CHEMISTRY OF MATERIALS

Toward High-Capacity Battery Anode Materials: Chemistry and Mechanics Intertwined‖

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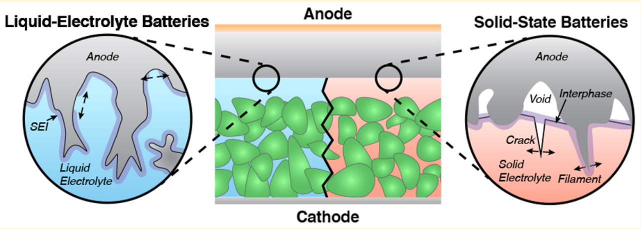

ABSTRACT: Lithium metal and lithium-rich alloys are high-capacity anode materials that could boost the energy content of rechargeable batteries. However, their development has been hindered by rapid capacity decay during cycling, which is driven by the substantial structural, morphological, and volumetric transformations that these materials and their interfaces experience during charge and discharge. During these transformations, the interplay between chemical/structural changes and solid mechanics plays a defining role in determining electrochemical degradation. This Perspective discusses how chemistry and mechanics are interrelated in influencing the reaction mechanisms, stability, and performance of both lithium metal anodes and alloy anodes. Battery systems with liquid electrolytes and solid-state electrolytes are considered because of the distinct effects of chemo-mechanics in each system. Building on this knowledge, we present a discussion of emerging ideas to control and mitigate chemo-mechanical degradation in these materials to enable translation to commercial systems, which could lead to the development of high-energy batteries that are urgently needed to power our increasingly electrified world.

1. CHEMO-MECHANICAL CONSIDERATIONS FOR BATTERY ANODES

Continued improvements and cost reductions of Li-ion batteries have enabled the rapid expansion of the electric vehicle market, but increased energy density and specific energy are required for further proliferation of electric vehicles as well as for emerging applications such as electric flight.[1,2] A promising pathway to higher energy is replacing the electrode materials in Li-ion batteries with materials that can hold more Li per unit weight and/or volume. The exchange of conventional graphite anodes with Li alloys, or even Li metal itself, could boost specific energy and energy density by 30–50% (Figure 1).[2−5] As such, the understanding, development, and engineering of alloy anodes and Li metal have received extensive research attention in recent years. The defining feature of these promising anode materials is that they undergo substantial morphological changes during charge and discharge with large volumetric expansion and contraction accompanied by structural transformations and interfacial reactions. This is in contrast to conventional Li-ion battery materials, which undergo intercalation reactions and thus reversibly incorporate Li^+ ions within largely invariant crystal structures.

The links between electrochemical transformations and solid mechanics often play a defining role in the behavior and stability of alloy and Li metal anodes. This connection is a consequence of the extensive morphological, volumetric, and structural changes during charge/discharge, which give rise to mechanical stress and cause chemo-mechanical degradation such as fracture or contact loss during cycling (Figure 2).[6,7] Moreover, stress and strain can influence chemical transformation pathways by altering kinetics or thermodynamics in the system,[8] and chemo-mechanics influences the formation of interphases between materials. While many high-capacity anode materials can undergo a few charge/discharge cycles without significant decay, the achievement of hundreds or thousands of cycles to match Li-ion batteries is a major challenge. Understanding and controlling how electrochemical reaction mechanisms and stability in high-capacity anode materials are affected by mechanical stress and damage are thus key steps for the development of next-generation batteries.

The goal of this Perspective is to describe how chemistry and mechanics are interrelated in determining reaction mechanisms, stability, and performance of high-capacity anode materials for batteries and, in so doing, reveal common themes and similarities among different materials and systems. These aspects then provide the foundation for an outlook on emerging ideas related to engineering these materials for battery applications. Three different topics are focused upon:

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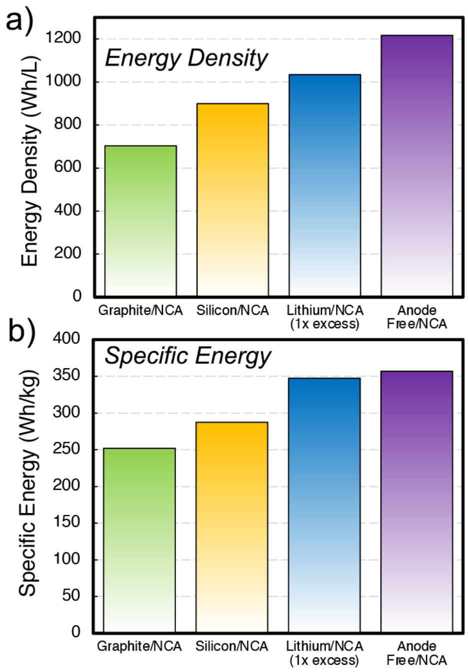

Figure 1. (a) Projected energy density (Wh/L) and (b) specific energy (Wh/kg) for combinations of different anodes (graphite, silicon alloy, and lithium) with a typical high-capacity intercalation cathode ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, NCA). "Anode-free" refers to the case when no extra Li metal is used in a cell, but all Li^+ is initially contained in the cathode. These calculations take into account the volume and mass of the electrodes and other cell components (see the Supporting Information and Figure S1 for details).

(1) Li metal anodes, (2) alloy anodes, and (3) the interface between electrode materials and the electrolyte. Both liquid-electrolyte and solid-state battery systems are considered, since chemo-mechanical phenomena within both systems are important but can be quite different. Although the development of high-capacity intercalation cathodes is also an important route to higher-energy batteries,[9] a discussion of such materials involves distinct scientific concepts and is not included herein. When one synthesizes the knowledge, perspectives, and ideas about these different classes of anode materials and battery systems, it is hoped that this Perspective will provide clarity toward designing new materials with controlled chemo-mechanical interactions for high-energy, long-lifetime batteries.

2. LITHIUM METAL ANODES

Li metal is the ideal anode for use in Li^+-based rechargeable batteries, as it can yield the highest specific energy and energy density of any Li-based anode.[3,5,10,11] Na metal is also attractive for use in Na^+-based systems.[12] Major challenges have prevented the use of alkali metals in rechargeable liquid-based batteries (Figure 2), including lack of control over the deposition morphology of the metal,[13] the formation of "dead" or inactive metal that is detached from the current collector,[14,15] dendritic electrodeposition of Li that can cause short circuits,[13,16] continuous solid-electrolyte interphase (SEI) formation,[10] and direct corrosion of the metal.[17] Recent work has also revealed related challenges when using alkali metals in solid-state batteries (SSBs),[18] including maintaining interfacial contact during stripping,[19−21] filamentary growth through dense solid-state electrolytes (SSEs),[22,23] and instabilities at the interface to form new interphase regions (Figure 2).[24−26] In both solid-state and liquid-based batteries, these challenges are compounded by the fact that minimal excess Li can be used to maintain high specific energy and energy density of the battery;[11,27−29] thus, any degradation process that consumes Li and reduces Coulombic efficiency will cause rapid capacity decay.[30] The interplay between chemical and mechanical effects is an important aspect of many

