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Published in:
ACS Energy Letters

DOI (link to publication from Publisher):
10.1021/acsenergylett.4c03578

Publication date:
2025

Document Version
Publisher's PDF, also known as Version of record

Citation for published version (APA):
Guo, J., Li, P., Piccolo, F., Jie, Y., Jia, H., Cao, R., Jiao, S., Adelhelm, P., & Xu, Y. (2025). Degradation and Failure Mechanisms of Lithium/LiNi$_x$Co$_y$Mn$_{1-x-y}$O$_2$ Batteries. *ACS Energy Letters*, *10*(5), 2318-2340. https://doi.org/10.1021/acsenergylett.4c03578

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Degradation and Failure Mechanisms of Lithium/$\mathrm{LiNi}_x\mathrm{Co}_y\mathrm{Mn}_{1-x-y}\mathrm{O}_2$ Batteries

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Cite This: *ACS Energy Lett.* 2025, 10, 2318−2340

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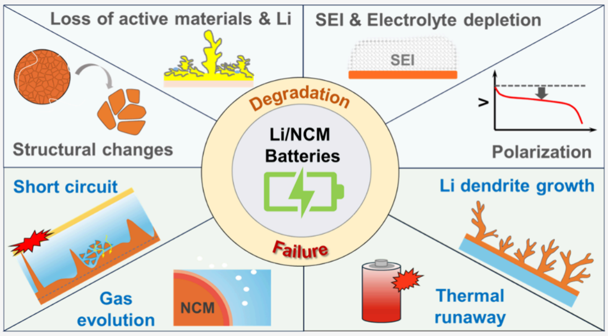
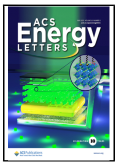
ABSTRACT: **Lithium (Li)/$\mathrm{LiNi}_x\mathrm{Co}_y\mathrm{Mn}_{1-x-y}\mathrm{O}_2$ (NCM) batteries are considered one of the most promising battery technologies for next-generation energy storage, but their commercial viability is still hampered by rapid capacity decay and safety concerns. Recently, the mechanistic understanding of Li/NCM battery degradation and failure processes has made significant progress thanks to advances in battery diagnostics and analysis. Herein we comprehensively review the current understanding of Li/NCM battery degradation as a function of the type of electrode materials, electrolytes, packaging formats, and cycling conditions, and discuss the degradation mechanisms related to the interplay between the Li metal anode and the NCM cathode. We also review the safety threats and eventual failure of Li/NCM batteries and their root causes. Moreover, we provide our perspectives on the future research necessary to gain a more complete understanding of the degradation and failure of Li/NCM batteries.**



Lithium (Li) ion batteries (LIBs) are the dominant energy storage technology in portable electronics and electric vehicles.[1,2] The excellent energy density and cycle life of LIBs has enabled their widespread use, while the search for more sustainable and energy-dense battery chemistries continues to drive the battery revolution as the market share of electric vehicles continues to grow.[3] As shown in Figure 1a, Li-ion storage materials with relatively low redox potential (typically < 2.0 V vs Li^+/Li), such as lithium titanate,[4] graphite,[5] silicon,[6] and Li,[7] are generally employed as the anode for Li-based batteries. Graphite is used in virtually all commercial LIBs thanks to its overall best trade-off in capacity, redox potential, and lifetime. Lithium titanate has been commercialized too, but the high redox potential of about 1.5 V vs Li^+/Li leads to a low energy density. Its use is therefore restricted to niche applications, see, e.g., the SCiB technology from Toshiba.[8] Due to its very high capacity, the use of silicon is being intensively researched, but the large volume expansion during lithiation limits cycle life and, for now, it can only be used in small amounts as an additive to graphite electrodes.[9] Among alternative electrode materials, Li metal has the lowest redox potential and a theoretical capacity ten times higher than that of the graphite anode in current commercial LIBs, which would thus increase the energy density by up to 60% at the cell level,[10] depending on the thickness of the Li metal. Among the cathode materials for Li-based batteries, LiFePO_4[11] has seen a significant diffusion in the market thanks to its modest cost, lack of critical elements, and high safety, but its low capacity (170 Ah kg^{-1}) limits its use in applications for which high energy densities are critical. Transition metal oxides, LMO_2[12] (M = Ni, Co, Mn), thanks to a wide redox potential window (between 2.9 and 4.6 V) and high capacity (up to 270 Ah kg^{-1}), significantly outperform other commercial cathodes.

The combination of a Li metal anode with a $\mathrm{LiNi}_x\mathrm{Co}_y\mathrm{Mn}_{1-x-y}\mathrm{O}_2$ (NCM) cathode could then be a promising strategy to maximize battery energy density.[13,14] Specifically, Li/NCM batteries (Figure 1b) can result in an output energy density exceeding 700 Wh kg^{-1}, almost three times that of state-of-art commercial LIBs (250 Wh kg^{-1}).[14] Therefore, the development of Li/NCM batteries with both liquid electrolytes (LEs) and solid electrolytes (SEs) for next-generation energy storage has attracted intensive research efforts.[15,16] However, these batteries still face tremendous challenges, such as limited cycle life and significant safety concern, when compared to the LIBs we have nowadays.[17,18] (Figure S1 and Tables S1 and S2)

Received: December 27, 2024
Revised: March 25, 2025
Accepted: April 4, 2025
Published: April 15, 2025



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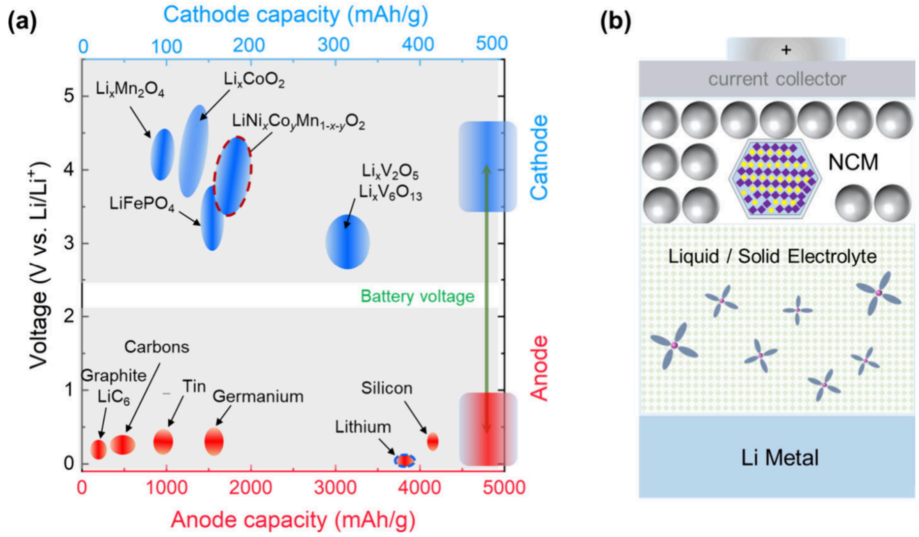

Figure 1. (a) Redox potentials and capacities of various cathode and anode materials.[19] Reproduced with permission from ref 19. Copyright 2009 Royal Society of Chemistry. (b) Schematic of a Li/NCM battery with a liquid or solid electrolyte (LE/SE).

In this Review, we provide a comprehensive review of the current understanding of the degradation and failure mechanisms of Li/NCM batteries based on both LEs and SEs, as well as the issues that they face in commercial pouch-cell applications. Although many review articles have been published on the mechanisms of Li metal anodes, NCM cathodes, and Li/NCM batteries, most focus on a single component (cathode, anode, or electrolyte). Mechanistic understanding of Li/NCM batteries under different battery designs and operating conditions remains relatively limited. Moreover, we provide perspectives for gaining new and deeper mechanistic insights into cell degradation and failure processes.

To understand the battery degradation and failure mechanisms, it is essential to consider the detailed influences of different battery materials (cathode, anode, and electrolyte), battery designs (coin cell, prismatic cell, and pouch cell), and operating conditions (e.g., current density, cutoff voltage, temperature, and stacking pressure).

■ FEATURES AND DEGRADATION OF LI/NCM BATTERIES

Features and Degradation of LE-Based Li/NCM Batteries. The performance of Li/NCM batteries is influenced by the battery chemistry (e.g., NCM stoichiometry, electrolyte formulation, and interlayer), cell format (e.g., coin- and pouch-cell), and configuration (e.g., anode-free, electrolyte-to-capacity (E/C) ratio, and negative-to-positive capacity (N/P) ratio), cycling protocols (e.g., dis-/charge cutoff voltages, C-rate, and pulse current charging), and external conditions (e.g., temperature, stacking pressure, battery use case, and customer habits) (Figure S2). For instance, nickel-rich NCM is increasingly favored for its higher capacity, but at the same time it is also prone to more severe degradation, mainly due to the rapid deterioration of the electrode structure, as well as side reactions between the cathode, electrolyte, and Li metal anode at high voltage, which together lead to the rapid decline of the entire battery. The same promise and issue apply also for the anode-free Li metal electrode due to the great volume change and zero-excess materials to compensate for the Li loss. Similarly, increasing the battery charge cutoff voltage to boost capacity, e.g., up to 4.7 V, increasing the C-rate, nowadays limited to 0.1 to 1 C, or raising the temperature leads to more severe capacity decay.[20] Regarding the cell format and configuration, significant efforts have been directed toward advancing Li/NCM batteries for prototyping, for which the amount of electrolyte and the thickness of the Li anode are minimized to maximize the energy density and minimize costs. However, the lifetime of these batteries remains poor, and most of them merely achieve a cycle life of <100 cycles. Finally, in the past years, intensive research efforts to engineer the materials and the interfaces of Li/NCM batteries, for instance, the use of 3D structured[21] and/or Li-composite electrodes,[22] surface-coated Li,[23] and NCM electrodes[24] have led to a further increase in the variability and complexity of the degradation mechanisms.

Features and Degradation of Solid-State Li/NCM Batteries. Compared to LE-based cells, there has been significantly less research on Li/NCM solid-state batteries (SSBs), with the majority still at lab scale. Reflecting this novelty, the SSB field still lacks a common platform when it comes to experimental setups and testing procedures, making a comparison between different studies often difficult, a problem highlighted in recent interlaboratory studies.[25,26] Studies investigating the operation of batteries under conditions different from these are rare. In particular, SSBs have always been expected to tolerate higher current densities and a wider operating temperature range compared to LIBs, but to date, this has not been tested for solid-state Li-metal/NCM batteries. The two most popular anodes in Li/NCM SSBs are Li foils and Li−In alloys, with other anode types (e.g., anode-less and other alloys[27]) being less common and yielding limited conclusions.[28,29] At the cathode, many NCM compounds have been explored as active materials (AM).

There is strong interest in reducing (and eventually eliminating) the carbon additives as they lower the specific capacity of the cathode and cause oxidative degradation of inorganic SEs.[30]

To understand the mechanisms involved in the degradation and failure of these batteries, it is important to first categorize them into different classes according to the employed SEs. We can divide the SEs into two families: solid polymer electrolytes[31] and inorganic solid electrolytes.[32] Although significant variations exist within each category, SEs within the same family generally share similar working mechanisms and failure modes. In contrast, the differences between these two categories are substantial. Here, we will not delve into the specific degradation mechanisms of composite SEs, such as polymer-inorganic composite electrolytes[33] and gel-polymer electrolytes,[34] as for them, being composites of different electrolytes, the degradation and failure mechanisms can be mostly traced back to a sum of their individual ones.

