Challenges and Opportunities for Fast Charging of Solid-State Lithium Metal Batteries

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Abstract

In this Perspective, we assess the promise and challenges for solid-state batteries to operate under fast charge conditions (e.g., <10-minute charge). We present the limitations of state-of-the-art lithium-ion batteries (LIBs) and liquid-based lithium metal batteries in context, and highlight the distinct advantages offered by SSBs with respect to rate performance, thermal safety, and cell architecture. Despite the promising fast charge attributes of SSBs, we must overcome fundamental challenges pertaining to electro-chemo-mechanics interaction, interface evolution, and transport-kinetics dichotomy to realize their implementation. We describe the mechanistic implications of critical features including plating-stripping crosstalk, metallic filament growth, cathode microstructure, and interphase formation on the fast charge performance of SSBs. Towards achieving the eventual goal of fast charge in SSBs, we highlight both intrinsic (*e.g.*, interface design, transport properties) and extrinsic (*e.g.*, temperature, pressure) design factors that can favorably modulate the mechanistic coupling and cross-correlations. Finally, a list of key research questions is identified that need to be answered to gain a deeper understanding of the fast charge capabilities and requirements of SSBs.

Widespread adoption of battery electric vehicles (EVs) will benefit from the rapid advancement of fast-charging technology that can compete with the refueling times of internal combustion engine vehicles and assuage ‘range anxiety’.[1] While fast-charging technology is dependent on a wide range of considerations including charging infrastructure, vehicle engineering, and techno-economics,[2, 3] the chemistry and design of batteries[4, 5] are central elements that dictate its successful deployment. Over the past three decades, lithium-ion batteries (LIBs) have revolutionized the energy storage sector and are the state-of-the-art technology across portable electronics and EVs. Although recent advances in electrode engineering,[6, 7] electrolyte design[8, 9] and cell architectures[10, 11] have enhanced energy densities and mitigated concerns of safety and degradation, fast charging at 400 kW (or under 10 min charge time) still remains an elusive target. Under charging rates of 6C and above, LIBs are confronted with major challenges with respect to electrolyte transport and thermal safety, resulting in reduced energy densities, deleterious side reactions, and accelerated capacity decay.[12] Electrodes with low areal capacities have demonstrated improved fast charging characteristics as compared to thicker battery electrodes.[13] However, since thinner battery electrodes still require a similar fraction of inactive materials such as current collectors and separators, this results in lower energy densities and imposes a larger cost constraint.[14] On the other hand, thicker electrodes with higher energy densities result in greater electrolyte concentration polarization and increased ohmic heat generation, which limits fast-charging capability. Hence, fast charging currently presents a tradeoff between energy and power density, with cost and thermal performance being key considerations.

While the adoption of fast charging for LIBs requires overcoming critical scientific and engineering barriers, solid-state batteries (SSBs) offer several intrinsic advantages over their liquid counterparts that can potentially unlock exciting opportunities.[15-17] Although SSBs have not historically been associated with high rates of charge or discharge because of limited ion transport rates in solids, this has changed in recent years due to the discovery and development of solid-state Li-ion conductors with ionic conductivity values approaching those of liquids.[18, 19] By replacing the organic liquid electrolyte with a non-flammable solid electrolyte, SSBs provide enhanced safety attributes over conventional LIBs. Upon pairing of solid electrolytes with a lithium metal anode, such systems present the possibility of engineering batteries with ultra-high energy density (>1000 Wh/L).

Owing to their inherent mechanical rigidity and high cationic transference number, solid electrolytes can potentially address challenges of unstable deposition and concentration gradients encountered in Li metal batteries with liquid electrolytes. However, despite their theoretical promise, there are a number of technical challenges and fundamental scientific advances necessary for SSBs to achieve reliable fast charging while retaining long cycle life. Ion transport during fast charging is often limited by electrolyte conductivity and ion percolation within all-solid-state composite cathodes, rather than the pure solid-state-electrolyte separator.[20, 21] Solid-solid interfaces within these systems also present electro-chemo-mechanical challenges, including Li metal penetration through the solid electrolyte, contact loss, and electrochemical decomposition.[22-26] In this regard, enhancing our fundamental understanding of aspects including electro-chemo-mechanics, evolution of solid-solid interfaces, thermal stability, and the transport/mechanical properties of constituent materials (Figure 1) will be critical to advance the bottom-up design of such systems and achieve fast charging in SSBs.

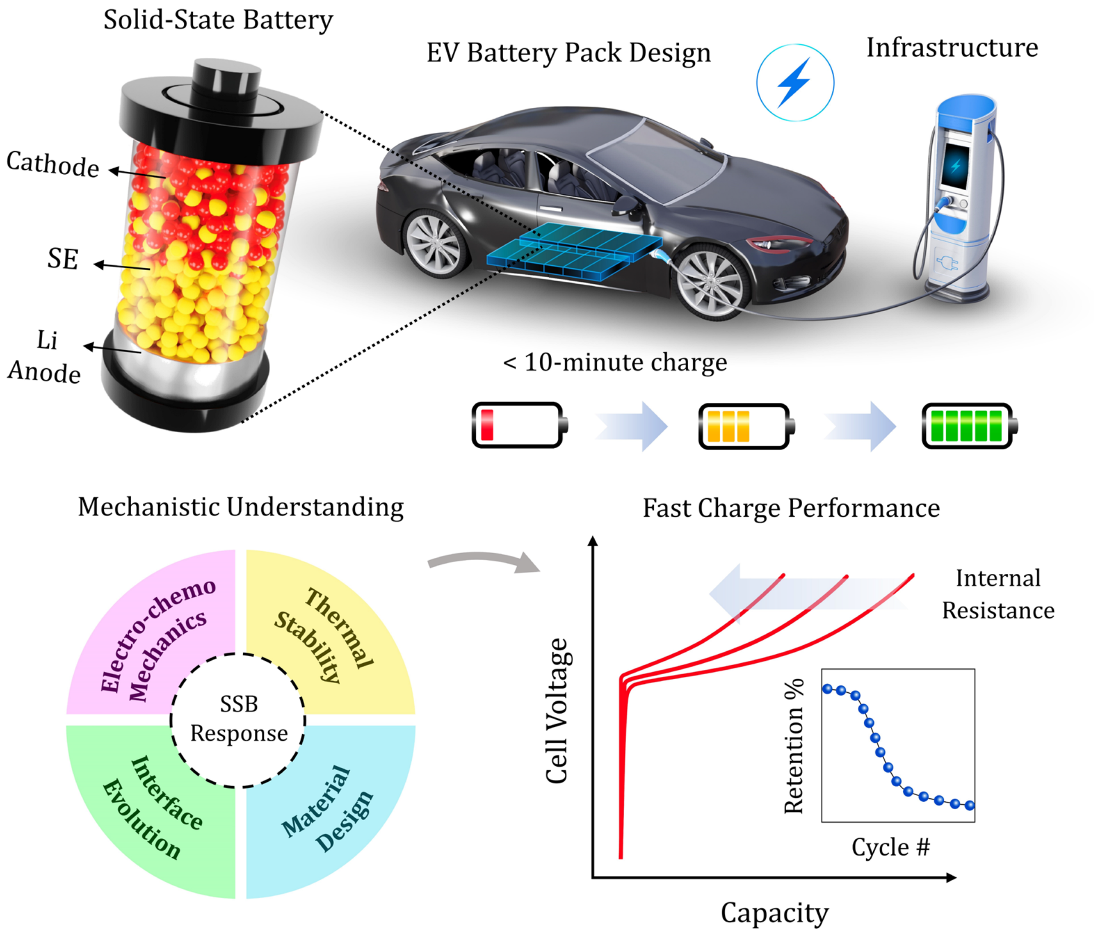

Figure 1. The development of SSBs offers an exciting opportunity to simultaneously achieve high energy density and fast charging rates. Despite presenting uniquely beneficial transport, thermal, and mechanical attributes, the rate performance of SSBs still faces significant bottlenecks.

