



Modeling the chemo-mechanical behavior of all-solid-state batteries: a review.

Donald Bistri · Arman Afshar · Claudio V. Di Leo 

Received: 1 February 2020 / Accepted: 5 July 2020
© Springer Nature B.V. 2020

Abstract Solid-state-batteries (SSBs) present a promising technology for next-generation batteries due to their superior properties including increased energy density, wider electrochemical window and safer electrolyte design. Commercialization of SSBs, however, will depend on the resolution of a number of critical chemical and mechanical stability issues. The resolution of these issues will in turn depend heavily on our ability to accurately model these systems such that appropriate material selection, microstructure design, and operational parameters may be determined. In this article we review the current state-of-the-art modeling tools with a focus on *chemo-mechanics*. Some of the key chemo-mechanical problems in SSBs involve dendrite growth through the solid-state electrolyte (SSE), interphase formation at the anode/SSE interface, and damage/decohesion of the various phases in the solid-state composite cathode. These mechanical processes in turn lead to capacity fade, impedance increase, and short-circuit of the battery, ultimately compromising safety and reliability. The article is divided into the three natural components of an all-solid-state architecture. First, modeling efforts

pertaining to Li-metal anodes and dendrite initiation and growth mechanisms are reviewed, making the transition from traditional liquid electrolyte anodes to next generation all-solid-state anodes. Second, chemo-mechanics modeling of the SSE is reviewed with a particular focus on the formation of a thermodynamically unstable interphase layer at the anode/SSE interface. Finally, we conclude with a review of chemo-mechanics modeling efforts for solid-state composite cathodes. For each of these critical areas in a SSB we conclude by highlighting the key open areas for future research as it pertains to modeling the chemo-mechanical behavior of these systems.

Keywords Solid-state battery · Chemo-mechanics modeling · Dendrite growth · Interphase instability · Composite cathodes

1 Introduction

Solid-state-batteries (SSBs) present a promising technology for next-generation batteries. In recent years, commercialization of SSBs has attracted significant research attention driven by their promise of superior performance compared to conventional Lithium-ion batteries (LIBs). Transition to SSBs has significant advantages including enhanced current density, faster charging time, wider electrochemical window, and

In honor of Professor J. N. Reddy for his 75th Birthday.

D. Bistri · A. Afshar · C. V. Di Leo (✉)
School of Aerospace Engineering, Georgia Institute of
Technology, 270 Ferst Drive, Atlanta,
GA 30332, USA
e-mail: cvdileo@gatech.edu

improved safety. Contrary to conventional LIBs which make use of graphite intercalation anodes, incorporation of Li metal anode enables for a 10-time increase in volumetric capacity, leading to a significant improvement in energy density (3860 mAh g^{-1}) [1–3]. Owing to their wider electrochemical window (0–5V), SSBs also enable for coupling of Li metal anode with high-voltage cathode materials as demonstrated by several recent studies [4–6]. From a safety perspective, replacement of toxic and flammable organic electrolytes with highly conductive ($\geq 10^{-3} \text{ S cm}^{-1}$), mechanically superior inorganic solid-state electrolytes (SSEs) can alleviate concerns associated with failure of batteries due to short-circuit or ignition [7–9]. A particularly attractive SSB architecture with high energy density features a lithium metal anode, a composite solid-state cathode and an inorganic SSE separating the electrodes. Figure 1 highlights these three particular areas of interest in an all-solid-state architecture as well as the mechanical modeling issues which must be addressed in order to understand and commercialize these systems.

Traditionally, SSEs are categorized into two groups, pertaining to organic solid polymers and inorganic solids (oxide or sulfide based). Among other

properties, successful integration of SSEs in SSBs requires meeting particular chemical standards, including negligible electronic conductivity, high ionic conductivity, good electrochemical compatibility as well as several mechanical standards including appropriate stiffness and fracture toughness to preserve mechanical integrity. While liquid electrolytes traditionally have a higher ionic conductivity and allow for excellent wetting of electrode surface, comparable ionic conductivity values have been achieved for several ceramic SSEs as reported in multiple studies [10–15]. Resolution of sluggish ionic conductivity, while a major improvement in research efforts to integrate SSEs in next-generation battery designs, addresses one of the multiple challenges hindering commercialization of SSBs.

Research efforts have recently shifted towards developing a comprehensive, multi-physics understanding of the complex nature of the solid-solid interfaces, as critical challenges associated with electrochemical and mechanical stability of SSEs exist there [16]. Among these issues, dendrite growth constitutes one of the most intricate challenges in SSBs, resorting to the interplay of both mechanical and chemical forces. Lithium dendrite infiltration through SSEs eventually leading to short-circuit of battery has been vastly reported for a multitude of representative SSEs [17–21]. Contrary to dendrite growth processes in liquid electrolyte systems, growth in SSBs depends on a fundamentally different mechanism hypothesized to be centered on morphology of SSE surface. Internal defects (pores, surface cracks and grain boundaries), inherent to the microstructural composition of inorganic SSEs serve as sites for non-uniform redistribution and infiltration of Li metal leading to potential dendrite growth. From a mechanics perspective, the process of Li dendrite growth depends on microstructural mechanical features including density of surface imperfections, defect-size distribution, local stress-state and viscoplastic deformation of the Li metal. This complex problem thus requires a comprehensive chemo-mechanical theoretical/computational framework [22].

Unwanted electrochemical reactions between the Li-metal anode and SSEs during cyclic charge/discharge of the battery can produce compounds which lead to the formation of a nonhomogeneous interphase layer of low ionic conductivity. This in turn can significantly limit ion transfer kinetics and

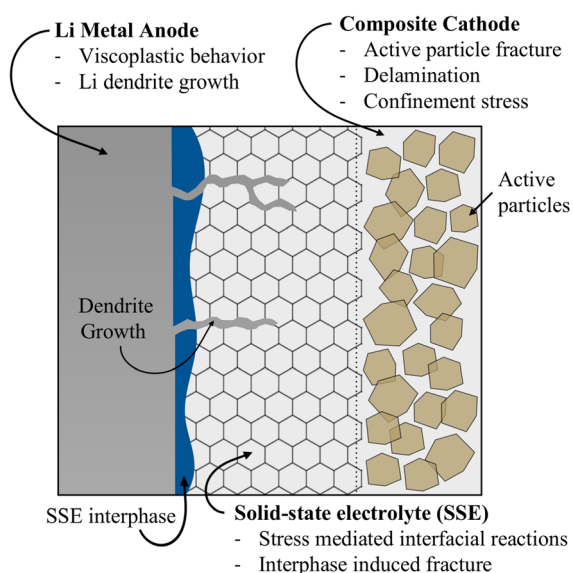


Fig. 1 Architecture of an all-solid-state battery composed of Li-Metal anode, solid-state electrolyte separator and composite cathode. Highlighted under each of these three main components are some of the key mechanics phenomena affecting the electrochemical performance of these systems

increase interfacial resistance as reported in several representative SSEs [5, 23–26]. Simultaneously, formation of nonhomogeneous interphase regions is accompanied by volumetric expansion, which in the context of densely packed all-solid-state architectures can induce high stresses resulting in fracture and degradation of the SSE [27].

Composite cathodes, as illustrated in Fig. 1, also present another area where mechanics plays a critical role. Composite cathodes in SSBs rely on a densely packed architecture of active material, surrounded by a conductive SSE to support ionic transport, in addition to complementary additives for electronic conduction. The active material undergoes volumetric expansion/contraction during insertion/extraction of ionic species, which, due to the confined nature of the all-solid-state architecture, can lead to generation of high stresses. Batteries employing liquid electrolytes isolate volumetric strains at the active particle level, given the incapacitation of liquid electrolytes to transfer stresses. As a result, in current battery designs, any morphological changes of the active particles do not tend to translate to interfacial delamination at the electrode-electrolyte interface, which continues to support ion transfer. The confined nature of the solid-state electrode allows for transmission of stresses through the stiff solid framework resulting in a complex coupled chemo-mechanical behavior which is prone to damage through failure of the active particles, the SSE itself, or delamination of the interface between the two [28, 29].

To overcome the aforementioned mechanical challenges we require an understanding of the interplay of chemo-mechanical phenomena at cell constituents. The objective of this review article is to provide a comprehensive overview of the present theoretical and computational frameworks relevant to the study of electro-chemo-mechanical phenomena in SSBs. However, certain aspects of chemo-mechanical modeling in SSBs (ex. interphase formation, dendrite growth) require a formal treatment, which extends beyond the realm of continuum mechanics. Therefore, where necessary, our review invokes additional modeling frameworks including both molecular dynamics (MD) and first-principles calculations. While not continuum in nature, the aforementioned computational frameworks give valuable insights for study of instabilities in SSBs in addition to helping establish a much

necessary framework for material characterization, be it for active electrode particles or SSEs.

Further, design of SSBs is inherently a multiscale and multiphysics problem by nature. A complete framework for modeling SSBs requires integration of models beyond continuum-level. From an optimization perspective, both continuum and first-principles models are integral components in development of hierarchical, data science frameworks. Here, first-principle calculations provide the necessary material properties, while continuum level frameworks solve the coupled chemo-mechanics problem. Optimal design of SSBs involves optimization of both material and geometry simultaneously, which in turn calls for an integrated use of both frameworks.

Significant efforts have been invested towards reviewing the chemo-mechanical behavior of SSBs in a series of past works from both an experimental and computational standpoint. Early review works [30, 31] focused exclusively on prospects of SSBs and assessment of potential SSE candidates with high ionic conductivity. However, no extensive connection to interface instabilities present in SSBs was made from a modeling perspective. Lewis et al. [32] studied interfaces in SSBs from an experimental standpoint. A special focus of their review centered on the potential of employing advanced characterization techniques (eg. tomographic imaging, spectroscopy) aside from conventional in-situ characterization methods to study interfaces in SSBs. A review of existing characterization techniques for study of SSBs as it applies to interphase formation and anode/cathode-SSE interface was also presented in the work of Xu et al. [33]. In-situ operando techniques were reviewed and potential use of non-destructive characterization techniques for future studies of interfaces were proposed. A design perspective on better engineering of interfaces in SSBs was introduced in the work of Shen et al. [34]. However, the scope of the review was only concerned with instabilities at the anode/SSE interface and issues associated with damage in composite cathodes were omitted. A departure from a purely experimental treatment of issues in SSBs towards a combined effort on reviewing of both experimental and theoretical/computational efforts is presented in the work of Wang et al. [35]. Here, major computational efforts in study of electrode-SSE interface are summarized. However, no insight is provided on limitations of current frameworks and potential

areas for improvement in future modeling efforts for study of SSBs. The review covers current modeling efforts on dendrite growth and damage of active particles and SSEs, but no connection from a modeling perspective is made to the phenomena of interphase formation and associated chemo-mechanical issues. A review on joint efforts, both experimental and theoretical in studying of SSBs is also presented in the work of Zhang et al. [36]. This review focuses primarily on mechanical damage in SSBs as it pertains to active particles, SSEs and dendrite growth. Modeling efforts reviewed in this work are limited to a select few and no identification of major limitations of current employed models is made from a theoretical perspective. Zhao et al. [37] focused their review on the transfer of already established chemo-mechanical frameworks in LIBs to model the behavior of SSBs.

The scope of our review paper intends to provide a comprehensive analysis of current computational framework for modeling the chemo-mechanical behavior of SSBs as it pertains to all its components including Li-metal anodes, SSEs and composite cathodes. In summarizing current modeling efforts, the focus of this work is to not merely showcase current efforts at the forefront of modeling of issues in SSBs. Here special attention is paid to identifying key assumptions/limitations upon which current modeling framework builds. In doing so, future research avenues for computational efforts in multi-physics modeling of SSBs are identified. Additionally, the authors propose available modeling tools from study of phenomena which share similarities with aforementioned issues in SSBs and can serve as starting points in the development of future modeling frameworks for addressing instabilities in SSBs. This paper is organized following the natural design of a SSB as shown in Fig. 1. We review the relevant chemo-mechanical phenomena and modeling for Li-Metal anodes and dendrite growth in Sect. 2, for solid-state electrolytes and electrode/SSE interfaces in Sect. 3, and for active materials and composite cathodes in Sect. 4.

2 Lithium metal anode

Use of inorganic SSEs with improved chemo-mechanical properties has the potential to alleviate failure of the cell due to short-circuit driven by dendrite growth or ignition as may be encountered in liquid

electrolytes. However, as discussed briefly in the introduction and elaborated in past studies, successful design and operation of SSBs is hampered by several challenges [30–32, 34, 35, 38, 39]. One major obstacle is tied to unstable deposition of Li at the Li anode/SSE interface, which can lead to the onset of dendrite formation and growth. Dendrite protrusions can initiate at perturbations of the interface or microstructural heterogeneities and subsequently grow through the SSE under continuous cycling, leading to short-circuit of the battery. It is critical thus to understand the mechanisms of Li plating/stripping, uneven deposition under non-uniform interface kinetics, and propagation of Li dendrites through the SSE. This section provides a review of the modeling efforts which have been developed to capture the mechanisms for dendrite initiation and growth. We begin by reviewing the research done in this area as it pertains to Li dendrite growth in liquid electrolyte systems as it is critical to understanding current research in SSBs.

2.1 Modeling of dendrite growth in liquid-electrolyte systems

One of the first models of dendrite growth was proposed by Barton and Bockris [40], who investigated electrolytic growth of spherical silver depositions in silver-nitrate electrolytes. Their formulation constitutes one of the early works in a series of efforts which model dendrite growth under pure diffusion control, disregarding the effect of migration in transport of ionic species. A first latent stage prior to dendrite growth is envisioned, during which protrusions emerging from the electrode surface were chemically controlled by the characteristic diffusion layer of the substrate. Having penetrated the diffusion layer, dendrite growth followed, as marked by a transition from linear to spherical diffusion at the tip. Additionally, surface tension forces were incorporated to regulate kinetics at the tip. This first proposed theoretical framework made use of linear kinetics (hence applicable to small overpotentials) and did not account for variations in concentration and potential near the vicinity of the dendrite tip during growth. Diggle et al. [41], improved this model by accounting for non-linear Tafel interface kinetics (higher overpotentials but below limiting current) to calculate the growth rate of zinc dendrites in alkaline zincate solutions as a function of overpotential, concentration

and temperature. Successive thinning of the dendrite tip enabled for spherical diffusion to dominate propagation, confirming the previous findings by Barton and Bockris [40].

In contrast to the aforementioned theories assuming diffusion-limited ionic transport, migration-limited mass transfer formulations of dendrite growth emerged with the work of Chazalviel [42] and later Brissot et al. [43]. These formulations investigated metallic electrodepositions in a high electric field (≈ 10 V), commensurate with cell currents above the limiting current density, a domain in which electroneutrality is invalid. The mechanism for dendrite initiation was stipulated to be a direct outcome of anion depletion in the vicinity of the electrode leading to a build up of space charge. This theoretical formulation also helped the development of dendrite growth modeling, however it is of limited use in the study of rechargeable batteries owing to their much lower current densities, as pointed out by Monroe and Newman [44].

An important technique in assessing the stability of electrodepositions, theoretical linear stability analysis emerged following the work of Mullins and Sekerka [45, 46]. Morphological stability of a spherical particle under linear diffusion control was investigated upon application of an initial harmonic perturbation. Resulting deformation was then modeled as a linear superposition of spherical harmonics and time dependence of expansion coefficients was assessed under the interplay of both concentration gradient and surface tension to judge stability. While initially specialized for spherical morphologies, the methodology was subsequently extended to non-spherical geometries. In doing so, assumption of an isotropic interface was employed, thus disregarding any crystallographic factors. Following Mullins and Sekerka, Aogaki and Makino [47] extended previous efforts and modeled the stability of electrode systems under diffusion-control non-steady depositions. Representing interfacial deformation as superposition of a series of two-dimensional waves, deposition growth and particle size were investigated as a function of variations in current density, bulk concentration and temperature. Theoretical predictions were subsequently compared against SEM crystal photographs [48]. Subsequent early contributions in study of stability of metal electrodepositions followed the work of Barkey et al.

[49], Pritzker and Fahidy [50] and Sundstrom and Bark [51].

Following the first observation of dendrite growth in lithium-polymer systems [52], a general framework describing dendrite growth in a parallel-electrode lithium-polymer cell during galvanostatic charging was proposed by Monroe and Newman [44]. A major improvement in their formulation centered on addition of well-defined thermodynamic points to capture the variations in concentration and potential ahead of the dendrite tip. Additionally, the assumption of a well-supported electrolyte was invalidated when solving for the transient concentration and potential profiles in the electrolyte. Henceforth, both diffusion and migration ion transfer mechanisms were incorporated in the formulation. Their findings concluded that dendrites accelerated across the cell at all conditions, with cell shortening occurring at current densities above 75% of the limiting current. A few limitations of this model are the assumption of a single emerging dendrite and unvarying transport properties. To address the aforementioned limitations, a simplified diffusion-reaction mathematical model for dendritic growth with concentration dependent diffusion coefficient following Stewart and Newman [53] was later proposed by Akolkar [54]. This formulation was further extended in a later work to incorporate the effect of temperature variations on Li-ion transport [55]. An Arrhenius-type temperature dependence of the diffusion coefficient was adopted. Given an operating current density, a critical temperature was evaluated below which dendrite formation proceeded in an unrestrained fashion. Noteworthy research efforts at this time also include the work of Ely and Garcia [56], who adopted a thermodynamic framework to devise a five-stage mechanism of dendrite initiation and early growth for reaction-rate limited systems undergoing heterogeneous depositions. A critical thermodynamic and kinetic radius was identified for growth of electrodepositions, below which emerging protrusions merely diffused in the electrolyte. Aside from theoretical efforts centered on understanding the mechanisms for dendrite initiation and growth in liquid electrolyte systems, modeling efforts with an emphasis on morphological evolution of dendrites have also been developed. Phase field models were extensively adopted for such purpose to different levels of complexity [57–62].

A common feature of all aforementioned theoretical frameworks is that they relied on surface tension as being the only mechanism to counter amplification of surface roughness. As a result, mechanical contributions were not accounted for in modeling of electrodeposition kinetics at interface [63].