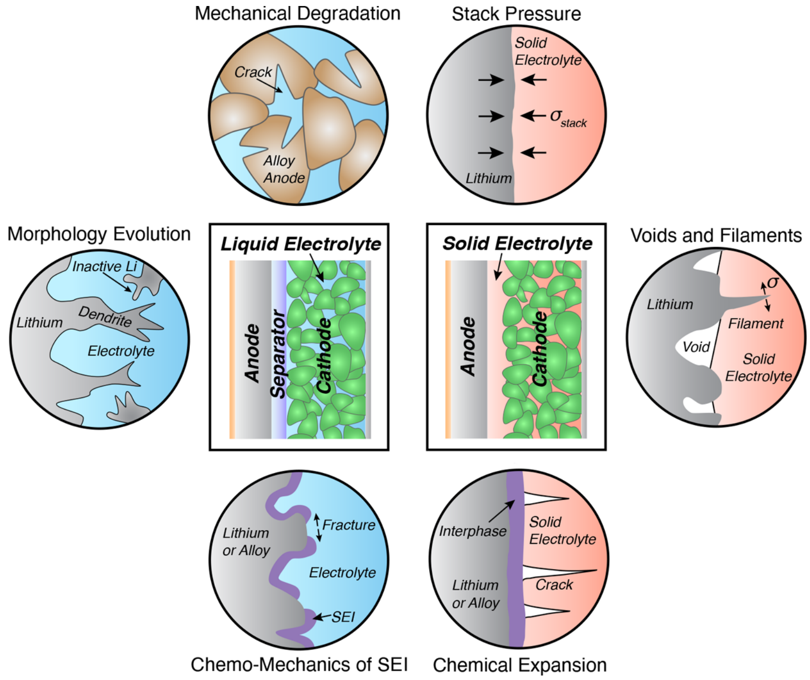

Figure 2. Chemo-mechanical phenomena in alloy and Li metal anodes for high-energy batteries. Various phenomena are shown for liquid-electrolyte batteries (left, with blue denoting liquid electrolyte) and solid-state batteries (right, with red denoting solid electrolyte).

of these degradation mechanisms, as mechanical stress generated within the material or externally applied to the cell can affect alkali metal morphology evolution during charge and discharge, among other factors. Chemo-mechanical effects are different in solid-state and liquid-based batteries, and both will be discussed in this section.

2.1. Mechanical Properties. To understand the effects of stress and strain on reaction pathways, it is important to consider the mechanical properties and deformation behavior of Li and other alkali metals. In general, measuring the mechanical properties of these materials is not straightforward due to their reactivity with moisture and other species, but a number of recent experimental efforts have developed innovative methods for reliable measurements.[31−41] Alkali metals exhibit low stiffness, and the bulk materials yield and flow at low applied stress. The yield strength of bulk Li has recently been measured to be below 1 MPa at room temperature (Figure 3a,b),[31,33,40] while that for Na is even lower (~0.25 MPa).[32,39] This is orders of magnitude below typical metals, and these low values indicate that these metals can flow and deform in response to the stress levels typically present within battery cells. Importantly, Li and Na have also been shown to undergo extensive creep deformation at room temperature,[31−33] meaning that the materials can undergo deformation in response to stresses even below their yield strength. Of particular relevance to batteries, both Li and Na metal have recently been shown to exhibit substantially higher yield strength at smaller length scales (Figure 3c),[35,39−42] indicating that small particles or grains that may form during electrodeposition could have very different mechanical properties than uniformly deposited Li. This finding may influence Li filament growth in SSBs as well as morphology evolution under stack pressure in liquid-electrolyte batteries, as discussed in the sections below. Finally, Li metal deposited in real batteries has been shown to exhibit different mechanical behavior than bulk Li due to differing microstructure and porosity,[37] demonstrating the importance of investigating materials created under realistic battery conditions.

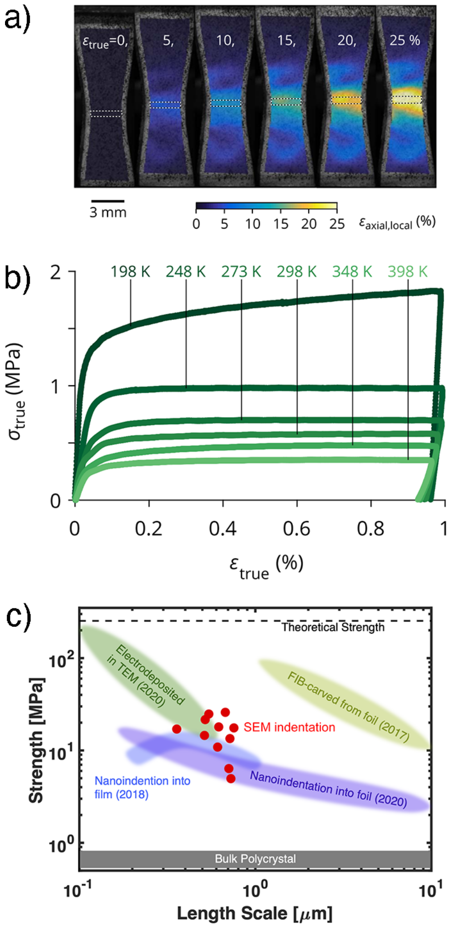

Figure 3. Measurement of the mechanical properties of Li metal. (a) Tensile tests on bulk Li using digital image correlation. (b) Stress–strain curves from bulk Li tensile tests at different temperatures. (a, b) Reproduced with permission from ref 31 without changes under the Creative Commons CC BY license (https://creativecommons.org/licenses/by/4.0/). Copyright 2019 IOPscience. (c) Size-dependent strength of Li. The plot shows results from SEM nanoindentation experiments measuring the strength of Li filaments directly grown from a solid-state battery (red points), along with general data trends from related studies. Reproduced with permission from ref 42. Copyright 2020 Cambridge University Press.

2.2. Li Morphology Evolution in Liquid Electrolytes. The growth of Li filaments (also termed *dendrites*) during charging has long plagued the development of rechargeable Li anodes, and this problem manifests in both liquid and solid-state batteries. Numerous problems arise from nonuniform metal deposition: filaments can grow across the cell to contact the cathode and short circuit the battery,[43] and filamentary growth can also increase the likelihood of physical disconnection of the metal from the electrode to create inactive "dead" Li.[10,15,44] In liquids, dendritic electrodeposition of Li can be driven by transport limitations in the liquid electrolyte or on surfaces,[16,45−47] as expected on the basis of classical theories of dendritic growth. However, factors other than transport also influence growth behavior: the morphology of Li varies widely when deposited in different liquid electrolytes,[48−51] with different particle sizes[52] and preferential filamentary growth in some systems,[53] as demonstrated in Figure 4a,b. Recent work has shown that temperature also

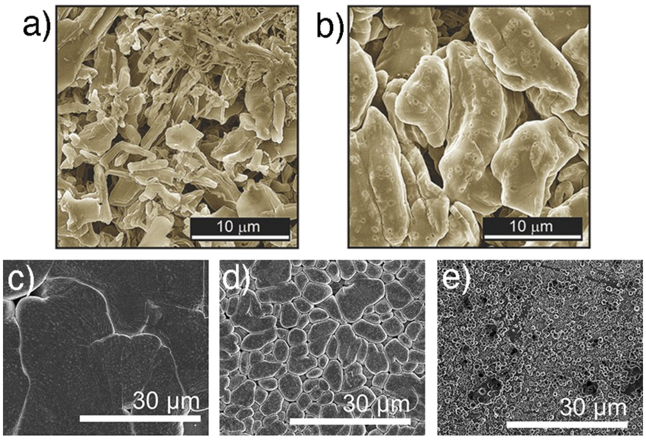

Figure 4. Differing morphologies of Li deposited under different electrochemical conditions. (a, b) SEM images of Li metal deposited in different electrolytes: (a) 1 M $LiPF_6$-EC/DMC electrolyte; (b) 4 M LiFSI-DME electrolyte. Reproduced with permission from ref 164. Copyright 2016 John Wiley and Sons. (c−e) SEM images of 4 mAh/cm^2 of Li metal deposited onto a steel substrate in a DOL/DME-based electrolyte at different temperatures: (c) 60, (d) 20, and (e) −40 °C. The deposited grain size decreases at lower temperatures. Adapted from ref 54. Copyright 2020 American Chemical Society.

strongly influences Li morphology in many liquid electrolytes (Figure 4c–e).[54−57] The variation of deposited Li morphology under different conditions can be critical for determining cyclability and Coulombic efficiency, since large deposited grain size and uniform films are generally preferred to minimize exposed surface area and inactive Li formation.[14,48,58] Recent work has found that the formation of inactive Li through the loss of the electronic connection to the current collector during dissolution of Li is the primary culprit in reducing Coulombic efficiency.[14,59]

In many of the cases mentioned above, the formation, properties, and (in)homogeneity of the solid-electrolyte interphase (SEI) are the major factors that control the Li morphology during growth in liquid electrolytes.[49] SEI films form on the surface of Li due to reductive decomposition of the electrolyte,[60] and different electrolytes cause SEI films to grow that contain different inorganic/organic constituents with divergent properties. Inhomogeneities in the SEI can cause varying reaction rates at different locations, leading to nonuniform Li growth.[50] Deposition temperature strongly affects SEI properties and uniformity, and tailoring the SEI through electrolyte control is a promising pathway to low-temperature batteries.[54] While precisely determining the interlinked dynamics of the simultaneous growth of Li and the SEI is at the forefront of current battery science, the mechanical properties of and physical constraint due to the SEI likely act both to influence the Li morphology during deposition and to cause Li detachment during cycling to result in inactive Li formation. The localized mechanical collapse of SEI shells on the surface of fibrous Li deposits,[14] which can be driven by current concentrations at particular regions of the SEI due to different structure and transport properties,[44] has been implicated in the formation of inactive Li. Such a process requires mechanical crumpling or buckling of the SEI surface layer during Li stripping, and thus, the mechanical properties of the SEI are important. The dynamic chemo-mechanical interactions between Li and the SEI will be further discussed with respect to SEI properties in Section 4.1.