It is usually hard to assign the degradation of a Li/NCM SSB to any single mechanism, as multiple simultaneous processes contribute to the degradation of the system, often interacting and reinforcing each other in nonlinear ways.[35] Based on the most evident causes and/or effects, we can classify these processes in (i) Mechanical processes, caused mostly by the imperfect contact between solids and whose effects are primarily physical in nature. Examples include the growth of dendrites at the anode and mechanical stress in the cathode; (ii) Electrochemical processes caused by the reactivity of the electrolyte with the active and/or conductive materials in the cell during normal operation. Note that issues related to the chemical stability of SEs[36−38] happen mostly outside of its normal operation, e.g., during battery assembly or storage (i.e., shelf life) or when in contact with air and/or moisture upon damage, and are therefore out of the scope of this article.

> *To advance Li/NCM batteries toward practical applications, it is crucial to promote interdisciplinary and collaborative research, joining efforts between academia and industries, integrating cutting-edge and emerging experimental and computational methods, and establishing a platform for data share to further and deepen the understanding of the degradation and failure mechanism of Li/NCM batteries toward performance improvement.*

Failure of Li/NCM Batteries. Both LE- and SE-based cells inevitably degrade over time and with use. Battery failure can stem from internal processes, like aging, which may lead to a gradual decrease in the battery's remaining capacity,[39] or external factors, such as improper use, which may instead lead to failures such as short circuits,[40] overcharging or over-discharging,[41] and swollen batteries.[42]

Battery failure caused by degradation processes like aging typically results from the impedance increase and the loss of positive and negative electrode active materials, which have the combined effect of decreasing capacity and increasing overpotentials.[43] A more hazardous failure is a battery short circuit,[44] which can occur due to dendrites growing from the surface of Li metal until they puncture the separator and make contact with the cathode.

Battery volume expansion is a common indicator of this type of failure, with the expansion occurring due to gas generation, typically from electrolyte decomposition or the release of

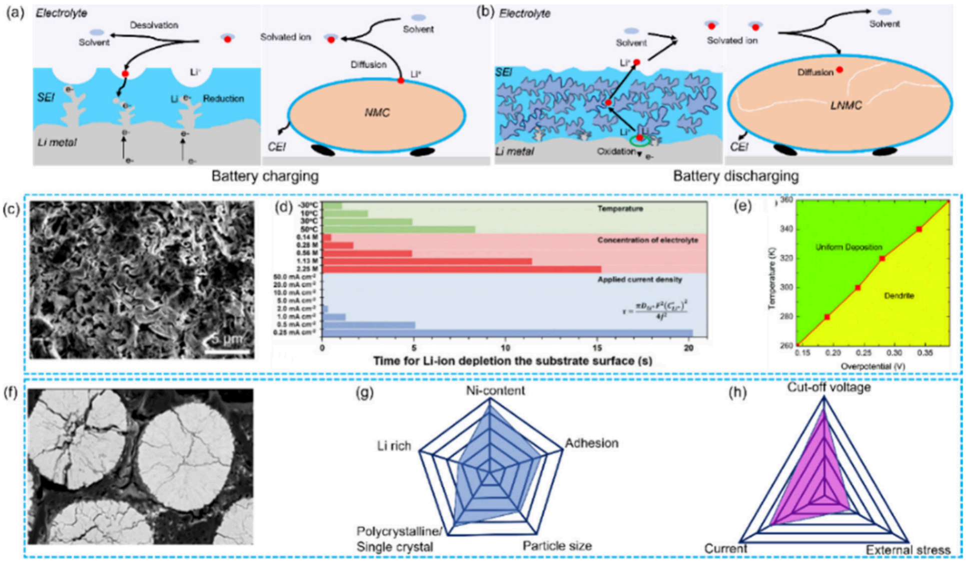

Figure 2. Increasing polarization of Li/NCM batteries related to structure changes of the Li and NCM electrodes. (a) Battery charging. (b) Battery discharging. (c) SEM image of plated Li metal.[16] Reproduced with permission from ref 16. Copyright 2019 Cell Press. (d) Time for Li-ion depletion the substrate surface in the influence of temperature, electrolyte concentration, and current density.[59] Reproduced with permission from ref 59. Available under CC-BY 4.0. Copyright 2020 Wiley. (e) Dendrite formation in function of temperature and overpotential.[56] Reproduced with permission from ref 56. Copyright 2018 Royal Society of Chemistry. (f) The SEM image of cracks in the cathode.[60] Reproduced with permission from ref 60. Copyright 2019 American Chemical Society. Crack formation as a function of (g) intrinsic factors of the cathode and (h) external factors.

oxygen from cathode materials,[45] or electrode thickening, primarily involving the Li metal anode.[46]

DEGRADATION MECHANISMS OF LI/NCM BATTERIES USING LES

During the charging process of LE-based Li/NCM batteries (Figure 2a), Li-ions are extracted from the NCM positive electrode, get solvated by the electrolyte solvent molecules, and migrate through the electrolyte toward the negative electrode. They are then desolvated and reduced to Li depositing on the anode surface. Due to the high reactivity of Li, the solvent molecules react vigorously with the Li metal deposits forming an inhomogeneous (in terms of thickness and composition) solid electrolyte interphase (SEI) film.[47] The diffusion of Li-ions through this layer strongly depends on the local composition and morphology, being faster where the SEI is thin or more Li-ion conductive and slower otherwise, resulting typically in an inhomogeneous Li deposition.[48,49] In the meantime, electrons tend to concentrate on the tips of nonuniform Li deposits due to the altered electrical field at the tips, inducing their fast growth and eventually an uncontrollable Li dendrite formation.[50] During the battery discharge process (Figure 2b), the reverse process happens, with Li-ions being stripped from the anode, transferred through the electrolyte, and then stored in the NCM cathode. During Li stripping, the dendrite root may become thinner and thus exhibit a higher local current density compared to the larger part of the tip, promoting the detachement of the dendrite from the bulk metal and its coverage by an insulating SEI film. This is also described as the formation of "dead" Li.[51] In addition to the specific issues of the individual electrodes, new problems emerge from their combined use, the interplay between the degradation processes of Li metal anode and NCM cathode. For instance, transition metals of the NCM cathode can dissolve into the electrolyte and get deposited on the Li metal surface, destabilizing the SEI layer and increasing the interfacial resistance. Moreover, the high redox potential of NCM leads to oxidative electrolyte decomposition with the formation of acidic compounds which also attack the Li metal anode, aggravating and complicating the SEI formation. These electrochemical processes lead to capacity degradation during cycling due to the following degradation processes.

Increased Polarization. During operation, the deviation of the terminal voltage from the equilibrium potential is known as battery polarization. As a battery ages, polarization increases, which can lead to capacity fading as the battery prematurely reaches its cutoff voltage.[52] Battery polarization is influenced by the characteristics of battery materials, dis-/charge protocols and external factors (e.g., temperature).[53]

As shown in Figure 2c, the accumulation of "dead" Li and interphases on the Li electrode surface not only inhibits the fusing of Li metal grains, leading to an increase in porosity, but restricts Li-ion transport at the grain boundaries.[54] At the same time, the thickness of the porous Li metal gradually increases, extending the path of Li-ion diffusion and reducing the kinetics for charge transfer.[54] As the mass transfer (i.e., Li-ion diffusion) is more sluggish than the electron transfer, this causes Li-ion depletion at the electrode surface which, coupled with the gradual building up of the SEI film from the reduction reaction of the solvent, further exacerbate the unevenness of Li deposition and eventually raises the electrode polarization.[3] Moreover, the unstable porous structure is prone to electrode pulverization upon repetitive Li deposition and stripping processes, which hinders electron transport as well.[3] All these mechanisms lead to impedance growth at the anode side.[54]

This process is influenced by several parameters. For example, using electrolytes with low Li salt concentration, high viscosity, or low ionic conductivity or cycling the cell at a low temperature further slows down Li-ion transport, while raising the applied current density to the battery, the concentration distribution of Li ions within the electrolyte becomes nonuniform.[55] This intensifies the polarization of the electrode interface and contributes to a more pronounced and irregular deposition of Li (Figure 2d). Hao et al.[56] found that a high overpotential promotes the growth of Li dendrites, while increasing the temperature allows for more uniform plating (Figure 2e). A number of composite anodes such as Li−C, Li−Ni, and Li-reduced graphene oxide have been explored, which utilize 3D skeletons, to decrease local current density, and thus reduce the overpotential for Li nucleation/growth, promote uniform Li plating/stripping, and eventually lower the electrode polarization during cycling.[57,58]

Polarization related to NCM cathodes, along with the mechanical degradation of the cathode material caused by NiO rock salt phase evolution and crack formation,[61] also leads to an increase in the battery's internal resistance. These deterioration processes are determined by the intrinsic properties of the NCM particles. As shown in Figure 2f, polycrystalline NCM cathodes are prone to crack along the primary particles' borders. This phenomenon is affected by both internal and external factors. For internal factors (Figure 2g), increasing the nickel content also increases the volume variations during cycling, causing greater mechanical stress, which ultimately results in more cracks inside cathode particles.[60,62,63] Besides, the particle crack formation is also related to the primary particle size, adhesion between particles, and single crystallinity or poly crystallinity.[64,65] The increase in primary particle size significantly reduces grain boundary resistance and is beneficial for the diffusion of Li ions, but makes it more difficult to release mechanical stresses, thus increasing the susceptibility to crack formation. As the adhesion between primary particles decreases, NCM secondary particles are also more prone to produce cracks.[66,67] Single crystal materials are less prone to crack formation because there is no agglomeration of primary particles.[65,68] Besides, crack formation is also related to battery operating conditions. High currents, high cutoff voltages, and external pressure produce more internal stress on the battery and can accelerate the process (Figure 2h).[69]

The formation and thickening of interface films on electrodes cause the internal resistance of the battery to increase as well. The SEI is brittle and prone to rupture due to the volume expansion of the electrode, thus leading to its continuous growth. The species on the Li metal SEI includes organic compounds, like ROLi, RCOOLi, ROCOLi, $RCOO_2Li$, and $ROCO_2Li$ (R = alkyl groups), and some inorganics, such as LiOH, LiF, Li_2O, and Li_2CO_3.[49] It has been reported that organic components of the SEI are more mechanically stable than the inorganic phases, but much less Li-ion conductive.[70] As the SEI layer thickens, diffusion of Li-ions becomes increasingly hindered. In addition, uneven Li deposition followed by stripping exposes a greater area of porous and freshly formed Li metal to the electrolyte, resulting in the accumulation of inactive "dead" Li and subsequent electrode pulverization, which can increase both the electrode volume and surface resistance. Similarly to the SEI on the Li

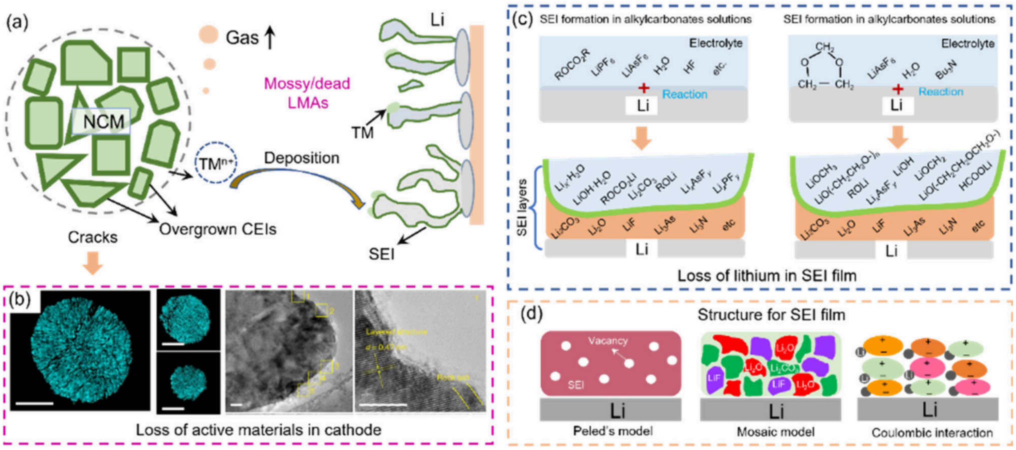

Figure 3. (a) Loss of active materials and loss of Li ions.[77] (b) Loss of active materials and structure change for cathode.[77] Reproduced with permission from ref 77. Available under a CC-BY 4.0. Copyright 2021 Springer Nature. (c) Side reactions and interface film formation process.[70] (d) Three SEI structure models for a Li metal battery.[70] Reproduced with permission from ref 70. Available under a CC-BY 4.0. Copyright 2015 Wiley.

