Fracture behavior in battery materials

Ping Li, Yibo Zhao, Yongxing Shen and Shou-Hang Bo

University of Michigan–Shanghai Jiao Tong University Joint Institute, Shanghai Jiao Tong University, 800 Dong Chuan Road, Minhang District, Shanghai 200240, People’s Republic of China

E-mail: shouhang.bo@sjtu.edu.cn and yongxing.shen@sjtu.edu.cn

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Abstract

The fracture of battery materials is one of the main causes of battery degradation. This issue is further amplified in emerging solid-state batteries, where the more robust interface between the liquid electrolyte and solid electrode in conventional batteries is replaced by a brittle solid–solid interface. In this review, we summarize the observed fracture behavior in battery materials, the origin of fracture initiation and propagation, as well as the factors that affect the fracture processes of battery materials. Both experimental and modeling analyses are presented. Finally, future developments regarding the quantification of fracture, the interplay of chemo-mechanical factors, and battery lifespan design are discussed along with a proposed theoretical framework, in analogy to fatigue damage, to better understand battery material fracture upon extended cycling.

1. Introduction

The Nobel Prize in Chemistry 2019 was awarded to John B. Goodenough, M. Stanley Whittingham, and Akira Yoshino to honor their contribution to the development of lithium-ion (Li-ion) batteries. Not only Li-ion batteries but all batteries are crucial for energy storage and transition. Although many sustainable energy technologies, such as solar, hydropower, and marine energy, have been developed in recent years, these energy sources are intermittent and unstable. Therefore, grid-scale energy storage systems that use batteries to store these renewable energy sources as they are generated are needed. Rechargeable batteries also currently dominate the portable electronics market and have penetrated the electric vehicle market. Batteries with a longer cycle life, higher energy density, increased safety, and reduced cost are thus highly desired.

State-of-the-art Li-ion batteries operate using two Li reservoirs, a cathode and anode, with different Li chemical potentials, as illustrated in figure 1. These two electrodes consist of three major components: active materials, which store and release Li ions and are redox active; an electronic conductor such as carbon; and a polymer binder that holds the electrode components together to form films of 10–100 µm in thickness. The cathode and anode are usually separated by a polymeric membrane soaked with a Li-ion-conducting, but electronically insulating, liquid electrolyte. During battery discharge, Li ions are extracted from the anode active material, travel across the liquid electrolyte, and are eventually inserted into the cathode active material. Meanwhile, electrons flow through an external circuit, powering electronic devices, such as electric vehicles and laptops. During battery charge, the process is reversed. As the chemical compositions (i.e. Li concentrations) of the cathode and anode active materials evolve during battery charge and discharge, volume changes at both the electrode and battery level are unavoidable, inducing the fracture of battery materials.

Fracture is a process in which a crack propagates and eventually leads to the separation of solids into pieces. There are two types of fractures depending on whether significant plastic deformation occurs before the fracture: brittle fracture, in which negligible plastic deformation exists before rapid fracture propagation, and ductile fracture, in which substantial plastic deformation takes place before fracture. Fracture in batteries is even more complex than typical mechanical fracture because of the coupling with electrochemistry. During battery operation, the chemical and mechanical properties of the electrode evolve. Stress is generated from the volume change of electrodes, which is driven by material composition change resulting from ion
Figure 1. Schematic illustration of chemomechanical interplay in solid-state batteries (SSBs). SSBs are composed of a solid-state electrolyte (SSE) and electrodes, where the electrodes are prepared by mixing active particles and carbon with SSE particles. During charging and discharging, the active particles undergo expansion or contraction as a result of Li insertion or extraction, respectively, which induces the formation of inter-/intragranular cracks in the active particles or SSE particles and delamination between active particles and the SSE particles. At the same time, interface decomposition and heterogeneous reactions also occur.

insertion or extraction. The stress can lead to the fracture of battery materials, which produces new surfaces and surface chemical species.

Battery material fracture is one of the main causes of battery capacity fading. Fracture can isolate active materials such that they are no longer in contact with electronic and/or ionic pathways in the electrode and become electrochemically inactive. One group of widely used cathode materials, layered transition metal oxides of the $\alpha$-NaFeO$_2$ structure (e.g. LiCoO$_2$) are largely affected by the fracture in this way because of the stress induced by lattice expansion and contraction. Fracture also generates fresh surfaces of active materials, which once in contact with a liquid electrolyte can result in a continuous reaction and solid-electrolyte interphase (SEI) build-up. This process reduces the cycling efficiency of batteries and accelerates electrolyte consumption, both of which can lead to a substantially reduced calendar life of batteries.

In emerging SSBs, the liquid electrolyte is replaced by an SSE, which poses two primary challenges at SSB interfaces, e.g. the interfaces between the SSE, electrode, and current collector, limiting the practical usage of SSBs (figure 1). First, chemical and electrochemical decomposition can occur at the electrolyte/electrode and electrolyte/carbon interfaces, leading to a substantial increase of the battery impedance and thus degradation of the battery performance [1–4]. Second, volume expansion and contraction of the electrode active materials, e.g. LiCoO$_2$ and Li metal, can lead to the formation of cracks at the interface and isolated active materials, which lose contact with the electrolyte and/or carbon. As a result, interfacial resistance increases and battery capacity fades [5, 6]. Cracks can also form in the SSE membrane as a result of electrode volume expansion. Such cracks in the SSE create voids, which can lead to short circuits and even catastrophic failure of the battery [7]. Although strategies have been proposed to tackle the chemical instability issue at SSB interfaces [8], the mechanical aspect of the interface instability appears to be more difficult to address. It is therefore important to understand the fundamental fracture mechanism of SSB materials.

Both experimental and computational methods have been utilized to study battery material fracture. Electron microscopy and X-ray tomography are commonly used to directly observe the initiation and propagation of cracks under different cycling conditions [9–13]. These imaging results shed light on the critical cycling conditions and particle morphology that affect the degree of fracture. X-ray diffraction has also been used to analyze the phase transitions of active materials during cycling [14, 15]. The diffraction patterns can be used to identify the origin of the fracture, such as the volume change resulting from phase transitions of Si anode particles. Computationally, various chemomechanical models have been developed to simulate the fracture process. In these models, the Li concentration distribution, responding stress distribution, and fracture initiation and propagation criteria have been considered [16–19].
In this review, we first present a microscopic description of fracture in battery materials as well as the related mechanisms in section 2. In section 3, we examine the modeling aspect of fracture. Then, previous studies on specific electrode and SSE materials are discussed in section 3 from both experimental and computational perspectives. In section 4, a summary of the intrinsic and extrinsic factors that affect the fracture behavior of battery materials is provided. Finally, challenges and future research directions for battery material fracture are highlighted. In this review, we aim to bridge fracture mechanics with electrochemistry to achieve a comprehensive understanding of the complex interplay between chemomechanical factors in SSE materials.

2. Mechanisms of battery material fracture

In this section, we will introduce the mechanisms of the fracture of battery materials. First, two types of fracture, intergranular and intragranular cracking, for cathodes, anodes, and SSEs will be discussed. Then, the origin of cracks in battery materials with different Li-ion storage mechanisms will be analyzed. Finally, volume changes of different active materials will be compared.

Broadly speaking, fracture in battery materials can occur via two paths: intragranular or intergranular cracking. Widely used cathode materials, such as layered transition metal oxides, are generally polycrystalline and are composed of numerous randomly oriented monocristalline grains with grain boundaries in between. These monocristalline grains (i.e. primary particles) often further aggregate into micron-size particles (i.e. secondary particles), as illustrated in figure 2 [14]. Intragranular cracks propagate within primary particles, whereas intergranular cracks grow between primary particles. The morphologies of these two types of cracks developed after cycling a Li[Li0.84Co0.15Mn0.05]O2 cathode are shown in figure 3 [20]. The intergranular crack is indicated by yellow arrows and grows across several primary particles. In contrast, the intragranular cracks propagate through the interior of a Li[Li0.84Co0.15Mn0.05]O2 primary particle and terminate at the edges. For alloying anodes, such as Si, Ge, and Sn, intragranular cracks occur on single-crystalline or amorphous materials, whereas both intergranular and intragranular cracks arise on polycristalline alloying anodes (particles and films). For graphite anode, an interlayer crack which propagates within the graphitic layer of graphite particles [21] is observed. Besides, the intragranular crack propagates along the boundaries of graphite particles [22]. For inorganic SSEs, intragranular cracks are induced in single-crystalline and amorphous materials, while intergranular cracks form along the grain boundary of polycristalline SSEs during Li electrodeposition.

The origin of intra- and intergranular cracks in intercalation cathodes is concentration gradient induced stress and two-phase-coherency stress on particles. In layered oxide cathode materials, oxygen release and phase transformation from layered to spinel and/or rocksalt phases generates a large strain during charging process [23]. Intragranular cracks are linked to material defects, such as vacancy and dislocation. In a layered transition metal oxide cathode such as LiNi1/3Mn1/3Co1/3O2, during crack incubation, Li or O vacancies first condense at the dislocation core. Then stress generated by the change in the material composition and volume drives the edge dislocation core to eventually develop into an intragranular crack [24], which is shown in figure 4. An anisotropic change of the lattice dimension during the single-phase solid solution stage (the ratio c/a of rhombohedral structure decreased from 5.07–4.89) [25] and the phase-transformation process (the lattice constants along the a and c directions increase by 4.48% and 0.74%, respectively, upon transformation from the layered to spinel and/or rocksalt phases) [26] is observed. Consequently, primary
particles with different orientations will experience strain mismatch. Thus, neighboring particles experience different strain sizes and shear stresses, which induce intergranular crack initiation and propagation [14], as shown in figure 5. For the spinel type [27] and olivine type [28] cathodes, two-phase-coherency stress is the origin of crack formation [29]. The large lattice mismatch between coexisting phases promotes a pre-existing flaw to extend [30] or crack formation on a disordered boundary [31].