2.3. Effects of Stack Pressure in Liquid Electrolytes.

In addition to the influence of local chemo-mechanical effects on Li metal morphology and filament growth, the global applied stack pressure within the battery cell can also affect the evolution of Li and other alkali metals during cycling. In conventional Li-ion batteries, a stack pressure between 0.1 and 1 MPa is typically applied by the rigid housing of the cell;[61] this pressure is necessary to ensure the full reaction of intercalation electrode materials without local irregularities. In liquid-electrolyte cells with Li metal anodes, the stack pressure plays an even more important role since the volume changes during deposition/stripping are more extreme than in intercalation electrodes. A number of studies have found that applied stack pressures on the order of 1 MPa are important for maintaining a dense and compact Li deposit within liquid-electrolyte batteries,[58,62−64] and this applied pressure also increases the Coulombic efficiency and stability during cycling.[62,65] This behavior likely arises due to the deformation of Li during electrodeposition under stresses that are greater than the yield strength, allowing for Li to yield and flow to fill in initially porous areas within the deposited film.[31] Furthermore, experimental observations have shown that mechanical pressure tends to diminish the formation of Li dendrites or filaments,[64] which has been postulated to be due to creep behavior of Li and pore closure in separators.[66] Finally, recent work has shown that filament growth under applied longitudinal stress, which is expected to be present when Li filaments impinge upon a polymer separator in liquid cells, can cause deformation and buckling of the whisker that increases the propensity for inactive Li formation.[47]

2.4. Lithium Filament Growth in Solid-State Batteries.

Li morphology evolution and filament growth also strongly influence the operation of SSBs. All-solid-state systems exhibit different chemo-mechanical behaviors than batteries with liquid electrolytes because (i) stress and strain can easily be transmitted across solid/solid interfaces, and (ii) the electrode materials are under mechanical constraint from their rigid surroundings, which is in contrast to the stress-relieving capabilities of liquid electrolytes. These concepts were discussed in detail in a recent review paper.[26] Regarding metal filament growth, multiple observations have revealed that Li has a tendency to grow through and fracture inorganic solid-state electrolytes during deposition within SSBs, resulting in short circuits and cell failure (Figure 5a–c).[22,67−69] Li filament growth through stiff inorganic SSEs was initially surprising given prior predictions that solid separators with a shear modulus twice that of Li metal should inhibit filamentary growth.[70] While a full understanding has yet to be attained, recent work has shown that plastic deformation of Li as well as

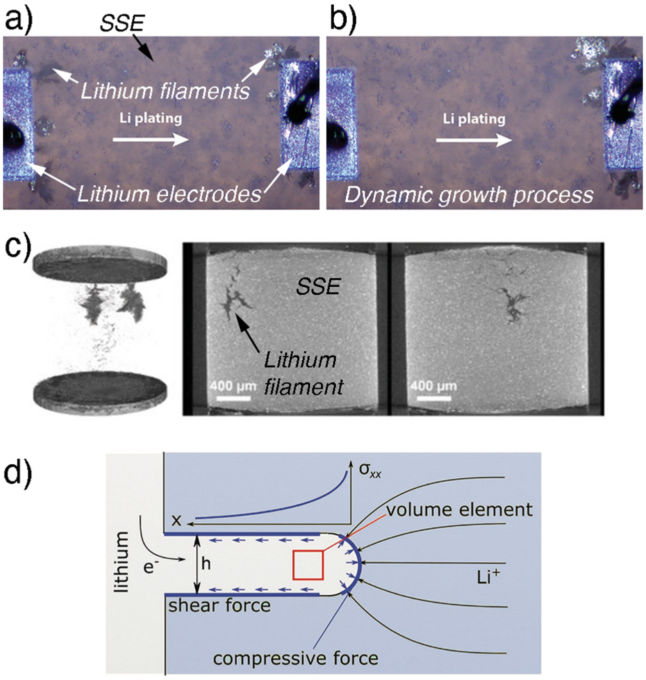

Figure 5. (a, b) *In situ* optical microscopy experiments showing the growth of Li filaments that cause cracks within the $Li_7La_3Zr_2O_{12}$ solid-state electrolyte (SSE). Panel (a) is a snapshot that comes before (b) in time, and the images show filaments receding at the left electrode and growing at the right electrode. Reproduced with permission from ref 23. Copyright 2020 Elsevier. (c) X-ray tomographic imaging of a filament that has penetrated a Li|Li_6PS_5Cl|Li symmetric cell; the left panel shows a 3D image, and the right panels show 2D slices. Reproduced with permission from ref 80. Copyright 2020 John Wiley and Sons. (d) Schematic from the mechanical model of Porz et al.[67] in which Li metal is deposited within a crack in an SSE (blue) and pressure buildup at the crack can cause crack growth and/or extrusion of Li out of the crack. Reproduced with permission from ref 67. Copyright 2017 John Wiley and Sons.

fracture toughness of the ceramic SSE are important in causing filament-induced fracture (Figure 5d).[67,71−74] The higher strength of Li at small length scales likely contributes to causing fracture of SSEs, as Li with nanoscale dimensions deposited at a crack tip could be strong enough to induce crack propagation instead of the metal undergoing plastic flow to be extruded out of the crack. Moreover, only a single filament growing across a solid-state cell is required to cause a short circuit, suggesting that the small fraction of filaments with appropriate structure and size to exhibit a high-enough strength could cause cell failure. Recent efforts have shown that the partial molar volume of alkali ions in both phases at a Li metal/SSE interface is critical for determining the stability of planar metal growth,[75,76] suggesting pathways to stable operation.[77] *In situ* optical microscopy experiments have revealed the variety of different filamentary growth/fracture modes that are possible (Figure 5a,b)[23] and that filaments can be reversibly grown and dissolved within cracks in the SSE. There has also been evidence that Li metal can deposit directly within the bulk of SSEs, potentially because of relatively high electronic conductivity of the SSE.[78] Finally, the confinement of the growing Li metal within controlled one-dimensional templates can aid the reversible growth/dissolution of Li in the solid state via creep along the boundaries with the confining phase.[79] Taken together, these studies have indicated that chemo-mechanical interactions largely determine Li growth behavior in SSBs, and also that improved control over Li morphology evolution is necessary for long-term stability.