In this Perspective, we first compare and contrast the fundamental electrochemical, transport, mechanical and thermal considerations for fast charging of LIBs and SSBs, and connect them to performance and degradation. Fast charge limitations of liquid-based Li metal batteries are also discussed in the context of morphological instability and rate capability, and their underlying interfacial mechanisms are compared with those in SSBs. Towards achieving the future target of <10 min fast charging in SSBs, we discuss the major electro-chemo-mechanical and transport challenges that need to be addressed. These limiting mechanisms are further linked to the intrinsic material evolution and interfacial complexations within the system. To overcome the underlying fast-charge challenges, intrinsic (e.g., interface design, material properties) and extrinsic (e.g., temperature, pressure) design factors that can modulate the electrochemical, transport and mechanical response of SSBs, and therefore fast charge capability, have been outlined. Lastly, we propose a list of critical research questions that must be answered to gain fundamental insight into the fast charge response of SSBs, and bridge the scientific gaps towards successful implementation.

Fast Charge Limitations of Conventional Li-ion Batteries

We begin by discussing the mechanisms that limit fast charge of conventional Li-ion batteries, which will enable comparison with SSBs in a later section. During fast charging, LIB operation involves non-equilibrium processes and exhibits a transition from reaction-limited to transport-limited conditions.[27] The low cationic transference number ($t_{Li+} < 1$) of liquid electrolytes engenders concentration gradients across the cell during charging, resulting in accumulation and depletion of Li^+ near reaction sites at the positive and negative electrodes, respectively. At higher rates of charging, mass transfer limitations intensify and lead to increased magnitudes of concentration overpotential and ohmic drop in the electrolyte phase, especially within the tortuous electrode framework[5, 28] (Figure 2(a)). Consequently, increased polarization drives the cell voltage towards cut-off at earlier stages of cell operation, resulting in a decrease in accessible capacity at high C-rates. Diminished concentrations of Li^+ at regions away from the interface between the negative electrode and separator can also lead to reduced intercalation kinetics and poor utilization of the active material within the electrode, which results in current focusing near the separator.

Under fast charge conditions, large kinetic overpotentials are also established to sustain the increased rates of applied current. In conjunction with the ohmic and concentration overpotentials, these irreversibilities in the system can push the local electrode potential below 0 V vs Li/Li$^+$.[29-33] This thermodynamically favors the formation of metallic lithium (Figure 2(b)), and results in competing kinetics between Li intercalation and plating on the graphite surface. Li plating poses major challenges and hazards including electrolyte decomposition, internal short-circuit risk, and capacity fade. Since the electrolytes in LIBs are optimized for graphite rather than Li metal, the reversibility of plated Li in these systems is generally poor. For a given C-rate, thick electrodes produce larger concentration gradients and kinetic overpotentials, leading to lower accessible capacities and an increased tendency for plating. Hence, the current strategy of increasing energy density with thicker electrodes results in a fundamental trade-off with charging rate.[34, 35]

Fast charging also amplifies the ohmic and kinetic heat generation modes within the battery and results in increased internal cell temperatures.[36, 37] Sufficiently high temperatures (~60^{o}C) can trigger side reactions[38] and electrode degradation, and can lead to thermal runaway in extreme circumstances (Figure 2(a)). In addition, intensified thermal effects can cause large diffusion-induced stresses within the active material host, thereby rendering a greater propensity for particle fracture.[39, 40] Active material cracking (Figure 2(b)) further facilitates electrolyte seepage and decomposition, and it can reduce the accessibility of electrochemical reaction sites. While high temperatures pose concerns of accelerated aging and thermal safety, fast charging at sub-zero temperatures is limited by sluggish kinetics and transport, eventually leading to Li plating[41, 42] and reduced energy densities. The degradation response of LIBs under fast charge conditions and the underlying mechanisms have been summarized in Figure 2.

In summary, fast charging of LIBs triggers mass transport limitations, deleterious side reactions, and excessive heat generation, which adversely affect their electrochemical performance, lifetime, and safety. Under fast charge conditions, these limiting mechanisms and degradation modes are further amplified (locally) by spatial heterogeneity in state-of-charge and current focusing. Fundamentally, fast charging of LIBs is constrained by electrolyte transport, Li plating, solid-state diffusion, and the restricted thermal window necessary for optimal electrochemical operation.

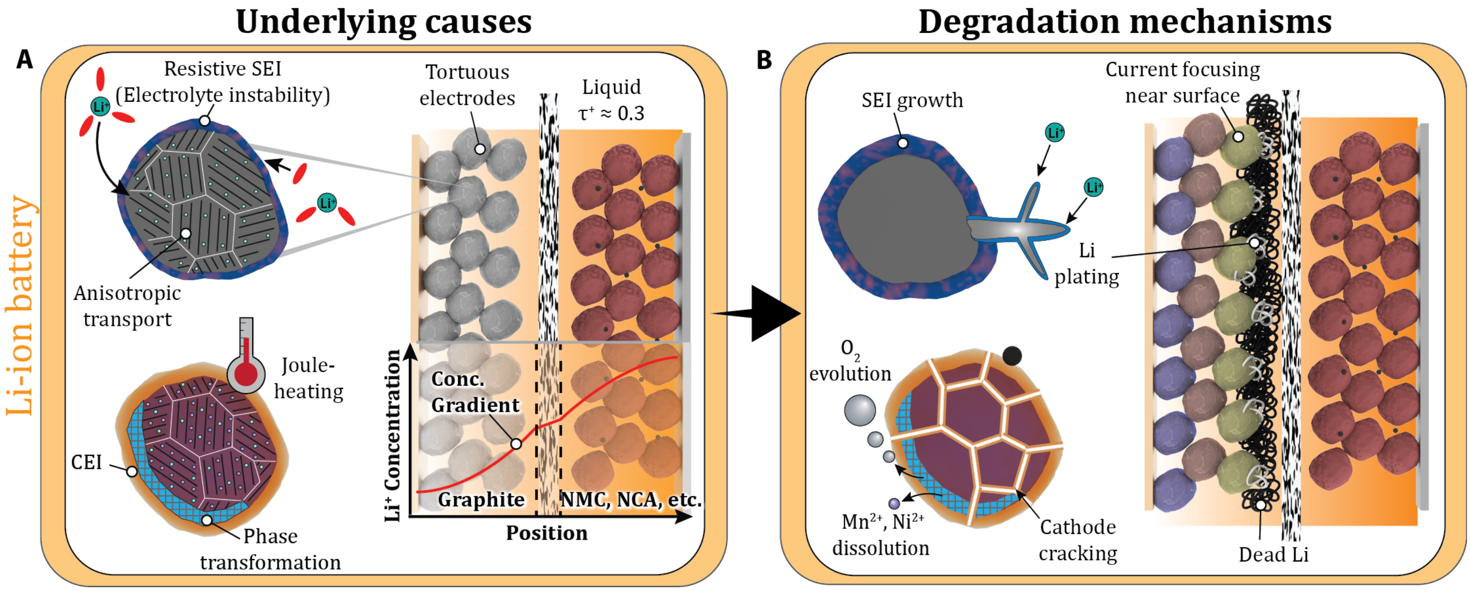

Figure 2. Fast charge implications on the electrochemical-thermal response and degradation of LIBs, with underlying causes shown in (a) and degradation mechanisms shown in (b). Electrolyte concentration gradients, intensified Joule heating, SEI (solid-electrolyte interphase) growth, Li plating, and cracking of the cathode material are major factors that limit the implementation of fast charge.