The origin of the fracture in the intercalation type graphite anode is due to the build-up of stress induced by volume change when Li ions intercalate into (or extract from) graphite layers and gas formation produced by surface side reactions, as shown in figure 6. Graphite can react with liquid electrolytes and Li ions to form a solid electrolyte interface (SEI) on the surface of an anode accompanied by gas evolution [32] and compressive pressure [33] existing inside the SEI. The SEI is highly cohesive and dense for ethylene carbonate-based electrolyte, which can prevent cointercalation of solvent and ions and further surface reaction. Cointercalation of solvent and ions leads to graphite layer exfoliation and eventually fracture in propylene carbonate-based electrolyte due to a loose and vulnerable SEI. Li ions’ intercalation into layers of
Figure 5. Virtual slices of transmission X-ray tomograms of LiNi\textsubscript{x}Co\textsubscript{y}Al\textsubscript{z}O\textsubscript{2} (NCA) (a) in its pristine state and (b) charged to 4.5 V after 93 cycles (2.7–4.5 V, C/20) showing substantial fracture after extended cycling. (c) Schematic illustration of the intergranular crack formation process in a secondary NCA particle. The arrow in each primary particle represents its crystal orientation. The first cycle causes the initiation of intergranular cracks. These intergranular cracks propagate in subsequent cycles. Reprinted with permission from [14]. © (2017) American Chemical Society.

Figure 6. Crack formation on graphite anode.

graphite, which forms LiC\textsubscript{6} through several stages, induces a 12.9% volume expansion [34]. This process generates tensile stress in the outer SEI which can be partially accommodated by the compressive stress inside the SEI. However, an SEI cannot fully accommodate the volume change of graphite during long cycles. As a result, solvent percolates through the SEI and reacts with graphite to generate gases between the layers, which leads to an interlayer crack in graphite. The volume change of a graphite particle can also induce crack formation between a graphite particle and matrix composed of a PVDF binder and acetylene in a composite electrode.

Intercalation cathodes and anodes have similarities and differences on crack origin. The similarity is that both the layered oxide cathode and graphite anode experience several stages of phase transformations accompanying an anisotropic change of the lattice parameters acting as the main origin of intergranular crack formation. However, there is a difference in the intercalation cathode and anode. Cointercalation of an ion with solvent in graphite is fatal because it not only induces layer exfoliation but also produces gases between the graphitic layers, while cointercalation of solvated ions does not occur in intercalation cathodes.
The origin of intra- and intergranular cracks in the alloying anode is two-phase-coherency stress induced by the expansion (or contraction) of electrode materials resulting from the phase transformation [35]. To understand the phase transformation process upon the insertion of Li ions into an alloying anode, we should turn to the phase diagram. Take the lithium–silicon (Li–Si) phase diagram (Figure 7 [36]) for example. During the charge process, Li ions are inserted into the Si, shifting the binary phase composition toward the Li-rich direction. When such an insertion process occurs at room temperature (RT; i.e. 300 K), thermodynamically, pure Si will sequentially transform into LiSi, Li$_{12}$Si$_7$, Li$_7$Si$_3$, Li$_{13}$Si$_4$, and Li$_{22}$Si$_5$ as lithiation progresses. These phase transformations result in a large volume expansion of almost 300% after full lithiation (or contraction during discharging), which creates a large stress on Si particles and therefore cracks. Besides the Si anode, other alloying anodes also experience large volume changes. When crystalline Ge nanowires transform to a c-Li$_{15}$Ge$_4$ phase, its volume increases by 260% [37]. Tin nanoparticle volume dilates by 159% after its first lithiation [38]. During delithiation, the volume of the alloying anode shrinks reversibly. Stress is generated between the two phases with a mismatched lattice parameter. When stress increases to some extent, fracture occurs on the alloying anode. Besides, anisotropic reaction kinetics accelerates fracture. For example, Si has a more severe lattice parameter change along the [110] direction than germanium does [39], because Li ions diffuse fast in the [110] direction in c-Si nanopillars. Consequently, the critical diameter of <111> Si pillars for lithiation-induced fracture is about 300 nm, while the critical diameter related to lithiation-induced fracture of <111> Ge pillars is ~1.2 µm.

The origin of the crack in the conversion type anode is structural reorganization and volume change during charging and discharging [40]. The reaction mechanism can be generalized as below:

$\text{M}_a\text{X}_b + (b \cdot n)\text{Li}^+ + (b \cdot n)e^- \xrightarrow{\text{discharge}} a\text{M} + b\text{Li}_n\text{X}$

where $\text{M}$ is the transition metal (Mn, Fe, Co, Ni, Cu, etc), $\text{X}$ is H, N, O, F, P, S, etc, and $n$ is the oxidation state of $\text{X}$ [41, 42]. For the Fe$_2$O$_3$ anode with a reticular structure, the reticular structure turns into nanoplates dispersing in a nanoparticle matrix after the first discharge which returns back to a reticular structure with a crack after the first charge [43]. This crack is also observed in other conversion anodes, such as Fe$_3$O$_4$, $\beta$–MnO$_2$, etc, which induces electrode pulverization [44].

Cracks also appear in SSEs. The origin of a crack in SSEs is stress from the growth of an interphase [45] and the volume change of the active material [46]. The crack formation in SSE can be seen in figure 8. Fracture in SSE initiates near the edge of the interphase growth by the reaction between the SSEs and electrodes and the volume increase of the electrode during charging. In SSEs, tensile radial stress induces circumferential cracks to form and tensile circumferential stress initiates radial cracks concentrated near the edge of the interphase. The circumferential and radial crack propagate in SSEs to form a web-like pattern [45]. In the composite cathode, active material will contract/expand during Li-ion extraction or insertion, which results in cracks initiating from the interface between the active particle and the SSE.

The origins of crack for different Li-ion storage mechanisms are all associated with volume change of active electrode materials. Large stress is generated with a large volume change according to the formula
The origin of crack in SSEs. Crack is induced by stress build-up from expansion of interphase formed between Li metal and SSEs and/or from contraction/expansion of active material.

PMVs of different battery active materials during delithiation. Reproduced from [35] with permission of The Royal Society of Chemistry.

\[ \Delta P = -\varepsilon_{\text{vol}} K \]

where \( K \) is the bulk modulus of the SSE and \( \varepsilon_{\text{vol}} \) is volume strain [35]. Quantification of the volume change is important to estimate the magnitude of the stress which causes the crack nucleation and propagation in electrode active particles and SSEs. Koerver et al used a partial molar volume (PMV) to quantify the volume change of active electrode materials. PMV is defined as the partial derivative of the volume of solid-solution phases with respect to the number of moles of inserted Li under constant temperature and pressure. For two-phase materials, the apparent PMV is defined as the difference in the molar volume between the delithiated and lithiated phases of two-phase active materials [35]. The PMVs of different active materials from crystallographic measurements are presented in figure 9. The PMVs are positive for all electrode materials shown in figure 9 except LiCoO₂. Ternary cathode materials show large PMVs at the deep charge state, which explains the severe crack with a large charge cutoff voltage.

3. Modeling of fracture

Depending on the mechanical properties of battery materials, the fracture behavior can be categorized as follows: linear elastic fracture mechanics (LEFM) or elastic plastic fracture mechanics (EPFM). LEFM
assumes that the material is linear elastic; thus, the stress field up to the crack tip can be calculated assuming 
elasticity. LEFM is only valid when the plastic zone is much smaller than the characteristic lengths of the 
solid, including the crack length and ligament width. For oxide electrolytes and cathode materials with high 
Young’s moduli, fracture analysis can be performed using LEFM. However, if a large plastic deformation 
zone develops near the crack tip, EPFM must be used.

One of the criteria to model crack initiation is the assumption that a crack initiates when the tensile stress 
exceeds a critical value, the fracture strength of the material [47–49]. The fracture strength is the ability of a 
material to resist fracture and is the final recorded point on the stress–strain curve of a material. It is 
determined with respect to different types of applied loadings. Guggenheim [26] studied Li-ion transport 
experimentally and computationally on a network-structured electrode where Si particles were attached to a 
carbon nanofiber. As expected, when the tensile hoop stress $\sigma_{ho}$ at the interface reached the fracture strength 
of the carbon matrix, crack initiation occurred at the contacting carbon matrix surface. Using large-scale 
atomistic simulations, Ding et al [50] observed a transition of the fracture mechanism from the intrinsic 
nanoscale cavitation to shear banding on amorphous lithiated Si, with increased Li concentration leading to 
this crack initiation phenomenon.

According to LEFM, once a crack appears, there are two commonly accepted and fundamentally 
equivalent criteria used to determine whether the crack propagates, the stress intensity factor (SIF) criterion 
and energy release rate criterion. For the SIF criterion, roughly speaking, a crack propagates when 
$K_\text{I} > K_\text{Ic}$, where $K_\text{I}$ is the mode I (opening mode) SIF and $K_\text{Ic}$ is the material fracture toughness. For electrode particles, 
$K_\text{I}$ depends on the charging time, pre-existing crack length, and current density, whereas $K_\text{Ic}$ is an intrinsic 
material parameter, which depends on the flaw geometry, loading conditions, and material properties. Chen 
et al [51] built an analytical model to predict crack propagation during phase transformation for a spherical 
Si electrode by applying this criterion. The pre-existing crack at the interface propagates when the SIF 
surpasses the fracture toughness of the electrode material during Li intercalation. Raghavan et al [52] 
identified fracture-free conditions using the SIF criterion in a study of pre-existing surface flaw propagation 
(a flaw is regarded as a pre-existing crack) under galvanostatic and potentiostatic boundary conditions.

The energy release rate criterion states that a crack will propagate when the strain energy release rate 
surpasses the surface energy of the newly created surface formed by cracking [51]. The strain energy release 
rate $G$ is defined as the elastic strain energy released when the crack extends a unit area, i.e. $G = -\partial\pi/\partial A$, 
where $\pi$ is the elastic strain energy and $A$ is the crack area. Zhao et al [53] built a finite-element model using 
this energy criterion to describe the concurrent reaction front movement and plastic deformation of a 
spherical c-Si electrode during lithiation. They observed that fracture can be avoided for lithiated Si with a 
low yield strength and small particle size.

Computational methods based on these crack initiation and crack propagation criteria can be used to 
predict the fracture behavior of materials. The phase field model [16–18, 54] and cohesive zone model 
[55–63] are the most common computational models.

The phase field model employs a continuous field variable to represent cracks. The evolution of crack 
surfaces follows from the solution of a set of partial differential equations. The advantage of the phase field 
model is that it does not require extra criterion to predict crack initiation and crack branching.