2.2 Modeling of dendrite growth in solid-state batteries

Modeling dendrite growth in SSBs requires a comprehensive understanding of the interplay of mechanics and electrodeposition kinetics. First modeling efforts in this area related to incorporating the role of mechanics on interfacial kinetics, without application to any particular problem. A seminal contribution in this area is the work of Monroe and Newman [63]. An extended electrodeposition framework which incorporated the effects of external pressure, elastic deformation and viscous stresses was proposed. Thermodynamic phases for proper description of the interface were accordingly introduced. Starting with balance of momentum and accounting for equilibrium conditions across the electrode-electrolyte interface, a relationship for the electrochemical potential difference ($\Delta\mu_{e-}$) induced by local deformations in terms of surface tension (γ), pressure (Δp), deviatoric ($\Delta\tau_d$) and viscous ($\Delta\tau_v$) stress differences across the interface was developed,

$$\Delta\mu_{e-}^{\alpha,\alpha'} = - \left(\frac{\bar{V}_M^{\alpha'} + \bar{V}_{M^{z+}}^{\beta'}}{2z^+} \right) \left\{ 2\gamma\mathcal{K} + \mathbf{e}_n^{\alpha} \cdot [\mathbf{e}_n^{\alpha} \cdot (\Delta\tau_d^{\alpha,\beta} + \Delta\tau_v^{\alpha,\beta})] \right\} + \left(\frac{\bar{V}_M^{\alpha'} - \bar{V}_{M^{z+}}^{\beta'}}{2z^+} \right) (\Delta p^{\alpha,\alpha'} + \Delta p^{\beta,\beta'}) \quad (1)$$

Here (α' , β') represent undeformed states of electrode and electrolyte while (α , β) represent the roughened electrode surface and its neighbouring electrolyte.

Additionally, \mathcal{K} is the mean curvature of the roughened surface, \bar{V}_M , $\bar{V}_{M^{z+}}$ are the molar volumes of reacting metal in electrode and cation in electrolyte, z^+ is the cation valence, while \mathbf{e}_n is the unit normal vector at the electrode-electrolyte interface.

In the limiting case where mechanical contributions are neglected, their work correctly predicted the earlier model proposed by Barton and Bockris [40],

in which surface kinetics are solely regulated by surface tension,

$$\Delta\mu_{e-}^{\alpha,\alpha'} = -2\gamma\bar{V}_M^{\alpha'}\mathcal{K} \quad (2)$$

Accounting for this, the impact of elastic deformation on deposition kinetics was assessed through a modified Butler-Volmer equation of the following form:

$$i_n = i_{0,ref} \cdot \exp \left[\frac{(1 - \alpha_a)\Delta\mu_{e-}}{RT} \right] \left[\exp \left(\frac{\alpha_a F \eta_s}{RT} \right) - \exp \left(- \frac{\alpha_c F \eta_s}{RT} \right) \right] \quad (3)$$

where F is the Faraday constant, T is temperature, R is the universal gas constant, $i_{0,ref}$ is the exchange current density pertaining to an undeformed configuration, α_a , α_c are anodic and cathodic charge transfer coefficients and η_s is the surface overpotential.

A more general framework for coupling mechanics to Butler-Volmer kinetics was developed by Ganser et al. [64]. In this work, the mechanical component of stress influencing the interfacial reaction need not be the hydrostatic stress but rather a measure of resolved stress in the direction of interfacial growth. Emergence of a theoretical framework to model the role of mechanics on electrodeposition kinetics created an avenue for further modeling efforts of dendrite growth in SSBs.

Monroe and Newman applied their framework [63] to study stability of Li-solid polymer electrolyte interfaces [65]. A linear elastic theory was employed to assess how variation in electrolyte properties modeled as a linear elastic material affected roughness at the interface. Small amplitude periodic displacements were applied at the interface, and analytical solutions for displacement distribution were afterwards computed by solving for a steady-state equation of motion with proper boundary conditions. Compressive stress, deviatoric stress, and surface tension at the interface were subsequently calculated and the contribution of each component to stability of the interface was assessed. While promoting interface stability at all conditions, surface tension was demonstrated to have a much smaller impact to electrode stability compared to deviatoric and hydrostatic stresses acting along the interface. A destabilizing effect, increasing with an increase in shear modulus of the electrolyte was found for deviatoric stresses. In

contrast, compressive stresses had a stabilizing effect with increase in shear modulus of the solid polymer electrolyte. Monroe and Newman's critical finding is that a region of stability for dendrite growth prevention existed, granted the shear modulus of solid polymer electrolyte is at least twice larger than that of Li-metal. Their findings, assessing the contribution of each factor to interfacial stability parameter are shown in Fig. 2a. Here, a state of $\Delta\mu < 0$, which $\Delta\mu$ - a stability parameter, represents stable electrodeposition and helps in turn mitigate surface roughening. In principle, these findings provided great promise for the

use of solid electrolytes as a mechanical barrier for preventing dendrite growth. However, several experimental observations have shown that inorganic SSEs still suffered from dendrite growth—despite satisfying the condition of having a shear modulus at least twice larger than that of Li-metal—leading to cell short-circuiting [17–21].

An alternative mechanism for initiation and propagation of dendrites through SSEs was proposed by Porz et al. [21], following their study of four SSEs subjected to different surface defect densities and internal microstructures. Contrary to the findings of

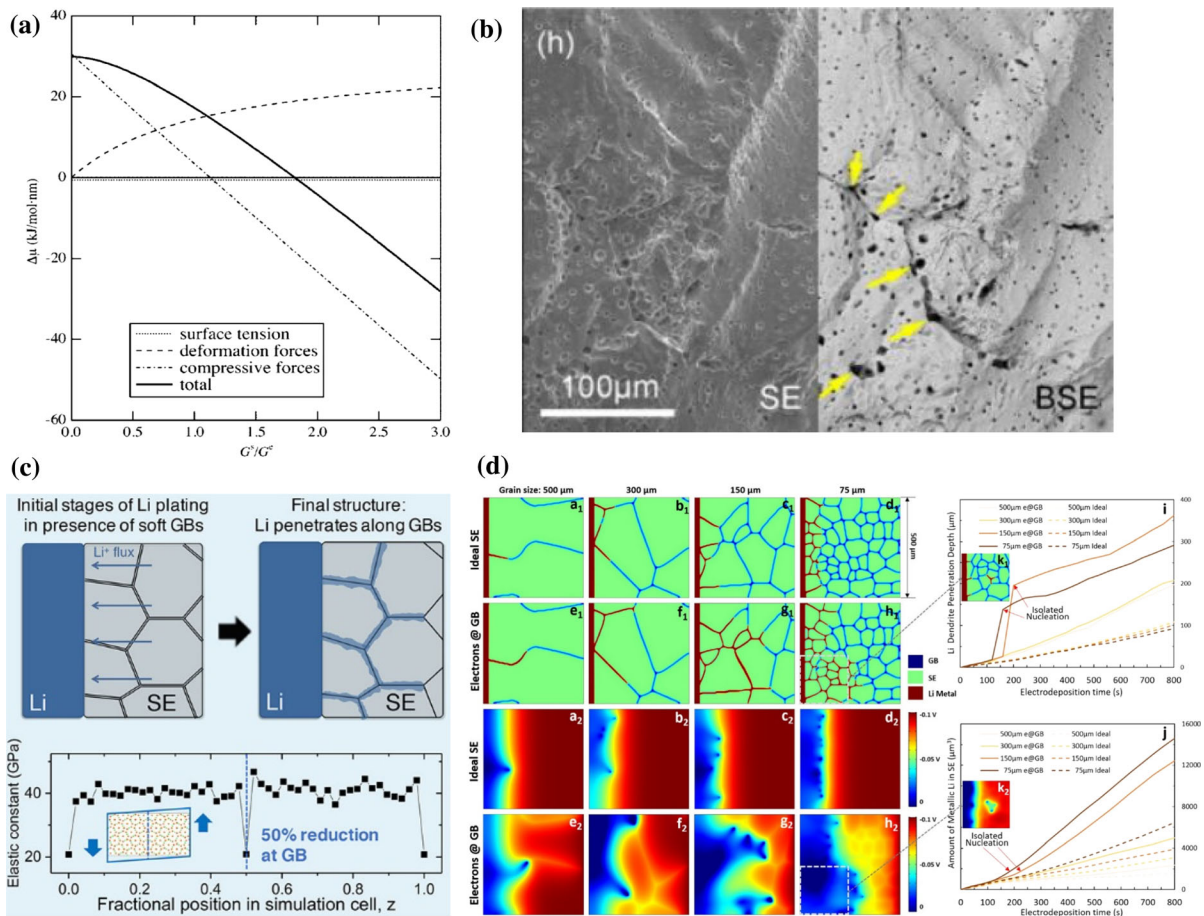


Fig. 2 Microstructural aspects of dendrite growth in SSBs. **a** Variation in contribution to interfacial stability of surface tension, deformation forces and compressive forces as a function of shear modulus of the solid polymer electrolyte. Reproduced with permission from [65]. **b** Interconnected pores in the vicinity of grain boundaries, providing pathways for dendrite growth in dense SSEs. Reproduced with permission from [17]. **c** Calculated elastic constant from MD simulations performed on a LLZO electrolyte as a function of position

normal to the grain boundary planes. A 50% reduction in elastic constant is obtained at the grain boundary relative to the bulk SSE. Reproduced with permission from [66]. **d** Phase-field simulation results on the effect of trapped excess electrons on Li-electrodeposition illustrating morphological differences between an ideal excess electron-free electrolyte configuration, and a real electrolyte configuration with trapped excess electrons at the grain boundaries. Reproduced with permission from [67]

Monroe and Newman, their observations suggested that Li infiltration through the SSE was independent of the shear modulus of the electrolyte and proceeded through a different mechanism than protrusions in liquid electrolytes. Surface morphology, particularly defect size and density were identified as the main factors for Li metal to plate in pre-existing imperfections which then drove crack propagation and dendrite growth through the SSE. A representative illustration of propagation of dendrites through surface imperfections in dense garnet-type SSEs is shown in Fig. 2b reproduced from the work of Ren et al. [17].

Following their experimental observations, Porz et al. [21] developed a simplified one-dimensional, chemo-mechanical formulation to model the stress build up at the crack tip as a function of Li-plating overpotential $\Delta\Phi$ through the relationship

$$\sigma_{0,max} = -\frac{F}{V_m^{Li}} \Delta\phi, \quad (4)$$

where F is the Faraday constant and V_m^{Li} is the molar volume of Lithium. Critical stresses at the tip for crack advancement through the SSE were evaluated as a function of defect size following a linear elastic fracture mechanics framework. This in turn enabled studying the variation in required overpotential for crack propagation with defect size. However, no formal treatment of the role of mechanics on electrodeposition kinetics is presented in this work.

More recently, Klinsmann et al. have modeled advancement of a lithiated crack adjacent to a Li metal negative electrode [68] with a more complete continuum-mechanics framework. Conditions under which pressure build up inside the crack due to Li plating can either promote unstable crack propagation or hinder it by blocking lithium insertion were explored. The critical pressure required for fracture propagation was subsequently translated to an equivalent surface overpotential regime in which safe operation of the battery is ensured, as described by the following relationship

$$|\eta| \leq \eta_c = \frac{K_C \Omega_M}{1.12F \sqrt{(\pi a)}}. \quad (5)$$

Here η_c defines the critical magnitude of the surface overpotential, K_C is the fracture toughness of the solid electrolyte, a is the initial crack size and Ω_M is the molar volume of metal.

The role of microstructural features in promoting uneven Li deposition and subsequent metal penetration through SSEs was also studied by Yu and Siegel [66]. They postulated that nanoscale softening of the SSE in the vicinity of grain boundaries provided a mechanism for preferential plating of Li, thus leading to dendrite growth. An important novelty of their work was accounting for heterogeneities at the SSE microstructure. Molecular dynamics simulations were performed on a representative LLZO electrolyte on two low-energy tilt and twist grain boundaries to measure the elastic properties in both the bulk of the electrolyte and near the grain boundaries. A 50% reduction in elastic modulus was observed locally at the grain boundaries as compared to the bulk. Representative data of the variation in elastic constants in the bulk and near the grain boundaries generated from MD simulations is shown in Fig. 2c. Tian et. [67] adopted a multiscale framework coupling density functional theory (DFT) with a phase-field model to investigate Li dendrite initiation and growth inside SSEs with microstructural and internal imperfections. DFT calculations were employed on four representative SSEs to evaluate the density of electronic surface states along with distribution of excess electrons in internal defects present in SSEs. As postulated in their earlier work, existence of electronic surface states served as a trapping mechanism for excess electrons, thus enabling the nucleation of Li metal depositions at surface defects [69]. Concentrations of surface excess electrons obtained from DFT results were then incorporated in a phase-field model to study morphology of dendrite evolution. Representative results from their work are shown in Fig. 2d. An increased intergranular dendrite growth rate and penetration depth was observed due to an increased electrochemical driving force from excess surface electrons. Additionally, the presence of trapped excess electrons in SSE defects leads to an increased probability of isolated nucleation. Their findings demonstrated a dominant effect of internal microstructural imperfections and their electronic conducting properties (band gap, distribution of excess electrons) on dendrite growth as opposed to shear modulus and fracture energy in the bulk of the SSE.

Parallel to these efforts, studies have been performed on the role of mechanics on electrodeposition kinetics. Earlier linear perturbation analysis in a Li-solid polymer electrolyte by Monroe and Newman

[65] was followed by a series of works, which employed a similar technique to study stability of electrodepositions at an interface. Barai et al. [70] considered an analogous morphological domain for dendrite initiation as Monroe and Newman, but revised the initial configuration of Li metal to be stress free, removing externally applied tractions at interface. This enabled for modeling of early dendrite growth behavior from a relaxed state. A small-strain finite element procedure was adopted to solve the mechanical equilibrium equation with a compressive distributed load on the electrolyte's side applied as a boundary condition. This allowed for more accurate modeling of the compressive stresses induced in both electrode and electrolyte by new phases of Li deposition. In contrast to the classical finding of Monroe and Newman, Barai et al. determined that an initial relaxed state of Li prevented dendrite growth at low current densities regardless of the shear modulus of the electrolyte. They proposed current distribution in the electrolyte as a dominant factor for dendrite growth. A comparison of the stability window with variation in shear modulus of solid electrolyte for both pre-stressed and relaxed initial Li states is shown in Fig. 3a. A more detailed framework of growth of electrode/SSE interface in the presence of an elastic prestress was formulated by Natsiavas et al. [73]. Interfacial growth was mathematically modeled under the interplay of numerous processes including the kinetics of ionic transport at both SSE and interface region, elastic stress due to built-in prestress and volumetric changes in SSE, and electro-mechanical interactions captured by Maxwell stress. A linear stability analysis was employed, specialized for planar growth in a Li-LiPON system and conditions for stable electrodeposition were studied as a function of stress state, elastic modulus, deposition kinetics and interfacial energy. The presence of prestress was determined to have a stabilizing effect on the electrode-electrolyte interface, enabling for a wider window of stable perturbation wavenumbers (k) as compared to a state of no prestress. This is schematically illustrated in Fig. 3d produced from [73]. Simulations employing a finite difference scheme also confirmed the advantageous effect of prestress on stability of electrodeposition growth, as demonstrated by significant reduction in amplitude of an initial perturbation upon application of a prestress, see Fig. 3e.

