

Building Better Li Metal Anodes in Liquid Electrolyte: Challenges and Progress

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ABSTRACT: Li metal has been widely recognized as a promising anode candidate for high-energy-density batteries. However, the inherent limitations of Li metal, that is, the low Coulombic efficiency and dendrite issues, make it still far from practical applications. In short, the low Coulombic efficiency shortens the cycle life of Li metal batteries while the dendrite issue raises safety concerns. Thanks to the great efforts of the research community, prolific fundamental understandings as well as the approaches of mitigating Li metal anode safety have been extensively explored. In this review, Li electrochemical deposition behaviors have been systematically summarized and the recent progress in

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electrode design and electrolyte system optimization have been reviewed. Finally, we discussed the future directions, opportunities and challenges of Li metal anode in applications.

1. INTRODUCTION

In the past three decades, the community have witnessed the tremendous boom of the energy storage market in different sectors such as portable electronic devices and electric vehicles. However, the current state-of-the-art lithium ion batteries are approaching a bottleneck of energy density limitations. Aware of the fast-growing energy storage demands, the quest for high-energy density batteries arouses a surge of interests in lithium metal anode in recent years. Li metal, is praised for its high theoretical capacity (3860 mAh g^{-1}) and the lowest electrochemical potential ($-3.04 \text{ V vs. standard hydrogen electrode}$), and it is thus considered as one of the most promising candidates for next-generation batteries. Despite the successful use of Li metal anode (LMA) in primary batteries, it encounters a poor cycle life and catastrophic safety issues due to low Coulombic efficiency (CE) and the formation of Li dendrites in rechargeable Li metal batteries. The replacement of Li metal anodes with carbon-based anodes has led to a successful realization of Li ion batteries (LIBs) in the early 1990s. However, the penalty is a much lower specific capacity (e.g., graphite, 372 mAh g^{-1}) that makes it hard to meet the increasing demands of higher specific energy density batteries. It is thus of the paramount significance to build better batteries based on a reliable LMA for next generation batteries.

For decades, the ongoing strides of solving these problems are also associated with the myriad efforts that dedicated to this area. Nevertheless, two main challenges of the Li metal pertain to the low CE and unstable Li electrochemical deposition, which hinder its practical

applications. Typically, the inhomogeneous deposition of lithium easily leads to a dendrite-like form, which may pierce through the separator and give rise to the safety hazards of cells by short circuit. The fracture of these dendrite-like Li becomes parts of “dead” Li and further contributes to a low CE due to the losing of electric contacts. In this regard, the realization of a stable Li electrochemical deposition is essential for solving these long-standing challenges of the Li metal. Herein, this review is intended to provide a complete picture on the Li electrochemical plating/stripping process in liquid electrolyte and further highlight the approaches for stabilizing Li metal electrodes. In particular, we specifically focus on recent new understandings as well as possible methods for future design of Li metal electrodes with an improved stability.

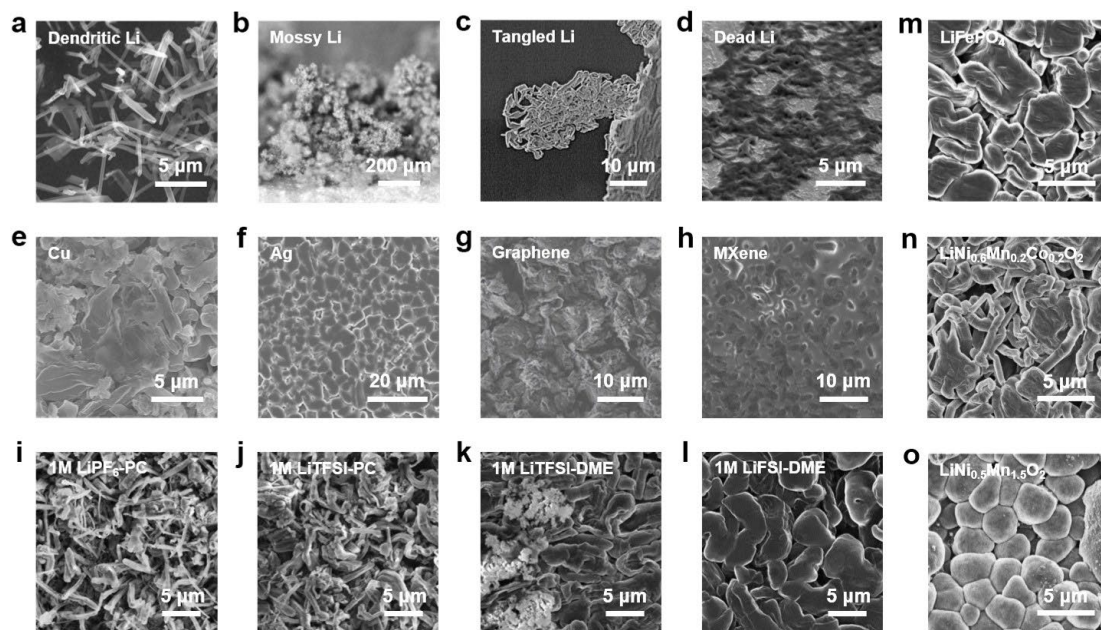


Figure 1. Li morphologies in battery cells. (a-d) Schematics of different Li micro-structure: (a) dendritic Li, reproduced with permission from ref. 1. Copyright 2018 American Chemical Society (b) mossy Li, reproduced with permission from ref. 2. Copyright 2016 American Chemical Society (c) tangled Li, reproduced with permission from ref. 3.

Copyright 1998 Elsevier. (d) dead Li. Reproduced with permission from ref. 4. Copyright 2019 Springer Nature. (e-h) SEM images of Li electrochemical deposition (1 M LiTFSI in DOL/DME based electrolyte, 2 mAh cm⁻²) on different substrates: (e) Cu, reproduced with permission from ref. 5. Copyright 2015 Springer Nature. (f) Ag, reproduced with permission from ref. 6. Copyright 2019 American Chemical Society. (g) Graphene, reproduced with permission from ref. 7. Copyright 2017 John Wiley and Sons. (h) MXene. Reproduced with permission from ref. 8. Copyright 2018 John Wiley and Sons. (i-l) Electrolyte based different Li deposition (0.5 mA cm⁻², 0.5 mAh cm⁻²) behaviors on Cu current collector: (i) 1 M LiPF₆-PC, (j) 1 M LTFSI-PC, (k) 1 M LiTFSI-DME, (l) 1 M LiFSI-DME. Reproduced with permission from ref. 9. Copyright 2014 Springer Nature. (m-o) Cathode effects on Li deposition: (m) LiFePO₄, (n) LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂, (o) LiNi_{0.5}Mn_{1.5}O₂. Reproduced with permission from ref.10. Copyright 2019 John Wiley and Sons.

2. LITHIUM PLATING/STRIPPING BEHAVIORS IN LIQUID ELECTROLYTE

Li dendrite suppression to achieve a stable electrochemical plating/stripping process is the prerequisite for the success of Li metal stabilization. In the course of electrochemical cycles, Li is prone to deposit in whisker forms, which is a basic issue of LMA. To overcome this issue, a clear fundamental understanding of its working principles in liquid electrolyte is required. In particular, we specifically focus on the mechanistic view of SEI formation, Li electrochemical deposition, and corresponding interfacial chemistries in this section. Relationship between electrochemical properties of Li anode and different variations including deposition substrates, electrolyte systems, and other factors, will be elucidated

to strengthen the insights of Li deposition behaviors.

