Solid-state lithium (Li) metal batteries (SSLMBs) have become a research hotspot in the energy storage field due to the much-enhanced safety and high energy density. However, the SSLMBs suffer from failures including dendrite-induced short circuits and contact-loss-induced high impedance, which are highly related to the Li plating/stripping kinetics and hinder the practical application of SSLMBs. The maximum endurable current density of lithium battery cycling without cell failure in SSLMB is generally defined as critical current density (CCD). Therefore, CCD is an important parameter for the application of SSLMBs, which can help to determine the rate-determining steps of Li kinetics in solid-state batteries. Herein, the theoretical and practical meanings for CCD from the fundamental thermodynamic and kinetic principles, failure mechanisms, CCD identifications, and influence factors for improving CCD performances are systematically reviewed. Based on these fundamental understandings, a series of strategies and outlooks for future researches on SSLMB are presented, endeavoring on increasing CCD for practical SSLMBs.

1. Introduction

Nowadays, the energy density of conventional lithium-ion batteries is gradually impeding their theoretical values. Li metal anode is an important precondition to realize a higher energy density, as it possesses a high specific capacity of 3860 mAh g\(^{-1}\) and the negative potential of \(-3.040 \, \text{V} \) versus \( \text{H}^+ / \text{H}_2 \).\(^{[1-4]} \) However, the formation of lithium dendrites will shorten the cycle lifespan and possibly trigger safety accidents in traditional batteries with organic liquid electrolytes.\(^{[5-7]} \)

The emerging solid-state electrolytes (SSEs) with high ionic conductivity, such as oxide garnets,\(^{[8,9]} \) sodium superionic conductor (NASICON),\(^{[10,11]} \) sulfide electrolytes,\(^{[12-24]} \) thin-film electrolytes (lithium phosphorus oxynitride, LiPON\(^{[25]} \)), lithium borohydrides,\(^{[26]} \) and solid-state polymers\(^{[27-30]} \) are believed to enable the practical applications of Li metal anodes.\(^{[31,32]} \) The high shear modulus of solid-state electrolytes can hinder free dendrite extension.\(^{[33]} \) Moreover, the high thermostability of solid-state electrolyte also enables a wide operation temperature, avoiding the issue of a thermal run away.\(^{[34]} \) Therefore, solid-state Li metal batteries (SSLMBs) are promising to realize an improved safety and energy density.\(^{[35-37]} \)

The maximum available current density of a solid-state battery is defined as critical current density (CCD), which is related to the power density of batteries and is of vital importance to solve the range anxiety of current electric vehicles (EV).\(^{[38-40]} \) CCD works as an important index to compare the performances of Li metal anodes and indicates many intrinsic behaviors at high current densities in solid-state batteries. Comprehensive understandings of CCD will help to unravel multiple hidden factors in Li-SSEs interfaces.\(^{[41]} \)

In fact, there are still large gaps of available current density in SSLMBs comparing with practical requirements (Figure 1). The industry standards for power batteries are shown in Table 1, including IEC (International Electrotechnical Commission, International), ISO (International Organization for Standardization, International), QC/T (Recommended Chinese Automobile Standards, China), GB/T (Recommended Chinese National Standards, China), NB/T (Recommended Standards of Chinese National Energy Administration, China), SAE (Society of Automotive Engineers, USA), and VDA (Verband Der Automobilindustrie, Germany), where a high working current (\(>4 \, \text{mA cm}^{-2}\)) and high single-cell capacity (\(>1 \, \text{Ah}\)) can deliver a current density of 0.5–1.5 mA cm\(^{-2}\) or even 10–40 mA cm\(^{-2}\) is usually required.\(^{[42-44]} \) However, lab-level SSLMBs are usually cycled at a current density lower than 0.5 mA cm\(^{-2}\). Much attention has been paid on pursuing the breakthrough on energy density, while the available current densities is also essential in the design towards practical Li metal pouch cells.\(^{[45-47]} \) As shown in Figure 1, the conventional pouch cells using Li metal anode with a satisfied energy density (>300 Wh kg\(^{-1}\)) and high single-cell capacity (>1 Ah) can deliver a current density of 0.5–1.5 mA cm\(^{-2}\) with liquid electrolyte.\(^{[48,49]} \) As reported by Samsung, the energy-dense solid-state pouch cells (900 Wh L\(^{-1}\)) can deliver the available current density of 3.4 mA cm\(^{-2}\) at 60 °C.\(^{[50]} \) Although currently the results measured with SSEs (e.g., 1–2 mA cm\(^{-2}\) for Li-garnet and Li-sulfide systems) still fall behind that measured with liquid electrolytes,
these results prove the potential of SSLMBs to achieve a higher power density.

Nowadays, the acquired CCD results cannot provide enough information due to the non-standard evaluations. Some measurements lack practical rationality (e.g., measured with a low areal capacity) and consistency (e.g., various evaluation protocols). Different measurement details can significantly influence the results. For example, cycling a battery under temperature higher than 100 °C can help to realize a current density of >20 mA cm\(^{-2}\) in garnet solid-state electrolyte systems.\(^{[51]}\) Practically, the electrode/electrolyte interfaces in SSBs dominate the CCD, while the understandings on the interfaces, including the: 1) mass transport of Li ions; 2) intrinsic interfacial physical and chemical properties; 3) the Li stripping and plating kinetics; and 4) interfacial evolution regularity\(^{[52]}\) still remain elusive. Hence, deeper and comprehensive theoretical understandings are essential to realize a quantum leap on CCD.

In this review, we underline the importance of the comprehensive understandings on CCD. The flow path on determining the CCD is shown in Figure 2. Underlying the Li anode/solid-electrolyte interfaces in SSBs, we systematically summarize the fundamental understanding on electrochemical mechanism of Li metal dynamics, the failure mechanisms of Li metal solid-state batteries and their critical influencing factors, trying to integrate the CCD with failure and limitation mechanisms to the emerging strategies. On the basis of these fundamental understandings, a series of solutions and previews for improving CCD performances are also put forward on the development for high-energy SSLMBs, promoting practical evaluation in future research.\(^{[2]}\)

Table 1. Standards for current densities towards a power battery for EVs.