The cohesive model uses elastoplastic fracture mechanics to model the interface damage and fracture 
process. The key component of a cohesive model is the traction-separation law, with an example shown in 
figure 10 [64]. In typical traction-separation law, the traction first increases with separation to a maximum 
value during the crack initiation stage and then drops to zero during the crack propagation stage, which leads 
to complete surface separation. Ryu et al [10] built a cohesive zone-finite element model in which 
the fracture of Si nanopillars is described as plastic growth of nanovoids; the nanovoids eventually link up 
during the lithiation process, as illustrated in figure 11. In this model, the void can grow isotropically from 
diameter $\alpha_0$ to diameter $\alpha$ (figure 11). A crack initiates from the small voids and propagates as the voids 
grow to a maximum diameter of $2\beta$. The cohesive law can also be applied to analyze the crack initiation 
process in originally crack-free electrodes. Bhandakkar and Gao [65] developed a cohesive zone model in a Si 
strip under diffusion-induced stresses.

### 4. Factors affecting fracture behavior

The factors affecting fracture behavior can be categorized into two types: intrinsic factors, which are related 
to inherent battery material properties, and extrinsic factors, which are related to battery cycling conditions, 
as illustrated in figure 12. In this review, we will discuss how the intrinsic factors (particle size, morphology, 
element composition, structure, pre-existing defects, and mechanical properties) and extrinsic factors 
(C-rate, cutoff voltage, cycling time, and thermal treatment) affect the fracture processes of battery materials.
Figure 10. Typical traction-separation curve in a cohesive zone model, where $x$ represents the displacement of the interface, and $y$ represents the cohesive force. Reprinted from [64], © (2016), with permission from Elsevier.

Figure 11. Plastic void growth model near the crack tip. (a) Nanovoids with radius $\alpha$ and a spacing of $2\beta$ are formed under a uniaxial tensile stress. (b) Nanovoids link up and lead to failure. (c) Hydrostatic stress state near the void modeled in a hypothetical bar assuming that the total volume of the bar is conserved because the volume increase at the edges is equal to the volume decrease resulting from void growth. $\alpha_0$ is the initial radius of the void and $w$ and $w_D$ are the current separation distance and separation distance when the void forms, respectively. Reprinted from [10], © (2014), with permission from Elsevier.

Below, we first discuss the effect of these factors on anode materials, followed by a discussion of their effect on cathode and SSE materials.

4.1. Anode materials
Commonly employed anode materials include graphite, alloys, and lithium titanate Li$_4$Ti$_5$O$_{12}$ (LTO). In SSBs, the anode is either a Li metal or a composite electrode containing anode active materials, carbon, and an SSE. Although Li metal is the most energy-dense battery anode, it is not stable when paired with most SSEs, resulting in interface decomposition and dendrite-growth-induced electrolyte cracks. A composite electrode is more chemically stable when combined with an SSE. However, a large volume change occurs in most anode active materials except LTO during Li-ion insertion/extraction [66].

Size-dependent fracture is observed for Si anodes. The indentation size effect is well known in the field of fracture mechanics which was first reported by Nix and Gao [67]. The indentation size effect relation is

$$\frac{H}{H_0} = \sqrt{1 + \frac{h}{h^*}}$$

where $H$ is the hardness for a given depth of indentation, $h$; $H_0$ is the hardness for an indentation of infinite depth; and $h^*$ is a characteristic length that depends on the indenter shape, shear modulus, and $H_0$. The indentation size effect indicates that the hardness of a crystalline material varies with the size of the indentation. Similarly, for battery materials such as Si, there is usually a critical particle size below which no fracture occurs. In addition, smaller-sized particles are more robust against the formation of cracks. Liu et al [68] observed that below a critical diameter of ~150 nm, Si nanoparticles will not fracture. In their study, the ratio of $t/D$ increased with decreasing $D$ when the first crack initiated at the interface, where $t$ is the thickness of the Li$_x$Si shell and $D$ is the diameter of the Si nanoparticle (figure 13). They built a
non-linear diffusion model to understand why the fracture behavior was size dependent and found that small nanoparticles release an insufficient amount of strain energy to drive crack propagation. Statistical data indicated that the critical diameter of Si nanowires is 220–260 nm, whereas the model indicated that the critical diameter is approximately 300–400 nm for lithiation and much larger for delithiation [69]. In this model, the maximum strain energy release rate is calculated for different sizes of pre-existing cracks and Si nanowires. The critical size of Si nanowires is determined by the values with the most rapid increase of the maximum strain energy release rate. The difference in the critical size determined from the statistical and modeling results is likely due to differences in the pre-existing crack sizes assumed in these two studies. For Si nanoparticles larger than the critical size of 150 nm, a surface crack first emerges near the particle surface [68, 70]. Size-dependent fracture behavior has also been observed for germanium and tin anodes. Wang et al [38] observed that the degree of the fracture of a tin anode has a positive relationship with the tin particle radius during the first lithiation and delithiation, as shown in figure 14. Lee et al [39] observed that a <111> Ge pillar has a larger critical diameter (~1.2 µm) than a <111> Si pillar (~300 nm). A SEM observation revealed that the anisotropic expansion of Ge pillars was less pronounced than that of Si pillars.

In addition to the size dependence, the morphology of active particles also affects the fracture behavior. For different particle morphologies, the fracture sites are different. For spherical c-Si particles, the crack initiates at the surface of the particle [53, 70]. For c-Si nanopillars, a finite element model in which diffusion induced swelling is treated as thermal expansion suggests that Si nanopillars with different crystallographic orientations have different preferred fracture sites. For nanopillars with a <100> crystallographic orientation, cracks initiate at the four corners between the (110) planes, where the maximum tensile stress lies during lithiation, leading to a cross shape, whereas for <110> and <111> crystallographic orientations, cracks also initiate at the maximum tensile stress sites, resulting in ellipsoidal and petal shapes, as shown in figure 15 [10]. The crack initiation sites are consistent with the experimental results shown in figure 16 [10]. For Si_{1-x}Sn_x alloy films, the crack patterns look like dried mud during delithiation. Cracks appear on a Si_{1-x}Sn_x working electrode at the first charge process during which the Li ions are removed, after which the particles undergo reversible expansion and shrinkage [71].
The crystallinity of the anode material also affects the fracture processes. For instance, both c-Si and amorphous Si (a-Si) can be employed as a battery anode. During the first lithiation process, a two-phase transition occurs for both c-Si and a-Si. In c-Si, the two-phase interface is c-Si/Li$_x$Si, whereas for a-Si, the two-phase interface is a-Si/Li$_x$Si. This difference leads to different fracture behaviors. First, the critical size of a-Si particles for fracture is larger than that of c-Si particles. Second, a-Si expands isotropically during lithiation, whereas c-Si expands anisotropically, resulting in anisotropic fracture. Third, the ratio between bond-breaking and the Li diffusion rate ($r_{\text{bond-breaking}}/r_{\text{Li diffusion}}$) is larger in a-Si lithiation than in c-Si lithiation. As a result, the Li-ion concentration gradient in the a-Li$_x$Si shell of a-Si may be larger than that in the a-Li$_x$Si shell of c-Si during lithiation. The large Li-ion concentration gradient, which affects the stress distribution, leads to different fracture behaviors [72].

The factors that affect fracture as we discussed above are all intrinsic physical properties of the battery anode; electrochemical parameters can also affect the fracture behavior. For example, opinions diverge as to the effect of the C-rate on crack propagation in Si nanoparticles. Liu et al [68] performed experiments on Si anode nanoparticles and observed that a slower charging rate did not prevent crack formation in large Si nanoparticles; in addition, a faster charging rate did not induce crack formation in small Si nanoparticles.
Liu et al. also observed that increasing both the C-rate and particle size synergistically propelled the fracture process. They suggested that the C-rate has little effect on crack formation in Si nanoparticles. However, modeling results of other researchers who used a cohesive method [65, 73] indicated that a larger C-rate would lead to higher stress in Si nanowires, which increased the possibility of crack nucleation and
propagation. In modeling studies, the Li diffusion rate was assumed to be isotropic, and can be directly calculated from the imposed current density on the basis of a diffusion equation \cite{74, 75}. We believe the reason for the disagreement between the experimental and computational studies is that the theoretical models did not take the facet-dependent lithiation rate into account. For example, many fracture models of Si spherical particles, whether applying electrochemical or thermal straining parameters, assume an isotropic and homogeneous Li diffusion rate and diffusion-induced deformation because of the amorphous nature of the Li$_x$Si layer. However, in real experiments, the lithiation rate at the reaction front (i.e. the surface that separates amorphous Li$_x$Si and c-Si) in the two-phase particles depends on the lattice surface at which lithiation occurs. Furthermore, we believe the particle size and the C-rate should be considered together to identify fracture-free conditions.

4.2. Cathode materials

Particle size, material composition, and defects are material intrinsic properties that can affect crack propagation in cathode active materials. Similar to anode materials, size dependence is also observed in the fracture of cathode materials. The critical particle size under which fracture will not propagate has been estimated and experimentally confirmed for many LCMs and olivine structured particles. Using synchrotron X-ray tomography, Xia et al \cite{9} showed that the degree of fracture has a positive relationship with the size of LiNi$_{0.6}$Mn$_{0.2}$Co$_{0.2}$O$_2$ (NMC622) secondary particles, as can be observed in figure 17. The particles with larger diameters have wider and longer cracks throughout the entire cross section of the particles. Hu et al \cite{76} determined that the critical particle size for olivine structure LiFePO$_4$ was ~56 nm using the crack propagation criterion of the energy release rate.

The composition of electrode materials can also affect the fracture of battery materials. Composition refers to the elemental concentration in the material. For LCMs such as Li$_{1-x}$Ni$_x$Co$_{1/3}$Mn$_{1/3}$O$_2$ (NCM), a higher Ni content results in the formation of more abundant and more severe cracks in the particle \cite{20, 77}. Ryu et al \cite{20} observed this phenomenon in NCM particles using SEM, as shown in figure 18 \cite{20}. The microcrack density increased with increasing Ni composition from $x = 0.6$ (figure 18(a)) to $x = 0.95$ (figure 18(d)) and was the main reason for capacity fade of the NCM cathode. The capacity fade of the NCM cathode with a higher Ni concentration was more severe than that of the NCM cathode with a lower Ni concentration.