Ahmad and Viswanathan later postulated a general stability criteria for electrodeposition at isotropic solid-solid interfaces [71]. A major contribution of their work was extending the previous formulation by Monroe and Newman to account for the effect of density changes of Li metal on the stability of electrodeposition at the interface. Their work specialized the earlier theory of Monroe and Newman [63] (refer to Eq. (1) for variable definitions)

$$\Delta\mu_{e-} = -\frac{1}{2z}(V_M + V_{M^{z+}})(-\gamma\mathcal{K} + \mathbf{e}_n \cdot [(\tau_d^\alpha - \tau_d^\beta)\mathbf{e}_n]) + \frac{1}{2z}(V_M - V_{M^{z+}})(\Delta p^{\alpha,\alpha'} + \Delta p^{\beta,\beta'}) \quad (6)$$

and introduced an extra parameter, the volume ratio ($v = \frac{V_{M^{z+}}}{V_M}$) to formally account for the effect of density changes of Li in the electrode versus the SSE. The stabilizing or destabilizing nature of the hydrostatic term was investigated as a function of the aforementioned parameter. Following this, a density-driven stability mechanism was postulated, in which case Li in solid electrolyte is more densely packed than Li in metal electrode. This provided an extension to the earlier work of Monroe and Newman [65] specialized for solid-polymer electrolytes in which hydrostatic pressure has a dominant effect over density changes on stability of electrodepositions. The interplay of both mechanisms for interfacial stability was investigated and a two-parameter stability plot including shear modulus ratio and molar volume ratio was generated. Two stability regimes were identified including a pressure dominated regime at high molar volume ratio ($v > 1$), and a density-driven regime at low molar volume ratio ($v < 1$), see Fig. 3b. Resistance to dendrite growth of representative SSEs was assessed based on their position in the stability diagram. Contrary to most previous studies, given that conventional inorganic SSEs have a low molar volume, softer SSEs were determined to be better at stabilizing dendrite growth. However all linear stability analyses studied at this point in time resorted to simplification of an isotropic elastic interface. Ahmad and Viswanathan extended their previous study to account for material anisotropy and assess its contribution to stability of electrodeposition at solid-solid interfaces [72]. A continuum mechanics framework was developed to solve for two-dimensional problems in

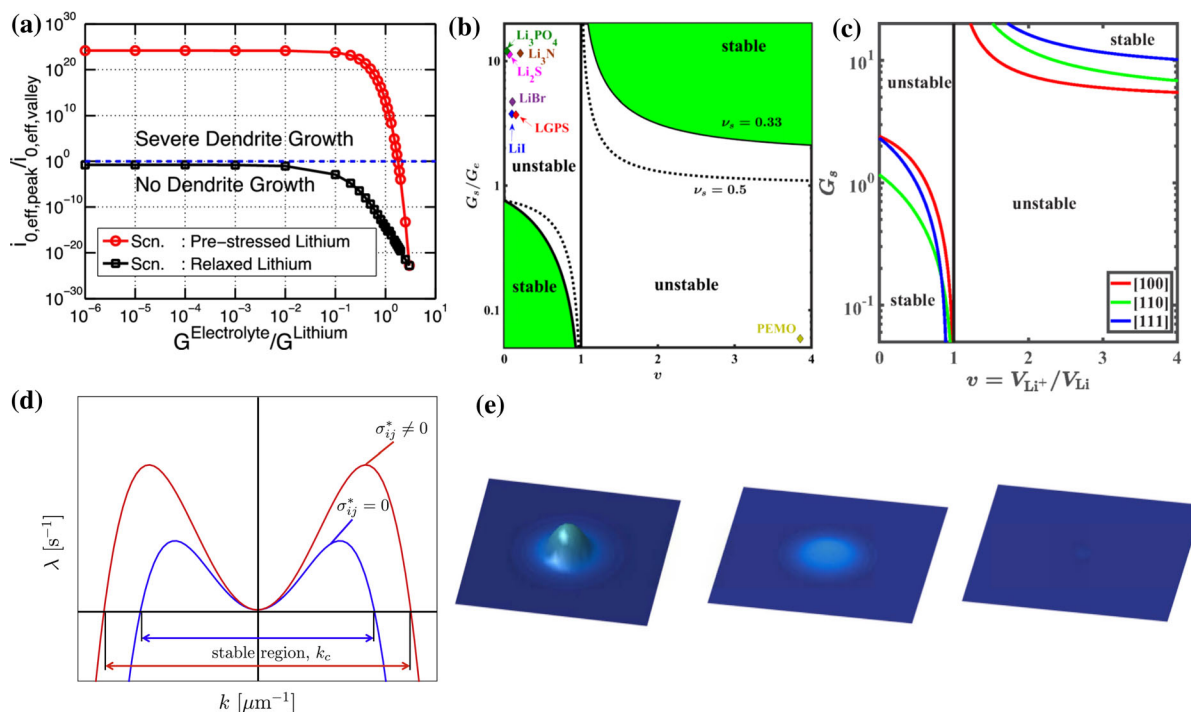


Fig. 3 Effect of mechanics on stability of electrodeposition kinetics. **a** Effective current density at the peak over the valley of dendritic protrusions plotted as a function of shear modulus of the solid electrolyte for both an initial relaxed Li-metal and a pre-stressed Li-metal. At low-current densities, an initially relaxed Li-metal is found to prevent dendrite growth irrespective of the effective shear ratio. Reproduced with permission from [70]. **b** Stability diagram for an isotropic Li anode/SSE interface with two regions of stable electrodepositions shaded in green. At low molar volumes (bottom-left) there is a density-

controlled stability regime, while at high molar volumes (top-right) there is pressure-controlled stability regime. Reproduced with permission from [71]. **c** Stability diagram for anisotropic Li anode-isotropic electrolyte system, demonstrating the variability in stability regions with crystallographic orientation of Li-metal. Reproduced with permission from [72]. **d** Effect of prestress on stability window of critical wavenumber of initial perturbation compared against a system with no prestress. **e** Stabilization of an initial perturbation upon application of a prestress. Reproduced with permission from [73]

anisotropic linear elasticity in terms of a crystallographic orientation-dependent elastic tensor. Similar to the case of an isotropic interface, two stability domains were identified for an anisotropic electrode-isotropic electrolyte interface combination. However, in the latter, critical shear modulus curves contouring regions of stability varied depending on the crystallographic orientation of Li-metal, see Fig. 3c.

Recently, McMeeking et al. [74] performed a linear perturbation analysis to investigate surface roughening of metal electrodes during plating. Their study employed an interfacial morphology consisting of a sinusoidal (amplitude of the peaks negligible to wavelength) stress-free electrode profile and a flat, undeformed electrolyte configuration. Bonding of the electrode to the electrolyte and successive plating

leads to the emergence of locally non-uniform stresses, however an average vanishing stress at the interface is maintained in the absence of external tractions. An Airy stress function was employed to derive the stress distribution at the interface, and results were incorporated in the theory of Ganser et al. [64] specialized for a single ion conducting solid electrolyte to capture the effect of mechanics on electrodeposition kinetics. Their findings also contradict the original model by Monroe and Newman, demonstrating that long wavelength protrusions (L) always amplify regardless of the stiffness of the SSE, as predicted by the following stability criterion

$$8\pi G_C \Omega_M \left[1 - \frac{(1 - 2\delta^{\text{electrode}})I}{\sqrt{(2i_o)^2 + I^2}} \right] [G_M(1 - v_C) + G_C(1 - v_M)] \\ \geq F\rho IL[G_C(5 - 6v_M - 6v_C + 8v_M v_C) + G_M(3 - 4v_C)] \quad (7)$$

where G_C , v_C , G_M , v_M denote the shear modulus and Poisson's ratio of electrolyte and electrode, Ω_M is the metal molar volume, I is the current density, i_o is a reference exchange current density, ρ is resistivity of electrolyte and $\delta^{\text{electrode}}$ is an influence coefficient which captures the effect of electrode energy state on redox reaction energy barrier. Similar conclusions for amplification of surface roughness irrespective of the stiffness of the SSE were derived provided the current density (I) is sufficiently large.

A common critical feature of all of the aforementioned modeling efforts is that they rely on an elastic interface. The Li metal anode behaves plastically (and viscoplastically) and has a low homologous temperature. Its plastic response has been the recent focus of a number of experimental investigations [76–81]. Development of a theoretical framework to incorporate the effect of plastic deformation on electrodeposition kinetics and dendrite growth spurred a new avenue in computational research efforts. Early contributions towards this goal emerged with the work of Ferrese and Newman [82]. Mechanical deformation of a Li-metal anode adjacent to a stiff solid-polymer electrolyte was studied under a framework of elastic-plastic deformation. An isotropic-hardening J_2 plasticity model was adopted utilizing the experimental stress-strain data of Li metal by Schultz [81]. However, viscoplastic effects were neglected. Similarly, Barai et al. [83] developed a computational framework coupling mechanics, charge balance and mass conservation equations to model stress evolution in both Li metal and polymer solid electrolytes. A nonlinear hardening law was adopted to account for plastic deformation. Plastic flow of Li metal was found to promote stable deposition at interface, as evidenced by a reduction in depth of penetration of dendrite protrusions as shown in Fig. 4a. This in turn enabled slower electrodeposition kinetics at the tip relative to the base of dendritic outgrowths. The effect of variation in yield strength of solid polymer electrolytes on dendrite growth was assessed. Barai et al. showed that increasing the yield strength in solid

polymer electrolytes promoted stability of dendrite protrusions even at shear modulus two orders of magnitude lower than that of Li metal. The effect of increasing the yield strength on the stability of electrodeposition is shown in Fig. 4b. Recently, Narayan and Anand [22] investigated dendrite growth through the use of a large deformation isotropic elastic-viscoplastic framework calibrated to the microindentation experiments of Wang and Cheng [76]. Figure 4c shows load versus indentation predicted by the calibrated model (solid lines) versus the experimental measurements (dashed lines) at various indentation rates. Their formulation builds upon a simple-power law to describe the effective plastic shear strain-rate $\dot{\epsilon}^p$ of the form

$$\dot{\epsilon}^p = \dot{\epsilon}_0 \left(\frac{\bar{\sigma}}{S} \right)^{\frac{1}{m}} \quad (8)$$

with flow resistance (S) evolving according to the following relationship

$$\dot{S} = \left(H_0 \left(1 - \frac{S}{S_s} \right)^a \right) \dot{\epsilon}^p. \quad (9)$$

Here $\dot{\epsilon}_0$ denotes a reference strain rate, m is a strain rate sensitivity parameter, $\bar{\sigma}$ is an equivalent tensile stress, while $\{H_0, S_s, a\}$ are strain hardening parameters with S_s defining a saturation flow strength. One major assumption employed here resorted to neglecting dependence of saturation flow strength on loading rate.

Two representative case studies of interest for modeling of SSBs were investigated including flattening of an asperity in Li metal due to compressive loading from the bounding SSE, and infiltration of Li metal into an imperfection on the surface of the SSE. Equivalent plastic strain and stress contours for the case of a pre-existing imperfection at the Li anode-SSE interface undergoing compression from the confining SSE are shown in Fig. 4d. Anand and Narayan recently revisited their formulation [84] following the experiments of LePage et al. [78] who provided stress strain data on polycrystalline Li foils. Here, earlier assumption of a constant saturation flow strength [refer to Eq. (9)] was modified to account for the experimentally observed strain hardening behavior of Li metal at high loading rates,

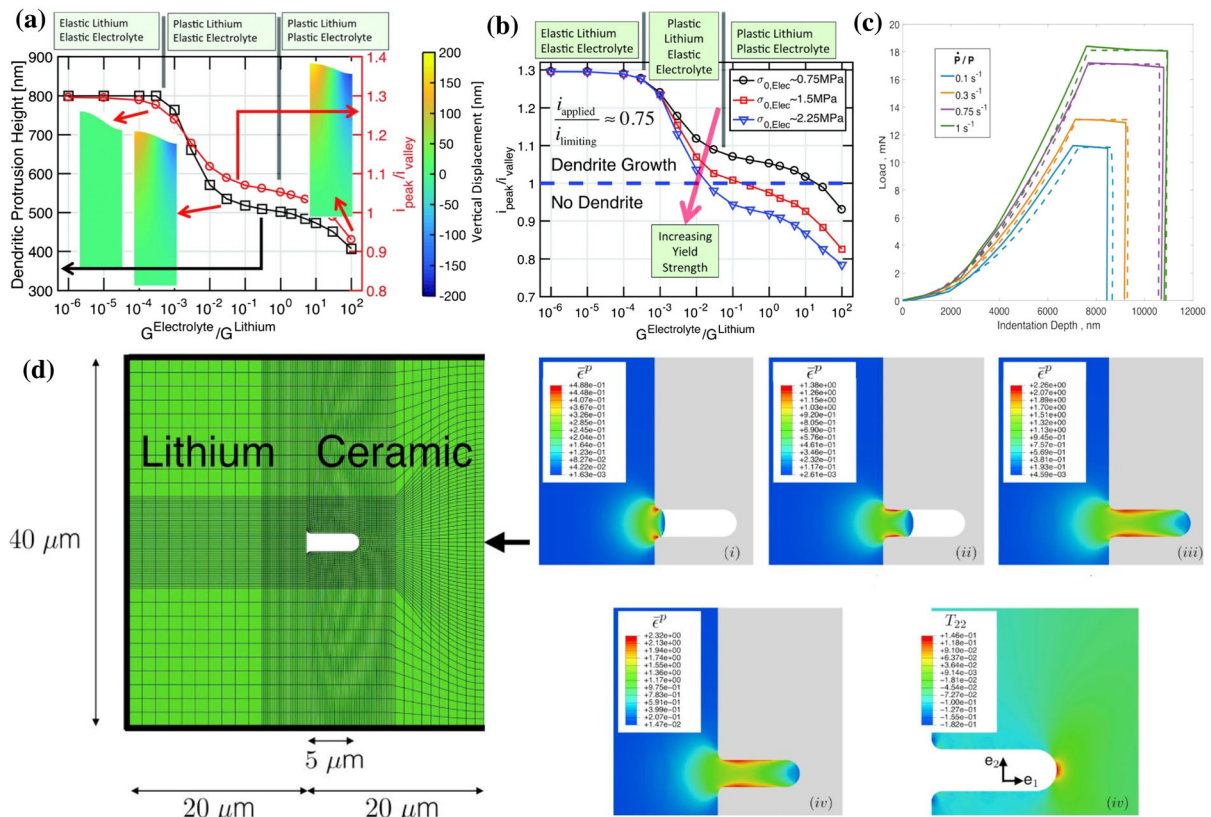


Fig. 4 Plastic modeling of Li metal and its role in dendrite growth. **a** Variation in amplitude of dendritic protrusions with shear modulus of solid electrolyte. For high shear modulus electrolytes, plastic deformation has a stabilizing effect, assisting in diminishing the height of dendritic protrusions. **b** Effect of increasing the yield strength of solid electrolyte on stability of electrodeposition, captured through the variation in ratio of current density at the peak over the valley of dendritic protrusions as a function shear modulus of electrolyte.

$$S_s = S^* \left[\frac{\epsilon \dot{\epsilon}}{A \exp(-\frac{Q}{RT})} \right]^n \quad (10)$$

where S_s denotes a saturation flow strength at a particular strain rate, S^* and n are strain hardening parameters, Q is an activation energy, A is a pre-exponential factor, R is the gas constant and T is temperature. To validate their theory, simulations of inhomogeneous tension and compression experiments were conducted and compared against experimental results by Masias et al. [79], demonstrating consistent results.

Reproduced with permission from [75]. **c** Comparison between numerically simulated load vs. indentation depth and experimental results by Wang and Cheng at different loading rates. **d** Simulation domain for modeling lithium infiltration in a pre-existing crack at the anode/SSE interface. Contour plots of equivalent plastic strain and induced stress due to compression of the SSE onto the Li anode. Reproduced with permission from [22]

2.3 Summary on modeling Li metal anodes and dendrite growth

As reviewed above, understanding Li metal anodes and the process of dendrite formation and growth is critical in enabling the design of an all-solid-state architecture which suppresses dendrite growth. We list here a few key areas of research the authors feel are of pressing relevance:

- At present, modeling efforts on dendrite growth have resorted to a linear elastic, isotropic interface, with modeling efforts which capture viscoplastic deformation of Li metal and effect of plastic flow on electrodeposition kinetics still at their infancy.

An experimentally validated constitutive theory for Li metal is required for modeling the manner in which stresses develop near the dendrite growth region and subsequently how these couple to the kinetics of growth.

- While several theoretical studies on the interplay of chemistry and mechanics on electrodeposition kinetics of Li metal have been proposed, from a modeling perspective, a fully coupled chemo-mechanical theory for modeling of dendrite initiation and growth within the solid-state electrolyte is still missing.
- Development of a microstructure-resolved description of the process of dendrite growth through the SSE microstructure is also lacking and necessary. In particular, this model should include considerations for the presence of SSE defects, cracks, and grain boundaries which can serve as nucleation and growth sites for Li dendrites.

3 Solid state electrolytes

As overviewed in Sect. 1 and also discussed within the context of Li-metal anodes in Sect 2, solid-state electrolytes (SSEs) are a critical component in enabling all-solid-state battery architectures. Presented here is a review of the literature addressing mechanics (and chemo-mechanics) phenomena in SSEs with a particular focus on phenomena associated with the formation and development of the interphase between the Li-metal anode and the electrolyte. As will become evident in this section, research as it pertains to mechanics of SSEs is in its infancy.

The interphase which forms at the anode/SSE interface is thermodynamically unstable, causing the SSE itself to go under oxidation and reduction during charge and discharge [5, 6, 26, 85, 86]. Figure 5a, shows the formation of this interphase due to chemical reactions. To summarize the current research in SSE behavior we divide this section into: (1) research addressing interphase formation and associated mechanical effects, (2) mechanical properties and failure of the SSE itself, and (3) delamination and damage of the interface.

3.1 Interphase induced stress and fracture

As presented in the work of Lewis et al. [32], the unwanted interphase has to be ionically conductive but electronically insulating for the battery to operate without failure, as an electronically conductive interphase allows for uncontrolled reaction of the pristine SSE and hence unstable growth of this undesirable mixed phase. In practical applications, electronically insulating interphases form, however the low ionic conductivity of the new mixture leads to high resistance of the cell, proving to be a challenging aspect of SSBs realization [24–26]. In addition to the undesirable low ionic conductivity of the interphase, there are critical mechanical issues accompanying its formation, particularly the volume expansion associated with the reaction that causes the new phase. Occurring in the confined all-solid-state architecture, this volume expansion introduces internal stresses, leading to possible fracture and degradation. Tippens et al. [87] showed the formation of cracks in $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ge}_{1.6}(\text{PO}_4)_3$ (LAGP) solid electrolyte using X-ray tomography, interestingly arguing that it is the presence of these cracks and the subsequent loss of contact that cause high impedance in the battery operation, and not the transport properties of the interphase itself. From a modeling perspective, the same team also studied the stress distribution in the aforementioned solid state cell using the chemo-mechanics continuum theory of Di Leo et al. [88]. The finite element model and contours of reaction coordinate are shown in Fig. 5b which by design agree well with the experimental observation shown in Fig. 5a. From Tippens et al. [87], Fig. 5d illustrates the evolution of a three-dimensional fracture network as the interphase forms during cell operation, along with a proportional increase in impedance depicted in Fig. 5e. It should be noted, however, that the model used to simulate the interphase formation and evolution relied on an ad-hoc description of the interphase where its position was determined a-priori rather than evolved according to the chemo-mechanical physics of the system. At present, capturing the phenomena of interphase formation and evolution remains one of the challenges for SSE realization from a modeling perspective. Other continuum formulations in chemo-mechanics of solid interphases, such as the one by Rejovitzky et al. [89], are more suited for modeling of growth of solid interphase in

