

Review on Modeling for Chemo-mechanical Behavior at Interfaces of All-Solid-State Lithium-Ion Batteries and Beyond

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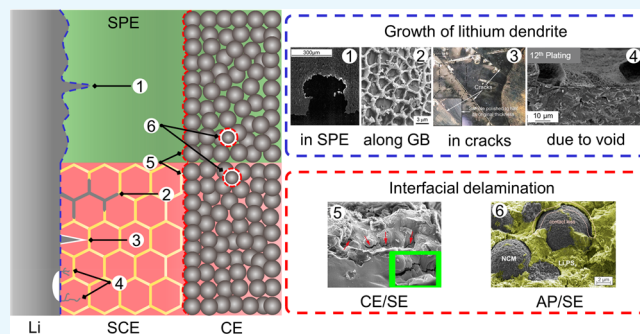
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ABSTRACT: The all-solid-state lithium-ion battery (ASSLIB) is a promising candidate for next-generation rechargeable batteries due to its high-energy density and potentially low risk of fire hazard compared with that of traditional lithium-ion batteries. However, the widespread application of ASSLIBs is unfortunately hindered by new critical issues arising from the all-solid-state structure, especially mechanical instability. First, employing solid electrolytes (SEs) in ASSLIBs is accompanied by a reduction of cell compliance. The SEs are normally much stiffer than liquid electrolytes, and they are no longer able to effectively accommodate the swelling and shrinkage of active particles during (de)lithiation. This may lead to the interfacial delamination and fragmentation of the active particles and electrolytes. In addition, although SEs are expected to mechanically suppress the growth of lithium dendrites at the lithium metal (Li)/SE interface, lithium dendrites are still observed frequently in battery cells employing SEs even with high stiffness. Hence, comprehending these phenomena and providing solutions to these issues are crucial to promote the application of ASSLIBs. A number of theoretical models have been developed to investigate the chemo-mechanical behavior of ASSLIBs in recent decades. This mini-review aims to comprehensively review them, focusing on the mechanically informed modeling on two main topics: (1) lithium dendrite initiation at the Li/SE interface and propagation through SEs and (2) delamination and fragmentation within a composite electrode due to (de)lithiation of an active particle. With this mini-review, we want to supply a more nuanced understanding for chemo-mechanical behavior at different interfaces in ASSLIBs from a modeling perspective.



1. INTRODUCTION

Lithium-ion batteries are widely used as mobile power sources because they have a high-energy density, power density, and Coulombic efficiency.¹ However, traditional lithium-ion batteries employ flammable and corrosive liquid electrolytes which leads to serious safety issues.² Moreover, it has been predicted that the theoretical limit will soon be reached with the current technology,² which can hardly catch up with the increasing demand for higher energy density. The urgent predicament of safety hazard and energy shortage has motivated a collection of new technologies, with the all-solid-state lithium-ion battery (ASSLIB) being the most promising one. An ASSLIB generally consists of a composite cathode, a solid electrolyte (SE) as the separator, and a composite anode (or a Li anode in an all-solid-state lithium-metal battery). ASSLIBs use SEs rather than organic liquid electrolytes to reduce the risk of fire hazard.² Moreover, the high stiffness of SEs is expected to enable the electrolytes to prevent the lithium dendrite from propagating and to secure the safe employment of the Li anode, which is the ultimate choice for high-energy batteries owing to its highest gravimetric and volumetric energy density.

Nevertheless, the employment of SEs in ASSLIBs brings about new challenges compared with conventional lithium-ion batteries. Among others, mechanical instability becomes increasingly critical for the stable operation of ASSLIBs. In lithium-ion batteries, the fluidity of the liquid electrolyte guarantees good accommodation of the deformation of the active particles and thus alleviates mechanical stresses upon charging and discharging cycles.¹ Therefore, the mechanical stress arising during (de)lithiation in the active particles can have a limited influence on the electrochemical performance and will not lead to destructive failure. On the other hand, the rigid nature of SEs, especially of the inorganic solid ceramic electrolytes, will not allow the active particles to swell and shrink freely, resulting in increased and more severe

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mechanical issues in ASSLIBs. The composite electrode in an ASSLIB is mainly composed of active particles surrounded by the SE. During cyclic charging and discharging, the active particles will continuously undergo swelling and shrinkage upon lithium inserting into and extracting from them. The whole process is accompanied by high stresses, not only in the active particles but also at the interfaces between the active particles and the SE in ASSLIBs. Consequently, the induced high stresses may lead to the fragmentation of the active particles and SE and the delamination at interfaces between them, as shown in Figure 1. It is thus crucial to understand the complex-coupled chemo-mechanical behavior during cyclic charging and discharging to develop rechargeable ASSLIBs with a long lifetime.