2.5. Void Formation at Metal Interfaces in Solid-State Batteries. Plating and stripping processes of Li metal anodes in SSBs are governed by different considerations than in batteries with liquid electrolytes. Specifically, a liquid electrolyte can flow to wet the surface of Li metal as it evolves, maintaining electrochemical contact at the interface (Figure 6a,b). An SSE cannot do this (Figure 6c,d), and the establishment and preservation of physical contact at the Li metal/SSE interface in SSBs are governed by chemo-mechanical phenomena.[21] The application of a stack pressure is usually necessary to enable sufficient contact between a Li metal anode and an SSE.[80] To maintain contact, Li metal atoms that are oxidized to Li^+ and removed across the interface must be replaced by new Li metal atoms from the underlying Li electrode. This replacement can happen either by self-diffusion of Li or by mechanical deformation and flow of the Li metal under the applied stack pressure to fill the vacancy.[19,21] Thus, stack pressures that are large enough to cause yielding and/or creep of Li can enable more uniform contact during Li stripping, which is necessary to allow for operation of the battery with low overpotentials.[19−21] If the applied current density (i.e., the rate at which Li is removed from the interface) is high relative to the rates of self-diffusion (which is dependent on temperature) and mechanical deformation (which is dependent on temperature and applied stack pressure), voids can form at the interface to reduce the interfacial contact area, resulting in diminished cell performance (Figure 6d). Moreover, the reduced interfacial contact area increases the local current density, which causes current focusing and can stimulate the nonuniform growth of Li as filaments that can penetrate the solid-state electrolyte during subsequent deposition cycles (Figure 6d), as already discussed.[20]

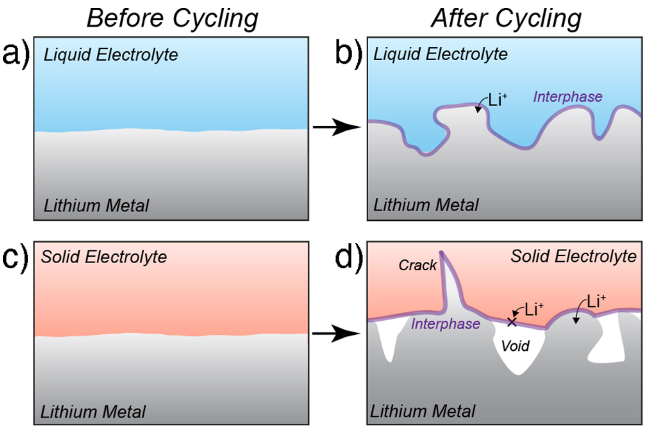

Figure 6. (a, b) Schematic of a Li/liquid electrolyte interface before (a) and after (b) electrochemical cycling, in which the metal exhibits increased roughness at the interface, but the liquid still wets the electrode. (c, d) Schematic of a Li/solid-state electrolyte interface before (c) and after (d) electrochemical cycling. There is a loss of physical contact at the interface due to void formation, and lithium has grown into the SSE to form a crack.

Electrochemical evidence for interfacial void growth has been seen in past decades in other solid-state electrochemical systems,[81] and recent electrochemical investigations have suggested that the formation of interfacial voids is a primary culprit for the degradation of Li-based SSBs as well.[19−21,82] The formation and growth of voids is stack-pressure dependent, with higher stack pressures shown to induce low-overpotential cycling likely through the dynamic filling of vacancies and voids at the interface via mechanical flow.[19] X-ray imaging of voids formed after stripping of Li and Na metal has been performed,[20,82] providing insight into this process that occurs in both alkali metals. A promising recent approach to overcome chemo-mechanical issues associated with contact loss is to use small quantities of alloying metals to direct the deposition and stripping morphology of Li metal[83,84] or to maintain contact at the interfaces.[85] The use of Ag particles in the anode enabled a prototype solid-state pouch cell to achieve 1000 cycles while retaining 80% of the initial capacity;[83] there are clear benefits to such an approach, but the chemo-mechanical action of alloy metals is unclear and needs further investigation. In particular, understanding solubility and interdiffusion in Li alloy materials, as well as probing how nucleation and growth of Li metal occur at the surface of Li-rich alloys with evolving morphology, are key research directions. The development of imaging methods that can dynamically track alkali metal morphology evolution and void formation[86] and relate these factors to electrochemistry will also provide important insight into the chemo-mechanics of SSBs and require future research attention.

3. ALLOY ANODES

As discussed in Section 1, alloy materials are also promising high-capacity anode candidates for batteries with higher energy density and specific energy. Examples of materials that undergo alloying reactions with Li include Si, Ge, Sn, and Sb.[4] Other materials, such as tin oxide, undergo "conversion" reactions. Alloy and conversion materials react to form Li-rich phases, with theoretical gravimetric capacities up to 10 times that of graphite, theoretical volumetric capacities up to three times that of graphite, and volume expansion up to 300% during the reaction.[87] The expansion and contraction of these materials during cycling give rise to chemo-mechanical challenges that include mechanical damage and electrical disconnection of the active material[6,88,89] as well as cyclic dimensional changes of particle surfaces that cause fracture and continuous growth of the SEI in liquid electrolytes, resulting in poor Coulombic efficiency.[90] In many ways, the challenges faced by alloy and conversion materials are related to those for alkali metals, as both classes of anode materials experience large volume/morphology changes and severe SEI growth. However, there is a fundamental and important difference: alkali metals are "hostless," meaning that they are deposited and grow directly on the current collector, while alloy materials act as "hosts" for the reaction and insertion of alkali atoms into the host structure. This difference has important implications for the mechanical stresses and degradation pathways experienced by host vs hostless materials.

3.1. Reaction-Induced Stress. Understanding reaction-induced stress evolution in alloy materials has been an important research area over the past decade.[6,7,91] Very large stresses, on the order of hundreds of megapascals to gigapascals, can be induced within alloy and conversion materials during Li insertion/extraction due to nonuniform volume changes within the materials.[6] These nonuniform volume changes arise from diffusion-induced concentration gradients or innate reaction pathways, and they are a consequence of the fact that the host material itself must deform to accommodate the inserted alkali species. Reactions that involve volume change across a sharp interface (i.e., two-phase reactions) can give rise to particularly large stresses,[92] and two-phase reactions have been implicated in the mechanical fracture of Si and Ge materials during the first lithiation step.[93−97]

A large body of work has focused on using *in situ* experiments to uncover reaction mechanisms in active alloy and conversion materials and to combine these observations with predictive modeling to understand how volume/structural changes cause stress evolution (an example is shown in Figure 7).[98−100] This work has been important for identifying the causes of various chemo-mechanical degradation processes as well as generally showing that smaller-scale (nanoscale) alloy materials are more resilient against fracture during battery reactions.[94] Furthermore, stresses induced within alloy materials have been shown to be large enough to affect the thermodynamics of the reaction itself,[8,101] which can slow reaction rates or prevent lithiation reactions from occurring in Si, for example. Knowledge of diffusion-induced stresses has been further used to engineer material architectures that controllably and reversibly change their shape in response to lithiation/delithiation cycles.[102] In addition to understanding reaction-induced stress, efforts have also focused on measuring mechanical properties of alloy materials at different states of charge;[103−105] these measurements are often *in situ* and require custom experimental systems that can monitor mechanical properties through wafer curvature techniques[103] or indentation[105] while maintaining an inert environment. In general, the yield strength and stiffness of most alloy metals decreases upon incorporating high concentrations of Li, which is consistent with the mechanical properties of Li itself. However, the mechanical degradation characteristics of different alloy materials depend both on the mechanical properties and the details of reaction mechanisms, resulting in varying behaviors among different materials.

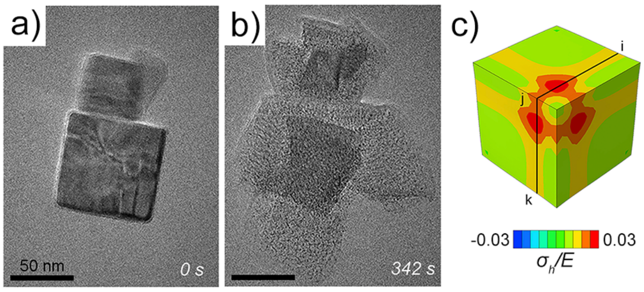

Figure 7. (a, b) *In situ* transmission electron microscopy (TEM) images of the lithiation reaction in FeS_2 nanocrystals, showing (a) pristine nanocrystals and (b) the same crystals after lithiation, where the crystals have fractured in multiple locations. (c) Finite-element modeling (FEM) of the hydrostatic stress (σ_h, normalized by Young's modulus E) that evolves on the basis of the experimentally observed reaction process. The model predicts stress concentrations at corners in agreement with observed fracture locations. Reproduced with permission from ref 97. Copyright 2018 Elsevier.

