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Li Metal Pouch Cells

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Progress and Perspectives on the Development of Pouch-Type Lithium Metal Batteries

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Abstract: Lithium (Li) metal batteries (LMBs) are the "holy grail" in the energy storage field due to their high energy density (theoretically $>500 \text{ Whkg}^{-1}$). Recently, tremendous efforts have been made to promote the research & development (R&D) of pouch-type LMBs toward practical application. This article aims to provide a comprehensive and in-depth review of recent progress on pouch-type LMBs from full cell aspect, and to offer insights to guide its future development. It will review pouch-type LMBs using both liquid and solid-state electrolytes, and cover topics related to both Li and cathode (including LiNi_xCo_yMn_{1-xy}O₂, S and O₂) as both electrodes impact the battery performance. The key performance criteria of pouch-type LMBs and their relationship in between are introduced first, then the major challenges facing the development of pouch-type LMBs are discussed in detail, especially those severely aggravated in pouch cells compared with coin cells. Subsequently, the recent progress on mechanistic understandings of the degradation of pouch-type LMBs is summarized, followed with the practical strategies that have been utilized to address these issues and to improve the key performance criteria of pouch-type LMBs. In the end, it provides perspectives on advancing the R&Ds of pouch-type LMBs towards their application in practice.

1. Introduction

The global warming crisis demands the utilization and storage of energy from renewable resources for future sustainability. As an efficient device for energy storage, rechargeable batteries have created a rapidly increasing market for e.g., smart phones and electric vehicles amounting to tens of billions of dollar so far.^[1] However, the stateof-the-art lithium (Li)-ions batteries (LIBs) suffer from limited energy densities (up to 300 Wh kg⁻¹) due to the low

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specific capacity of nowadays commercial graphite (Gr) anode (372 mAh g^{-1}) ,^[2] which cannot meet the increasing demand for future energy storage.

Driven by the eagerness of enhancing the energy density, Li metal anode has attracted enormous research & development (R&D) interest, due to its high theoretical specific capacity of 3861 mAh g^{-1} that is >10-fold of Gr anode^[3] and the highest battery output voltage realized by the lowest electrochemical redox potential (-3.04 V vs. the standard hydrogen electrode). Besides, Li metal batteries (LMBs) also render various choices of cathode materials, such as Licontaining transition metal oxides (e.g., LiNi_xCo_vMn_{1-x-v}O₂ (NCM) and LiCoO₂ (LCO)), polyanion compounds (e.g., LiFePO₄ (LFP), and conversion-type Li-free materials (e.g. bxygen (O_2) and sulfur (S), which can boost the energy lensity $> 500 \text{ Wh} \text{kg}^{-1}$.^[4,5] This is even more appealing than Silicon (Si)-based LIBs, which has reached 450 Whkg⁻¹ so ar.^[6] However, severe challenges like dendrite growth and serious side reactions still impede the implementation of LMBs.^[7] Recent R&Ds of LMBs focus on addressing all the bove issues, through advanced liquid or solid electrolyte nd surface/interface modification, etc.[7-9]

The R&Ds of LMBs occur on various cell capacity evels, typically spanning from < 0.01 Ah (coin cells) in the aboratory level to 0.01-10 Ah (e.g., pouch and cylindrical cells) heading for practical applications, and even >100 Ah prototype LMBs released by several startup companies. At the cell capacity level >1 Ah, battery modules and packs in he pouch-type have higher specific energy density than the other two commercial battery configurations (cylindrical nd prismatic) thanks to the lightweight of aluminum plastic ases, which can maximize the specific energy density of MBs at the cell level. Therefore, the development of oouch-type LMBs has gained tremendous momentum ecently,^[10] particularly for industrial prototyping. Startup companies like SolidEnergy Systems (SES), QuantumScape nd Solid Power have demonstrated liquid or solid-state bouch-type LMB prototype cells with various layers (1-25 +) of electrodes, whose energy density reaches up to 75 Whkg⁻¹ verified by the third party. Meanwhile, many ar manufacturers (BMW, Ford, General Motor, Hyundai, tc.) have collaborated with these startup companies to accelerate the deployment of pouch-type LMBs on electric

vehicles. In the academic community, the number of publications on pouch-type LMBs is surging in recent years, either using liquid or solid-state electrolytes. Figure 1 shows the recent developments of pouch-type LMBs in terms of energy density and cycle life (determined by 80% capacity retention). The specific energy density of cells using liquid electrolyte has increased from 250-350 Whkg⁻¹ to 300-500 Wh kg⁻¹ in the past five years, while the typical cycle life remains <100 cycles, with few reaching >200 cycles.^[11] Meanwhile, cells using solid-state electrolytes have realized a volumetric energy density of $>900 \text{ Wh } L^{-1}$.^[12] However, there is no comprehensive review article on the progress of Li metal pouch cells, except for a couple of review articles on Li–S pouch cells,^[13–15] and the key parameters of Li metal pouch cells have yet been established, which results in the lack of guidance on the future R&Ds of Li metal pouch cells.

This article introduces the key performance criteria, which include energy density, cycling stability and safety, and the major challenges facing the development of Li metal pouch cells using liquid or solid-state electrolytes, and reviews the recent progress on both fundamental understandings and practical strategies for improving the performance of Li metal pouch cells. Note that there are many review articles that have comprehensively discussed the general problems of LMBs,^[5,7,16] this review focuses onto the specific issues of Li metal pouch cells, especially the cycle life, cell swelling and safety. In terms of the progress that have been achieved, we summarize both the mechanistic understandings of degradation of electrodes and electrolytes and the practical strategies that have been utilized to address





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2. The key performance criteria of Li metal pouch cells

Many parameters (e.g., energy density, cycle life, power density, rate capability, working temperature range, voltage range, etc.) have been used to evaluate the performance of batteries. Here we define the key performance criteria of Li metal pouch cells for practical applications, namely energy density, cycling stability/cycle life, and safety.

2.1. Energy density

The most appealing characteristic of LMBs over LIBs is its high specific and volumetric energy density. Electrode materials with high specific capacities and large potential difference are desired to achieve high energy densities. Meanwhile, the electrode porosity (or density) should be considered for increasing the volumetric energy density. In general, the cathode materials of high R&D interest cannot simultaneously deliver high output voltage and high specific capacity. Figure 2 shows the calculated specific and volumetric energy densities of 5 Ah-level Li-based pouch cells made of Li metal, Gr or Si anode and NCM, LCO, S or O_2





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Figure 1. a) Roadmap of the recent developments of Li metal pouch cells in terms of energy density and lifespan. Results with cycle number < 5 are not included. *The energy density was not obtained from direct measurement of the pouch cell, but by calculation based on the available cell parameters in the report. #No electrochemical data is available. All references in the figure are shown in Table S2–S4 in the Supporting Information. b–f) Strategies enabling the representative developments marked in Figure 1a.



Figure 2. Estimated energy densities of 5 Ah Li-based pouch cells with different anode-cathode pairs. For comparison, all batteries in this chart have comparable cell parameters (e.g., areal capacity, N/P ratio and E/C ratio). Detailed cell parameters used for the calculation are listed in Table S1.

cathode under almost equal condition with similar parameters listed in Table S1, to make a relatively fair comparison of energy density between different systems. High-voltage cathode materials (>4 V vs Li⁺/Li) such as NCM offers a specific capacity of merely $< 300 \text{ mAh g}^{-1}$, while conversiontype cathode materials (e.g., O_2 and S) have up to >10 times higher specific capacities but lower working voltages of < 3 V vs Li⁺/Li. The compromise in voltage and capacity renders comparable specific energy densities (350-500 $Wh\,kg^{-1}\!,$ as shown in Figure 2) of Li–NCM and Li–S/ Li-O₂ batteries. So far, there is still no standard in the field to determine the energy density of a pouch cell. Many papers claim the energy density that is obtained at a low Crate (mostly 0.05 and 0.1 C) but report the cycle number achieved at a high C-rate (typically > 0.2 C, with lower energy density). Besides, in many papers, the calculation of specific energy density often does not include the weight of

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all cell components (particularly packaging), which is termed as "calculated energy density" in this work. For those that are measured based on the weight of whole pouch cell including packaging, we continue to use the term "energy density".

2.2. Stability & cycle life

The stability & cycle life is another critical parameter for rechargeable pouch-type LMBs. Herein, the stability & cycle life is normally evaluated by the cycle number of Li metal pouch cells retaining 80% of its initial discharge capacity. Currently, the stability & cycle life of Li metal pouch cells remains unsatisfactory (typically <100 cycles), which is a magnitude shorter than the state-of-the-art LIBs with a cycle life of >1000 cycles. The poor stability & cycle life is a

significant challenge impeding the commercialization of Li metal pouch cells. Therefore, tremendous efforts have been devoted to improve the stability & cycle life of Li metal pouch cells recently, which will be summarized in the following section.

2.3. Safety

Safety is also a key performance criteria of pouch-type LMBs, since it dictates the application scene of Li metal pouch cells and even substantial affects the operation state of electronics. In general, the safety of Li metal pouch cells can be evaluated from the microscopic- to macroscopiclevel. Microscopically, the cell safety can be evaluated by whether Li dendrite grows and gas evolution takes place in the batteries. At the macroscopic level, it is crucial to assess the cell safety by considering whether the cell swells, thermal runaway or even explosion occurs during cycling, and it resists external circumstances such as mechanical vibration, shock, cell damage, external short-circuit, and temperature change. Safety standards of LMBs have been introduced in files like UN38.3 and EURCA Hazard Levels, which contain various safety tests including shock, vibration, short-circuit, and overcharge. However, in general, the safety of Li metal pouch cell has not yet received enough research attention, as a higher priority has been given to the improvement of stability & cycle life at the current stage.

In an ideal condition, a Li metal pouch cell is anticipated to reach a high energy density of $> 500 \text{ Wh kg}^{-1}$, nearly two-fold of the state-of-the-art LIBs, and a long cycle life

comparable to LIBs (>1000 cycles). Besides, it is crucial to have good operational safety without severe hazards such as cell swelling and explosion over long-term cycling. Tables S2–S4 show the energy density, cycle life and other important parameters of pouch-type Li–NCM, Li–S and Li–O₂ batteries achieved in the recent reports.

The parameters of these pouch cells exhibit some notable trends and relations as shown in Figure 3. Specifically, (i) for Li-NCM pouch cells, the specific energy density is in a positive relation with the charge cut-off voltage and in an inverse relation with the electrolyte amount to capacity (E/C) ratio and the areal negative/positive capacity (N/P) ratio (Figure 3a, 3b and 3c). Note that there do not exist perfect linear relationships as the energy density is determined not by a single parameter, but by all three parameters. Meanwhile, a way to achieve a specific energy density > 500 Wh kg⁻¹ is satisfy a charge cut-off voltage > 4.6 V, E/C ratio < 2.3 gAh⁻¹ and N/P ratio < 1.5. On the other hand, a charge cut-off voltage >4.2 V, E/C ratio <3 gAh⁻¹ and N/P ratio <3 is the minimum requirement for >300 Wh kg⁻¹. (ii) For Li-S pouch cells, the specific energy density and the electrolyte volume/sulfur mass (E/S) ratio is in an inverse relation (Figure 3d), though deviated from linearity due to variations of the average discharge voltage and N/P ratio, etc. (iii) Figure 3e shows the relation of the volumetric and specific energy densities of the three types of Li metal pouch cells, among which Li-NCM pouch cells have the highest volumetric energy densities at the same specific energy densities, and the volumetric energy density increases sharply as the specific energy density increases. (iv) Figure 3f shows that Li-NCM pouch cells have the largest



Figure 3. Relations between selected cell parameters of Li metal pouch cells reported in literature. a) Specific energy density vs. E/C ratio. b) Specific energy density vs. cut-off charge voltage. c) Specific energy density vs. N/P ratio. d) Specific energy density vs. E/S ratio. e) Volumetric energy density vs. Specific energy density. f) Effective density vs. Specific energy density. References are given in Tables S2–S4.