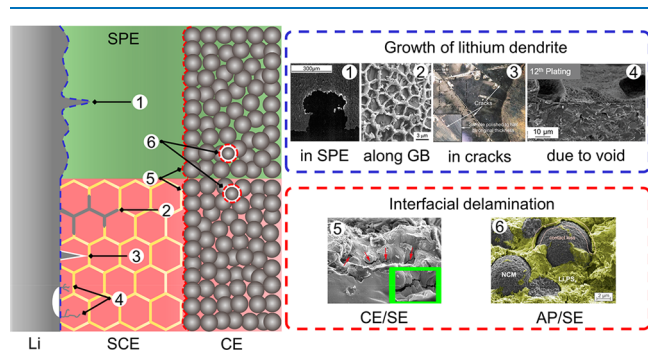


Figure 1. Schematics of interfacial failures in a solid-state battery, which uses Li as the anode, solid polymer electrolyte (SPE, top) or solid ceramic electrolyte (SCE, bottom) as the electrolyte and composite electrode (CE) as the cathode. We identify six interfacial failures in this mini-review: lithium dendrite formation at Li/SE interface ① in solid polymer electrolytes,^{5a} ② along grain boundary (GB),^{5b} ③ in cracks,^{5c} and ④ due to lithium voiding,^{5d} interfacial delamination of ⑤ CE/SE^{5e} and ⑥ active particle (AP)/SE.^{5f} The subgraphic ① is reprinted in part with permission from ref 5a (copyright 1999 Elsevier); ② from ref 5b (copyright 2017 Elsevier); ③ from ref 5c (copyright 2017 John Wiley & Sons); ④ from ref 5d (copyright 2020 American Chemical Society); ⑤ from ref 5e (copyright 2017 Elsevier); and ⑥ from ref 5f (copyright 2017 American Chemical Society).

Another critical issue concerning all-solid-state lithium–metal batteries is the dendritic formation at the interface between the Li anode and the SEs. It has been anticipated that SEs are stiff and tough enough to prevent lithium dendrites from penetrating,³ which is a major driving force for the employment of SEs. To our disappointment, SEs—organic and inorganic SEs alike—cannot resist Li to penetrate through,^{4a} which is against theoretical predictions,^{4b,c} as shown in Figure 1. A new mechanistic theory accounting for the lithium dendritic formation and propagation in SEs is thus necessary and urgent for a successful implementation of SEs in all-solid-state lithium–metal batteries.

It is also noticed that a few recent works have already reviewed the mechanical behavior of ASSLIBs from a modeling perspective. Zhao et al.'s review¹ aims to facilitate the knowledge transfer of mechanically coupled modeling in lithium-ion batteries to the study of ASSLIBs, but only with a slight touch upon the topic of the latter. A thorough review especially for ASSLIBs is nonetheless lacking in Zhao's review. Bistri et al.^{6a} comprehensively reviewed the efforts on the modeling of chemo-mechanical behavior of the Li anode, SEs, and composite cathodes in ASSLIBs. The connection and

difference between the modeling of traditional lithium-ion batteries with liquid electrolytes and that of ASSLIBs are not explicitly reviewed. Wang et al.^{6b} summarized associated electro-chemo-mechanical issues at the interfaces of ASSLIBs, shedding light on both experimental observations and computational analyses. However, their review mainly focuses on the observation and conceptual understanding of coupled electro-chemo-mechanical behaviors, and various mathematical models and their validations are missing. There are also some excellent works from Tang et al.,^{6c} Zhang et al.,^{6d} Lewis et al.,^{6e} and Wang et al.,^{6f} who summarized the research of electro-chemo-mechanics in ASSLIBs and conducted in-depth discussions for mechanical behavior at interfaces. However, these works are more from an experimental perspective rather than from a modeling one. Therefore, this review aims to summarize the current updates on the extensive collection of modeling efforts for ASSLIBs, with a dedication to the modeling for mechanical behavior at different interfaces in ASSLIBs. Note that this mini-review only concerns models at continuous level, and models based on molecular dynamics and first-principles can be found in some other works.^{6g} Furthermore, considering the limit on the number of references in the mini-review, the work after 2020 is mainly reviewed in this review, whereas that before 2020 can be found in previous reviews.^{6a–f}