<table>
<thead>
<tr>
<th>Country</th>
<th>Standard code</th>
<th>Measurement standard (cycle)</th>
<th>Current density [mA cm(^{-2})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>International</td>
<td>IEC-62660:2-2010</td>
<td>1/3 C for BEV</td>
<td>1.34</td>
</tr>
<tr>
<td></td>
<td>ISO-12405-4:2018</td>
<td>1 C, 2 C (standard), 10 C (if applicable) for a high-power pack</td>
<td>4, 8, 40 (if applicable)</td>
</tr>
<tr>
<td></td>
<td>GB/T-31467.2-2015</td>
<td>1/3 C (standard), 1 C, 2 C (if applicable) for a high-energy pack</td>
<td>1.34, 4, 8 (if applicable)</td>
</tr>
<tr>
<td>China</td>
<td>QC/T 743-2006</td>
<td>1/3 C (basic unit for measurement)</td>
<td>1.34</td>
</tr>
<tr>
<td></td>
<td>GB/T-33024-2016</td>
<td>1 C for room temperature</td>
<td>4</td>
</tr>
<tr>
<td>USA</td>
<td>SAE J2929-2011</td>
<td>High-energy type: 0.5 C</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High-power type: 1 C</td>
<td>4</td>
</tr>
<tr>
<td>Germany</td>
<td>VDA 2007</td>
<td>1 C, 10 C, 20 C</td>
<td>4, 40, 80</td>
</tr>
</tbody>
</table>

Notes: Current density is calculated by areal capacity in a commercial Li ion battery (4 mAh cm\(^{-2}\)); HEV: Hybrid Electric Vehicle; BEV: Battery Electric Vehicle; PHEV: Plug-in Hybrid Electric Vehicle; IEC: International Electrotechnical Commission; ISO: International Organization for Standardization; QC/T: Recommended Chinese Automobile Standards; NB/T: Recommended Standards of Chinese National Energy Administration; GB/T: Recommended Chinese National Standards; SAE: Society of Automotive Engineers; VDA: Verband Der Automobilindustrie.
2. The CCD Theory Underlying Solid Interface

2.1. The Development of CCD

The development of CCD can be traced back to the application of solid-state sodium batteries. The timeline of development history on CCD in SSLMBs is shown in Figure 3. In 1980s, the available maximum current density is measured in Na/β′-Al₂O₃/Na symmetric cells to indicate the interfacial wettability.[53] With the emergence of many new types of SSEs in lithium batteries, the concept of CCD is first put forward by Sakamoto et al. in an Li/LiₓLa₃Zr₂O₁₂ (the doped ones (e.g., LiₓLa₃Zr₂₋ₓMₓO₁₂ M = Ta, Nb; LiₓLa₃NₓZr₂O₁₂ N = Al, Ga, etc.) are also simplified as LLZO system,[51] exceeding which battery failure will occur. In solid-state Li metal batteries, Li dendrite penetration constitutes the main causes for short circuit. Recently, improving CCD has been treated as an important target for SSLMB research. Naturally, the CCD can be involved into a series of topics underlying metallic lithium/solid-electrolyte interfaces, including the current density dependent interfacial kinetics (e.g., ionic diffusion, Li metal nucleation/growth, and void production/annihilation), thermodynamics (e.g., parasitic reactions), and intrinsic quality of SSEs (e.g., degradation of the interfaces and the electrolytes). Deepened understandings will promote the development of CCD and contribute to standardizing future research.

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**Figure 2.** Schematic diagram of key issues on determining the critical current density.

**Figure 3.** Timeline of the development of critical current densities (CCDs) in solid-state batteries.[8,13,15,17,41,53,71,80,126,144,158] Reproduced with permission.[41] Copyright 2017, American Chemical Society. Reproduced with permission.[80] Copyright 2017, Elsevier. Reproduced with permission.[88] Copyright 2018, the Royal Society of Chemistry.
2.2. Interface Lithium Chemistry

Theoretically, CCD reflects the maximum available ionic transportation and charge transfer at the unit area and the time without fatigue system damage. The unit ionic flux passing across the interfaces and interfacial charge transfer rate co-determine the CCD value. This is actually related with the interfacial lithium chemistry and is the reflection of the essence of solid interfaces. The related lithium chemistry processes can be categorized into: a) interfacial lithium kinetics including the formation/consumption of Li ions and the elimination/formation of Li atoms at working interfaces; b) interface morphological evolution including the void formation and atom diffusions; and c) interface degradation and failure.

2.2.1. Basic Lithium Kinetics

There are a series of models for lithium deposition based on liquid electrolytes, such as heterogeneous nucleation model, space charge model, and solid-electrolyte interphase induced dendrite growth model.[5,54,56] The lithium deposition in solid-state systems share some similarities, while the unique chemical/mechanical state of various solid electrolytes will lead to novel lithium kinetics.

The lithium nucleation process is analyzed based on surface energy and chemical potential,[57] where the overpotential contributes to overcoming the surface energy and triggers Li embryo formation (Figure 4a). The lithium nucleation in solid-state systems is first observed in LiPON thin-film batteries.[58] Amorphous LiPON delivers good stability and high mechanical strength, avoiding the grain boundary to form a uniform local ionic distribution. Motoyama et al. took Cu as current collectors to probe the plating behaviors of Li nuclei (Figure 4b). The nucleation overpotential and nuclei sizes are directly related to the Young’s modulus of the current collectors.[59] The rigid current collector provides sustained high inner pressure, resulting in the larger size of nuclei with fewer nuclei sites at the same current density. The relationship between the overpotential and the nuclei size is as follows:

\[
\eta = \frac{\varepsilon EM}{\rho(1-\nu)} \left( \frac{3(r_i + r_f)^3}{2(r_i + r_f)^3 - r_i^3} \right) \frac{V}{1-\nu} \tag{1}
\]

where \(\eta\) represents overpotential, \(\varepsilon\) represents strain at \(\theta\) direction, \(E\) represents Young’s modulus, \(\nu\) represents Poisson ratio, \(r_i\) represents the nuclei radius, \(M\) and \(\rho\) represent the molar mass and density of lithium metal, respectively. These results prove that the increased Young’s modulus is related to increased overpotential, resulting in smaller Li nuclei.

The current densities also influence the initial morphologies of the plated lithium. Iriyama et al. systematically probed the role of current densities on the morphology of deposited lithium based on LiPON electrolyte.[60] The nucleation overpotentials are dependent on the current densities in a cell. The nucleation overpotentials can be predicted by the deviation of peak potential \(\eta_{NC}\). According to the Nernst equation, the Li plating process is described as:

\[
E = E_0 + \frac{RT}{F} \ln \frac{a_{LiPON}^{ad}}{a_{ad}} \tag{2}
\]

where \(a_{ad}^{p}\) represents the activity of polarized and adsorbed Li atom, \(a_{LiPON}^{ad}\) represents the activity of Li in bulk LiPON.

The overpotential is marked as \(\eta\). The activity of \(a_{ad}\) at different current densities is calculated as:

\[
a_{ad} = a_{ad}^{p} \exp \left( \frac{F\eta_k}{RT} \right) \tag{3}
\]

\[\Delta\mu = F\eta_k. \tag{4}\]

The increased chemical potential \(\Delta\mu\) influences the critical radius and the Gibbs free energy of nucleation. As calculated, subsequent formulas are given as follows

\[
r_i = \frac{\gamma V}{F\eta_k} \tag{5}\]
\[\Delta G = \frac{\pi \gamma^2}{\eta_k} \frac{V}{\hbar} \]

where \(r_c\) represents critical radius, \(\gamma\) represents unit Gibbs free energy of the nuclei, \(V\) represents atomic volume, and \(\eta_k\) represents the height of deposited nuclei. These calculations are also accomplished by Iriyama et al.\(^{[60]}\) (Figure 4c).