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effective cell densities (determined by the cell mass in relative with the cell volume, equivalent to the volumetric/specific energy density ratio), while $\text{Li}-\text{O}_2$ pouch cells are the least efficient in storing energy in terms of volume. These results suggest that Li-NCM pouch cells are denser and occupy less space in devices for a specific energy.

2.4. Interplay and trade-off between the key performance criteria

2.4.1. Energy density vs. stability/cycle life

The energy density of Li metal pouch cells normally has an inverse relation with the stability/cycle life, because prevalent approaches for enhancing the energy density often compromise the cycling stability. For instance, the energy density could be increased through lowering the mass of inactive materials (e.g., electrolyte and copper (Cu) current collector, which usually occupies >20 % and 5 % of the total cell mass, respectively) as well as excessive Li which is often needed to compensate the irreversible Li losses (e.g., to solid-electrolyte-interphase (SEI) and "dead" Li). However, reducing the amount of electrolyte would accelerate its depletion and cause cell dry-out during cycling,^[10,17] while lowering the thickness of Cu current collector would aggravate the non-uniform Li deposition and Li corrosion during electrochemical cycling, hence compromising the cell performance. The energy density can also be increased by using cathodes with high specific capacities, such as oxygen. However, Li–O₂ pouch cells >400 Wh kg⁻¹ suffer from very limited cycle life (typically <5 cycles^[18-23]) due to the extremely sluggish kinetics and poor reversibility of O2/ Li₂O₂ conversion reactions.^[24] Cathode with a high active material (AM) loading is another approach to increase the energy density due to the decreased mass ratio of inactive materials (e.g. separator, current collector, package materials, etc.) in the cell. However, the cycling stability would deteriorate, since the Li metal anode cycled at a high areal capacity exhibits much worse stability with pronounced increase in the porosity and electrode thickness after cycling,^[25] accelerating the decomposition and depletion of electrolytes.

There might exist an exception of increasing the energy density without sacrificing the stability/cycle life, which could be achieved e.g., by using more layers of electrodes in the pouch cells to decrease the mass ratio of packing materials. Tables S5–S6 show the energy densities of cells with variable number of electrode layers, which has seen ≈ 25 % rise from 1 Ah to 20 Ah cells.

2.4.2. Energy density vs. safety

In general, the energy density of Li metal pouch cells is inversely related with the safety. The increase in energy density of pouch cells is usually realized by using a high mass ratio of AMs, such as cathode with high AM loading, more electrode layers, less electrolyte and thinner Li, which

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would pronouncedly increase the safety hazards. Specifically, (1) cathode with high AM loading would severely increase the porosity and thickness of Li over cycling and yield more dendritic Li, which aggravates the risks of shortcircuit and thermal runaway; (2) More electrode layers increase the amount of Li metal and capacity of cells, which leads to increased heat release at the cell level and the amount of pulverized Li; (3) The reduced amount of electrolyte would lead to more rapid electrolyte depletion,^[10] which tremendously aggravates non-uniform Li deposition resulting in more porous Li and heat production.

Anode-free Li metal pouch cells may be a strategy to simultaneously increase the energy density and improve the safety. It decreases the amount of active Li, which might promote the safety of cycled cells.^[26] Besides, the utilization of safer electrolyte/separator, particularly solid-state electrolyte, would be another solution to increase energy density while also improving the safety.

2.4.3. Stability/cycle life vs. safety

The stability/cycle life of pouch-type cells is usually positively related with the safety of cells, as both depend on the stability of electrodes and interfaces. In general, stable Li metal anode is achieved by compact and dendrite-free Li deposition, which promotes the stability/cycle life of pouch cells. Meanwhile, compact Li deposition with small volume expansion would suppress the swelling of cells and mitigate the short-circuit and thermal runaway hazards, which improves the safety of cells. The compact Li deposition can even prevent flaming when contacting water.^[27] Moreover, compact Li reduces the surface area and thus suppresses the electrolyte side reactions and the resultant gassing, which also mitigates the cell swelling. Besides, stable cathodes, especially those can be stabilized at high voltages with decreased amount of lattice oxygen release,^[28] simultaneously improve the capacity retention and hence stability/ cycle life of cells and reduce safety concerns related to gassing and cell swelling.

3. Challenges facing the R@Ds of Li metal pouch cells

Comprehending the electrochemical processes and the degradation mechanisms of Li metal pouch cells is of vital importance for optimizing cell design towards performance improvement. In this section, the main challenges of Li metal pouch cells in mechanistic understandings and development of cycling performance are comprehensively summarized.

3.1. Limited understanding of the electrochemical processes in Li metal pouch cells

In recent years, progress has been made in the mechanistic understanding of the electrochemical processes in LMBs, mostly in coin cells. Nevertheless, the working mechanism of LMBs that has been obtained with coin cells may not be applicable in Li metal pouch cells, due to the differences in cell configurations and cycling conditions (electrolyte amount, pressure, electrode area, etc.).^[10] Understanding in detail the electrochemical processes involved in the operation of Li metal pouch cells are in pressing demand.

3.1.1. Unclear cell degradation or failure mechanism

The degradation and failure of LMBs can be caused by many reasons, including the loss of AMs and electrolytes by the formation of SEI/cathode-electrolyte-interphase (CEI) and "dead" Li,^[10] the drastically increased cell polarization related to the thickening interphase lavers and the cell drying-out,^[17,29] the capacity fade of cathode by the structural deformation of cathode materials, the cell-swelling due to the volumetric change of Li metal anode and gas evolution,^[30] and the short-circuit of cells caused by Li dendrites.^[31] Notably, the major cause for the degradation and/or failure of Li metal pouch cells depends on the cycling conditions (e.g., current rate, temperature, stacking pressure, etc.) and cell parameters (AM loading of electrodes, N/P ratio, E/C ratio, etc.),^[31,32] and might vary drastically once the parameters are different. Therefore, the major degradation and/or failure mechanism(s) for cells working at various conditions remain to be identified. In particular, the stacking pressure has substantial effect on the cell behavior and degradation. However, although the pressure effect has been investigated in Li metal coin cells, [33,34] it has not been well understood in Li metal pouch cells. And the pressure condition is different between coin cells and pouch cells. Unlike coin cells where pressure is applied during the packaging, pressure is applied on pouch cells through the external clamp.^[26] Besides, the applied pressures on Li metal pouch cells are various in literatures, which makes the horizontal comparison difficult.

3.1.2. Poor understanding of the electrolyte evolution and re-/distribution during cell operation

The electrolyte plays a decisive role in the chemistry and structure of the electrode-electrolyte interphases, which eventually determines the interfacial stability of anode/ cathode and the cycling stability of the pouch cells.^[8] However, the electrolyte constantly changes in composition during cycling due to its progressive decomposition on the cathode and anode side,^[26] which consequently alters its decomposition behaviors at the electrode-electrolyte interfaces and the chemistry/structure of SEI and CEI, thus affecting the stability of cells. Moreover, the redistribution of liquid electrolytes^[27] driven by the structural changes of

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the electrodes, internal electrical field, and gas evolution would severely influence the Li-ion distribution inside cells (e.g., local concentration and homogeneity) and eventually the electrochemical behaviors of electrodes and the entire cell, which is particularly relevant for large-sized pouch-cells. Therefore, it will be of great interest to monitor the dynamic changes (i.e., composition, amount and distribution) of electrolyte inside Li metal pouch cells in service, which helps predict the cycle life of the cell and to rationalize the cell design toward improvement.

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3.1.3. Limited understanding of the structural evolution and degradation of electrodes

Electrodes in Li metal pouch cells constantly undergo dynamic and drastic evolution in structure/morphology due to multiple factors, which strongly affects the cycling stability and safety of cells. Specifically, Li metal anode tends to form various morphologies such as mossy Li, columnar Li, dendritic Li and needle-like Li, etc.,^[31] which evolves and changes dynamically along cycling. Meanwhile, the Li growth mode may transform during cycling (e.g., from dendrite-free to dendritic),^[27] as the composition and concentration of electrolyte constantly changes affecting the behavior of Li deposition. Moreover, the repetitive Li plating/stripping causes pronounced volumetric changes of the Li metal anode,^[11] drastically affecting the cycling stability of Li metal pouch cells. However, the above processes are still unclear.

On the cathode side, electrode also undergoes significant and complex structural changes (e.g., the evolution of intercrystalline and intragranular cracks of NCM/LCO particles^[35] and the structural degradation of elemental sulfur caused by the large volumetric change during charge/ discharge processes) and phase transformation of highvoltage cathode (e.g., the layered-to-rock salt and layeredto-spinel transformation due to over-delithiation).

3.2. Poor performance of high-energy-density Li metal pouch cells

Practical Li metal pouch cells with high energy density use electrodes with high areal capacity (typically >4 mAh cm⁻²) and low electrolyte amount (generally E/C ratio <3 gAh⁻¹). Under such a harsh condition, Li metal pouch cells exhibit poor cycle life, safety and rate capability, together with tremendous cell swelling and distortion (Figure 4).

3.2.1. Poor stability and cycle life

A big and urgent challenge pouch-type LMB needs to resolve is its poor stability and cycle life under the harsh cycling condition (particularly high areal capacity of electrodes and lean electrolyte). The poor cycle life is directly related with the poor stability of electrode-electrolyte interfaces and electrode material itself.

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Figure 4. The major challenges of pouch-type Li metal batteries.

• Interface instability

The Li and cathode interfaces possess high reactivity endowed by the extreme electrode potential, which triggers severe side reactions and rapid depletion of electrolyte leading to the cell failure.^[10] And unlike coin cells, the lifespan of pouch-type LMB cannot be prolonged through increasing electrolyte amount, as it would decrease the cell energy density.^[10] Moreover, porous and even dendritic Li grows on the anode side, which not only aggravates the side reactions but also accelerates the accumulation of dead Li during cycling,^[36] exacerbating the interfacial instability and cell polarization.

• Electrode instability

Both anode and cathode of LMBs suffer from poor structural stability. On the anode side, non-uniform and porous Li grows during charge and inhomogeneous stripping occurs with the formation of "dead" Li upon discharge, leading to great volumetric change of Li electrodes upon dis-/charge and pulverization of the Li electrode, and eventually leading to rapid cell degradation and failure. On the cathode side, the strain-induced cracks of insertion-type cathode materials during cycling causes structural deforma-

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tion of the electrode and cell capacity fade,^[37] while conversion-type S (or O_2) cathode undergoes repetitive deposition and dissolution of Li₂S/S (or Li₂ O_2) with large volumetric change during battery dis-/charge, which also largely destabilizes the electrode structure and threatens the cycling stability.^[38]

3.2.2. Poor safety

Pouch-type LMB still has severe potential safety hazards like thermal runaway, short-circuit, cell swelling and even explosion. Most of those issues are related with dendrite, electrode volume expansion, gassing and electrolyte flaming.

