



TOPICAL REVIEW

Fracture behavior in battery materials

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Abstract

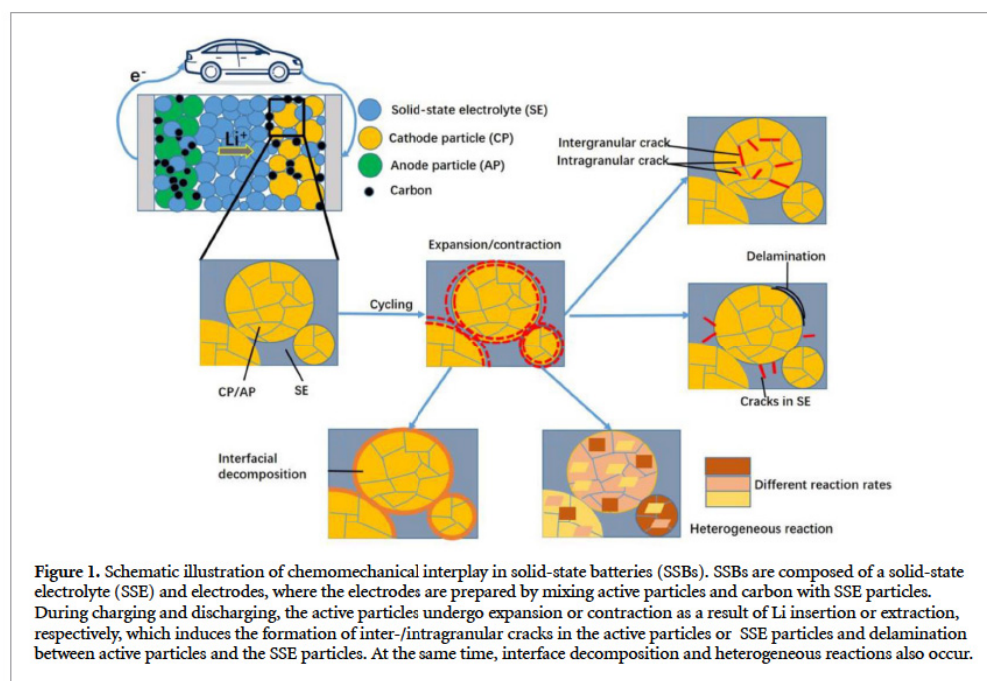
The fracture of battery materials is one of the main causes of battery degradation. This issue is further amplified in emerging solid-state batteries, where the more robust interface between the liquid electrolyte and solid electrode in conventional batteries is replaced by a brittle solid–solid interface. 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

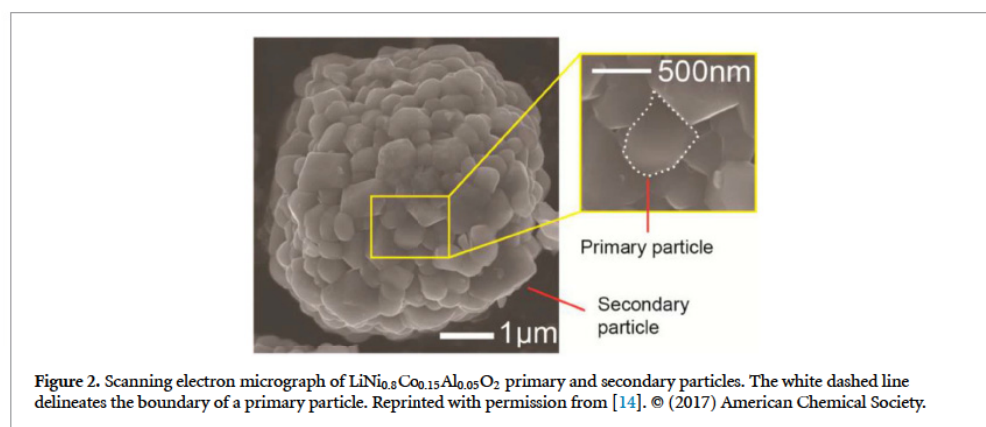


insertion or extraction. The stress can lead to the fracture of battery materials, which produces new surfaces and surface chemical species.

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 α - 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, through which working ions such as Li^+ cannot pass, increasing the impedance of the battery. These cracks also create space for Li dendrite growth, 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 SSB 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 SSB 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 monocrystalline grains with grain boundaries in between. These monocrystalline 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 $\text{Li}[\text{Ni}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}]\text{O}_2$ 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 $\text{Li}[\text{Ni}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}]\text{O}_2$ 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 polycrystalline 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 intergranular 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 polycrystalline 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 $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$, 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

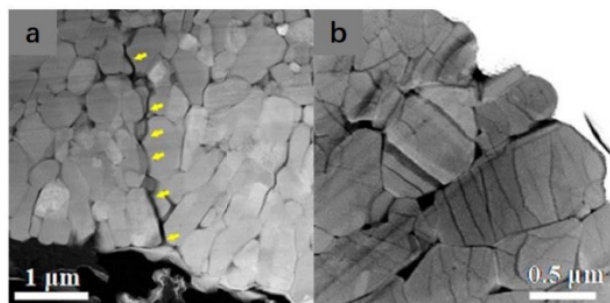


Figure 3. Morphology of intergranular and intragranular cracks. (a) Scanning electron microscopy (SEM) image of intergranular cracks in $\text{Li}[\text{Ni}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}]\text{O}_2$ cathodes after 100 cycles. The yellow arrows indicate the intergranular cracks. (b) Transmission electron microscopy (TEM) image of intragranular cracks in the primary particles of a $\text{Li}[\text{Ni}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}]\text{O}_2$ cathode after cycling. Reprinted with permission from [20]. © (2018) American Chemical Society.

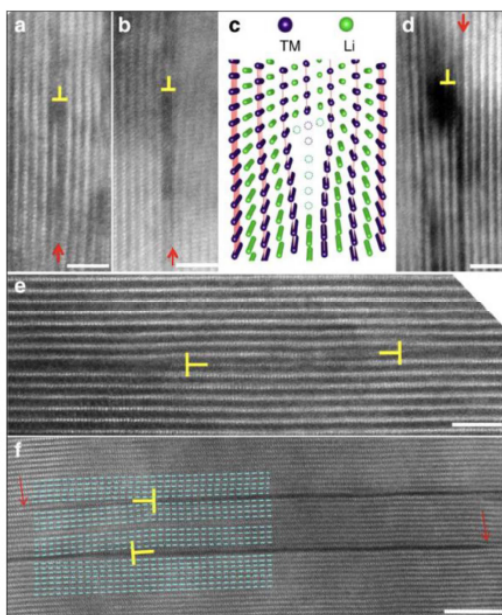
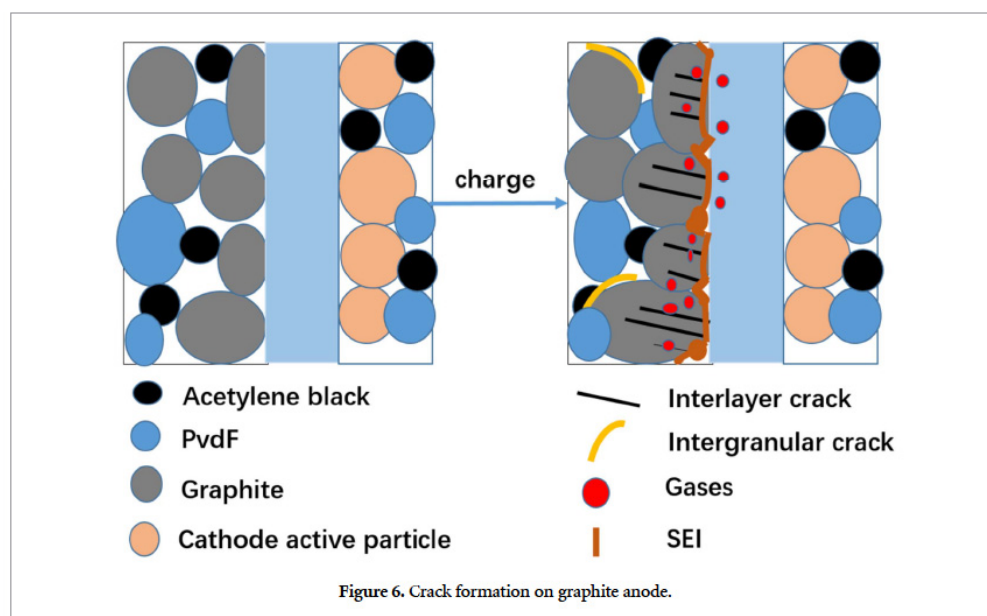
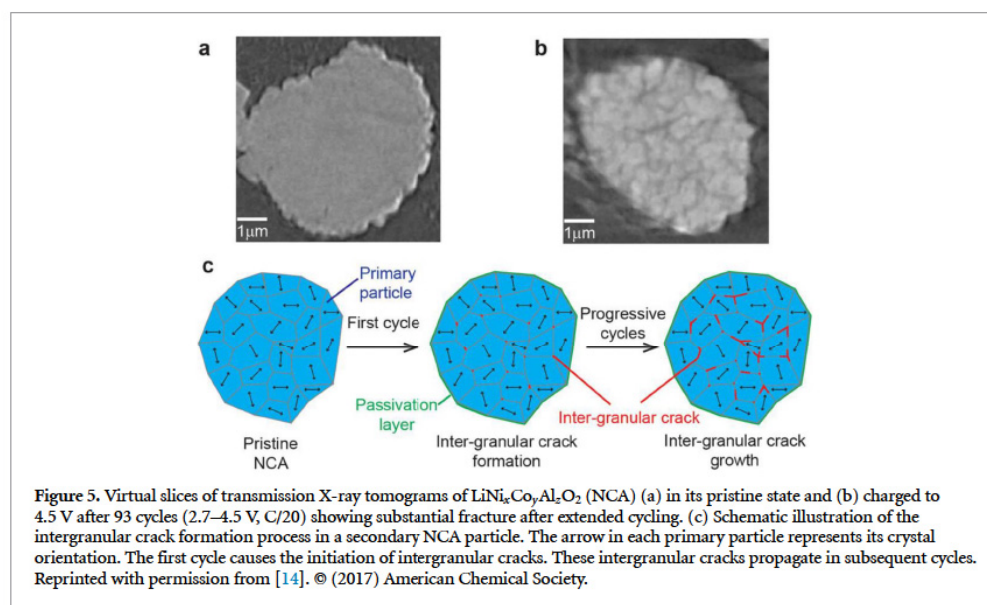