These calculations prove that a higher overpotential \((\eta_k)\) reduces the critical radius (nuclei size). The nuclei sizes and morphologies are also detected. The large nuclei with whisker growth are formed with low current density \((5 \mu A \text{ cm}^{-2})\) and the small nuclei of about 200 nm are formed with a current density of 500 \(\mu A \text{ cm}^{-2}\). Therefore, the higher current density can render tiny lithium nuclei, which is in accordance with the experimental observations. These nucleation estimations are based on the amorphous LiPON electrolytes. However, the utilization of polycrystalline oxide or sulfide electrolytes introduces more interfacial defects.

### 2.2.2. Interface Evolution and Degradation

Nowadays, a series of theoretical models have been proposed to predict the lithium plating/stripping behaviors. The density-driven model put forward by Ahmad et al. adopted shear modulus and molar volume ratio as critical parameters.\(^{[61]}\) Garnet-type Li$_7$L$_a$Z$_{r}$O$_{12}$ (LLZO) solid-state electrolyte exhibits high stability against Li metal, serving as an optimal model for the research on interfacial kinetics to exclude the contribution of parasitic reactions.\(^{[62,63]}\) Krauskopf et al. employed Al-doped Li$_{0.55}$Al$_{0.23}$La$_{0.2}$Z$_r$O$_{12}$ as a model system to probe the fundamental phenomena of the Li metal.\(^{[64]}\) During the stripping process, the Li atom \((\text{Li})\) will become \(\text{Li}^+\) and be transported into the SSE, leaving an electron and lithium vacancy \((\text{Li}_v)\). Repeated stripping processes result in gradually-accumulated vacancies forming continuously a void layer without external pressure. The \(\text{Li}^+\) combines with an electron and fills into the \(\text{Li}_v\) during the plating process. These processes are represented as following formula:

\[\text{Li} \leftrightarrow \text{Li}^+ + e^- + \text{Li}_v \]  

(7)

The relationship between interfacial impedances and the voltage profiles are measured during the dissolution and deposition, unraveling the formation and annihilation of the void layer at electrode–electrolyte interfaces (Figure 5a).\(^{[52]}\) The interfacial voids dominate the interfacial impedance (or charge transfer impedance).\(^{[64]}\) The essences of interfacial impedance are derived from the interfacial ionic conductive resistance at SEI layers \((R_{\text{SEI}})\) and charge transfer processes \((R_{\text{ct}})\).

\[R_{\text{ct}} = R_{\text{SEI}} + R_{\text{ct}} \]

(8)

\[R_{\text{ct}} = \frac{RT}{i_{\text{ct}}} \]

(9)

As displayed, \(R_{\text{ct}}\) is charge transfer impedance, and \(i_{\text{ct}}\) is the exchange current density. Actually, the charge transfer of \(\text{Li}^+/\text{Li}\) at the solid-state interfaces is extremely rapid. It is measured that the exchange current density can reach as high as \(>50 \text{ mA cm}^{-2}\) in the Li/LLZO and Li/Li$_2$S-P$_2$S$_5$ system, proving the intrinsic rapid charge-transfer.\(^{[64-66]}\) As measured with LLZO, the \(R_{\text{ct}}\) mainly contributes the \(R_{\text{int}}\), because of the extremely weak \(R_{\text{SEI}}\). Hence considering the \(R \propto \frac{1}{A}\), \(A\) representing the real active contact interfacial area, the continuously increasing \(R_{\text{int}}\) indicates the constant loss of contacts. In contrast, the reduced lithium atoms will refill in the vacancies at the interfaces, recovering the interfacial contacts during the deposition process. Therefore, the evolution of \(R_{\text{int}}\) is reversible during lithium plating and stripping at a low current density of 100 \(\mu A \text{ cm}^{-2}\). The kinetics process is accurately displayed by galvanostatic electrochemical impedance spectroscopy.\(^{[67]}\) The time–polarization and time–impedance profiles clearly represent the interfacial evolution tendency. Koshikawa et al. also measured the evolution of \(R_{\text{int}}\) during lithium plating and stripping utilizing a three-electrode system.\(^{[68]}\) Actually, the interfacial kinetics of lithium is much more complicated due to the inhomogeneity of the surface microstructures including flaws, crystal orientations, grains, grain boundaries, and contaminates.\(^{[69,70]}\) and these defects will amplify the differences under high current densities. In order to unravel the surficial asperities on influencing the lithium deposition, the Li-free deposition in half cells are observed.

The solid-state half cells can clearly distinguish the lithium kinetics. Most of measurements toward anodic evaluation in solid-state batteries (SSBs) are conducted in symmetric cells. The pre-existing lithium can easily be deformed and contacted with SSEs well concealing the actual lithium kinetics.\(^{[67]}\) In solid-state half cells, the kinetics of lithium growth can be recognized. Initially, the Li-LLZO-Cu half batteries can clearly capture the continuous impedance evolution that indicates lithium appearance and vanishing. The interfacial lithium content can be reflected in the discharge and charge profiles in half cells. The plating lithium results in the reduction of interfacial impedance. The depletion on stripped lithium is consistent with the drastically emerging \(R_{\text{int}}\) (Figure 5b). The homogenous LiPON film is appropriate to eliminate the influence of the interfacial asperity and conduct optical observations. The growth of lithium whiskers is monitored at LiPON-Cu interfaces. After the nucleation, the lithium whiskers can rapidly penetrate the current collectors and sprout out above the current collectors.\(^{[59]}\) The rapid discovery of lithium whisker on probing can prove the rapid charge transfer (Figure 5c).\(^{[64]}\) The uncontrollable lithium deposition can exhibit variable morphologies. Krauskopf et al. and Hu et al. both observed special deposition morphologies of lithium in half cells. The Cu films or carbon nanotube foams are pressed on solid-state electrolyte to assemble the Li-LLZO half cells.\(^{[67,71]}\) Dendrite-like lithium nucleates and grows underneath the Cu film. The free lithium also displays whisker growth on LLZO surfaces (Figure 5d).\(^{[72]}\) The diameters of the whiskers range from hundred nanometers to several micrometers, which are determined by the pinhole cavities on electrolyte surfaces. The whiskers with short length and thick roots are achieved at a low current density, while whiskers with thin and long length morphology are delivered at a high current density. These phenomena reflect that the lithium nucleation and deposition behaviors are fully controlled by the surficial morphology, current densities, and the surficial crystal nucleation kinetics.\(^{[67]}\) Wang et al. utilized carbon nanotube foam as current collectors to investigate
lithium deposition. They discovered the “lithium mushroom” in the carbon networks, which derived from the special interfacial contacts (Figure 5e). These results confirm that the initial lithium kinetics also obey the nucleation and growth process. The nucleation is determined by the surficial morphology and current density, and the growth is highly relied on the formed nucleation sites.