• Li dendrite growth

The Li dendrite could penetrate through the separator, causing electrical short-circuit of cell during cycling. The cell short-circuit process is accompanied by tremendous Joule heat release, which can even lead to cell explosion. Besides, Li dendrite growth drastically increases the porosity and surface area of reactive Li metal, which aggravates the safety threats of thermal runaway, especially when contacting with the ambient air and water. The electrodes of Li metal pouch cells, especially Li metal anodes, undergo large volumetric changes during cycling. For instance, Li metal anode could expand from $\approx 100 \ \mu m$ to $\approx 400 \ \mu m$ after 20 cycles,^[17] corresponding to a 300 % volumetric change. Besides, cathode particularly S and O₂ electrodes also undergo large volume expansion during the discharge process. Unfortunately, soft-packed pouch cells are susceptible to structural deformation. The large volume expansion of electrodes would exert large stress on the cell package, which causes cell distortion and swelling. The cell distortion and swelling raise the interfacial contact issue and the explosion risk, which imposes tremendous threats for commercial introduction of Li metal pouch cells.

• Gassing

The gas evolution in Li metal pouch cells is also a severe safety issue. One contribution of gassing is electrolyte decomposition at electrode-electrolyte interfaces,^[26,39] which forms gases like H₂, CH₄, C₂H₄ on the anode side and CO₂ on the cathode side, etc. Another source of gassing is the lattice oxygen releasing from transition metal oxide cathode materials upon charging to a high voltage (>4.2 V).^[28] The gassing would lead to formidable cell swelling, which substantially raises the safety risk.

• Electrolyte flaming

Pouch-type LMBs using organic liquid electrolytes are also confronted with potential hazards of electrolyte flaming upon cell damages (e.g., leakage and broken).^[40] The use of solid electrolytes can largely suppress this problem,^[41] yet many polymer-based electrolytes can burn when subjected to a flame.

3.2.3. Low rate capability

Li metal pouch cells suffer from poor fast-charge/discharge capability due to various kinetic limiting factors.

• Poor charge capability

High charge current (e.g., $>2 \text{ mA cm}^{-2}$) of LMBs would aggravate the Li-ion depletion region (i.e., space charge layer) and non-uniform charge distribution across the electrode, which accelerates the non-uniform Li deposition and Li dendrite growth,^[31] dramatically compromising the safety and lifespan. Moreover, fast-charging of Li-NCM pouch cells results in the rapid and inhomogeneous extraction of Li-ion from NCM, inducing large strains that destabilize the NCM structure, while the fast-charging of Li–S and Li–O₂ pouch cells is limited by the poor kinetics of S/O₂ for the electrochemical conversion reactions.

· Limited discharge capability

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During the discharge process, the moderate ion diffusion limits the large rate for high-voltage transition metal oxide cathodes, which causes cell capacity fade. Although high discharge rate of > 2 C has been reported for their based Li metal pouch cells, many of those results only show high-rate cycling for several cycles.^[42,43] More efforts are required for high-rate long-term cycling. Besides, fast-discharging of Li–S/O₂ pouch cells is also challenged by their sluggish conversion reaction kinetics.

4. Progress on the R&Ds of Li metal pouch cells

In this section, we summarize the recent progress of Li metal pouch cells that has been achieved in the mechanistic understandings of the electrochemical processes and failure mechanism, the improvement of energy density and stability, and the enhancement of safety.

4.1. Mechanistic understandings of the electrochemical processes in pouch-cell LMBs

In this section, we review the mechanistic understanding on the evolution of Li metal anode, cathode and electrolyte, respectively.

4.1.1. Major mechanism of cell degradation and/or failure

Understanding of the degradation and/or failure mechanism of Li metal pouch cells remains underdeveloped. Nevertheless, the depletion of electrolyte has recently been identified as a major cause of the failure of Li metal pouch cells. Liu et al. found that Li NCM622 pouch cells underwent rapid capacity drop after 12 cycles when filled with 3 gAh⁻¹ conventional carbonate ester electrolyte,^[17] and retained only $\approx 40\%$ capacity after 14 cycles (Figure 5a). For comparison, the capacity decreased moderately after 15 cycles at EC/ratio of 6 gAh⁻¹ (Figure 5b). Moreover, when refilling the same amount of electrolyte (3 gAh^{-1}) into a cycled and dead Li metal pouch cell, $\approx 50\%$ of the original capacity could be recovered (Figure 5c), which suggests the deteriorated cell kinetics due to the depletion of electrolyte is a major failure mechanism of pouch-cell LMBs. The depletion of liquid electrolytes hinders the ion transport between the anode and cathode, which fails the battery operation.

4.1.2. Electrolyte evolution and re-/distribution study during cell operation

Prior to depletion, the electrolytes undergo complicated compositional evolution. The challenge of studying the electrolyte compositional evolution in pouch-type cells is the poor penetration depth of many radiation sources like photons and electrons. Meanwhile, common in situ spectroscopic techniques like Raman spectroscopy and Fourier-



Figure 5. Degradation/failure of Li metal pouch cells related to electrolyte evolution and re-/distribution during cell operation. a, b) Cycling performance of Li metal pouch cells with different E/C ratios. c) Cycling performance of pouch cell at an E/C ratio of 3 gAh⁻¹ before and after electrolyte refilling. Copyright 2019, Macmillan Publishers Ltd.^[17] d) Electrolyte depletion during cycling and (e) corresponding cycling performance of Li metal pouch cells. Copyright 2019, Macmillan Publishers Ltd.^[26] Ultrasonic transmission mapping of anode-free Li metal pouch cells with f) low and g) high stacking pressure. Copyright 2020, Macmillan Publishers Ltd.^[27]

transformed infrared spectroscopy can barely provide quantitative information.

As a solution, techniques like nuclear magnetic resonance (NMR) and inductively coupled plasma-mass spectrometry could reveal quantitative information on the chemical evolution of electrolytes. Dahn et al. studied the electrolyte compositional change through NMR measurements of electrolytes extracted from Li metal pouch cells before and after cycling (Figure 5d and 5e).^[26] Notably, the salt concentration after the initial cycle was apparently lower

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than the pristine, indicating severe consumption of Li salts to form the SEI and CEI. Also, the salt concentration dropped to very low values (<0.1 M) and in the meantime the capacity decreased drastically after cycling, which suggests that the cell failure is strongly associated with the consumption of Li salts. Dahn et al. also studied the electrolyte redistribution and depletion in Li metal pouch cells during cycling through ultrasonic transmission mapping (Figure 5f and 5 g).^[27] The electrolyte wetting of electrodes gradually deteriorated as the Li metal anode became more and more porous along cycling, which also depends on the stacking pressure of cells. The transmission dropped to almost zero after 50 cycles under a low stacking pressure (Figure 5f), which suggests at least one layer of the electrode in pouch cells was dried out. In comparison, the electrodes remained wetted after 80 cycles under a high stacking pressure (Figure 5g).

4.1.3. Structural evolution and degradation investigation of Li metal anodes

Li metal electrodes evolve in morphology/structure and degrade gradually during the cycling of Li metal pouch cells, which are affected by various factors.

One is the electrolyte formulation, which influences the solvation structure of Li ions and the SEI chemistry and structure, eventually regulating the Li plating/stripping behavior and the stability of Li metal anode. Liu et al. found that in the conventional 1 M LiPF₆-ethylene carbonate (EC)/ethyl methyl carbonate (EMC) + 2 wt % vinylene carbonate (VC) electrolyte, two-sided compact Li electrode in the pouch cell evolved from 50 µm to a thick and very porous structure (160 and 250 µm, respectively, for the two sides), and the cell rapidly failed merely after ≈ 20 cycles.^[17] In comparison, the cycled Li evolved to 140 and 190 µm after 50 cycles in the 1.2 M lithium bis(fluorosulfonyl)imide (LiFSI) dissolved in the solvent triethyl phosphate (TEP) and the diluent bis(2,2,2-trifluoroethyl) ether (BTFE)electrolyte, which exhibits better cycling stability.

The morphological evolution and degradation of Li electrode is also highly dependent on the cycling rate and areal capacity. Zhang et al. investigated the morphologies of Li metal anode in pouch cells with various current densities and areal capacities spanning from 1 mA cm⁻² and 1 mAh cm^{-2} to 10 mA cm^{-2} and 10 mAh cm^{-2} (Figure 6a– 6f),^[31] which found that the failure mechanisms of Li metal anode can be classified into three regions on the map of the failure mechanism of Li metal anode at varied current and capacities (Figure 6g): polarization, short-circuit, and transition/combination between these two mechanisms. Specifically, pulverization and increased polarization are the main origin for the failure of Li metal anode at small current densities and areal capacities, and short-circuit is the main failure cause at large current densities and capacities. There also exists a transition region where all these processes (pulverization, polarization or short-circuit) contribute to the cell failure.

The working temperature is another factor affecting the morphological evolution of Li metal anode. Compared with the regular working temperature of ≈ 25 °C Dahn et al. achieved better cycling performance of Li metal pouch cells at 40 °C. Moreover, the stacking pressure affects the flatness and compactness of Li deposition, which influences the amount of "dead" Li and eventually impacts the reversibility and structural stability of the Li metal anode.^[32]

Additionally, the morphological evolution of Li metal anode is influenced by the thickness of Li foil. Liu et al. reported that for a moderate N/P ratio >1, a thinner Li foil could enhance the cycling stability of pouch-cell LMBs benefiting from the balanced interfacial reactions (i.e., SEI formation).^[11] The authors found that for the pouch cells using 20, 50 and 100 µm Li foil, the lifespan gradually shortened from ≈ 600 to 430 and 330 cycles, respectively, which might be caused by the thicker SEI layers accumulated during the cycling of cells. For the 50 µm Li foil, the thickness increased to 130 µm after 460 cycles (Figure 6h), while the 20 µm Li increased to 70 µm after 600 cycles (Figure 6i). The porous and thick cycled Li which evolved from 50 µm to 130 µm requires more electrolyte to wet, which causes local drying of the electrode and drastically increased impedance and sudden failure of the cell, as illustrated in Figure 6j.

4.1.4. Degradation mechanism of cathode

Compared to Li metal anodes, fundamental understanding of the degradation of cathodes in Li metal pouch cells remains limited. In general, Li-ion insertion/intercalation cathodes have much better stability compared to Li metal anodes, and their failure mechanism in Li metal pouch cells has captured less attention with few reports.^[29] The existing studies have focused on the degradation of conversion-type cathode such as sulfur in Li metal pouch cells.^[44,45]

Liu et al. assembled Li-S pouch cells with a range of energy densities up to 313 Whkg⁻¹ to investigate the failure mechanism (Figure 7a).^[45] The pouch cell with the highest energy density used 50 µm Li foil as anode and sulfur cathode with an areal capacity of $> 6 \text{ mAh cm}^{-2}$, and the E/S ratio was controlled at 2.5 mLg⁻¹. In comparison, the cell with a higher E/S ratio of 3 and 6 mLg⁻¹ maintained a stable discharge capacity for 30 and 90 cycles, respectively. Further investigation of the cycled cell of 313 Wh kg⁻¹ revealed that the cycled sulfur electrode exhibited significant inhomogeneity in the morphology and composition throughout the electrode (Figure 7b). This suggests that the decomposition of electrolyte results in non-uniform reactions of the sulfur electrode, which finally causes the failure of Li-S pouch cell at a low E/S ratio. This is different from the high E/S ratio condition in which the shuttle effect of lithium polysulfides is the dominant mechanism of capacity decay.