The reason why more severe micro-cracks appear with a higher Ni concentration is that the NCM cathode with a higher Ni concentration undergoes a larger volume change because of the higher degree of delithiation and larger change of nickel-ion radius upon oxidation \cite{78-80}, which leads to the formation of an intergranular crack network between the primary particles. The phase transitions from the original layered structure to three different sequential hexagonal phases (H$_1$, H$_2$, and H$_3$) during charging are usually inferred from $dQ/dV$ profiles in the Li extraction process. During the H$_2$ $\rightarrow$ H$_3$ transition process (approximately 4.1 V vs. Li$^+$/Li), Yoon et al \cite{81} observed an abrupt contraction of the c-axis lattice parameter of LiNiO$_2$, whereas the a-axis lattice parameter remained nearly unchanged. When the Ni concentration is low, such as for a LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (NMC333) cathode, the H$_3$ phase only appears at potentials above 5 V vs. Li/Li$^+$ \cite{82}. When the Ni concentration is intermediate, such as for a LiNi$_{0.8}$Mn$_{0.2}$Co$_{0.2}$O$_2$ (NMC622) cathode, the H$_2$ $\rightarrow$ H$_3$ transition occurs near 5 V during the charge process \cite{83}.

In addition to the particle size and material composition, pre-existing defects can also affect the fracture behavior of the cathode. For LiMn$_2$O$_4$, Hovington et al \cite{84} observed that during discharging, cracks are most likely to propagate when the defect is located in the center of the particle; in contrast, during charging, cracks are most likely to propagate when the defect is located at the surface of the particle. They used the extended finite element method to investigate the effect of the current density, particle size, and particle aspect ratio on defect propagation. A larger current density and particle size promoted defect propagation, with a particle aspect ratio of 1.5:1 resulting in the most severe fracture. For LiCoO$_2$ particles \cite{85}, TEM-observable defects such as dislocations, strain contours, and micro-cracks in particles appeared after 50 cycles. For LiFePO$_4$ particles, researchers using TEM and selected area electron diffraction observed that defects such as twin crystal boundaries are initiation sites of cracks \cite{86, 87}. The Li ions diffuse preferably along the b-axis, leading to the development of an internal anisotropic high strain along the a-axis and c-axis. Such anisotropic high strain induces crack initiation at twin crystal boundaries.

State-of-charge heterogeneity on a cathode accelerates crack formation. State-of-charge heterogeneity is defined as heterogeneous distribution of the oxidation state of a transition metal element on a cathode at multiple length scales, ranging from secondary particles to electrodes \cite{9, 16, 88-90}. Chemical outliers exist on nickel-rich layered secondary particles at the discharge state, which means the oxidation state of Ni is more reduced on the surface of particles, while it is more oxidized in the bulk \cite{91}. Chemical outliers may result in concentration gradient stress, and eventually facilitates crack formation. Unbalanced electron and
ion transport distance and rate lead to reaction heterogeneity at the electrode scale. Consequently, depth-dependent particle fracture is observed, which means a more severe crack occurs in the electrode near the separator more than near the current collector [92]. The experiment shows that the mechanical properties of a cathode degrade with a deep delithiation process and cycles [93], which is believed to be the consequence of state-of-charge heterogeneity and crack formation.

Extrinsic factors, including cycling time, cutoff voltage, and temperature, can also affect fracture behavior. During cycling, electrochemically caused fragments are commonly detected in layered composite cathode materials, including NMC and NCA. Lithium batteries using layered composite cathode materials exhibit significant capacity fading after the first charge–discharge cycle. Capacity fading slows down in the following cycles. A consistent phase change during long-time cycling induces further strain development, which is followed by micro-crack formation. Figure 19 shows the capacity fading phenomenon for Li(Li$_{0.2}$Ni$_{0.2}$Mn$_{0.6}$)O$_2$ (LNMO), observed by Gu et al [37]. In figures 19(a)–(c), capacity fading slowed down after the first cycle. The first cycle was considered to cause a certain degree of destruction to the layered active materials, as indicated by the fading tendency. The authors believed that the fading was a consequence of the phase transition of active materials from the layered to the spinel structure, as indicated by the green arrow in figure 19(d). This phase transition was a result of transition-metal-ion sites and Li sites disordering in the lattice and moving further into the interior from the surface of one active material particle. Micro-cracks were observed on LNMO particles after 300 cycles at a rate of C/3 at RT, as shown in figure 20 [90]. The cracks were the result of large strain created by Li insertion/removal and oxygen release during phase transitions in cycling, and the resulting resistance increase is shown in figure 20(b).
The cutoff voltage can affect the crack types and crack density, especially for layered cathode materials. Intergranular and intragranular cracks were observed under different cycling cutoff voltages. High voltage leads to both inter- and intragranular cracks, whereas low voltage only leads to intergranular cracks. Yan et al \[9, 24, 77\] experimentally showed that during electrochemical cycling, intergranular cracks can be observed in layered cathode particles under both high and low cutoff voltages, whereas intragranular cracks can only be observed under high cutoff voltages. Figures 21(e)–(g) shows the intergranular cracks observed in NMC333 secondary particle after 100 cycles under cutoff voltage ranges up to 4.2, 4.5, and 4.7 V, respectively. Therein, intragranular cracks only existed under 4.7 V, as indicated by the yellow arrows. In addition, the capacity fading phenomenon was more severe under the high cutoff voltage, as indicated by the blue triangles in figure 21(a). The density of the intragranular cracks in NMC333 cathodes abruptly increases upon cycling at a high cutoff voltage \[24\]. Yoon et al \[81\] observed that the c-axis lattice constant increases at
a higher cutoff charge voltage, which may explain why the cracking is more severe at a high cutoff charging voltage because of the larger volume change in the electrode.

Thermal runaway, the phenomenon of a battery releasing a large amount of heat when cycling, is a severe issue for batteries. Recently, Feng et al [86] noted that Li cells cycled at HT (e.g. 110 °C) exhibit higher thermal stability than those cycled at low temperature (e.g. −10 °C). However, active material loss, in their case intercalated Li in a graphite anode, is more severe when cycling at HT. In their study, the thermal runaway process can reach a temperature of 700 °C–800 °C. The thermal response of the cathode active material is also an important characteristic for practical use of a battery and is related to cathode active material particle fracture. Researchers have observed that active material fracture can also be induced by temperature. Thermal abuse, for example, produces results similar to those after long-term electrochemical cycling of composite layered cathode active materials, leading to the formation of nano- or micro-cracks in primary particles; as a result, thermal treatment has been used in place of electrochemical cycling as an analysis method for fracture in layered cathode particles [87, 94]. An NMC622 secondary particle with pre-existing micro-cracks contained more cracks after thermal abuse at 380 °C for 4 h, as can be observed in figures 22(a) and (b). In addition, the experimental results of Wei et al indicated that the porosity and surface area increased after thermal abuse, as shown in figure 22(c). Thus, thermal treatment at 300 °C–400 °C can induce the propagation of micro-cracks in cathode active particles, and thermal runaway could take the entire cell packet to 700 °C–800 °C. It is reasonable that thermal runaway makes the cracks more severe, which will consequently cause high resistivity in the cell because of fracture-induced active material separation. This will, in turn, result in more severe thermal runaway and thus lower thermal stability.
4.3. SSEs
The commonly used SSEs for Li SSBs are Li-based NASICONs [95, 96], garnets [97–99], and sulfides [97, 100, 101]. Li-based NASICONs are oxides with a large Young’s modulus. Among all Li-based NASICONs, the maximum conductivity of 7 mS cm\(^{-1}\) is achieved for the glass ceramics of \(\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_{3-x}\text{Li}_2\text{O} (x = 0.0–0.20)\) at RT [102]. A typical garnet material is \(\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}\) whose Li-ion conductivity reaches up to 1.62 mS cm\(^{-1}\) at RT [103]. \(\text{Li}_{10}\text{GeP}_2\text{S}_{12}\) is one of the best conducting sulfides, reaching a Li-ion conductivity of 12 mS cm\(^{-1}\) at RT [104]. However, compared with oxides, sulfides are more compliant with a smaller Young’s modulus. Fracture in SSEs is usually analyzed by examining the metal dendrite growth path and mechanical properties of SSEs to guide the selection of SSEs. The mechanical properties, crystallinity, and defects of SSEs can affect the fracture behavior.

Both experimental and modeling results have shown that mechanical properties can affect the fracture behavior of SSEs. Bucci et al [58] built a 2D cohesive zone model based on intrinsic constitutive behavior. In this model, anode active materials are surrounded by a sulfide SSE and carbon matrix. Cracks induced by tensile stress initiate at the corner of anode particles, as indicated by the black dot in figure 23 and propagate into the SSE during the charge process. The crack propagation path is marked with black lines in the SSE (figure 23). The crack nucleation and propagation rate depend on the elastic properties of the SSE. Crack nucleation is delayed for an SSE with a larger fracture energy (the energy needed to open a new crack). The crack propagation rate and the final length of the crack decrease with the increased fracture energy of the SSE. The model results indicate that a sulfide SSE with a Young’s modulus of 15 GPa assists crack propagation compared with an SSE with a larger Young’s modulus, indicating that a compliant sulfide SSE is easy to crack. As a result, large tensile stress forms in the sulfide SSE, which contradicts the common belief that sulfide SSEs are more suitable for SSBs than oxide SSEs [105] because they were believed to accommodate the deformation and volume change of active materials [106]. Instrumented indentation and ultrasonic measurement are common methods to measure elastic modulus (E), hardness (H), and fracture toughness (\(K_{IC}\)) [35, 107, 108]. These mechanical properties then determine the ability of the SSE to withstand stresses from the two electrodes during battery cycling [106, 109].

The crystallinity and defects of SSEs can also affect the fracture behavior. For polycrystalline electrolytes, a crack is generated by the deposition of Li metal along the grain boundaries. For a single-crystalline electrolyte, although there are no grain boundaries, artificial flaws are present on the surface. A crack extends stably under the crack-opening stress. The crack-opening stress is produced by Li metal deposition inside the flaw.

![Figure 22. Nano-tomography of a selected NMC622 secondary particle (a) before and (b) after thermal treatment at 380 °C for 4 h. (c), (d) Comparison of micro-crack formation and other properties before and after thermal treatment of the particle. Reproduced from [87] with permission of The Royal Society of Chemistry.](image-url)
Figure 23. Finite element analysis of composite electrodes: (a) boundary conditions and geometry of the modeling and evolution of Li concentration and corresponding stress at different charge times and at (b) $t = 150$ s, (c) $t = 400$ s, and (d) $t = 900$ s. When Li ions are inserted into active material particles, compressive stress develops inside the particles and tensile stress develops at the corners of active particles. Eventually the tensile stress is large enough to initiate crack propagation from corner to corner, which blocks the diffusion path for Li ions and electrons. Reproduced from [58] with permission of The Royal Society of Chemistry.