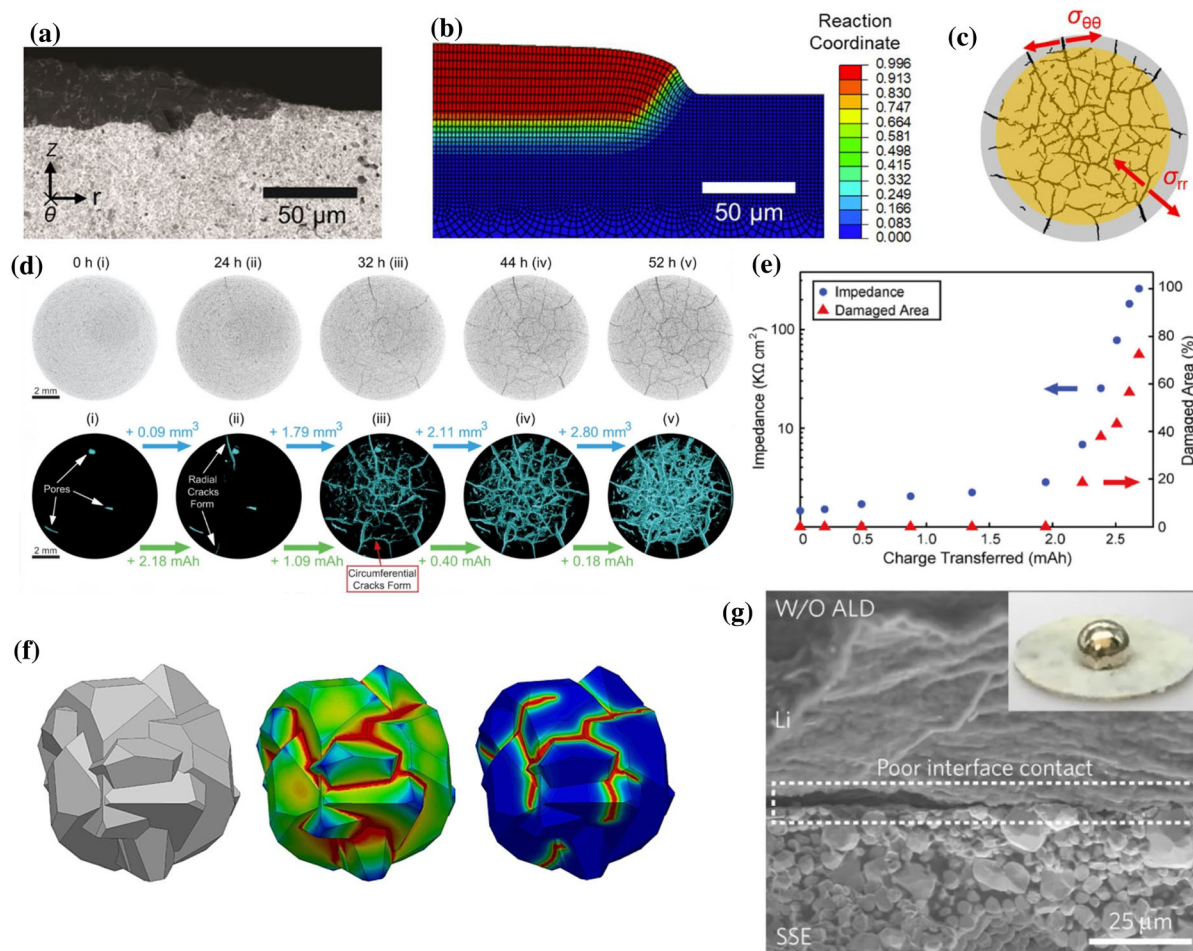


Fig. 5 Mechanical effects of reaction induced interphase growth. **a** Interphase formation at the interface of Li anode and LAGP SSE. **b** Finite element model of the swollen interphase showing contours of reaction coordinate. **c** Stress distribution in the cell, leading to both radial and circumferential cracks. **d** Network of extensive crack propagation in the SSE. **e** Direct correlation between extent of crack propagation and

increase in the impedance. **a–e** are reproduced with permission from [87]. **f** Phase field model of fracture growth in an active electrode LiMn₂O₄ particle, starting from left to right: model geometry, stress distribution and crack pattern, respectively. Reproduced with permission from [98]. **g** Delamination of a SSE interface resulting in poor contact. Reproduced with permission from [99]

conventional LIBs, as opposed to structural and phase changes associated with interphase formation at the anode-electrolyte interface in SSBs; treatment of growth models in LIBs are fundamentally different from a reaction model relevant to SSBs. There are, however, models in the mechanics community from which useful formulations for interphase growth can be drawn as they describe physical phenomena that share similarities with interface reactions in SSBs. Particularly, the research conducted on modeling oxidation in thermal barrier coatings [90–94], and on modeling hydrogen assisted cracking in metals

[95–97] might provide a potential starting point for building more specific models of interface reactions in SSBs. These models are particularly useful given the framework for oxidation/corrosion phenomena build upon similar governing equations, in that species balance law obeys a diffusion reaction equation of the form

$$\dot{c} = m \nabla^2 \mu - R \quad (11)$$

where $\{c, m, \mu\}$ denote concentration, mobility and chemical potential. Here, R defines the species consumption rate, specific to the type of chemical

reaction, be it oxidation, SSE interphase formation, etc.

A major difference in these existing formulations to modeling phenomena in SSBs is in the distinct chemical driving forces controlling each reaction. Hence, enhancing current frameworks with models specific to reaction kinetics of interphase formation in SSEs presents an appealing avenue for future efforts.

To capture the bulk mechanical behavior of SSEs, Ganser et al. [100] proposed a thermodynamically consistent theory of transport in a host material using a Helmholtz energy formulation which accounts for species transport, elastic deformation and electrostatics. They extended the concentrated solution theory of Newman and Thomas-Alyea [101] to incorporate the effects of mechanics, and then specialized their formulation to the case of binary electrolytes. Effect of deformation and mechanical stresses on reaction kinetics and ionic transport were assessed upon solving the coupled problem. Part of their study also focused on capturing the role of interfacial morphological change on concentration profile and its potential association with dendrite formation. A similar thermodynamically consistent treatment is also presented in the work of Bucci et al. [102] who modeled ionic transport in crystal lattices. Noteworthy to mention here is also the analytical work of Grazioli et al. [103] on solid polymer electrolytes that addressed the effects of mechanics.

The aforementioned models provide a foundation for modeling ionic transport in solids, however, these works, including those by the authors, neglect the fundamental physics of interphase formation and growth, that is the reaction induced structural phase transformations and the associated coupling to mechanical deformation and stress. It is the reaction induced mechanical effects of the newly formed interphase, and its associated chemical and structural phase changes, which cause mechanical degradation in the SSE [87]. A diffusion deformation reaction theory capable of accommodating chemically induced phase transformation is currently lacking in the mechanics literature and is a potential avenue for potential future research.

In addition to interphase formation induced stresses in SSEs and their effect on driving forces for diffusion and reaction, a critical mechanism for SSE failure is the formation and propagation of cracks. At present, the authors could not identify an existing model in the

literature for fracture in SSEs. However, there are a number of studies dedicated to modeling of crack propagation in electrode particles, which can be adopted as a starting point for addressing chemo-mechanics of SSEs in the presence of cracks. The literature on modeling fracture of ceramics might also serve as a relevant foundation for the development of modeling techniques specific to SSEs [104–112]. Although the physical mechanisms governing crack formation in SSEs are likely to differ from that of active particles, in which diffusion and reaction induced stresses govern, the methods developed for active particles should serve as a suitable starting point for modeling crack formation in SSEs.

Phase-field damage models have been developed for damage in active particles. These models can incorporate the crack degradation parameter as an additional internal variable to the chemical variable set, taking into account both its initiation and propagation. Particularly, Miehe et al. [98] presented a finite strain chemo-elasticity theory coupled with phase field modeling to investigate fracture in Li-ion electrode particles. Their regularized crack model uses a principal stress criterion for failure surface, and a degradation function to “damage” both the stored energy and the mobility of species across the crack faces. They also regularized reaction kinetics at the fracture surfaces, replacing it with a source term in the conservation equations. Using FEM to solve the resulting partial differential equations, they demonstrated the versatility of the phase field method in simulating crack propagation in chemo-mechanics problems. Figure 5f shows a representative three-dimensional simulation of fracture in a coupled chemo-mechanics framework. Zhang et al. [113] extended these works to model diffusion induced plasticity and fracture in both amorphous and crystalline silicone (Si) electrodes using a similar variational based phase field damage model. Employing an efficient time integration scheme, they successfully simulated fracture of Si nano-particles and nanopillars and investigated how energy release rate affected the electrode damage behavior. A similar work on effects of fracture propagation on mechanics and subsequently on Li concentration and phase separation in polycrystalline particles of LiCoO_2 was conducted by Yamakawa et al. [114], in which they estimated the effect of grain size and crystal orientation on the extent of fracture. In Anand et al. [97] the

Table 1 Compounds studied in Deng et al. [116] using DFT to obtain the elasticity tensor

Compound	Family
LiTi ₂ (PO ₄) ₃ , NaZr ₂ (PO ₄) ₃	NASICON
Li ₃ PO ₄	Phosphate
Li _{1/2} La _{1/2} TiO ₃ , Li _{1/8} La _{5/8} TiO ₃	Perovskite
Li ₇ La ₃ Zr ₂ O ₁₂ (LIZO), Li ₅ La ₃ M ₂ O ₁₂	Garnet
Li ₃ OCl, Li ₃ OBr, Na ₃ OCl, Na ₃ OBr	Antiperovskite
Li ₃ PS ₄ , Li ₁₀ GeP ₂ S ₁₂ (LGPS), Li ₇ P ₃ S ₁₁ , Na ₃ PS ₄	Thiophosphate

authors developed an alternative thermodynamics based damage model, in contrast to the aforementioned variational based phase-field approaches. Available phase-field models for treatment of chemo-mechanical fracture in LIBs are transferable to address the reaction induced crack propagation in SSE. Damage evolution in current phase-field models is governed by an equation of the form

$$\dot{\eta} = (1 - d)\mathcal{H} - [d - l^2 \nabla^2 d] \quad (12)$$

where $\{\eta, d, l\}$ denote the viscous regularization parameter, the damage variable and the characteristic length scale. Here \mathcal{H} defines the damage driving force which depends on the underlying material and chemistry of interest. Both stress and energy based criteria have been used in the literature to formulate \mathcal{H} , and may include elastic, inelastic, or chemo-mechanical coupling terms. Damage evolution in SSEs can be captured by a form similar to Eq. (12) provided the constitutive framework for damage driving force is specialized to account for effect of reaction in addition to capturing the specific fracture behavior of the SSE material.

3.2 Mechanical characteristics of solid-state electrolytes

In the process of developing an understanding of the mechanical behavior of SSEs, it is necessary to understand and model the mechanical behavior and properties of the SSE itself, as the elastic, plastic and fracture properties of the electrolyte will determine how it responds to dendrite growth, induced stresses due to interphase formation, crack propagation and other relevant mechanical issues [115]. For instance, a ductile electrolyte is more desirable for accommodating deformation and maintaining contact with the lithium anode during battery operation, while a high

fracture toughness and high stiffness one is better at resisting lithium dendrite growth [116].

As the scope of this review is concerned with modeling, here we summarize the reported mechanical properties for a range of SSEs, all of which are obtained from first-principle calculations. The results of these Ab-initio estimations can be used as inputs to continuum models to optimize SSE designs, potentially in a hierarchical multi-scale, multi-physics paradigm. Deng et al. [116] used density functional theory (DFT) with projected augmented wave method [117] for ions interaction, to obtain a complete description of the elasticity tensor for the compounds shown in Table 1. They reported the following hierarchy of elastic moduli: thiophosphate < antiperovskite < phosphate < NASICON < garnet < perovskite. It was also determined that Na counterparts of the studied SSEs had smaller Young moduli compared to the aforementioned Li compounds. From a microstructural standpoint, it was determined that tetragonal structures exhibited a higher elastic modulus compared to cubic ones among garnet based SSEs. Regarding brittle vs ductile behavior, the DFT calculations revealed thiophosphates as the most ductile, with oxides being the most brittle compounds. It should be noted, however, that the employed metric in assessing ductile vs brittle behavior resided solely on simple shear over bulk ratio or Pugh's number [118], and not on a complete stress strain constitutive curve.

Wu et al. [119] adopted a similar technique for characterization of antiperovskite Li₃OCl material. Upon calculation of three elastic constants of the cubic material, it was determined that Li₃OCl is softer than LLTO and LIZO, but harder than LGPS. They also calculated a Pugh's ratio of 1.35, indicating its brittleness. As mentioned in their work, this inherent brittleness makes this material susceptible to interphase induced fracture during cell operation and can

severely limit its potential integration in SSBs as a practical SSE. Their reported value of 0.22 for Poisson's ratio is also typical of ionic crystals [120]. In a similar fashion, Wang et al. [121] studied LGPS along with $\text{Li}_4\text{P}_2\text{S}_7$ and $\text{Li}_3\text{P}_7\text{S}_{11}$, which unlike the tetragonal structure of the LGPS, have triclinic formations. They reported that LGPS has higher elastic constants compared to the two aforementioned LISICON compounds. They also calculated a Pugh's number of 2.12 for LGPS, indicating its relative ductile nature. A detailed study on two β and γ phases of Li_3PS_4 was performed by Yang et al. [122], demonstrating that the γ phase is a stiffer material than its β counterpart. Both materials also showed relative ductility, characterized by Pugh's ratio of 2.26 and 2.89 for γ and β phases, respectively. Similarly, compounds of Metal Borohydrides $\text{M}_2\text{B}_{10}\text{H}_{10}$ (with M being the place holder for different ions of Li, Na, K) were studied in the work of Chen and Hong [123]. Their study illustrated the Li compound to be stronger than the sodium and potassium counterpart, observing a decrease in stiffness as the ion becomes larger. While referred works resort purely to material properties obtained by first-principle calculations, experimental efforts have also invested in characterizing properties of SSEs. A review of such efforts has been provided in tabulated form by Wang et al. [35] and Zhang et al. [36] and are not replicated for conciseness in this review.

Finally, Ahmad and Viswanathan [124] realized the uncertainties associated with calculating energies around the equilibrium state in DFT calculations, improving the previous works by quantifying this uncertainty. They performed the calculations on an ensemble of energies on four compounds of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, Na_3PS_4 , LiI , and Na_3OCl , obtaining probability distributions for mechanical properties with quantified standard deviations. These probabilistic results can be put into a continuum model, leading to probabilistic design of SSBs. Also equally important to consider and currently lacking in the DFT literature is the mechanical properties of the reacted interphase, as it seems natural to expect the properties of this mixed phase to be different from the bulk unreacted material. Future DFT simulations can shed some light on how the properties of this structurally crucial layer are changing during battery operation.

As appealing as these DFT results are for mechanical design of SSEs, they suffer from the inherent

computational complexity and uncertainties associated with quantum mechanical calculations. It has been shown that mechanical phenomena during battery operations heavily depend on the choice of the SSE material. While DFT simulations can help overcome the need for complex experimental characterizations, they are still relatively time consuming given the vast combination of potential SSE compounds. A possible avenue to accelerate the mechanical design of SSEs is to take advantage of data science approaches, which by now have reached a relatively mature state in the material science community [125–130]. This particular approach has previously been used for generic liquid electrolyte battery design [131, 132], but Ahmad et al. [133] recently extended this work by employing machine learning techniques to scan a space of over 12000 inorganic SSE compounds, identifying the ones that have the best mechanical properties to suppress dendrite growth. It should be noted, however, that their data was only trained on structural features of the compounds and they considered elastic properties of the SSE to be the only dominant factor for dendrite suppression. As reviewed in Sect. 2, the phenomena of dendrite growth is complex and governed not just by the choice of elastic properties of the SSE. Addressing this phenomenon requires a continuum chemo-mechanical model that accounts for microstructure, defects, geometry, boundary conditions, etc. Adding the results acquired from fully coupled chemo-mechanical continuum models as features to the training space of these data science approaches constitutes one area for potential improvement in pursuit of robust mechanical designs of SSBs.

3.3 Mechanical compatibility at the interface

We conclude this section with another important mechanical problem in SSEs, namely void formation and loss of contact at the lithium anode-SSE interface [35, 99]. This phenomenon is depicted in Fig. 5g from the experimental work of Han et al. [99] on improving resistance in LLCZN garnet based SSEs. This problem is specific to SSBs as traditional liquid electrolyte cells maintain excellent wetting properties during operation. In SSBs, on the other hand, continuous plating and stripping of Li, accompanied by its volume expansion during cycling, leads to formation of voids and partial delamination of the interface. This partial

loss of contact slows the transport of Li ions across the interface, significantly increasing the impedance [99, 134]. In the authors knowledge, there seems to have been no attempts in the literature at modeling void formation and loss of contact at the Li anode/SSE interface. Potential models addressing this issue should incorporate the micro-scale mechanisms of void formation and growth, along with the macro-scale deformation and morphology evolution of the interphase. Models should also aim to relate the void formation and morphology change to impedance increase at the interface in a coupled chemo-mechanics framework.

3.4 Summary on modeling solid-state electrolytes

As reviewed above, modeling of solid-state electrolytes is in its infancy. In particular modeling the interphase which forms at the anode/SSE interface is critical for understanding stress generation, fracture, and delamination and there are currently no validated models for this phenomenon. We list here a few key areas of research the authors feel are of pressing relevance:

- At present, capturing the phenomena of interphase formation and evolution remains one of the challenges for SSE realization from a modeling perspective. A diffusion deformation reaction theory capable of accommodating chemically induced phase transformation is currently lacking in the mechanics literature and needs to be developed to address the issue of interphase formation in SSEs.
- Damage and fracture modeling of SSEs is lacking with no calibrated model currently available. In particular, models should be capable of capturing both the mechanical degradation and the electrochemical degradation in the form of an increase in impedance.
- In the pursuit of robust mechanical SSEs it could be beneficial to use fully coupled chemo-mechanical continuum models as features to the training space of new data science approaches for material discovery.
- The process of void formation and loss of contact at the anode/SSE remains unaddressed. A calibrated model for this phenomena must be developed in order to understand the relevant material

properties, microstructural characteristics, and operational requirements to prevent this form of damage.

4 Composite electrodes

Solid-state composite electrodes represent another critical component of an all-solid-state Li-Ion battery where mechanical effects will play a crucial role, cf. [32]. Both cathodes and anodes not composed of pure solid Li metal will consist of a composite of active particles surrounded by a solid-state electrolyte matrix. During cycling, the active particles will undergo electrochemically induced expansion and contraction while the SSE provides an ion pathway for Li diffusion. Developing models for these systems requires an understanding of three critical components: (1) the behavior of the active particles themselves, (2) the behavior of the solid state electrolyte, and (3) the combined behavior of the composite. This section will mainly focus on this third aspect of modeling composite behavior since it is in its infancy. Within this context, one must consider the composite behavior from a pure chemo-mechanical perspective, the behavior of the interfaces and possible delamination, as well as the potential for fracture/damage within the active particles and SSE. Modeling of the active particles will be briefly reviewed in Sect. 4.1 as significant work has been made in this area and models are fairly mature and predictive. The state of the art in modeling solid-state electrolytes was reviewed in Sect. 3 and is not considered here.