The kinetics of Li deposition will be regulated through the alternation of substrates. The formation of alloyed lithium solid solutions render very limited nucleation overpotential and thus guide the lithium nucleation in an alloy anode. Lithium ions insert into the metal (e.g., Au, In) to form an alloy layer and get deposited. The introduction of Li-Au alloy layer is demonstrated to retard the dendrite penetration and reduce the void generation during the Li stripping process. While, excessive lithium leads to the dispersion of alloy elements, causing the failure of alloy layers. Generally, the alloy can accelerate the lithium diffusion and contribute to suppressing Li accumulation (Figure 5f).

The polymer electrolyte is the special case in SSEs. The polymer electrolytes exhibit a low mechanical strength, which can be easily penetrated by lithium filaments. The ionic transportation is fulfilled by the coordinated Li ions at the polymer chains. The dendrite propagation is similar to that in liquid electrolytes. Monroe et al. simulated the dendrite formation process in polymer SSEs.

Briefly, both surface homogeneity and current density are the most important factors on interfacial kinetics. Introducing a lithium alloy contributes to reducing Li deposition overpotential and inhibiting Li dendrite penetration. Guiding Li growth at a high current density with an imperfect surface is essential to achieve a stable cycling at high rates.

Figure 5. The lithium kinetics during plating and stripping in SSBs. a) The dynamic processes during lithium plating and stripping in symmetric cells. In continuous cycling, the interfacial voids of lithium metal continuously produce and annihilate. Reproduced with permission. Copyright 2019, American Chemical Society. b) The lithium plating and stripping in solid-state Li-Cu batteries. The interfacial impedance exhibits obvious changes and the bulk almost remains at a constant. Reproduced with permission. Copyright 2019, Elsevier. c) The rapid charge transfer induces the discovery of the lithium whiskers. The lithium whiskers of different sizes at LLZO interface. The different morphologies of lithium whiskers are also determined by the current densities. Reproduced with permission. Copyright 2019, Elsevier. e) The lithium “mushroom” at the CNT-LLZO interface proves the importance of the existence of a current collector for stable lithium plating. Reproduced with permission. Copyright 2017, American Chemical Society. f) The tendency of lithium growth with different current collectors. The free plating of lithium metal exhibits an obvious tendency for dendrite propagation, and the alloy interlayers or the pre-existing lithium metal can guide the uniform plating. Reproduced with permission. Copyright 2019, Elsevier.
2.2.3. Interface Failure

The anodic failure including the short circuit and open circuit determines the CCD value. Lithium dendrite is widely observed in different type of SSEs. The dendrites tend to extend along the grain boundaries (Figure 6a). The grain boundaries in garnet SSEs can be fully penetrated by Li filaments (Figure 6b). In contrast, due to the poorer adhesion between sulfide particles, the resistance for dendrite growth is lower than that in oxide SSEs, exhibiting clear dendrites (Figure 6c) in sulfide SSEs. The tree-like and needle-like lithium whiskers can be observed in polymer SSEs (Figure 6d). Except for dendrite-induced failures, the voids-induced open circuit is also an important type for battery failures. The interfacial void accumulation can also be detected in polymer based (Figure 6e) SSLMBs and the inorganic SSLMBs (Figure 6f).

Different types of failure mechanisms in solid-state batteries are introduced below.

(1) Hard short circuit

Hard short circuit in SSLMBs derives from the rapid dendrite penetration. The dendrites directly connect the anode and cathode, which is unable to be recovered. The dendrites can be valued as parallel leakage resistance in the fitting circuit of impedance spectra. The electrochemical phenomena and the corresponding fitting circuits are summarized in Figure 7. In galvanostatic measurements, the voltage or polarization exhibit a sudden and drastic drop. The hard short circuits are usually difficult to forecast. Under some circumstances, this hard short circuits are accompanied with severe polarizations. This kind of short circuit generally occurs in stiff inorganic SSEs. Especially, the low strength areas (e.g., grain boundaries and defects) exhibit lower shear modulus than that of bulk SSEs, which are preferred areas for these completely dendrite propagations.

(2) Partly short circuit

Partly short circuit is the primary stage of the complete short circuit, but the short circuit pauses or terminates subsequently. The lithium filaments just penetrate the interfaces, not the whole bulk SSEs. The polarization voltage drops slightly, which represents the partial reduction of the bulk impedance. Because of the existence of bulk electrolyte impedance, the partly short circuit cannot be regarded as a complete failure of a solid-state battery. As displayed by Lu et al., the polarization will increase following the Ohm’s law with the increase of external currents.

(3) Soft short circuit

Soft short circuit refers to the slight voltage drop during battery operations, embodied in the severe fluctuation of charging curves. After regulating the external factors (e.g., current density, pressure, or temperature), the soft short circuit can be recovered. The soft short circuit usually occurs in polymer electrolytes or solid–liquid hybrid electrolytes. Distinguished from the stiff inorganics, the partial fluidity enables polymer materials to form uniform interfacial contacts. The soft short circuit is resulted from the formation and dissolution of tiny dendrites. The high viscosity of the polymer/partial liquid restrains the size of dendrites. These tiny dendrites can be easily fused, providing chances for battery recovery. However, the soft short circuit will induce a severe overcharge phenomenon, leading to a waste of energy.

(4) Contact loss

The electrode–electrolyte contact loss is mainly attributed to the vacancy accumulation at interface and the volume expansion/shrinkage in the continuous stripping of Li metal. The escape of Li atoms will generate vacancy sites during the lithium stripping. Vacancy accumulation leads to the formation of pores and...
defects at the working interfaces. These defects gradually reduce the effective interfacial area, inducing the partially concentrated Li-ion flux. The concentrated Li-ion flux will further exacerbate the contact loss. Kazyak et al. observed the inhomogeneous Li depletion and void accumulation at high current densities and high areal capacities (Figure 8).[83] It is proved that the interfacial capacitances are mainly derived from the interfacial voids. The microelectrodes are employed to observe the void accumulation (Figure 8a). Obvious lithium depletions can be observed after lithium stripping with the capacity of 1.07 and 1.47 mAh cm$^{-2}$ (Figure 8b,c). The depleted regions indicate the contact loss areas, resulting in the increased polarization (Figure 8d) and interfacial impedance (Figure 8e). During lithium plating, the huge volume expansion will also lead to more cracks and consequently accelerate lithium pulverization.[84] Besides, volume changes of cathode materials will also lead to contact loss in the cathodic structure. Contact loss is a dynamic behavior and is accumulated over cycles. Therefore, maintaining a conformal interface during repeated cycling is essential to extend the life span of SSLMBs.