Figure 4. Crack incubation process in cycled $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$. (a), (b) Early incubation stages, showing vacancy condensation at the dislocation core; (c) corresponding schematic illustration. (d)–(f) Scanning transmission electron microscopy (STEM) images showing that cracks form from the dislocation. The red arrows indicate the crack tips. The scale bars are 2 nm except for that in (f), which is 5 nm. Reproduced with permission from [24]. © (2017) Springer Nature.

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



graphite, which forms LiC_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.

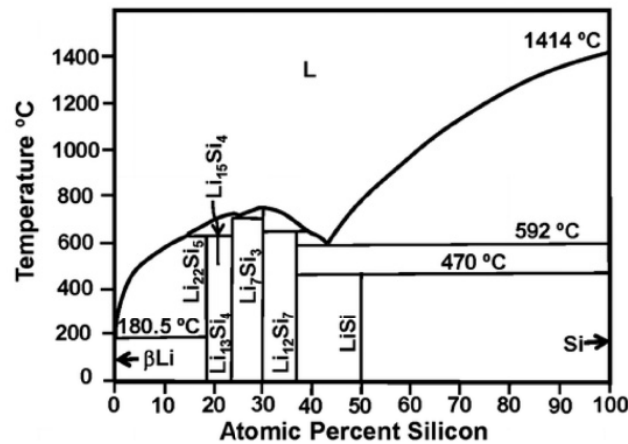
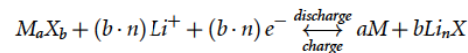


Figure 7. Li-Si phase diagram. Reprinted with permission from [36]. © (2013) American Chemical Society.

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, Li₁₂Si₇, Li₇Si₃, Li₁₃Si₄, and Li₂₂Si₅ 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-Li₁₅Ge₄ 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.

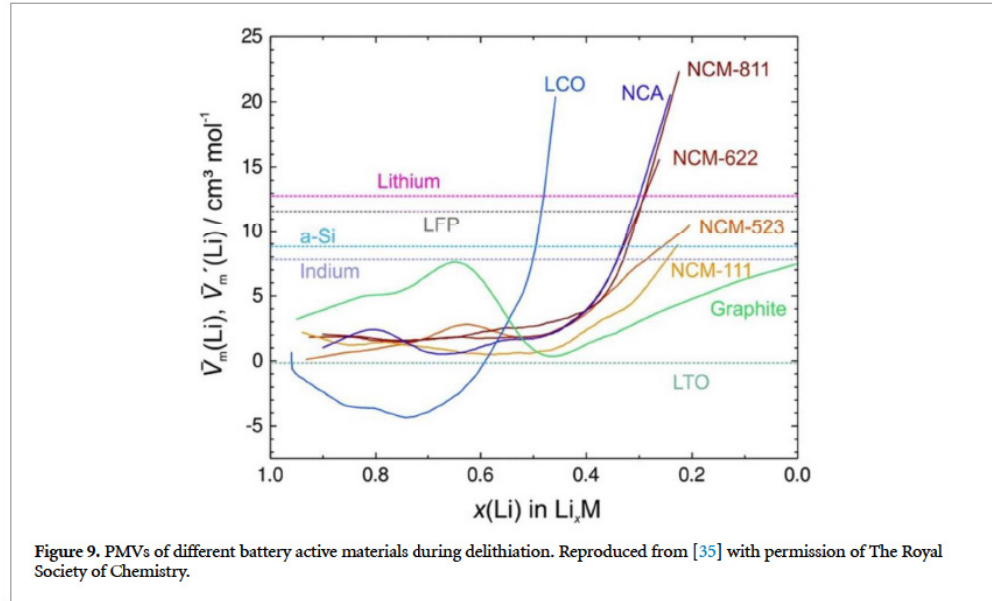
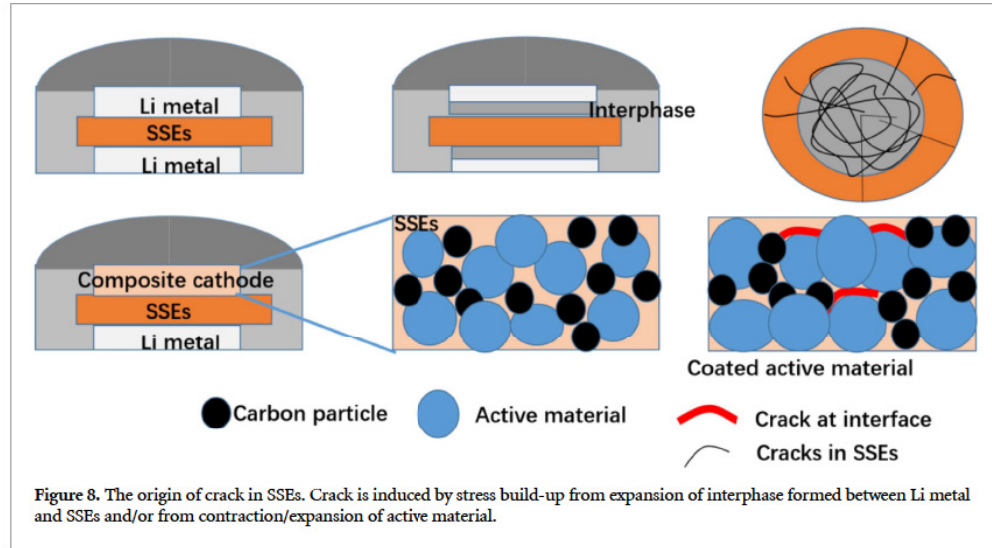
The origin of the crack in the conversion type anode is structural reorganization and volume change during charging and discharging [40]. The reaction mechanism can be generalized as below:



where M is the transition metal (Mn, Fe, Co, Ni, Cu, etc), X is H, N, O, F, P, S, etc, and n is the oxidation state of X [41, 42]. For the Fe₂O₃ 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 Fe₃O₄, β-MnO₂, 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



$\Delta P = -\varepsilon_{vol}K$, where K is the bulk modulus of the SSE and ε_{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 LiCoO_2 . 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 $\sigma_{\theta\theta}$ 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 $K_I > K_{Ic}$, where K_I is the mode I (opening mode) SIF and K_{Ic} is the material fracture toughness. For electrode particles, K_I depends on the charging time, pre-existing crack length, and current density, whereas K_{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 π 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.