4.1 Chemo-mechanical continuum modeling of active particles

With respect to the active particles, coupled chemo-mechanical models have been developed for a number of different active materials. To different degrees of complexity and success, models have been developed both for intercalation electrodes [135–141], where deformations are generally elastic and on the order of 10% strain, and for conversion electrodes [88, 142–146], where deformations are elastic-inelastic in nature and chemical strains are on the order of 100% or more, including aspects of failure modes and damage [147].

Within the context of small deformations and intercalation electrodes, some of the earliest works considered isotropic elastic intercalation electrodes and within this restriction studied the critical geometrical, material, and electrochemical parameters to prevent fracture using a linear elastic fracture mechanics approach [135, 136]. For certain types of electrodes such as Graphite and LiFePO_4 , phase-segregation (i.e. staging) occurs during lithiation and models have been developed based largely on the Cahn–Hilliard phase-field model to capture these phenomena, cf. [137–139]. These models have been shown to accurately predict the electrochemical performance of these individual particles as well as the manner in which mechanical strains can affect the morphology of the phase-segregation [138, 148, 149] or even suppress it entirely [137, 150]. Models have also been extended to include large elastic deformations and Cahn–Hilliard-type phase-segregation [141, 144, 151]. With an accompanying finite-element implementation of the coupled chemo-mechanics theoretical framework, researchers have demonstrated in two and three-dimensional simulations the manner in which lithiation morphology is critically influenced by mechanical deformation, e.g. [141, 152]. Although the aforementioned models have been developed within the context of LIBs, they are particularly focused on the chemo-mechanical behavior of active particles and should be equally applicable to modeling of these active materials in the context of composite cathodes in SSBs. There are potential chemical interface stability issues that might have to be considered for particular active particle/SSE combinations which might require different theoretical models for capturing interfacial kinetics. However, the bulk behavior of the active particle in a SSB composite cathode should still be well described through the above models.

Conversion electrodes—such as Silicon which has been extensively studied—generally undergo very large elastic-inelastic deformations with chemical strains on the order of hundreds of percent [153]. Continuum models have been developed for these systems which account for large elastic-inelastic deformations accompanied by species diffusion and chemical strains [142–144, 146]. Closed form analytical solutions have been developed for a few simple cases. For example, Bower et al. [155] developed analytical solutions for the problem of an elastic-plastic spherical particle undergoing diffusion induced

deformations with a sharp propagating phase boundary. A number of studies use simplified geometries (i.e. spherical or radially symmetric) to simplify to a one-dimensional problem which may be solved numerically [142, 154]. Huang et al. [154], for example, demonstrated the manner in which stresses develop in spherical particles undergoing large chemically induced elastic-plastic deformations with or without the presence of a sharp interface. Figure 6a–c shows results from the work of Huang et al. [154], where (a) shows the single-phase and two-phase configurations. Figure 6b shows the distribution of equivalent σ_e , radial σ_r , and hoop σ_θ stresses across the normalized particle radius R/A for the single-phase simulation while Fig. 6c shows the same result for the two-phase simulation. One particularly important finding of this work is the manner in which the hoop stress may be either tensile or compressive on the surface due to the presence of inelastic deformations and two-phase lithiation. This has important implications in modeling fracture of these materials.

Amorphous Silicon (a-Si) has been widely studied in the literature for its potential as a high-capacity anode. Bucci et al. [146] and Di Leo et al. [88] have both calibrated continuum mechanics theories and demonstrated an ability to predict the Voltage vs. Charge behavior of simple a-Si electrodes coupled to their mechanical behavior. Figure 6d, e, reproduced from the work of Bucci et al. [146], show the evolution of cell potential and film stress in a thin-film a-Si electrode undergoing potentiostatic cycling. The model developed by Bucci et al. is calibrated and contrasted against the experimental results and demonstrated the ability of these models to accurately predict both stress evolution and cell performance. Examples from Di Leo et al. [88] are shown in Fig. 6f–i where a large-deformation elastic-plastic chemo-mechanical theory and accompanying finite-element simulation is used to predict the behavior of hollow double-walled nano-tubes experimentally realized by Wu et al. [156]. Figure 6f shows the finite-element discretization of the geometry and (h) the resulting prediction of voltage vs. state-of-charge (SOC) for two different C-rates. It is important to note that no parameters are calibrated in this prediction. An important aspect of this and similar studies is on the role of inelasticity as demonstrated in Fig. 6i which shows Voltage vs. SOC for two simulations with and without plastic deformation. (g) Shows contours of the

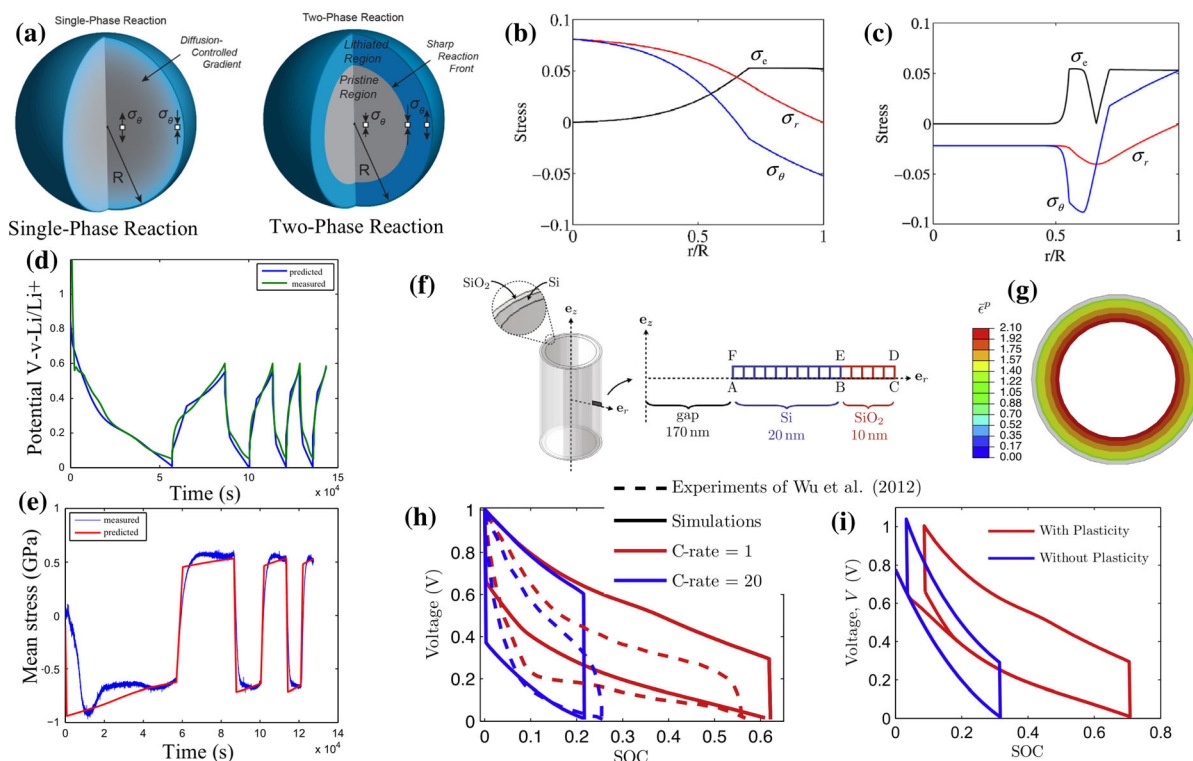


Fig. 6 Representative simulations of active particles. **a–c** Demonstrate a simulation using spherical symmetry considering both single-phase and two-phase lithiation within an elastic-plastic electrode. **b** Shows the distribution of equivalent σ_e , radial σ_r , and hoop σ_θ stresses across the normalized particle radius R/A for the single-phase simulation while **c** shows the same result for the two-phase simulation. Reproduced with permission from [153] and [154]. Evolution of **d** cell potential and **e** thin-film stress during the potentiostatic cycling of an a-Si

thin-film electrode. Reproduced with permission from [146]. **f–i** Modeling of a hollow double-walled nanotube. **f** Shows the finite-element discretization with **h** showing the resulting simulation prediction against experimental measurements of Voltage vs. State-of-Charge (SOC). **i** Shows the effect on V vs. SOC of ignoring plastic deformation and **g** shows contours of equivalent plastic strain, $\bar{\epsilon}^p$ after three half-cycles. Reproduced with permission from [88]

equivalent plastic strain $\bar{\epsilon}^p$ developed during three half-cycles of the hollow double-walled nanotube.

Critical in the calibration of these theories is experimental data which shows both the voltage/charge and stress/charge behavior of the system. In recent years substrate curvature techniques [157–160] have been used to measure the mechanical stress in thin films of active materials during lithiation. These experiments provide crucial information for modelers as they quantify both the electrochemical and mechanical performance of the material. Fig. 6d, e show an example of the cell potential and film stress which can be measured during potentiostatic cycling of a thin-film a-Si electrode. Experiments using substrate curvature techniques have elucidated phenomena including the stress-potential coupling [157], strain-rate sensitivity [160], and fracture properties

[159, 161]. The technique however is more complex when considering composite materials, such as the composite solid-state electrodes under consideration, since the stress measured is an average over the various phases and local stress state cannot be resolved. Researchers have recently begun investigating the use of substrate curvature techniques for composite materials but there is at present no clear route for how these experiments will aid in the calibration and validation of composite electrode models [162–164]. It must also be noted that it is possible to inform aspects of the continuum mechanics models through molecular dynamics or first-principles [165–169]. Zhao et al. [165] for example performed first-principle studies based on density functional theory to elucidate the manner in which lithium insertion in Silicon leads to a decreased stiffness,

strength, and a brittle-to-ductile transition. Sharma and co-workers have developed techniques based on enhancing molecular dynamics with autonomous basin climbing, kinetic Monte Carlo, and transition state theory to gain insight into the diffusivity of Li in a-Si [167], its inelastic response [168, 169]. Continuum chemo-mechanics models for active materials are relatively mature and a number of theoretical frameworks and numerical techniques have been developed, calibrated, and validated which may serve as the foundation for the more pressing work of understanding all-solid-state composite cathodes.

4.2 Modeling of composite cathodes

Composite electrodes, both anodes and cathodes, are critical in the function of any Li-Ion battery. As reviewed in Sect. 4.1 above, the lithiation/delithiation of active particles can cause significant deformations. Beyond the generation of stresses within the particles, these deformations can lead to significant particle-to-particle interactions as well as interactions with the surrounding matrix. In a solid-state electrode, in contrast to a liquid electrolyte electrode, these interactions are enhanced as the high stiffness of the electrodes leads to further confinement of the particles. Stresses exerted on the SSE can lead to a loss in electrochemical performance through damage/fracture of the SSE or delamination of the active particles from the SSE resulting in a loss of ionic conductivity, e.g. [170, 171]. Further, it is possible that all-solid-state composite electrodes will exhibit longer-range effects than liquid electrolyte systems where particle-to-particle mechanical interactions are enhanced due to the presence of the stiff electrolyte matrix, e.g. [172].

Building on the theoretical frameworks developed for single active particles as reviewed in Sect. 4.1, the first progression towards modeling full battery behavior has been to consider half- or full-cell models with solid electrodes e.g. [151, 173]. Bower et al. [151] developed a half-cell continuum chemo-mechanics model including an accounting for mechanical deformation and stress on the anode, cathode, electrostatic field and electrochemical reaction. Figure 7a shows a schematic of the model under consideration, which was applied to modeling a one-dimensional thin-film half-cell. The potential vs. time and capacity time plots are derived from the full-cell behavior and show

good agreement with experiments also published in their work. These chemo-mechanical continuum models introduce important aspects of the role of mechanics on interfacial electrochemistry but are still limited to solid electrodes.

An enhancement to these types of full-cell models which accounts for the composite nature of the electrodes has been developed around porous electrode theory, e.g. [176–179]. In such frameworks, the electrodes are treated as a homogenized porous medium. Renganathan et al. [176] developed a full-cell model with porous electrode theory used for both electrodes. In this work the authors enhance traditional porous electrode theory to account for stress effects on diffusion. Christensen [177] performs a similar analysis including the role of fracture by assuming some degree of pre-existing fractures in the electrode. Significant efforts have been developed in the theory of porous electrodes by Bazant and co-workers. In Ferguson et al. [178], porous electrode theory is developed with a detailed Cahn–Hilliard model to account for phase-separation in active particles. The role of strain is introduced in the chemical potential by considering variations of the local concentration from its volume averaged quantity. Through this analysis the authors were able to demonstrate the importance of mechanics in suppression of phase-separation and promotion of homogeneous filling. Porous electrode theory has the distinct advantage of producing a computationally efficient solution while still maintaining a fairly rich description of the porous nature of the microstructure. However, as with any homogenization technique, it is impossible to retain all details of the behavior at the microstructure and one loses for example an understanding of stress distribution at the active particle scale and the manner in which damage might occur either through active particle failure, matrix failure, or interface delamination.

An alternative approach is to fully-discretize the microstructure or a representative volume thereof, e.g. [174, 175, 180]. Garcia et al. [174] developed a two-dimensional finite element description of a detailed composite cathode microstructure with cylindrical particles coupled to a simplified model for the separator and anode behavior. Mechanical deformation was captured through the use of isotropic elastic active particles with chemically-induced strains. Figure 7b shows an example result using their simulation tool for an electrode with graded porosity. Using this

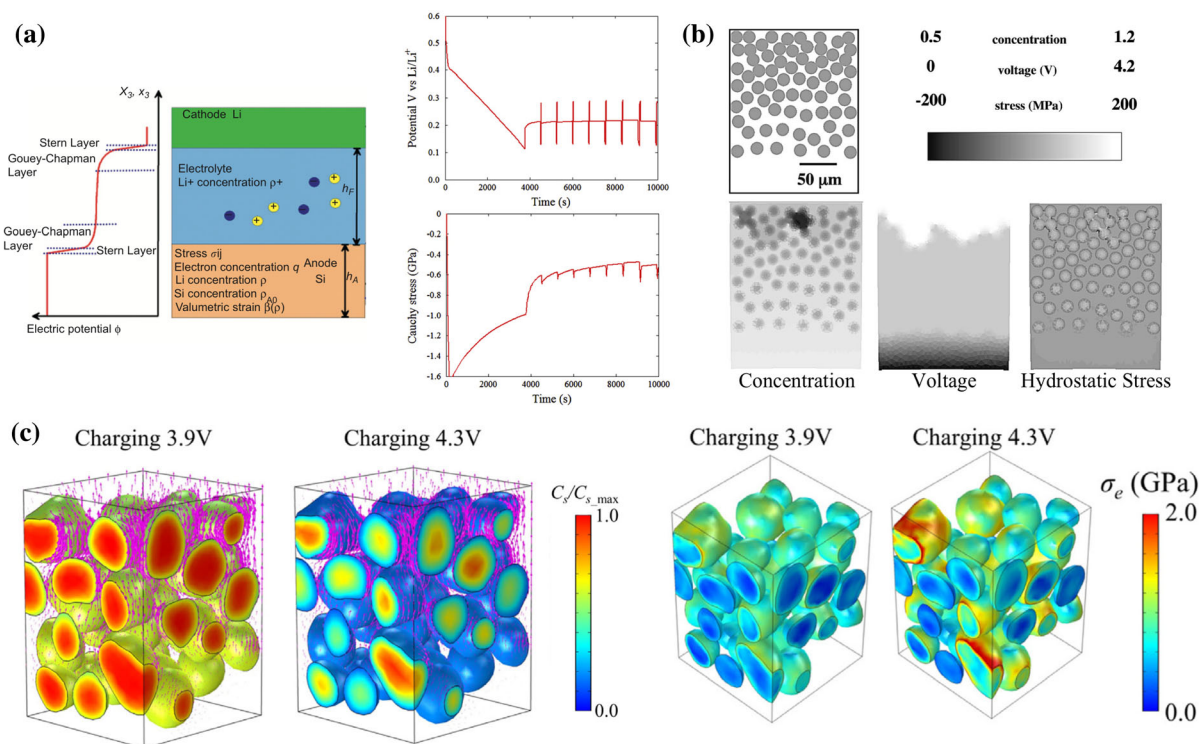


Fig. 7 Representative simulations of traditional electrode architectures. **a** Shows a schematic of a continuum chemo-mechanics representation of a half-cell Li-Ion system with the accompanying predictions for potential and capacity vs. time. Reproduced with permission from [151]. **b** Results of a 2D numerical simulation of a composite cathode microstructure with a liquid electrolyte. The bottom three images in (b) show

contours of normalized concentration, voltage, and hydrostatic stress. Reproduced with permission from [174]. **c** Results of a 3D numerical simulation of a composite NMC cathode informed by X-Ray tomography. The first two contours are of normalized concentration at varying charging voltages while the second two contours show equivalent stress at the same charging conditions. Reproduced with permission from [175]

tool researchers studied the role of particle size and distribution on electrochemical and mechanical performance. More recently, Xu et al. [175] performed three-dimensional finite element simulations to numerically resolve the microstructure of $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC) composite cathodes. Synchrotron X-ray tomography was used to inform the microstructural modeling and to validate model predictions. Here, the composite cathodes modeled used a homogenized matrix consisting of the electrolyte and the carbon-binder matrix while active particles were fully resolved. Although modeling a traditional liquid electrolyte material, a small stiffness (4GPa) is attributed to the homogenized matrix. Damage was modeled both in the active NMS particles through cohesive zone modeling, and at the particle interfaces by penalizing interfacial resistance as a function of the normal displacement of the interface. Figure 7c shows an example result of their numerical model where the

first two results show contours of normalized concentration at two different voltages during charging as well as a quiver plot of flux. The third and fourth results in Fig. 7c show contours of equivalent stress at the same charging conditions. Using this detailed simulation tool, the authors quantified the manner in which mechanical damage influences battery performance. For example they quantified the manner in which electrochemical impedance is affected by interfacial debonding. Using experimentally relevant microstructures is critical and recent trends, as demonstrated in Xu et al. [175], have seen the use of X-Ray tomography to develop experimentally accurate simulation domains. This of course adds computational and experimental cost. Recently, Hofmann et al. [180] performed numerical simulations similar to those referenced above but importantly provided a comparison on the use of synthetically generated microstructures vs. experimentally “exact”

descriptions. In this approach one still needs to understand the key experimental descriptors of the microstructure such as a particle size and shape distributions, but need not simulate the exact experimental microstructure.