Fast Charge Limitations in Li Metal Batteries with Liquid Electrolytes

The promise and possibility of enabling higher energy densities has motivated a recent resurgence of research on the use of Li metal anodes (high specific capacity = 3860 mAhg^{-1}, low density and the lowest standard electrode potential = –3.04 V vs. SHE) with liquid electrolytes.[43, 44] Unfortunately, many of the challenges associated with the irreversibility of Li metal plating under fast-charge conditions in LIBs are exacerbated in these cells, which intentionally plate Li metal during charge. It is noted that the electrolytes used in LIBs are not tuned for Li plating, which makes them even worse for plating in LIBs. While these challenges can be partially addressed by controlling the electrolyte chemistry to be optimized for Li metal electrodes rather than graphite,[45-47] significant hurdles still remain.

During charging, spatial heterogeneities along the Li metal surface (grain boundaries, SEI species, defects, pits, etc.) lead to local current focusing and subsequent growth of high-surface-area ‘dendrites’.[48, 49] The newly plated Li exposes fresh surface area, reacting with the electrolyte and consuming the Li reservoir. Stripping from these dendritic structures is typically inefficient, isolating regions of metallic Li from the electrode, forming “dead Li”.[50, 51] Accumulation of dead Li during extended cycling has been shown to be a key cause of failure in cells with Li metal anodes. In particular, the tortuous dead Li layer exacerbates mass transport limitations in the liquid electrolyte, which results in a decrease in the achievable power density (and thus fast-charging performance) during extended cycling.[50]

To increase Coulombic efficiency (CE) for Li metal anodes in liquid electrolytes, previous studies have explored the influence of charge/discharge protocol. It has been reported that CE increases during slow charging and fast discharging.[52, 53] Unfortunately, this is the opposite of what is desired for EV applications. Interestingly, there seem to be competing effects during fast charging, where nucleation density of plating increases with increasing current density[48, 54, 55] (which is beneficial), but the subsequent growth morphology under fast charge conditions can promote a higher surface area, which exacerbates SEI formation and irreversible capacity loss.

These competing effects have motivated investigations of methods to decouple nucleation density from surface area. In particular, some of the highest Coulombic efficiency values to date have been reported for 3-D electrode architectures with "lithiophilic" surface modifications.[56-61] This strategy reduces the kinetic overpotentials during fast charging while promoting uniform growth. Without a lithiophilic coating, the reduction in local current density from a high-surface-area current collector will result in a decreased nucleation density, which can lead to a steric hinderance to plating of large, low-density deposits within the structure.[58] However, when adding a reactive coating that alloys with Li metal, a sufficiently high nucleation density can be achieved, allowing for the entire electrode surface to be active.

Regardless of whether the electrode is planar or 3-dimensional, the local current density during charging plays an important role in the plated Li morphology. A variety of morphologies have been observed, including needle-like, mossy, and fractal dendrites.[62-64] Furthermore, transitions in reaction pathway can occur during plating and stripping, which are driven by spatially-varying kinetics along the electrode surface.[65] One potentially catastrophic transition in morphology that has been observed is the transition from mossy Li to fractal dendritic growth at the onset of electrolyte diffusion limitations.[66] While the mossy Li deposits are typically larger than the pore size of separators, the fractal dendrites have been observed to more easily penetrate the separator and cause dangerous short-circuits.

The evolution of concentration gradients within the electrolyte during fast charging will be further exacerbated by mechanical deformation of plated Li. When dendrites are plated and stripped repeatedly, the non-planar Li morphologies experience compressive deformation, which results in the formation of a compact and tortuous interphase.[62] This viscoplastic deformation of Li metal will be influenced by the strong dependence of Li on strain rate and temperature.[67-69] Under fast-charging conditions, the compressive strain rate of Li will increase, resulting in a higher flow stress. The higher flow stress would make it more difficult for mossy Li to form the compact morphological layer that is required to achieve high CE in Li metal batteries. Additionally, this would increase the propensity for Li dendrites to penetrate the polymer separator. The coupled nature of electro-chemo-mechanical phenomena will have implications in solid electrolyte cells, as discussed in the following sections.

Many approaches have been explored to stabilize Li metal cycling in liquid electrolytes, including electrolyte design,[45-47] electrode architectures,[70, 71] coatings,[57] elevated cell temperatures[72-74] and more.[75] While these mitigation strategies have made significant progress, long-term cycling, in particular with fast-charging, remains challenging. In addition, the intrinsic safety challenges of Li metal anodes in flammable liquid electrolytes are of significant concern for many applications.

Theoretical Advantages of Solid-State Batteries for Fast Charge

Solid electrolytes offer inherently unique transport, thermal, and mechanical characteristics that can potentially address the fast charging barriers of safety, performance, and degradation exhibited by their liquid counterparts. Moreover, through the incorporation of lithium metal anodes instead of graphite, SSBs can potentially provide gravimetric and volumetric energy densities 40% and 70% higher than LIBs, respectively.[15] The combination of the potential for high energy content and fast charge provides strong motivation to develop these systems. This section discusses the theoretical advantages of SSBs that make them prospective candidates for fast charge; the challenges associated with many of these potential advantages are discussed in a later section.

Transport in Solid-State Batteries

As discussed previously, concentration polarization in liquid electrolytes is one of the primary factors that limits the fast charge performance of LIBs. Such concentration gradients result in asymmetric concentration profiles across the positive and negative electrodes.[76] While the local depletion of charge carriers limits ionic conductivity inside the negative electrode, large salt concentrations result in overlapping of ion solvation shells, and thereby provide restricted ionic mobility within the positive electrode. Hence, liquid electrolytes offer a relatively narrow window of salt concentrations to achieve optimal ionic conductivities. Given the large concentration gradients that manifest at high charging rates,[5] liquid electrolytes pose a major bottleneck for fast-charge operation of LIBs.

In contrast, inorganic solid electrolytes (ISE) such as $Li_7La_4Zr_2O_{12}$ (LLZO), Li_3PS_4 (LPS), Li_6PS_5Cl and $Li_{10}GeP_2S_{12}$ (LGPS) are typically single-ion conductors that exhibit a transference number (t_{Li+}) of effectively 1.0. Unlike liquid electrolytes that present solvation environments for ion transport, Li^+ travels through the rigid anion framework of the crystal lattice of ISEs. Hence, ionic concentration does not vary dynamically with the passage of current as it does in liquid systems. In recent years, sulfide single-ion conductors such as $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$ and $Li_{9.6}P_3S_{12}$ have been developed with exceptional room-temperature ionic conductivities as high as 25 mS cm^{-1},[18] which is higher than most liquid/separator composites. In addition, such systems do not experience the process of de-solvation at the electrode-electrolyte interface and thus have been observed to offer minimal charge transfer resistances.[18, 77] The high cationic transference number (~1) and mechanical rigidity of such ISEs also have the potential to prevent local ion depletion and enable compact deposition morphologies, which are critical challenges faced in liquid-based metal battery systems.[78] To summarize, ISEs bypass concentration gradients and along with the utilization of a Li metal anode, have the unique potential to simultaneously enable high energy densities and sustain fast charging rates.