2.3. Rational Identifications for CCD

2.3.1. Basic Measurement Protocols

The detection towards battery failure with specific current density is the identification for CCD. Generally, the CCD is measured by stepwise increasing currents. However, with the progressing of solid-state batteries, various measurement protocols for CCD are developed and lead to the different CCD results.[92] The schematic illustrations of internal evolutions of different measurement protocols are illustrated in Figure 9a,b. The protocols of evaluating CCDs can be categorized as follows:

(1) Time control

A time-control test is that the time is set in same particular length (10 min, 30 min, 1 h, or even longer) in every cycle, while the current density is increased in a fixed step. As displayed in Figure 9a, the capacity is gradually increasing with each current step. Figure 9c exhibits an example of time-control measurement, where the polarization increases continuously until a short-circuit failure in time–voltage profiles. This method helps to assess the endurance with simultaneously increased current density and capacity.

(2) Capacity control

The capacity control method is based on equal areal capacity in each cycle (e.g., 0.2, 0.5, 1 mAh cm$^{-2}$, or more). The operation time gradually shrinks with the extended cycle because the capacity is constant (Figure 9b,d). This protocol is effective to evaluate the influence of capacity during cycling.

(3) Endurable time control

The measurement only set as one cycle in each current density in the time-control test. The measurement remains for several cycles in each current density at this protocol.
This method can effectively evaluate the role on current density and cycling number simultaneously.

(4) Long cycling

This is the commonly-used protocol for measuring the stability of lithium/SSE interface in symmetric cells, which aims at evaluating the interfacial accumulation effects during long-time operation. However, the operation current is relatively low in most of reports.

2.3.2. “Fake Stable” Phenomena

The erroneous identification for CCD should be avoided. Most CCDs are identified by the voltage polarization curves. However, the impedance spectra before and after cycling indicate that short circuits occur before the voltage profile drops to zero.

As aforementioned in Section 2.2.2, the total impedance for symmetric cells is composed of bulk impedance of SSEs, $R_{ct}$ and $R_{SEI}$. The polarizations are also derived from the interfacial overpotential and the Ohm impedance from the bulk SSEs. According to the DC Ohm’s law, the polarization voltage ($U_{pol}$) can basically obey the $R_{pol} = \frac{U_{pol}}{I_{measure}}$. The erroneous identification on CCD usually happens at extremely high current density or high temperature. Although a short circuit occurs due to dendrite formation, weak electronic impedance will still remain and contribute to the polarization increase with elevated current densities.

Herein, our experimental results are provided to unravel the “fake stable” phenomena. This result is measured at 60 °C, with a cycling capacity of 2 mAh cm$^{-2}$. The current density is ranged from 0.5 to 10 mA cm$^{-2}$. As displayed in Figure 10a, the dashed square marks the real failure points in symmetric cells. However, a stable polarization increase is still accompanied with the elevated current densities. It is a typical “fake stable phenomena”, which exhibits a continuous increased polarization without a voltage drop. The EIS at room temperature before cycling is 70–80 Ohm (Figure 10b), while the much-decreased impedance (6 Ohm) at room temperature proves that the short circuits have occurred (Figure 10b, insert). After the short circuits, this symmetric cell exhibits a flat polarization without fluctuation when cycled at a high current density of 10 mA cm$^{-2}$ (Figure 10c). A flat polarization with a high current density or capacity is also a common characteristic of the “fake stable” phenomenon.

Two methods can help to identify the “fake stable” phenomenon when measuring CCD. The most direct method is to compare the initial impedance and the cycled impedance under room temperature, where a sudden impedance decrease indicates short circuits. Moreover, it renders a stable cycling if the calculated DC resistance by Ohm’s law is at the same magnitude with the result from impedance spectra, which is effective for room-temperature measurements. However, a high temperature operation will shrink the polarization which is not convenient for identification, where the polarization profiles can also indicate the “fake stable” phenomena. A standard polarization profile with a high current density or high capacity will exhibit a polarization increase due to the void accumulation at the interfaces (Figure 10d). In comparison, the “fake stable” will show an unusual flat and stable polarization where no void accumulation phenomena can be observed. Once an extremely high “CCD” with a flat polarization has occurred, it can probably be attributed to “fake stable” phenomena unless a rapid Li$^0$ diffusion is determined to eliminate the influences of void accumulations such as in a Li alloy system. Consequently, an EIS evaluation before and after cycling is essential to validate the results of CCD.
2.4. Rate-Determining Steps for CCD

The major target for CCD is used to evaluate the anodic dynamic stability with a series of current density and capacity. The CCD aims at evaluating the rate-determining steps for the Li metal and SSE interfaces. The solid–solid Li kinetics are determined by three main processes: ionic transport, charge transfer reaction, and the Li self-diffusion (Li adatom diffusion and voids production and annihilation), which are displayed in Figure 11.

The Li kinetics is highly relied on the quality of solid–solid interfaces. The exchange current density of intrinsic Li charge transfer reactions is as high as 50 mA cm\(^{-2}\).[66] Hence the effective area of for charge transfer is one of the main rate-determining processes. The mass transport at the interface is also an important factor. The ionic diffusion in inorganic SSEs (10\(^{-9}\)–10\(^{-7}\) cm\(^2\) S\(^{-1}\), room temperature)[18,93] are basically much faster than that of the Li atom self-diffusion (10\(^{-12}\)–10\(^{-11}\) cm\(^2\) S\(^{-1}\)).[77]

Another main rate-determining process for mass transport can be attributed to the Li atom transport for inorganic systems. If a polymer electrolyte is employed, the mass transport determining factor should be reconsidered due to the low transference number (\(t^+ 0.2–0.3\)) and Li\(^+\) diffusion coefficient (10\(^{-9}\) cm\(^2\) S\(^{-1}\) at 60 °C).[94] These models are based on a perfect SSE without external influence factors. Virtually, other

influence factors can also alter the rate-determining process of Li deposition. And the CCD will display special changes under different factors.

3. The Influence Factors of CCD

The CCD can be affected by many internal and external factors. These factors are usually coupled with each other. Because of the poor interfacial adjustments in a solid-state system, the CCD in solid batteries is more sensitive to external factors than those with liquid electrolytes. The major issues are summarized in Figure 12 and are discussed as follows.