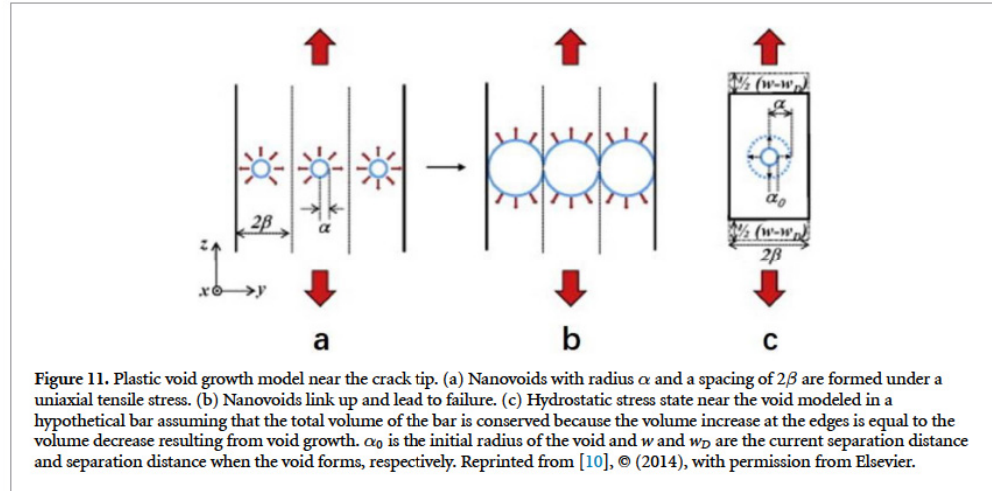
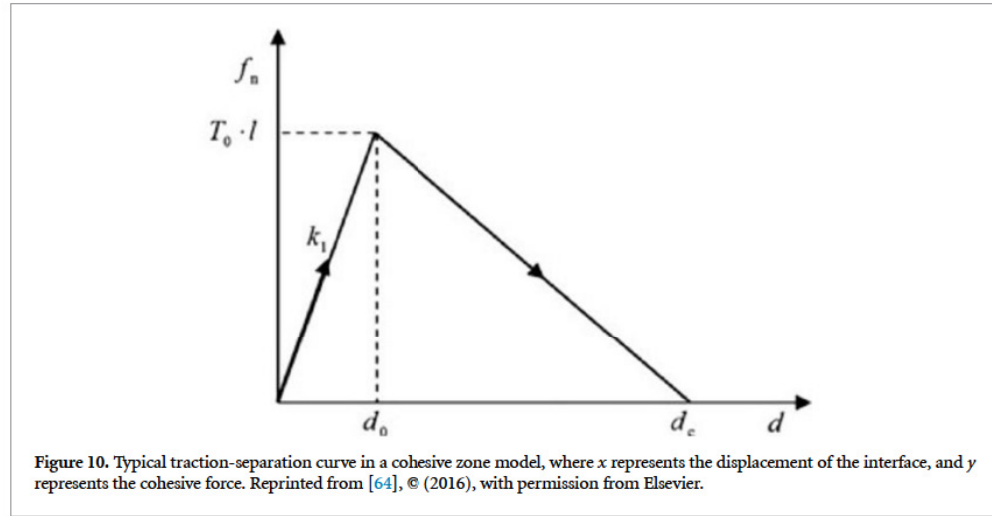
Computational methods based on these crack initiation and crack propagation criteria can be used to predict the fracture behavior of materials. The phase field model [16–18, 54] and cohesive zone model [55–63] are the most common computational models.

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 α_0 to diameter α (figure 11). A crack initiates from the small voids and propagates as the voids grow to a maximum diameter of 2β . 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.

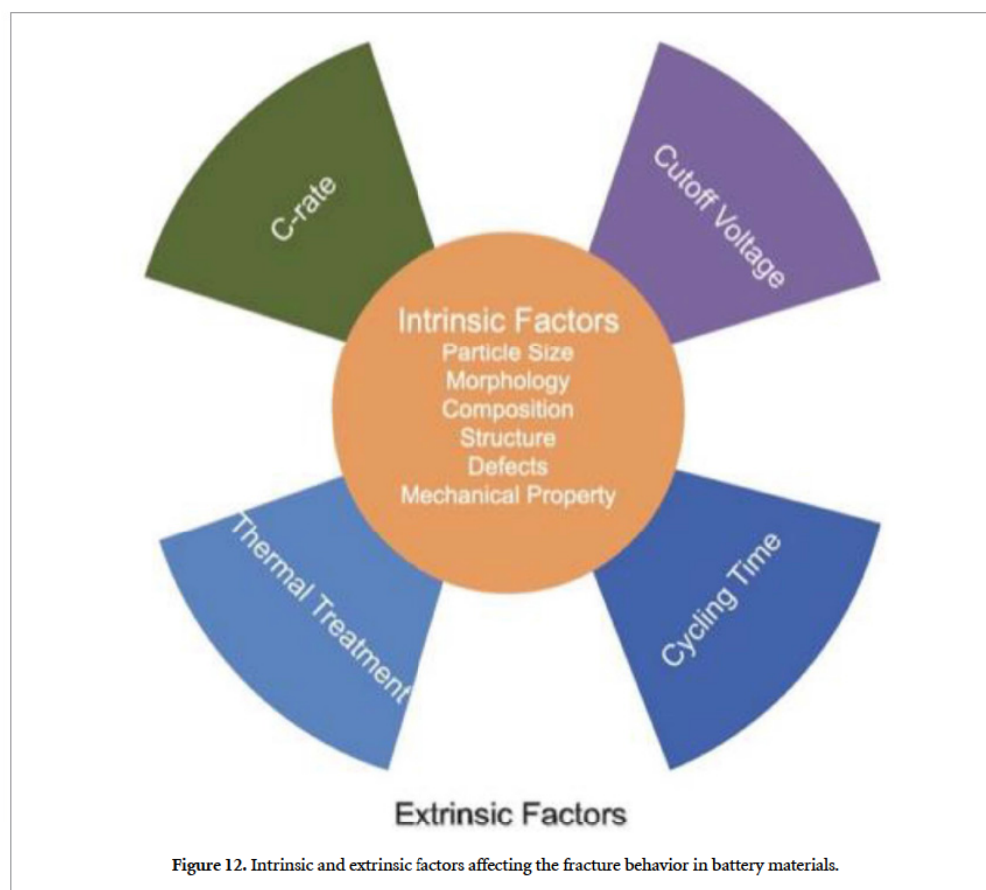


Below, we first discuss the effect of these factors on anode materials, followed by a discussion of their effect on cathode and SSE materials.