The main body of this article focuses on the mechanically informed modeling on two main topics: (1) lithium dendrite initiation at the Li/SE interface and propagation through SEs and (2) delamination and fragmentation within composite electrodes due to (de)lithiation of active particles. In section 2, the modeling for the mechanical influence on the formation and propagation of lithium dendrites at Li/SE interfaces will be reviewed, whereby polymer and ceramic electrolytes are discussed separately. In section 3, we will review the modeling for chemo-mechanical behavior at interfaces within composite electrodes, discussing, in particular, the influence of particle size, spatial distribution, and volume fraction of active particles on the interfacial delamination and particle fragmentation during (de)lithiation.

2. MODELING AT Li/SE INTERFACE: LITHIUM DENDRITE FORMATION

The formation of lithium dendrites is generally caused by unstable lithium deposition at the Li/SE interface, whose electrochemical and mechanical mechanism is yet to be understood. It seems that uneven deposition can take place regardless of the interface types and roughness. Moreover, the penetration of soft lithium through SEs remains mysterious. On one hand, metallic lithium is a substance that is elastically compliant with a Young's modulus of 1.9–7.98 GPa,^{7a,b} is ductile with very low yielding strength (around 0.41–2 MPa^{6f}), and can undergo considerable diffusional creep under low stresses at room temperature.^{7c} The SEs, on the other hand, normally consist of stiffened polymers or ceramics with great elastic moduli, which are considered mechanically “strong” to prevent the lithium from protruding. The counterintuitive fact that the “fluid-like” lithium can penetrate “strong” SEs and short the battery also appeals urgently for a corresponding theory to comprehend the phenomenon.

The early attempt that tried to connect the mechanical stresses and surface roughness with the initiation of lithium dendrites at the Li/SPE interface was made by Monroe and Newman,³ who treated both Li and SPE as pure linear elastic

materials and developed a kinetic model that took surface roughness into consideration through linear perturbation analysis. Their model, though, has led to an arguable conclusion and has inspired a series of works. Thus, we would like to briefly review their model here. In the Monroe–Newman model, a lithium ion is assumed to be the only charge carrier in the cell, and the amount of lithium plating on the anode per second per unit area is proportional to the current density (i), which is perturbed by a roughened electrode surface with the displacement subject to a sinusoidal function (u_1):

$$u_1(0, x_2) = A \cos \omega x_2 \quad (1)$$

In eq 1, x_1 and x_2 directions are normal and tangential to the electrode surface, respectively (Figure 2a). The surface is

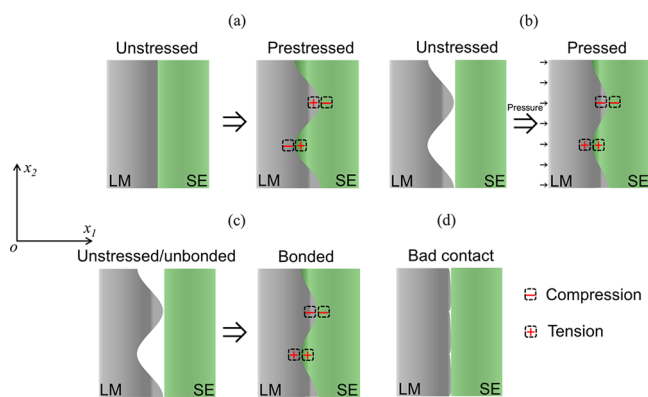


Figure 2. (a) Prestressed model (Monroe–Newman model), (b) pressure model, (c) bonded model, and (d) bad contact at the Li/SE interface.

subjected to a periodic displacement in the x_1 direction with amplitude A and frequency ω . The electrode surface lies at $x_1 = 0$, and the current density on the surface is determined by the Butler–Volmer equation:

$$i = i_{0,\text{ref}} \exp\left[\frac{(1 - \alpha_a)\Delta\mu_{e^-}}{RT}\right] \left[\exp\left(\frac{\alpha_a F \eta_s}{RT}\right) - \exp\left(-\frac{\alpha_c F \eta_s}{RT}\right) \right] \quad (2)$$