Figure 6. Degradation/failure of Li metal pouch cells related to the structural evolution and degradation of Li metal anodes. Morphologies of cycled Li at (a) 3 mAcm^{-2} , 3 mAhcm^{-2} , (b) 7 mAcm^{-2} , 7 mAhcm^{-2} and (c) 10 mAcm^{-2} , 10 mAhcm^{-2} . Cross-section view of cycled Li at (d) 3 mAcm^{-2} , 3 mAhcm^{-2} , (e) 7 mAcm^{-2} , 7 mAhcm^{-2} , 10 mAhcm^{-2} . (g) Failure mechanism map of cycled Li at varied current and capacities. Copyright 2019, Wiley.^[31] Evolution on the morphology and thickness of h) 50 µm and i) 20 µm Li foils before and after cycling. j) Schematic of the degradation mechanisms and pouch cell fading models with different thickness of Li foils. Copyright 2021, Macmillan Publishers Ltd.^[11]

4.2. Practical strategies for improving the performance of Li metal pouch cells

As energy density, stability and cycle life, and safety are three key performance criteria for pouch-type LMBs, the recent progress summary of the performance of Li metal pouch cells focus on the improvement of those parameters. Meanwhile, recent progress on the rate capability improvement is reviewed, as the rate capability is also a huge challenge.

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4.2.1. Improvement of energy density & stability and cycle life of LMBs with liquid electrolytes

For practical application, the stable cycling of Li metal pouch cells is equally if not more important than being dense in energy, which however remains challenging due to the reverse relationship between these two criteria as detailed in Section 2.4. The stability and cycle life of pouchtype LMBs is determined not only by the stability of Li metal anode, but also by the cathode stability. Therefore, it

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Figure 7. Degradation mechanisms of sulfur cathodes in Li-S pouch cells. a) Cycling performance of Li-S pouch cells with different E/S ratios. b) Optical image of the sulfur electrode from the cycled 313 Whkg⁻¹ Li-S pouch cell. c, d, f, g, i, j) X-ray fluorescence (XRF) mapping of 3 different regions of the cycled sulfur electrode. e, h, k) X-ray absorption spectroscopy (XAS) spectra of the corresponding regions. Copyright 2020, Royal Society of Chemistry.[45]

is of essence to stabilize both electrodes, which is realized by strategies like electrolyte regulation, electrode protection and solid-state electrolytes.

In this section, we summarize the recent progress on simultaneous improvement of the energy density and the cycling stability of Li metal pouch cells, through electrolyte regulation and electrode protection.

4.2.1.1. Electrolyte regulation

Tuning the electrolyte formulation is an effective strategy to promote the reversibility of the Li metal anode and cycling stability of Li metal pouch cells. Electrolyte formulation plays a key role in the composition and structure and thus the physicochemical properties of the SEI, e.g., Li-ion conductivity, mechanical property, and thermal stability. Since it is widely accepted that the properties of the SEI

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affect the Li nucleation and growth behaviors, tuning of electrolyte formulations would regulate the Li plating morphology and the stability of Li metal anode. Meanwhile, the electrolyte could react with the freshly exposed Li to in situ repair the broken SEI layer.

So far, a prevalent trend in the development of advanced electrolytes for Li metal full cells is to adopt the strategy

through which Li salts are dissolved by comparable numbers of solvents (solvent/salt molar ratio <2), and low-dielectricconstant solvents which do not dissolve Li salts act as the diluent to decrease the viscosity of electrolytes (Figure 8a). In general, this kind of electrolyte is called "localized highconcentration electrolyte (LHCE)" due to the similar coordination chemistry as concentrated electrolyte (e.g.,



Figure 8. Electrolyte regulation for improving the energy density & stability and cycle life of Li metal pouch cells. a) Schematic of the electrolyte regulation strategy with LHCEs for improving the performance of Li metal pouch cells. b) A pie chart of the mass distribution of cell components in the Li metal pouch cell. c) Cycling performance of the 1 Ah Li metal pouch cell using a phosphate-based LHCE. Copyright 2019, Macmillan Publishers Ltd.^[17] d) Cycling performance of Li metal pouch cells with 20 µm Li foils using an ether-based LHCE. Copyright 2021, Macmillan Publishers Ltd.^[11]

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numerous contact ion pairs and aggregates in electrolytes vs. dominant solvent-separated ion pairs in conventional electrolytes). Such a unique solvation chemistry promotes the formation of inorganic-rich SEI and CEI due to the sacrificial decomposition of anion,^[46] improving the interfacial stability between the electrolyte and electrodes, which effectively improves the stability and cycle life of Li metal pouch cells. Another prevalent trend is to use Li salt or solvent with a high fluorine content, which can decompose to form LiF-rich SEI.^[47,48] LiF is thought be a unique component with low diffusion barrier for Li ions and high electronic resistivity, which promotes the planar Li deposition.^[47] But some recent literatures show that the LiFrich SEI does not act in all systems,^[8] i.e., there is no simplistic mono-correlation between Coulombic efficiency (CE) and fluorine content among a wide range of electrolytes. For instance, some Li salts (such as LiPF₆) exhibit large scattering in CE in contrast to others (e.g., LiFSI).

Recently, new electrolyte formulations have been explored to enable stable cycling of high-energy-density Li metal pouch cells.^[11,17,43,49-57] In 2019, Liu et al. reported an impactful research that stable cycling of 300 Whkg⁻¹ Li metal pouch cells was realized through the use of a LHCE which consisted of 1.2 M ILiFSI dissolved in the solvent tTEP and the diluent BTFE (TEP and BTFE 1:2 by molar ratio).^[17] The LHCE enables compact Li deposition, which mitigates the cell swelling from 111% after 10 cycles in conventional carbonate electrolyte to 74% after 50 cycles. This effectively suppresses the irreversible consumption of the electrolyte at interfaces, which enables the lowering of the E/C ratio to 3.0 gAh^{-1} , corresponding to a mass ratio of \approx 24.1 % of the cell (Figure 8b) without apparently sacrificing the cycle life. The cell operated over 200 cycles with 86% capacity retention and 83% energy retention (Figure 8c).

In later research, many cell parameters were further optimized to achieve higher energy densities, such as the use of cathode materials with higher specific capacities (e.g., NCM811 and LiMnO₂) and thinner Li foil (e.g., 20 µm), and electrolyte with lower E/C ratio ($<2 \text{ g Ah}^{-1}$). Liu et al. demonstrated the Li metal pouch cell with an advanced LiFSI-1,2-dimethoxyethane (DME)-1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) (1:1.2:3 by molar ratio) LHCE, which increased the energy density to $\approx 360 \text{ Wh kg}^{-1}$ through the use of 20 µm Li electrode.^[11] Meanwhile, the pouch cell had an excellent lifespan of 600 cycles with 70 % capacity retention thanks to the excellent compatibility between ether-based electrolytes and Li (Figure 8d), which remains to be the best cycling performance of Li metal pouch cells till far.

4.2.1.2. Design and engineering of Li metal anodes

• Surface Engineering of Li metal anodes

The stability of Li metal anode can also be improved through the pretreatment of Li surface to form an artificial protective film.^[30,58-67] The artificial films formed before

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cycling can mitigate the contact between the reactive Li metal and the electrolytes, thus alleviating the consumption of electrolytes and promoting the cycle life of LMBs. Meanwhile, the artificial films are more homogeneous and less complex in chemistry (usually containing less than three components), compared to the SEI formed in batteries derived from the complicated decomposition of electrolytes. Such a uniform layer might help to homogenize the Li-ion transport on the surface of Li and suppresses localized Li deposition.

Recently, Wei et al. reported a silanized artificial film on Li metal anode for high-energy-density Li metal pouch cells.^[30] The silanized film could promote faster and more uniform Li-ion flux and thus dense Li plating in Li metal pouch cells (Figure 9a). The authors fabricated 300 Whkg⁻¹ pouch cells in which thin Li foils (\approx 50 µm) were paired with a high areal capacity (3.38 mAh cm⁻²) NCM523 cathode and a lean electrolyte (E/C ratio of 2.7 gAh^{-1}). The cells using silanized Li could deliver a long cycle life of 160 cycles, twofold of that with unprotected Li (80 cycles) (Figure 9b). The silanized film could mitigate the pulverization of Li metal anode, as shown in Figure 9c, where the thickness of the utilized Li was 10 and 25 µm after 20 and 85 cycles. Therefore, the gassing due to the side reactions of electrolyte with pulverized Li has been suppressed, which largely mitigates the cell swelling. In comparison, the pristine Li without artificial film resulted in a thickness of over 18 and 51 µm after 20 and 85 cycles.

• 3D conductive current collector

Three dimensional (3D) conductive current collector for Li metal anode can lower the local current density and provide more Li nucleation sites compared with planar current collector due to its large specific area, which mitigates non-uniform Li deposition and detrimental Li dendrite growth, promoting the stability of Li metal anode (Figure 9d). Also, some 3D current collectors decorated with lithiophilic materials have been developed to improve the wettability of Li metal, which promotes more uniform Li deposition. Lu et al. reported a porous reduced graphene oxide (rGO) framework with dispersed MgF₂ nanoparticles as the host for Li metal anodes.^[68] The MgF₂-rGO film accommodates liquid Li metal through the sparkling process, during which Li metal reacts with MgF₂ forming Mg_xLi_y alloy and LiF (Figure 9e). The Li-Mg alloy acts as the lithiophilic site for Li nucleation and deposition, which facilitates the uniform Li plating with a low nucleation overpotential. The authors assembled Li metal pouch cells with the MgF₂-Li-rGO electrode and a high areal capacity (3.93 mAh cm⁻²) NCM811 cathode, along with a low N/P ratio of 1.445 and an E/C ratio of 2.9 gAh⁻¹. The cell delivered a very high first-cycle energy density of \approx 400 Wh kg⁻¹ at 0.1 C and 371 Wh kg⁻¹ at 0.2 C/0.4 C charge/discharge rates, with 85% of retention after 150 cycles (Figure 9f).

Despite the promising electrochemical performance, the complicated and costly fabrication of many 3D current collectors limit their potential for practical applications.



Figure 9. Design and engineering of Li metal anodes for stabilizing Li metal pouch cells. a) Schematic of the mechanism of artificial protective film for stabilizing Li metal anodes and improving the performance of Li metal pouch cells. b) Cycling performance of 1 Ah Li metal pouch cells (300 Wh kg^{-1}) with or without pretreated Li. c) Morphological and thickness evolution of the Li electrode with and without artificial film after cycling. Copyright 2019, Wiley.^[30] d) Schematic of the mechanism of 3D current collector for stabilizing the Li metal anode and improving the performance of Li metal pouch cells. e) Schematic of the synthesis process of the MgF₂-rGO film. f) Cycling performance of Li metal pouch cell with the MgF₂-rGO film. Copyright 2017, Elsevier.^[68]

Meanwhile, a large amount of electrolytes have to be used and consumed to effectively passivate the large specific areas of the 3D current collectors, which, together with the considerable weight of the (usually metallic) 3D hosts, compromises the energy density of the cells. Therefore, the systematic optimization of material design and specific area of 3D current collectors is required.