3.2. Chemo-Mechanics of Hollow Particles in Liquid Cells. The fundamental investigation of chemo-mechanics in alloy and conversion materials has coincided with substantial efforts to develop structured alloy anodes with high capacity and extended cycle life,[90,106−108] with most efforts focused on liquid-electrolyte batteries. Anode materials must be carefully structured to avoid mechanical/physical disconnection within composite electrodes during volume changes, while also maintaining dimensionally stable outer surfaces to enable self-limiting SEI growth. Academic efforts have shown the promise of engineered nanostructured hollow materials,[109] which can expand and contract toward their hollow interiors while maintaining dimensionally stable surfaces. "Yolk−shell" materials, in which alloy anode particles are surrounded by hollow space and an external shell, have shown particularly encouraging performance.[106,110] In many cases, however, these engineered nanostructures require complex synthetic procedures that preclude industrial-scale manufacturing. Furthermore, it is difficult to pack nanoscale particles closely enough to achieve the tap densities necessary for high energy density. The concepts embodied in these studies (i.e., simultaneously controlling internal material morphology evolution and surface dimensions) have guided other promising approaches, including efforts focused on improving performance of micron-scale particles that feature a lower surface area for SEI growth and thus can feature higher Coulombic efficiency. For example, new polymeric binders have been developed that can mechanically stretch while still maintaining connectivity among micron-scale particles to minimize the formation of new surface area.[111] Tailoring the SEI composition on micron-scale particles to reduce mechanical adhesion between the SEI and active material has also been shown to be a promising approach for improving cyclability.[112]

In the context of these efforts, we have recently reported an advance in the understanding of the chemo-mechanics of core−shell alloy anode particles.[113] In this study, very small (~15 nm diameter) antimony nanocrystals with native oxide layers were found to expand upon lithiation to form the Li_3Sb phase, as expected. Instead of simply shrinking when Li was removed, as has been observed in most studies of larger alloy anodes,[114,115] the particles were observed to form internally voided structures during delithiation, leaving the external surface dimensions largely unchanged (Figure 8a−c).[113] Reversible refilling/voiding of each individual core−shell

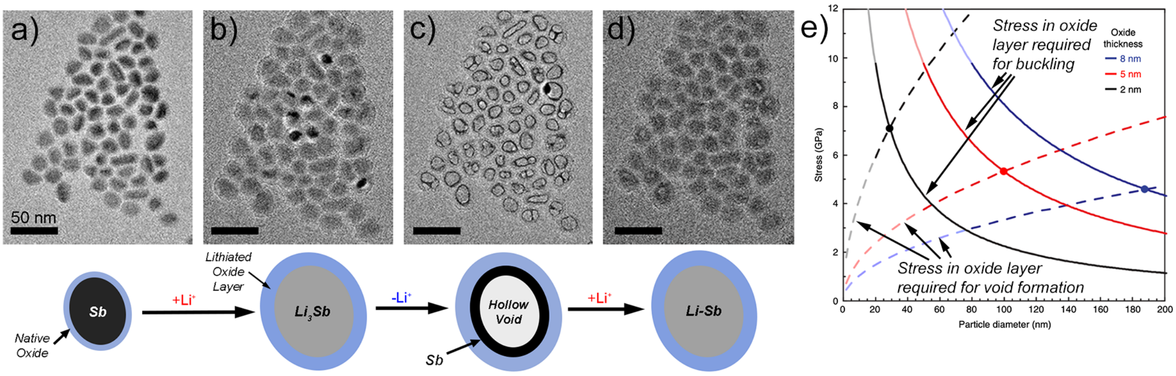

Figure 8. (a−d) *In situ* TEM images of a group of Sb nanocrystals before lithiation (a), after lithiation to form Li_3Sb (b), after delithiation (c), and after the second lithiation (d). During delithiation, each particle forms a hollow void structure with the outer dimensions largely unchanged, as shown in the schematics below the images. (e) A chemo-mechanical model that shows that void formation is favored in smaller particles, but buckling of the oxide shell is favored in larger particles. Reproduced with permission from ref 113. Copyright 2020 Springer Nature.

particle then persisted with further cycling with insignificant changes of the surface dimensions (Figure 8d). The observed voiding behavior was found to be caused by the chemo-mechanical constraint of the native oxide shell, which was stiff enough to maintain its shape during delithiation without buckling to avoid shrinkage of the structure. Modeling showed that this behavior should only occur in small particles due to the reduced thermodynamic surface energy penalty for the formation of voids (Figure 8e). This study thus demonstrates the importance of mechanical constraint within core−shell structures in determining morphological evolution pathways of battery materials. The findings suggest that other alloy metals could also be engineered to undergo reversible voiding behavior though engineering surface layers with high stiffness and, furthermore, that constrained alkali metals could also be made to exhibit such reaction pathways.

3.3. Alloy Foils as Anodes. Although there has been considerable progress made in understanding and controlling reaction mechanisms in particulate alloy anodes, the translation to commercial applications has been challenging because of difficulties in manufacturing complex structures and persistent SEI growth on particle surfaces within electrodes. To bypass these problems, a number of groups have recently begun to focus on engineering macroscale metallic foils as alloy anodes. As highlighted in a recent perspective,[116] foils offer the advantage of high volumetric capacity since they are completely dense, and manufacturing is more straightforward than nanostructured particles. Historically, however, foils have undergone rapid mechanical pulverization during cycling due to stress generation in the relatively thick (20−50 μm) materials.[117] Furthermore, charge/discharge rate capability could be limited because of the necessity for solid-state diffusion to occur across the foil thickness. Recent efforts have shown that alloy foils containing separate phases (for example, the Zn−Sn−Bi foils shown in Figure 9) can exhibit high volumetric capacity, appropriate rate capability, and promising electrochemical stability, while resisting mechanical degradation,[118−121] which is thought to be at least partially due to enhanced mechanical integrity provided by the multiphase matrix. Stress concentrations generated in pure Li−Al foil anodes during Li removal have been reported to be alleviated with alloying elements[122] as well as by controlling the dimensionality of volume changes through tuning hardness values.[123] Alloy foils with high Li content can also enable relatively reversible cycling.[124,125] Despite the recent promising results, further work is required to obtain a deep understanding of how stress and mechanical damage are linked to microstructural evolution within foil-based alloy anodes.

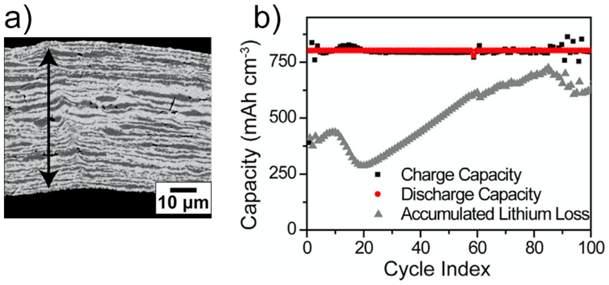

Figure 9. (a) Image of a $Zn_{44}Sn_{55}Bi_1$ foil cross section, in which dark regions are Zn-rich and light regions are Sn-rich. (b) Galvanostatic cycling behavior with an areal capacity of 1.7 mAh/cm^2 in a Li half cell with liquid electrolyte. The data show relatively stable capacity over 100 cycles. Reproduced with permission from ref 118. Copyright 2019 Elsevier.