It is to be noted that polymer-based solid electrolytes still involve mass transport limitations and provide lower ionic conductivities at room temperature than ISEs.[79] Due to the limited rate performance of current polymer electrolytes, we do not discuss them in detail here for fast-charge applications.[15]

Thermal Performance and Safety

Replacing the liquid electrolyte with a non-flammable ISE enhances the thermal stability window when compared to organic liquid electrolytes,[18] and it reduces the risk of thermal runway when internal short-circuits occur. Designing high-energy-density batteries via higher active material packing or by incorporating thicker electrodes is associated with increased ohmic heat generation rates that lead to a rise in internal temperatures. Hence, achieving the fast charge goals in the high-energy-density systems needed for EVs requires critical consideration of thermal performance and safety aspects.[37] While LIBs tend to exhibit accelerated side reactions and degradation at elevated temperatures (~60 °C), SSBs based on ISEs have demonstrated excellent cycling stabilities up to 100 °C.[18] SSBs can potentially sustain the large thermal fluctuations during fast charge without undergoing additional degradation mechanisms and thus retaining long-term stability. In fact, while elevated temperatures are often avoided in conventional LIB packs through battery management systems,[80-83] they are potentially beneficial for transport and fast charge in SSBs and could be incorporated into the design of optimal SSB modules and packs. It is noted that elevating the operating temperature in LIBs can also improve fast charge performance, particularly at low ambient temperatures.[10] Solid electrolytes offer enhanced thermal stability at high temperatures and comparable ionic conductivity with liquid electrolytes at room temperature.[18] The morphological stability of the anode and electrochemical performance of the SSB depend on the kinetics of transport and reaction, and hence the thermal environment in the vicinity of different solid-solid interfaces within the system. Temperature-dependent mechanisms such as vacancy diffusion and viscoplasticity (creep) of lithium play a pivotal role in preserving the anode morphology during electrochemical operation.[84-86] Additionally, further enhancement in ionic transport within the solid electrolyte has also been considered beneficial towards achieving homogenized reaction distributions at the anode interface[87] and improved ionic percolation within the cathode microstructure.[20, 88]

Operating the SSB at elevated temperatures that can thermally activate the kinetics of mechanisms such as ionic transport within the electrolyte/cathode, vacancy transport within lithium, and lithium creep behavior theoretically offers significant advantages in terms of interface stability, reduced internal resistance and improved cell performance. However, low-temperature operation of the SSB would result in reduced kinetics of such transport mechanisms, potentially having a deleterious effect on interface behavior and performance. Hence, it is important to assess the efficacy of such temperature-dependent mechanisms on the cold-start ability and fast charge operation of SSBs at low ambient temperatures.

In future, the development of solid electrolyte materials with higher thermal conductivities would be important to mitigate thermal hot spots and homogenize internal cell temperatures during fast charging. In addition, the cathode microstructure design can also be tailored to modulate the internal heat generation and temperature rise within the battery.[89, 90] Overall, solid electrolytes offer improved safety and reduced degradation for fast-charge operation.

Cell Architecture and Interface Control

The rigid nature of ISEs also affords several advantages with respect to the cell architecture and control of the electrode/electrolyte interface. In liquid cells, the electrolyte flows to contact the entire exposed area of the electrode. While this provides intimate contact for charge transfer, it can also lead to continuous side-reactions and result in the formation of undesirable interphases. In particular, Li metal electrodes undergo large volume expansion and generate fresh interfaces with the electrolyte, which results in repeated SEI formation and consumption of the active metal reservoir. Similar phenomena occur in the positive electrode, where active particle cracking occurs and exposes interior surfaces to the electrolyte. Under high charging rates, these mechanisms can intensify and eventually lead to accelerated degradation of the electrode-electrolyte interfaces within the system.

In contrast, the rigid nature of ISEs can help in preserving their shape during cycling, and fresh regions of the electrolyte are less likely to be continuously exposed to the electrode in the same way as when surrounded by a liquid. This means that once a passivating SEI is formed (either during manufacturing or during formation), subsequent side reactions and SEI growth can potentially be minimized. For Li/SSE interfaces, the regions prone to SEI formation after the formation step are those where fresh lithium metal is deposited, such as around a penetrating lithium filament in the solid electrolyte. This dimensional stability affords researchers an enhanced ability to engineer the electrolyte/electrode interface using myriad avenues including 3D architectures, wetting layers, self-healing, nucleation layers, and more.[91-94]

Challenges for Fast Charge of Solid-State Batteries

Despite the exciting potential of SSBs for achieving fast charge, there are fundamental electro-chemo-mechanical challenges at various solid-solid interfaces within these systems that must be overcome. Dynamic processes at interfaces between the electrode materials and the solid electrolyte are particularly critical, as instabilities at solid-solid interfaces can degrade kinetics and lead to capacity and/or power fading. Importantly, many aspects of active material and interface evolution can potentially be controlled by either engineering the materials/interfaces or by modifying the electro-chemo-mechanical conditions. With respect to the solid-state cathode, ion percolation, electrochemical contact and chemo-mechanical degradation are major factors that limit the fast-charge performance of SSBs. On the other hand, the morphological instability (e.g., filament growth above the 'critical current density' (CCD)) of the Li anode is a major aspect that limits high charging rates. In this section, we summarize the key challenges in achieving fast charging in SSBs and connect them to the material evolution and various interfacial interactions in the system. We discuss the fundamental mechanisms that can limit charge rates in SSBs, with the goal of highlighting materials challenges that must be addressed.