Figure 24. Ex-situ optical microscopy image of single-crystal LLZTO, focused on a subsurface Li filament. A crack without Li metal propagates from the Li filament tip. Republished with permission of Electrochemical Society, Inc. from [110]; permission conveyed through © Clearance Center, Inc.

as shown in Figure 24 [110], a crack propagates from the deposited Limetal tip on a single-crystal electrolyte. For an amorphous electrolyte, no grain boundary exists. Porz et al [11] used optical microscopy to observe Li deposition on a 70/30 mol% amorphous Li$_2$S–P$_2$S$_5$ SSE with and without surface defects. No crack appeared on the surface of a 70Li$_2$S–30P$_2$S$_5$ solid electrolyte without surface defects, whereas cracks were observed to grow from the surface defect site on a 70Li$_2$S–30P$_2$S$_5$ SSE with surface defects. The authors studied Li penetration mechanisms in four types of SSEs (amorphous 70/30 mol% Li$_2$S–P$_2$S$_5$, polycrystalline $\beta$-Li$_3$PS$_4$, and single-crystalline and polycrystalline Li$_6$La$_3$ZrTaO$_{12}$ (LLZTO) garnet) [11]. They observed that Li infiltration on pre-existing defects in the electrolytes led to crack tip stress accumulation and subsequent crack propagation.

We have discussed the fracture mechanism, modelling, and factors that affect the fracture behaviors of battery materials above. Table 1, comparing the fracture mechanism, fracture effects, and factors affecting the fracture for anodes, cathodes, and SSEs is developed below to better understand the similarities and differences of fracture among anodes, cathodes, and SSEs.
Table 1. Comparisons of the fracture mechanism, fracture effects, and factors affecting the fracture for anodes, cathodes, and SSEs.

| Fracture mechanism | Anodes | Cathodes | SSEs |
|--------------------|--------|----------|------|
|  | Alloying | Two-phase-coherency stress, anisotropic reaction kinetics | Stress induced by volume change, gas formation, counterintercalation of solvated ion | Concentration gradient stress and two-phase-coherency stress |
| | Intercalation (graphite) | Stress induced by volume change, gas formation, counterintercalation of solvated ion | Stress induced by growth of interphase or volume expansion of active material |
| | Conversion | Structure reorganization and volume change | Porosity increases, impedance increase, overpotential increase |
| Fracture effect | Specific area of active material increases, impeded diffusion of ions and electrons | Exfoliation, impedance increase, capacity fade | Resistance increase, capacity fading |
| | Mechanical properties, solvent type | Structure pulverization, decayed capacity, inferior cycling stability. | |
| Factors affecting fracture | Size, morphology, crystallinity, C-rate | Particle size, material composition, pre-existing defects, state-of-charge heterogeneity, cycling time, cutoff voltage, temperature | Mechanical properties, crystallinity, defects |
| | Mechanical properties, solvent type | Particle size, material composition, pre-existing defects, state-of-charge heterogeneity, cycling time, cutoff voltage, temperature | Mechanical properties, crystallinity, defects |

5. Discussion

5.1. Quantification of fracture and its effect on electrochemistry

Many experiments have qualitatively visualized the degree of fracture. However, to quantify the effect of fracture on battery performance, it is necessary to quantify the degree of fracture using the specific area and porosity. A new surface area is created when a crack forms on an active material. The absolute surface area, which is the entire surface exposed to the electrolyte or air, will increase after cracking without volume contraction. However, the absolute surface area may remain constant or decrease when crack propagation is accompanied by volume contraction, which may not indicate the exact degree of the fracture of battery materials. Therefore, other variables are needed to describe the degree of fracture. The specific area is defined as the surface area per unit volume, which reflects the true degree of fracture. Wang et al [38] quantified the degree of fracture in an electrode from the increase of the specific area $(S_v)$ compared with that of a particle without fracture that had undergone the same volume change. For a spherical particle with radius $r$, $S_v$ can be calculated as follows:

$$S_v = \frac{4\pi r^2}{3\pi r^3} = \frac{3}{r}.$$  

If the particle undergoes volume expansion/shrinkage without fracture, the specific area change in percentage is

$$dS_v = \frac{\Delta S_v}{S_{v1}},$$  

where $S_{v1}$ is the specific area before volume expansion. If the radius of the particle changes from $r_1$ to $r_2 = ar_1$, where $a$ is a constant, the specific area change in percentage is calculated as

$$dS_v = \frac{\Delta S_v}{S_{v1}} = \left(1 - \frac{1}{a}\right) = \frac{r_1 - ar_1}{ar_1} = \frac{1 - a}{a}.$$  

The specific area change is a constant if the particle expands/shrinks without fracture according to equation (3). An additional crack surface $A$ is generated in the particle with fracture. As a result, the specific area change is $dS_v' = dS_v + A$, where $A > 0$. For more severe fracture on the particle, more crack surface is generated; therefore, the specific area change deviates more from $dS_v$.

Use of the specific area provides a solution to obtain a quantitative description of the degree of fracture rather than a qualitative one. Transmission X-ray microscopy (TXM) can be used to monitor the 3D...
microstructure evolving in the electrode at the submicron scale. The specific area change in a particle can be measured by TXM. In figure 25 [38], the blue line represents the specific area evolution, and the red line represents the surface area evolution during the first and second cycles. The absolute surface area (figure 25) increases via the combined effect of volume expansion and fracture during each lithiation (stages 0–1 and 2–3) while remaining constant with crack extension and particle volume shrinkage during delithiation (stages 1–2 and 3–4). Instead of using the change of the absolute surface area, the change of the specific area is a valid parameter to quantify the degree of fracture by considering the combined effect of volume change and crack propagation. The specific area (figure 25) continuously increases during each discharge and charge, which indicates that the degree of fracture is becoming more severe. The specific area increases sharply during the first delithiation and second lithiation (from stage 1–2 and from stage 2–3 in figure 25), which indicates that these two stages play a dominant role in electrode fracture.

Another way to quantify fracture is to use the change of porosity of the particles. After cracks form on SSB materials, the morphology will change within the material, such as an increased void space [9]. Porosity is defined as the volume ratio of the void space within materials. The change in porosity before and after electrochemical cycles, which results from crack growth, can be used to quantify the degree of fracture. Synchrotron X-ray tomography can provide a 3D grayscale map of a particle. A threshold for voxels can be set such that the void space is indicated by the value below the threshold. Xia et al [9] observed that the C-rate and particle size can affect fracture and that the degree of fracture could be quantified using the porosity. In this work, the porosity increased with increasing C-rate and particle size, as shown in figure 26, which indicates that the degree of fracture increases with increased C-rate and particle size.

The effect of cracks on battery performance can be quantified by electrochemical characterization. Because of the fracture of the electrode, the electrode is separated into several parts, blocking the diffusion path of ions. Consequently, the diffusion path of Li ions in the electrode change, leading to a change in charge transfer resistance. Therefore, EIS of an electrode before and after fracture can be used to quantify the effect of cracking on a material. Newman et al proposed a lattice spring model to quantify mechanical
degradation on the impedance response of an electrode [111]. They used the lattice spring model to simulate the interaction between two atoms, as shown in figure 27(a). They derived the concentration gradient of Li ions by solving a diffusion equation. The Li ion concentration gradient induces stress inside the electrode. The integral of force and displacement is the energy of a spring. Fracture is assumed to occur if the energy of the spring exceeds the breaking threshold. As a result, the EIS spectra of an electrode with and without fracture contains two parts (in figure 27(b)): a semicircle, which represents the charge transfer resistance, and a tail, the slope of which represents the solid phase diffusion resistance. A smaller charge transfer resistance indicates better battery performance, as indicated by a semicircle with a smaller diameter in the EIS spectrum. The charge transfer resistance is affected by the concentration of Li ions on the particle surface and the particle size. In Newman’s model, if the particle size distribution remains constant, the concentration of Li ions on the particle surface will differ with and without cracks, which results in different concentration gradients, ultimately leading to different charge transfer resistances.

5.2. Interplay of chemical and mechanical effects
Chemical and mechanical effects play an important role in the fracture of composite electrodes. The volume expansion and contraction of active material particles is restricted by the SSE matrix, which induces stress in both the active material particle and the SSE matrix itself. The stress can cause mechanical failure such as cracks and delamination at the interface of both the active particles and SSE matrix. Moreover, active material particles may chemically react with SSEs under electrochemical cycling. Both modeling and experiments are needed to investigate the chemomechanical evolution at the interface. SEM can be used to observe the morphology of the interface, and X-ray tomography is a powerful tool to see how the interior cracks in active material particles evolve. In addition to experimental observation, modeling is another effective way to study the electrochemical reaction, Li-ion diffusion, and crack initiation and propagation together. The results of some simulations yield the Li-ion distribution, stress distribution, and SIF, and predict when and where cracks will occur. The relationship of the C-rate, particle size, $K_{IC}$, and current density can be illustrated with a diagram in which the safe zone and crack zone are given [30, 51, 52]. However, to obtain a deeper understanding of the chemomechanical effects, the design of new experiments that enable the chemical and mechanical evolution on the interface of a composite electrode to be monitored is needed.

5.3. Design criterion for long-term battery cycling
Controlling the primary particle size can affect the battery cycling life. Based on the models discussed above, the critical size is related to the state of charge, the interface orientation, and the particle morphology. Woodford et al [112] built a model to predict the critical size for polycrystalline ensembles with micro-cracks.
at the grain boundaries and another model for a single-crystal particle with an intragranular crack, as shown in figures 28 and 29, respectively. In the grain boundary micro-crack model, the SIF is a function of the flaw size, and the polycrystalline ensembles are treated as Eshelby inclusions for calculating the stress field. In the Eshelby inclusion model, an inclusion is cut from the matrix and undergoes a stress-free transformation strain. Then, a surface force is applied on the inclusion to return it to the previous shape. After that, the inclusion is returned to the matrix, and the relaxation force is calculated, which gives the stress field. The critical size is derived when the maximum SIF is equal to the fracture toughness. In the intragranular cracking model, the strain energy release rate is a function of the crack length. The critical size is derived by estimating the strain energy release rate as the orientation-dependent surface energies. The critical size varies with the interface orientation. To avoid both intergranular and intragranular cracks, the critical size of the primary crystal should be the minimum. Future work is needed to build a model to accurately calculate the particle critical size to synthesize particles with sizes smaller than the critical size.