metal anode, a cathode electrolyte interphase (CEI) grows on the positive electrode, which results from the reactions between the cathode and the electrolyte, especially when charged to a high voltage.[71] The CEI composition is similar to the SEI, as it is composed of Li_2CO_3 and alkyl carbonates oxidized from the electrolyte solvent, and $Li_xPO_yF_z$ oxidized from the electrolyte salt.[72] The formation of SEI and CEI typically leads to a slow but steady increase in resistance and hence electrode degradation. Moreover, SEI- and CEI-forming reactions consume the electrolyte, causing the battery to dry out and fail prematurely.[73,74]

Loss of Active Materials (LAM) and Loss of Li (LLI). The battery capacity is directly determined by the capacity of the electrodes; therefore, any loss of electrochemically active material in the cell is directly linked to a capacity loss. On the anode side, this loss is mostly caused by SEI formation and formation of dead Li. On the cathode side, an important degradation mechanism is the dissolution of transition metals, i.e., the loss of the redox sites. These two processes, are connected.[54] When cycling, especially at high temperatures, transition metal elements are dissolved into the electrolyte and deposited on the anode surface, a process promoted by acids such as the HF derived from degraded electrolyte salts (e.g., $LiPF_6$ and LiTFSI).[75,76] Such solvation-migration-deposition process not only causes the loss of cathode material, but also the destabilization of the SEI by the transition metal deposition on the anode surface, resulting in further SEI formation and hence loss of anode active materials (Figure 3a).[77] The loss of active material is promoted also by the cathode particles crackdue to the large volume changes in the unit cell during de/lithiation caused by the lattice anisotropy along the c-direction (Figure 3b) . The *c*-lattice parameter in fact initially increases due to the reduced electrical shielding effect of fewer Li ions and the concomitant increase in repulsive force between the transition metal oxide layers. The subsequent rapid contraction and collapse of the lamellar structure is caused by charge transfer between the O and Ni bands, which leads to a decrease in the effective O charge and its repulsive strength.[78] At the same time, the oxygen release from the lattice and the reduction of reactive high-valent substances (e.g., Ni^{4+}) to more stable Ni^{2+} can additionally lead to cation mixing, where transition metal (TM) ions migrate to vacant Li sites.[79] In particular, Ni^{2+} has a high tendency to occupy the Li^+ site due to their similar ionic radii, causing the Li^+/Ni^{2+} cationic mixing and increasing Li^+ diffusion impedance.[80] Both effects lead to a transition from lamellar to spinel and finally to rock-salt type phases. The latter consists of low-valent TM oxides (e.g., NiO) that are soluble in the electrolyte. The released oxygen moreover contributes also to the decomposition of electrolyte, which leads to the formation of H_2O,[81] which hydrolyzes $LiPF_6$ salts producing HF, which in turn leads to the formation of slightly soluble MF_2 (M = Mn, Co, Ni) compounds.[76]

Similarly, at the anode, the inhomogeneous electrochemical dissolution process of Li metal induces electrode pulverization and the formation of "dead" Li. The "dead" Li, defined as Li totally encapsulated by the electronically insulating SEI, loses electrical contact with the rest of the anode and therefore cannot participate in the subsequent electrochemical reactions.[16] The combined formation of SEI and "dead" Li causes the loss of Li^0 and the capacity fade, although dead Li can potentially be reactivated in some cases.[82] Next to the Li^0 loss, the loss of Li^+ also occurs, e.g., due to the irreversible SEI/CEI formation.[83] When a current is applied and/or simply when Li metal is exposed to the electrolyte, Li rapidly reacts with electrolyte species, typically within milliseconds (Figure 3c),[70,84] as the reduction potentials of the common organic electrolyte solvents, including ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), and ethylmethyl carbonate (EMC), are all below 1.0 V (vs Li^+/Li).[85] The mechanism of SEI formation on Li metal anodes and its composition depend on numerous parameters and are subjects of considerable controversy. These parameters include electrode materials, electrolyte salts, solvents, purity of the involved chemicals, and environmental conditions (i.e., temperature). Three widely discussed mechanisms include the following: (i) The early model by Peled suggests that the surface reaction is stepwise, involving preferential reduction of certain electrolyte components. It further suggests that the interphase layer formed as a result exhibits a uniform structure.[86] (ii) The mosaic model suggests multiple reductive decompositions simultaneously occur on the Li anode surface. This leads to the deposition of a mixture of insoluble and multiphase products on the anode, resulting in the formation

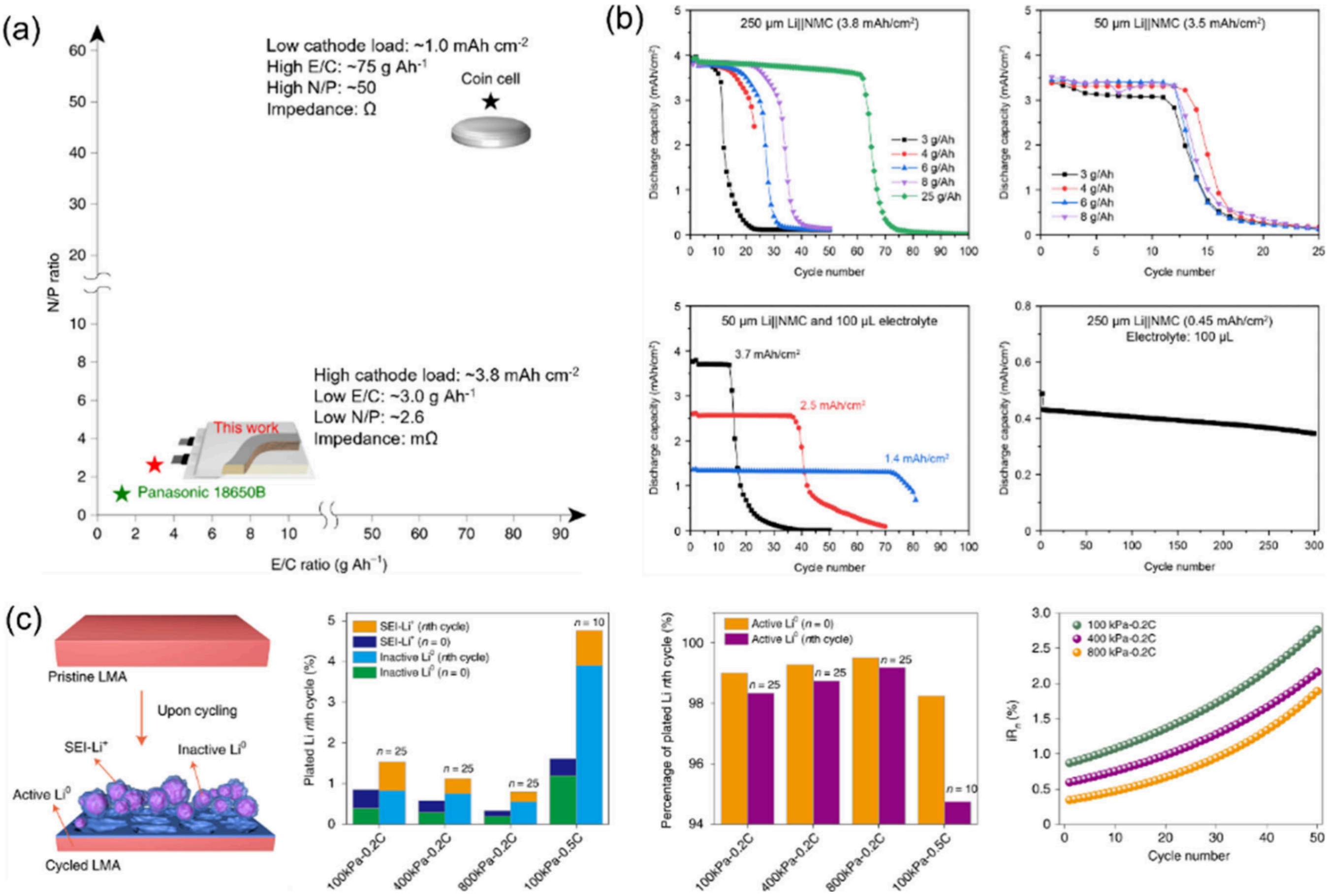

Figure 4. (a) Different parameters design for coin cell and pouch cell.[89] Reproduced with permission from ref 89. Available under a CC-BY 4.0. Copyright 2019 Springer Nature. (b) Influence of electrolyte amount on the battery performance for a high N/P coin cell, and a low N/P coin cell, and different cathode load (N/P) for battery performance, and a stable battery with high N/P and high E/C.[16] Reproduced with permission from ref 16. Copyright 2019 Elsevier. (c) Influence of external pressure on the Li plating component.[94] Reproduced with permission from ref 94. Available under a CC-BY 4.0. Copyright 2022 Springer Nature.

of an interphase layer with a mosaic morphology. This mosaic structure permits Li ions to migrate across the boundaries of the multiphase products.[87] (iii) The Coulombic interaction mechanism (Figure 3d),[70] in which, after the initial surface reaction, the decomposition products are lined up with positively charged Li^+ as "head" and the partially positively charged Li^0 electrode as "foot". The unique structure of the electrical double layer allows the products to adhere to the existing interphase layer stably.[88]

Degradation Mechanisms vs Battery Design. The aging of the battery is strongly associated with battery design parameters, such as cathode load, E/C ratio, and N/P ratio. Usually, the amount of Li metal and electrolyte are in excess in coin cells, as shown in Figure 4a.[89] However, in pouch cells the thickness of Li metal and the amount of electrolyte are minimized, which can lead to battery dry-out or Li depletion.[90,91] Chen at al[16] investigated the effects of electrolyte amount (i.e., E/C) and Li metal thickness (i.e., N/P) on battery performance by coin cell (Figure 4b). When the electrolyte amount increased to 4, 6, and 8 g/Ah, the battery cycling performance improved significantly. Further increasing the electrolyte amount to 25 g/Ah increased the battery lifetime by 6 times but lowered the practical cell-specific energy due to the large amount of electrolyte, preventing its adoption in real cells. Regarding the N/P ratio, when it is low, the battery will quickly fail due to Li metal depletion.[92] When the N/P is high and the electrolyte is in excess, the cycle life of battery can be extended.[93]

A critical issue inherent to Li metal batteries is battery expansion. It is not usually a problem for small conventional coin cells, but it is apparent in the pouch cells, where the electrode stacks are thick and the tiny fluctuations are magnified. The flat Li foil is converted into large solid Li particles covered with SEI components, which leads to rapid volume expansion of the anode, resulting in a rapid thickening of the pouch cell.[95] External pressure can positively influence the Li deposition, inhibiting the tip and promoting the lateral growth, therefore ensuring contact between the Li particles deposited at the Li anode and the preservation of a conduction percolation network for ions and electrons.[96] However, as the external pressure increases, the risk of Li dendrite root fracture increases, converting "active" Li to "dead" Li,[95,97] resulting in the loss of active material and ultimately reducing the Coulombic efficiency of the cell.[98]

To further quantify the effect of external pressure, Deng et al.[94] used the inductively coupled plasma-optical emission spectrometry to quantify the active and inactive Li plating for Li metal anode under different pressures (Figure 4c). With the external pressure increasing from 100 to 800 kPa, the inactive Li and SEI-Li decreased after 25 cycles at 0.2 C, which is due to the more flattened morphology of Li at higher pressure reduces the cracking possibility of SEI. Besides, the value of