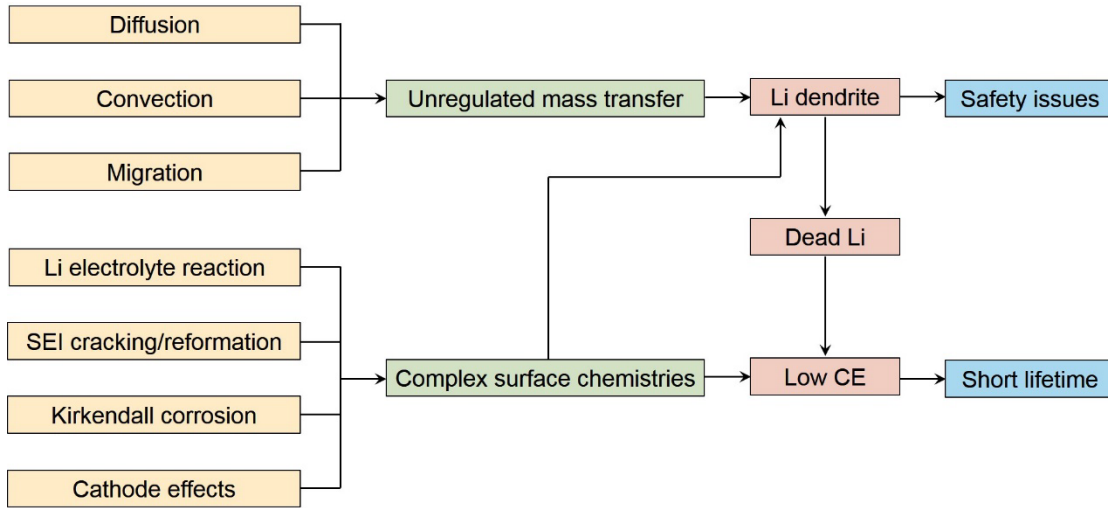


Figure 2. The main challenges related to LMA.

2.1 Unstable Li plating/stripping. Upon the electrodeposition process, three mass transfer modes are involved, namely diffusion, convection, and migration of lithium ions¹¹. In theory, Li ions move from the bulk of the electrolyte to the surface of the Li anode through mass transfer. Such an unavoidable mass transfer (including diffusion, convection and migration, generally, convection is negligible) of Li ions results in concentration gradients between the bulk of electrolyte and electrode surface. Li ions start to nucleate when the diffusion current density approaches the limiting current density (i_{lim}) at a steeper concentration gradient site, because depleted Li ions cannot be fully replenished immediately by diffusion¹². Once the current exceeds the diffusion limitation ($\sim i_{lim}$), the Li ion concentration near the electrode surface reduces to zero at a certain time, which is known as “Sand’s time” (t_{sand}).¹³ These mass transfer processes in dilute electrolyte give rise to a formation of space-charge, which has been shown to form dendrites at Sand’s time¹⁴⁻¹⁶. This uneven deposition process further worsens the electrical field and potential

distribution, then accelerates the propagation of dendrite growth¹⁷. However, it has been found that limiting current density i_{lim} is not an effective indicator to predict Li dendrite formation because dendrite growth has been observed even at a current density lower than 20% of the i_{lim} ,¹⁸ which is different from other metal deposition (e.g. Cu)¹⁹. In particular, apart from Li protrusions, subsurface structures have been revealed by X-ray microtomography, which suggests a complicated mass transfer process is involved in Li dendrite development²⁰. Along with the Li whisker growth, a sequence of behaviors such as buckling, kinking, yielding may occur under stress, further complicates the Li plating/stripping process²¹. As a consequence, a great deal of intricate deposition microstructures has been reported in practical battery cells including dendritic Li (Fig. 1a), mossy Li (Fig. 1b), tangled Li (Fig. 1c), to name a few. All these results exemplified that the growth of Li dendrite was not solely controlled by mass transfer process. Thus, several Li dendrite growth models have been developed with an incorporation of thermodynamics reference points¹⁷. For example, a heterogeneous nucleation model has been proposed, in which an overpotential-controlled critical radius is highlighted for dendrite formation thermodynamically²². Moreover, a critical kinetic radius is defined by surface tension and overpotential driving forces, which is related to the growth and shrinkage of the isolated embryo. All these findings highly suggest a kinetically and thermodynamically controlled mechanism for Li dendrite growth.

On the other hand, a Kirkendall-type corrosion has been proposed recently on the stripping process, that is, a galvanic process between lithium and the copper current collector renders the fast Li corrosion²³. Typically, the Li metal and Cu serve as the anode and cathode for

this galvanic cell, respectively. Thus, a new electron transfer pathway is enabled from Li to electrolyte through Cu cathode, along with the outward diffusion of Li^+ on the Li surface through the SEI layer. The observed void Li could be accounted well by the dominant outward diffusion as Kirkendall-type corrosion. These void Li caused by Kirkendall corrosion is further vulnerable to dendrite germination in subsequent plating. What's more, the initial sequence of Li plating and stripping process has been found may give rise to different full cell cycling performance, morphologies evolutions, and electrochemical potential evolutions.²⁴ All these complex plating/stripping processes encumber a comprehensive understanding of Li electrochemical behaviors in practical cells. After a complete stripping process, certain amount of metallic Li^0 is isolated and remains unreacted due to the losing of electric contacts, which, typically, refers as “dead Li” (Fig. 1d). These dead Li account for a wide range from ~1% to 75% of deposited lithium capacity, as varied with different electrolyte systems⁴, which explains the low CE of Li metal to a certain extent. In such a scenario, an underlying cognition of electrochemical behaviors of Li metal is still under exploration in light of its convoluted mechanism. Along with the Li deposition, a solid electrolyte interphase (SEI) layer forms on the surface of Li structure by virtue of the reactions between Li and electrolyte²⁵⁻²⁹. The formation of SEI could be traced to the electrochemical window (EW) of the electrolyte, which is associated with the difference between the energy level of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO)³⁰. The deposition potential of Li metal is around 0.000 V (vs. Li/Li^+), which is much lower than the reduction potential of electrolyte (i.e. equivalent HOMO energy). Hence, electrolyte decomposes to SEI at the Li surface spontaneously³¹⁻³². Passivation by the SEI prevents the further reaction between Li and

electrolyte, while allows the Li ion conduction. However, the porous and mechanically fragile SEI may crack along with the repeated Li deposition/dissolution processes. The induced re-exposure of fresh Li to electrolyte renders a reduced CE and the depletion of electrolyte after long time cycling³³⁻³⁴. These issues impose imperative challenges for stabilizing Li metal anodes.