The pre-existing crack length plays an important role in the battery cycling life. Although defects, micro-cracks, and porosity cannot be avoided during battery processing, the initial crack length below which crack propagation will not occur can be controlled. Aifantis et al. [113] built an anode model in which Si nanospheres were embedded in an inert matrix, as illustrated in figure 30. They assumed that the crack would initiate at the interface of the active material and inert matrix. The critical crack length is defined as $\rho - a$. The hoop tensile stress will induce the propagation of radial cracks. By setting the hoop tensile stress equal to the ultimate tensile strength of the matrix, a critical crack length is obtained. The pre-existing crack length should be made smaller than the critical crack length to achieve a longer cycling lifespan.

In addition to controlling the particle size and initial crack length, controlling initial defects such as the porosity of the electrode material is appropriate for designing battery cycling life. The porosity can be defined as the difference between the actual volume and the predicted volume, normalized by the actual volume [114]:

$$\text{porosity} = \frac{V_{\text{actual}} - V_{\text{predicted}}}{V_{\text{actual}}}.$$  

Many researchers have reported the relationship between the specific energy of a battery and the porosity of an electrode [114–119]. Some methods can be applied to reduce the adverse effect of porosity. Aifantis et al. [113] observed that coating a porous Si film anode with gold can delay cracking. Other coatings such as copper on porous Si film anodes can also improve the cycling number of the battery [120]. However, few researchers have reported a quantitative relationship between the initial porosity and the cycling life of the battery.
The structural design of the SSE is considered in battery life design. Wu et al [121] recently designed a core–shell structure for a sulfide SSE by controlling the synthesis parameters. In their core–shell structure, the core is crystalline Li$_{10}$GeP$_2$S$_{12}$ (LGPS) or Li$_{9.45}$Si$_{1.74}$P$_{1.44}$S$_{11.7}$Cl$_{0.3}$ (LSPS-Cl), and the shell is amorphous.
LGPS or LSPS-Cl with a high Si content. The computational results indicate that the shell layer with a higher mechanical strength can suppress expansion and decomposition of the electrolyte. Consequently, the stability window of this electrolyte is opened up. In the future, particle structure design can be explored to prevent crack propagation.

5.4. Fatigue damage of batteries

Battery electrode materials experience periodic contraction and expansion during electrochemical cycling. During each process, stress induced by volume change is applied on the electrode material, which is a form of fatigue fracture where a periodic force is applied on a material. Researchers have used fatigue formulas to predict the lifespan of materials with pre-existing cracks [122]. We can also design the cycle life of a battery from the fatigue viewpoint.

Paris’ law is a crack propagation equation that regards the SIF as the driving force for pre-existing cracks to grow. The crack length will increase by a small increment $\Delta a$ in each cycle when a periodic force is applied. The relationship between the increase of the crack length $da$ and the increase of the cycle number $dN$ is

$$\frac{da}{dN} = C(\Delta K)^m,$$

where $a$ is the crack length, $N$ is the cycle number, $\Delta K$ is the SIF range defined as $\Delta K = K_{\text{max}} - K_{\text{min}}$ for each load cycle, and $C$ and $m$ are material parameters. In the initial stages of crack propagation, the rate is slow, and we can use Paris’ law to describe crack growth. When the crack grows to a critical length $a_{\text{crit}}$ (where $K_{\text{max}} \approx K_{\text{IC}}$), it then propagates rapidly, leading to complete fracture. The crack propagation lifespan is

$$N = \int_{a_0}^{a_{\text{crit}}} \frac{da}{C(\Delta K)^{m}}.$$

This formula is valid in the linear elastic fracture regime, under tensile loading, and for long cracks. We can assume a discharge and charge process as a cycle during which the SIF changes periodically. Nix and Gao [67] first built a model to couple electrochemistry and chemical degradation with mechanical degradation. Using Paris’ law, the crack depth as a function of cycle numbers is obtained. However, in practice, the condition is more complicated. First, the material parameters $C$ and $m$ will change with an increasing electrochemical cycling number because the structure of the material changes as a result of phase transition. Another problem is that during each electrochemical cycle, the Li concentration, and thus $C$ and $m$, may change over time. Moreover, the exact SIF range will also vary with respect to the cycle number. Overall, quantitative prediction of the crack length with battery cycle number is worth exploring in the future to enable the realization of a crack-resistant design.

6. Conclusions

Fracture failure is a large obstacle for batteries with a long cycle life and high capacity retention. The fracture of batteries is a complex electro–chemical–mechanical coupled process. Therefore, a deep understanding of fracture is important to mitigate fracture and prolong the lifespan of batteries. In this review, the fracture mechanism of battery materials was discussed from both modeling and experimental viewpoints. We summarized not only the intrinsic properties of battery materials but also the extrinsic (dis)charge conditions that can affect fracture behavior. Furthermore, we proposed the following directions worth pursuing to alleviate fracture in batteries: quantification of fracture and its effect on electrochemistry, in-depth investigation of chemical and mechanical interplay, and the design of battery lifespan from fatigue. By achieving these goals, batteries with high capacity and performance reliability can be better designed. In the emerging SSBs, fracture will become even more pronounced. Interdisciplinary research bridging fracture mechanics with electrochemistry will play an increasingly important role in the development of SSBs.

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ORCID iDs

Ping Li  https://orcid.org/0000-0001-5958-0853
Yongxing Shen  https://orcid.org/0000-0001-9397-3853
References

[1] Zhu Y Z, He X F and Mo Y F 2015 Origin of outstanding stability in the lithium solid electrolyte materials: insights from thermodynamic analyses based on first-principles calculations ACS Appl. Mater. Interfaces 7 23685–93
[2] Richards W D, Miaira L I, Wang Y, Kim J C and Ceder G 2016 Interface stability in solid-state batteries Chem. Mater. 28 266–73
[3] Tian Y, Shi T, Richards W D, Li J, Kim J C, Bo S-H and Ceder G 2017 Compatibility issues between electrodes and electrolytes in solid-state batteries Energy Environ. Sci. 10 1150–66
[4] Tian Y S, Sun Y Z, Hannah D C, Xiao Y H, Liu H, Chapman K W, Bo S H and Ceder G 2019 Reactivity-guided interface design in Na metal solid-state batteries Joule 3 1037–50
[5] Zhang W et al 2017 Interfacial processes and influence of composite cathode microstructure controlling the performance of all-solid-state lithium batteries ACS Appl. Mater. Interfaces 9 17835–45
[6] Koerver R, Aygün İ, Leichtweiß T, Dietrich C, Zhang W, Binder J O, Hartmann P, Zeier W G and Janek J 2017 Capacity fade in solid-state batteries: interphase formation and chemomechanical processes in nickel-rich layered oxide cathodes and lithium thio phosphate solid electrolytes Chem. Mater. 29 5574–82
[7] Janek J and Zeier W G 2016 A solid future for battery development Nat. Energy 1 16141
[8] Tikekar M D, Choudhury S, Tu Z Y and Archer L A 2016 Design principles for electrolytes and interfaces for stable lithium-metal batteries Nat. Energy 1 1–7
[9] Xia S H et al 2018 Chemomechanical interplay of layered cathode materials undergoing fast charging in lithium batteries Nano Energy 53 753–62
[10] Ryu I, Lee S W, Gao H J, Cui Y and Nix W D 2014 Microscopic model for fracture of crystalline Si nanopillars during lihiation J. Power Sources 255 274–82
[11] Porz L, Swaney T, Sheldon B W, Rettenwander D, Fromling T, Thaman H L, Berendts S, Uecker R, Carter W C and Chiang Y M 2017 Mechanism of lithium metal penetration through inorganic solid electrolytes Adv. Energy Mater. 7 1701003
[12] Cheng J, Sharafi A and Sakamoto J 2017 Intergranular Li metal propagation through polycrystalline Li4La3Zr2O12 ceramic electrolyte Electrochim. Acta 223 85–91
[13] Kim Y, Jo H, Allen J L, Choe H, Wolfenstine J and Sakamoto J 2016 The effect of relative density on the mechanical properties of hot-pressed cubic Li4La3Zr2O12 J. Am. Ceram. Soc. 99 1367–74
[14] Liu H, Wolf M, Karki K, Yu Y S, Stach E A, Cabana J, Chapman K W and Chupas P J 2017 Intergranular cracking as a major cause of long-term capacity fading of layered cathodes Nano Lett. 17 3452–7
[15] Bak S-M, Hu E, Zhou Y, Yu X, Senanayake S D, Cho S-J, Kim K-B, Chung K Y, Yang X-Q and Nam K-W 2014 Structural changes and thermal stability of charged LiNi0.5Mn1.5O4 cathode materials studied by combined in situ time-resolved XRD and mass spectroscopy ACS Appl. Mater. Interfaces 6 22594–601
[16] Zhao Y, Yu B X, Stein P and Gross D 2016 Phase-field study of electrochemical reactions at exterior and interior interfaces in Li-ion battery electrode particles Comput. Methods Appl. Mech. Eng. 312 428–46
[17] Zhang X X, Krishnan A R and Linder C 2016 A variational framework to mode diffusion induced large plastic deformation and phase field fracture during initial two-phase lithiation of silicon electrodes Comput. Methods Appl. Mech. Eng. 312 51–77
[18] Zuo P and Zhao Y P 2015 A phase field model coupling lithium diffusion and stress evolution with crack propagation and application in lithium ion batteries Phys. Chem. Chem. Phys. 17 287–97
[19] Zhang X, Lee S W, Lee H W, Cui Y and Linder C 2015 A reaction-controlled diffusion model for the lithiation of silicon in lithium-ion batteries Extreme Mech. Lett. 4 61–75
[20] Ryu H H, Park K J, Yoon C S and Sun Y K 2018 Capacity fading of Ni-rich Li[Ni0.5Mn1.5O4−x/2−x/2]O2 (0.6 ≤ x ≤ 0.95) cathodes for high-energy-density lithium-ion batteries: bulk or surface degradation? Chem. Mater. 30 1155–63
[21] Bhattacharya S, Rahn A and Alpas A T 2011 A transmission electron microscopy study of fracture and propagation in electrochemically cycled graphite electrode in lithium-ion cells J. Power Sources 196 8719–27
[22] Zheng H, Zhang L, Liu G, Song X and Battaglia V S 2012 Correlation between electrode mechanics and long-term cycling performance for graphite anode in lithium-ion cells J. Power Sources 217 530–7
[23] Mu L et al 2018 Oxygen release induced chemomechanical breakdown of layered cathode materials Nano Lett. 18 3241–9
[24] Yan P F, Zheng J M, Gu M, Xiao J, Zhang J G and Wang C M 2017 Intragrannular cracking as a critical barrier for high-voltage usage of layer-structured cathode for lithium-ion batteries Nat. Commun. 8 14101
[25] Yabuuchi N, Kim Y-T, Li H H and Shao-Horn Y 2008 Thermal instability of cycled Li[Ni0.5Mn1.5O4]O2 electrodes: an in situ synchrotron x-ray powder diffraction study Chem. Mater. 20 4936–51
[26] Guggenheim E A 1985 Thermodynamics—An Advanced Treatement for Chemists and Physicists 7th edn (Amsterdam: North-Holland Physics Publ.)
[27] Wu H M, Belharouak I, Deng H, Abouinmara A, Sun Y K and Amine K 2009 Development of Li[Ni0.5Mn1.5O4]/Li4Ti5O12 system with long cycle life J. Electrochem. Soc. 156 A1047–50
[28] Padhi A K, Nanjundaswamy K S and Goodenough J B 1997 Phospho-olivines as positive-electrode materials for rechargeable lithium batteries J. Electrochem. Soc. 144 1188–94
[29] Woodford W H, Chiang Y-M and Carter W C 2013 Electrochemical shock in ion-intercalation materials with limited solid-solubility J. Electrochem. Soc. 160 A1286–92
[30] Woodford W H, Chiang Y-M and Carter W C 2010 “Electrochemical shock” of intercalation electrodes: a fracture mechanics analysis J. Electrochem. Soc. 157 A1052–9
[31] Chen G Y, Song X Y and Richardson T J 2006 Electron microscopy study of the LiFePO4 to FePO4 phase transition Electrochem. Solid State Lett. 9 A295–8
[32] Aurbach D, Zingrad E, Cohen Y and Teller H 2002 A short review of failure mechanisms of lithium metal and lithiated graphite anodes in liquid electrolyte solutions Solid State Ionics 148 405–16
[33] Mukhopadhyay A, Tokranov A, Xiao X and Sheldon B W 2012 Stress development due to surface processes in graphite electrodes for Li-ion batteries: a first report Electrochem. Acta 66 28–37
[34] Ohzuku T, Iwakishi Y and Sawai K 1993 Formation of lithium-graphite intercalation compounds in nonaqueous electrolytes and their application as a negative electrode for a lithium ion (shuttlecock) cell J. Electrochem. Soc. 140 2349–54
[35] Koerver R, Zhang W, de Biasi L, Schweidler S, Kondrakov A O, Kolling S, Brezesinski T, Hartmann P, Zeier W G and Janek J 2018 Chemomechanical expansion of lithium electrode materials—on the route to mechanically optimized all-solid-state batteries Energy Environ. Sci. 11 2142–58
[36] Gu M, Wang Z G, Connell J G, Perea D E, Lauhon L J, Gao F and Wang C M 2013 Electronic origin for the phase transition from amorphous Li$_2$Si to crystalline Li$_x$Si$_{1-x}$ ACS Nano 7 6303–9