3.4. Alloy Anodes in Solid-State Batteries. Chemo-mechanical aspects of alloy anodes for solid-state batteries have also received increased research attention in recent years. Expansion of the alloy material must be accommodated within the all-solid battery architecture, which can lead to high stresses and accelerated mechanical damage compared to liquid-based batteries.[26] Indeed, Janek and co-workers found that cycling of a full SSB cell with a $LiCoO_2$ cathode and an indium metal alloy anode caused approximately megapascal-level variations in stress over each cycle, whereas the use of "zero-strain" $Li_4Ti_5O_{12}$ anodes resulted in ∼20 times lower stresses.[126] X-ray imaging studies of solid-state composite anodes with micron-scale Sn active material showed that the expansion of the Sn particles during lithiation caused extensive cracking of the surrounding SSE phase, increasing tortuosity, and impeding ion transport.[127] In addition, the arrangement of active particles was found to strongly influence the local fracture characteristics, indicating that stress concentrations and interactions among particles can contribute to degradation.[127] Improved cycling stability of alloys in SSBs has been attained through the use of smaller particles: antimony nanocrystal composite anodes achieved Coulombic efficiencies above 99.9% when cycled at 95 °C.[128] This result suggests that reducing alloy particle size could be an effective way to minimize chemo-mechanical damage of the solid-state composite, as has widely been observed in liquid-based systems. Thin-film alloy materials have shown a tendency to delaminate from the SSE material due to volume changes,[129] although thicker layers were achieved in SSB configurations compared to those in liquid electrolytes. The internal porosity contained within alloy anode materials has also been shown to be an important factor for achieving high capacity as well as stable cycling, as internal porosity can accommodate volume expansion during lithiation while minimizing mechanical damage.[130] Finally, composite Si electrodes containing sulfide SSEs have been shown to exhibit promising cycling behavior despite some mechanical damage of the electrode, which was thought to be due to buffering of displacements by the SSE separator layer.[131]

4. SOLID-ELECTROLYTE INTERPHASE

As previously discussed, the solid-electrolyte interphase (SEI) is a surface film that forms due to reductive (electro)chemical decomposition of the electrolyte at the anode interface (interphases can also form at cathode interfaces but will not be discussed here). Virtually all liquid electrolytes are unstable in contact with anode materials (including Li metal, lithiated graphite, and many alloy anodes), and liquid electrolytes therefore decompose to form SEI films. These films are composed of a mixture of phases, with the commonly reported "mosaic" structure consisting of small inorganic crystallites (e.g., Li_2O, Li_2CO_3) dispersed within an amorphous organic or polymeric matrix (Figure 10a,b).[60] Most SSE materials are also unstable when in contact with Li metal,[24] and they react to form an interphase (here, the solid-state analogue to the SEI formed in liquid electrolytes will simply be called the *interphase*). Although the SEI has been mentioned numerous times throughout this Perspective, a discussion of the chemo-mechanics of the SEI deserves its own section.

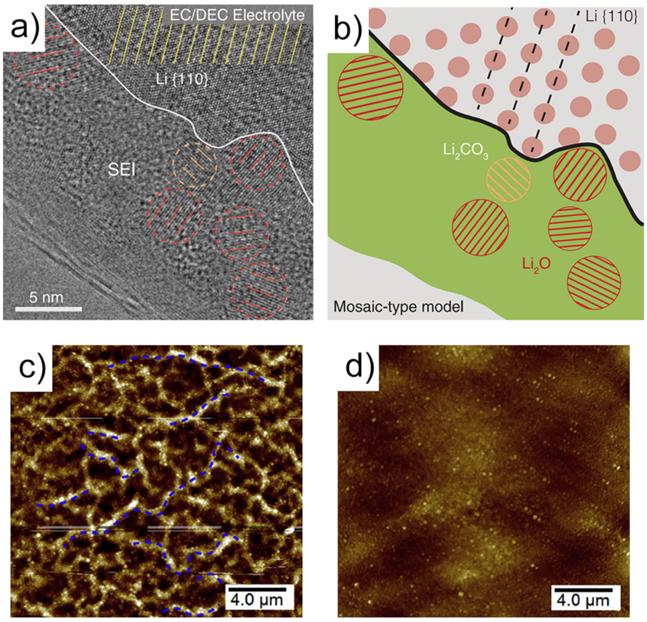

Figure 10. Cryo-TEM image (a) and schematic (b) of a mosaic-type SEI layer grown on a Li metal filament in a liquid electrolyte (with ethylene carbonate (EC)/diethyl carbonate (DEC) solvents). Reproduced with permission from ref 135. Copyright 2017 AAAS. (c) AFM image of the topography of an SEI film under 5.6% strain, showing cracks along the blue lines. This film was grown in an electrolyte only containing EC solvent. (d) AFM image of the topography of a different SEI film under 6.2% strain, showing deformation without cracks. This film was grown in an electrolyte containing EC and FEC solvents, indicating the potential of FEC to prevent SEI fracture. Reproduced with permission from ref 141. Copyright 2020 Elsevier.

4.1. Chemo-Mechanics of the SEI in Liquid Electrolytes. A primary goal in the development of next-generation anodes for rechargeable batteries is to create materials that allow for the formation of an SEI that is chemo-mechanically stable, has uniform morphology, and allows for sufficient ion transport. This is because fracture or delamination of the SEI can cause the bare surface of the electrode material to be re-exposed to the electrolyte, consuming more electrolyte to grow additional SEI in the process, which reduces Coulombic efficiency and causes cell degradation.[132] From a chemo-mechanical perspective, SEI films in liquids should have a high modulus and sufficient fracture toughness to resist fracture, and it is generally agreed that the mechanical adhesion at the electrode material interface should be strong enough to prevent delamination.[133] Furthermore, the SEI should exhibit structural and morphological uniformity to prevent nonuniform reaction processes in the electrode beneath the film.[134] However, it is a major challenge to create stable SEI films that can adhere to electrode materials such as alkali metals or alloy anodes since they undergo such substantial volumetric changes during charge/discharge. This challenge is complicated by the fact that the complex electrolyte reduction reactions that occur during SEI formation can be difficult to control or even determine, and the structure/property relationships of the SEI material itself are usually inferred due to the complicated structure of the SEI that is difficult to interrogate with conventional techniques.[133] This lack of control and understanding has traditionally limited our ability to beneficially engineer the SEI with appropriate mechanical and transport properties for improved performance.

Despite long-standing challenges, recent progress has been made in understanding the structure and mechanical properties of SEI films formed in liquid electrolytes. Cryogenic transmission electron microscopy (TEM) has been particularly useful for investigating the atomic-scale structure and chemistry of SEI films and interfaces (Figure 10a,b).[55,56,135−138] Cryogenic conditions and inert-gas transfer were found to be necessary to stabilize SEI films against environmental and electron-beam-induced degradation due to the sensitivity of the Li-containing compounds in these structures. A number of studies have found distinctive structural characteristics that correlate to electrochemical cycling behavior, such as layered vs mosaic SEI structures.[135] Studies designed to uncover the mechanical properties and fracture behavior of SEI films on different electrode materials have also been carried out. A number of studies have measured the elastic properties of SEI films,[139,140] with a wide variation in results that is likely due to limitations of various measurement techniques, as well as differing properties of SEI films formed under slightly different conditions. A recent investigation developed a membrane-bulge experimental technique in combination with atomic force microscopy (AFM) to precisely measure elastic modulus as well as fracture behavior of SEI grown on Li metal.[141] Interestingly, the results showed that the addition of fluoroethylene carbonate (FEC) to the electrolyte increased the elastic modulus by 80% and also substantially increased the resistance to fracture (Figure

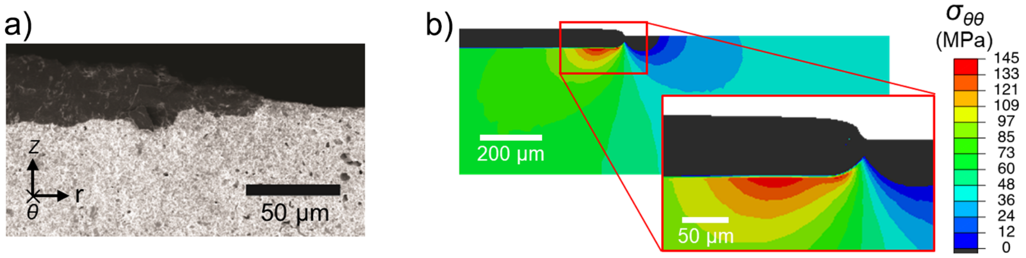

Figure 11. (a) SEM image of a $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ solid-state electrolyte after reacting with lithium to form an interphase (the dark region at the top of the image). (b) Finite element modeling of tensile stresses generated within the SSE due to interphase formation. Reproduced from ref 159. Copyright 2019 American Chemical Society.