The aforementioned research efforts focused on LIBs, and although the results are not directly applicable as the higher stiffness of the SSE is a critical component, they have served to pave the way for current models developed specifically for all-solid-state-batteries and solid-state composite cathodes in particular. Specifically, models for LIBs using a fully-discretized microstructure contain suitable models for the behavior of active particles and an existing framework for constitutive modeling of the matrix (be it liquid or SSE) and an accounting for potential damage through delamination using cohesive elements. With the development of proper chemo-mechanical constitutive theories for the SSE material and the active particle/SSE interfaces, these works can serve as a starting point for modeling composite cathodes in SSBs. From a purely electrochemical perspective Mykhalov et al. [184] considered an all-solid-state construction with the use of porous electrode theory, without consideration for mechanical deformation and stress, and achieved closed-form or semi-closed form solutions for the performance of the system. Bielefeld et al. [185] used a three-dimensional description of the composite cathode microstructure to investigate its percolation characteristics.

Bucci and co-workers have done arguably the most extensive work on modeling the chemo-mechanics of solid-state composite cathodes without [172] and with [182, 183, 186] the inclusion of damage modeling. In [172], the authors focus on how constraint induced stresses modify cell performance using both an analytical approach and numerical finite element simulations. Figure 8a shows analytical results for the open-circuit potential for Silicon vs Li with varying stiffness of the electrolyte matrix. As is clear from the figure, increasing matrix stiffness results in larger compressive stresses which have the effect of shifting the open-circuit potential and reducing storage capacity. A two-dimensional finite element description of a representative microstructure (similar to that shown in Fig. 8d) was used to investigate this behavior further. Through this analysis, Bucci and co-workers found that there is a critical volume ratio of active material, Silicon to SSE at which one achieves

maximum capacity for the composite electrode, see Fig. 8b. Below this critical number, one is under-utilizing the available space, and above this number one is generating excessive stresses due to particle-particle interactions. Similar to the work of Bucci et al. [172], existence of a critical volume fraction of active material for cathode compositions was investigated in the work of Al-Siraj et al. [187]. Here, a linear decay in effective diffusivity of SSE with increase in active particle volume fraction was determined. Above a critical volume fraction, effective diffusivity of SSE becomes negligible in magnitude, thus limiting performance. Modeling damage in composite solid-state cathodes is critical. Bucci et al. [182] present arguably the first quantitative study on the role of mechanical damage in composite all-solid-state cathodes. In this work, cohesive zone modeling is used to capture damage in the SSE during cycling of the composite cathode. Figure 8d shows the simulation domain used by the authors while (e) shows contours of normalized concentration and hydrostatic stress with cracks shown in black during lithiation to a state-of-charge of 0.7. Although the active particles are expanding due to chemically-induced strains, regions of tensile stresses develop in the SSE resulting in the micro-cracks shown in Fig. 8e. Critically, the authors demonstrated that compliant SSEs are more prone to micro-cracking. Delamination of the active particles from the SSE was not considered in [182] and was studied in a separate investigation by the same authors [183]. There the interface between the active particle and the SSE is studied through a one-dimensional radially symmetric model with the microstructure approximated by stacking of truncated octahedrons, see Fig. 8f. The authors found that very compliant electrodes and high fracture energies are required to delay the onset of delamination. The phase-map in Fig. 8f shows the necessary volume contraction required to initiate delamination as a function of SSE stiffness and fracture energy. Even at small volume changes, delamination is expected for a broad range of engineering relevant properties. Inelastic deformation of the SSE was considered in this simplified geometry and can contribute significantly to potentially delaying the onset of delamination by releasing energy through inelastic deformation of the SSE. Clearly the coupled chemo-mechanical behavior of composite cathodes is complex and there is at present no clear understanding of the desired

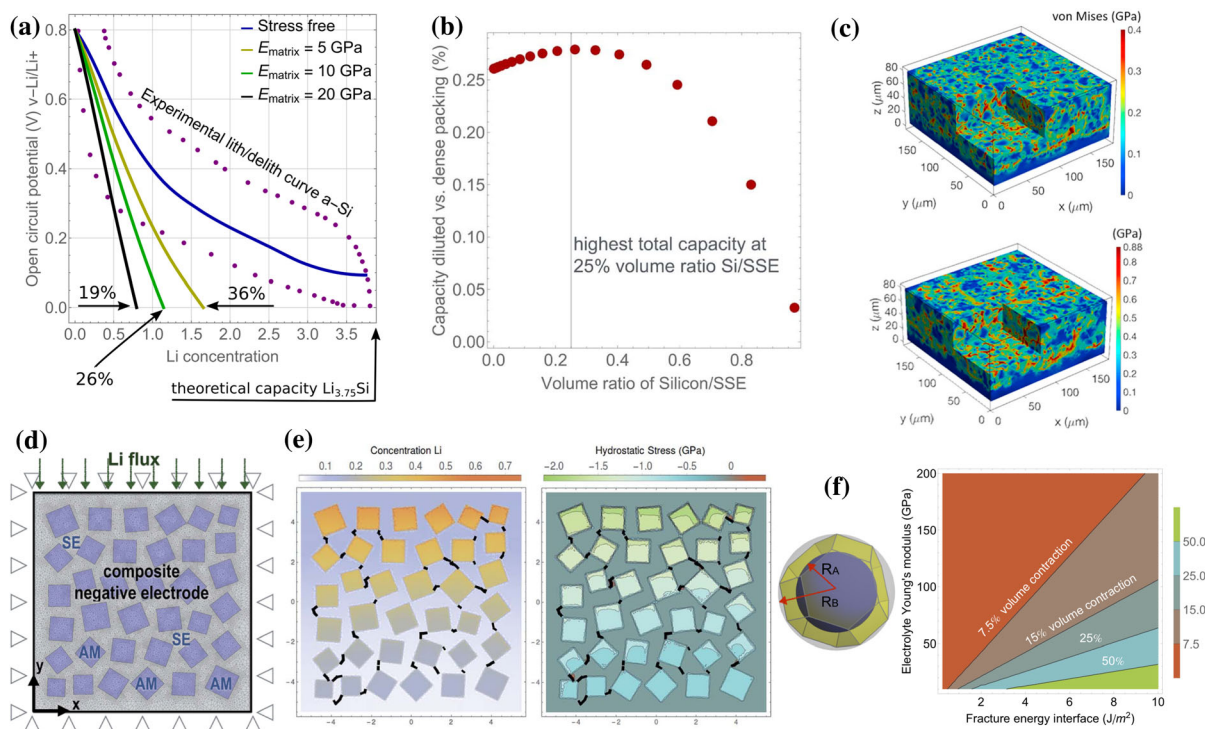


Fig. 8 Representative simulations for composite solid-state cathodes. **a** Shows analytical results for the open-circuit potential for Silicon vs Li with varying stiffness of the electrolyte matrix. **b** Capacity (percent dilute vs. dense packing) of Si in a representative two-dimensional microstructure as a function of volume ratio of Silicon vs. SSE. The highest capacity is achieved due to a tradeoff between packing and stress generation. Reproduced from [172] under creative commons license CC BY-NC-ND 4.0. **c** Shows contours of equivalent (von Mises) stress generated due to thermal contraction (top) and delithiation (bottom) for a simulation performed using the smoothed boundary method (SBM). Reproduced with

permission from [181]. **d** Simulation domain for capturing fracture of the SSE during lithiation, note that the SSE domain is discretized with cohesive elements to simulate fracture. **e** Shows contours of normalized concentration and hydrostatic stress with cracks shown in black during lithiation to a state-of-charge of 0.7. Reproduced with permission from [182]. **f** Shows a schematic of the one-dimensional radially symmetric model with the microstructure approximated by stacking of truncated octahedrons used to study delamination. The phase-map in **f** shows the necessary volume contraction required to initiate delamination as a function of SSE stiffness and fracture energy. Reproduced with permission from [183]

properties of SSEs for improved performance. Recent studies suggest that compliant SSEs are beneficial to prevent delamination while stiff SSEs are beneficial to delay microcracking. Further, the SSE material will also serve a role at the anode side of the cell in dendrite suppression as reviewed in Sect. 2, and the effect of its mechanical behavior there must also be considered.

Damage, either of the active particles, the SSE, or the interface is critical to understanding composite cathodes, and its investigation remains in its infancy. Use of cohesive elements to discretize interfaces provides one potential mechanisms for understanding interfacial failure. This has been studied for electrochemical systems but outside of the context of solid-state batteries, e.g. [143, 188, 189]. Another method

which deserves attention in future investigations is the use of phase-field continuum damage models, also discussed briefly in Sect. 3.1 above. In this approach, damage can initiate at any given location and proceed in any direction without the need for a pre-defined crack path as is the case for intrinsic cohesive zone models. The general theory of phase-field continuum damage models is relatively mature [190, 191], and there have been a few recent examples of its application mainly towards modeling damage of active particles, e.g. [98, 113, 192–195]. It will be relevant as a future research direction to investigate the use of these techniques also in the context of modeling damage of SSEs.

Finally, we conclude by noting that direct numerical simulation by finite element analysis is not exclusively the only technique for modeling the behavior of solid-state composite cathodes. Recently, Hao et al. [196] developed a Kinetic Monte Carlo (KMC) model to solve the electrochemistry formulation and coupled it to a finite element solution where each cell in the KMC corresponds to an FEA model to account for chemically induced volume changes of the active particles. Yu et al. [181], used smoothed boundary method (SBM) to solve mechanical equilibrium and compute stresses due to thermal dilatation as well as chemically induced deformations. Figure 8c shows representative results from Yu et al. [181] for equivalent (von Mises) stress generated due to thermal contraction (top) and delithiation (bottom). This study is unique as one of the only ones currently investigating the role of stress generation due to thermal misfit between components of the composite cathode.

4.3 Summary on modeling composite cathodes

As reviewed above, composite cathodes will play a critical role in all-solid-state Li-Ion battery architectures. Study of their coupled mechanical-chemical behavior is in its infancy, and a number of research avenues remain to be explored. We list here a few key areas of research the authors feel are of pressing relevance:

- There is a need for detailed continuum modeling of experimentally relevant, three-dimensional solid-state cathode microstructures. Research along this vein has been performed for liquid electrolytes (cf. Xu et al. [175]), but has not yet been realized for solid-state composite cathodes. The inclusion of damage, discussed in the third bullet point, is critical.
- Within the context of direct simulation of experimentally relevant microstructures, there is a need for improved constitutive descriptions of the relevant phases of the microstructure. Anisotropic properties, thermo-mechanical behavior, inelastic deformations all need to be rigorously accounted for. Further, appropriate boundary conditions for simulating these representative volume elements have not been extensively studied.
- As elucidated by the recent work of Bucci and co-workers [182, 183, 186], the role of damage on performance of solid-state cathodes is critical. There is first a need to develop simulations with the combined effects of possible active particle failure, SSE failure, and delamination of the two. Three-dimensional simulations, although computationally expensive, should be realized in order to get an experimentally relevant understanding of 3D crack formation and propagation. Within this context, research needs to be performed to assess what are the most promising damage modeling techniques for each of the aforementioned phenomena.
- Finally, we began our review with a discussion of porous electrode theory, a form of homogenization. Once there is a solid fundamental understanding of the detailed microstructural behavior of solid-state composite cathodes there is a need to develop efficient homogenized models. These computationally efficient models, if predictive, can subsequently be used to explore the design space of all-solid-state batteries and identify promising candidates for next-generation materials. There is a strong possibility that data analytics (i.e. machine-learning) can play a role in the development of these new homogenization tools.

5 Conclusion

The commercialization of next-generation all-solid-state battery architectures will rely on the development of predictive models for the various components of the cell capable of capturing the complex interplay between chemistry and mechanics. The sheer number of possible material combinations as well as the design of the microstructure limit the possibility of studying these systems from a purely experimental perspective. Modeling techniques are required to identify key possible candidates for materials and design at all levels of the SSB. In this review article we have summarized the state-of-the-art in chemo-mechanical modeling for (1) Li-metal anodes and dendrite growth, (2) solid-state electrolytes, and (3) composite cathodes. In doing so one key takeaway is that modeling of these systems is very much at its infancy. A few key areas have been researched extensively. Driven in large part by the objective of improving active materials for traditional liquid electrolyte cell designs, there have been sustained efforts in the areas of

modeling Li-dendrite growth through stability analysis as well as in modeling the chemo-mechanical behavior of active intercalation and reaction electrode particles. However, as illustrated in this review, there are significant new challenges in modeling the all-solid-state battery architecture.

A major challenge is in modeling the solid-state electrolyte and in particular the unstable formation and propagation of thermodynamically interphases at the anode/SSE boundary. This is a fully coupled problem in that the driving force for reaction at these interfaces is coupled to the local stress state and the stresses are significantly influenced by the volumetric expansion resulting from the formation of the new interphase. Modeling SSE behavior is perhaps the least well understood component of SSBs. A number of important research avenues in this area are presented in Sect. 3.4.

With respect to Li-metal anodes, significant research has gone into predicting the onset and growth of dendrites at the anode/SSE interface. A number of contradicting models have been developed for conditions in which dendrite growth is suppressed. However, at present, most models have been proven inaccurate by experimental observations. There is a critical need in this area to develop fully-coupled, high-fidelity chemo-mechanical models for dendrite growth problem with a detailed accounting for the role of surface imperfections and grain boundaries on the effect of Li dendrite growth at the anode/SSE interface. Further, better constitutive models for the behavior of Li metal itself are only now being developed and these still require significant attention. Future research avenues with respect to Li metal anodes and dendrite growth are presented in Sect. 2.3.

Finally, modeling efforts were with respect to solid-state composite cathodes. Unlike the other portions of the battery, here significant research exists for the behavior of the individual active particles which are expected to be deployed in these composite materials. A number of the main mechanical modeling challenges thus lie in understanding the damage and failure in these materials under cycling. There is a need here for experimentally relevant (or exact) numerical descriptions of the composite cathode microstructure integrated with fully-coupled chemo-mechanical models for the individual constituents. Further, these models should include all possible mechanisms of damage. Through such a detailed model one can make

accurate predictions on what the range of SSE/active material properties need to be in order to mitigate damage. Further, one may study the design of the microstructure to understand how key descriptors such as particle and shape size distribution impact mechanical degradation. Other future avenues for research, including development of new homogenization techniques, are presented in Sect. 4.3

Acknowledgements C.V.D.L. acknowledges funding from the National Science Foundation under Award No. CMMI-1825132.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Armand M, Tarascon JM (2008) Building better batteries. *Nature* 451:652
2. Bruce PG, Freunberger SA, Hardwick LJ, Tarascon JM (2015) Li-O₂ and Li-S batteries with high energy storage. *Nat Mater* 11:19
3. Yao X, Liu D, Wang C, Long P, Peng G, Hu YS, Li H, Chen L, Xu X (2016) High-energy all-solid-state lithium batteries with ultralong cycle life. *Nano Lett* 16(11):7148
4. Li J, Ma C, Chi M, Liang C, Dudney NJ (2015) Solid electrolyte: the key for high-voltage lithium batteries. *Adv Energy Mater* 5:1401408
5. Zhu Y, He X, Mo Y (2015) Origin of outstanding stability in the lithium solid electrolyte materials: insights from thermodynamic analyses based on first-principles calculations. *ACS Appl Mater Interfaces* 7(42):23685
6. Richards WD, Miara LJ, Wang Y, Kim JC, Ceder G (2015) Interface stability in solid-state batteries. *Chem Mater* 28(1):266
7. Roth EP, Orendorff CJ (2012) How electrolytes influence battery safety. *Electrochem Soc Interface* 21(2):45
8. Yang C, Fu K, Zhang Y, Hitz E, Hu L (2017) Protected lithium-metal anodes in batteries: from liquid to solid. *Adv Mater* 29(36):1701169
9. Zhang W, Nie J, Li F, Wang ZL, Sun C (2018) A durable and safe solid-state lithium battery with a hybrid electrolyte membrane. *Nano Energy* 45:413
10. Hayashi A, Ohtomo T, Mizuno F, Tadanaga K, Tatsumisago M (2003) All-solid-state Li/S batteries with highly conductive glass-ceramic electrolytes. *Electrochem Commun* 5(8):701
11. Murugan R, Thangadurai V, Weppner W (2007) Fast lithium ion conduction in garnet-type Li₇La₃Zr₂O₁₂. *Angew Chem Int Ed* 46(41):7778
12. Thokchom JS, Gupta N, Kumar B (2008) Superionic conductivity in a lithium aluminum germanium phosphate glass-ceramic. *J Electrochem Soc* 155(12):A915