where constants of $i_{0,\text{ref}}$, R , T , F , α_a , and α_c are the reference exchange current density, the gas constant, absolute temperature, Faraday constant, and anodic and cathodic transfer coefficients, respectively. $\Delta\mu_{e^-}$ is the electrochemical potential change of the electrons in the metal electrode from undeformed (unstressed) to deformed (stressed) state, and η_s is the electric overpotential between the electrode and the electrolyte. By solving the stress state and electric field under the surface perturbation of eq 1, $\Delta\mu_{e^-}$ and η_s can be obtained, and the current density distribution i on the electrode surface can thus be calculated through eq 2. When current density i at the lithium electrode “peak” ($x_2 = 0, 2\pi/\omega\dots$) is greater than that at the lithium “valley” ($x_2 = \pi/\omega, 3\pi/\omega\dots$), the electrode surface becomes rougher and lithium dendrite initiation is likely to occur. Through their analysis, they concluded that the roughening at the Li/SPE interface can be mechanically inhibited when the shear modulus of SPE is more than twice that of lithium. However, accumulated studies have shown that their conclusion is debatable and stiff electrolytes cannot effectively prevent lithium penetration.^{4a,b} Variations based on

the Monroe–Newman model are thus proposed to consider different effects.

First, in the Monroe–Newman-type models, the employment of Butler–Volmer equations indicates that the surface reaction is assumed as the limiting factor for lithium deposition. It should be argued whether this assumption is solid. Tikekar et al.^{8a} assume that, instead of reaction, ion transport is the limiting factor for the lithium deposition, and lithium ions can be reduced immediately on site when they arrive at the lithium electrode surface. Thus, the amount of lithium deposited on the Li surface is governed by the chemical-potential-gradient-driven flux instead of a Butler–Volmer-type reaction. Based on their model, they found that the stable electrodeposition can be realized in a SPE by immobilizing a small fraction of anions in the separator and using SPE with a moderate shear modulus. In a different study, Mistry and Mukherjee^{8b} discussed the competing effects between lithium bulk transport and surface reaction. They revealed that the mismatch between lithium molar volume in SEs and that in the lithium anode, rather than the stiffness of SEs, is fundamentally responsible for unstable electrodeposition. Ganser et al.^{8c} employed a rigorous electrochemo-mechanical description of the bulk transport and interfacial reaction kinetics to predict the interface stability. Their results showed that stiffness and transport properties of the electrolyte are equally important for interface stability. A right trade-off among the electrochemical and mechanical properties should be found rather than unconditionally increasing the stiffness of the SPE.

Second, the implementation of the boundary condition for the perturbed surface of eq 1 introduces an unrealistic external traction at the electrode/electrolyte interface, as shown in Figure 2a. Although this unrealistic traction can be understood as a coupled “thermodynamic stress” induced by volume change of the conversion of a lithium ion in the electrolyte to a lithium atom in the electrode at the electrode/electrolyte interface,⁹ this treatment indeed leads to the violation of force balance at the interface because there is no external loading applied explicitly in reality. A different approach with modified boundary condition has been proposed by Barai et al.,^{10a} who assumed that the Li electrode already has a perturbed surface due to nonuniform stress-free lithium deposition, and the SE initially has a flat surface, as shown in Figure 2b. In their treatment, however, compression always exists in the electrode due to their treatment to maintain the conformability of the two surfaces, and the mechanical effect arising from applied compression cannot be decoupled from the surface effect. In view of that, McMeeking et al.^{10b} proposed that the unstressed Li electrode has a sigmoidal surface with the shape of eq 1. By bonding the Li electrode surface with the flat surface of the electrolyte together, stresses are generated naturally without introduced unrealistic external traction at the interface or compression in the electrode, as shown in Figure 2c. The electrochemical change of $\Delta\mu_{e^-}$ is simplified to $-\sigma_n \Omega_M$, where σ_n is the stress normal to the electrode surface and Ω_M is the molar volume of lithium metal. The variation of electric field—and the consequent overpotential η_s —along the interface due to the surface perturbation is also treated explicitly. They derived an analytical expression for the amount of lithium deposited on the roughened interface. Based on the expression, they discussed the role that surface roughness has played and showed that, regardless of the elastic stiffness of the SEs, the amplitude of the sinusoidal roughness of Li surface will always