4.2.1.3. Improving stability of cathode materials

• Insertion-type cathode materials

Compared with Li, insertion-type high-voltage cathode especially prevalent Ni-rich oxide cathode (i.e., Ni ratio > 0.6) is more stable at the charge cut-off voltage of 4.3 V after tremendous efforts on stabilizing the cathode interface and structure through doping and surface coating. The capacity increase is negligible through increasing the charge cut-off voltage (e.g., $\approx 200 \text{ mAh g}^{-1}$ at 4.3 V and 220 mAh g⁻¹ at 4.5 V for NCM811), while it would cause severe oxidation of electrolytes and poor cycling stability of cells.^[39,69] Efforts have been made on improving the cathode with high cut-off

charge voltage recently.^[35,70] Lu et al. reported a singlecrystalline LiNi_{0.88}Co_{0.09}Mn_{0.03}O₂ (SNCM) cathode material stabilized through Al/Zr co-doping.^[35] Al and Zr relieve the internal strain and suppress the phase transformation, which enables the improved cycling of Li metal pouch cells with a high cut-off charge voltage of 4.6 V.

In comparison, Li–Mn-rich layered oxides (a mixture of Li_2MnO_3 and NCM) could largely increase the specific capacity (up to 300 mAh g⁻¹) but suffer from poor structural stability like oxygen release over repetitive Li-ion insertion/ extraction and rapid capacity/voltage decay, and the realization of the very high theoretical capacity requires charging the cathode to an elevated voltage (>4.7 V) which leads to the afore-mentioned oxidation issues. Liu et al. reported the elimination of oxygen release via tuning the distribution of superlattice domain, which enables the cycling of 500 Wh kg⁻¹ Li metal pouch cell over 50 cycles.^[28]

• conversion-type cathode materials

Considerable advances have been obtained for pouchcell LMBs with conversion-type cathode materials, e.g., S and O_2 , thanks to the electro-/chemical stability of ether GDCh

electrolytes that are used for Li–S and Li–O₂ batteries against Li metal anodes and within the low operating voltages of these batteries (<4 V vs. Li⁺/Li). Here we briefly summarize the recent progress of S^[71–96] and O₂^[18–23,97–101] cathodes for Li metal pouch cells.

Li-S batteries suffer from the poor conversion kinetics from electron-insulating elemental sulfur (S_8) to long-chain lithium polysulfides (Li₂S₄, Li₂S₆ and Li₂S₈) and to shortchain and electron-insulating lithium sulfides (Li_2S_2 and Li₂S), along with the high solubility and thus severe crossover of the polysulfide intermediates in the liquid electrolytes between the anode and the cathode.^[102,103] The electronic conduction property of the sulfur electrode can be improved through the incorporation of nanostructured carbon materials, $^{\left[104,105\right]}$ and the conversion kinetics of S/Li2S2 can be improved through the liquid-phase reaction of enabled by the dissolved lithium polysulfides in highly polar solvents or increased amount of electrolytes.^[106,107] However, the electrodes of sulfur impregnated within conductive carbon frameworks are very porous with low electrode tap density as mentioned above, which severely decreases the volumetric energy density, while the increase in the amount of electrolytes also decreases the specific energy density, and the high solubility of polysulfides aggravates the shuttle effect.

Another approach to promote the electrochemical reaction kinetics of sulfur electrode is to introduce catalytic sulfur-host materials, typically transition metal compounds which strongly coordinate with lithium polysulfides to catalyze their reduction to $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ and oxidation into S_8 .^[84,108] Zhao et al. designed a microporous carbon framework with binary metallic compounds as sulfur host.^[71] They embedded single-atom Co–N–C catalyst and ZnS nano-

particles into the microporous carbon network, where lithium polysulfides (Li₂S₄, Li₂S₆ and Li₂S₈) strongly bind with ZnS or Co-N-C due to the synergetic effects of the metallic compounds (Figure 10a). Density functional theory calculations reveal that the reduction of S₈ into Li₂S is more favorable on the catalytic Co-N-C surface (Figure 10b), which improves the redox kinetics of the sulfur electrode. Besides, the strong interactions between lithium polysulfides and the transition metal compounds can immobilize lithium polysulfides and thus suppress the shuttle effect. Ah-level Li-S pouch cells based on such sulfur cathode design achieved a calculated energy density up to $\approx 317 \text{ Wh} \text{kg}^{-1}$ given an N/P ratio of 2.6, an E/S ratio of 4 mLg⁻¹, and an areal capacity of $>6 \text{ mAh cm}^{-2}$, with a capacity retention of \approx 74 % after 80 cycles (Figure 10c). Note that, the mass ratio of the electrolyte in relative with the whole cell reached \approx 50 %, which is much higher than the Li-insertion cathode based Li metal pouch cells (≈ 20 %). Therefore, the electrochemical conversion kinetics of the sulfur electrodes need further improvements to lower the E/S ratio for practical pouch cells with higher energy densities.

Transition metal sulfides that exhibit considerably enhanced electronic conductivity and reaction kinetics have also been explored as sulfur-equivalent cathodes for pouchcell Li–S batteries.^[108] Li et al. proposed a metallic sulfide to improve the kinetics of the sulfur electrode.^[72] They designed an intercalation-conversion hybrid cathode (HMSC electrode), which mixed sulfur with a Chevrel-phase Mo_6S_8 with a good electronic conductivity (Figure 10d). The lithiated Mo_6S_8 could improve the adsorption of lithium polysulfides onto the electrode, which promotes the conversion kinetics. Meanwhile, Mo_6S_8 acted as the electronconductive agent to partially replace the carbon materials,



Figure 10. Designing strategies of sulfur/air cathodes for Li–S/Air pouch cells. a) Designing strategy of microporous host for sulfur electrode. b) Free energy of reactions from S_8 to Li₂S on the bare graphene and Co–N–C surfaces. c) The cycling performance of Li–S pouch cell with the microporous host. Copyright 2021, Macmillan Publishers Ltd.^[71] Schematic of the d) HMSC electrode and e) traditional S electrode. Copyright 2019, Macmillan Publishers Ltd.^[72] f) The voltage and specific capacity of Li₂O-based electrode vs. the insertion-type cathode materials. g) The cycling performance of Li-Li₂O pouch cell with catalyst. Copyright 2020, Elsevier.^[97]

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so the mass ratio of carbon materials (≈ 10 wt % for the whole electrode) could be much lower than the typical sulfur electrodes (containing ≈ 30 wt% carbon materials). In addition, Mo_6S_8 has a higher density (5.04 g cm⁻³) compared to sulfur (2.07 g cm^{-3}) . Therefore, a compact electrode with a thickness of 121 µm could be realized, thinner than the tradition porous sulfur electrode mixing S with carbon (167 µm, Figure 10e). Moreover, Mo₆S₈ contributed capacity for Li-ion storage within the charge/discharge window of S (1.7-2.8 V vs. Li⁺/Li) through the intercalation/deintercalation of Li ions. Therefore, the volumetric energy density of the Li-S pouch cells could be effectively increased. The Li-S pouch cell with the HMSC electrode exhibited a high calculated specific energy density of 366 $Wh\,kg^{-1}$ and a volumetric energy density of 581 $Wh L^{-1}$ at a very harsh condition of E/S ratio: 1.2 mLg⁻¹, and showed a good capacity retention even at a high current density of $1 \,\mathrm{mA}\,\mathrm{cm}^{-2}$.

Element oxygen is lighter than sulfur and has an even higher specific capacity for Li-ion storage, which envisions an ultrahigh theoretical energy density for Li-O2 batteries.^[38] Nevertheless, the practical implementation of Li-O₂ pouch cells is challenging due to the poor reaction kinetics and high reactivity of intermediate species.[24] Intensive research efforts have been devoted to improving the kinetics of O₂ electrode, and Li–O₂ pouch cells with high energy densities have been demonstrated in recent years.^[18-23,97-100,109,110] Long et al. prepared a palladium (Pd)induced metallic (1T) MoS₂ nanosheet array which was supported on carbon textiles to catalyze the O_2 reactions.^[20] The Li-O₂ pouch cells with this composite electrode obtained a high specific energy density of 441.6 Whkg⁻¹. Wang et al. reported a free-standing 3D CuCo₂S₄ nanosheet array to accelerate the transition of O_2/Li_2O_2 redox,^[101] and fabricated a Li metal pouch cell which can delivers a high energy density of 536 Whkg⁻¹ at 100 mAg⁻¹. Although some reports have demonstrated Li-O₂ pouch cells with very high energy densities $(>480 \text{ Wh kg}^{-1})$,^[23] rechargeable Li–O₂ pouch cells have been rarely reported, plagued by the poor reversibility and cycling stability of these cells. Besides, most of these pouch cells are single-layer cells with relatively low capacities (typically < 0.5 Ah).

To avoid the issues raised by the highly reactive intermediates like superoxide, Zhou et al. developed a $Li_2O-Li_2O_2$ redox-based oxygen electrode to prolong the cycle life of Li– O_2 batteries without evidently sacrificing the energy density of oxygen electrode (Figure 10f).^[97] The $Li_2O-Li_2O_2$ redox can provide a specific capacity of ≈ 750 mAh g⁻¹, much higher than prevalent transition metal oxide electrodes (150–200 mAh g⁻¹), together with a moderate average discharge voltage (≈ 2.5 V vs. Li⁺/Li) and low charge voltage indicating good kinetics. The key to realizing this kind of chemistry is to use a carbon skeleton modified by Ni nanoparticles (carbon-alloy-catalyst framework with Ni) to catalyze the reaction of Li_2O electrode, which successfully demonstrates a 500 Wh kg⁻¹ Li metal pouch cell with a lifespan of 100 cycles (Figure 10g).

4.2.2. Development of stability & cycle life of solid-state Li metal pouch cells

The development of pouch-cell solid-state Li metal batteries (SSLMBs) has attracted great R&D interest but is still at their infant stage. There exist many review articles on the solid electrolytes for SSLMBs,^[111-114] which will not be repeated in this review. In this section we just highlight the R&D progress that has been achieved on solid electrolytes and their interfaces with electrodes for pouch-cell SSLMBs.

4.2.2.1. Pouch-type solid-state LMBs with Li-ion intercalation/insertion cathodes

The fabrication of pouch-cell SSLMBs based on inorganic solid electrolytes (ISEs) has been tremendously challenging due to the lack of high stacking pressure inside pouch cells, which, however, is essential for maintaining good electrical contact for battery operation. To date, there are only a few reports^[12,115] of pouch-cell SSLMBs using ISEs. Zhu et al. reported Li₄Ti₅O₁₂ (LTO)|Li pouch-cell SSLMBs with a Li₇P₃S₁₁ (LPS) solid electrolyte, which could achieved a stable capacity retention of 120 mAhg⁻¹ at 1 C after 20 cycles when dis-/charged at 1.4–2.4 V.^[115] Stable cycling was achieved by varying the working voltage range, which could regulate the redox behaviors of the sulfide electrolyte toward reversible interfacial reactions (Figure 11a–b).