4.1. Anode materials

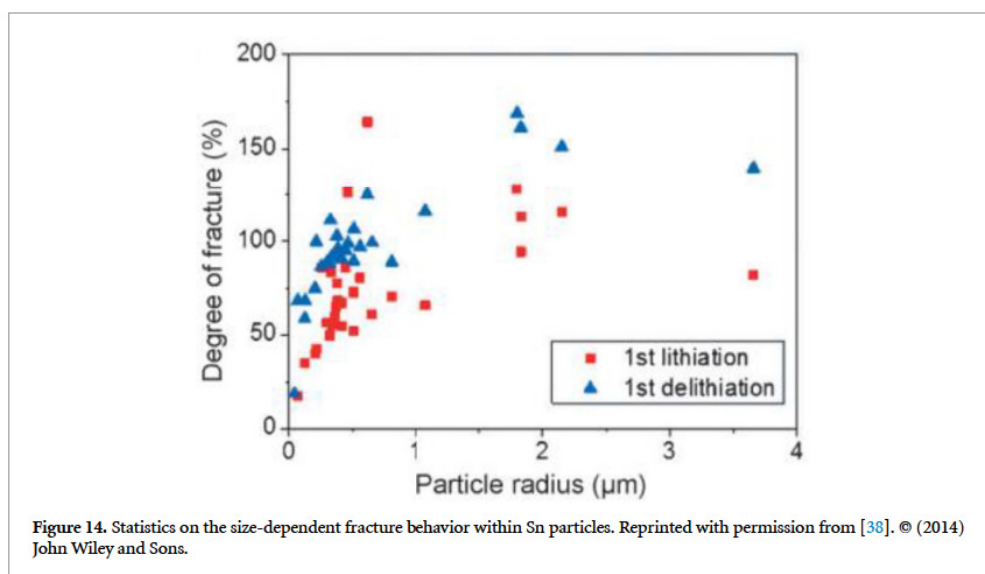
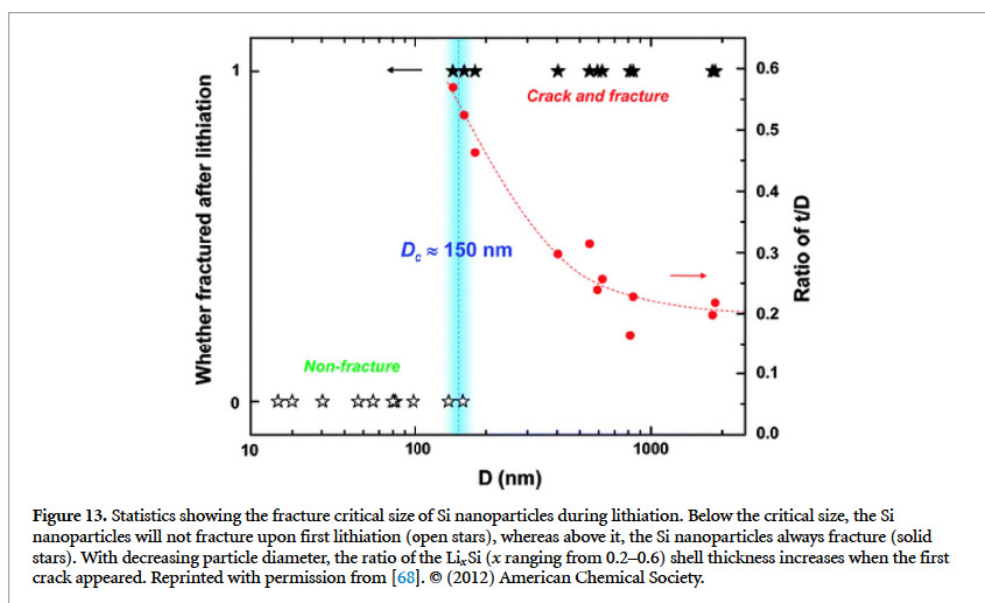
Commonly employed anode materials include graphite, alloys, and lithium titanate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO). In SSBs, the anode is either a Li metal or a composite electrode containing anode active materials, carbon, and an SSE. Although Li metal is the most energy-dense battery anode, 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_xSi shell and D is the diameter of the Si nanoparticle (figure 13). They built a



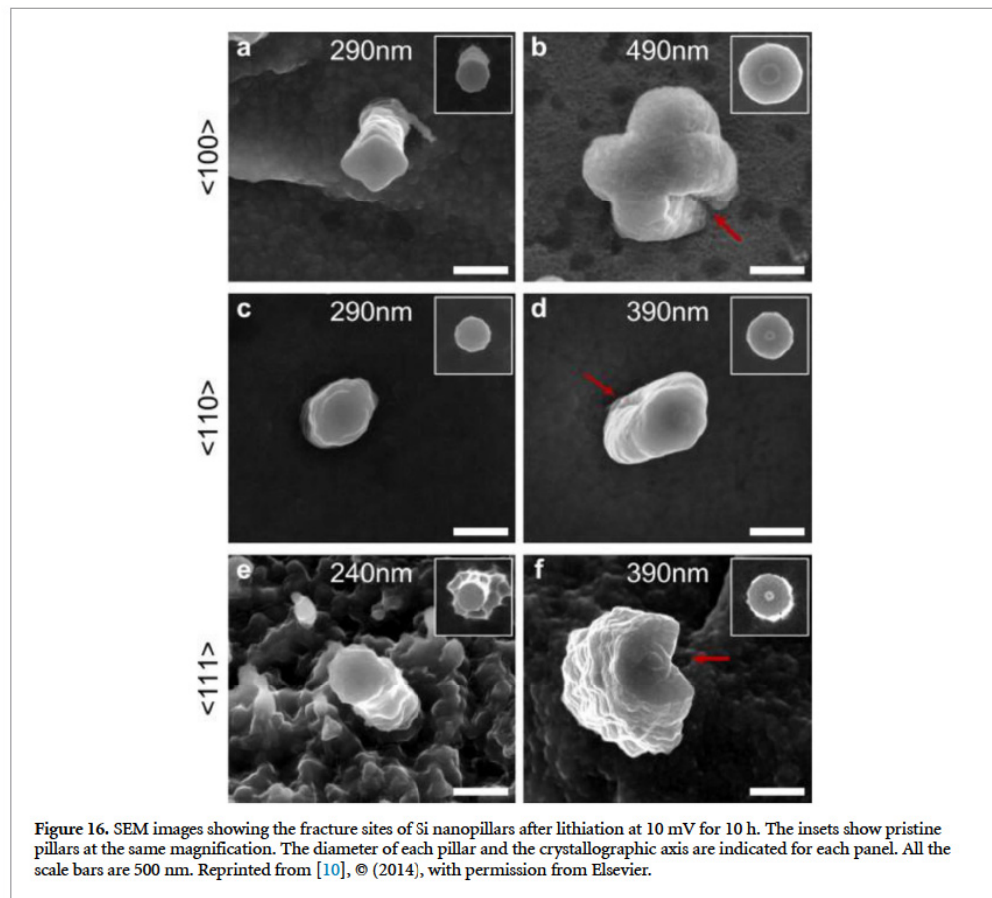
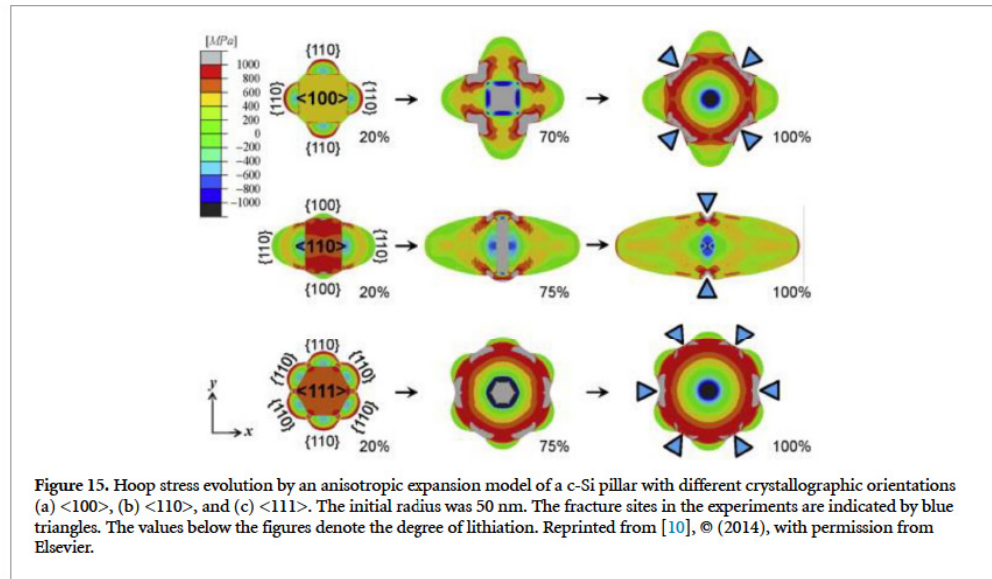
non-linear diffusion model to understand why the fracture behavior was size dependent and found that small nanoparticles release an insufficient amount of strain energy to drive crack propagation. Statistical data indicated that the critical diameter of Si nanowires is 220–260 nm, whereas the model indicated 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 $\langle 111 \rangle$ Ge pillar has a larger critical diameter ($\sim 1.2 \mu\text{m}$) than a $\langle 111 \rangle$ Si pillar ($\sim 300 \text{ nm}$). 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 $\langle 100 \rangle$ 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 $\langle 110 \rangle$ and $\langle 111 \rangle$ crystallographic orientations, cracks also initiate at the maximum tensile stress sites, resulting in ellipsoid 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 $\text{Si}_{1-x}\text{Sn}_x$ alloy films, the crack patterns look like dried mud during delithiation. Cracks appear on a $\text{Si}_{1-x}\text{Sn}_x$ 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_xSi , whereas for a-Si, the two-phase interface is a-Si/ Li_xSi . 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 ($t_{\text{bond-breaking}}/t_{\text{Li diffusion}}$) is larger in a-Si lithiation than in c-Si lithiation. As a result, the Li-ion concentration gradient in the a- Li_xSi shell of a-Si may be larger than that in the a- Li_xSi 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 [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_xSi layer. However, in real experiments, the lithiation rate at the reaction front (i.e. the surface that separates amorphous Li_xSi 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* [9] showed that the degree of fracture has a positive relationship with the size of $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (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* [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 $\text{Li}_{1-x}\text{Ni}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ (NCM), a higher Ni content results in the formation of more abundant and more severe cracks in the particle [20, 77]. Ryu *et al* [20] observed this phenomenon in NCM particles using SEM, as shown in figure 18 [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 [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 $\text{H}_2 \rightarrow \text{H}_3$ transition process (approximately 4.1 V vs. Li^+/Li), Yoon *et al* [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 $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC333) cathode, the H_3 phase only appears at potentials above 5 V vs. Li/Li^+ [82]. When the Ni concentration is intermediate, such as for a $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NMC622) cathode, the $\text{H}_2 \rightarrow \text{H}_3$ transition occurs near 5 V during the charge process [83].