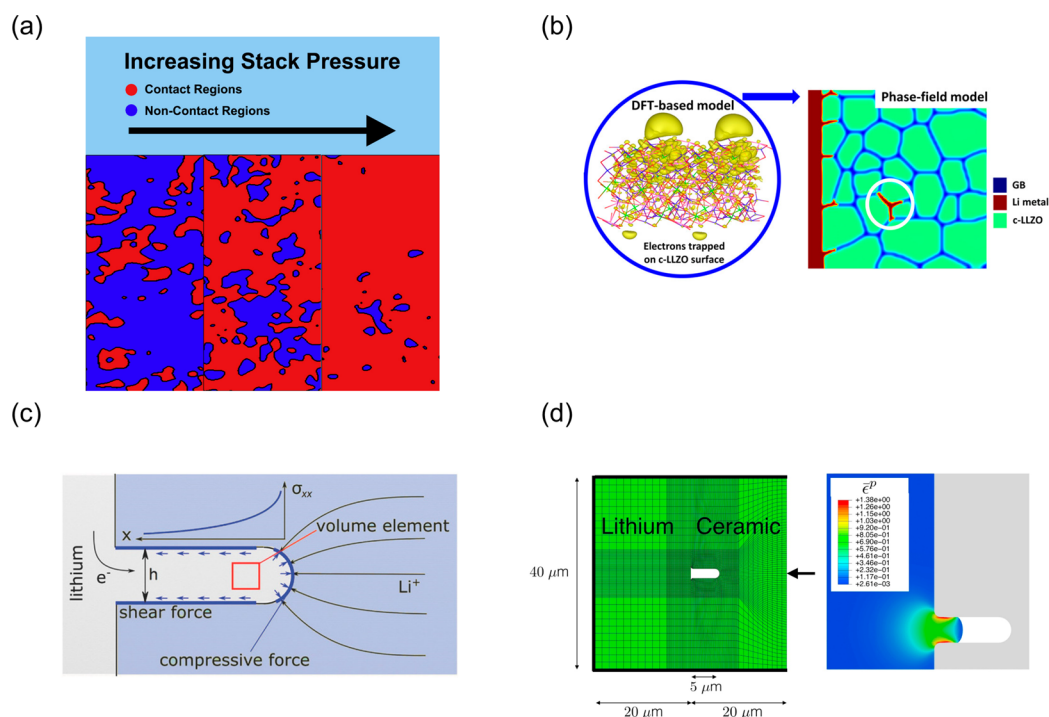


Figure 3. Collection of mechanisms for lithium dendrite formation in Li/SCE systems: (a) variation of Li contact stress under various stack pressures,^{12a} (b) multiscale model for dendrite formation in grain boundary,^{13c} (c) pressurized crack modeling for propagation of dendrite via extending crack,^{5c} and (d) Li intrusion the crack in SCE through elastic–viscoplastic deformation.^{18a} The subgraphic (a) is reprinted in part with permission from ref 12a (copyright 2020 Elsevier); (b) from ref 13b (copyright 2019 American Chemical Society); (c) from ref 5c (copyright 2017 John Wiley & Sons); and (d) from ref 18a (copyright 2018 Elsevier).

increase if the wavelength is long. They have also shown that, for small wavelength roughness, high current density permits the growth of the lithium dendrites, which again cannot be suppressed by increasing the stiffness of the SEs.

Third, studies have shown that rather than the bulk properties of SEs, Li/SE interface characteristics play key roles in lithium dendritic formation. Stone et al.¹¹ pointed out that the prediction by Monroe and Newman is not implementable experimentally because interface adhesion cannot be maintained as perfectly in reality as in the theoretical model, as shown in Figure 2d. Thus, a high shear modulus cannot guarantee a dendrite-free battery system; instead, increased adhesion of the Li/SPE interface can help alleviate the problem of dendrites. This can be realized by external pressure at the cell level.^{12a,b} Zhang et al.^{12a} identified a preferred stack pressure of at least 20 MPa that can decrease void volume and maintain relatively small interface resistance (Figure 3a). Using effective properties, the model was also used to model SCE. Tu et al.^{12b} analyzed factors that affect interfacial stability, such as stack pressure, interfacial charge transfer coefficient, and mass transfer rate in the SEs. They showed that a low stack pressure (3–5 MPa) hardly affects the interfacial deposition, but low ionic conductivity and low interfacial area-specific resistance will increase lithium deposition inhomogeneity. Verma et al.^{12c} employed and developed the model to discern the impact of external stack pressure on interfacial instability in the polycrystalline/amorphous solid electrolyte structure. The microstructure of the SEs of interest including grains, grain boundary, and voids is characterized by effective transport and mechanical parameters. They showed that the external pressure, high

temperature, and low surface roughness can realize the stable deposition.