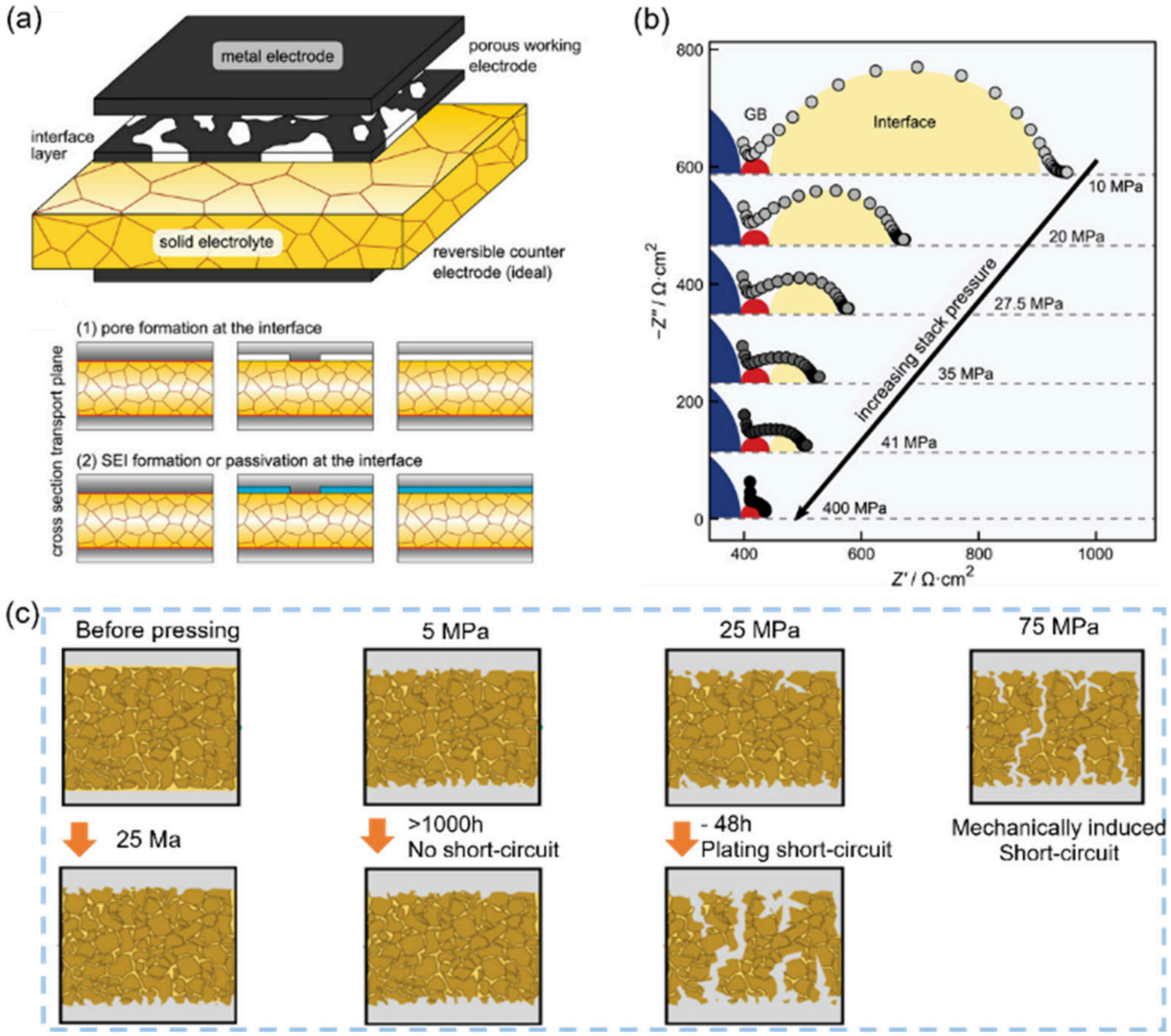

Figure 5. Mechanical degradation of the Li-SE interface and the ambivalent effect of the stack pressure. (a) Loss of contact between the Li and the $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$.[112] Reproduced with permission from ref 112. Available under a CC-BY 4.0. Copyright 2023 Wiley. (b) Impedance caused by loss of contact can be prevented by increasing the stack pressure.[112] Reproduced with permission from ref 112. Available under a CC-BY 4.0. Copyright 2023 Wiley. (c) Increasing the stack pressure also increases the evolution of dendrites at the Li|Li_6PS_5Cl interface.[113] Reproduced with permission from ref 113. Copyright 2020 Wiley.

$iR_n(Li^0)$ decreases at both 400 and 800 kPa compared to 100 kPa, indicating that elevated stack pressure primarily prevents the degradation of electron and ion transport thanks to reduced formation of dendritic Li. However, when the pressure is over 4 MPa, the mechanical instability increases.[95]

Compatibility of Electrolytes. Different electrolytes show different compatibilities with either NCM cathodes or Li metal anodes. Ether-based electrolytes are compatible with Li metal anodes, but are unsuitable for cathodes operating above 4 V due to their low oxidation potential.[99] Coversely, conventional carbonate solvents (e.g., ethylene carbonate (EC), ethyl methyl carbonate (EMC), and dimethyl carbonate (DMC)) are compatible with high-voltage cathodes,[100] butundergo side reactions with Li metal, leading to the formation of the SEI and the accumulation of dead Li. Therefore, conventional 1.0 m $LiPF_6$ carbonate-based electrolytes, commonly used as benchmarks, exhibit inferior stability and shorter cycle life.[101] Studies have demonstrated that incorporating a dual-salt electrolyte consisting of 0.05 m $LiPF_6$ with Li bis(trifluoromethanesulfonyl)imide (LiTFSI) and Li bis(oxalate)borate (LiBOB) enhances Li metal stability and suppresses dendrite growth, thereby maintaining stable cycling performances even at high current densities. Besides, a bifunctional additive, adiponitrile ($C_6H_8N_2$), also can effectively stabilize both the Li metal anode and Ni-rich NCM cathode interfaces.[102]

Localized high-concentration electrolytes (LHCEs) have emerged as a promising research direction. Based on high-concentration electrolytes (HCEs), LHCEs mitigate the limitations of HCEs by incorporating diluents, thereby improving compatibility with both high-voltage cathodes and Li metal anodes.[103] HCE has lower bulk ionic conductivity than dilute $LiPF_6$ but higher cell conductivity, indicating greater thermodynamic stability against electrodes.[104] The improved performance stems from HCE's higher stability with a Li metal anode.

Interplay between Li Metal Anodes and NCM Cathodes. Cathode−anode crosstalk is bidirectional, including both cathode-to-anode and anode-to-cathode crosstalk and is generally detrimental. It not only accelerates battery self-

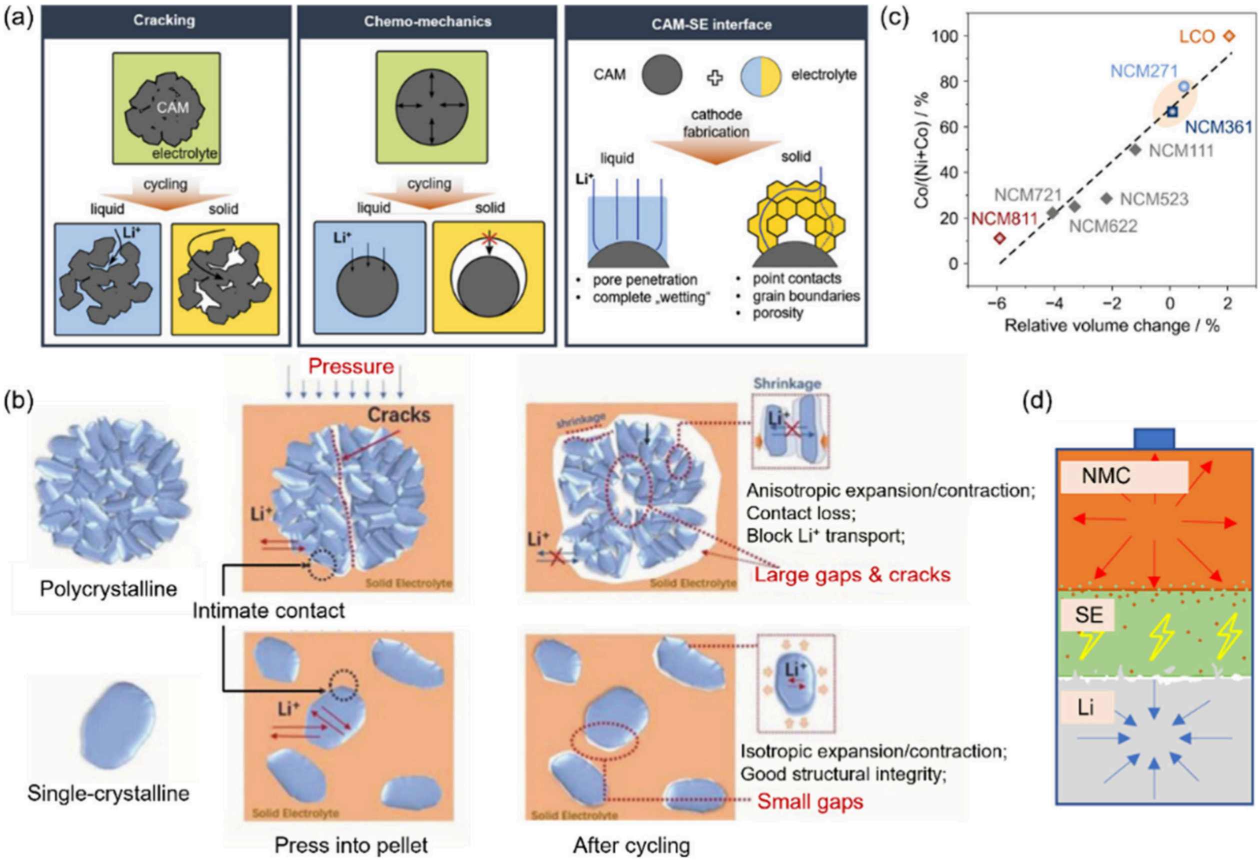

Figure 6. (a) Mechanical degradation effects with SEs compared to that with LEs from Minnmann et al.[117] Reproduced with permission from ref 117. Copyright 2022 Wiley. (b) Schematic of cross section morphological change during electrode pressing process and electrochemical cycling.[118] Reproduced with permission from ref 118. Copyright 2021 Wiley. (c) Molar ratio of Co/(Ni + Co) versus the relative change in unit cell volume for various layered oxide cathode active materials (from operando XRD of LIB pouch cells charged to 4.4 V vs Li^+/Li). The dashed line is a linear fit to the experimental data. Note that LCO refers to $LiCoO_2$.[119] Reproduced with permission from ref 119. Copyright 2020 American Chemical Society. (d) Expected stress on the separator layer caused by opposite volume fluctuations at the anode and cathode and element diffusion from cathode to anode through the solid electrolyte.

discharge but also reduces Coulombic efficiency, promotes continuous SEI/CEI growth, and leads to issues such as gas accumulation, Li dendrite formation, and "dead" Li, ultimately shortening the battery lifetime and even causing self-heating and thermal runaway. The primary mechanisms include TM dissolution and migration, oxygen release, and electrolyte oxidation.[105]

The reaction between the cathode and anode generally begins with the dissolution of TMs from the NCM cathode material, which is exacerbated at higher temperatures. Lüchtefeld et al.[106] found that Ni and Co dissolve more easily than Mn. The TM migration through the electrolyte to the Li metal anode, especially in the case of Ni that is reduced to its metallic state, leads to its incorporation into the SEI in small clusters. This locally alters the chemical composition and nanostructure of the SEI, which alters Li-ion and electron transport properties within the SEI, accelerating electrolyte decomposition, increasing "dead" Li formation, and resulting in a thicker SEI, ultimately leading to battery failure.[107]

In addition to TM dissolution, oxygen release is also a key factor in cathode-anode crosstalk. The structural instability of NCM materials leads to the release of lattice oxygen in the form of singlet oxygen, superoxide anions, molecular oxygen, and other oxidative species. During delithiation, NCM materials generate a significant amount of O_2, which enters the electrolyte and undergoes a series of side reactions with the anode. Ultimately, the released oxygen is consumed by Li metal, accompanied by intense exothermic reactions. Further details on this process are provided in the battery failure section.