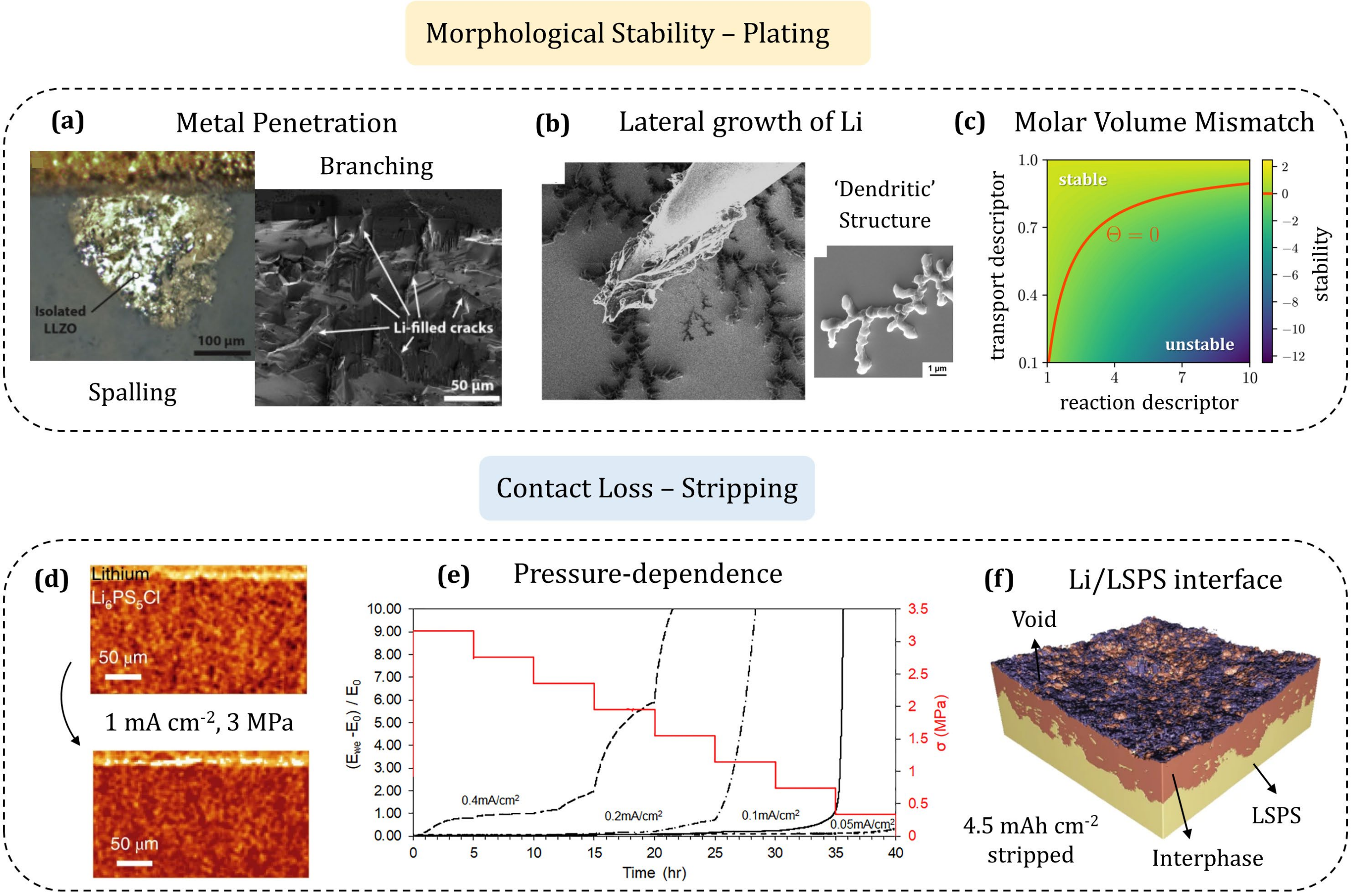

Figure 3. Morphological stability during plating: (a) Formation of various Li penetration morphologies (e.g., spalling, branching) observed using *operando* video microscopy[25] (Reproduced with permission from [[25]]. 2020 Elsevier) (b) Scanning electron microscopy (SEM) images showing lateral growth of Li along an ISE surface[77] (Reproduced with permission from [[77]]. 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim) (c) Mechanistic description of interface stability during plating based on the concept of molar volume mismatch of interacting species.[95] (Reproduced with permission from [[95]]. Copyright 2020 The Electrochemical Society ("ECS")) Contact loss during stripping: (d) Void growth (white regions) at 3 MPa and 1 $mAcm^{-2}$ for the Li/Li_6PS_5Cl interface.[96] (Reproduced with permission from [[96]]. 2019 Springer Nature)

(e) Pressure-dependent potential response due to stripping[97] (Reproduced with permission from [[97]]. Copyright 2019 Elsevier) (f) Formation of voids at the Li/$Li_{10}SnP_2S_{12}$ interface during stripping. (*operando* X-ray tomography).[98] (Reproduced with permission from [[98]]. 2021 Springer Nature)

Electrodeposition Stability

Despite the theoretical potential of dendrite suppression by mechanically rigid ISE separators, solid electrolytes have been widely reported to exhibit inhomogeneous electrodeposition and Li metal penetration,[25, 84] which can lead to mechanical failure and internal short circuiting. With the high current densities (10-20 mA/cm^2) necessary for sub 10-min charging, such risks of system failure are further exacerbated. Above the CCD,[78] filamentary growth/short circuiting has been observed across a wide range of solid electrolytes including the garnet-based $Li_7La_4Zr_2O_{12}$, Li_3PS_4, Li_6PS_5Cl, and Li_2S-P_2S_5.[99, 100] Recent studies have highlighted the dependence of CCD on different aspects such as external pressure,[101] temperature,[85, 86] interface resistance,[102] and discharge conditions.[96] Preferential plating at surface flaws and electrode edges has been observed at fast charging rates, leading to crack formation and mechanical failure of the solid electrolyte.[103] Figure 3(a) illustrates the formation of different Li penetration morphologies such as spalling and branching in the Li-LLZO system that have been observed using *operando* video microscopy.[25] The lateral growth of lithium along the surface of ISEs has been identified to be an important mechanism limiting the application of high current densities during charging.[77] Figure 3(b) depicts the SEM images showing the lateral growth of Li on crystalline LLZO surface, along with a magnified image of the dendritic structure.[77] Filament propagation has also been attributed to microstructural features including pore connectivity and density that are linked to electrolyte synthesis conditions.[104-107] Fundamentally, the lithium metal-solid electrolyte interface hosts a coupled set of electrochemical, chemical, transport, mechanical and morphological interactions that impact the performance and safety of SSBs. It is to be noted that mechanisms leading to non-uniform deposition in inorganic solid electrolytes are significantly different from liquid and polymer-based electrolytes.[78]

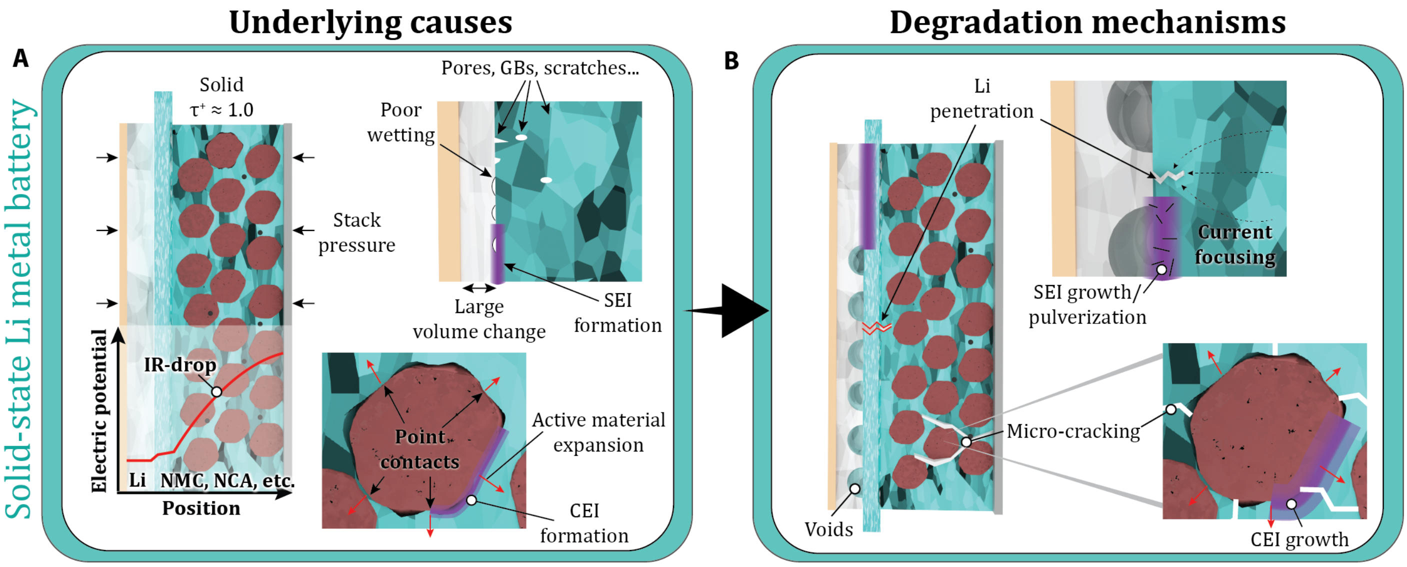

Figure 4. Major fast-charge limitations for SSBs, with underlying causes shown in (a) and degradation mechanisms shown in (b). Filament propagation through the solid electrolyte, loss of solid-solid contact area, and mechanical degradation of the active materials are important aspects that currently limit fast charging of SSBs.[17]