For SCEs, because ceramics have various defects, the ideal linear elastic model for electrolyte material from Monroe–Newman finds even less validations in ASSLIBs with SCEs. Experiments have shown that lithium dendrite can be found in the grain boundary, cracks, and voids of SCEs.^{4a,b,12d} The defects in the SCEs are playing equally, if not more, important roles than stiffness of Li and SCEs in the dendrite formation in ASSLIBs with SCEs.

The grain boundary in the SCEs can account for intergranular dendritic formation due to different reasons. First, the ionic resistivity of the grain boundary is generally found to be high, which may trap the lithium and invite lithium dendrites to grow.^{4a,b} However, experiments also show that even a lower resistivity of the grain boundary cannot guarantee a dendrite-free electrolyte.^{4c} Second, a grain boundary, in general, has lower shear modulus compared to that of the grain, which may also be the reason for dendrite growth inside the grain boundary.^{4a,b} Barai et al.^{13a} employed a two-step computational model and showed that the current density induced by effective stress in the grain boundary is higher than that in the grain interior because the former is mechanically softer than the latter, which leads to enhanced lithium deposition in the grain boundary. Third, recent studies have also shown that high electronic conductivity of SCE may fundamentally account for lithium dendrite formation.^{13b} Tian et al.^{13c} conducted a multiscale simulation coupling density functional theory calculation with the phase-field method. They revealed that the $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ surfaces can trap significant excess electrons and produce isolated lithium nucleation, as shown in Figure 3b. Tantratrian et al.^{13d}

developed an electro-chemo-mechanical phase-field model to further reveal the influence of mechanical and electronic properties of the grain boundary on the lithium nucleation and propagation in polycrystalline SCE. Based on the simulation, they provided a phase map of lithium morphologies as a function of elastic modulus and trapped electron concentration.

Apart from the grain boundary, pre-existing cracks may also function as “soft spots” that may invite a lithium dendrite to initiate there. Porz et al.^{5c} found that monocrystal SCEs cannot resist the propagation of lithium dendrites due to small scratches on the crystal surface. The Li will wedge open the pre-existing defect on the grain surface, independent of the shear modulus of the single crystal. They developed a 1D electro-chemo-mechanical model for growth of lithium-filled cracks (Figure 3c) and explained that the pressure generated by filled Li is sufficiently large to penetrate brittle SCEs by Griffith-like crack extension. Barroso-Luque et al.¹⁴ developed a mathematical model of electrodeposition-induced plastic flow, which showed that the maximum value for pressure from deposition at an isolated flaw is determined by the boundary traction potential. Yuan et al.^{15a} proposed a coupled electro-chemical–mechanical phase-field model for crack propagation and lithium dendrite growth. They found that the crack propagation and dendrite growth are promoted by both a longer defect with a sharp edge and angle as well as a stacking pressure above 10 MPa. They^{15b} also developed a physics-based and fully coupled electrochemical–mechanical model considering the battery model, mechanical model, phase-field model, and short-circuit model. Their model revealed that the electrochemical failure of the cell can be accelerated by high charging rate and low conductivity of SCE because the overpotential-driven stress promotes dendrite growth in the crack and penetrates the SCE. However, that pressurized crack model of dendrite growth exists as a paradox that if a pressure is high enough to extend the crack in SCE with high fracture toughness, that pressure can also squeeze the “soft” lithium into a Li anode, thus relieving the pressure in the crack.¹⁶ A new mechanism is proposed by Shishvan et al.,^{17a} who treated the dendrite growth as a climbing edge dislocation, which can spontaneously occur without excess constant chemical potential of Li⁺. The free energy provided by Li⁺ flux into the dendrite tip is sufficient to grow the dendrite, whose growth rate can also be calculated from the model.^{17b}

Although the electrochemical and mechanical response of SEs are considered to be the prime factor that accounts for lithium dendritic formation, the properties of Li electrodes are also important to capture the whole picture. Narayan and Anand^{18a} proposed an elastic–viscoplastic model with large deformation for lithium and worked out the material parameters in the model from the nanoindentation data. Then they applied the theory in a finite element simulation and showed that the lithium dendrite can be flattened and the Li can infiltrate the cavity of SE when Li and SE are mechanically pushing against each other, as shown in Figure 3d. Moreover, to address the important role of the flow of lithium in the growth of lithium dendrites, Yang^{18c} introduced a non-Newtonian flow model to describe the flow of lithium and studied the growth of a Li sphere and a Li whisker in the electrolyte. The results indicated that the growth of such lithium dendrites can be alleviated through suppressing the cycling-induced strain energy. Furthermore, Shishvan et al.^{18b} have also pointed out that, during stripping, the classical

Butler–Volmer equation, which disregards the dislocation-induced creep of the Li electrode, fails to predict voiding formation. They developed a modified form of Butler–Volmer kinetics for the interface flux that is associated with a deforming Li electrode. They showed that Li creep around an imperfection can enhance flux focusing significantly. Interestingly, treating lithium as a power-law creeping solid, Roy et al.^{18d} studied the void growth from a pre-existing small imperfection at the Li/SCE interface, which showed that the void can only initiate from an unrealistically large pre-existing imperfection with a size greater than 1200 μm . Their results showed that there is still a long way before we finally find out the mechanism for lithium voiding and the subsequent lithium dendrite formation.