Im, et al. fabricated a sliver-carbon composite film which adhered to a stainless steel current collector for SSLMBs based on ISEs.^[12] The composite film was used to separate the electrolyte and electrode for mitigating the reactions between Li metal and the electrolyte, while the Ag nanoparticles uniformly dispersed in the carbon black framework were used to guide the uniform Li deposition due to the good affinity of Ag towards Li (Figure 11e). Interestingly, Li tends to form deposits close to the current collector side after the first charging, while a large amount of Ag exists in the Li deposits, which suggests the diffusion of Ag towards the current collector and the formation of Li-Ag alloys. Since the Li deposits are close to the current collector, the carbon layer can block the contact between Li and the solid electrolyte. This improves the durability of the solid electrolyte, prevents the Li metal penetration, and mitigates the consumption of Li metal reacting with the solid electrolyte to form interphases. The authors paired the Ag-C composite layer with a thick NCM ($\approx 6.8 \text{ mAh cm}^{-2}$) to enable anode-free Li metal pouch cells with a high calculated energy density $> 900 \text{ Wh L}^{-1}$. Notably, the anode-free pouch cell showed an excellent capacity retention of $\approx 89\%$ after 1000 cycles, with an extremely high average CE of \approx 99.8 %. Nevertheless, the working temperature was still high (60 °C) (Figure 11d).

Solid polymer electrolytes (SPEs) have also been explored as the electrolyte for pouch-cell SSLMBs,^[116-124] due to their high manufacturability of membrane preparation and cell assembly, but their low ionic conductivity and demanding working conditions (e.g., at elevated temper-



Figure 11. Strategies for improving the performance of solid-state Li metal pouch cells. (a) Stable cycling of the LTO | Li pouch cell with a LPS solid electrolyte at a voltage range of 1.4–2.4 V and (b) the underlying mechanism.^[115] Copyright 2020, Elsevier. (c) 0.3 Ah LFP | Li pouch cell with a garnet-rich PEO/LLZNO CSE membrane electrolyte showing a cycle life of > 4000 cycles when tested at 60 °C.^[125] Copyright 2021, Elsevier. (d) Schematic of the anode-free LiNi_{0.90}Co_{0.05}Mn_{0.05}O₂ | Li pouch cell with a Ag–C composite anode and (e) the capacity retention over long-term cycling.^[12] Copyright 2020, Macmillan Publishers Ltd. (f) The cycling stability of a pouch-cell Li–S batteries tested under repetitive stretching/ release at a maximum strain of \approx 80%, enabled by an IL-PVDF-HFP based GPE.^[126] Copyright 2021, Elsevier. (g) The cycling performance of NCM811 | Li pouch cell with a MOF-based quasi-solid electrolyte under harsh working conditions.^[127] Copyright 2022, Macmillan Publishers Ltd.

ature of ≈ 60 °C) have largely hindered their realization in practice.

To address the issues of ISEs and SPEs, polymer/ inorganic composite solid electrolytes (CSEs) have attracted great research attention for pouch-cell SSLMBs and various approaches have been applied to simultaneously improve the interfacial stability and to stabilize the cycling performance of CSE-based batteries,^[41,125,128–137] demonstrating their

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GDCh

great promise for the realization of SSLMBs in practice. Yang et al. developed anacre-like poly(ether-acrylate)/Li1+ _xAl_xGe_{2-x}(PO₄)₃ (LAGP) CSE with a "brick-and-mortar" microstructure, which exhibits a high mechanical robustness. The LFP|Li pouch cell based on this CSE achieved excellent mechanical and cycling stability, retaining 95.6% capacity after 100 cycles even when an external point load was applied. Kvasha et al. developed a 0.3-0.4 Ah LFP Li pouch cells using CSE membranes containing inorganic Li₇La₃Zr_{1.75}Nb_{0.25}O₁₂ (LLZNO) garnet or alumina nanoparticle and poly(ethylene oxide) (PEO)-lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) host polymer electrolyte, which exhibited a long cycle life up to 4000 cycles when tested at $60 \degree C$ (Figure 11c).^[125,138]

Moreover, building layered structure of CSEs, which could have well-controlled and further enhanced interfacial stability, has gained emerging interest.^[139–142] For instance, Yang et al. synthesized a freestanding a tri-layer CSE membrane containing Al-doped lithium lanthanum zirconate oxide (LLZO), and NCM811|Li pouch cells using the membrane achieved a capacity retention of 95.6 % after 30 cycles.^[139] Yang et al. reported NCM622|Li pouch cells with a modified tri-layer membrane for suppressing Li dendrite growth, which demonstrated the stable cycling for 100 cycles with a high specific capacity of NCM622 of up to 159 mAhg⁻¹.^[140]

The utilization of liquid-containing quasi-solid-state electrolytes^[127,143–146] and gel polymer electrolytes (GPEs)^[147-151] is a compromised solution to SSLMBs, which substantially avoids interfacial contact issues and enables fast charge transfer. Zhou et al. reported NCM811 | Li pouch cells using a metal-organic framework (MOF)-based quasisolid-state electrolyte,^[127] which could deliver high and stable cycling performance even at very harsh conditions (171 mAh g^{-1} for 300 cycles and 89% capacity retention at a high temperature of 90 °C; retained capacity of 164 mAh g⁻¹ after 100 cycles after cutting). (Figure 11g). Guo et al. reported a NCM622|Li pouch cell using a hybrid solidliquid electrolyte, with both the CEI and SEI stabilized via in situ synergistic conversion of lithium difluoro-(oxalato)borate (LiDFOB) and $\rm LiBF_{4}\!.^{[143]}$ Benefiting from the stabilized interfaces, the pouch cell achieved an outstanding cycling stability over 100 cycles even at high areal capacity (5 mAh cm⁻²), high charge cut-off voltage (4.5 V), and high temperature (45°C) conditions, leading to a highenergy-density of 456 Wh kg⁻¹.

4.2.2.2. Pouch-type Li-S and Li-O₂ solid-state LMBs

Li–S and Li– O_2 batteries suffer from much worse cycling stability compared to LMBs based on insertion/intercalation-type cathodes, due to the unstable Li deposition and large structural changes of the cathodes, and sluggish electrochemical conversion reaction kinetics, which has been aggravated in pouch cells due to poor interfacial contact and lack of stacking pressure to restrain the structural changes. Besides, high AM loading and low amount of inactive components such as electrolyte are also extremely challeng-

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ing for pouch-cell Li–S and Li– O_2 batteries that are targeted at improved energy density, which is rooted in the electronic insulating property of sulfur/oxygen and the conversion products and the poor electrochemical conversion kinetics.

GPEs^[152] can enable the application of a low E/S ratio and a high sulfur mass loading for Li-S batteries, next to its functionality of flexibility and even stretchability, making them particularly suitable for their based pouch cells. Jin et al. developed a super-stretchable Li-S pouch cell using an ethyl-3-methylimidazolium bis(trifluoromethvlsulfonyl)imide (EMI-TFSI) ionic liquid (IL)poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) based GPE membrane,^[126] which enables a high areal sulfur loading (up to 14 mg cm⁻²) and stable cycling even being stretched and released at a maximum strain of $\approx\!80\,\%$ (Figure 11f).

Moreover, the shuttle of lithium polysulfides could be avoided when ISEs^[154] are used, and sulfide-based SEs are the most promising ISEs for Li–S batteries due to their high ionic conductivity and compatibility with sulfur. However, they are not stable against metallic Li. To solve this issue, Yin et al. introduced a quasi-sold-state pouch-cell Li–S batteries,^[155] using [Li(triglyme)]]⁺[TFSI]⁻ solvent-salt complex to stabilize the Li-Li₁₀GeP₂S₁₂ interface by creating a stable SEI derived from in situ electrochemical reduction of the complex on Li. The interfacial stability against Li could also be improved through the application of halide-doped lithium argyrodites (Li₆PS₅X, X=Cl, Br or I) or garnet solid electrolytes that have much enhanced compatibility with Li.^[156]

Similar to Li–S pouch cells, most pouch-type Li– O_2 batteries that have been developed employing quasi-solidstate or polymer/inorganic CSEs, and engineering of multiple components of the batteries is often required to achieve stable cycling.^[22,100,157-160]

4.2.3. Progress of stability & cycle life of anode-free Li metal pouch cells

Anode-free LMBs are the kind of Li batteries which uses metallic current collectors (without Li) as the anode, while Li sources from lithiated cathode materials and is plated on the anode side during the battery charging process. Anodefree Li metal pouch cells get rid of excess Li on the anode, thus enabling high (especially volumetric) energy densities. Figure 12a shows the thicknesses of anode-free Li metal pouch cell and commercial Li-ion pouch cell with the same capacity, which shows that anode-free Li metal pouch cells have apparent advantage in volumetric energy density $(1200 \text{ Wh } \text{L}^{-1} \text{ vs. } 700 \text{ Wh } \text{L}^{-1}$, as shown in Figure 12b and 12c).^[27] However, stable cycling of anode-free Li metal pouch cells have been extremely challenging since no additional Li source can remedy the loss of electrochemically active Li due to the formation of SEI and accumulation of "dead" Li over repetitive Li plating/stripping processes.

Recently, anode-free Li metal pouch cells have achieved tremendous progress, through electrolyte regulation, anode medication and cathode engineering.^[12,26,27,161–169]



Figure 12. Approaches enabling anode-free Li metal pouch cells. a) Optical images of anode-free Li metal pouch cell and Li-ion pouch cell with the same capacity. The volumetric energy densities of b) Li-ion pouch cell and c) anode-free Li metal pouch cell. d) Comparison for the driving ranges of electrical vehicles and cost for the same range using LIBs (blue) and anode-free LMBs (purple). e) The cycling performance of anode-free Li metal pouch cells with different electrolyte formulations. Copyright 2020, Macmillan Publishers Ltd.^[27] f) Schematic for the working mechanism of anode-free LMBs with a Li-rich high-voltage NCM811 cathode. The cycling performance of g) 60 mAh level single-layer and h) 300 mAh level multi-layer Li metal pouch cells with different anodes (Li or anode-free) and NCM811 cathodes (Li-rich or normal). Copyright 2021, Wiley.^[161]

• Electrolyte engineering

Dahn et al. constructed anode-free Li metal pouch cells to achieve a high volumetric energy density and long cycle life,^[27] which was enabled by a concentrated electrolyte composed of 2.0 M LiDFOB and 1.4 M LiBF4 in fluoroethylene carbonate (FEC)/diethyl carbonate (DEC) (1:2 v/ v) forming stable fluorinated SEI and CEI. The plated Li exhibited a compact and dendrite-free morphology, which enables the good reversibility for Li metal plating/stripping. Besides, the Li metal pouch cells were discharged to an elevated cut-off voltage of 3.6 V vs. Li⁺/Li (instead of the commonly used 2.8 V). At such a high cut-off voltage, plated Li remains partially unstripped on the anode side after the discharge process, which behaves similar to thin Li foils and promotes the reversibility of Li plating/stripping thanks to the better plating morphology of Li on Li metal compared to that on Cu current collector. The anode-free Li metal pouch cells delivered a calculated energy density up to $\approx\!1200~Wh\,L^{-1}$ (Figure 12c), and still retained $\approx\!700~Wh\,L^{-1}$ after 200 cycles (Figure 12e).