For the sake of clear elucidation of these electrochemical processes, many *ex-situ* and *in-situ* characterization techniques have been developed and applied. The first observation of Li dendrite formation could date back to 1980 by Epelboin et al³⁵. In 1998, the texture of lithium has been visualized with the plenty of grain boundaries by scanning electron microscopy (SEM) and atomic force microscopy (AFM). These columnar-like structures are coated by a passive layer, namely SEI layer, which consists of Li_2CO_3 , Li_2O , and reduction products of electrolyte³⁶⁻³⁷. The strong crystallographic texture of deposited Li has been further corroborated by X-ray diffraction pole-figure analysis³⁸. By *in-situ* optical microscopic imaging, a large number of pits and defects have been captured after plating/stripping, and these pits further serve as nucleation sites ready for dendrites growth^{2, 39}. All these findings underline the lithium surface state is one of the key parameters for dendrite growth apart from electrolyte gradient concentration (mass transfer controlled process). Cryo-electron microscopy as an emerging powerful technique also have been utilized to correlate atomic and nanoscale structure of electron-sensitive Li metal anode structure. It has been found that Li grows along with (111) (preferred), (110), and (211) facets to form dendrites structure⁴⁰. Recently, two types of dendrites structure with different composition have been revealed using cryo-transmission electron microscopy

(cryo-TEM)⁴¹. Type I dendrite structure has an extended SEI layer, while type II structure consists of lithium hydride rather than lithium metal itself. Moreover, other imaging approaches such as neutron imaging and X-ray tomography, provide in-depth insights towards lithium metal^{20, 42-44}. To the best of our knowledge, two main reasons of unregulated mass transfer and complicated surface chemistries interpret the failure mechanisms of Li metal upon electrochemical cycles, and a brief summary has been presented in Fig. 2.

Current density and temperature are two main external factors that affect the Li electrochemical plating/stripping behaviors. It has been widely accepted that larger current density is favorable for the dendrites formation. As a result, a shorter cycling lifetime and lower CE of LMA has been widely observed at high current density situation^{3, 45-47}. Nevertheless, the thin needle-like lithium filaments have been further revealed at a small current density below the limiting current, and the authors discriminated these “whiskers” from those common used term “dendrite”.⁴⁸ Even at a small current, a transition of these Li mossy structures (formed by interweaved Li whiskers) to dendritic lithium happens once the deposition capacity is over Sand’s capacity. In this regard, current density is not sufficient to judge the tendency of the growth of Li dendrite solely. Modeling results based on thermodynamically consistent theory further demonstrates that three dendrite growth mechanism could be existed, that is, base-controlled growth, tip-controlled growth, and diffusion-limited growth, which gives a further detailed explanation.⁴⁹ In general, smaller and more distributed Li nuclei has been deposited at larger current density while dendrites formation is favorable at certain current density region with charge-transfer-controlled

growth mechanism⁵⁰⁻⁵¹. On the other hand, suitable temperature range is required, otherwise, insufficient dynamics at low temperature and high reactivity at elevated temperature may leads to failure of LMA⁵²⁻⁵⁶. It has been reported that needle-shaped Li is easily deposited on Cu foil at -15°C , and SEI components is also influenced with different operating temperature⁵⁷. Elevated temperature (e.g. $>55^{\circ}\text{C}$) generally brings the exacerbation of irreversible side reactions in light of the high chemical reactivity of Li metal⁵⁸⁻⁵⁹. What's more, the thermal decomposition of SEI may occur at an elevated temperature, which brings the cycling stability issues.⁶⁰⁻⁶³ To pursue a wide working temperature range for LMA, the exploration of new electrolyte system is imperative⁶⁴⁻⁶⁶.

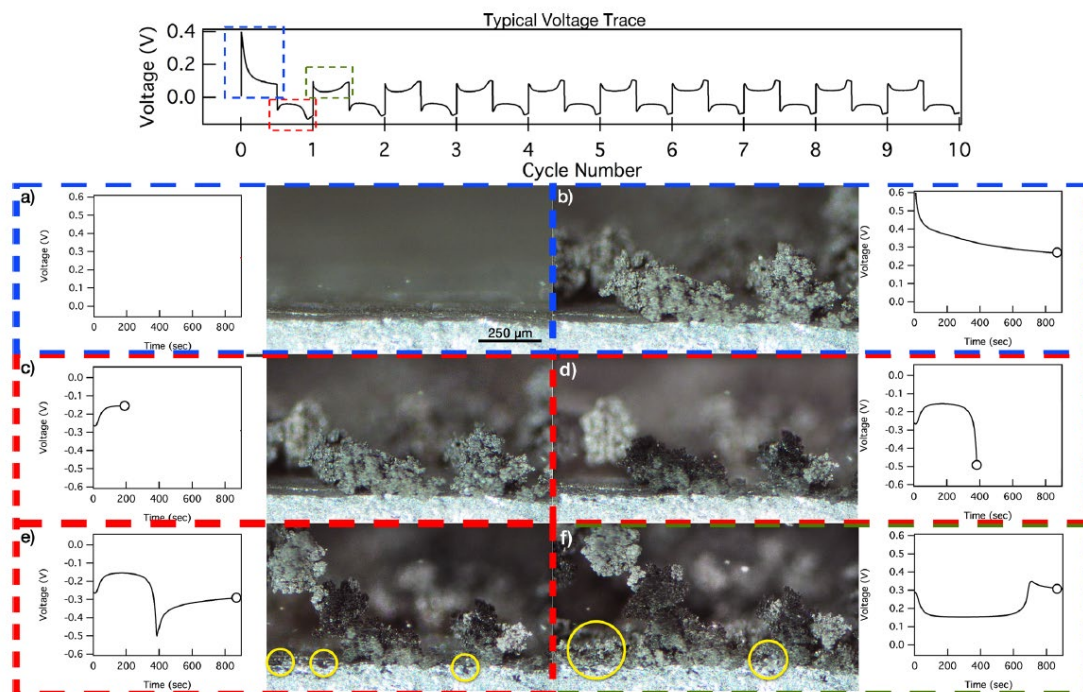


Figure 3. Operando video microscopy captured Li electrode morphologies (Li-Li symmetric cell) associated with corresponding voltage trace. Reproduced with permission from ref. 2. Copyright 2016 American Chemical Society.

The failure mechanisms of Li metal in practical cells have been intensively investigated. A Li-Li symmetric cell provides the simplest cell configuration for the investigation in depth. Utilizing operando video microscopy, Dasgupta et al studied the morphology evolution of Li metal anodes in Li-Li symmetric cells, and the morphologies of dendrites were directly correlated with the trace of corresponding voltage (Fig. 3)². It has been found that the pitting occurs at the electro-dissolution process, and Li dendrites preferentially nucleate and grow within these pits. The reactivity of the local surface of Li metal with the electrolyte is vital for the longtime stability. The sharp increase or decrease of the voltage hysteresis has been widely recognized as failure criterions for the cycling of Li-Li symmetric cells, which is corresponding to electrolyte depletion or short circuit, respectively³³. The electrolyte depletion is highly induced by the surface reaction between Li metal and electrolyte. Similar failure mechanism retains in Li metal full cells. Once a limited amount of Li cycled with corresponding cathode materials, a sudden drop of capacity occurs with traditional electrolytes⁶⁷. Considering the requirements of a balance among electrolyte amount, Li metal thickness, and cathode loading in practical pouch cells⁶⁸, the surface reaction should be carefully controlled, in other words, a high CE should be emphasized⁶⁹. Very recently, a Li-Li pouch symmetric cell has been utilized for the exploration of Li metal failure mechanism in a more practical working situation⁷⁰. Varied working conditions such as current density, capacity, Li utilization have been investigated and a related failure map is demonstrated in three categories: polarization, transition, and short-circuit, which exhibits huge challenges of Li metal pouch cells at practical harsh working conditions.