It can be seen from this section that lithium dendrite formation is a rich topic and has inspired a series of modeling work. However, from the authors' point of view, no single work has agreed with the experiments in every respect. Hence, the theoretical modeling for formation and propagation of lithium dendrite is still an ongoing investigation.

3. MODELING FOR COMPOSITE ELECTRODES: DELAMINATION AND FRAGMENTATION

Composite electrodes in an ASSLIB are, in general, composed of active particles embedded in a SE. A significant mechanical challenge in such composite electrodes is that the active particles cannot swell freely during lithium insertion and extraction, which will result in high stresses and fracture, not only inside active particles but also at particle/SE interfaces, as shown in Figure 1. During lithiation, active particles swell, pushing against the surrounding SE and generating stresses. When the stresses are sufficiently high, fracture at different places occurs, including intergranular fragmentation inside active particles and cracks in electrolytes. During delithiation, active particles shrink, detaching themselves from the surrounding material, and delamination occurs. Fracture in composite electrodes leads to a decrease in ion transport, an increase in internal resistance, and a reduction in capacity. In this section, we will briefly review the theoretical models developed to understand mechanical behavior of the interface within composite electrodes of ASSLIBs during charging and discharging. Because some problems like intergranular fracture of active particles and delamination of electrodes from separators and current collectors are already observed in traditional LIB systems, models concerning these phenomena can be directly adapted from previous models treating the same problems. Thus, one can also refer to works such as Zhao et al.¹ for a more comprehensive review regarding these problems. This mini-review only concentrates on the debonding of active particles from an electrolyte matrix.

Bistri and Di Leo¹⁹ showed that the interfacial stress between the active particle and SE is not controlled by the size of active particles nor their spatial distribution but is enhanced by the increasing volume fraction of active particles. However, the amount of active particles cannot be increased without a limit. Bucci et al.^{20a} derived an analytical model based on a cohesive theory of fracture and reported that decreasing particle size does not help to avoid interfacial delamination of an active particle, which will initiate when its volumetric change reaches about 7.5%, as shown in Figure 4a. They found that compliant SEs ($E < 25$ GPa) can accommodate the volumetric change and delay the occurrence of interfacial delamination.^{20a} However, their previous work^{20b} also showed