[37] Gu M, Yang H, Perea D E, Zhang J-G, Zhang S and Wang C-M 2014 Bending-induced symmetry breaking of lithiation in germanium nanowires Nano Lett. 14 6622–7

[38] Wang J, Chen-Wiegart Y C K and Wang J 2014 In situ three-dimensional synchrotron x-ray tomography of the (de)lithiation processes in tin anodes Angew. Chem. Int. Ed. 53 4660–4

[39] Lee S W, Ryu I, Nix W D and Cai Y 2015 Fracture of crystalline germanium during electrochemical lithium insertion Extreme Mech. Lett. 2 15–19

[40] Wu H B, Chen J S, Hng H H and Lou X W 2012 Nanostructured metal oxide-based materials as advanced anodes for lithium-ion batteries Nano尺度 6 2526–42

[41] Cao K, Jin T, Yang L and Jiao L 2017 Recent progress in conversion reaction metal oxide anodes for Li-ion batteries Mater. Chem. Front. 1 2213–42

[42] Poizot P, Laruelle S, Grugone S, Dupont L and Tarascon J M 2000 Nano-sized transition-metal oxides as negative-electrode materials for lithium-ion batteries Nature 407 496–9

[43] Jiang T, Hu M, Zhang D, Yuan T, Sun W, Xu X and Yan M 2014 Transition metal oxides for high performance sodium ion battery anodes Nano Energy 5 60–66

[44] Chen C, Ding N, Wang L, Yu Y and Lieberwirth I 2009 Some new facts on electrochemical reaction mechanism for transition metal oxide electrodes J. Power Sources 189 552–6

[45] Tippets J, Miers J C, Afshar A, Lewis J A, Cortes F J Q, Qiao H, Marchese T S, Di Leo C V, Saldana C and McDowell M T 2019 Visualizing chemomechanical degradation of a solid-state battery electrolyte ACS Energy Lett. 4 1475–83

[46] Zhang W, Schroeder D, Arlt T, Manke I, Koerver R, Pinedo D A, Sann J, Zeier W G and Janek J 2017 (Electro)chemical expansion during cycling: monitoring the pressure changes in operating solid-state lithium batteries J. Mater. Chem. A 5 9929–36

[47] Xu Z-L, Gao K, Abuoli S, Garakani M A, Huang J, Huang J-Q, Heidari E K, Wang H and Kim J-K 2016 Study of lithiation mechanisms of high performance carbon-coated Si anodes by in-situ microscopy Energy Storage Mater. 3 40–54

[48] Gu M, Li Y, Li X, Hu S, Zhang X, Xu W, Thevuthasan S, Bae D R, Zhang J-G and Liu J 2012 In situ TEM study of lithiation behavior of silicon nanoparticles attached to and embedded in a carbon matrix ACS Nano 6 8439–47

[49] Hvizdol P, Tatarko R, Duszova A and Dusza J 2013 Failure mechanisms of ceramic nanocomposites and R Banerjee et al Ceramic Nanocomposites (Cambridge: Woodhead Publishing)

[50] Ding B, Li X, Zhang X, Wu H, Xu Z P and Gao H J 2015 Brittle versus ductile fracture mechanism transition in amorphous lithiated silicon: from intrinsic nanoscale cavitation to shear banding Nano Energy 18 89–96

[51] Chen B B, Zhou J Q and Cai R 2016 Analytical model for crack propagation in spherical nano electrodes of lithium-ion batteries Electrochem. Acta 210 7–14

[52] Raghavan R S, Kumar A M and Narayana Rao 2015 Intercalation induced surface cracking in electrode particles Z. Angew. Math. Mech. 95 845–58

[53] Zhao K J, Prath M, Wan Q, Wang W L, Kaxiras E, Vlassak J J and Suo Z G 2012 Concurrent reaction and plasticity during initial lithiation of crystalline silicon in lithium-ion batteries J. Electrochem. Soc. 159 A238–43

[54] Huttin M and Kamlah M 2012 Phase-field modeling of stress generation in electrode particles of lithium ion batteries Appl. Phys. Lett. 101 13

[55] Chew H B 2014 Cohesive zone laws for fatigue crack growth: numerical field projection of the micromechanical damage process in an elasto–plastic medium Int. J. Solids Struct. 51 1410–20

[56] Bhandakkar T K and Gao H 2010 Cohesive modeling of crack nucleation under diffusion induced stresses in a thin strip: implications on the critical size for flaw tolerant battery electrodes Int. J. Solids Struct. 47 1424–34

[57] Bower A P and Guduru P R 2012 A simple finite element model of diffusion, finite deformation, plasticity and fracture in lithium ion insertion electrode materials Model. Simul. Mater. Sci. Eng. 20 4

[58] Bucci G, Swamy T, Chiang Y-M and Carter W C 2017 Modeling of internal mechanical failure of all-solidstate batteries during electrochemical cycling, and implications for battery design J. Mater. Chem. A 5 19422–30

[59] Chen L, Feng Y P and Ding K Q 2018 Int. Conf. on Automatic Control, Mechatronics and Industrial Engineering (Boca Raton, FL: CRC Press)

[60] Lee S, Park J, Yang J and Lu W 2014 Molecular dynamics simulations of the traction–separation response at the interface between PVDF binder and graphite in the electrode of Li-ion batteries J. Electrochem. Soc. 161 A1218–23

[61] Lee S, Yang J and Lu W 2016 Debonding at the interface between active particles and PVDF binder in Li-ion batteries Extreme Mech. Lett. 6 37–44

[62] Meng Q-D, Gui L, Zhang X-L, Zhang L-W, Geng D-F and Lu Y-Q 2014 Delamination study of InSb infrared focal plane arrays using a cohesive zone model Acta Phys. Sin. 63 118503

[63] Zhang Y, Zhao C and Guo Z 2019 Simulation of crack behavior of secondary particles in Li-ion battery electrodes during lithiation/de-lithiation cycles Int. J. Mech. Sci. 153 178–86

[64] Sun G, Sui T, Song B, Zheng H, Lu L and Korsunsky A M 2016 On the fragmentation of active material secondary particles in lithium ion battery cathode particles induced by charge cycling Extreme Mech. Lett. 6 91–8

[65] Bhandakkar T K and Gao H J 2011 Cohesive modeling of crack nucleation in a cylindrical electrode under axisymmetric diffusion induced stresses Int. J. Solids Struct. 48 2304–9

[66] Schweidler S, de Biase L, Schiele A, Hartmann P, Brezesinski T and Janek J R 2018 Volume changes of graphite anodes revisited: a combined operando x-ray diffraction and in situ pressure analysis study J. Phys. Chem. C 122 8829–35

[67] Nix W D and Gao H J 1998 Indentation size effects in crystalline materials: a law for strain gradient plasticity J. Mech. Phys. Solids 46 411–25

[68] Liu X H, Zhong L, Huang S, Mao S X, Zhu T and Huang J Y 2012 Size-dependent fracture of silicon nanoparticles during lithiation ACS Nano 6 1522–34

[69] Ryu I, Choi J W, Cui Y and Nix W D 2011 Size–dependent fracture of Si nanowire battery anodes J. Mech. Phys. Solids 59 1717–30

[70] McDowell M T, Ryu I, Lee S W, Wang C M, Nix W D and Cai Y 2012 Studying the kinetics of crystalline silicon nanoparticle lithiation with in situ transmission electron microscopy Adv. Mater. 24 6034

[71] Beaulieu L Y, Eberman K W, Turner R L, Krause L J and Dahn J R 2001 Colossal reversible volume changes in lithium alloys Electrochem. Solid State Lett. 4 A137–40