3.1. Interfacial Contact

The interfacial contacts are directly related to the interfacial physical contacts and chemical stability. The physical contact is one of the most fundamental prerequisites for SSBs. The interfacial contacts are directly related to the interfacial physical contacts and chemical stability. The physical contact is one of the most fundamental prerequisites for SSBs. Without

![Figure 10](image1.png)

**Figure 10.** The “fake stable” phenomena measured in Li/Li$_2$P$_2$S$_5$/Li symmetric cells at 60 °C. a) The cycling profiles for CCD with constant capacity of 2 mAh cm$^{-2}$ and current density range from 0.5–10 mA cm$^{-2}$. b) The impedance before cycling (outside) and after cycling (inside). c) The time–voltage profiles of typical “fake stable” phenomena. d) The demonstration for normal cycling and “fake stable” cycling.

![Figure 11](image2.png)

**Figure 11.** Theoretical model of CCD and the corresponding rate-determining steps. Data sources: The diffusion coefficient of inorganic SSEs$^{[18,93]}$ and polymer SSEs.$^{[94]}$ The exchange current density$^{[65,66]}$ and charge transfer impedance.$^{[64]}$
the fluidities to connect the electrolyte and the electrode, the transport pathway of Li ions can only be built by solid–solid contacts.[96]

The SSEs and electrodes (e.g., Li metal) possess unique mechanical properties such as hardness, flexibility, and creep deformation. The theoretical model and practical analysis are shown in Figure 13. Persson and co-workers[97] reviewed the basic contact mechanics theories, pointing out that the contact regions are determined by the elastoplasticity, the squeezing force, and the roughness. The solid–solid contacts are usually formed between the soft matrices and comparatively hard matrices. The soft substances are squeezed into the interfacial gaps to form a face-to-face contact (Figure 13a). A perfect face-to-face contact is hard to accomplish. At microscopic view, tiny voids will remain at the rough places of the interfaces. If there are contamintates at the boundaries or when operated under low pressure, the electrode/electrolyte interface will render a point-to-point contact (Figure 13b, left) or uneven face-to-face contact (Figure 13b, right). The limited physical contact contributes to high local current densities, consequently accelerating Li dendrite growth.[52,98]

The interfacial reactions between electrolytes and Li metal anodes induce volume changes, generate additional products, and therefore determine the interfacial contacts.[99] Virtually, many kinds of SSEs exhibit poor chemical stability against the Li metal. The decomposition of some SSEs with high-valence metal element will continue until battery failure if a mixed conducting layer is formed. This kind of interphase is
defined as mixed conductive interphase (MCI). For instance, \( \text{Ge}^{4+} \) in \( \text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3 \) will be reduced into Li-Ge. The reduced high-valence metal element will retain the electronic conduction ability, facilitating the continuous decomposition.\(^{[62,106–103]}\) Meanwhile, the heterogeneous morphologies lead to uneven interfacial chemical reactions, which is a

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**Figure 13.** The interfacial contacts: from the theoretical description to the experimental phenomena. a) Theoretical mode. Reproduced with permission.\(^{[97]}\) Copyright 2006, Elsevier. b) Interfacial contacts in LLZO.\(^{[92,94]}\) Reproduced with permission.\(^{[92]}\) Copyright 2019, American Chemical Society. Reproduced with permission.\(^{[94]}\) Copyright 2018, Elsevier. c) Chemical degradation of Li/SSSE \(^{[102,110,172]}\) Reproduced with permission.\(^{[102]}\) Copyright 2019, American Chemical Society. Reproduced with permission.\(^{[110]}\) Copyright 2018, Elsevier. Reproduced with permission.\(^{[172]}\) Copyright 2018, the Royal Society of Chemistry. d) Void induced short circuit. Reproduced with permission.\(^{[114]}\) Copyright 2019, Elsevier. e) Lithium pulverization in Li/LLZO. Reproduced with permission.\(^{[84]}\) Copyright 2018, Elsevier.
potential inducement for dendrite propagation (Figure 13c). Polyethylene oxide (PEO) exhibits the thermodynamic tendency to be decomposed into Li₂O, C₂H₄, H₂, and LiₓCᵧ, etc.[104,105] The Li₂S-P₂S₅(-LiX X = Cl, Br, or I) sulfide solid-state electrolyte will be decomposed into Li₂S and Li₃P.[106–109] These decomposition products are electronically insulated, which are similar to the solid-electrolyte interphase (SEI) layer derived from the direct reactions between lithium and organic electrolytes in liquid-based battery systems.[55] However, the artificial interfaces might be degraded by the volume expansion during cycling.[107,110,111] A perfect interface guarantees face-to-face contacts, providing homogenous Li-ion flux. The LLZO electrolytes possess high chemical stability in a wide temperature range, which permits the lithium melting treatment on the LLZO electrolyte at a high temperature (>200 °C).[112,113] After the melting treatment on LLZO, the molten Li fills into the surficial fluctuations forming a static face-to-face contact. Nevertheless, the stable status cannot be hold in the continuous dynamic operations. The high current density results in a rapid injection of vacancies, and the voids will accumulate at the areas with high impedance, reflecting a partial contact loss (Figure 13d).[114] The stepwise generated contact loss is related to the continuous concentrating on Li-ion flux, finally causing the dendrite penetration. Besides, the volume expansion and subsequent pulverization are also discovered in prolonged cycling (Figure 13e). This self-activated anodic deterioration stimulates the dendrite formation.

3.2. Intrinsic Properties of Electrolyte

The intrinsic properties of the SSEs include the relative density, compacted density, chemical components, and mechanical strength.[115] Most SSEs are polycrystalline, which are composed of multiple single crystals, grain boundaries, isolated SSE particles, impurities, and internal flaws. These internal factors determine the internal ionic flux and guide the nucleation or extension of lithium filaments. Different chemical components (e.g., dopants or functional additives) will also determine the intrinsic properties of SSEs.[116]

The relative density of a solid-state electrolyte deteriorates the critical behavior of SSLMBs. For instance, the LLZO solid-state electrolytes are inclined to display a statement of “abnormal grain growth” during the sintering of an LLZO electrolyte.[89] The abnormal grains will destroy the internal homogenous situation of SSE, including the ionic conduction and the mechanical strength.[70,117,118] After the molten lithium treatment, there are fragmentations of LLZO SSEs with abnormal grain growth, due to the reduced mechanical strength and inhomogeneous internal thermal conduction (Figure 14a).[119]

The ionic conductivities at grain is generally higher than that at the grain boundary, hence the abnormal grain growth will concentrate the Li-ion flux. As calculated by Srinivasan et al., a phase map between applied current density and grain size is predicted. Similarly, the current distributes at the grain boundaries with the rise of grain size. The dendrite filaments are inclined to extend through these areas along the grain boundary. 