2.2 Deposition substrates. The lithium electrochemical deposition could be influenced by other external variables as well. For example, the different substrates possess disparate nucleation barriers,⁷¹ and may further guide Li deposition behaviors (Fig. 1e-h). It is favorable for Li nucleation and cycling stability on substrates with little nucleation barriers. As a consequence, smaller deposition overpotential and nucleation overpotential are presented in these substrates with superior affinity with Li, where the nucleation overpotential is defined as the difference between sharp tip voltage (deposition overpotential) and the later stable mass-transfer-controlled overpotential^{7, 72}. In analogy with hydrophilicity, the concept of “lithiophilicity” has been widely accepted as a guide rule to achieve stable Li deposition^{6, 73-78}. For this purpose, the binding energy between Li and specific functional group (or matrix) has been considered to evaluate the lithium bond quantitatively, and different Li affinities could be explained in this regard^{7, 72, 79-82}.

An epitaxial electrodeposition process has been uncovered recently for metal anodes, that is, the deposited metal layer arranges into coherent or semicoherent lattice interface on substrate⁸³. Once a low lattice mismatch is within reach, the deposited crystalline layer (epilayer) demonstrates a correlated orientation in line with the substrate. What’s more, low residual stresses are enabled in this deposition process. This epitaxy regulation strategy drives a locked crystallographic orientation of metal deposition, and an exceptional reversibility has been realized, providing another considerable way to regulate electrochemical deposition process on certain substrates. However, some researchers argue the clear evidence of the epitaxial deposition mechanism, the jury is still out⁸⁴⁻⁸⁵.

2.3 Electrolyte Systems. Since the mass transfer process plays a crucial role in Li plating process as discussed above, an electrolyte system consists of Li salts, solvent, and additives, is highly relevant to LMA performance (Fig. 1i-l). Moreover, Li salts and electrolyte additives directly participate in the formation of the SEI layer with electrolyte solvent. The SEI layer is electrically insulated, but allows for the Li^+ conduction, thus, Li atom is always deposited beneath SEI layer. The generated compressive stress in this process may leads to SEI layer cracks if a fragile and mechanical weak SEI is formed. Thus, a careful selection of Li salts and electrolyte additives benefits the formation of high quality SEI layer. Very recently, the solvent molecule cooperation effects have been revealed, that is, the extent of electrolyte decomposition (SEI components) is dependent of the combinations of different solvents in electrolyte⁸⁶. These solvent combinations dominate the solvation chemistry of Li^+ . In this regard, both mass transfer process and surface chemical reaction are heavily dependent with electrolyte systems.

Electrochemical window (EW) of an electrolyte is the stable potential range, in which the electrolyte is neither oxidized nor reduced, and the reduction potential and the oxidation potential of the electrolyte refer as the cathodic limit and the anodic limit, respectively. Typically, a high anodic stability of the electrolyte solvent has been pursued to fulfill the electrochemical stability with high voltage cathode materials⁸⁷. Thus, in traditional lithium ion batteries, carbonate based solvents, such as ethylene carbonate (EC), ethyl methyl carbonate (EMC), propylene carbonate (PC), dimethyl carbonate (DMC), and diethyl carbonate (DEC)⁸⁸⁻⁸⁹, have been widely utilized due to their high anodic stability compared with ethers-based and esters-based solvent. Despite the success of these solvent in LIBs,

low CE and short cycling life has been encountered of carbonate-based electrolyte for LMA⁹⁰. Recently, the role of the carbonates in Li metal deposition has been investigated by *in-situ* environmental transmission electron microscopy (ETEM)²¹. It has been discovered that an addition of very small amount of EC (0.2 wt. %) in baseline electrolyte leads to an obvious Li whiskers formation, which is called “electrolyte-poison”. Given this situation, ethers including 1,3-dioxolane (DOL), 1,2-dimethoxyethane (DME) with lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) as lithium salt, have been widely accepted as a baseline electrolyte for stabilizing Li metal anode due to their high cathodic stability compared with carbonate based solvent.

While the present evaluation of the stability of Li metal anode is mainly based on half-cell, the selection of the cathode materials may have a great impact on its plating/stripping behaviors¹⁰ (Fig. 1m-o). The Li deposition overpotentials and morphologies vary with different cathode materials (LiFePO₄, LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂, LiNi_{0.5}Mn_{1.5}O₄). The trace dissolution of the transition metal into electrolyte has been identified as one of main reasons leads to above mentioned different behaviors, which further delineates the significance of the electrolyte for Li electrochemical performance.

3. STABILIZING LMA ELECTROCHEMICAL CYCLING

Based on the fundamental understanding of LMA upon the electrochemical deposition/stripping process, a great deal of the approaches has been proposed and explored to stabilize the Li electrochemical cycling. In this section, we have summarized the main state-of-the-art approaches to stabilize LMA, and their representatives have been

demonstrated in Fig. 4. These approaches will be discussed and reviewed in detail.