While recent efforts have focused on explaining the chemo-mechanical mechanisms governing lithium deposition, plastic flow, and penetration/fracture,[23] a comprehensive understanding of lithium filament nucleation and growth has not yet been attained. Various candidate mechanisms such as current focusing at grain boundaries,[108-110] molar volume mismatch of interacting species,[95] interphase morphology,[98, 107, 111] electronic conductivity of the solid electrolyte[112, 113] and poor electrochemical contact at the solid-solid interface[96] have been studied to understand the underlying reasons for interfacial instability and cell failure (Figure 4(a) and 4(b)). Their implications on interface degeneration, filament propagation and mechanical failure of the solid electrolyte typically intensify at high charging rates or repeated charge/discharge of the battery. The effect of a candidate interface instability mechanism, species molar volume mismatch, has been illustrated in Figure 3(c).[95] It is inferred that the evolution of mechanical stresses fundamentally alters the reaction kinetics and ion transport interactions at the solid-solid interface, which jointly regulate the electrodeposition stability of the anode. In this regard, the development of advanced computational models that can evaluate the morphological stability of the anode including factors such as the thermodynamic properties of the interacting species,[95] ionic transport in the solid electrolyte microstructure,[106] plasticity[87, 114] and creep behavior[115] of lithium would be critical to gain a mechanistic understanding of the fast charge response. Preserving the morphological stability of the Li metal anode and preventing unwanted mechanical penetration of Li continues to be a major challenge that must be addressed to achieve fast charging in SSBs.

Plating-Stripping Crosstalk

A distinct feature of SSBs featuring Li metal anodes is the effect that discharge can have on the deposition stability of a subsequent charging operation. During discharge (Li stripping), the kinetics of Li self-diffusion and creep compete with local rates of electrochemical reaction at the metal-electrolyte interface.[84, 96] In principle, if stripping rates are larger than the rates of metal replenishment via mechanical deformation and self-diffusion, voids can form and grow at the interface.[23, 98, 116] In recent studies, the void growth mechanism has been analyzed using various techniques including three-electrode measurements and *operando* X-ray tomography. Based on three-electrode cell analysis, critical stripping current has been identified as an important factor influencing the growth of filaments during charging.[96] Figure 3(d) shows *in situ* X-ray computed tomography images, illustrating the formation of voids at the Li/Li_6PS_5Cl interface.[96] Depending on the creep behavior of Li, the propensity for void growth and concomitant effect on overpotential response at the interface is a function of applied pressure in the system (See Figure 3(e)).[97] In solid electrolytes such as $Li_{10}SnP_2S_{12}$ (LSPS), the void growth process is further linked with the formation of an interphase at the anode.[98] Based on *operando* X-ray computed microtomography experiments, Figure 3(f) depicts the complex interplay between void formation and interphase growth during stripping at the Li/LSPS interface.[98]

In turn, this deterioration in interfacial contact (Figure 4(a) and 4(b)) will lead to current constriction and manifests in the form of increased cell polarization during stripping.[25, 98] During subsequent Li plating upon charging, the pre-existence of voids results in the reduction of electrochemically active area and a consequent increase in local current densities. More importantly, contact loss due to stripping can potentially result in the formation of isolated contact regions and interfacial discontinuities that experience larger current focusing. The preferential nucleation of new Li at local hot spots will increase the driving force for filament penetration and mechanical failure of the solid electrolyte. Hence, preventing contact loss during discharge is critical to achieve uniform reaction currents and mitigate the risk of internal short-circuit during fast charging of SSBs.

To address this challenge, larger stack pressures and temperatures have been shown to enhance the ability to maintain a continuous contact area and enable higher discharge rates.[86, 97] This points toward the critical role of the mechanical properties of Li metal in determining both void formation during stripping and CCD. In particular, the viscous flow of Li, either in the form of viscoplastic deformation in the solid phase[67, 68] or fluid flow of molten Li,[85] has been shown to be a critical parameter to increase the rate capability of Li metal-solid electrolyte interfaces.[117] Furthermore, increasing temperature also affects interfacial kinetics and ionic transport in the solid electrolyte, which can reduce current focusing and counteract the driving force for fracture.[118]

While large stack pressures improve interfacial contact, they can also result in greater risk of damaging internal cell layers and mechanically driving Li metal into the solid electrolyte;[119] this can also adversely impact internal cell resistance. Moreover, the application of large stack pressures in commercial cell housings may be impractical. While extrinsic parameters like stack pressure can improve the point to point contact area between the solid electrolyte and Li metal up to a certain degree, intrinsic properties like wettability between the two materials, depending on their surface characteristics and morphology, would also jointly contribute to determine the homogeneity of plating and stripping at the solid-solid interface. Owing to the vastly differing limiting mechanisms at play during plating and stripping, stack pressure and thermal design considerations to achieve optimal performance and interface stability during plating and stripping may be significantly different. In Figure 4(a) and 4(b), the overall set of underlying mechanisms and electrodeposition responses of solid electrolyte-metal anode systems are highlighted.