[72] Wang J W et al 2013 Two-phase electrochemical lithiation in amorphous silicon Nano Lett. 13 709–15
Chan C K, Peng H L, Liu G, Mcllwraith K, Zhang X F, Huggins R A and Cui Y 2008 High-performance lithium battery anodes using silicon nanowires Nat. Nanotechnol. 3 31–35
Kalnais S, Rhodes K and Daniel C 2011 A study of lithium ion intercalation induced fracture of silicon particles used as anode material in Li-ion battery J. Power Sources 196 8116–24
Pharr M, Suo Z and Vlassak J J 2014 Variation of stress with charging rate due to strain-rate sensitivity of silicon electrodes of Li-ion batteries J. Power Sources 270 569–75
Hu Y H, Zhao X H and Suo Z G 2010 Averting cracks caused by insertion reaction in lithium-ion batteries J. Mater. Res. 25 1007–10
Sun H H and Manthiram A 2017 Impact of microcrack generation and surface degradation on a nickel-rich layered LiNi0.5Co0.2Mn0.3O2 cathode for lithium-ion batteries Chem. Mater. 29 8486–93
Ishizuku K, Oka Y and Nakamura T 2016 Lattice volume change during charge/discharge reaction and cycle performance of Li[Ni1/3Co1/3Mn1/3]O2 Solid State Ion. 288 176–9
Kondrakov A O, Schmidt A, Xu J, Geßwein H, Mönig R, Hartmann P, Sommer H, Brezesinski T and Janek J R 2017 Anisotropic lattice strain and mechanical degradation of high- and low-nickel NCM cathode materials for Li-ion batteries J. Phys. Chem. C 121 3286–94
de Biasi L, Kondrakov A O, Geßwein H, Brezesinski T, Hartmann P and Janek J R 2017 Between scylla and charybdis: balancing among structural stability and energy density of layered NCM cathode materials for advanced lithium-ion batteries J. Phys. Chem. C 121 26163–71
Yoon C S, Jun D W, Myung S T and Sun Y K 2017 Structural stability of LiNi0.5Co0.2Mn0.3O2 cycled above 4.2 V ACS Energy Lett. 2 1150–5
Yoon W-S, Chung K Y, McBreen J and Yang X-Q 2006 A comparative study on structural changes of LiCo0.2Ni0.6Mn0.2O2 and LiNi0.5Co0.15Al0.3O2 during first charge using in situ XRD Electrochem. Commun. 8 1257–62
Tian C X, Nordlund D, Xin H L, Xu Y H, Liu Y J, Sokaras D, Lin F and Doeff M 2018 Depth-dependent redox behavior of Li[Ni0.5Mn0.2Co0.3]O2 J. Electrochem. Soc. 165 A690–704
Hovington P, Donfigny M, Guerfi A, Trottier J, Lagace M, Mauger A, Julien C M and Zaghib K 2014 In situ scanning electron microscope study and microstructural evolution of nano silicon anode for high energy Li-ion batteries J. Power Sources 248 457–64
Wang H H, Jiang Y I, Huang B Y, Sadoway D R and Chiang Y T 1999 TEM study of electrochemical cycling-induced damage and disorder in LiCoO2 cathodes for rechargeable lithium batteries J. Electrochem. Soc. 146 473–80
Feng X N, Ren D S, Zhang S C, He X M, Wang L and Ouyang M G 2019 Influence of aging paths on the thermal runaway features of lithium-ion batteries in accelerating rate calorimetry tests Int. J. Electrochem. Sci. 14 44–58
Wei C X et al 2018 Thermally driven mesoscale chemo-mechanical interplay in Li(Ni0.5Mn0.2Co0.3)O2 cathode materials J. Mater. Chem. A 6 20355–61
Xu Z, Rahman M M, Mu L, Liu Y and Lin F 2018 Chemomechanical behaviors of layered cathode materials in alkali metal ion batteries J. Mater. Chem. A 6 21859–64
Xu Z et al 2020 Charge distribution guided by grain crystallographic orientations in polycrystalline battery materials Nat. Commun. 11 83–83
Zheng J M, Gu M, Xiao J, Zuo P J, Wang C M and Zhang J G 2013 Corrosion/fragmentation of layered composite cathode and related capacity/voltage fading during cycling process Nano Lett. 13 3824–30
Mao Y et al 2019 High-voltage charging-induced strain, heterogeneity, and micro-cracks in secondary particles of a nickel-rich layered cathode material Adv. Funct. Mater. 29 18
Yang Y et al 2019 Quantification of heterogeneous degradation in Li-ion batteries Adv. Energy Mater. 9 25
Xu R, Sun H, de Vasconcelos L S and Zhao K 2017 Mechanical and structural degradation of Li[Ni0.5Mn0.2Co0.3]O2 cathode in Li-ion batteries: an experimental study J. Electrochem. Soc. 164 A3333–41
Sun Y K, Chen Z H, Noh H J, Lee D J, Jung H G, Ren Y, Wang S, Yoon C S, Myung S T and Amine K 2012 Nanostructured high-energy cathode materials for advanced lithium batteries Nat. Mater. 11 942–7
Anantharamulu N, Rao K K, Rambabu G, Kumar B V, Radha V and Vithal M 2011 A wide-ranging review on Nasicon type materials J. Mater. Sci. 46 2821–37
Goodenough J B and Manivannan V 1998 Cathodes for lithium-ion batteries: some comparisons Denki Kagaku 66 1173–81
Knauth P 2009 Inorganic solid Li ion conductors: an overview Solid State Ionics 180 911–16
Murugan R, Thangadurai V and Weppner W 2007 Fast lithium ion conduction in garnet-type Li1.2Al2Zr2O7 Angew. Chem. Int. Ed. 46 7778–81
Thangadurai V, Narayanan S and Pinzar D 2014 Garnet-type solid-state fast Li ion conductors for Li batteries: critical review Chem. Soc. Rev. 43 4714–27
Kato Y, Hori S, Saito T, Suzuki K, Hirayama M, Mitsuji A, Yonemura M, Iba H and Kanno R 2016 High-power all-solid-state batteries using sulfide superionic conductors Nat. Energy 1 16030
Mizuno F, Hayashi Y, Tadanaka K and Tatsusimao M 2005 New, highly ion-conductive crystals precipitated from Li2S–P2S5 glasses Adv. Mater. 17 918
Xu X, Wen Z, Wu X, Yang X and Gu Z 2007 Lithium ion-conducting glass-ceramics of Li1.5Al5Ge2.5(PO4)3–xLi2O (x=0.0–0.20) with good electrical and electrochemical properties J. Am. Ceram. Soc. 90 2802–6
Wu J-F, Pang W K, Peterson V K, Wei L and Guo X 2017 Garnet-type fast Li-ion conductors with high ionic conductivities for all-solid-state batteries ACS Appl. Mater. Interfaces 9 12461–8
Kamaya N et al 2011 A lithium superionic conductor Nat. Mater. 10 682–6
Sakuda A, Hayashi A and Tatsusimao M 2013 Sulfide solid electrolyte with favorable mechanical property for all-solid-state lithium battery Sci. Rep. 3 2261
McCrogan F P, Swamy T, Bishop S R, Eggleton E, Porz L, Chen X W, Chiang Y M and Van Vliet K J 2017 Compliant yet brittle mechanical behavior of Li2S–P2S5: lithium-ion-conducting solid electrolyte J. Electrochem. Soc. 164 712
Sharafi A, Haslam C G, Kems R D, Wolfenstine J and Sakamoto J 2017 Controlling and correlating the effect of grain size with the mechanical and electrochemical properties of Li2Li2Zr2O7 solid-state electrolyte J. Mater. Chem. A 5 21491–504
Herbert E G, Tenhaeff W E, Dudney N J and Pharr G M 2011 Mechanical characterization of LiPON films using nanoindentation Thin Solid Films 520 413–18
Hu X, Qiang W and Huang B 2017 Preparation and properties of Li1.2Al2Zr2O7 perovskite oxide electrolytes J. Am. Ceram. Soc. 100 4153–8
[110] Swamy T, Park R, Sheldon B W, Rettenwander D, Porz L, Berendts S, Uecker R, Carter W C and Chiang Y M 2018 Lithium metal penetration induced by electrodeposition through solid electrolytes: example in single-crystal Li$_6$La$_3$ZrTaO$_{12}$ garnet J. Electrochem. Soc. 165 A3648–55

[111] Chen C F, Barai P and Mukherjee P P 2014 Diffusion induced damage and impedance response in lithium-ion battery electrodes J. Electrochem. Soc. 161 A2138–52

[112] Woodford W H, Carter W C and Chiang Y M 2012 Design criteria for electrochemical shock resistant battery electrodes Energy Environ. Sci. 5 8014–24

[113] Aifantis K E, Hackney S A and Dempsey J P 2007 Design criteria for nanostructured Li-ion batteries J. Power Sources 165 874–9

[114] Marks T, Trussler S, Smith A J, Xiong D J and Dahn J R 2011 A guide to Li-ion coin-cell electrode making for academic researchers J. Electrochem. Soc. 158 A51–A57

[115] Pope M A and Aksay I A 2015 Structural design of cathodes for Li-S batteries Adv. Energy Mater. 5 16

[116] Newman J and Tiedemann W 1975 Porous-electrode theory with battery applications AIChE J. 21 25–41

[117] Srinivasan V and Newman J 2004 Discharge model for the lithium iron-phosphate electrode J. Electrochem. Soc. 151 A1517–29

[118] Srinivasan V and Newman J 2004 Design and optimization of a natural graphite/iron phosphate lithium-ion cell J. Electrochem. Soc. 151 A1530–8

[119] Lopez C M, Vaughay J T and Dees D W 2009 Morphological transitions on lithium metal anodes J. Electrochem. Soc. 156 A726–9

[120] Sethuraman V A, Kowolik K and Srinivasan V 2011 Increased cycling efficiency and rate capability of copper-coated silicon anodes in lithium-ion batteries J. Power Sources 196 393–8

[121] Wu F, FitzHugh W, Ye L H, Ning J X and Li X 2018 Advanced sulfide solid electrolyte by core-shell structural design Nat. Commun. 9 4037

[122] Deshpande R, Verbrugge M, Cheng Y-T, Wang J and Liu P 2012 Battery cycle life prediction with coupled chemical degradation and fatigue mechanics J. Electrochem. Soc. 159 A1730–8