Electrolyte oxidation plays a crucial role in these interelectrode reactions. Li et al.[108] studied the cross-effects between NCM cathode and Li metal anode in ether- and ester-based electrolyte systems. The ester-based electrolyte exhibited a good electrochemical performance with minimal cross-effects. In contrast, the ether-based electrolyte, due to its poor oxidative stability, led to significant dissolution of transition metal ions. Recent studies of electrolyte design, particularly in LHCE systems, have begun to shed light on these reactions. The electrolyte consists of lithium bis(fluorosulfonyl)imide (LiFSI), 1,2-dimethoxyethane (DME), and 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether (TTE) in a molar ratio of 1:1.2:3. The study explores the impact of high-nickel cathodes on Li metal anodes, as well as the reciprocal effect of Li metal anodes on high-nickel cathodes.[109] Compared to graphite/NCM batteries, Li/NCM batteries exhibit a faster capacity decay, at a rate two to three times higher than the former. Notably, despite the more severe capacity fade, the CEI thickness is reduced by approximately 3-fold. This increased degradation is primarily attributed to the enrichment of sulfur and nitrogen species and the loss of fluorine rather than merely changes in CEI thickness, which adversely affects the cathode. The influence of the cathode on the Li metal anode is equally significant. Li metal anode benefits from an increased fluorine content. Compared to Li/Li, the SEI thickness in Li/NCM batteries is reduced by three times while exhibiting a higher fluorine content and lower sulfur and nitrogen content. The preferential defluorination of the LiFSI salt by the Li metal anode is the key factor driving these cross-interface effects, ultimately enhancing electrochemical performance.

DEGRADATION MECHANISMS OF SOLID-STATE LI/NCM BATTERIES

Degradation of Li Metal Anodes and Li-SE Interfaces. The growth of Li dendrites is the main mechanical failure process happening at the anode of solid-state Li/NCM batteries, ultimately leading to the electrical short-circuit of the cell. Although this problem also occurs in LE-based Li/NCM batteries, its origin and evolution are different in SSBs due to the different chemical and mechanical natures of the Li-SE interface. Multiple causes (e.g., low sheer module of SE, presence of cracks/defect points, residual electronic conductivity of SE) have been proposed to explain their formation and evolution,[110,111] but it is still unclear which ones prevail.

A secondary but still significant mechanical problem at the anode is mechanical degradation of the Li-SE interface. This can manifest as uneven Li plating/stripping, which can lead to the formation of pits during discharge, reducing the contact area, and protruding Li grains, which can evolve into dendrites or "dead" Li. The impact of these issues on the cell behavior depends on the type of SEs and anode materials, as well as the cycling conditions (Figure 5). For example, softer SEs, such as polymers or sulfides, are better able to accommodate the electrode changes and maintain the Li-SE contact,[111,114] while anodes with minimal or no excess Li, such as thin Li-foils or Li-free anodes, are more sensitive to interface deterioration, as losing even a small amount of Li can mean losing a significant cell capacity.[115]

The interface between the Li anode and SE is also significantly affected by electrochemical degradation. The reason lies in the limited electrochemical stability window (ESW) of most solid electrolytes, indicated as the voltage interval between the onset of electrolyte oxidation and reduction. In particular, as the electrochemical reduction potentials of SEs are always higher than that of Li (−3.04 V vs standard hydrogen electrode), it is always thermodynamically favorable for Li to reduce SEs, except for the full-reduced ones.[116] The Li/SE electrochemical degradation leads to an increase in the internal resistance of the cell, which can be one-off (with formation of a stable SEI) or continuous (unstable and growing SEI), resulting in an increasing overpotential and capacity loss along cycling.

As both Li dendrites and Li interface degradation are common challenges for all Li SSBs, regardless of the cathode material, we will not provide an in-depth analysis here. Instead, we refer the reader to other literature for more informations.[38,111,114]

Degradation of NCM Cathodes and NCM-SE Interfaces. Compared with what happens in LE-based Li/NCM batteries, mechanical stress in SSBs contributes to a much larger extent to the degradation of cathodes. LEs can compensate, and in some cases even turn into a benefit, the cracking and volume fluctuations of the cathode, filling the new pores and fractures as soon as they are generated and guaranteeing the functionality of the transport network.[65] As SEs obviously do not have this ability, in SSBs mechanical stress always leads to formation of voids and contact loss, resulting in reduced active contact area, increased length of transport pathway, and limited utilization of AMs (Figure 6a).

Many studies have analyzed the mechanical degradation happening at the NCM cathode of SSBs. The fabrication procedure of SSB cathodes can already cause irreversible mechanical damage, as demonstrated by Yamamoto et al.,[120] who showed that the densification procedure during assembly, can cause cracking and pulverization of the $LiNbO_3$-coated NCM333 particles under pressures between 111 and 166 MPa, significantly lowering the cell capacity. Given the higher (sometimes much higher) pressures commonly applied during battery fabrication, it cannot be excluded that some degradation seen during cycling actually occurs already prior to cycling. In another study, Liu et al.[118] observed the cracking of polycrystalline NCM811 secondary particles after pressing, while single crystal NCM particles could endure pressures as high as 1020 MPa without cracking. The same study also gives some insights into the mechanical degradation during cycling (Figure 6b). Specifically, it shows how polycrystalline NCM811 particles are structurally unstable when charged above 4.15 V vs Li^+/Li, when large anisotropic volume change takes place, causing formation of voids and cracks between the randomly oriented grains.[121] This causes the gradual pulverization of the cathode and the loss of AMs and of contact with the SEs. Moreover, sustained breathing of the electrode put continuously in contact AMs with SEs, causing progressive thickening of the CEI layer.[122] The consequence of this process is the continuous growth of interfacial resistance due to the reducing contact area and thickening SEI, and capacity fading caused by the detachment of AMs from the conductive networks and its consumption by the reactions with the SE. In contrast, single crystal particles are much less affected by these processes, with their capacity retention further improveable by coating them.[123]

Wang et al.[124] and Conforto et al.[125] also came to similar conclusions. Lou et al.[126] also tested polycrystalline NCM622 in PEO-based SSBs, in which the softer nature of polymers ensures good physical contact with the AM particles and better accommodates volume changes inside the cathode, limiting the effect of interface degradation. Even in this setup they could notice cracks along the boundaries between the single crystalline NCM622 primary particles, caused by strong heterogeneities in their SoC distribution, confirming the degradation is independent from the electrolyte chosen.[127] The cracks in turn further aggravate the SoC distribution heterogeneity, causing a feedback loop that accelerate failure.

Apart from single crystals, other structures can also exhibit reduced susceptibility to mechanical degradation. Jung et al.[128] showed that radially oriented rod-shaped polycrystalline $NCM_{7.5/1/1.5}$ particles with a concentration gradient of Ni and Mn (Ni concentration higher in the core, Mn concentration higher on the surface) can accommodate the volume changes during cycling without cracking. Moreover, the lower Ni content on their surface also limited the side reactions with the SEs. We would like to point out that, while micro/nanostuctured NCM materials have sometime been reported in the literature, to the best of our knowledge this is the only study that investigated them in a SSB.

Finally, different NCM cathode compositions undergo different volume fluctuations upon cycling and therefore suffer mechanical degradation to different extents. Strauss et al.[119] demonstrated that increasing the Ni content of NCM increases the volume change upon Li-ion insertion/extraction, with NCM811 reaching 6%. Co-rich compounds are instead much less affected by this degradation process, with NCM271 and NCM361 showing <1% unit-cell volume variation (Figure 6c).

Moreover, similar to the anode side, the electrochemical decomposition of the SE at the cathode causes the growth of a resistive interphase, increasing the internal cell resistance and consuming AMs. The SE included in the cathode has the strongest impact on the cell performance and is highly susceptible to degradation, given the high contact area between SE and NCM particles. Usually, the same SE is also used as a separator between the anode and cathode. Few SEs are stable (thermodynamically or kinetically) against NCM, and the reaction processes and products are often very different among them (for an in-depth analysis of the electrochemical degradation of SEs we point the reader to the cited literature[38,114]). Koerver et al.[129] have demonstrated that β-Li_3PS gets oxidated during the first charge, causing the formation of a resistive interphase which slowly grows further over the subsequent cycles, while Zhang et al.[130] studied the interface evolution between Li_6PS_5Cl and NCM811, highlighting the strong influence of the space charge layer, caused by the Li^+ redistribution at interface, on the interfacial impedance growth during the first cycles.

Note that the reactivity of the SE may however not always be detrimental, as shown by Auvergniot et al.,[131] which proved that the elemental sulfur, Li polysulfides, phosphates, and LiCl produced by the decomposition of Li_6PS_5Cl do not hinder the cyclability of the Li/NCM battery, and may even, participating in the redox reactions, increase the reversible capacity of the batteries.

The electrochemical and mechanical degradation of NCM cathodes may also be hindered by the presence of a coating layer on the NCM particles. The most studied and employed coating material is $LiNbO_3$,[118−120,132−135] which has repeatedly proven to form interfaces with the SE that exhibit good mechanical contact and limited electrochemical decomposition. Other reported coating materials on NCM include Li_3PS_4,[135] Li_6PS_5Cl,[136] $LiNbTaO_3$,[124] Li_2CO_3,[133] and Li_2ZrO_3,[134] sometimes used in combination with $LiNbO_3$.[133,135]

Interplay between the Degradation Processes of the Anode and Cathode. Different from LE-based Li/NCM batteries, the degradation processes at the two electrodes in solid-state Li/NCM batteries are mostly independent from each other, as the solid nature of the SE layer prevents the migration of species other than Li^+ from one electrode to the other. However, elemental interdiffusion between the cathode and the solid electrolyte can still happen, as Zhang et al.[137] showed by demonstrating that transition metals can diffuse from the cathode material ($NCM_{85/10/5}$) particles into the bulk of SE (Li_6PS_5Cl). Many questions, however, still need to be answered about this phenomenon, such as where does the migration occur (i.e., along the voids, grain boundaries, Li sites), how deep can it penetrate in the bulk, how fast, with which SEs is it present, and how does it progress with cycling. Only once these questions are answered will it be possible to clarify how common this phenomenon really is and how much influence (if any) holds on the degradation of the battery.

Another specific issue that could arise in solid-state Li/NCM batteries is the internal pressure mismatch between the anode and cathode (Figure 6d) as the volume fluctuations during cycling of the two electrodes are different and, differently from LE cells, cannot be compensated by electrolyte migration. In the worst-case scenario, this growing interelectrode stress could further contribute to the mechanical degradation of the interfaces and the formation of cracks inside the SE layer. A further problem we can envisage is related to the wide potential difference between the anode and cathode, wider than the stability window of any single SE and that, unless much more stable SEs are developed, will keep causing intense electrochemical degradation at the anode and/or cathode side, Nevertheless, to the best of our knowledge, no dedicated study on the interelectrode degradation process of solid-state Li/NCM batteries has been reported.