In addition to the particle size and material composition, pre-existing defects can also affect the fracture behavior of the cathode. For LiMn_2O_4 , Hovington *et al* [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 [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 [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 [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 [91]. Chemical outliers may result in concentration gradient stress, and eventually facilitates crack formation. Unbalanced electron and

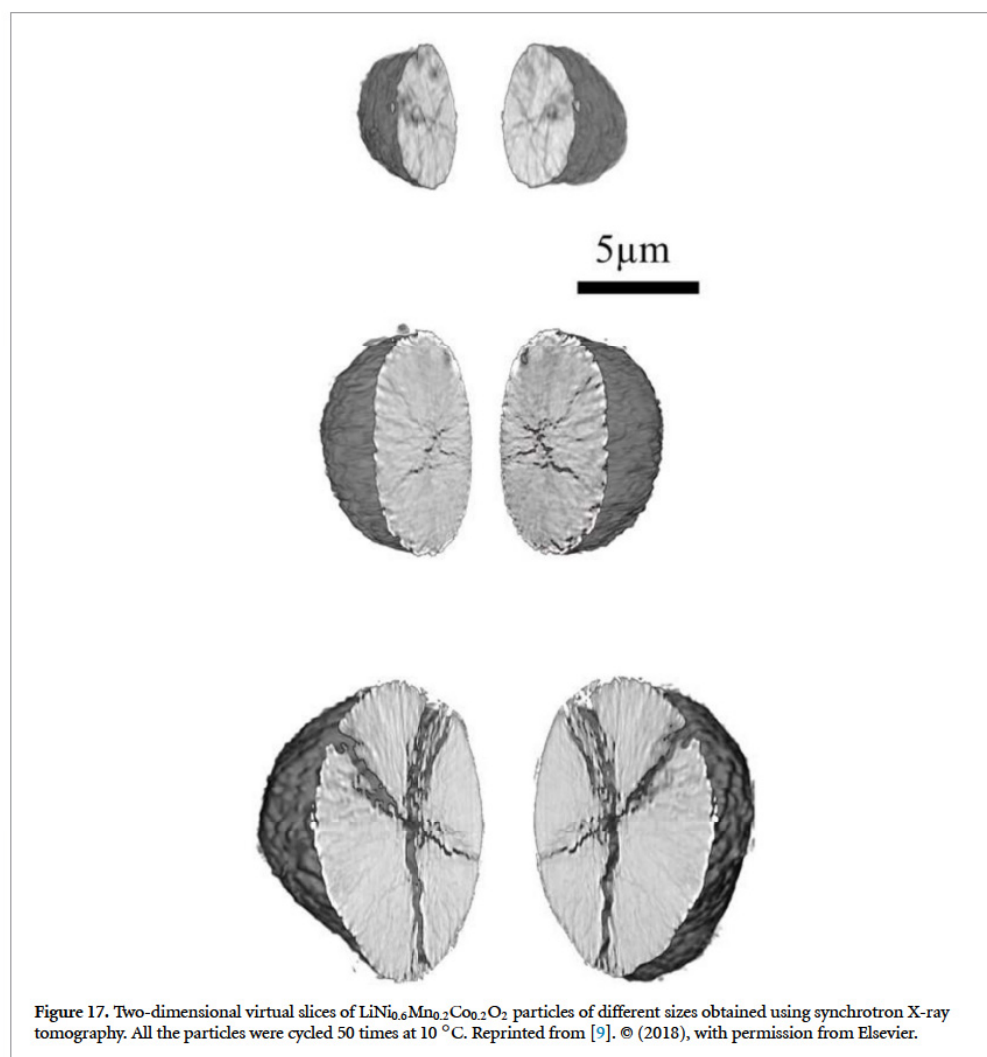


Figure 17. Two-dimensional virtual slices of $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ particles of different sizes obtained using synchrotron X-ray tomography. All the particles were cycled 50 times at 10°C . Reprinted from [9]. © (2018), with permission from Elsevier.

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 $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$ (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).

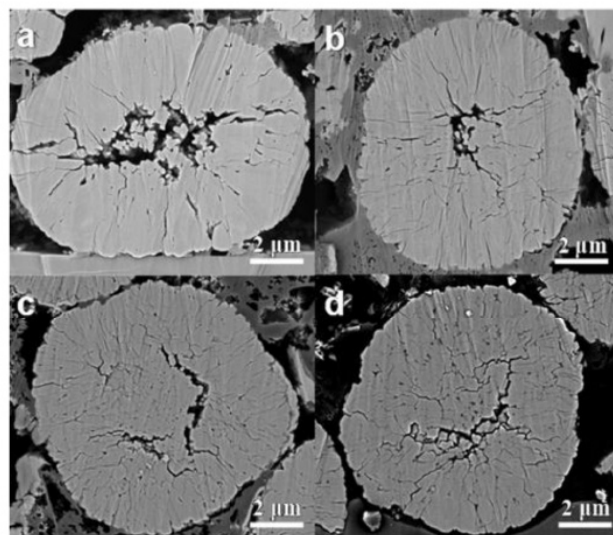


Figure 18. Cross-sectional SEM images of NCM cathodes charged to 4.3 V in the first charge cycle: (a) $x = 0.6$, (b) $x = 0.8$, (c) $x = 0.9$, and (d) $x = 0.95$. Reprinted with permission from [20]. © (2018) American Chemical Society.

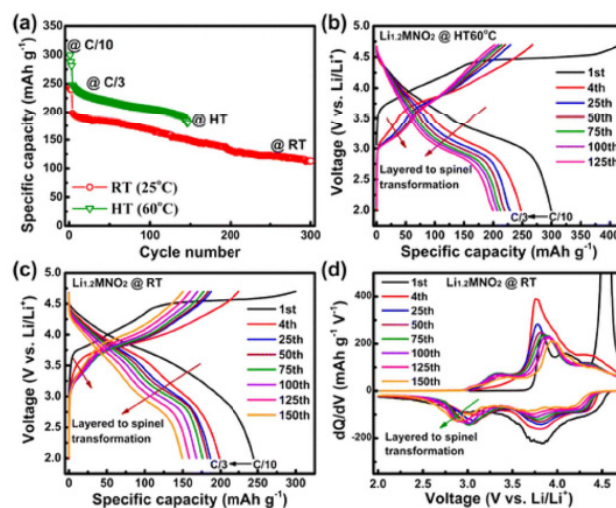


Figure 19. (a) Cycling performance and (b), (c) charge–discharge electrochemistry curves of LNMO at high temperature (HT; 60 °C) and RT (~25 °C); (d) dQ/dV curves at RT for the same cathode. Reprinted with permission from [90]. © (2013) American Chemical Society.