10c,d). This may help explain why FEC has been widely shown to improve cycling performance in investigations of alloy anodes and Li metal. Other work has investigated the fracture behavior of SEI films on Si electrodes.[142] Modeling investigations have provided insight into mechanical properties of SEI components[143] and how interface adhesion of different compounds affects mechanical deformation of the SEI,[144] as well as developed frameworks for finite-element modeling of SEI deformation.[145] Further work to bridge the gap between experiments and modeling in this area would be useful.

A variety of experimental strategies have been developed to overcome chemo-mechanical degradation of SEI films in liquid electrolytes. For alloy anodes, encapsulated particles and hollow structures with dimensionally stable outer surfaces have shown stability advantages,[90] as has already been discussed in this article. Such strategies are beneficial because they minimize the mechanical stress applied to the SEI from the underlying material undergoing expansion or contraction, since empty space is available within the structure into which the material can expand. Beyond this strategy, recent work on microsized alloy anode particles has suggested that stiff SEI films with low adhesion strengths to the active material can be beneficial, as they allow for the external SEI film to remain structurally and morphologically intact while the internal active material can detach from the SEI to create open hollow space.[112] This concept is somewhat counterintuitive, since strong adhesion to SEI films has generally been desired,[133] but the performance of alloy anodes with such SEI films is encouraging. This idea is conceptually similar to the recently reported voiding transformations in small Sb nanocrystals under the mechanical constraint of native oxide shells,[113] as discussed in Section 3.2. The parallels between these studies suggest that engineering SEI films to be stiff and to exhibit high interfacial energy (low adhesion strength) could enable a wide variety of particulate alloy materials to achieve improved cycling stability.

For alkali metals in liquid electrolytes, researchers have focused on developing electrolyte systems in which compact metal films are deposited with minimal surface area to reduce the total amount of SEI that forms.[48] "Artificial SEI" layers have also been engineered,[133,146−148] with the goal of creating surface layers that direct the deposition of alkali metals beneath these layers so the alkali metal does not contact the electrolyte. Li-containing compounds[149,150] and alloy materials[151] have been used for such purposes, showing improved stability and Coulombic efficiency. While substantial progress has been made, greater control over SEI evolution is necessary to enable alkali metal anodes with high enough Coulombic efficiency to match the stability of graphite electrodes in Li-ion batteries.

4.2. Chemo-Mechanics of Interphase Formation in Solid-State Batteries. In a similar fashion to liquid electrolytes, most Li-based SSEs are unstable at low potentials[24,25,152] and will naturally evolve to form an interphase region at the anode.[153−157] Interphase formation in SSBs can have exacerbated chemo-mechanical consequences compared to liquid-electrolyte batteries.[26] The formation of an interphase involves an electrochemical or chemical reaction of the solid-state electrolyte to form a new phase or mixture of phases.[154,157] Many SSEs feature interphases that continuously grow, and the extent of growth as well as the structure and properties of the interphase layer are important for determining the chemo-mechanical consequences of its formation.

Interphase formation involves volume expansion since Li is incorporated into the interphase, and this expansion necessarily causes mechanical stress and strain to be generated because the interphase is constrained by the surrounding solid materials.[157−159] The growth of the interphase at Li metal anodes in SSBs has been shown to induce stresses that are high enough to cause fracture in certain oxide SSEs (Figure 11).[157,159−161] In the NASICON SSE material $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ (LAGP), *in situ* X-ray tomography has revealed that fracture induced by interphase growth is the dominant degradation mechanism, rather than degradation due to the impedance of the interphase itself (Figure 12). In addition, large applied stack pressures have been implicated in extending the electrochemical metastability of the SSE and altering decomposition pathways.[162] It is also possible that compressive stress present in the interphase region due to its growth could alter diffusion kinetics of ions through the interphase. These chemo-mechanical effects are largely absent from liquid-electrolyte batteries and arise because of the constraint of the full solid-state stack, and new engineering concepts will be required to overcome or take advantage of these phenomena.

5. MITIGATING CHEMO-MECHANICAL DEGRADATION: TOWARD APPLICATIONS

The high-capacity anode materials discussed in this Perspective represent a new frontier for rechargeable alkali ion batteries. Whereas Li-ion battery technologies have been built upon a scientific understanding of crystal chemistry and intercalation processes, the next generation of electrode materials requires different science and engineering concepts, in which control over morphology evolution and chemo-mechanical degradation is necessary to attain reversibility and long cycle life. As such, worldwide efforts have been dedicated to understanding the links among chemical transformations, stress evolution, and

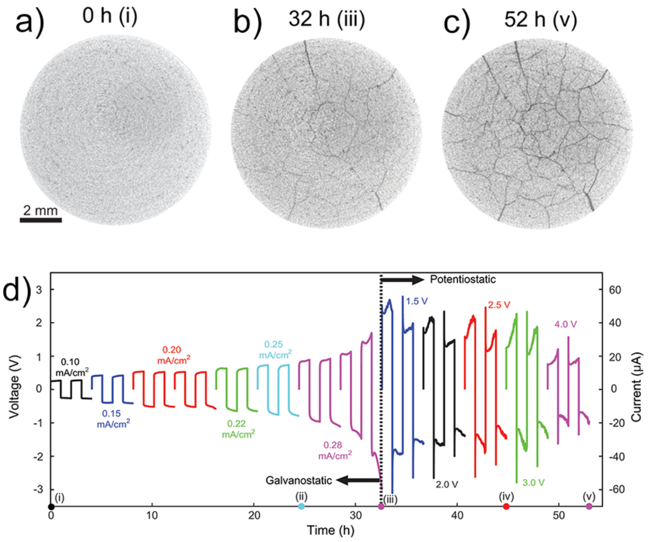

Figure 12. (a−c) *In situ* X-ray tomographic imaging of a NASICON-type oxide solid-state electrolyte material ($Li_{1+x}Al_xGe_{2-x}(PO_4)_3$) that fractures during battery cycling due to the growth of the interphase. Each image is a single slice from the center of the ceramic pellet, and the cell is a symmetric cell with Li on both sides of the pellet (not visible). (d) Electrochemical measurement for this sample, in which galvanostatic cycling and potentiostatic cycling were used as denoted. Reproduced from ref 159. Copyright 2019 American Chemical Society.

chemo-mechanical damage accrual in these electrode systems, with the goal of using this knowledge to engineer higher-capacity electrodes that can achieve or surpass the stability of current Li-ion battery electrodes. Building on the overview provided in this article, this section highlights possible future research directions that could advance these materials toward use in applications.

5.1. Alkali Metals. When one looks toward the future of alkali metal anodes, it is critical to devise methods for creating controlled chemo-mechanical environments to enable reversible deposition/stripping. Different approaches are likely necessary for liquid vs solid systems, but some fundamental concepts are similar; both are discussed here.

5.1.1. Anode-Free Cells with Liquid Electrolytes. In the context of liquid-electrolyte batteries, a promising configuration is the "anode-free" cell in which an anode current collector is paired with a conventional Li-containing cathode, and charging involves directly electrodepositing Li metal onto the current collector from the cathode.[48,64,163,164] Since there is initially no active material at the anode, this configuration enables very high energy density and specific energy, and manufacturing would be very similar to conventional Li-ion batteries. However, achieving stable cycling is challenging because there is no excess Li^+ in the system to mitigate persistent Li^+ inventory loss when using Li metal anodes. While recent years have seen improvements in the Coulombic efficiency of anode-free cells primarily through electrolyte design, the best research cells can currently only cycle ∼100 times before degradation.[48,165] Improved stability may be achieved through careful control of the interconnected evolution of the Li metal and the SEI so that the SEI is mechanically stable as Li is deposited/stripped underneath. Future development of encapsulation schemes for alkali metals could take advantage of the chemo-mechanical knowledge gained through studying core−shell alloy materials, as discussed herein. Carefully engineered shells with appropriate transport and mechanical properties are necessary to allow for ion ingress while maintaining encapsulation, enabling Li metal to reversibly grow and recede within shell structures.