SAFETY THREATS AND CELL FAILURE

Ensuring the safety of Li/NCM batteries is crucial for their large-scale applications. However, as batteries degrade, a series of issues gradually aggravates and safety threats arise, such as short circuits, gassing and thermal runaway, resulting in sudden battery death or even explosion.[138] Here we give a comprehensive overview of the safety issues of Li/NCM batteries and their underlying degradation mechanisms.

Short Circuit Related to Li Dendrite Growth. Short circuits, caused by mechanical shock, bending, nail penetration, cutting, dendritic Li, etc., are the most hazardous threat to battery safety. This is because the large current emerging where the short circuit occurs can generate a large amount of ohmic heat in a short time, causing a dramatic increase in the internal temperature of the cell and significantly increasing the risk of thermal runaway (see details in Degradation Mechanisms vs Battery Design) and even fire or explosion. In particular, short circuiting is a common problem associated with the growth of sharp Li dendrites in Li/NCM batteries.

Among the many factors associated with the Li dendrite short-circuit, the effect of external pressure is known to be significant, especially for pouch cells, but the exact mechanism remains unclear. External pressure not only deforms batteries (e.g., shape and volume) but also influences the microstructures of electrodes.[139,140] At the same time, Li metal anodes undergo a large volume expansion during cycling, causing electrode pulverization and accumulation of “dead” Li. This volume change is for the most part constricted in the presence of rigid casings (i.e., coin cells), resulting in an increase in mechanical stress accumulating in the battery materials. By contrast, more flexible casings (i.e., pouch cells) can more easily accommodate volume fluctuations, resulting in less internal mechanical stress. Zhang et al.[95] quantitatively described the evolution of mechanics, electrochemical reactions, and ion transport in Li cells by constructing a mechanical-electrochemical phase field model using a pouch cell as a model system. The results show that the morphology of Li deposition becomes smoother and more compact (i.e., less branches) when the external pressure is increased from 2.0 to 14.0 MPa, indicating that the Li deposits adopt a compressed state when the applied external pressure is greater than the intrinsic stress.[95] This proves that the effects of external pressure on cell operation are double-sided. On one hand, it can smooth Li electrodes limiting the evolution of dendrites, while on the other hand, it increases internal mechanical stress and the risk of mechanical short circuiting.

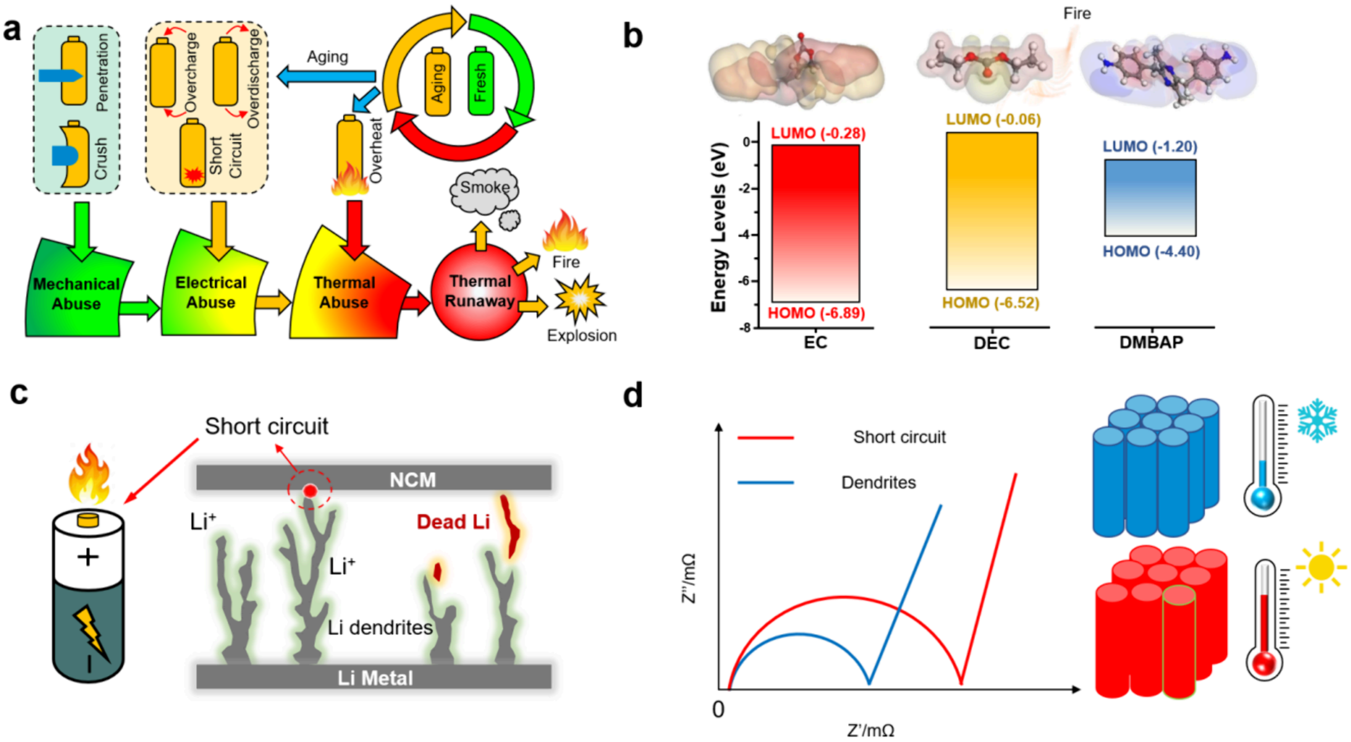

Figure 7. Important factors related to thermal runaway. (a) Cell abuses. Reproduced with permission from ref 160. Copyright 2018 Elsevier. (b) Volatile and flammable organic electrolytes. (c) Short circuit and Li dendrites. (d) Ohmic impedance.

Therefore, moderate external pressure might be required to improve the safety of Li/NCM batteries.

Gassing. Gases generated during battery degradation pose serious safety threats, not only because they contain large amounts of flammable components but also because they cause the deformation/swelling of batteries, especially pouch cells. Therefore, it is extremely important to understand the mechanism of gas evolution and control it.

The high vapor pressure of organic LEs influences the gassing behavior of Li/NCM batteries.[141] It has been reported that the saturation vapor pressure of EC is several orders of magnitude lower than that of DMC (e.g., 24 and 1913 Pa for EC and DMC, respectively, at 45 °C), which leads to a strong temperature dependence of the solvent content in the gas phase in the case of DMC.[142,143] Therefore, electrolyte solvents with a high vapor pressure have considerable advantages in inhibiting gas production. However, given the high flammability of these organic solvents, the electrolyte with a high vapor pressure of the solvent also brings about more severe safety concerns upon cell breakage or short-circuit.

Gas evolution occurs due to overcharging, primarily resulting from reactions between metallic Li and electrolytes. These reactions are the main cause of gas formation and pouch cell swelling.[144,145] Li^+ attacks O atoms in EC, DEC, and EMC, breaking molecular bonds and forming free radicals like $^\bullet OCH_3$ and $^\bullet OC_2H_5$.[146] These radicals recombine to release flammable gases (C_2H_6, C_3H_8, and C_4H_{10}), as summarized in Table S5. H_2 mainly forms from Li reacting with trace H_2O,[147] while CO_2 originates from H_2O reacting with electrolyte decomposition intermediates and can further reduce to CO.[148] Alkynes in combustible gases may result from alkane dehydrogenation in the presence of a strong electric field, active Li, and H_2O.[144]

Thermal Runaway. Battery failure can be caused by several types of abuses during operation, such as electrical (e.g., short circuit and overcharge/overdischarge),[149−151] mechanical (e.g., penetration, crush, free fall, and rollover),[152−154] and thermal abuse (e.g., heating and burning on fire),[155−157] all possibly leading to thermal runaway (Figure 7a).

Thermal runaway is the process by which a spontaneous exothermic reaction in the battery can in turn trigger an uncontrolled exothermic chain reaction between the rest of battery materials and the ignition of organic electrolytes.[158−161] This issue is more severe for volatile and flammable electrolytes (Figure 7b) and may be caused by the growth of Li dendrites, which may puncture the separator and cause a short circuit with the cathode.[162,163] Such a process is controlled by the thermal balance between the heat generated and dissipated by the battery[164,165] and can further worsen with overcharging, since the oxygen released during the phase transformation of the NCM cathode can fuel the reactions.

The main cause of thermal runaway is electrical short circuits, which may originate both during abuse and during the normal operation of the battery. The separator is the main component responsible for preventing electrical short circuits, but these can still happen through two main processes: puncturing of the separator by the growing Li dendrites (especially with thin separators) and thermal melting of the separator.

Ohmic impedance is one of the factors affecting the risk of battery thermal runaway. Ohmic impedance increases over time due to factors such as Li dendrite growth, SEI formation, and electrode degradation.[166,167] The increase of internal impedance causes the battery to generate more heat during charging and discharging, and affects the temperature rise rate of the battery.[168] Additionally, Li deposited on the anode may react with the electrolyte, resulting in a further increase in impedance and release of a large amount of heat. More dramatically, the formation of Li dendrites can puncture the separator and cause internal short circuits in the battery (Figure 7c). A high current peak occurs during a short circuit, which generates a lot of heat in a short period of time, causing its temperature to rise rapidly.[169,170] These shorts bypass a portion of the battery's active area, causing localized heating and possible thermal runaway. An increase in the ohmic impedance may also correlate with a loss of capacity in the battery. As the battery ages, the crystal structure of the active material changes, leading to changes in the internal contact resistance of the electrodes.[171,172] In addition, the further attenuation of the battery capacity will cause the contact area between the electrodes and the electrolyte to decrease, which in turn will cause an increase in the ohmic impedance of the battery.[173] Therefore, the capacity loss will cause the battery to generate more heat during high-load operation, increasing the risk of thermal runaway (Figure 7d). Moreover, ohmic impedance causes the voltage within the battery to drop rapidly during high-current operation, causing uneven current distribution and localized heating, leading to thermal instability and possible thermal runaway.

SUMMARY OF THE DEGRADATION AND FAILURE MECHANISMS OF LI/NCM BATTERIES

The performance of Li/NCM batteries achieved so far varies a lot and is generally encouraging. However, the lack of standardized cell designs and testing procedures seriously complicates the comparison between different studies, making it difficult to identify the state-of-the-art in this active and rapidly developing research field. We have identified, however, some major challenges and research necessities. Here we summarize the degradation and failure mechanisms of Li/NCM batteries on several levels, from the AMs to electrodes and cells, and identify which processes and mechanistic understandings remain unclear. The specific aging mechanisms are shown in Figure 8.

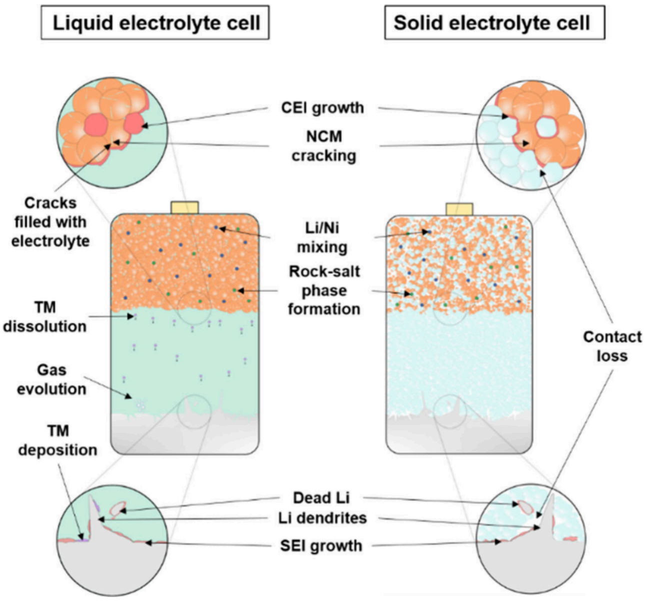

Figure 8. Summary of the degradation and failure mechanisms of Li/NCM batteries with LEs and SEs.