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

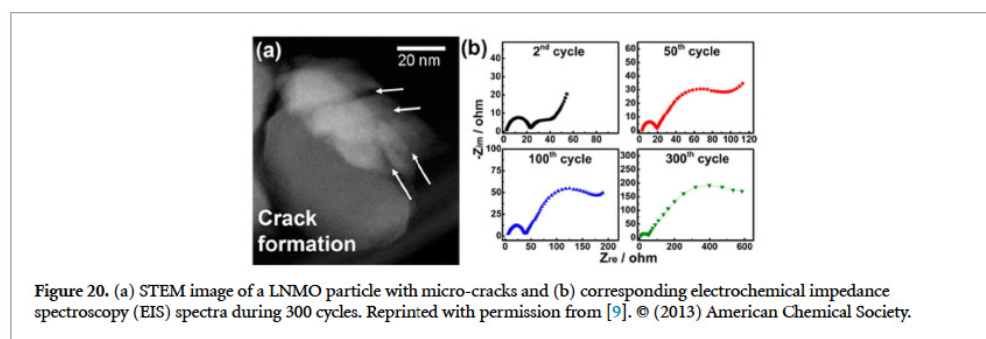


Figure 20. (a) STEM image of a LNMO particle with micro-cracks and (b) corresponding electrochemical impedance spectroscopy (EIS) spectra during 300 cycles. Reprinted with permission from [9]. © (2013) American Chemical Society.

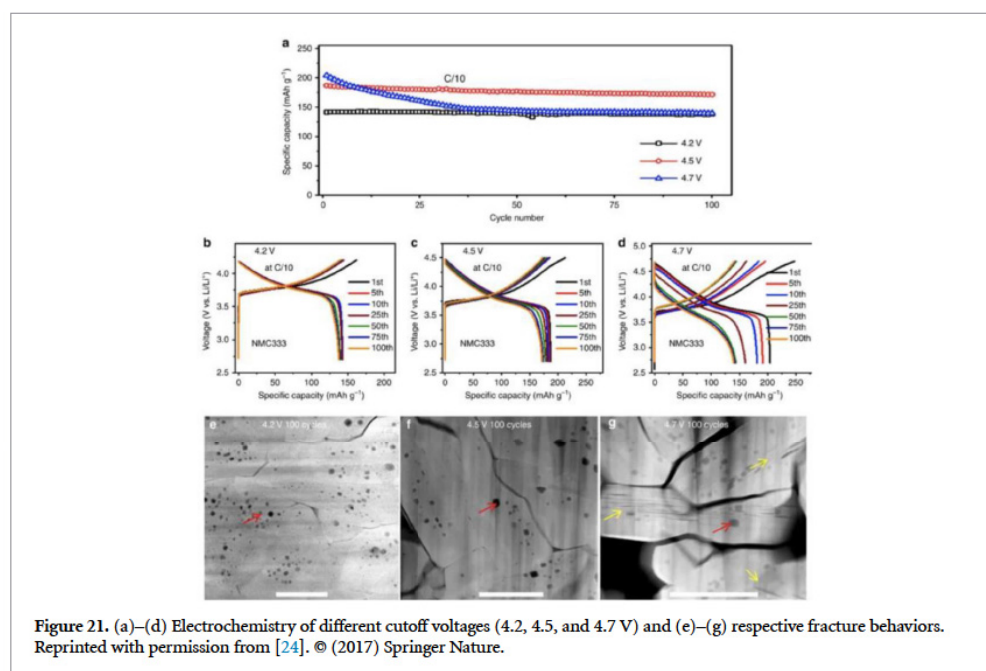
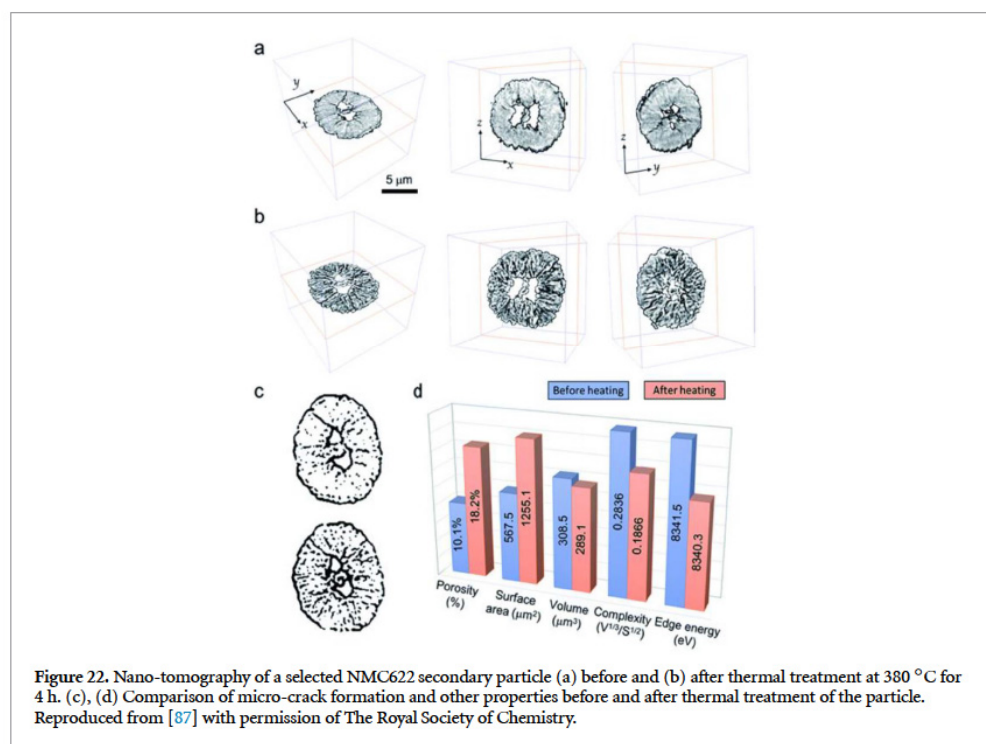


Figure 21. (a)–(d) Electrochemistry of different cutoff voltages (4.2, 4.5, and 4.7 V) and (e)–(g) respective fracture behaviors. Reprinted with permission from [24]. © (2017) Springer Nature.

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.