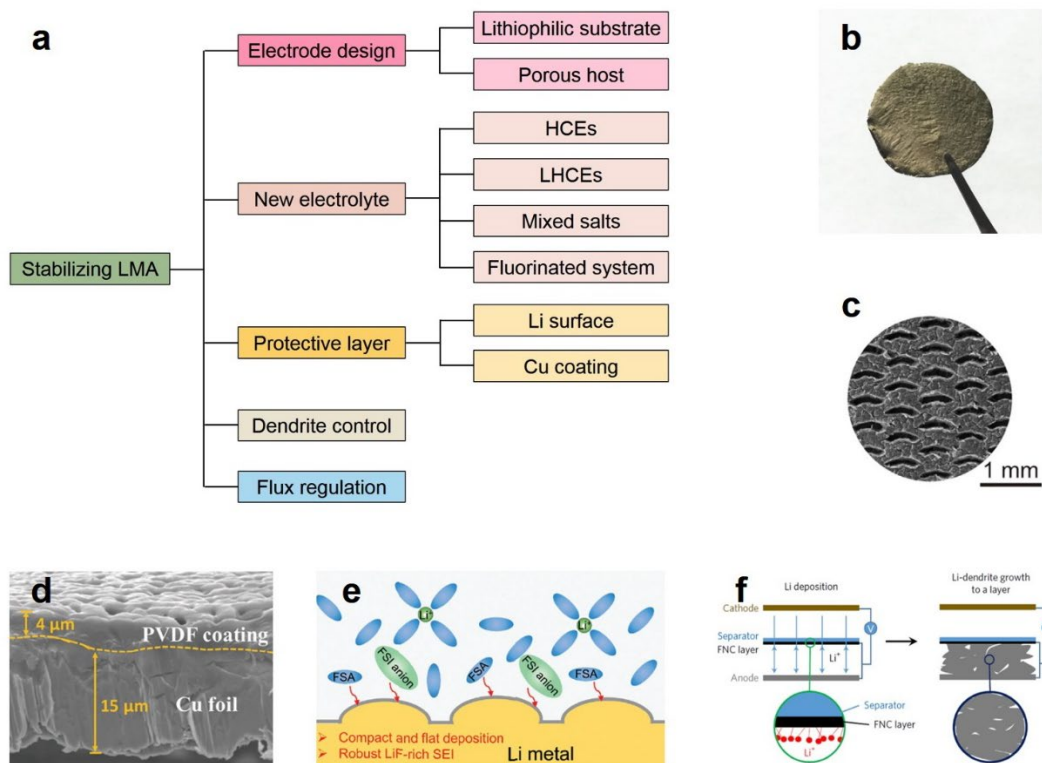


Figure 4. Stabilizing approaches for LMA and related representatives. (a) Schematics of main approaches to stabilize LMA. (b) Lithiophilic reduced graphene oxide paper as Li substrate. Reproduced with permission from ref.72. Copyright 2016 Springer Nature. (c) Periodic patterned porous graphene mesh for stable LMA. Reproduced with permission from ref.91. Copyright 2018 Elsevier. (d) Poly (vinylidene difluoride) (PVDF) coating on Cu current collector. Reproduced with permission from ref. 92. Copyright 2017 John Wiley and Sons. (e) Full fluorosulfonyl electrolyte for high voltage Li metal batteries. Reproduced with permission from ref.93. Copyright 2020 Royal Society of Chemistry. (f) Stabilizing LMA by the control of dendrite growth direction. Reproduced with permission from ref. 94. Copyright 2017 Springer Nature.

3.1 Electrode design. To address the problem of inhomogeneous deposition, materials with excellent Li affinity have been utilized to guide Li plating. Up to now, lithiophilic materials such as Si⁹⁵, Au⁷¹, Ag^{6, 76, 96}, ZnO^{78, 97}, CuO⁷³⁻⁷⁴, SiO⁹⁸, SnO⁷⁷, TiC⁹⁹, MXene^{8, 100}, to name but a few, has been explored for a stable LMA. For these metals, Cui et al discovered the selective deposition behaviors of Li on some specific metals like Ag and Au, and a largely reduced over-potential is presented on these metal compared with Cu (current collector materials)⁷¹. It has been found that there are no nucleation barriers for metals (e.g. Ag, Au) exhibiting a definite solubility in lithium. Given this understanding, these metals have been utilized as substrate materials to guide Li deposition for a uniform distribution^{76, 96}. As for metal oxide (e.g. ZnO, CuO, Co₃O₄), due to the negative of the free energy ($\Delta G < 0$) between Li and metal oxide, a spontaneous reaction between Li and metal oxide is enabled^{73, 77, 101}. Thus, these metal oxides not only decrease the kinetic barrier of adhesion of Li metal but also facilitate the Li⁺ transport. In summary, Li wettable substrates are beneficial for the dendrite suppression and further ameliorates its cycling stability. These lithiophilic substrates could produce a smaller nucleation overpotential and leads to a more homogeneous Li nucleation (e.g., reduced graphene oxide paper, Fig. 4b). Among these substrates, carbon based materials received considerable attention in light of its outstanding electrical conductivity, high chemical stability, facile fabrication process and plenty of structural diversity¹⁰². For the sake of achieving higher Li affinity of these carbon substrates, chemical functionalization as well as structure design have been widely explored¹⁰³. For example, the attachment of amine (-NH) groups to the surface of the carbon fibers contributed to a smooth and stable Li layer¹⁰⁴. On the other hand, the direct modifications of the Cu current collector with good Li affinity have been evidenced as an effective

strategy to improve the cycling stability as well^{5, 75, 105-110}.

Apart from the wettability tuning of the substrates, porous structure design offers direct host space to regulate Li deposition and meanwhile minimize the volume change upon plating/stripping cycles¹¹¹. Furthermore, the high surface area of these porous structure lowers the local current density and current density distribution is improved^{107, 112}. Given this reason, a great deal of porous hosts has been devised to accommodate Li plating/stripping^{98, 113-118}. One typical example is graphene substrates with periodic patterned voids (Fig. 4c)⁹¹. By the simply constructed periodic voids on graphene structure, the Li dendrites have been fundamentally suppressed due to the horizontal centripetal plating behaviors, that is, the Li nucleates at the void edges and then grows horizontal centripetally to fill these voids. As a result, a stable voltage profiles maintained as long as 2000 hours at a high current density of 10 mA cm⁻².

For practical application, pre-storing of Li metal into these substrates is required. Electrodeposition and thermal infusion are two main methods to pre-store Li into these hosts as Li metal composite anodes. Various current collectors with decent conductivity have been used as hosts for Li metal by electrodeposition approach¹¹⁹⁻¹²¹. The amount of the pre-stored Li could be precisely controlled by deposition time and corresponding current density. However, the electrodeposition process is operated in a symmetrical cell using Li metal as counter/reference electrode and desired host as working electrode, thus sacrificial cells are required for the obtainment of the final composite LMA. Tedious preparation procedures such as cell disassembly, electrode cleaning, and full cell re-

assembly hinders the scale-up of electrodeposition approach. Regarding the relatively low molting point of Li metal (~ 180.5 °C), thermal infusion has been proved as a prominent strategy for uniform Li pre-storing^{72, 78, 116}. Compact and homogeneous Li infusion is enabled and sacrificial cells could be avoided in thermal infusion method. Nevertheless, considerable thermal stability and wettability of liquefied Li for the substrate materials are the prerequisites for thermal Li infusion.

3.2 New electrolyte. Development of new electrolyte systems including solvent, lithium salts, and additives has been regarded as one of the most potent ways to strive for a stable LMA. As previously discussed, the electrolyte components directly participate in formation and propagation of the SEI layer on Li metal surface. Furthermore, an electrolyte as the medium to bridge the mass transfer process between the cathode and anode, which determines the main morphology of the deposited Li. A brief summary of the development electrolyte system for Li metal has been presented in Fig. 5. The high concentration of lithium salts improves the electrolyte reductive stability by reducing availability of reactive solvent as well as sacrificial anion reduction. What's more, fast Li plating/stripping is enabled by the elevated Li^+ concentration⁹. Furthermore, the high Li salt concentration increases the limiting current density and facilitates the replenishment of the ions depleted by Li deposition and thus suppress Li dendrite formation. In this regard, the high concentration electrolytes (HCEs) has been sought as a potent method¹²²⁻¹²⁵. For example, a solvent-in-salt HCEs has been reported with 7M LiTFSI in DOL and DME mixture solvent for Li-S batteries in 2013, a high CE approaches 100% is demonstrated¹²². Later, 4 M lithium bis(fluorosulfinyl)imide (LiFSI) in DME as HCEs has been proposed and results