5.1.2. Understanding and Utilizing the Effects of Temperature. Recent work has revealed that Li metal electrodes evolve differently at different temperatures in liquid electrolytes; specifically, the deposited particle/grain size and Coulombic efficiency decrease at lower temperatures in many electrolytes.[55] Although tailoring the electrolyte and SEI can improve Coulombic efficiency,[54,166,167] this finding highlights that Li metal batteries will likely exhibit widely varying behavior as a function of temperature, especially compared to Li-ion batteries. Temperature is often ignored as a variable in the development of Li metal anodes, but it may be able to be used beneficially to improve electrochemical and chemo-mechanical behavior. For instance, charging (i.e., Li plating) under controlled temperature conditions could enable the formation of Li films with optimal structure and SEI characteristics, followed by discharge under whichever conditions are necessary for the application. High temperatures (60 °C) have been found to allow for the growth of dense, uniform Li films in certain electrolytes.[56] These elevated temperatures could enhance mechanical creep of Li metal under applied stack pressure as well as self-diffusion and surface diffusion rates, which may contribute to the formation of optimal films. On the other hand, high temperatures may also accelerate detrimental SEI formation. Improved understanding of electrochemical and chemo-mechanical behavior under a variety of temperature conditions, and especially under varying temperature conditions designed for specific charge/discharge regimens, would be useful for further development of Li-based anodes in liquid electrolytes.

5.1.3. Controlling Metal Evolution in Solid-State Batteries. SSBs are an attractive alternative that could enable the use of Li metal anodes without any detrimental interactions with liquid electrolytes. As discussed in this Perspective, however, an entirely new set of chemo-mechanical challenges arises in SSBs, including adhesion issues and loss of contact at solid interfaces as well as filamentary growth of the metal to fracture the SSE. The strategic incorporation of materials that alloy with alkali metals into anode architectures could further improve the cycling behavior of alkali metal anodes. Interestingly, while the incorporation of small amounts of alloy materials could have advantages in both solid and liquid systems for seeding alkali metal growth in controlled locations, the purpose and action of these materials in solid vs liquid systems are subtly different. In SSBs, engineered alloy structures could (i) enable the deposition of Li metal with controlled morphology and stress distribution[83] and (ii) prevent void formation at the solid-state electrochemical interface during stripping by maintaining physical contact.[85] While there has been some exploration of these strategies, accelerated development of Li metal anodes in SSBs will require improved understanding of how the alloy material and Li evolve in concert within the anode architecture during charge/discharge, which will likely necessitate *in situ* or *operando* experiments. Finally, anode-free designs for SSBs are also extremely attractive from an energy density standpoint, and alloy-directed growth may be a pathway toward SSBs with no excess (or minimal excess) Li.

5.1.4. Lithium vs Sodium for Solid-State Batteries. Li metal has received far more attention for use in SSBs in recent years than Na metal due to the high specific energy of Li metal-based batteries. However, there are a variety of Na^+-ion-conducting SSEs that have been known for many years, and recent work has shown that Na metal may have particular benefits over Li due to its mechanical properties and chemo-mechanical behavior in SSBs.[32,168] Na has a lower yield strength and elastic modulus than Li, and it undergoes creep deformation even more readily because of its low melting point (98 °C).[32] Furthermore, the self-diffusivity of Na in Na metal is about 100 times that of Li at room temperature.[168] Na metal anodes used in conjunction with the Na-β''-alumina solid-state electrolyte have been shown to exhibit about an order of magnitude higher "critical current density" before initiation of filament growth and failure, as compared to Li.[168] This is likely due both to the easier mechanical deformation and to the higher self-diffusivity of Na that enables void-filling to avoid current hot spots and filament growth. As highlighted by Battaglia and co-workers,[168] such performance is promising for commercialization if appropriate high-energy Na-based cathode materials competitive with the current $LiNi_xMn_yCo_zO_2$ chemistries used in Li-ion batteries can be found, and thus, work is urgently needed in this area.

5.2. Alloy Anodes. Alloy anode materials are further along the commercialization spectrum within rechargeable batteries compared to alkali metals. This is largely because alloy materials act as hosts for Li insertion, which can enable greater control over morphology evolution compared to hostless alkali metals. Low concentrations of Si or SiO_x are currently added to graphite anodes to slightly boost capacity in some commercial batteries.[1,169] Progress toward higher concentrations of alloy materials, and thus higher-energy batteries, is contingent upon implementing materials with controlled volume changes and regulated SEI formation. The complex nanostructures that have shown promising performance in small-scale cells have had limited success in translating to commercial applications for a number of reasons, including high cost, high surface area, low tap density, and difficulty in scaling synthetic procedures.[90,170] However, the research community's improved understanding of the chemo-mechanics of alloy-based anodes has provided an important scientific framework, and the further implementation of alloy materials in commercial batteries will likely continue to take advantage of this knowledge, with a primary focus on developing chemo-mechanically stable microscale materials that can be manufactured at large scales while achieving commercially relevant areal capacities (2−4 mAh/cm^2) within cells. For example, progress has been made by companies in developing particulate materials that are compatible with conventional Li-ion manufacturing processes,[171,172] and controlling the extent of lithiation will also likely be important.

5.2.1. The Promise of Alloy Foils. Beyond this focus, the idea of incorporating dense foil electrodes instead of particle-based electrodes is quite attractive from a manufacturing standpoint, but more research is required to engineer foils that retain mechanical integrity while exhibiting sufficient mass transport capabilities and areal capacity to achieve high power and energy density. The incorporation of conceptual advances attained through research on particulate alloy materials, such as the advantages of core−shell structures, could enable improved performance of alloy foils that contain controlled porosity or other internally engineered structures. A better understanding of how stress and mechanical damage evolve in alloy anode foils with complex microstructures is also necessary, which will likely require the interlinked use of *in situ/operando* experiments and modeling over multiple length scales.

5.3. The Frontiers of Chemo-Mechanics in Batteries. Although our knowledge of chemo-mechanical effects in battery anode materials has substantially improved in the past decade, there is much more scientific progress to be made that could also impact technology. A major challenge is that the mechanical properties of individual active components, whether they are alloy anode particles or different grains of an alkali metal electrode, can vary as a function of the Li content, domain size, and/or defect characteristics. While we may have general knowledge about the mechanical properties of an active material, it would often be advantageous to know the properties of individual particles or domains within an electrode in real time to be able to predict the heterogeneous response of such a material to a load or deformation. Future work could approach this issue by combining large-scale imaging of particle dynamics with statistical knowledge of mechanical property variations. In addition, while large-scale mechanical degradation within a cell can be straightforward to track, it is often much more difficult to determine the spatial and temporal location of the origin of such failure. It is therefore critical to pinpoint and understand the chemo-mechanical evolution of materials inside batteries at short time scales (milliseconds) and length scales (tens of nanometers) to understand how nanoscale mechanical mechanisms (such as crack initiation or strain-induced delamination at in interface) can propagate to larger length and longer time scales. Such efforts will likely require close links between *operando* experiments and predictive modeling as well as extensive analytics applied to combined data sets.

5.4. Conclusions. The development of anode materials with increased ion storage capacity is a key step in the creation of next-generation energy storage technologies. Both alkali metals and alloy anodes offer the possibility of batteries with higher energy density and specific energy, but chemo-mechanical degradation of these electrode materials and their electrolyte interfaces has been a barrier to the implementation in commercial battery technologies. This Perspective highlights chemo-mechanical considerations that contribute to reaction processes in these materials in both liquid-electrolyte and solid-state battery systems. Careful engineering of materials across length scales as well as further understanding of materials transformation and degradation processes are critical for combating chemo-mechanical degradation. Building on the substantial progress made in the past decade, the future is bright for these high-capacity materials for emerging battery technologies.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.0c02981.

Description of the cell stack architectures and material properties used to calculate the energy metrics in Figure 1 (PDF)

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Notes

The authors declare no competing financial interest.

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