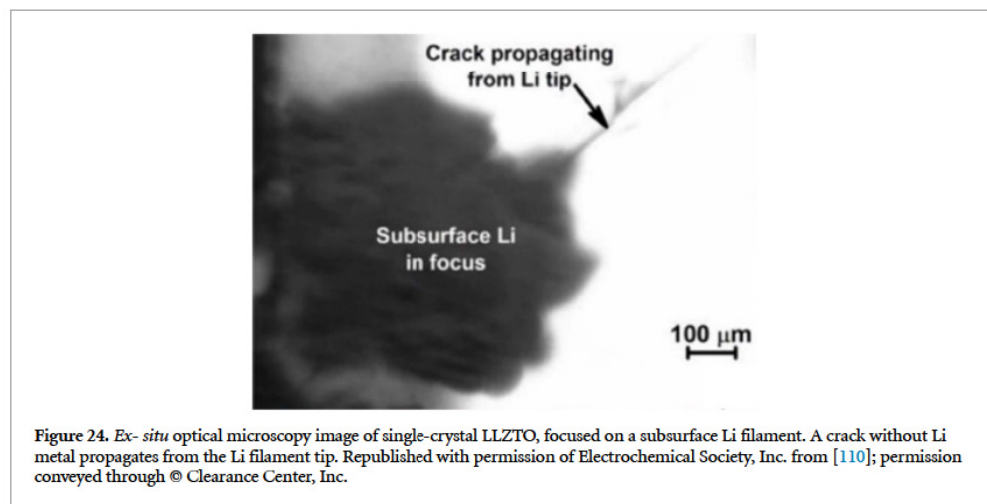
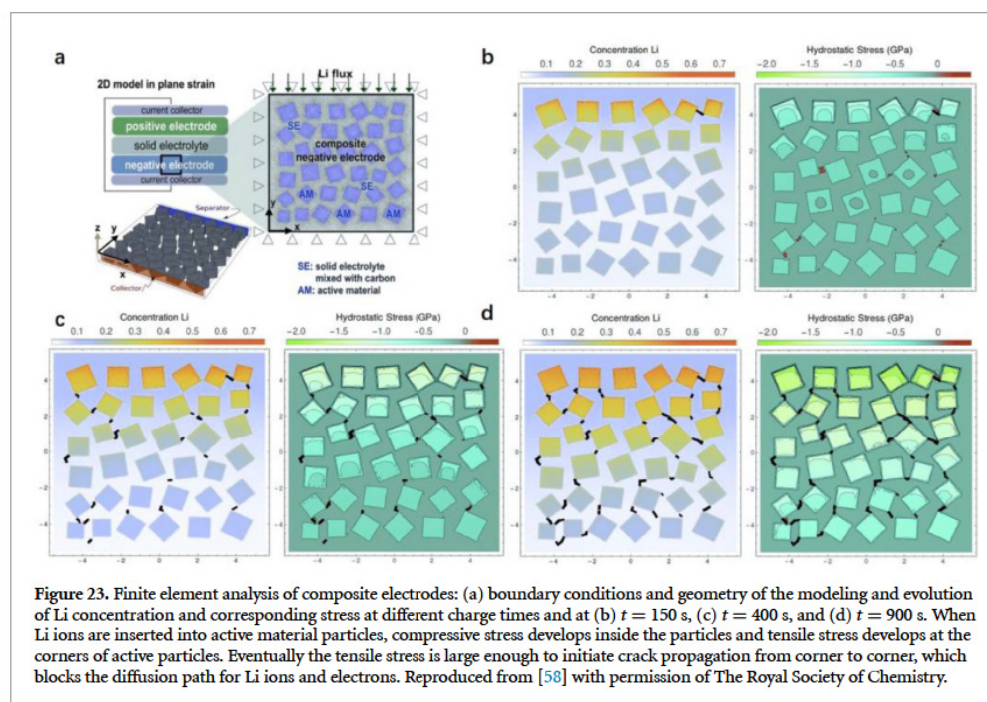


1.3. SSEs

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 Li_{1.5}Al_{0.5}Ge_{1.5}(PO₄)_{3-x}Li₂O ($x = 0.0-0.20$) at RT [102]. A typical garnet material is Li₇La₃Zr₂O₁₂, whose Li-ion conductivity reaches up to 1.62 mS cm⁻¹ at RT [103]. Li₁₀GeP₂S₁₂ 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.



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 $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ SSE with and without surface defects. No crack appeared on the surface of a 70 Li_2S -30 P_2S_5 solid electrolyte without surface defects, whereas cracks were observed to grow from the surface defect site on a 70 Li_2S -30 P_2S_5 SSE with surface defects. The authors studied Li penetration mechanisms in four types of SSEs (amorphous 70/30 mol% $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$, polycrystalline $\beta\text{-Li}_3\text{PS}_4$, and single-crystalline and polycrystalline $\text{Li}_6\text{La}_3\text{ZrTaO}_{12}$ (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.

	Anodes			Cathodes	SSEs
	Alloying	Intercalation (graphite)	Conversion	Intercalation	NASICONs, garnets, sulfides
Fracture mechanism	Two-phase-coherency stress, anisotropic reaction kinetics	Stress induced by volume change, gas formation, cointercalation of solvated ion	Structure reorganization and volume change	Concentration gradient stress and two-phase-coherency stress	Stress induced by growth of interphase or volume expansion of active material
Fracture effect	Specific area of active material increases, impeded diffusion of ions and electrons	Exfoliation, impedance increase, capacity fade	Structure pulverization, decayed capacity, inferior cycling stability.	Resistance increase, capacity fading	Porosity increases, impedance increases, overpotential increase
Factors affecting fracture	Size, morphology, crystallinity, C-rate	Mechanical properties, Solvent type	Morphology, material composition, structure	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:

$$S_v = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r}. \quad (1)$$

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

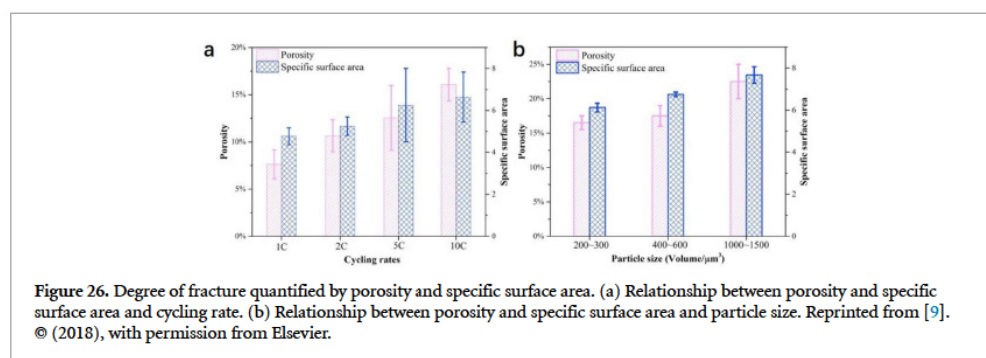
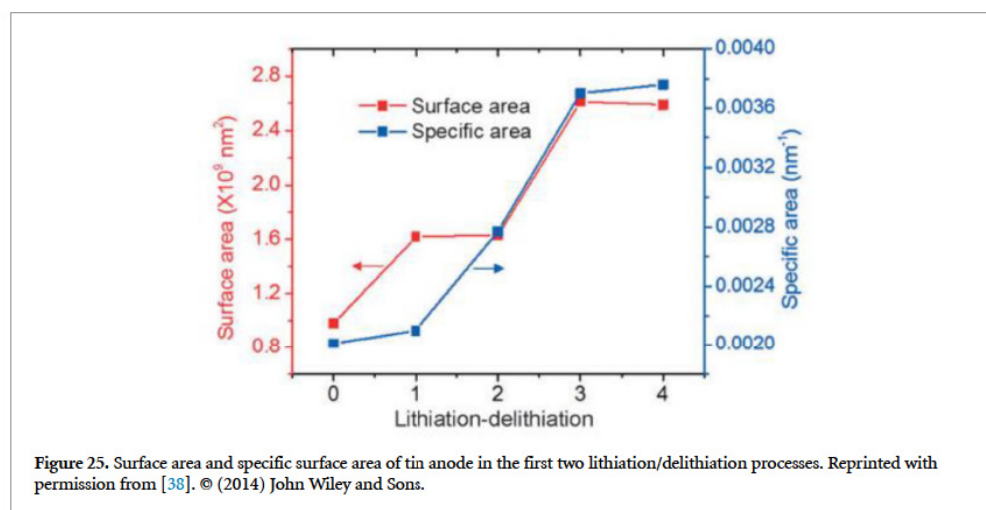
$$dS_v = \frac{\Delta S_v}{S_{v1}}, \quad (2)$$

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

$$dS_v = \frac{\Delta S_v}{S_{v1}} = \frac{\frac{3}{r_2} - \frac{3}{r_1}}{\frac{3}{r_1}} = \left(\frac{r_1 - r_2}{r_2} \right) = \frac{r_1 - ar_1}{ar_1} = \frac{1-a}{a}. \quad (3)$$

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 .