![Figure 14. Detects in SSEs influencing CCD. a) The SSEs with abnormal grain growth smash after contacting with molten lithium. Reproduced with permission.[119] Copyright 2019, Elsevier. b) The relationship between internal defects and CCD value. The low relative density of SSEs results in an uneven ionic flux and a large space for dendrite extension. Reproduced with permission.[88] Copyright 2018, the Royal Society of Chemistry. c) The dendrite propagation induced by surficial flaws in SSE single crystals[121] and d) the lithium deposition induced the crack propagation in SSEs. Reproduced with permission.[122] Copyright 2017, Wiley-VCH. e) The schematic illustration of dendrite-induced high inner stresses on degrading the interfaces. Reproduced with permission.[122] Copyright 2017, Wiley-VCH.](image)
in these circumstances. The grain size is less than 100 nm; the current concentration also decreases gradually, reflecting as a high CCD.\[85\]

The dendrite penetration can be clearly induced by internal defects.\[88\] Although the Li-Al alloy can help to increase the CCD, LLZO with defects also cannot endure a high current density. It is demonstrated that the relative density (LLZO) of >97% can achieve a CCD of >0.7 mA cm\(^{-2}\). The decreased relative density of 92–93% leads to the drop of a CCD value of 0.4 mA cm\(^{-2}\). A LLZO with an extremely low relative density (<90%) can be penetrated at a low current density of 0.2 mA cm\(^{-2}\) (Figure 14b).\[88\] Nevertheless, a good or even perfect interfacial contact is realized, internal flaws will also drastically weaken the CCD behaviors. Shen et al. also analyzed the pore connectivity in LLZO on influencing the CCD value. A low porosity of LLZO reflects on higher CCD.\[120\] In subsequent studies, lithium filament propagation can be induced from surficial to internal crystals. Chiang et al. systematically evaluated the dendrite propagation in a garnet single crystal by controlling the surface flaws.\[121,122\] The lithium tips can induce the crack propagation in single crystal SSEs. Even a single crystal LLZTO can be split by the Li dendrites (Figure 14c). The micro-electrodes are utilized to monitor these processes. As shown in Figure 14d, cracks will be rapidly developed during continuous Li plating, which will finally lead to Li penetration. The lithium metal preferentially gathers in the flaws, and then the lithium ion flux concentrates at the flaw area leading to overpotential. The overpotential is the driven factor of the stress, which is determined by the size of flaws. The subsequent deposition of lithium will impose an additional stress including shear force, triggering the crack of the SSEs (Figure 14e). This research is also validated by a finite element modeling to assess the current density in SSEs.\[122\]

The CCD is not only dependent on the densities of SSEs influence, but also the dopants in solid-state electrolytes.\[123,124\] Persci et al. demonstrated the relation of dopants with CCD in an LLZO electrolyte. It is measured that the grain boundary capacity, the bulk capacity, and total ionic conductivity exhibit an obvious discrepancy with different dopants, which are determined as the derivation on the different results towards CCD.\[125\] Zhu et al. also discovered the Nb doped LLZO exhibited a lower CCD than the Al and Ta doped ones.\[123\] Different dopants significantly affect the stability against the Li metal and subsequently influence the CCD performance.

3.3. Capacity on Lithium Plating and Stripping

The raising areal capacity during Li stripping results in severe contact loss in all-solid-state systems. As reported, 1 mAh cm\(^{-2}\) corresponds to a lithium thickness of 4.9 µm (Figure 15a).\[126\] Nowadays, although some reported solid batteries exhibit a long lifespan, the cycling capacities are far from practical batteries. In commercial lithium ion batteries, the cathodic areal capacity should exceed 4 mAh cm\(^{-2}\). After being fully discharged, the thickness of the void layer will reach nearly 20 µm. The stripped void layer represents the contact loss, and a higher current density will accelerate the void accumulation (Figure 15b).\[83\] In addition, massive lithium cycling will lead to a high volume expansion, accelerating the contact loss. The loss of active plating/stripping sites is difficult to recover due to the sluggish and uncontrollable surficial Li adatom diffusion according to the terrace-ledge-kink model. It is discussed in Section 2.2.2. that the lithium growth exhibits a complexity which is highly related
with initial morphology and the current density. In a high capacity cycling it is difficult to fulfill a reversible morphological evolution, and high current density also deteriorates the morphological reversibility, which results in the poor CCD performance in a working cell.

### 3.4. Temperature

The batteries are expected to be stably-operated in a wide temperature range in practical applications under harsh conditions. The working temperature significantly affects the value of CCD. The corresponding mechanism is divided into two aspects, including the intrinsic physical properties of lithium and the electrochemical properties (e.g., ionic conduction in lithium SSEs and the interface and the diffusion coefficients in an electrode–electrolyte system). As measured by Krauskopf et al., the interfacial activation energy is similar to that of the bulk LLZO electrolyte (Figure 16a). Both the interfacial conductivity and bulk conductivity obey the Arrhenius formula. Hence the interfacial impedance can theoretically achieve a low value.

In addition, the temperature determines the local strain rate of lithium. The lithium softens at a higher temperature and embrittles at a low temperature. The deformation of softened lithium will contribute to improving the interfacial contacts under a same stack pressure. Hence the interfacial impedances are reduced with the increasing temperature. The reduced impedance still remains after recovering to room temperature. It is concluded that the increased temperature is beneficial to construct conformal interfaces. According to the practical measurements by Sakamoto et al., the interfacial impedance can be reduced to 2.7 $\Omega$ cm$^{-2}$ at 175 °C with the ascending temperature. The CCD can also reach a high value of 20 mA cm$^{-2}$ at 160 °C (Figure 16b). The reduced interfacial impedance is directly related to the improved CCD. The interfacial impedance can also achieve a low value of <2 $\Omega$ cm$^{-2}$ through some other interfacial modification strategies at room temperature. However, their corresponding CCDs don't fulfill a similar value of over 10 mA cm$^{-2}$. The improved temperature exerts enormous functions on other aspects in the SSBs. The low interfacial impedance is only a fundamental precondition to permit the high Li$^+$ flux, but it is not a determinant.

Another reason on the high CCD at high temperature can be ascribed to the improved diffusion of Li$^0$/V$_{Li}$ and Li$^+$. These factors are also temperature-dependent. A high CCD indicates a rapid diffusion of lithium ions and lithium atoms at interfaces.

![Figure 16. The diffusion issues of Li$^0$/V$_{Li}$ at the interfaces. a) The evolution tendency of the impedances of bulk, grain boundaries, and interfaces at different temperatures. Reproduced with permission.[42] Copyright 2019, Elsevier. b) The extremely improved CCD performances at 160 °C. Reproduced with permission.[51] Copyright 2016, Elsevier. c) The Li$^0$ accumulation due to the insufficient voids at the interfaces. Reproduced with permission.[42] Copyright 2019, Elsevier. d) The diffusion dominated model for the flux balance between Li vacancies in the Li metal electrode and the Li$^+$ in LLZO SSEs. Reproduced with permission.[52] Copyright 2019, American Chemical Society.](image)
a solid-state electrolyte, and bulk lithium metal. The rapid rise of these diffusion factors accelerates the lithium diffusion in electrode, electrolyte, and the interfaces, which can delay the existence of the diffusive mismatch at ascending current densities. Hence the diffusion balance of electrode–electrolyte can be realized at a higher current density. This can be treated as a rational interpretation for the high CCD value at high temperature.