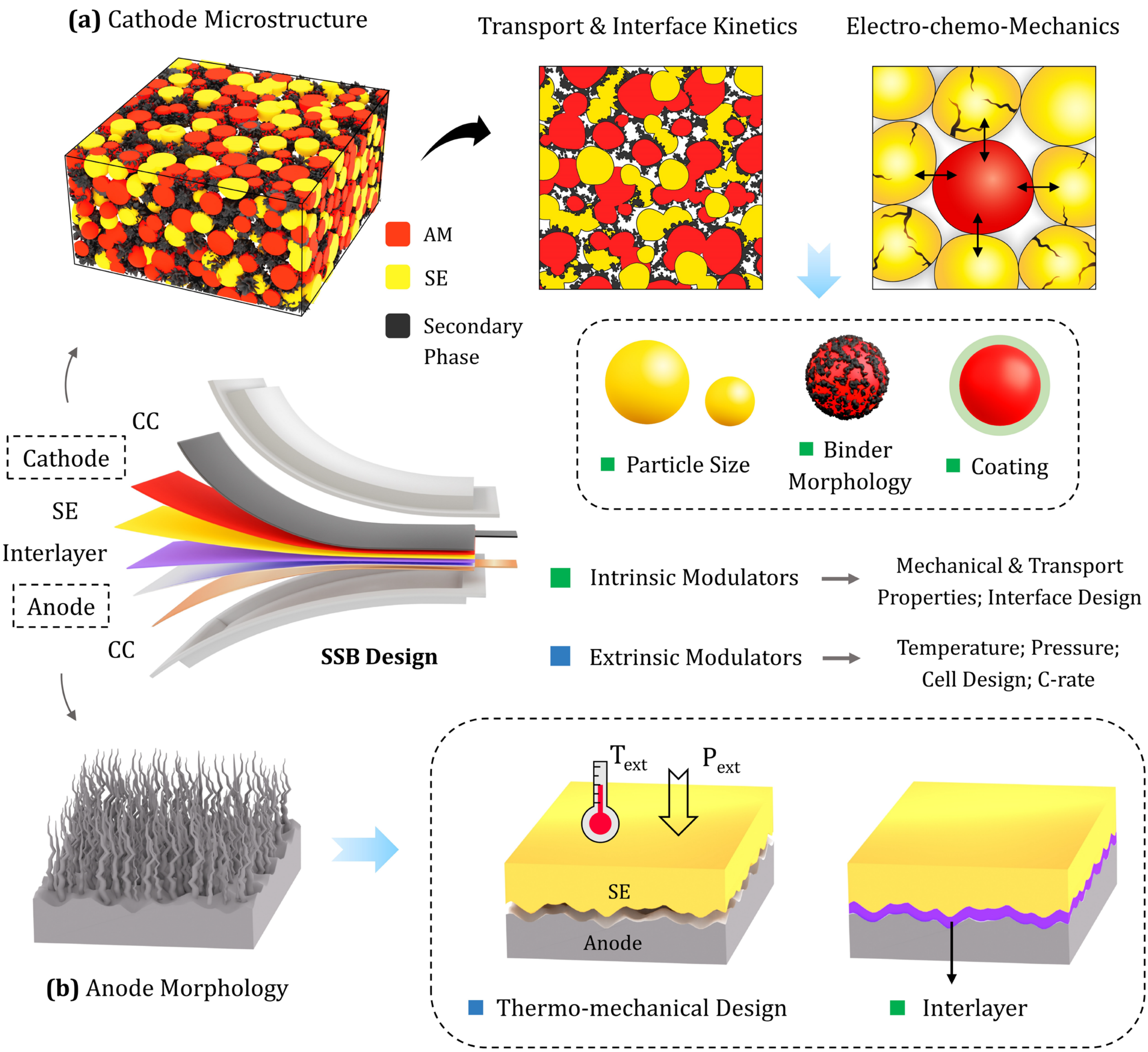

Figure 5. Summary of design factors for intrinsic and extrinsic modulation of the fast-charge response of SSBs. (a) In the cathode, ionic percolation, electro-chemo-mechanics, and interfacial kinetics are key governing mechanisms. Identifying optimal regimes of particle size, binder morphology, and active material coating are all required to tailor the overall cathode architecture to sustaining fast charge rates, without exhibiting ion transport and chemo-mechanical limitations. (b) In the anode, optimized

thermo-mechanical design of the cell and the incorporation of interlayers that can enhance active contact and reaction homogeneity are key design factors that can modulate the potential unstable evolution of the metal anode during fast charge and subsequent discharge.

Other Anode Material Candidates

The challenges associated with contact loss during stripping and short-circuiting during plating of lithium metal have motivated the investigation of other high-capacity anode material candidates. Alloy anodes, such as silicon and tin, have long been studied for conventional Li-ion batteries but have only recently begun to be more widely investigated for solid-state batteries[120-122]. While alloy anodes offer the potential for high energy density and significantly reduce the risk of lithium dendrite growth, they present different mechanistic challenges to fast charging. In particular, alloy anodes require solid-state diffusion over the thickness of the electrode, which can be a kinetically limited process regardless of whether the solid-state electrolyte is mixed with the alloy material. This highlights an advantage of Li regarding fast charge: the electrodeposition of Li occurs at the electrode/electrolyte interface and the kinetics are not dependent on long-range diffusion in the electrode material. Furthermore, the non-uniform expansion of alloy anodes can cause large local and global stresses to be exhibited,[121] which can cause uncontrolled morphological changes. In short, dedicated further effort is required to determine the energy storage and fast charge characteristics of alloy anodes in SSBs.

Microstructure and Design of the Cathode

An important aspect of single-ion conductors towards electrode design is the absence of concentration gradients in response to ionic current. However, a major bottleneck for fast charging in SSBs is related to kinetics within solid-state cathodes, including ion transport and electrochemical reactions at interfaces. Achieving enhanced fast charge performance in SSBs requires designing cathode microstructures that provide sufficient electrochemically active area and ionic/electronic percolation pathways, while retaining interfacial stability and long-term cyclability. Given the limited ionic conductivity of cathode materials such as $LiCo_xNi_yMn_zO_2$, the cathode active particles must be mixed with a solid electrolyte to obtain low-impedance ionic transport pathways throughout the electrode[21] (Figure 5(a)). Despite incorporating solid electrolytes directly into the composite cathode, transport in this layer is often rate-limiting for SSBs[21] (Figure 5(a)). A large fraction (~ 30-50 wt.%) of electrolyte particles is often used within the cathode to ensure ion percolation, which penalizes energy density.[123] With an increase in active material loading to achieve higher energy densities, ion percolation limitations within the cathode architecture become more critical. In this context, recent studies have reported a decrease in rate performance at higher active material loading. (~ 80 wt.%).[88, 124, 125] This has been attributed to a higher electrostatic potential (IR) drop within the composite electrode structure, which results in spatial heterogeneity in state-of-charge throughout the electrode thickness.[88] Therefore, energy and power density tradeoffs exist in composite cathodes in SSBs, analogous to Li-ion batteries.

Solid-state cathodes can also be limited by insufficient interfacial area for charge-transfer reactions.[126] The presence of voids and the incorporation of secondary phases including the conductive additive and polymer binder can further reduce the active interfacial area and impede ion percolation pathways. The microstructure of the composite structure including aspects such as particle size, distribution, porosity, and tortuosity also plays an important role in electrochemical performance along with ionic conductivity and active area. Together, these factors dictate the ohmic and kinetic losses within the cathode composite. In addition, while conductive additives can enhance electronic conductivity, they have been found to promote oxidative decomposition of the solid electrolyte,[127] which makes interfacial engineering through coatings more complicated in composite cathodes.

While design and construction of solid-state composite cathodes has been dominant in SSB research (Figure 5(a)), it is necessary to critically evaluate the compatibility of this design approach with fast charging. At higher charging rates, chemo-mechanical challenges including interfacial delamination and particle cracking due to severe volume fluctuations of the active material need to be understood and addressed.[128-131] Therefore, the relative mechanical compliance of the active material and surrounding matrix of solid electrolyte must be considered under a range of volumetric strain conditions. This mechanical damage can potentially be mitigated by using single crystal cathode particles instead of polycrystalline materials.[132] In addition, cathode particles should not be completely surrounded by electrolyte to avoid electronic isolation from neighboring particles while maintaining both electronic and ionic percolation networks throughout the electrode. Moreover, the stack pressures required to maintain particle contact within the cathode during high charging rates need to be optimized. In summary, a wide spectrum of design parameters (Figure 5) including the mechanical properties and particle sizes of the active material and solid electrolyte,[123, 133] morphology of the conductive-binder domain, and electrode thickness must be considered to simultaneously achieve high energy density and fast-charge operation of SSBs.

Creating sufficient ionic and electronic percolating pathways in thick cathodes may demand new cathode chemistries and architectures. For example, one approach is to create thick, dense cathodes that intrinsically possess higher electronic and ionic conductivity; this has been recently demonstrated[134] using a thick electrodeposited $LiCoO_2$ cathode with no conductive diluents.[135] Electrodeposited cathodes can be grown with preferred crystallographic facets that allow optimized ion transport pathways and charge transfer to enable fast charge, although the limits of charge/discharging rate need to be determined. Another approach[136] is to fabricate 3D templates that provide bi-continuous electronic and ionic pathways, to minimize tortuosity and simultaneously enable high active material loading. To bypass the challenges of constructing all-solid-state cathodes with high rate capability, recent studies have also incorporated liquid or gel electrolytes in the cathode to enhance rate performance.[137, 138] While this approach can, in principle, mitigate some of the disadvantages of all-solid-state composite cathodes, the introduction of a flammable liquid or gel component can also negate some of the safety benefits.

Interphase Formation

Interfaces between practical solid electrolytes and electrodes experience some degree of interphase formation that can irreversibly consume lithium ions and increase impedance. Most ISEs with relatively high ionic conductivity are thermodynamically unstable against Li metal, although this growth may be self-limited through the formation of stable interphase products. It is noted that ISEs that exhibit poor stability at high voltages are also susceptible to interphase formation in contact with conventional cathodes, an effect that is typically mitigated by coating cathode particles with ultrathin layers to stabilize the interface. In contrast to liquid electrolyte systems, SSBs do not necessarily allow for continuous wetting of new surfaces that are formed due to volume changes during cycling. This can be beneficial for limiting interphase formation compared to liquid-based batteries, particularly those with Li metal anodes.