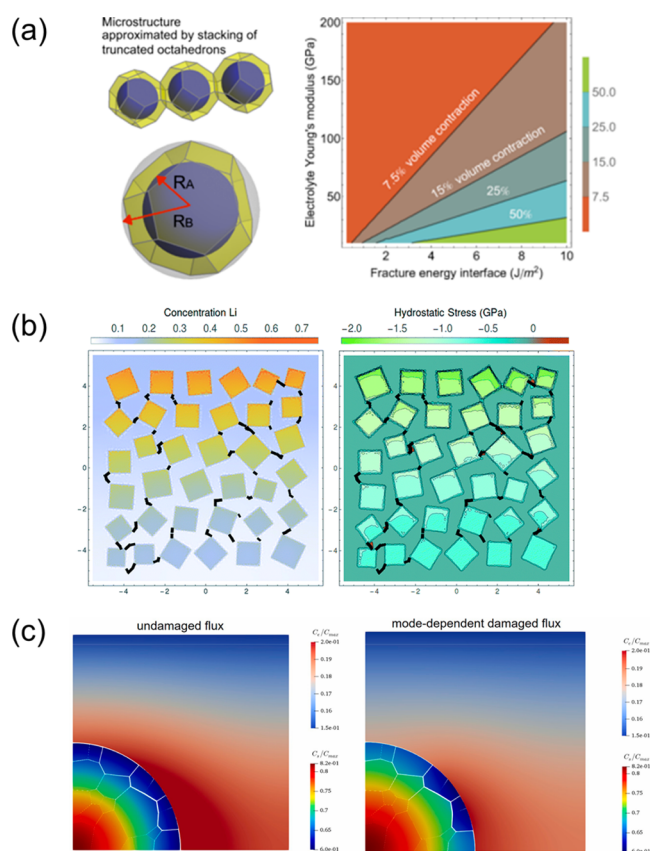


Figure 4. (a) Schematic of the one-dimensional radially symmetric model and the relative volume contraction of electrode particles.^{20a} (b) Damage in the solid electrolyte material after charging^{20b} and (c) intergranular fragmentation inside active particles.²¹ The subgraphic (a) is reprinted in part with permission from ref 20a (copyright 2018 American Physical Society); (b) from ref 20b (copyright 2017 Royal Society of Chemistry); and (c) from ref 21 (copyright 2021 Elsevier).

that the microcracks are more likely to take place in compliant SEs as the higher stress concentrations are caused by a larger deformation of compliant SEs, as shown in Figure 4b. A more comprehensive chemo-mechanically coupled cohesive fracture model was developed by Rezaei et al.,²¹ who showed that the model can be applied to study the dominant degradation mechanism in the ASSLIB, such as intergranular fragmentation inside active particles (Figure 4c). Fathiannasab et al.²² developed a chemo-mechanical model based on the reconstructed morphology of a composite electrode to elucidate the influence of the particle/electrolyte interface and void space on the lithiation-induced stress evolution. They found that a void can alleviate the stress formation through accommodating swelling of active particles. The external pressure being used to improve ion pathways may cause fracture, and a SE with a lower stiffness can relax the stress in the composite electrode and exacerbate the anisotropic displacement of active particles. Song et al.²³ developed a fully coupled electro-chemo-mechanical model for thin-film batteries and showed that the thin-film batteries can be bent toward the cathode to enhance the lithiation capacity and reduce the stress at the electrode/electrolyte interface. Wan and Ciucci²⁴ reported that the interfacial stress is also enhanced by the strong electric fields at the interface. Sultanova and Figiel²⁵ proposed a nonlinear microscale diffusion mechanics model to study the effects of viscoplas-

ticity and interfacial damage on the in situ diffusive mechanical behavior of a composite electrode. The results suggested that the value of the interfacial opening displacement is reduced by the plastic deformations of SPE, and a smaller interfacial gap is generated by a softer polymer response at slower charging rates. Furthermore, the linear elastic models will overpredict the interfacial opening compared with the elasto-viscoplastic models.

The above research studies show that the particle size, spatial distribution, volume fraction of active particles, and the characteristics of voids in the composite electrode have a great influence on the interfacial stability within composite electrodes and the performance of ASSLIBs. However, there are still more factors that can account for the electrochemical and mechanical performance of the composite cathode, such as the realistic microstructure. Therefore, much work remains to be done in this area.

4. CONCLUSIONS

The wide application of ASSLIBs with high-energy density and safety to replace traditional lithium-ion batteries is hindered by problems such as dendrite growth and mechanical instability. To comprehend and solve these issues, various coupled chemo-mechanical models have been developed in recent decades. This mini-review aimed to supply a more nuanced understanding of the interfacial chemo-mechanical issue in ASSLIBs from a modeling perspective.

This mini-review summarized different mechanisms for dendrite growth in solid electrolytes, which we consider would be the biggest concern should all-solid-state lithium-metal batteries be implemented. The surface reaction, ion transport, interfacial stress state, and interfacial contact characteristics have been considered to account for the lithium deposition at the Li/SPE interface. For SCE, apart from the factors considered in SPE, defects such as grain boundaries, cracks, and voids are also considered to contribute to dendrite initiation and propagation. On the cathode side, the models for fracture in composite electrodes are reviewed. Particle size, spatial distribution, volume fraction of active particles, and the characteristics of voids are primarily responsible for interfacial stability within composite electrodes and the performance of ASSLIBs.

Although we reviewed these phenomena separately, it should be noted that they are not independent failure mechanisms. Rather, they may occur simultaneously during charging and discharging cycles. However, due to the limited computational capability, it is very much unlikely that all factors are considered in one model and one simulation throughout. Thus, a comprehensive multiscale model is urgently needed that accounts for these failure mechanisms at the same time. Moreover, some issues such as lithium dendrite formation are still not fully understood. A convincing model that agrees with most—if not all—experimental observations is yet to be developed. In view of this, we believe that much work remains to be done in modeling chemo-mechanical behavior at the interfaces of ASSLIBs.

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Notes

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