy. The model of mechanical stress during Li plating, and interface kinetics. Reproduced with permission.[30] Copyright 2022, Elsevier.

electrolyte on dead Li accumulation when it replaces a standard LE.[205] X-ray tomography can monitor the Li-metal thickness during cycling: its increment is related to an increased Li porosity.[206] As the porosity increases, the electrolyte becomes insufficient to wet all the cell components. Kazyak et al.[30] followed the deformation of Cu metal foil with operando 3D microscopy technique: the authors could detect the morphology of plated Li by varying the pressure (0–10 MPa) through a conductive sapphire window (**Figure 10**). Cosby et al.[207] used synchrotron for in-situ measurements to analyze a Cu||NCM pouch cell observing that Li metal inhomogeneities mainly develop after the second charge. ^{7}Li Nuclear Magnetic Resonance (^{7}Li NMR) is a non-invasive technique that allows following the accumulation of dead Li as reported by Gunnarsdóttir et al.[207]The authors observed that the Li-metal peak (≈260 ppm) remains at the end of the discharge as a consequence of the formation of dead Li. The electrolyte decomposition products can be accurately quantified by ex-situ NMR,[208] Zhou et al. designed a new data fitting protocol to analyze the electrolyte of a cycled coin cell based on Cu|| $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM523) is diluted in deuterated dimethyl sulfoxide (DMSO-d6) solvent with the addition of chromium III acetylacetonate [Cr(acac)$_3$] as relaxation enhancer. In-situ NMR measurement[209] is a promising option to quantify the irreversible Li losses in anode-free batteries, with the possibility to distinguish losses due to SEI formation[40,69] and fractions of dead Li. Recently Tao et al. could determine the content of inactive Li by using mass spectrometry with high reproducibility.[210]

6. Prospects and Outlook

Li metal-based SSBs are considered a promising technology because of their higher energy density than LIBs. However, the battery's performance remains unsatisfactory for commercialization, primarily owing to the inability of the inorganic SEs to hinder Li dendrite propagation and short circuits. The anode-free design is a milestone in the development of AFLMBs and AF-SSBs. The AFLMBs with significantly increased energy density and ease of assembly (**Table 1**).[22] Current LIBs include multiple stacks of anodes, anode CCs, separators, and cathodes soaked in an electrolyte. The AFLMBs comprise an anode CC and a cathode with a separator in between, as well as LEs or SEs. SSB technologies (semi, quasi, and fully) will bring mass production compared to the traditional conventional LIBs. These three types of SSBs are coming to market sooner than expected and their market penetration rate will be higher than estimated in 2030.[212–214] This could be the highest possible energy density by eliminating the anode material and utilizing the maximum possible voltage output from the cathode. From a practical point of view, eliminating Li-metal excess during cell manufacture and simplifying cell assembly are significant advantages.

Table 1. A comparison of different battery chemistries with their performances.

	LIBs	SSBs	LMBs	LMSSBs	AFLIBs	AFSSBs
Gravimetric energy density (Wh kg^{-1})	277	266	406	393	423	408
Volumetric energy density (Wh L^{-1})	751	751	1197	1197	1514	1514
Cycling performance	5000 cycles, 90% capacity retention at 1C-1C	1000 cycles, 90% capacity retention, at C/5-C/5	1000 cycles, 90% capacity retention, at C/3-C/3	700 cycles, 80% capacity retention at C/2-C/2	100 cycles, 80% capacity retention at C/5-C/5	50 cycles, 80% capacity retention at C/5-C/5
Temperature (°C)	RT	60	RT	RT	RT	RT
Reference	[215]	[216]	[217]	[218]	[26]	[155]

A new strategy of introducing better CC design plays a big role to void the dendrite or dead Li formation [219] Furthermore, AFSSB can reduce the cost per kWh by reducing materials consumption as well as energy demands during electrode production. AFLMBs are currently the focus of research, as they will offer high capacity combined with improved safety with the choice of electrolytes (LEs and SEs). Despite this interesting progress toward AFLMBs,many challenges are still open. Likewise, the suitable CC design in terms of structure and choice of materials, interface optimizations, pressure, and stress monitoring during the cycling process. These challenges could be considered to meet the benchmark requirements for the industrial scale viable for commercialization applications (**Figure 11**).