The formation of interphases is dependent on the electrode potential, and high rates of charge could cause excursions to extreme potentials that aggravate interphase formation. This may be particularly important in cathodes that employ surface coatings[127, 139] to protect the solid electrolyte against decomposition. Formation of such interphases can also alter ion transport and reaction kinetics at the anode, along with hindering ion percolation within the cathode. The effect of decomposition and interphase growth at the solid electrolyte-active material interface in the cathode has been mathematically described below:

Charge conservation within the active material (equation 1) and solid electrolyte phases (equation 2) are expressed as:

$$\nabla \cdot (\sigma^{eff} \nabla \phi_s) - j_{BV} = 0 \tag{1}$$

$$\nabla \cdot (\kappa^{eff} \nabla \phi_e) + j_{BV} = 0 \tag{2}$$

Here, ϕ_s and ϕ_e represent the electric potential for electron transport (effective conductivity: σ^{eff}) in the active material and ion transport (effective conductivity: κ^{eff}) in the solid electrolyte, respectively. j_{BV} is the reaction current density at the solid electrolyte-active material interface, which is expressed as:

$$j_{BV} = a_s\, i_0 \left(exp\left(\frac{\alpha_a F}{RT}\eta\right) - exp\left(-\frac{\alpha_c F}{RT}\eta\right)\right) \tag{3}$$

Here, a_s is the active area for reaction, i_0 is the exchange current density, α_a and α_c are the charge transfer coefficients, R is the gas constant, T is the operating temperature, η is the overpotential and F is the Faraday constant. Formation/growth of a resistive interphase modifies the reaction kinetics:

$$\eta = \phi_s - \phi_e - U_{eq} - i_{BV}\, R_{interphase} \tag{4}$$

Here, U_{eq} represents the equilibrium potential; the interphase resistance ($R_{interphase}$) depends on the conductivity (k_{film}) and thickness/growth dynamics (δ_{film}) of the passivating products:

$$R_{interphase} = \frac{\delta_{film}}{k_{film}} \tag{5}$$

It is noted that the above formalism depicts how the formation of an interphase alters the lithiation/de-lithiation kinetics in the cathode. In addition to the lithiation/de-lithiation currents, consumption of lithium ions for interphase formation can extract a fraction of the total applied current.[29, 36] Overall, while fast charge can aggravate the formation of such interphases, depending on their transport properties and growth dynamics, the reaction landscape at the solid-solid interfaces is further modified.

Interphase-driven instabilities in the cathode will depend on both the mechanical and chemical properties of the active material and solid electrolyte, due to the deformation and decomposition processes that occur.[140] While there is a growing understanding of the nature of the interphase products that form and how they grow at open circuit and slow cycling rates, there is still the need to understand how interphase processes deviate under fast charge conditions that involve large overpotentials. In particular, it is important to know if the same passivating products that comprise stable interphases and enable reversible cycling are present during fast charging.

Design Strategies to Overcome Fast-Charge Challenges in Solid-State Batteries

Figure 5 summarizes key design considerations to address challenges relating to fast charge of SSBs, including interface evolution, ionic transport, and chemo-mechanics pertaining to the composite cathode and metal anode in SSBs. As presented in Figure 5(a), microstructural arrangement largely governs the coupled transport-kinetic interactions and mechanical response of the cathode. To eliminate rate limitations from the cathode, it is important to collectively optimize design parameters including the thickness, particle sizes (solid electrolyte/active material), interfacial coating on the active material, and morphology of the secondary phases (e.g., binder). On the other hand, while the incorporation of interlayers (Figure 5(b)) has yielded promising results for the anode in retaining interfacial contact,[94] it is critical to gain deeper insights into the underlying mechanisms regarding chemical and morphological (in)stability at interfaces. Additionally, the thermo-mechanical design of the cell should be evaluated, considering implications from both the anode and cathode. Overall, enabling fast charge in SSBs mandates a mechanistic analysis and comprehensive optimization of materials and architecture design. Critically, while interface characteristics, microstructure, mechanical properties and transport properties of the components can intrinsically modulate SSB behavior, factors such as temperature, stack pressure and cell design/architecture can act as extrinsic modulators[141] that could also be beneficially controlled for enabling fast charge characteristics (Figure 5).

As the scientific community investigating various aspects of SSBs grows, there is an excellent opportunity to comprehensively assess the challenges and opportunities for fast charge of SSBs and establish a strong fundamental knowledge base through this effort. In addition to the ideas presented in this Perspective, we propose the following set of research questions to guide future efforts:

(i) What is the effect of high overpotentials during fast charge on the distinct formation/growth dynamics of interphases at the anode and cathode? Can the individual responses at the anode and cathode be decoupled, for example through the use of three-electrode measurements?

(ii) How does internal heat generated during fast charge affect local reaction kinetics and (electro)chemical interface degradation? Can this internal heating be rationally controlled to enhance fast charge while minimizing degradation?

(iii) How do heterogeneities in the microstructure and interfaces within solid electrolyte/composite cathodes alter fast charge response in terms of local ion transport and reaction kinetics?

(iv) Can the successful implementation of interlayer design concepts preserve the morphological stability of alkali metal anodes even at high charging/discharging rates, and thus mitigate the requirement of large stack pressures and elevated temperatures?

(v) Along with materials and cell-level improvements, how can pack design and extrinsic modulators (temperature, pressure) be synergistically controlled to leverage the architectural advantages of SSBs and enable fast charge capabilities, high energy density, and long cycle life?

Summary

SSBs hold the potential to enhance the fast charge performance and safety of state-of-the-art LIBs; however, successful realization is predicated on systematic investigation and understanding of ionic transport, reaction kinetics, chemo-mechanical evolution, interface dynamics and thermal behavior of these systems. Despite the promise of SSBs for fast charge applications, key challenges must be overcome to enable optimal performance. As outlined in this Perspective, morphological stability and interphase growth at the anode, as well as microstructure-driven interactions and chemo-mechanics of the cathode, are important considerations to achieve enhanced performance, safety and minimized degradation during repeated fast charge operations. To accomplish the eventual goal of fast charge of 80% capacity in <10 min, it will likely be important to integrate system-level advancements, along with materials and cell-level improvements. A concerted effort involving research laboratories and industry will be critical to bridge the associated scientific and engineering gaps and accelerate progress in development of SSB technologies to enable a wide variety of electrified transportation.

Conflicts of interest

There are no conflicts to declare.

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Quotes for the paper:

Solid electrolytes offer inherently unique transport, thermal, and mechanical characteristics that can potentially address the fast charging barriers of safety, performance, and degradation exhibited by their liquid counterparts.

Preserving the morphological stability of the Li metal anode and preventing unwanted mechanical penetration of Li continues to be a major challenge that must be addressed to achieve fast charging in SSBs.

Achieving enhanced fast charge performance in SSBs requires designing cathode microstructures that provide sufficient electrochemically active area and ionic/electronic percolation pathways, while retaining interfacial stability and long-term cyclability.

Critically, while interface characteristics, microstructure, mechanical properties, and transport properties of the components can intrinsically modulate SSB behavior, factors such as temperature, stack pressure and cell design/architecture can act as extrinsic modulators that could also be beneficially controlled for enabling fast charge characteristics.