• Modification of Li metal anode

Suo et al. applied an epitaxial-induced plating currentcollector (E–Cu) to promote the performance of anode-free LMB.^[164] The E–Cu was fabricated by coating a Ga–In-Sn

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liquid metal layer on Cu substrate, which initiates Li storage by an alloying reaction forming an epitaxial-induced layer. Such an epitaxial-induced layer accelerates the surface diffusion of Li ions, which induces an epitaxial plating behavior of Li metal. Therefore, anode-free pouch-type LMB with calculated energy density of 420 Wh kg⁻¹ (excluding packaging weight) has increased capacity retention from 66 % to 84 % within 50 cycles.

• Engineering of cathode

The performance of anode-free LMB can also be promoted by using Li-rich cathode. Suo et al. reported a Lirich Li_{1.31}Ni_{0.8}Co_{0.1}Mn_{0.1}O₂ cathode materials to improve the cycling performance of anode-free LMBs. The cathode could release an excessive amount of Li to partially remedy during cycling.^[161] The the irreversible Li loss Li_{1.31}Ni_{0.8}Co_{0.1}Mn_{0.1}O₂ cathode was converted to normal NCM811 after the first cycle (Figure 12f), so the anode-free Li metal pouch cell with the $Li_{1.31}Ni_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathode behaved like Li metal pouch cells with an N/P ratio of 0.31. Such a cell construction could provide a high specific energy density up to 349.5 Whkg⁻¹ at an E/C ratio of 2 gAh⁻¹ (Figure 12g and 12 h), but the cycling performance of the Li metal pouch cell was not satisfactory due to the limited excessive Li in the Li-rich NCM cathode.

Note that, despite the progress of anode-free Li metal pouch cells that have been made recently, their cycle life

typically cannot beat Li metal pouch cells, except for the report of anode-free solid-state Li metal pouch cell using an Ag–C composite anode that achieved a cycle life of 1000 cycles,^[12] where the carbon layer suppresses Li loss through preventing direct contact between Li and the solid electrolyte. In general, an ultra-high CE of >99.9% for Li metal plating/stripping would be crucial for the commercial introduction of anode-free Li metal pouch cells, which still needs significant R&D breakthroughs.

4.2.4. Safety improvement

The operational safety is gaining increasing attention when moving toward commercialization, e.g., at the stage of prototyping, of Li metal pouch cells. So far, R&D efforts have been devoted to improving the safety of Li metal pouch cells through different strategies, such as modifying the electrolytes and decreasing the reactivity of cycled Li. To evaluate the safety of Li metal pouch cells, safety tests like nail penetration, corner-cut, bending, and electrolyte flaming test have been performed in literatures.

4.2.4.1. Electrolyte modification

Commonly used electrolytes for Li-based batteries predominantly use ester- or ether-based solvents,^[170,171] due to their relatively high electrochemical stability and the high solubility and ionization degree of Li salts in these solvents. However, most of these electrolytes are highly flammable, which may cause thermal runaway and even explosion when the cells are electrically shorted or broken. Ether-based electrolytes are more stable against Li metal anodes, but they are even more flammable compared with ester-based electrolytes.

Formulating electrolytes with high-flash-point solvents can largely decrease the flammability. However, many solvents with high flash points are highly reactive with Li metal. Fortunately, the severe reactions with Li metal can be suppressed through increasing the concentration of Li salts in the electrolytes, due to the higher content of anions in the concentrated electrolytes, which decomposes to suppress the reactions between the solvents and Li, promoting the stability of Li metal anode.^[40,51] Cui et al. reported a concentrated electrolyte composed of 2.5 M LiTFSI and 0.5 M LiDFOB in succinonitrile (SN).^[40] The solvent SN has a good stability against flaming due to its high flash point of >110 °C and it has a low molar ratio in the electrolyte. Both factors contributed to the decreased flammability of the electrolyte, which did not catch fire when placed on a heating plate at 200 °C. For comparison, the ester electrolyte composed of 1 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) was highly flammable. The authors also tested the safety of Li metal pouch cells with the nonflammable electrolyte. The pouch cell with the concentrated electrolyte did not swell after cycling and thermal shock test. By contrast, the cell with ester electrolyte swelled after cycling and got short-circuit after the

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thermal shock test. The pouch cell with the concentrated electrolyte worked well even after nail penetration and corner-cut tests, demonstrating its outstanding safety.

Though concentrated liquid electrolytes have shown enhanced safety for LMBs,^[172,173] their high price and potential safety issue at extreme conditions hinder their commercial introduction. Solid electrolytes could potentially further improve the safety of LMBs and various types of solid electrolytes,^[41,122] especially polymer/inorganic CSEs,^[120,121] have been developed to enhance the safety of Li metal pouch cells. However, many CSEs are still flammable due to the C–O bonds in the polymers and require significant advancements to enhance the safety of their based Li metal pouch cells.

4.2.4.2. Decreasing the reactivity of cycled Li metal

Li metal vigorously reacts with electrolytes in batteries and with the ambient air especially in the humid atmosphere, which raises the safety concern. This issue is significantly aggravated when Li metal anode becomes porous with high specific surface areas, e.g., after cycling, which is even worsened for Li metal pouch cells that are more vulnerable to external damages of the plasticized cell package and are prone to evolution toward porous Li electrode due to the lack of stacking pressure.

Dahn et al. reported the improved safety of the cycled Li metal electrode in a dual-salt electrolyte.^[27] Li metal cycled in the LiDFOB-LiBF₄-FEC/DEC dual-salt electrolyte was compact with a low specific surface area, which merely produced gases and foams when submerged in water (Figure 13a). In sharp contrast, the cycled Li in 1.2 M LiPF₆-FEC/DEC and EC/DEC electrolytes were highly mossy and porous, which exploded when submerged in water. Besides, the pouch cells with the dual-salt electrolyte kept at a temperature of < 100 °C during nail penetration test, while the cells with the LHCE and concentrated electrolyte (1.73 M LiFSI DME-TTE and 4 M LiFSI FEC-DEC) underwent uncontrollable thermal runaway and violent explosions, with the temperature skyrocketing to 500°C and 370 °C, respectively, when subjected to nail penetration tests (Figure 13b). The results emphasize the importance of the rational design of electrolyte composition and controlling of the Li plating morphology for enhancing the safety of Li metal pouch cells. Also, even Li metal pouch cells with concentrated electrolytes are not safe enough over longterm cycling.

4.2.5. Rate capability improvement

Despite the poor rate particularly charge rate capability, high rate pouch-type LMBs have been reported in some recent literatures. To access the high rate capability, good kinetic of electrolyte is of essence. This requires electrolyte has high ionic conductivity, transference number and good de-solvation kinetic. Recently, a novel asymmetric Li salt with high donor number and diploe moment was reported,^[42]



Figure 13. Improving the safety of Li metal pouch cells by reducing the reactivity of Li with electrolytes. a) Safety test of cycled electrodes submerged in water. The electrodes were cycled in different electrolytes as shown in the figure. b) Temperature vs. time profiles of cycled pouch cells during the nail test using different electrolytes. Copyright 2020, Macmillan Publishers Ltd.^[27]

which could increase the transference number of carbonate electrolyte. Besides, it facilitates the formation of inorganic-rich SEI through a self-clean mechanism that dissolve the organic species in the SEI. With the high transference number and inorganic-rich SEI, Li metal pouch cell exhibits a good rate capability, demonstrating up to 1 C charge/discharge rate with 5 cycles in the rate test, and a 0.4/1 C charge/discharge rate for the long-term cycling.

Even high charge rate for the long-term cycling has also been reported recently. Xie et al. reported the supergravity enables the improved performance of Li metal pouch cells at high rate.^[63] They found that by applying supergravity corresponding to 50 gravity coefficient (G), the interaction between Li⁺ and anions is strengthened, which promotes the production of LiF and inorganic-rich SEI formation. Therefore, Li metal pouch cell can operate 200 cycles at a high 2 C charge/discharge rate.

5. Perspectives on the development of Li metal pouch cells

In summary, great progress has been made on the understandings of the chemical and morphological evolution and the degradation mechanisms of electrolytes and electrodes in Li metal pouch cells in the past few years. Meanwhile, pouch-type prototype LMBs with liquid and solid-state electrolytes have been demonstrated with high energy densities of up to 500 Whkg⁻¹ and extended cycle life (typically 50–200 cycles, with an exception of 1000 cycles). However, many open questions concerning the mechanistic understandings remain to be resolved. Besides, the cycling stability and cycle life of Li metal pouch cells remain unsatisfactory, and its safety is still threatened by Li dendrite, gassing and the resultant cell swelling. And only a few solid-state LMBs have reported the energy density based on the mass of all cell components including package. Other challenges like the poor rate capability also limit the applications of Li metal pouch cells in practice.

In the future R&Ds of Li metal pouch cells, new insights into the degradation and failure mechanism and tremendous advances on the cell performance are in pressing demand. Below we list the most important requirements of Li metal pouch cells and provide our perspectives on the potential solutions to their realization.

5.1. Requirements for future Li metal pouch cells

(1) Boosting the energy density towards $> 500 \text{ Wh kg}^{-1}$ and lifespan > 1000 cycles. Li metal pouch cells for practical applications are anticipated to simultaneously offer a high energy density of $> 500 \text{ Wh kg}^{-1}$, a long lifespan of > 1000cycles (with 80 % capacity retention). Previous reports have shown that LMBs can exceed 500 Wh kg⁻¹ at the cell level, which is nearly two-fold of the state-of-the-art LIBs ($\approx 300 \text{ Wh kg}^{-1}$). However, a satisfactory lifespan (>1000 cycles) of 500 Wh kg⁻¹ Li metal pouch cells is highly required for many practical applications such as consumer electronics. To achieve this, it is necessary to enhance the CE of Li plating/stripping towards >99.9 %.

(2) Marginal cell swelling and good cycling performance under low stacking pressure. Currently, implementing controlled and high stacking pressure (>10 MPa) has been commonly applied onto pouch cells during electrochemical testing in research labs to maintain intimate interfacial contact and to minimize the cell swelling, which effectively improves the performance of Li metal pouch cells. In comparison, the lifespan of Li metal pouch cells without external pressure remains poor (<50 cycles), and the cell swells drastically (e.g., from 2.7 mm to 4.7 mm after cycling^[17]), due to the formation of much porous Li metal anode during cycling. However, the application of external pressure requires additional tools and thus has poor feasibility in practical applications. Overall, compact Li deposition and a minimal swelling (<20%) of pouch cells free of stacking pressure is highly desired.

(3) Improving safety, especially at the module/pack level. The safety of Li metal battery module/pack, which consists of many Li metal pouch cells closely packed together, is of vital importance, since high energy and tremendous explosive materials in module can cause much more severe safety hazards than a single cell. Moreover, the failure of one cell may cause the explosion of the whole module/pack. At the cell level, the swelling, flaming and explosion of cells are concerning for the safety issues. Compact Li deposition which facilitates small swelling of pouch cells is desired and yet realized. Meanwhile, the gas evolution especially at elevated temperatures and overcharge conditions should be mitigated. In addition, non-flammable and stable electrolytes against Li can also promote the safety of Li metal pouch cells. Solid electrolytes might be one of the most promising solutions to promoting the safety of practical Li metal pouch cells. In addition to the strategies for improving safety, the safety standards for LMBs should also be established. Herein, safety standards for LIBs can be taken

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as reference (such as non-flammability and non-explosion at $130 \,^{\circ}$ C for 30 min; non-flammability and non-explosion at 55 $\,^{\circ}$ C upon short-circuit; resistance to overcharging for 2 h).