In summary, the following key factors should be considered for future research and development:

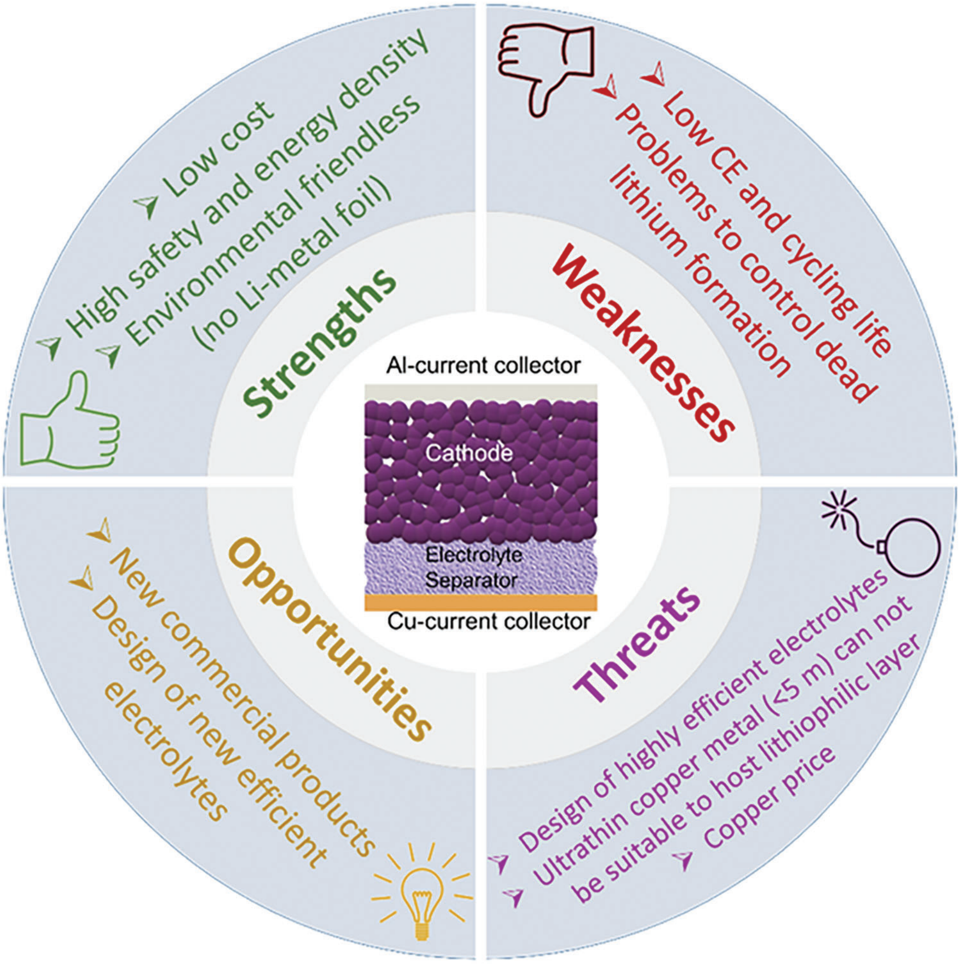

Figure 11. A SWOT analysis of AFLMBs.

i. The structure of CC substrate (micro to nano level) could affect the long-term cycling stability.[220] Moreover, it is suggested to analyze the relative difference between theoretical simulations and the practical results, which could open a new pathway for the design and fabrication of novel CCs for AFLMBs or AFSSBs. Modeling-based estimations indicate very high CEs ≥ 99% are required in AFSSB to be competitive with the well-established LIB technology.
ii. Maintaining a high CE is extremely important for all battery chemistries, particularly for AFLMBs that have limitations on the amount of Li present at the cathode. The CE is contingent upon the cell's type and composition, making it challenging to arrive at a definitive conclusion. Nevertheless, modification of the CC surface to make a stable Li-metal deposition/stripping, as well as optimizing the electrolytes, can enhance the CE and prolong the battery's cycling life.
iii. The CC/SE interface has a significant influence on the Li nucleation behavior, which in turn affects Li growth characteristics.[221] To avoid the dendritic growth of Li through the solid-electrolyte separator and associated cell failure, a targeted choice of materials and interface design is required. In AFLMBs, the LEs show a significant dependency of the Li plating mechanism on the type and surface states of CC material. Such correlations should be further investigated for SEs, where only a few studies have been reported. Furthermore, it has also not yet been investigated how unavoidable current density inhomogeneities in pouch cells affect Li deposition and whether homogeneous plating is possible.
iv. Most of the knowledge gained from lab-scale-level research on different CCs used for AFLMBs employing LEs can be transferred to the nascent field of AFSSB to accelerate the development process.[221] Synergistic approaches that combine the advantages of host structures, lithiophilic coatings, protective layers, pressurization, and specific formation protocols appear to be highly promising in combination with SEs. Initial CE and reversibility of Li-plating/stripping during cycling are extremely critical to the practical energy density and cycle life of AFSSB.
v. Interfacial issues related to the thermodynamic stability of SE[222] need to be tackled by using protective coatings at the anode-free CC and the cathode active material as well as by the development of novel SE materials. It requires promising interface design strategies for realizing high performance and long-term cyclability. The optimization of the interfaces represents an important challenge to developing highly efficient AFLMBs and AFSSBs. Designing an artificial interface layer on the CC using thin film technologies (e.g. thermal evaporation technique, electron beam evaporation, pulsed-layer deposition, sputtering, and chemical route deposition) could greatly improve the performance of both chemistries. However, the cost of processing technology may limit the practical fabrication process, which will drawback to the commercialization process.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

anode-free, current collectors, interfaces, liquid electrolytes, lithium metals, solid electrolytes

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