The current understanding is that the most significant degradation issues in Li metal batteries are primarily caused by problems of the Li metal anode and its interfaces, including dendrites, polarization, active material loss, and Li loss. The rational design of electrode materials (e.g., NCM cathodes with low nickel content and a single crystal structure, Li metal with electrode structuring and/or surface protection), battery design (e.g., optimized N/P and E/C ratios), and operating conditions (e.g., low C-rate and charge cutoff voltage) can help alleviate battery aging and safety issues in Li/NCM batteries to some extent. However, these solutions currently also introduce some new problems, such as reduced energy density and higher materials and processing costs. Furthermore, the implementation of these measures increases the complexity of the battery system and creates a wider range of aging paths.

The main problems afflicting solid-state Li/NCM batteries, as discussed above, consist of mechanical and electrochemical degradation at the Li anode (Li dendrites, SEI growth, "dead" Li, etc.) and NCM cathode (cracking, CEI, contact loss, etc.). However, their exact causes and consequences during battery operation are still unclear.

The electrochemical behaviors of both LE- and SE-based Li/NCM batteries are influenced by the working conditions, e.g., pressure, temperature, and current density, but the exact mechanisms are different. (i) Applying appropriate external pressure during cycling can help suppress dendrite growth or alter dendrite morphology, thereby enhancing battery cycle performance and reducing safety risks. For solid-state batteries, high external pressure (tens to hundreds of MPa) is essential to decrease the contact resistance between SEs and electrodes and enable battery function. In contrast, external stacking pressure is not mandatory but crucial for stable cycling of Li/NCM pouch cells with LEs. Applying moderate pressure (hundreds of KPa) onto pouch cells during testing can help maintain the mechanical stability of Li electrodes (flattening Li deposits), suppress cell swelling caused by gas generation, maintain interfacial contact, thereby enhancing battery performance and test consistency, while high pressure (>1 MPa) may deteriorate the performance. (ii) Compared to SE-based Li/NCM batteries, LE-based batteries are more sensitive to the variation of operating temperature. At low temperatures, the diffusion rate of Li ions in electrolytes decreases, leading to aggravated Li dendrite formation. At high temperatures, electrolyte decomposition and interfacial side reactions intensify, increasing battery polarization and causing capacity degradation. (iii) The effects of current on these two battery systems are similar. High current density accelerates dendrite growth on Li metal anodes, leading to more significant "dead" Li formation and reduced battery lifespan.

On the other hand, there are also differences in LE- and SE-based Li/NCM batteries. For instance, transition metal dissolution is one major degradation process in LE-based batteries, while the solubility of NCM cathode materials and their diffusion to the anode side in solid-state Li/NCM batteries remain unclear.

Factors Limiting the Current Understanding of the Aging Mechanisms. Although a large number of experimental works and theoretical simulations have been devoted to studying the degradation mechanism of Li/NCM batteries, mechanistic understanding of the battery degradation mechanisms is still very limited due to the complexity of electrode materials, cell designs, and operating conditions.

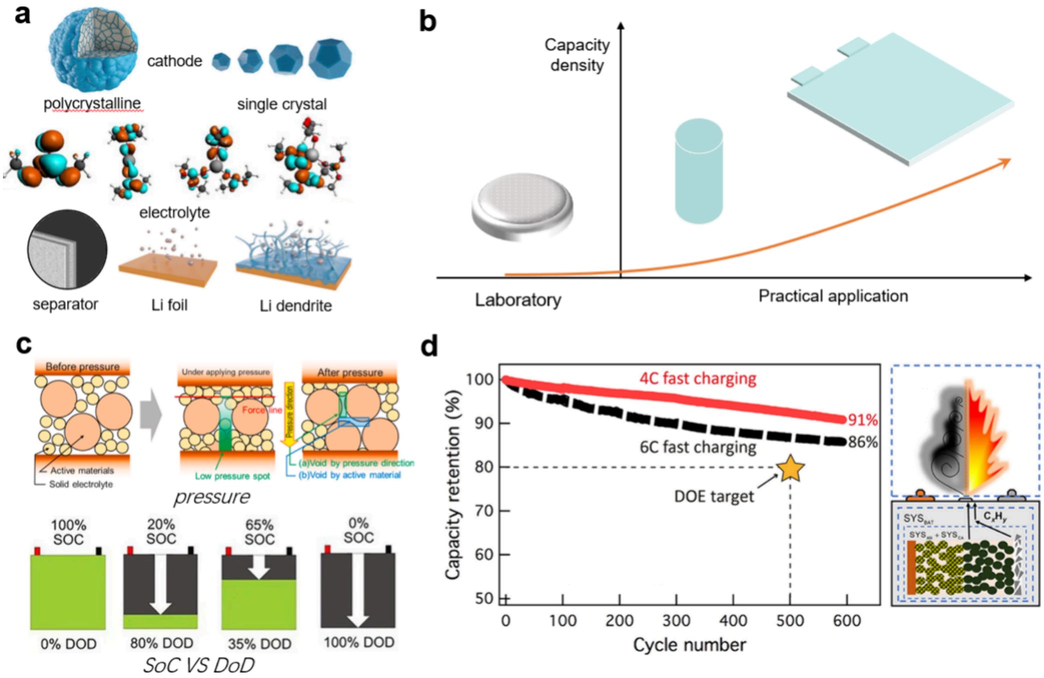

Figure 9. Effects of some important factors on cell aging. (a) Cell material. (b) Cell configuration. (c) Cycle conditions.[187] Reproduced with permission from ref 187. Copyright 2023 Elsevier. (d) Fast charging and discharging for accelerated degradation.[188,189] Reproduced with permission from ref 188. Copyright 2020 Elsevier; Reproduced with permission from ref 189. Copyright held by the authors.

On the material level, different chemistries of anode/cathode materials result in different battery performances. Even for the same electrode materials, the particle size and morphology can vary, resulting in different degradation pathways.[65] Besides, the reactions at individual interfaces and the interplays between battery components (e.g., between Li metal anode and NCM cathode) are complex and difficult to probe during battery operation, while the theoretical models and simulations (e.g., Li dendrite growth, SEI formation, and gassing) are based on greatly simplified or ideal conditions that significantly deviate from the actual situation.

On the cell level, the degradation mechanism of the Li/NCM battery is dependent on the cell design. As there is not yet a standardized cell design (including N/P ratio, E/C ratio, area capacity of electrodes, materials of separator, current collector, and packages, etc.) and cycling protocol (constant current, constant voltage, pulse current, fast charging, different depths of discharge (DoDs), etc.) in the field, comparison between studies is difficult. External operating conditions such as pressure and temperature also have a significant impact on the battery degradation modes, an impact difficult to assess given the unevenness of these parameters inside the battery.[174]

The current techniques and methods for battery analysis have a lot of limitations, returning each of them to only a fraction of the processes happening (e.g., SEI/CEI chemistry and structure, electrode cracking, charge transport at grain boundaries, etc.). Even more advanced *in situ* techniques present challenges due to their strict requirements for battery casings, sample preparation, and transfer, and so on.

PERSPECTIVES FOR DEEPENING THE UNDERSTANDING OF DEGRADATION AND FAILURE MECHANISMS

Systematic Investigation of Cell Degradation. The battery materials determine the battery's performance and stability (Figure 9a). The stoichiometry of NCM cathode material (e.g., NCM811, NCM622, NCM523) determines the battery's operating voltage, capacity, and cycle life.[175] To overcome the Li dendrite issue, various solutions have been explored, such as structured/surface-coated Li and Li alloys (e.g., Li–Sn and Li–Si) or composites (mostly with carbonaceous materials), but these engineered Li anodes present different interfacial behaviors with the electrolytes and hence different degradation pathways. Conventional liquid organic electrolytes, such as carbonate esters, are prone to decomposition and formation of SEI and CEI layers on the electrode surface, which can hinder Li-ion transport and accelerate battery degradation.[176] As an alternative, ionic liquids have shown promise in improving battery stability and safety but exhibit limited Li-ion conductivity and poor fast-charge capability.[110] The use of SEs, an alternative considered safer thanks to its expected ability to mechanically suppress Li dendrite penetration and less susceptibility to thermal runaway, necessitates further research.

The configuration of a cell is usually indicated in terms of cell format (e.g., coin-, cylindrical- and pouch-cell) (Figure 9b), type of Li metal anode (e.g., Li foil, 3D Li composite, anode-free, etc.) and NCM cathode (e.g., AM/binder/carbon ratio, areal AM loading, porosity, etc.), areal capacity ratio of negative to positive electrode (N/P ratio, [−]) and electrolyte volume to battery capacity ratio (E/C ratio, [mL Ah^{-1}]), all parameters that have a significant impact on the degradation and failure mechanisms of Li/NCM batteries. The use of pouch cells, for example, can increase the risk of cell swelling and threaten the operational safety of the battery. Current studies indicate that the N/P ratio of Li/NCM batterys is typically more than twice that of commercial Li-ion batteries (N/P ratio ≈ 1.1).[177] This design compensates for Li loss during cycling to enhance cycling performance. However, using thin (<50 μm) Li foil as the anode can reduce the N/P

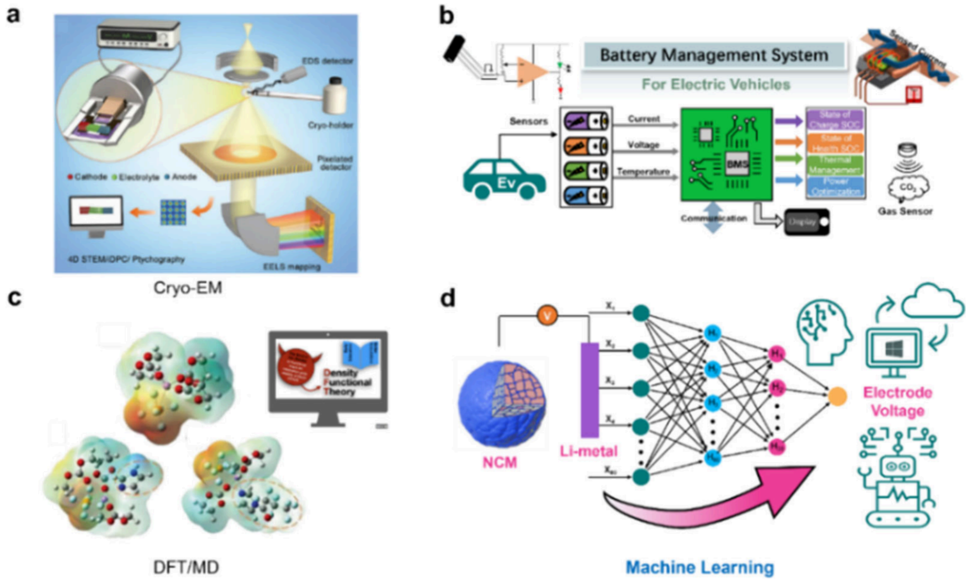

Figure 10. Methods for understanding the aging processes of Li/NCM batteries. (a) Cryo-EM characterization.[211] Reproduced with permission from ref 211. Copyright 2021 Cell Press. (b) Degradation sensing and battery management system (BMS). (c) DFT/MD simulations.[212] Reproduced with permission from ref 212. Available under a CC-BY 4.0. Copyright 2022 Wiley. (d) Machine Learning (ML) methods.[213] Reproduced with permission from ref 213. Copyright 2019 American Chemical Society.

ratio, thereby improving the overall energy density of the battery.[16] At the same time, the continuous Li loss during cycling limits the life of the battery. Employing thin Li foils would also significantly complicate the scale-up of the technology. The E/C ratio determines the degradation related to electrolyte consumption and cell dry-out, resulting in the formation and thickening of SEI/CEI layers and an increasing polarization.