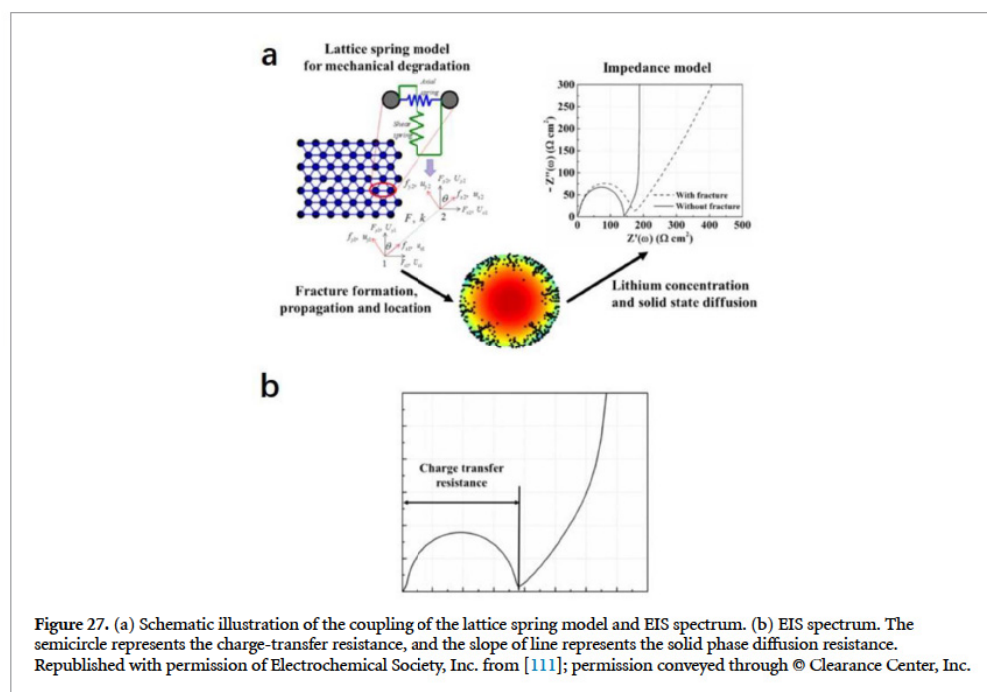
Use of the specific area provides a solution to obtain a quantitative description of the degree of fracture rather than a qualitative one. Transmission X-ray microscopy (TXM) can be used to monitor the 3D



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

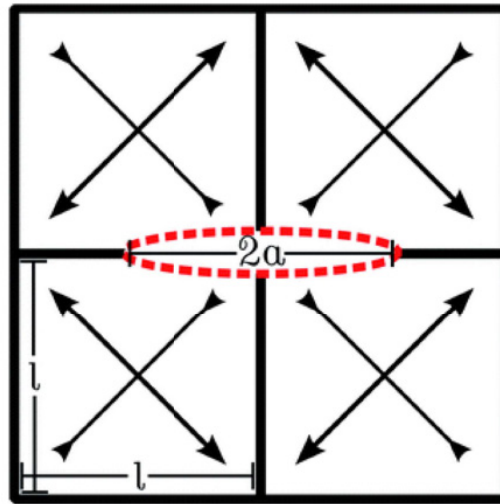


Figure 28. Grain boundary microcrack model containing four grains. The arrows in each grain indicate the principal axes of the crystallographically anisotropic Vegard strain. l is the grain side length and $2a$ is the length of the pre-existing crack at the quadruple junction. Around the four-grain ensemble is an infinite isotropic linear elastic matrix. Reproduced from [112] with permission of The Royal Society of Chemistry.

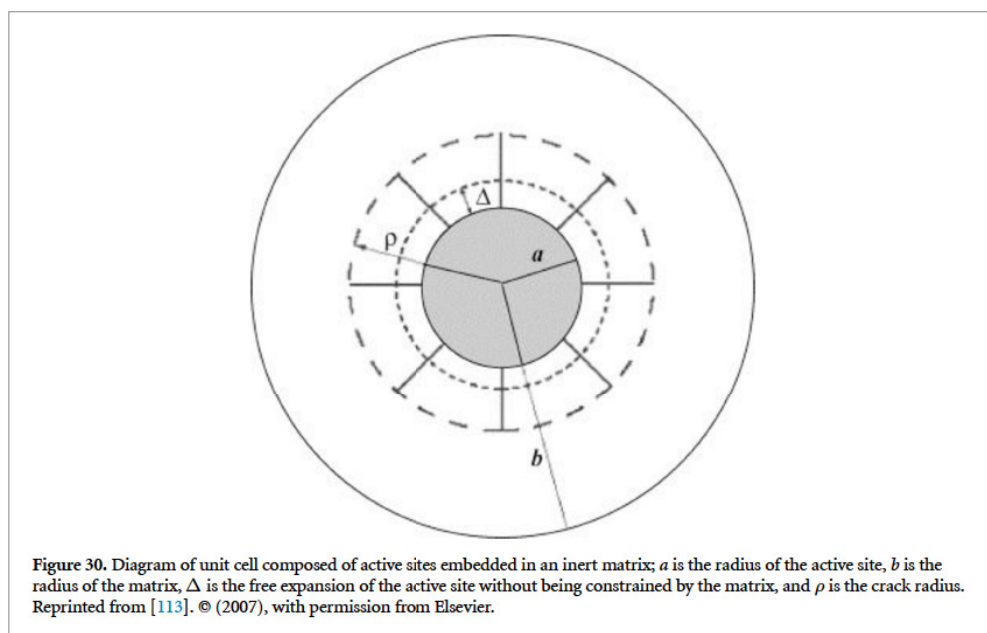
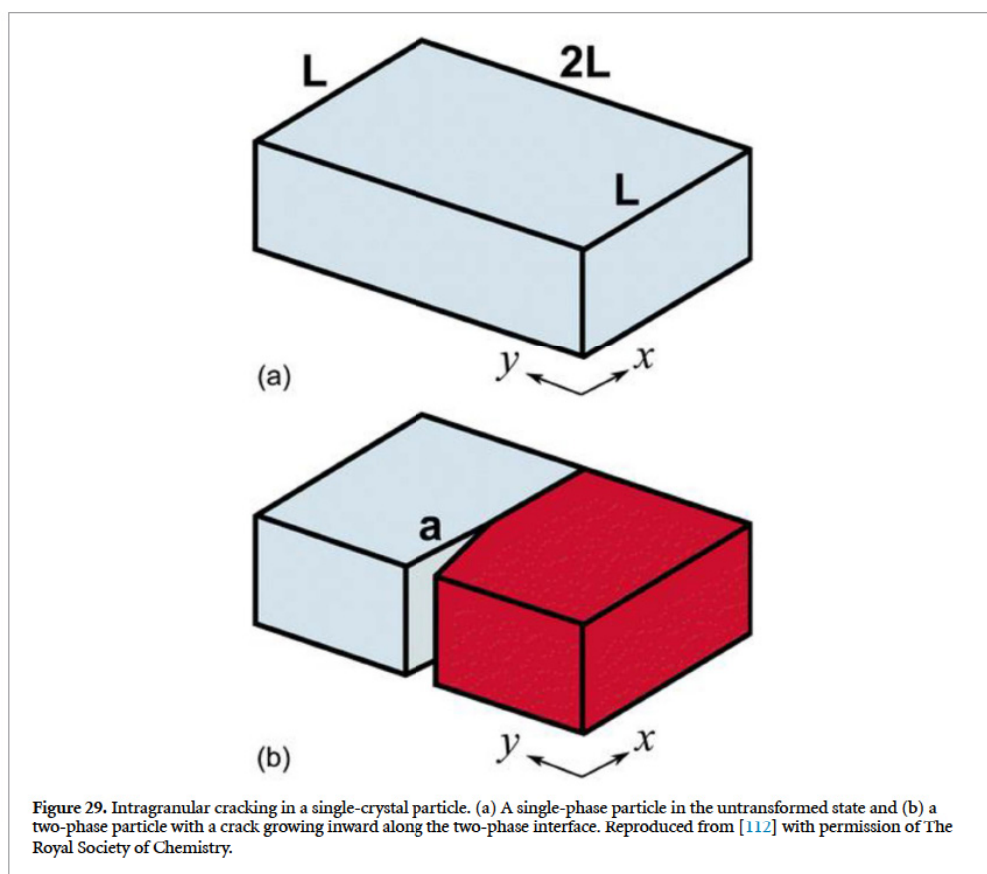
at the grain boundaries and another model for a single-crystal particle with an intragranular crack, as shown in figures 28 and 29, respectively. In the grain boundary micro-crack model, the SIF is a function of the flaw size, and the polycrystalline ensembles are treated as Eshelby inclusions for calculating 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 $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) or $\text{Li}_{9.45}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$ (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 Δa 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, ΔK is the SIF range defined as $\Delta K = K_{\max} - K_{\min}$ 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_{crit} (where $K_{\max} \approx K_{\text{IC}}$), it then propagates rapidly, leading to complete fracture. The crack propagation lifespan is

$N = \int_{a_0}^{a_{\text{crit}}} \frac{da}{C(K_{\max} - K_{\min})^m}$. 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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