13. Allen J, Wolfenstine J, Rangasamy E, Sakamoto J (2012) Effect of substitution (Ta, Al, Ga) on the conductivity of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$. *J Power Sources* 206:315
14. Seino Y, Ota T, Takada K, Hayashi A, Tatsumisago M (2014) A sulphide lithium super ion conductor is superior to liquid ion conductors for use in rechargeable batteries. *Energy Environ Sci* 7:627
15. Thangadurai V, Pinzaru D, Narayanan S, Baral A Kumar (2015) Correction to “Fast solid-state Li ion conducting garnet-type structure metal oxides for energy storage”. *J Phys Chem Lett* 6(3):347
16. Song X, Lu Y, Wang F, Zhao X, Chen H (2020) A coupled electro-chemo-mechanical model for all-solid-state thin film Li-ion batteries: the effects of bending on battery performances. *J Power Sources* 452:227803
17. Ren Y, Shen Y, Lin Y, Nan CW (2015) Direct observation of lithium dendrites inside garnet-type lithium-ion solid electrolyte. *Electrochem Commun* 57:27
18. Sharafi A, Meyer HM, Nanda J, Wolfenstine J, Sakamoto J (2016) Characterizing the $\text{Li-Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ interface stability and kinetics as a function of temperature and current density. *J Power Sources* 302:135
19. Cheng E, Sharafi A, Sakamoto J (2016) Intergranular Li metal propagation through polycrystalline $\text{Li}_6.25\text{Al}_0.25\text{-La}_3\text{Zr}_2\text{O}_{12}$ ceramic electrolyte. *Electrochim Acta* 223:85
20. Aguesse F, Manalastas W, Buannic L, Lopez del Amo JM, Singh G, Llord A, Kilner J (2017) Investigating the dendritic growth during full cell cycling of garnet electrolyte in direct contact with Li Metal. *ACS Appl Mater Interfaces* 9(4):3808
21. Porz L, Swamy T, Sheldon BW, Rettenwander D, Frmling T, Thaman HL, Berendts S, Uecker R, Carter WC, Chiang YM (2017) Mechanism of lithium metal penetration through inorganic solid electrolytes. *Adv Energy Mater* 7(20):1701003
22. Narayan S, Anand L (2018) A large deformation elastic-viscoplastic model for lithium. *Extreme Mech Lett* 24:21
23. Kobayashi T, Yamada A, Kanno R (2008) Interfacial reactions at electrode/electrolyte boundary in all solid-state lithium battery using inorganic solid electrolyte, thio-LISICON. *Electrochim Acta* 53(15):5045
24. Sakuda A, Hayashi A, Tatsumisago M (2010) Interfacial observation between LiCoO_2 electrode and $\text{Li}_2\text{S-P}_2\text{S}_5$ solid electrolytes of all-solid-state lithium secondary batteries using transmission electron microscopy. *Chem Mater* 22(3):949
25. Santhanagopalan D, Qian D, McGilvray T, Wang Z, Wang F, Camino F, Graetz J, Dudney N, Meng YS (2014) Interface limited lithium transport in solid-state batteries. *J Phys Chem Lett* 5(2):298
26. Wenzel S, Randau S, Leichtweiß T, Weber DA, Sann J, Zeier WG, Janek J (2016) Direct observation of the interfacial instability of the fast ionic conductor $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ at the lithium metal anode. *Chem Mater* 28(7):2400
27. Lewis JA, Cortes FJQ, Boebinger MG, Tippens J, Marchese TS, Kondekar N, Liu X, Chi M, McDowell MT (2019) Interphase morphology between a solid-state electrolyte and lithium controls cell failure. *ACS Energy Lett* 4(2):591
28. Koerver R, Zhang W, de Biasi L, Schweidler S, Kon-drakov AO, Kolling S, Brezesinski T, Hartmann P, Zeier WG, Janek J (2018) Chemo-mechanical expansion of lithium electrode materials-on the route to mechanically optimized all-solid-state batteries. *Energy Environ Sci* 11(8):2142
29. Zhang W, Richter FH, Culver SP, Leichtweiss T, Lozano JG, Dietrich C, Bruce PG, Zeier WG, Janek J (2018) Degradation mechanisms at the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{LiCoO}_2$ cathode interface in an all-solid-state lithium-ion battery. *ACS Appl Mater Interfaces* 10(26):22226
30. Goodenough JB, Kim Y (2010) Challenges for rechargeable Li batteries. *Chem Mater* 22(3):587
31. Takada K (2013) Progress and prospective of solid-state lithium batteries. *Acta Mater* 61(3):759
32. Lewis JA, Tippens J, Cortes FJQ, McDowell MT (2019) Chemo-mechanical challenges in solid-state batteries. *Trends Chem* 1:845–857
33. Xu L, Tang S, Cheng Y, Wang K, Liang J, Liu C, Cao YC, Wei F, Mai L (2018) Interfaces in solid-state lithium batteries. *Joule* 2(10):1991
34. Shen Z, Zhang W, Zhu G, Huang Y, Feng Q, Lu Y (2020) Design principles of the anode-electrolyte interface for all solid-state lithium metal batteries. *Small Methods* 4:1900592
35. Wang P, Qu W, Song WL, Chen H, Chen R, Fang D (2019) Electro-chemo-mechanical issues at the interfaces in solid-state lithium metal batteries. *Adv Funct Mater* 29(27):1900950
36. Zhang F, Huang QA, Tang Z, Li A, Shao Q, Zhang L, Li X, Zhang J (2020) A review of mechanics-related material damages in all-solid-state batteries: mechanisms, performance impacts and mitigation strategies. *Nano Energy* 70:104545
37. Zhao Y, Stein P, Bai Y, Al-Siraj M, Yang Y, Xu BX (2019) A review on modeling of electro-chemo-mechanics in lithium-ion batteries. *J Power Sources* 413:259
38. Albertus P, Babinec S, Litzelman S, Newman A (2018) Status and challenges in enabling the lithium metal electrode for high-energy and low-cost rechargeable batteries. *Nat Energy* 3:16
39. Kerman K, Luntz A, Viswanathan V, Chiang YM, Chen Z (2017) practical challenges hindering the development of solid state Li ion batteries. *J Electrochem Soc* 164(7):A1731
40. Barton JL, Bockris JO, Ubbelohde ARJP (1962) The electrolytic growth of dendrites from ionic solutions. *Proc R Soc Lond A* 268(1335):485
41. Diggle JW, Despic AR, Bockris JO (1969) The mechanism of the dendritic electrocrystallization of zinc. *J Electrochem Soc* 116(11):1503
42. Chazalviel JN (1990) Electrochemical aspects of the generation of ramified metallic electrodeposits. *Phys Rev A* 42:7355
43. Brissot C, Rosso M, Chazalviel JN, Baudry P, Lascaud S (1998) In situ study of dendritic growth in lithium/PEO-salt/lithium cells. *Electrochim Acta* 43(10):1569
44. Monroe C, Newman J (2003) Dendrite growth in lithium/polymer systems: a propagation model for liquid electrolytes under galvanostatic conditions. *J Electrochem Soc* 150(10):A1377

45. Mullins W, Sekerka R (1963) Morphological stability of a particle growing by diffusion or heat flow. *J Appl Phys* 34:323
46. Mullins WW, Sekerka RF (1964) Stability of a planar interface during solidification of a dilute binary alloy. *J Appl Phys* 35(2):444
47. Aogaki R, Makino T (1981) Theory of powdered metal formation in electrochemistry-morphological instability in galvanostatic crystal growth under diffusion control. *Electrochim Acta* 26(11):1509
48. Aogaki R (1982) Image analysis of morphological instability in galvanostatic electrocrystallization: I. General expression for the growth mode of surface irregularities. *J Electrochem Soc* 129(11):2442
49. Barkey DP, Muller RH, Tobias CW (1989) Roughness development in metal electrodeposition: II. Stability theory. *J Electrochem Soc* 136(8):2207
50. Pritzker MD, Fahidy TZ (1992) Morphological stability of a planar metal electrode during potentiostatic electrodeposition and electrodisolution. *Electrochim Acta* 37(1):103
51. Sundström LG, Bark FH (1995) On morphological instability during electrodeposition with a stagnant binary electrolyte. *Electrochim Acta* 40(5):599
52. Selim R, Bro P (1974) Some observations on rechargeable lithium electrodes in a propylene carbonate electrolyte. *J Electrochem Soc* 121(11):1457
53. Stewart SG, Newman J (2008) The use of UV/vis absorption to measure diffusion coefficients in LiPF₆ electrolytic solutions. *J Electrochem Soc* 155(1):F13
54. Akolkar R (2013) Mathematical model of the dendritic growth during lithium electrodeposition. *J Power Sources* 232:23
55. Akolkar R (2014) Modeling dendrite growth during lithium electrodeposition at sub-ambient temperature. *J Power Sources* 246:84
56. Ely DR, Garcia RE (2013) Heterogeneous nucleation and growth of lithium electrodeposits on negative electrodes. *J Electrochem Soc* 160(4):A662
57. Guyer JE, Boettinger WJ, Warren JA, McFadden GB (2004) Phase field modeling of electrochemistry. II. Kinetics. *Phys Rev E* 69(2):021604
58. Shibuta Y, Okajima Y, Suzuki T (2007) Phase-field modeling for electrodeposition process. *Sci Technol Adv Mater* 8(6):511
59. Liang L, Qi Y, Xue F, Bhattacharya S, Harris SJ, Chen LQ (2012) Nonlinear phase-field model for electrode-electrolyte interface evolution. *Phys Rev E* 86(5):051609
60. Ely DR, Jana A, García RE (2014) Phase field kinetics of lithium electrodeposits. *J Power Sources* 272:581
61. Chen L, Zhang HW, Liang LY, Liu Z, Qi Y, Lu P, Chen J, Chen LQ (2015) Modulation of dendritic patterns during electrodeposition: a nonlinear phase-field model. *J Power Sources* 300:376
62. Cogswell DA (2015) Quantitative phase-field modeling of dendritic electrodeposition. *Phys Rev E* 92(1):011301
63. Monroe C, Newman J (2004) The effect of interfacial deformation on electrodeposition kinetics. *J Electrochem Soc* 151(6):A880
64. Ganser M, Hildebrand FE, Klinsmann M, Hanauer M, Kamlah M, McMeeking RM (2019) An extended formulation of butler-volmer electrochemical reaction kinetics including the influence of mechanics. *J Electrochem Soc* 166(4):H167
65. Monroe C, Newman J (2005) The impact of elastic deformation on deposition kinetics at lithium/polymer interfaces. *J Electrochem Soc* 152(2):A396
66. Yu S, Siegel DJ (2018) Grain boundary softening: a potential mechanism for lithium metal penetration through stiff solid electrolytes. *ACS Appl Mater Interfaces* 10(44):38151
67. Tian HK, Liu Z, Ji Y, Chen LQ, Qi Y (2019) Interfacial electronic properties dictate Li dendrite growth in solid electrolytes. *Chem Mater* 31(18):7351
68. Klinsmann M, Hildebrand FE, Ganser M, McMeeking RM (2019) Dendritic cracking in solid electrolytes driven by lithium insertion. *J Power Sources* 442:227226
69. Tian HK, Xu B, Qi Y (2018) Computational study of lithium nucleation tendency in Li₇La₃Zr₂O₁₂ (LLZO) and rational design of interlayer materials to prevent lithium dendrites. *J Power Sources* 392:79
70. Barai P, Higa K, Srinivasan V (2017) Effect of initial state of lithium on the propensity for dendrite formation: a theoretical study. *J Electrochem Soc* 164(2):A180
71. Ahmad Z, Viswanathan V (2017) Stability of electrodeposition at solid-solid interfaces and implications for metal anodes. *Phys Rev Lett* 119:056003
72. Ahmad Z, Viswanathan V (2017) Role of anisotropy in determining stability of electrodeposition at solid-solid interfaces. *Phys Rev Mater* 1:055403
73. Natsiavas P, Weinberg K, Rosato D, Ortiz M (2016) Effect of prestress on the stability of electrode-electrolyte interfaces during charging in lithium batteries. *J Mech Phys Solids* 95:92
74. McMeeking RM, Ganser M, Klinsmann M, Hildebrand FE (2019) Metal electrode surfaces can roughen despite the constraint of a stiff electrolyte. *J Electrochem Soc* 166(6):A984. <https://doi.org/10.1149/2.0221906jes>
75. Barai P, Higa K, Srinivasan V (2017) Lithium dendrite growth mechanisms in polymer electrolytes and prevention strategies. *Phys Chem Chem Phys* 19:20493
76. Wang Y, Cheng YT (2017) A nanoindentation study of the viscoplastic behavior of pure lithium. *Scr Mater* 130:191
77. Xu C, Ahmad Z, Aryanfar A, Viswanathan V, Greer JR (2017) Enhanced strength and temperature dependence of mechanical properties of Li at small scales and its implications for Li metal anodes. *Proc Natl Acad Sci* 114(1):57
78. LePage WS, Chen Y, Kazyak E, Chen KH, Sanchez AJ, Poli A, Arruda EM, Thouless MD, Dasgupta NP (2019) Lithium mechanics: roles of strain rate and temperature and implications for lithium metal batteries. *J Electrochem Soc* 166(2):A89
79. Masias A, Felten N, Garcia-Mendez R, Wolfenstine J, Sakamoto J (2019) Elastic, plastic, and creep mechanical properties of lithium metal. *J Mater Sci* 54(3):2585
80. Fincher CD, Ojeda D, Zhang Y, Pharr GM, Pharr M (2020) Mechanical properties of metallic lithium: from nano to bulk scales. *Acta Mater* 186:215
81. Schultz RP (2002) Lithium: measurement of young's modulus and yield strength. Tech. rep. Fermi National Accelerator Lab., Batavia, IL (US)

82. Ferrese A, Newman J (2014) Mechanical deformation of a lithium-metal anode due to a very stiff separator. *J Electrochem Soc* 161(9):A1350
83. Barai P, Higa K, Srinivasan V (2017) Lithium dendrite growth mechanisms in polymer electrolytes and prevention strategies. *Phys Chem Chem Phys* 19(31):20493
84. Anand L, Narayan S (2019) An elastic-viscoplastic model for lithium. *J Electrochem Soc* 166(6):A1092
85. Wenzel S, Sedlmaier SJ, Dietrich C, Zeier WG, Janek J (2018) Interfacial reactivity and interphase growth of argyrodite solid electrolytes at lithium metal electrodes. *Solid State Ion* 318:102
86. Wang S, Xu H, Li W, Dolocan A, Manthiram A (2017) Interfacial chemistry in solid-state batteries: formation of interphase and its consequences. *J Am Chem Soc* 140(1):250
87. Tippens J, Miers J, Afshar A, Lewis J, Cortes FJQ, Qiao H, Marchese TS, Di Leo CV, Saldana C, McDowell MT (2019) Visualizing chemo-mechanical degradation of a solid-state battery electrolyte. *ACS Energy Lett* 4:1475–1483
88. Leo CVD, Rejovitzky E, Anand L (2015) Diffusion deformation theory for amorphous silicon anodes: the role of plastic deformation on electrochemical performance. *Int J Solids Struct* 67–68:283
89. Rejovitzky E, Di Leo CV, Anand L (2015) A theory and a simulation capability for the growth of a solid electrolyte interphase layer at an anode particle in a Li-ion battery. *J Mech Phys Solids* 78:210
90. Loeffel K, Anand L (2011) A chemo-thermo-mechanically coupled theory for elastic-viscoplastic deformation, diffusion, and volumetric swelling due to a chemical reaction. *Int J Plast* 27(9):1409
91. Busso EP, Qian ZQ (2006) A mechanistic study of microcracking in transversely isotropic ceramic-metal systems. *Acta Mater* 54(2):325
92. Karlsson AM, Xu T, Evans A (2002) The effect of the thermal barrier coating on the displacement instability in thermal barrier systems. *Acta Mater* 50(5):1211
93. Loeffel K, Anand L, Gasem ZM (2013) On modeling the oxidation of high-temperature alloys. *Acta Mater* 61(2):399
94. Zhao Y, Chen Y, Ai S, Fang D (2019) A diffusion, oxidation reaction and large viscoelastic deformation coupled model with applications to SiC fiber oxidation. *Int J Plast* 118:173
95. Salvadori A, McMeeking R, Grazioli D, Magri M (2018) A coupled model of transport-reaction-mechanics with trapping. Part I—small strain analysis. *J Mech Phys Solids* 114:1
96. Di Leo CV, Anand L (2013) Hydrogen in metals: a coupled theory for species diffusion and large elastic-plastic deformations. *Int J Plast* 43:42
97. Anand L, Mao Y, Talamini B (2019) On modeling fracture of ferritic steels due to hydrogen embrittlement. *J Mech Phys Solids* 122:280
98. Miede C, Dal H, Schänzel LM, Raina A (2016) A phase-field model for chemo-mechanical induced fracture in lithium-ion battery electrode particles. *Int J Numer Methods Eng* 106(9):683
99. Han X, Gong Y, Fu KK, He X, Hitz GT, Dai J, Pearse A, Liu B, Wang H, Rubloff G et al (2017) Negating interfacial impedance in garnet-based solid-state Li metal batteries. *Nat Mater* 16(5):572
100. Ganser M, Hildebrand FE, Kamlah M, McMeeking RM (2019) A finite strain electro-chemo-mechanical theory for ion transport with application to binary solid electrolytes. *J Mech Phys Solids* 125:681
101. Newman J, Thomas-Alyea KE (2012) *Electrochemical systems*. Wiley, New York
102. Bucci G, Chiang YM, Carter WC (2016) Formulation of the coupled electrochemical-mechanical boundary-value problem, with applications to transport of multiple charged species. *Acta Mater* 104:33
103. Grazioli D, Zadin V, Brandell D, Simone A (2019) Electrochemical-mechanical modeling of solid polymer electrolytes: stress development and non-uniform electric current density in trench geometry microbatteries. *Electrochim Acta* 296:1142
104. Zavattieri P, Raghuram P, Espinosa H (2001) A computational model of ceramic microstructures subjected to multi-axial dynamic loading. *J Mech Phys Solids* 49(1):27
105. Templeton DW, Holmquist TJ, MEYER HW, Grove DJ, Leavy B (2002) A comparison of ceramic material models. *Ceram Trans* 134:299
106. Deshpande VS, Gamble EN, Compton BG, McMeeking RM, Evans AG, Zok FW (2011) A constitutive description of the inelastic response of ceramics. *J Am Ceram Soc* 94:s204
107. Deshpande V, Evans A (2008) Inelastic deformation and energy dissipation in ceramics: a mechanism-based constitutive model. *J Mech Phys Solids* 56(10):3077
108. Holland CC, McMeeking RM (2015) The influence of mechanical and microstructural properties on the rate-dependent fracture strength of ceramics in uniaxial compression. *Int J Impact Eng* 81:34
109. Espinosa HD, Zavattieri PD, Dwivedi SK (1998) A finite deformation continuum\discrete model for the description of fragmentation and damage in brittle materials. *J Mech Phys Solids* 46(10):1909
110. Ashby M, Sammis C (1990) The damage mechanics of brittle solids in compression. *Pure Appl Geophys* 133(3):489
111. Kimberley J, Ramesh K, Daphalapurkar N (2013) A scaling law for the dynamic strength of brittle solids. *Acta Mater* 61(9):3509
112. Rice RW (1977) Microstructure dependence of mechanical behavior of ceramics. In: *Treatise on materials science & technology*, vol 11. Elsevier, pp 199–381
113. Zhang X, Krischok A, Linder C (2016) A variational framework to model diffusion induced large plastic deformation and phase field fracture during initial two-phase lithiation of silicon electrodes. *Comput Methods Appl Mech Eng* 312:51
114. Yamakawa S, Nagasako N, Yamasaki H, Koyama T, Asahi R (2018) Phase-field modeling of stress generation in polycrystalline LiCoO₂. *Solid State Ion* 319:209
115. Ke X, Wang Y, Ren G, Yuan C (2019) Towards rationally mechanical design of inorganic solid electrolytes for all-solid-state lithium ion batteries. *Energy Storage Mater* 26:313–324