in a high average Coulombic efficiency of 98.4%⁹. Along this line, a concentration as high as 10 M LiFSI in DMC not only realize a superior CE of ~99.3% but a high cutoff voltage of 4.6 V due to the utilization of excellent anodic stability solvent of DMC¹²⁶. However, the high concentration of the lithium salts exhibits a high viscosity and further leads to a cost concern for practical application. Recently, localized high concentration electrolytes (LHCEs) has been proposed to address these concerns^{67, 127-130}. Typically, a co-solvent has been introduced to dilute the HCEs to obtain LHCEs and it is required that the diluent do not affect the solvate structure between the original solvent molecules and Li salts. For example, one of LHCEs has been develop by Zhang's group by diluting HCEs (5.5 M LiFSI in DMC) with bis(2,2,2-trifluoroethyl) ether (BTFE)¹³¹. Furthermore, a significantly improved cycling performance of Li metal anode has been reported at the same group based on sulfone-based LHCE in which tetramethylene sulfone (TMS) serves as solvent and 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) serves as the diluent⁶⁷. On the other hand, despite the successful application of the ether-based electrolytes in LMA (e.g., 1 M LiTFSI in DOL-DME) due to their high reductive stability, their unsatisfactory anodic stability (normally < 4 V) highly limits the selection of the cathode materials. Given this situation, electrolyte systems using nitrile¹³²⁻¹³³, carbonate¹²⁶ which are gifted with a higher anodic stability, have been carefully considered. Among these high-voltage electrolytes, fluorinated system is of great interests in this community¹³⁴⁻¹³⁵. Fluorinated solvents such as fluoroethylene carbonate (FEC), 3,3,3-fluoroethylmethyl carbonate (FEMC), 1,1,2,2-tetrafluoroethyl-2',2',2'-trifluoroethyl ether (HFE), tris(2,2,2-trifluoroethyl)orthoformate (TFEO), have been employed for high-voltage Li metal batteries^{89, 136-137}. Very recently, "full fluorosulfonyl" (FFS) electrolyte consists of LiFSI,

LiPF₆, and *N,N*-dimethylsulfamoyl fluoride (FSA) has been evaluated for LMA, and such FFS electrolyte has been corroborated their good compatibility with high-voltage cathode materials (Fig. 4e)⁹³. It has been widely recognized that the SEI plays a crucial role in the stability of LMA¹³⁸⁻¹³⁹. Mixed salts electrolytes including dual salts¹⁴⁰⁻¹⁴¹, ternary salts¹⁴²⁻¹⁴³, offer a facile approach to optimize the SEI components and thus improve the stability. Finally, other strategies, for instance, ionic liquids¹⁴⁴⁻¹⁴⁵, viscoelastic electrolyte¹⁴⁶, and liquid/liquid two phase electrolyte interface protection¹⁴⁷, to name but a few, offer new directions for the development of new electrolyte system for LMA. Among these systems, the fluorinated system stands out as a competitive candidate. The high anodic stability imparts a wide range of compatibility for cathode materials selection, especially for 4-V class lithium metal batteries. Moreover, it does not need high concentration of lithium salt and thus avoids the high cost and high electrolyte viscosity.

Apart from the careful consideration of the solvents and lithium salts, the electrolyte additives optimize the SEI components and stability, and may tune the lithium solvation structure to achieve smooth plating as well. Typically, the electrolyte systems consist of solvents, anions, and solvents solvated cations (e.g. Li⁺), and a de-solvation process involved once these solvated Li⁺ ions get inserted or deposited on the electrode surface. Hence, the Li ion solvation structure is an important index for the performance and electrochemical behaviors of LMA¹⁴⁸. For example, the introduction of anions (e.g. NO₃⁻) has been found that could alter the solvation sheath of the solvation structure and thus promotes the decomposition of lithium salt anions¹⁴⁹⁻¹⁵⁰. A uniform SEI layer with an abundance of specific components is further enabled. In most cases, additives have been

selected to directly optimize SEI microstructures such as vinylene carbonate¹⁵¹, LiNO₃¹⁵², LiF¹⁵³, and so on¹⁵⁴⁻¹⁵⁵. Fluorinated SEI structure, that is, high LiF content, is particularly pursued which benefits the uniform diffusion of the Li ions through this SEI¹⁵⁶⁻¹⁵⁸. The other type of electrolyte additives does not take part in the SEI formation, however, adjust the electrolyte properties to suppress Li dendrite formation^{150, 159}. For example, dendrite formation can be fundamentally altered with the addition of selected cations (e.g., Cs⁺, Rb⁺), which harnessed by a self-healing electrostatic shield (SHES) mechanism¹⁶⁰. With a suitable concentration, these selected cations possess an effective reduction potential that is less than the Li deposition potential, thus, a positively charged electrostatic shield covers the initial growth tip of the deposited Li by these cations and repels the incoming Li⁺ to prevent the dendrite propagation. In a summary, direct and indirect modifications of SEI structure could be enabled by electrolyte additives for stabilizing LMA. The former directly participate in the SEI formation along with the Li metal deposition, while the latter modify the SEI components indirectly by the tuning of Li solvation sheath.

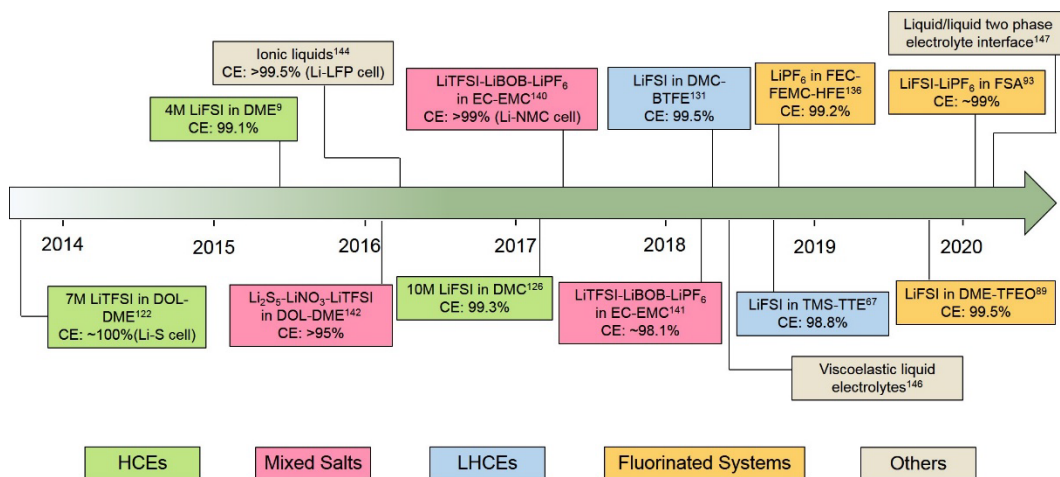


Figure 5. A brief timeline summarizing the development of electrolyte system for Li metal anode. It is worth noting that the evaluation of the CE may be based on different test

condition.