(4) Fast-discharging capability at >5 C and charging capability >2 C. The discharging capability which determines the output power density is also an important parameter for Li-based batteries, especially those used in electric vehicles and unmanned aerial vehicle. High discharging capability of >5 C with high capacity retention (> 80% compared with 0.1 C) is desired for enhanced user experience of Li metal pouch cells. Meanwhile, charging capability of >2 C is particularly needed for electric vehicles.

(5) Wide working temperature range between -20 and 40 °C. Most of the reported Li metal pouch cells were tested at a constant temperature of 25 °C inside a climate chamber, which, however, is not viable for practical applications. Operation under a realistic (e.g., fluctuating) temperature condition is essential. Moreover, the working temperature of Li metal pouch cells need to be widened between -20 and 40 °C which is commonly used for the testing of pouch-cell LIBs.

(6) Self-discharge and calendar life need more research attention. Considering that pulverized and porous growth of highly reactive Li is inevitable on Li metal anode, selfdischarge of Li metal pouch batteries is probably one of the most challenging problems for practical application. Selfdischarge leads to significant capacity degradation, and thus reduces the calendar life. Nevertheless, calendar life is one of the most important performance indexes for electric vehicle batteries that is usually neglected by researchers. More attention is needed on the study of the critical characteristics of batteries under practical conditions to accelerate the application of Li metal batteries.

(7) Sustainability should be considered. Material and energy sustainability is crucial for our modern society and economy. Currently, tremendous efforts on LMBs go to NCM cathode materials, due to its higher operating voltage and better cycling stability compared with conversion cathode materials such as S and O₂. Meanwhile, fluorinerich electrolyte is a prevalent choice for stabilizing LMBs. However, the Co resource is globally limited and fluorine is highly toxic, which compromises the sustainability. Therefore, Li–S and Li–O₂ batteries with high material abundance and better compatibility with low-fluorine electrolyte deserve more considerations as future energy storage solutions. Co-free high-voltage cathode materials such as LFP and LiNi_{0.5}Mn_{1.5}O₄ (LNMO) are also more sustainable alternatives to NCM.

5.2. Deepening the mechanistic understandings of Li metal pouch cells

(1) Li plating/stripping behavior. To understand the mechanism of Li plating/stripping, the Li nucleation, growth and dissolution processes under different operating conditions (e.g., temperature, stacking pressure, electrolytes, and electrochemical protocols) need to be systematically investigated



in order to conclude the thermodynamic and kinetic factors influencing the morphology of Li deposits and stripping behaviors. Particularly important is to elucidate the role of SEI in shaping Li deposits.

(2) Degradation/Failure mechanism. The past research on Li metal pouch cells have focused on the cycling stability, while the degradation and failure mechanisms with different cell parameters (including electrode materials and electrolytes, areal capacity, N/P ratio, and E/C ratio, etc.) and under various operating conditions (including temperature, pressure, charge and discharge protocols, etc.) are to be identified through comprehensive and in-depth investigations. In particular, understanding of the degradation mechanisms of conversion-type cathode materials (e.g., S and O₂) requires intensive further investigations. Moreover, the self-discharge and aging effects during shelf life remains unexplored, which could be revealed through e.g., operando electrochemical impedance spectroscopy (EIS) over longterm rest periods coupled with advanced material characterization methods.

(3) Monitoring of the dynamic evolution of cell components. The chemistry of electrolyte and the compositions and morphologies of electrodes and interphases evolve from time to time during cycling. Advanced in- & ex situ and operando techniques, such as cryogenic electron microscope (cryo-EM), in situ scanning and transmission electron microscope (STEM), NMR, X-ray spectroscopy (e.g., XAS and Xray photoelectron spectroscopy (XPS)) and operando X-ray microscopy (e.g., X-ray computed tomography (XCT) and transmission X-ray microscopy (TXM)), are required to elucidate the dynamic morphological and chemical evolution of cell components during cycling. In particular, the

evolution of electrode-electrolyte interphases should be precisely deciphered.

5.3. Rational design of future Li metal pouch cells

(1) Strategies for improving the key performance criteria of Li metal pouch cells. Li metal pouch cells fulfilling the high energy density, good stability & cycle life, and safety are highly desirable for future applications. Figure 14 shows the viable strategies to improve the performance and safety of Li metal pouch cells. Specifically, thin Li and lean electrolyte are prevalent strategies to increase the energy density, and interfacial engineering is a common approach to improve the interfacial stability of Li metal anode and cathode and thus the stability of pouch cells. 3D structuring of Li electrodes can facilitate uniform Li deposition and accommodate the volumetric change, which improves the cell safety by suppressing the cell swelling. Utilization of solidstate electrolytes can improve the cell safety since they are non-flammable, and the use of thin solid-state electrolyte film can increase the energy density of cells. Enhancing the lithiophilicity of Li metal anodes and interfaces which promotes uniform nucleation of Li could suppress growth of Li dendrites and depletion of electrolyte, which improves the stability of Li metal anode and pouch cells and facilitates the use of thin Li and lean electrolyte for enhancing the energy density of Li metal pouch cells.

(2) Stabilization of electrode-electrolyte interfaces. Stable electrode-electrolyte interfaces are essential for the stable cycling of Li metal pouch cells. One common solution is to modify the electrolyte formulation, e.g., using concen-



Figure 14. An overview of the strategies for improving the energy density, stability & cycle life, and safety of Li metal pouch cells.

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trated electrolytes^[172] and electrolyte additives (e.g., fluorinated carbonate ester,^[174] LiNO₃,^[175] polysulfides,^[176] etc.), to facilitate the formation of stable SEI and CEI, effectively suppressing dendritic Li growth and mitigating cracks and phase transformation of cathode materials. Another important way to stabilize the electrode-electrolyte interfaces is to construct artificial interfaces, which have been widely used to improve the interfacial stability, especially against Li metal anode, and could be further functionalized to enhance the lithiophilicity and structural stability of electrodes. On the anode side, the Li metal can be coated with a polymeric and Li-ion conducting film as an artificial film to mitigate Li metal from exposure to liquid electrolytes, suppressing the continuous SEI formation and enhancing the cycling stability. Meanwhile, the polymeric film could improve the operational safety of Li metal pouch cells through alleviating the volumetric change of Li metal anode during the cycling of pouch-type cells, which has been adopted by the SES company, and guiding the Li-ion flux at the interface, which would suppress localized Li deposition and growth of Li dendrites. Note that polymeric materials with good reductive stability are required to avoid severe decomposition and vigorous reactions with Li metal. On the cathode side, surface coating of cathode materials, e.g., coating NCM particles with Li₃PO₄,^[177] has demonstrated great promise in enhancing the stability of cathode materials and the interface with electrolytes.

(3) 3D structured Li metal anode. 3D Li anode is a composite of Li metal and a 3D nanostructured Li-host. The 3D host should be electrically conductive and lithophilic (such as a carbon or metallic nanostructures with lithiophilic coating^[178]) to facilitate the homogeneous Li deposition and to accommodate the volumetric change upon Li plating/ stripping, which could be a solution to high-rate and low-swelling Li metal pouch cells. However, large-scale manufacturing of 3D Li anode remains challenging. Compared to the reported methods of Li pre-electrodeposition and high temperature Li infiltration, mechanical rolling exhibits better viability for industrial applications.

(4) Optimization of cell design and parameters. The realization of Li metal pouch cells in practice also requires the rational cell design and optimization of the cell parameters. (i) Many cell parameters have to be considered in the rational design of Li metal electrodes and batteries, such as the geometry of pouch cell format, the number of electrode layers, the areal capacity, thickness and porosity of electrodes. (ii) The position and number of electrical tabs should be optimized to promote the uniformity of the current density and heat distribution. The overhang between separator and anode should be maintained to improve the safety. (iii) The N/P ratios and E/C ratios should be optimized. As discussed in Section 2.4, excess Li and flooded electrolyte would reduce the energy density, while thin Li and lean electrolyte cause rapid failure of Li metal pouch cells. Optimizing the N/P and E/C ratios, e.g., by adjusting the thickness of Li foil and the amount of electrolyte, is required for balancing the cycle life and energy density of Li metal pouch cells.

(5) Solid-state Li metal pouch cells. SSLMBs that utilize mechanically strong, electro-/chemically stable and non-flammable solid-state electrolytes may be the ultimate solution to overcome the critical obstacles related to pouch-type Li metal batteries. The realization of energy-dense pouch-cell SSLMBs requires the utilization of thin and robust solid electrolytes.

(6) Non-flammable and flame-retardant materials for cell production. The utilization of non-flammable materials for fabricating Li metal pouch cells, such as flame-retardant separator and current collector, electrolyte retardant additives, and fire-proof packing materials, are required to further enhance the safety of Li metal pouch cells.

(7) Enhancement of processability and manufacturability. It is highly desired to enhance the production and processing of thin (e.g., $<20 \ \mu\text{m}$) Li electrodes in a scalable way. Meanwhile, roll-to-roll (R2R) preparation of largearea solid electrolyte films, especially brittle ceramic inorganic solid electrolytes with a thickness of $<50 \ \mu\text{m}$, is crucial for realizing energy-dense solid-state Li metal pouch cells.

(8) Optimization of cycling protocols. External conditions, such as stacking pressure and temperature, and cycling protocols (e.g., pulse charge, voltage range, and current rate) of Li metal pouch cells should be systematically investigated to optimize the cycling protocols for improving the cycling performance and safety.

(9) Establishment of battery monitoring and management system. A reliable monitoring and management system is to be developed to monitor the state (e.g., temperature, internal pressure, stress, instant charge/discharge voltage, etc.) of cells under operation, to determine the time-node for the scrapping of unhealthy cells, and to cut-off the link between the abnormal cell(s) and other cells for preventing sudden and severe safety hazards.

All in all, the problems of Li metal pouch cells are complicated, and it is unlikely to resolve all the challenges and to simultaneously improve their key performance criteria through a single strategy. Mechanistic understandings and novel practical strategies have been developed to stabilize the cell performance and to enhance the operational safety, but significant further R&Ds are still in pressing demand to simultaneously achieve Li metal pouch cells with high energy density, good cycle life and safety. What is of particular importance and urgency is to gain new and comprehensive mechanistic insights into the operating and degradation mechanisms of Li metal pouch cells to guide rational materials and cell deign, which requires advanced and integrated operando and post-mortem characterization techniques accompanied with theoretical computations and simulations to comprehend the electrochemical behaviors of Li metal pouch cells on various levels (including atom-, material-, electrode- and cell-level) at all relevant time- and length-scales during battery operation. Tremendous and joint efforts on experimental and theoretical methods are required to minimize and bridge the gap between the fundamental research and practical applications of Li metal pouch cells.



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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Energy Density · Lithium Metal Anode · Lithium Metal Battery · Mechanistic Understanding · Pouch Cell

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