The degradation of Li/NCM batteries also depends on the cycling conditions, including external temperature and stacking pressure, the dis-/charge current, state of charge (SoC), depth of discharge (DoD) (Figure 9c), cutoff voltages, and cycle number. (i) High temperatures can accelerate electrolyte degradation.[178] However, at a low temperature, the kinetics for Li-ion transport are sluggish, resulting in a large overpotential and more uncontrollable Li dendrite growth, accelerating the battery degradation and increasing the risk of electrical short-circuit. (ii) Stacking pressure is known to influence the Li dendrite growth behavior and hence the failure mechanism of the Li/NCM batteries, but the exact effects of stacking pressure on the electrochemical performance remain elusive. (iii) Deeper discharge, e.g., a larger DoD, can cause greater strain change in the NCM cathode materials and faster degradation.[179] Charging a Li/NCM battery to a high cutoff voltage leads to degradation related to the collapse of the NCM crystal structure and lattice oxygen release. In particular, under a high SoC (>75%), the unit cell volume of NCM shrinks sharply (7.8 ± 1.5)%,[180] and TM ion dissolution, lattice oxygen evolution, and particle cracking will occur.[181] This not only worsens the loss of AMs but also triggers parasitic reactions with the electrolyte solvent. (iv) High C-rates can cause increased heat generation, which can lead to accelerated electrolyte degradation. The battery may explode upon a high-current overcharge, and cell swelling occurs during a low-current overcharge.[182] (v) Repeated battery charge and discharge can cause cumulative structural damage to the electrodes and electrolyte consumption, leading to increased cell polarization.

Accelerated battery degradation test is frequently used to enable fast analysis of the degradation mechanisms of Li/NCM batteries, which could be realized by aging the batteries at fast dis-/charge (Figure 9d).[183] Heat generation is one of the most hazardous problems of Li/NCM batteries during rapid dis-/charging,[184] The Joule heating causes the cell temperature to rise rapidly, which intensifies the parasitic reactions between the electrodes and the electrolyte and destabilizes the interphases, leading to further growth of SEI/CEI layers. The uneven distribution of heat is another key factor leading to the accelerated degradation of electrodes and electrolytes. Cell parameters, such as electrode thickness, areal AM loading, porosity, and tortuosity, influence the charge distribution, thereby affecting the heat uniformity and deteriorating the battery operation. Besides, the structures of NCM cathode materials are unstable during fast charging,[185] during which also the growth of Li dendrites is promoted.[186]

***In Situ* and *Operando* Characterization at Various Time- and Length-Scales.** The interfacial reactions, microstructure, and dynamic behaviors in Li/NCM batteries have been intensively and extensively studied with conventional microscopic and spectroscopic techniques, such as S/TEM, AFM, XPS, XRD and FTIR. Future developments of Li/NCM batteries call for the development of more advanced and complementary tools, especially *in situ* and *operando* characterization of sensitive electrochemical materials and interfaces at the relevant time and length scales. Electrochemical dilatometry[190] coupling electrochemical and mechanical measurements, provides information on the thickness/volume changes of the electrodes and cells during operation, while Differential Electrochemical Mass Spectrometry (DEMS),[191] combining electrochemical testing with mass spectrometry, enables *real-time* analysis of gas evolution (e.g., H_2 on Li anode and O_2 on NCM cathode. These methods have been explored, but their application remains rather limited due to the complexity of *operando* cell design and data analysis. The emerging environmental transmission electron microscopy (ETEM)[192] combines electron microscopy and ambient gas control technology, which can reveal the dendrite growth and gas production behaviors of batteries in real operating conditions. However, vacuum technology faces challenges (such as the evaporation of liquid electrolytes) as well as challenges in sample transfer. Three-dimensional electron tomography techniques enable high-resolution 3D imaging and *in situ* observation of the internal structure of NCM materials and cracks within SSBs. The morphology of electron-sensitive Li dendrites can be captured in a frozen state (e.g., −196 °C with liquid nitrogen) with cryogenic electron microscopy (cryo-EM)[193] (Figure 10a). Meanwhile, by freezing the specimen under cryogenic conditions, the (close-to) native state of the SEI/CEI films on the electrodes can be preserved. The combination of cryo-EM and electron energy loss spectroscopy (EELS) enables *in situ* visualization of the interface layers and analysis of the chemical composition and distribution, which determines Li-ion diffusion and charge transfer processes. Besides, the decomposition of electrolytes is an important factor affecting the interface stability and cycle life of Li metal batteries. *In situ* nuclear magnetic resonance (NMR) is particularly suitable for detecting the composition of electrolytes and hence the associated parasitic reactions.[194] By comprehensively analyzing the multimodal *operando* and *in situ* data, the degradation and failure mechanisms of Li/NCM batteries can be revealed.

Advancement of Electrochemical Analysis and Sensing for Degradation Diagnoses. Next to material characterization, electrochemical analysis is also essential for diagnosing the degradation of Li/NCM batteries. To understand in-depth the electrochemical behavior and the degradation processes, typical galvanostatic voltage profile, differential voltage analysis (DVA) and cyclic voltammetry (CV) have been commonly used to unveil the formation of SEI/CEI and phase transformation of NCM and also to reveal overpotentials caused by, e.g., the structural changes of electrodes, interphase formation and accumulation, and electrolyte dry-out. Electrochemical impedance spectroscopy (EIS) can identify and quantify the impedance contributions of different processes, such as ohmic resistance, interphases, and charge transfer resistance, while *operando* EIS also allows monitoring their variations during battery cycling.[195] Exchange current density analysis and galvanostatic intermittent titration technique (GITT) can be used to estimate the kinetics for charge transfer and Li-ion diffusion in NCM cathode material, respectively.[196] However, these techniques cannot elucidate the problematic microstructural changes of Li metal electrodes in Li/NCM batteries, and therefore, further developments in electrochemical analytics are needed. Electrochemical noise analysis (ENA) can be used in detecting dendrite morphology.[197,198] The potentiostatic intermittent titration technique (PITT) can detect the rate of battery capacity decay, and evaluate battery lifetime, and reliability.[199] Additionally, polarization curve analysis (PCA)[200] and polarization potential sweep (PPS)[201] are also emerging techniques that have shown advantages in examining the polarization, electrode interface, and charge transport behavior of batteries. Sensing technology is a promising solution to detect degradation and early failure of Li/NCM batteries, but it is still very underdeveloped (Figure 10b). Due to the nonuniform Li plating behavior on the Li metal anode, the inhomogeneous temperature distribution is particularly prominent in Li/NCM batteries, and temperature sensors can detect hot spots or abnormal temperature patterns.[202] *Real-time* monitoring of the gas evolution behavior of Li metal batteries, e.g., with gas sensors,[203] can trigger preventive measures to avoid such failure. The external pressure sensors could be integrated into Li/NCM batteries to monitor the pressure distribution and variation and better regulate battery operation. Besides, advanced optical and acoustic sensors have recently also been reported to give information on the state of health of batteries, but these technologies still require significant further developments.[204] Moreover, an intelligent battery management system (BMS) that integrates the aforementioned sensors is essential to provide real-time monitoring, diagnostics, and protection/healing functions to minimize degradation and maximize cycle life and safety.

Theoretical Computation and Simulation at All Relevant Time- and Length-Scales. All the above-mentioned experimental techniques for degradation studies exhibit limitations, especially when investigating processes at the atomic/molecular level, and therefore should be complemented with theoretical computations and simulations at all relevant time and length scales. Density functional theory (DFT) and *ab initio* molecular dynamics (AIMD) could reveal information on the electro-/chemical instability of electrolytes, which is of particular importance for high-voltage NCM materials[205] (Figure 10c). Molecular dynamics (MD) methods can also be used to study the ion solvation and diffusion, electrode−electrolyte interfacial reactions, and phase transition of NCM, but are limited to a short length- and time-scale (usually <nm and <~ns).[206] For simulations at large scales, kinetic Monte Carlo (KMC) and Phase Field (PF) simulations can reveal details related to Li dendrite growth and SEI/CEI formation.[207] To unveil the internal temperature, stress, and rate-dependent mechanical responses of Li/NCM batteries, physics-driven machine learning (PD-ML) algorithms and finite element methods (FEM) when jointly applied can capture complex deformations in solids involving multifield and multiscale mechanics.[208,209] Nevertheless, due to the simplifications and boundary conditions required for computations, far away from the complex systems in real batteries, the efficiency and accuracy of these methods are still rather limited and further developments are necessary.

Emerging and Cross-Disciplinary Methods. There are several emerging and cross-disciplinary methods that will significantly accelerate the study of degradation mechanisms in Li/NCM batteries. One is robot-assisted and automated experimentation (including cell fabrication and testing). While many laboratories worldwide have begun adopting this technology, challenges remain in refining robot control algorithms and improving operational accuracy. Additionally, no fully automated laboratories capable of long-term operation have been established.

Another promising approach is virtual reality (VR) technology, which involves the creation of a digital battery model and the simulation of its operation, may also be a powerful tool, with VR visualization technology facilitating the understanding of the results.[210] However, VR technology relies heavily on mathematical models, which may introduce prediction errors, particularly when both application scenarios and battery designs are modified simultaneously. As a result, the conclusions drawn may not always align with real-world outcomes. Developing highly accurate models and optimized control algorithms will be essential to accelerating progress in these interdisciplinary methods.

Both methods are high-throughput, which allows for systematic and accelerated investigation of a whole set of cell parameters (e.g., areal AM loading, electrolyte composition, N/P ratio, E/C ratio, etc.), cycling protocols (e.g., C-rate, cutoff voltage, continuous *or* pulse dis-/charging, etc.), and testing conditions (e.g., temperature and stacking pressure). Besides, the VR methods are particularly useful to safely study degradation under extreme conditions, eliminating the risk for physical accidents (e.g., explosions). Moreover, both methods would produce a large amount of data, which would require high-throughput and automated data analysis combined with machine learning (ML) algorithms to enhance efficiency and accuracy (Figure 10d). In addition, the development of open-access and collaborative platforms is also of crucial importance to facilitate the sharing of materials and data and to accelerate the understanding of the degradation mechanisms of Li/NCM batteries.

Overall, Li/NCM batteries have received increasing attention but face various issues toward stabling cycling, such as issues toward stabling cycling, such as dendrite growth, “dead” Li, cathode cracking, electrolyte depletion, SEI/CEI formation, and gassing. To understand the battery degradation and failure mechanisms, it is essential to consider the detailed influences of different battery materials (cathode, anode, and electrolyte), battery designs (coin cell, prismatic cell, and pouch cell), and operating conditions (e.g., current density, cutoff voltage, temperature, and stacking pressure). In-depth understanding of the interactions between the degradation processes of the cathode and anode is also required, particularly for solid-state Li/NCM batteries. To advance Li/NCM batteries toward practical applications, it is crucial to promote interdisciplinary and collaborative research, joining efforts between academia and industries, integrating cutting-edge and emerging experimental and computational methods and establishing a platform for data sharing to further and deepen the understanding of the degradation and failure mechanism of Li/NCM batteries toward performance improvement. Moreover, as these degradation processes of Li/NCM batteries are not unique and most of them are observed also in Li metal batteries with other cathode materials, e.g., $LiFePO_4$ and sulfur, the understanding of the degradation mechanisms of Li/NCM batteries can benefit the advancement of other types of Li metal batteries as well toward practical applications in future energy storage.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.4c03578.

> Literature summary of Li/NCM battery degradation and their relationship with cell design parameters, common electrodes materials and their major degradation mechanisms, and gas evolution reactions of Li/NCM batteries (PDF)

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■ ACKNOWLEDGMENTS

S.J. acknowledges the financial support from the National Natural Science Foundation of China (Grant Nos. 52225105 and 22279127).

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