Due to the progress of the high CE new electrolytes for LMA, a novel battery configuration of “anode-free” has been inspired.¹⁶¹⁻¹⁶⁴ For traditional LIBs, the Li ion extracted from cathode materials diffuse through electrolyte and then store into anode materials during charge process. However, for “anode-free” rechargeable batteries, only a current collector (copper foil) is used for the extracted Li ions plating, and the current collector with plated Li metal further serves as LMA for battery discharge/charge. This configuration of batteries is referred as “anode-free rechargeable lithium metal battery” (AFLB). The anode active materials free design of AFLB significantly reduced the overall weight of a whole battery, and then energy density could therefore be increased to a great extent compared with traditional LIBs. However, the negative/positive capacity ratio (N/P ratio) is determined (1:1), thus the CE of AFLB is crucial for its cycling performance.¹⁶⁵⁻¹⁶⁷ Assuming a AFLB could sustain an excellent cycling capacity (e.g. 80% retention after 1000 cycles), a CE as high as 99.98% is required. Such CE is still far from the reach of LMA, and the contribution of the cathode capacity loss make it even worse for AFLB. Up to now, the longest lifetime of 200 cycles (80% capacity retention) has been realized by Dahn’s group using dual-salt carbonate electrolyte.¹⁶⁸ Given this situation, future progress is still demanded for the practical application of AFLB. For detailed information on this part could be found in comprehensive review elsewhere.¹⁶⁹

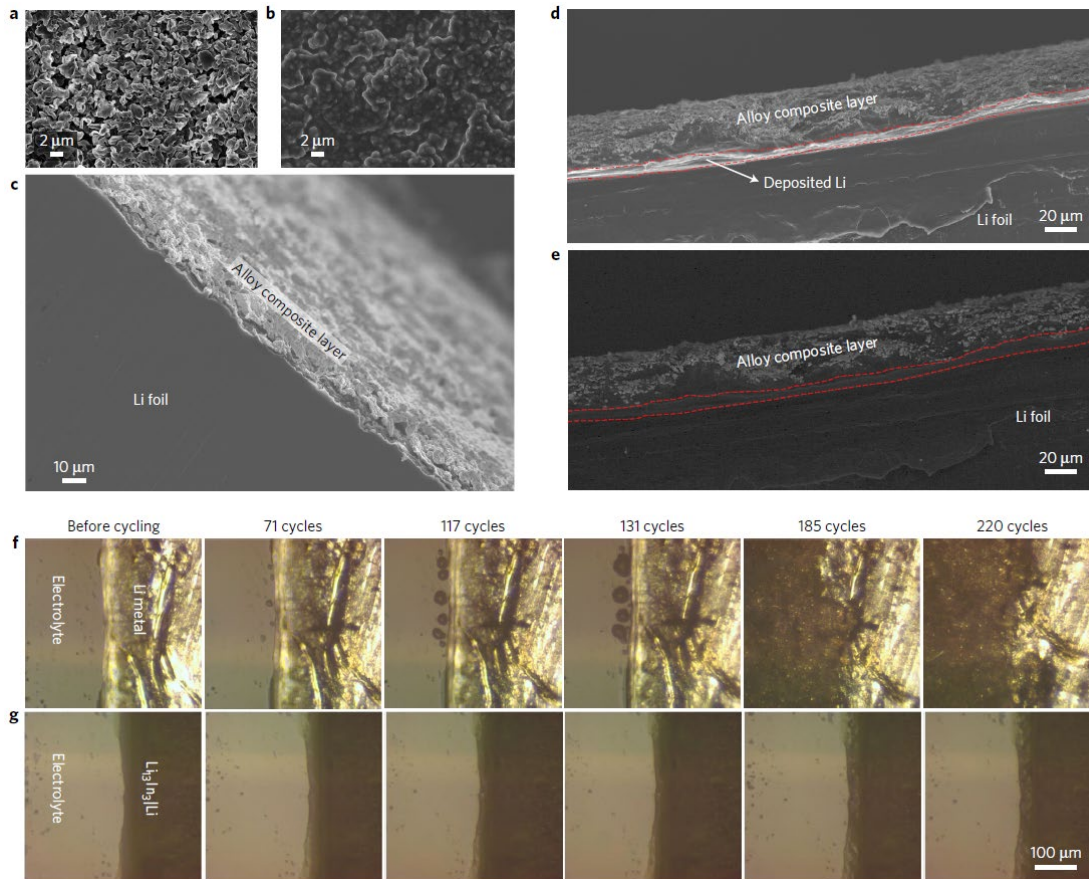


Figure 6. Electrochemical behaviors of alloy protected lithium metal SEM images of fresh lithium metal (a) and $\text{Li}_{13}\text{In}_3$ protected lithium metal (b) plated with 2 mAh cm^{-2} of Li. Cross view SEM images of $\text{Li}_{13}\text{In}_3$ protected lithium metal before (c) and after (d-e) 2 mAh cm^{-2} Li plating. Operando optical microscopy images of fresh Li metal (f) and $\text{Li}_{13}\text{In}_3$ protected lithium metal in a symmetric transparent cell (g). Reproduced with permission from ref. 170. Copyright 2017 Springer Nature.

3.3 Protective layer. Since a stable SEI layer is imperative for LMA, construction of protective layer on Li surface, sometimes refers as artificial SEI, has stood out as a reliable approach to regulate Li plating/stripping behaviors^{79, 171-175}. A large body of materials such as metals¹⁷⁶, polymers¹⁷⁷⁻¹⁸⁰, oxides¹⁸¹⁻¹⁸², nitrides¹⁸³⁻¹⁸⁵, sulfides¹⁸⁶⁻¹⁸⁷, and so on, has been

utilized as a protective layer to prevent the side reaction between Li surface and electrolyte. A typical example is the artificial interphases constructed by a facile ion-exchange chemistry between Sn^{2+} and Li metal¹⁸⁸, and this Sn-Li anode exhibited a reduced interfacial impedance and higher exchange current density. Due to the Sn alloying reaction with Li (Li_5Sn_2), a reversible Li ion conduction is enabled through this constructed layer. A prerequisite of these protective layers pertains to the unimpeded transport of the Li ions, which enable the lithium deposition under the layer (Fig. 6)¹⁷⁰. In analogy with Sn metal, a Li_xSi alloy protective layer has reported with mechanical robustness and high Li ion conductivity¹⁷⁵. The fast Li ion diffusion is allowed through this thin alloyed surface layer. Furthermore, the robust mechanical stability and chemical stability of such a layer are desired. For example, Wang's group has proposed a polymer-inorganic SEI which consists of polymeric lithium salts, lithium fluoride and graphene oxide sheets¹⁸⁹. This artificial SEI layer has manifested excellent passivation properties and mechanical stability, imparting high-efficiency Li deposition and durable cycle life. Apart from the direct modification of the Li foil, the fabrication of a Li^+ conductive protective layer on Cu current collector provides the similar effects^{1, 190}. Polymer based artificial SEI layers are especially in vogue due to their structure flexibility and elastic nature, which accommodate the Li volume change upon cycling and overcome the SEI fragility issue (e.g., PVDF coating, Fig. 4d)^{92, 180, 191-192}. For more information, review articles focusing on protective coating could be found elsewhere.¹⁹³⁻¹⁹⁵

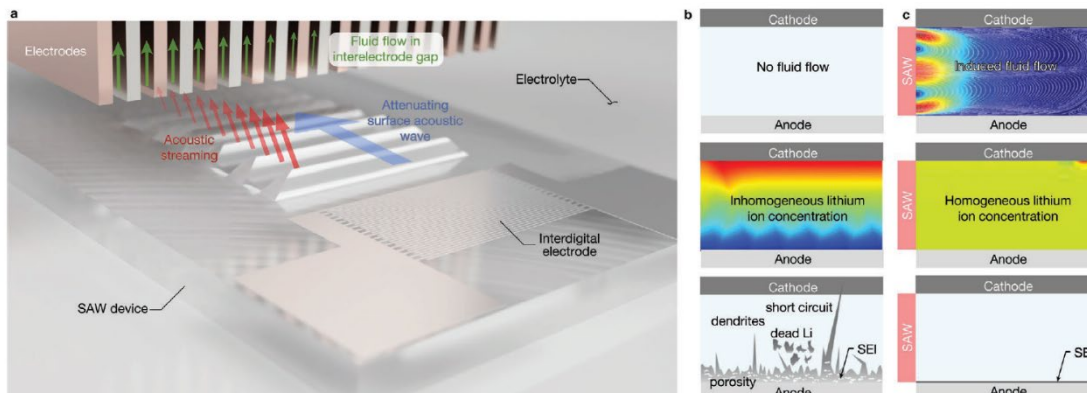


Figure 7. Working principles of traditional and SAW-driven Li metal batteries. (a) Schematics of the mechanisms of acoustic streaming drives electrolyte flow in the gap between the electrodes. The homogeneous ion distribution and uniform Li deposition in a SAW Li metal battery (c) compared with traditional Li metal battery (b). Reproduced with permission from ref.196. Copyright 2020, John Wiley and Sons.