116. Deng Z, Wang Z, Chu IH, Luo J, Ong SP (2016) Elastic properties of alkali superionic conductor electrolytes from first principles calculations. *J Electrochem Soc* 163(2):A67
117. Kresse G, Joubert D (1999) From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys Rev B* 59(3):1758
118. Pugh S (1954) XCII. Relations between the elastic moduli and the plastic properties of polycrystalline pure metals. *Lond Edinb Dublin Philos Mag J Sci* 45(367):823
119. Wu M, Xu B, Lei X, Huang K, Ouyang C (2018) Bulk properties and transport mechanisms of a solid state antiperovskite Li-ion conductor Li₃ OCl: insights from first principles calculations. *J Mater Chem A* 6(3):1150
120. Mattesini M, Soler JM, Ynduráin F (2006) Ab initio study of metal-organic framework-5 Zn₄ O(1,4- benzenedicarboxylate)₃: an assessment of mechanical and spectroscopic properties. *Phys Rev B* 73:094111
121. Wang Z, Wu M, Liu G, Lei X, Xu B, Ouyang C (2014) Elastic properties of new solid state electrolyte material Li₁₀GeP₂S₁₂: a study from first-principles calculations. *Int J Electrochem Sci* 9(2):562
122. Yang Y, Wu Q, Cui Y, Chen Y, Shi S, Wang RZ, Yan H (2016) Elastic properties, defect thermodynamics, electrochemical window, phase stability, and Li⁺ mobility of Li₃PS₄: insights from first-principles calculations. *ACS Appl Mater Interfaces* 8(38):25229
123. Chen H, Hong T (2019) First-principles investigation of the mechanical and thermodynamic properties of the metal-borohydrides as electrolytes for solid-state batteries. *J Electrochem Soc* 166(4):A493
124. Ahmad Z, Viswanathan V (2016) Quantification of uncertainty in first-principles predicted mechanical properties of solids: application to solid ion conductors. *Phys Rev B* 94(6):064105
125. White A (2012) The materials genome initiative: one year on. *MRS Bull* 37(8):715
126. Kaufman L, Ågren J (2014) CALPHAD, first and second generation—birth of the materials genome. *Scr Mater* 70:3
127. Jain A, Ong SP, Hautier G, Chen W, Richards WD, Dacek S, Cholia S, Gunter D, Skinner D, Ceder G et al (2013) Commentary: the materials project: a materials genome approach to accelerating materials innovation. *Apl Mater* 1(1):011002
128. Rajan K (2005) Materials informatics. *Mater Today* 8(10):38
129. Ramprasad R, Batra R, Pilania G, Mannodi-Kanakkithodi A, Kim C (2017) Machine learning in materials informatics: recent applications and prospects. *NPJ Comput Mater* 3(1):54
130. Agrawal A, Choudhary A (2016) Perspective: materials informatics and big data: realization of the “fourth paradigm” of science in materials science. *Apl Mater* 4(5):053208
131. Makeev MA, Rajput NN (2019) Computational screening of electrolyte materials: status quo and open problems. *Curr Opin Chem Eng* 23:58
132. Bhowmik A, Castelli IE, Garcia-Lastra JM, Jørgensen PB, Winther O, Vegge T (2019) A perspective on inverse design of battery interphases using multi-scale modelling, experiments and generative deep learning. *Energy Storage Mater* 21:446–456
133. Ahmad Z, Xie T, Maheshwari C, Grossman JC, Viswanathan V (2018) Machine learning enabled computational screening of inorganic solid electrolytes for suppression of dendrite formation in lithium metal anodes. *ACS Central Sci* 4(8):996
134. Tsai CL, Roddatis V, Chandran CV, Ma Q, Uhlenbruck S, Bram M, Heitjans P, Guillon O (2016) Li₇La₃Zr₂O₁₂ interface modification for Li dendrite prevention. *ACS Appl Mater Interfaces* 8(16):10617
135. Woodford W, Chiang Y, Carter W (2010) “Electrochemical shock” of intercalation electrodes: a fracture mechanics analysis. *J Electrochem Soc* 157(10):A1052
136. Zhao K, Pharr M, Vlassak JJ, Suo Z (2010) Fracture of electrodes in lithium-ion batteries caused by fast charging. *J Appl Phys* 108(7):073517
137. Bai P, Cogswell D, Bazant M (2011) Suppression of phase separation in LiFePO₄ nanoparticles during battery discharge. *Nano Lett* 11(11):4890–4896
138. Cogswell DA, Bazant MZ (2013) Theory of coherent nucleation in phase-separating nanoparticles. *Nano Lett* 13(7):3036
139. Bohn E, Eckl T, Kamlah M, McMeeking R (2013) A model for lithium diffusion and stress generation in an intercalation storage particle with phase change. *J Electrochem Soc* 160(10):A1638
140. Purkayastha R, McMeeking R (2016) Stress due to the intercalation of lithium in cubic-shaped particles: a parameter study. *Meccanica* 51(12):3081
141. Di Leo C, Rejovitzky E, Anand L (2014) A Cahn–Hilliard-type phase-field theory for species diffusion coupled with large elastic deformations: application to phase-separating Li-ion electrode materials. *J Mech Phys Solids* 70:1
142. Zhao K, Pharr M, Cai S, Vlassak J, Suo Z (2011) Large plastic deformation in high-capacity lithium-ion batteries caused by charge and discharge. *J Am Ceram Soc* 94(s1):s226–s235
143. Bower AF, Guduru P (2012) A simple finite element model of diffusion, finite deformation, plasticity and fracture in lithium ion insertion electrode materials. *Modell Simul Mater Sci Eng* 20(4):045004
144. Anand L (2012) A Cahn–Hilliard-type theory for species diffusion coupled with large elastic-plastic deformations. *J Mech Phys Solids* 60(12):1983
145. Cui Z, Gao F, Qu J (2012) A finite deformation stress-dependent chemical potential and its applications to lithium ion batteries. *J Mech Phys Solids* 60(7):1280
146. Bucci G, Nadimpalli S, Sethuraman V, Bower A, Guduru P (2014) Measurement and modeling of the mechanical and electrochemical response of amorphous Si thin film electrodes during cyclic lithiation. *J Mech Phys Solids* 62:276
147. Lyu D, Ren B, Li S (2019) Failure modes and mechanisms for rechargeable Lithium-based batteries: a state-of-the-art review. *Acta Mech* 230(3):701
148. Cogswell DA, Bazant MZ (2018) Size-dependent phase morphologies in LiFePO₄ battery particles. *Electrochem Commun* 95:33
149. Nadkarni N, Rejovitsky E, Fraggadakis D, Di Leo CV, Smith RB, Bai P, Bazant MZ (2018) Interplay of phase boundary anisotropy and electro-auto-catalytic surface

- reactions on the lithium intercalation dynamics in Li X FePO₄ plateletlike nanoparticles. *Phys Rev Mater* 2(8):085406
150. Zhang T, Kamlah M (2019) Phase-field modeling of the particle size and average concentration dependent miscibility gap in nanoparticles of Li_xMn₂O₄, Li_xFePO₄, and Na_xFePO₄ during insertion. *Electrochim Acta* 298:31
151. Bower A, Guduru P, Sethuraman V (2011) A finite strain model of stress, diffusion, plastic flow, and electrochemical reactions in a lithium-ion half-cell. *J Mech Phys Solids* 59(4):804
152. Zhang T, Kamlah M (2020) Mechanically Coupled Phase-Field Modeling of Microstructure Evolution in Sodium Ion Batteries Particles of Na_xFePO₄. *J Electrochem Soc* 167(2):020508
153. McDowell MT, Xia S, Zhu T (2016) The mechanics of large-volume-change transformations in high-capacity battery materials. *Extreme Mech Lett* 9:480
154. Huang S, Fan F, Li J, Zhang S, Zhu T (2013) Stress generation during lithiation of high-capacity electrode particles in lithium ion batteries. *Acta Mater* 61(12):4354
155. Bower AF, Guduru PR, Chason E (2015) Analytical solutions for composition and stress in spherical elastic-plastic lithium-ion electrode particles containing a propagating phase boundary. *Int J Solids Struct* 69:328
156. Wu H, Chan G, Choi JW, Ryu I, Yao Y, McDowell MT, Lee SW, Jackson A, Yang Y, Hu L et al (2012) Stable cycling of double-walled silicon nanotube battery anodes through solid-electrolyte interphase control. *Nat Nanotechnol* 7(5):310
157. Sethuraman VA, Chon MJ, Shimshak M, Srinivasan V, Guduru PR (2010) In situ measurements of stress evolution in silicon thin films during electrochemical lithiation and delithiation. *J Power Sources* 195(15):5062
158. Sethuraman VA, Van Winkle N, Abraham DP, Bower AF, Guduru PR (2012) Real-time stress measurements in lithium-ion battery negative-electrodes. *J Power Sources* 206:334
159. Nadimpalli SP, Sethuraman VA, Bucci G, Srinivasan V, Bower AF, Guduru PR (2013) On plastic deformation and fracture in Si films during electrochemical lithiation/delithiation cycling. *J Electrochem Soc* 160(10):A1885
160. Pharr M, Suo Z, Vlassak JJ (2014) Variation of stress with charging rate due to strain-rate sensitivity of silicon electrodes of Li-ion batteries. *J Power Sources* 270:569
161. Pharr M, Suo Z, Vlassak JJ (2013) Measurements of the fracture energy of lithiated silicon electrodes of Li-ion batteries. *Nano Lett* 13(11):5570
162. Sethuraman VA, Nguyen A, Chon MJ, Nadimpalli SP, Wang H, Abraham DP, Bower AF, Shenoy VB, Guduru PR (2013) Stress evolution in composite silicon electrodes during lithiation/delithiation. *J Electrochem Soc* 160(4):A739
163. Nadimpalli SP, Sethuraman VA, Abraham DP, Bower AF, Guduru PR (2015) Stress evolution in lithium-ion composite electrodes during electrochemical cycling and resulting internal pressures on the cell casing. *J Electrochem Soc* 162(14):A2656
164. Zhang Y, Luo Y, Fincher C, McProuty S, Swenson G, Banerjee S, Pharr M (2019) In-situ measurements of stress evolution in composite sulfur cathodes. *Energy Storage Mater* 16:491
165. Zhao K, Wang WL, Gregoire J, Pharr M, Suo Z, Vlassak JJ, Kaxiras E (2011) Lithium-assisted plastic deformation of silicon electrodes in lithium-ion batteries: a first-principles theoretical study. *Nano Lett* 11(7):2962
166. Huang S, Zhu T (2011) Atomistic mechanisms of lithium insertion in amorphous silicon. *J Power Sources* 196(7):3664
167. Yan X, Gouissem A, Sharma P (2015) Atomistic insights into Li-ion diffusion in amorphous silicon. *Mech Mater* 91:306
168. Yan X, Gouissem A, Guduru PR, Sharma P (2017) Elucidating the atomistic mechanisms underpinning plasticity in Li-Si nanostructures. *Phys Rev Mater* 1(5):055401
169. Darbaniyan F, Yan X, Sharma P (2020) An atomistic perspective on the effect of strain rate and lithium fraction on the mechanical behavior of silicon electrodes. *J Appl Mech* 87(3):031011
170. Koerver R, Aygn I, Leichtweiß T, Dietrich C, Zhang W, Binder JO, Hartmann P, Zeier WG, Janek J (2017) Capacity fade in solid-state batteries: interphase formation and chemomechanical processes in nickel-rich layered oxide cathodes and lithium thiophosphate solid electrolytes. *Chem Mater* 29(13):5574
171. Zhang W, Schröder D, Arlt T, Manke I, Koerver R, Pinedo R, Weber DA, Sann J, Zeier WG, Janek J (2017) (Electro) chemical expansion during cycling: monitoring the pressure changes in operating solid-state lithium batteries. *J Mater Chem A* 5(20):9929
172. Bucci G, Swamy T, Bishop S, Sheldon BW, Chiang YM, Carter WC (2017) The effect of stress on battery-electrode capacity. *J Electrochem Soc* 164(4):A645
173. Wan TH, Ciucci F (2020) Electro-chemo-mechanical modeling of solid-state batteries. *Electrochim Acta* 331:135355
174. Garcia R, Chiang Y, Carter W, Limthongkul P, Bishop C (2005) Microstructural modeling and design of rechargeable lithium-ion batteries. *J Electrochem Soc* 152(1):A255
175. Xu R, Yang Y, Yin F, Liu P, Cloetens P, Liu Y, Lin F, Zhao K (2019) Heterogeneous damage in Li-ion batteries: experimental analysis and theoretical modeling. *J Mech Phys Solids* 129:160
176. Renganathan S, Sikha G, Santhanagopalan S, White R (2010) Theoretical analysis of stresses in a lithium ion cell. *J Electrochem Soc* 157(2):A155
177. Christensen J (2010) Modeling diffusion-induced stress in Li-ion cells with porous electrodes. *J Electrochem Soc* 157(3):A366
178. Ferguson T, Bazant M (2012) Nonequilibrium thermodynamics of porous electrodes. *J Electrochem Soc* 159(12):A1967
179. Purkayastha R, McMeeking R (2012) A linearized model for lithium ion batteries and maps for their performance and failure. *J Appl Mech* 79(3):031021
180. Hofmann T, Westhoff D, Feinauer J, Andrä H, Zausch J, Schmidt V, Müller R (2020) Electro-chemo-mechanical simulation for lithium ion batteries across the scales. *Int J Solids Struct* 184:24
181. Yu HC, Taha D, Thompson T, Taylor NJ, Drews A, Sakamoto J, Thornton K (2019) Deformation and stresses

- in solid-state composite battery cathodes. *J Power Sources* 440:227116
182. Bucci G, Swamy T, Chiang YM, Carter WC (2017) Modeling of internal mechanical failure of all-solid-state batteries during electrochemical cycling, and implications for battery design. *J Mater Chem A* 5(36):19422
 183. Bucci G, Talamini B, Balakrishna A, Chiang Y, Carter W (2018) Mechanical instability of electrode-electrolyte interfaces in solid-state batteries. *Phys Rev Mater* 2(10):105407
 184. Mykhaylov M, Ganser M, Klinsmann M, Hildebrand F, Guz I, McMeeking R (2019) An elementary 1-dimensional model for a solid state lithium-ion battery with a single ion conductor electrolyte and a lithium metal negative electrode. *J Mech Phys Solids* 123:207
 185. Bielefeld A, Weber DA, Janek J (2018) Microstructural modeling of composite cathodes for all-solid-state batteries. *J Phys Chem C* 123(3):1626
 186. Bucci G, Swamy T, Chiang YM, Carter WC (2017) Random walk analysis of the effect of mechanical degradation on all-solid-state battery power. *J Electrochem Soc* 164(12):A2660
 187. Al-Siraj M, Stein P, Xu BX (2020) The effect of morphology changes and mechanical stresses on the effective diffusivity of solid electrolyte for lithium ion batteries. *J Electrochem Soc* 167(2):020535
 188. Bhandakkar T, Gao H (2010) Cohesive modeling of crack nucleation under diffusion induced stresses in a thin strip: Implications on the critical size for flaw tolerant battery electrodes. *Int J Solids Struct* 47(10):1424
 189. Bhandakkar T, Gao H (2011) Cohesive modeling of crack nucleation in a cylindrical electrode under axisymmetric diffusion induced stresses. *Int J Solids Struct* 48(16–17):2304
 190. Miehe C, Welschinger F, Hofacker M (2010) Thermodynamically consistent phase-field models of fracture: variational principles and multi-field FE implementations. *Int J Numer Methods Eng* 83(10):1273
 191. Borden M, Verhoosel C, Scott M, Hughes R, Landis C (2012) A phase-field description of dynamic brittle fracture. *Comput Methods Appl Mech Eng* 217:77
 192. Miehe C, Welschinger F, Hofacker M (2010) A phase field model of electromechanical fracture. *J Mech Phys Solids* 58(10):1716
 193. Klinsmann M, Rosato D, Kamlah M, McMeeking R (2016) Modeling crack growth during Li insertion in storage particles using a fracture phase field approach. *J Mech Phys Solids* 92:313–344
 194. Klinsmann M, Rosato D, Kamlah M, McMeeking RM (2016) Modeling crack growth during Li extraction in storage particles using a fracture phase field approach. *J Electrochem Soc* 163(2):A102
 195. Klinsmann M, Rosato D, Kamlah M, McMeeking RM (2016) Modeling crack growth during Li extraction and insertion within the second half cycle. *J Power Sources* 331:32
 196. Hao F, Mukherjee PP (2018) Mesoscale analysis of the electrolyte-electrode interface in all-solid-state Li-ion batteries. *J Electrochem Soc* 165:A1857

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.