3.4 Li flux regulation. During Li electrochemical reduction, the movement of the solvated Li^+ ions is driven by the concentration difference between the electrode surface and the bulk of the solution, which refers as the diffusion. However, uncontrollable natural convection exists and is unpredictable for Li^+ transportation. These solvated Li^+ ions desorb the solvent molecules once approaching the SEI layer, and migrate through SEI and are reduced to Li atoms. These three processes, namely diffusion, convection, and migration, explicates the mass transfer process of Li deposition¹¹. The sharp concentration gradient produced upon unregulated mass transfer process is one of the main reasons, which gives rise to the inhomogeneous distribution of Li^+ flux. This inhomogeneous distribution of Li^+ flux further results in the non-uniform deposition. Given this situation, advanced strategies in achieving uniform Li deposition by regulating Li^+ flux have been

proposed¹⁹⁷. For example, external electric field¹⁹⁸ and magnetic field¹⁹⁹⁻²⁰⁰ have been applied to promote the uniform distribution of lithium ions to suppress dendrite formation. Considering the high energy consumption of these external fields, surface acoustic wave (SAW) as an emerging technique has been developed (Fig. 7)¹⁹⁶. Li dendrites and porosity have been avoided using SAW device to realize a homogeneous lithium ion concentration by acoustic forces. In recent years, the effect of charging method has received growing attention. Li et al have investigated the molecular mechanism of pulse current charging for LMA, and it has been found that the loose interaction between cations and anions boosts the Li⁺ transportation, which stabilizes the Li deposition²⁰¹. Moreover, compared with direct current (DC) electrodeposition, needle-like lithium could be avoided and the cycling efficiency was improved by pulse plating under diffusion controlled conditions²⁰²⁻²⁰³.

3.5 Dendrite growth control. Instead of the suppression of the Li dendrite fundamentally, the control of dendrite growth direction has been validated as a novel approach to the cycle lifetime of LMA by our group⁹⁴. The potential difference between the tips and bottom of a Li dendrite is the thermodynamic driving force for the propagation of the dendrites. By using a functionalized nanocarbon (FNC) coated separator, the Li dendrites grow toward each other from both FNC separator and Li metal anode. A dense Li layer is formed once these dendrites meet each other, which prevents the uncontrollable growth of the Li dendrites and the safety hazards (Fig. 4f). By the way, the design of the functional separators also has been extensively investigated in recent years²⁰⁴⁻²⁰⁸. Since the affinity between the Li and substrates has been widely examined, the separator wettability with electrolyte as well as the affinity between separator and Li should be carefully considered

as well²⁰⁹⁻²¹⁰.

4. OUTLOOK

Table 1. Summary of different approaches to stabilize LMA.

Approaches	CE	Dendrite	Comments
Electrode design	Fair	Good	Li deposition behavior is physically regulated, but the side reaction between Li and electrolyte may hardly be avoided.
New electrolyte	Excellent	Good	Both low CE and dendrite issues can be regulated due to the improved surface chemistries.
Protractive layer	Good	Excellent	Interface between Li and electrolyte is ameliorated thus suppress dendrite formation and improve CE.
Li flux regulation	Fair	Good	Uniform Li deposition is enabled to prevent dendrite propagation. However, external energy is required.
Dendrite growth control	Good	Excellent	Dendrite issue is physically controlled, and CE could be improved.

The growing energy storage markets are unprecedentedly demanding the higher energy density rechargeable batteries with high reliability and safety. As a captivating candidate,

LMA stands out from others and receives prevalent investigations. However, the dendrite formation and low CE, these two issues intrinsically hinder the practical application of LMA. In this perspective, unregulated mass transfer process and complex surface chemistries have been outlined as two main reasons that induce these issues. Despite the approaches underlined here to stabilize LMA (Summarized in Table 1), there are still future concerns remain to be judiciously considered as below.

1. The current state-of-the-art evaluation of the stability mainly based on high Li metal loading, which means low depth of discharge (DOD) of LMA. To fully utilize the great potential of the high capacity of Li metal, a suitable N/P ratio should be highlighted and implanted to the cell level assessment, especially in pouch cell, which will be potential addressed in the near future.
2. Considering the cathode effects on Li metal, a better understanding based on the full cell level should be taken into account. More detailed information such as Li morphology and SEI components is encouraged to investigate at full cell level not only limit to the symmetric Li cells. These observations will greatly facilitate the understanding of the lithium metal batteries at practical situation.
3. Improving the CE of the LMA is one of the most important factors to ensure the long-time battery cycling. For this purpose, an extremely high CE (i.e. >99.9%) is anticipated. Given a simple calculation, only 60.6% capacity has been retained after 500 cycles if a CE of 99.9% has been assumed. Moreover, a standard measurement of CE protocol is encouraged to avoid the conflicting values in different literatures ²¹¹. The rapid development of new electrolyte system as well as optimization of the electrolyte systems among lithium salts, solvents, and additives will still be a powerful

way to address the low CE issue.

4. Suppression of Li dendrites. The development of commercial Li metal batteries depends on not only the high energy density and long cycle life, but also reliable safety. Thus, a non-dendritic LMA is of great significance. A deep understanding of the interfacial mechanisms such as the side reactions of Li and electrolyte, SEI formation and components, Li ion transportation in SEI and so on, are vital for the suppression of Li dendrites. In fact, the Li dendrites could be notably suppressed by the synergetic integration of all approaches toward to the cell components including Li metal itself, electrolyte system, and separator, not limit to an individual component optimization.
5. Lean electrolyte LMA. The dendrite growth related SEI formation leads to a continuous electrolyte loss. Thus, a rise of voltage hysteresis is one of the main failure mechanism of Li symmetric cell. In this respect, the electrolyte usage effects towards LMA is vital for its both energy density and cycling stability, thus a lean electrolyte LMA is expected²¹².
6. Future challenges and outlook. The low CE and dendrite issues have been ameliorated by means of as-discussed approaches developed in recent years. However, practical Li metal batteries requires a careful balance among cathode, anode, and electrolyte. The utilization of thin Li foil (suitable N/P ratio) and electrolyte compatibility with cathode still remains as the daunting challenges regarding the fast capacity fading. The future of the LMA is associated with the developments of the fundamental understanding of the Li metal and novel approaches.

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Notes

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