### 3.5. Interfacial Diffusion Balance

As mentioned in Section 3.4, a higher temperature can significantly improve the CCD in SSBs because of the increasing diffusive capability of Li\(^+\). In liquid electrolytes, a diffusion-limited model is adopted to interpret the dendrite formation at a high current density. The interfacial mass transportation plays vital roles on constraining current densities. The analogous conjecture is proposed in a solid state system. As claimed by Sharafi et al., a higher CCD represents a larger Li ion flux at the unit area on the interfaces\(^{[42]}\). The ionic transference number is considered as 1 in a solid-state electrolyte. All the operation current can be ascribed to the Li\(^+\) transport. Hence the flux of Li\(^+\) migration \(J_m\) is displayed as:

\[
J_m = \frac{I}{e} \quad (10)
\]

There is a reversible transition between Li\(^0\) (Li atom) and Li\(^+\) at the interfaces in an Li metal electrode. The stack pressure induces the creep deformation of Li metal. The mass transport on the stripping of Li\(^0\) in Li metal is denoted as Li\(^+\) flux \(J_{0d}\):

\[
J_0 = J_{\text{diffusion}} + J_{\text{creep}} \quad (11)
\]

There is a discrepancy of the diffusive capability between Li\(^0\) in the Li metal and Li\(^+\) in the solid-state electrolyte. The diffusion coefficient of Li\(^+\) in the LLZO is measured as 2.15 × 10\(^{-9}\) cm\(^2\) s\(^{-1}\). Comparatively, the self-diffusion coefficient of the Li metal is reported as 5.6 × 10\(^{-11}\) cm\(^2\) s\(^{-1}\). If the current density remains in a low value \(J_m < J_0\), the diffusion of Li\(^0\) is sufficient to supply the Li loss at the interfaces and leave homogenous vacancy sites for a new lithium deposition. The plated Li\(^+\) flux can also replenish the vacancy sites with sufficient speed by diffusion and creep during the plating process. Therefore, the planar morphology can remain at low current densities. In contrast, the Li\(^0\) is not rapid enough to migrate into the bulk lithium upon the plating of fresh Li\(^0\) at high current densities \(J_m > J_0\). The new plated Li\(^+\) can only compulsively accumulate at the interfaces, resulting in the “non-planar” character (Figure 16c). The accumulated Li metal works as new nuclei sites, which induces the morphological instability, even the dendrite penetration. The mass transport limitation occurs in the lithium electrode (adatom diffusion), which is in contrast to that in a liquid electrolyte. In a liquid electrolyte, Li\(^+\) diffusion is the major limitation on mass transport. Moreover, the concentration and diffusion of vacancy are not negligible. In EIS spectra, the increase of \(R_{\text{int}}\) directly reflects the phenomena of contact loss. As described in the Kroger–Vink notation, taking an LLZO electrolyte as example, the interfacial elementary process is denoted as the following formula:\(^{[52]}\)

\[
Li \rightleftharpoons \left[ Li_{\text{Li}}^{\text{Li}} + V_{\text{Li}}^\text{Li} (\text{LLZO}) \right] + e^- (Li) + V_{\text{Li}}^0 (Li) \quad (12)
\]

During lithium stripping, at the surface, a lithium vacant site \(V_{\text{Li}}^\text{Li}(Li)\) and electron \(e^- (Li)\) are left in the bulk Li metal, and the Li ion transports into the available Li ion channel in the LLZO, which is the vacant site \(V_{\text{Li}}^\text{Li} (\text{LLZO})\) or interstitial site of LLZO at the interface (Figure 16d). These leftover Li vacancies can migrate into the bulk metal. It can be speculated that the combined effect on the migration of Li vacancy in the electrode and the mobility of Li ions in the SSE determine the interfacial dynamics. As aforementioned, the mobility of Li\(^+\) in SSE is much faster than that of Li\(^0\) in bulk metal. It is concluded that not only the Li\(^0\) adatom diffusion determines the interfacial phenomena, but the vacancy diffusion dominates the interfacial dynamics. According to the vacancy mode, a detailed description on these dynamics processes is put forward as follows: the internal diffusion of vacancy is fast enough to deal with the Li solution at low current densities. The vacancy sites can migrate into the bulk, which helps to retain a stationary vacancy concentration at the interface. The vacancy pile-up occurs at the interface once the production of vacancies surpasses their diffusion speed, which results in the morphological instability. Janek and Schmalzried et al. also put forward the defect relaxation model. They took Ag and Ag\(^+\) SSE as examples, which is similar to Li\(^+\) in LLZO.

\[
j_v = \left(1 - \frac{c_v(\xi = 0)}{c_v^0} \right) \sqrt{D_v \tau_v} \quad (13)
\]

\[
i_{\text{crit}} = zF \cdot j_v \quad (14)
\]

\(V\) is the vacancy in Li metal, \(\tau_v\) is the relaxation time, \(D_v\) is the diffusion coefficient of Li metal vacancies \(D_v = D_{Li} \cdot x_c^{-1}\), \(j_{V\text{crit}}\) is the limiting flux of vacancy, \(c_v\) is the vacancy concentration \(c_v^0 = 5 \times 10^{-9} \text{ mol cm}^{-3}\), and \(\tau_v\) is the relaxation time to establish the vacancy equilibrium in the electrodes. The limiting flux of the vacancy is defined as \(j_v\). When the concentration of the vacancy reaches the maximum value at the interface \(c_v(\xi = 0)\), the vacancy supersaturation status is defined as \(j_{V\text{crit}}\). Once the current density exceeds the critical vacancy diffusion, more vacancy will remain at the interfaces, resulting in the accumulation of voids near the interface. This should be seen as the beginning of a morphological collapse. If there is no vacancy diffusion process in SSBs, contact loss will rapidly happen for a planar electrode in a short time at any current density because of the rapid formation of the vacancy. However, SSBs can fulfill a high areal capacity at a low working current density virtually. It validates the rationality of this theory. In addition, these parameters including \(\tau_v\), \(D_v\), and \(c_v^0\) are also exponential temperature dependent. Therefore, the fulfilled critical current can be estimated theoretically under different temperatures. In conclusion, the vacancy diffusion model obeys the practical phenomena, which provides a powerful mechanism understanding on interfacial dynamics in Li metal SSBs.

The weakness of diffusion is derived from the metal electrode in inorganic electrolyte systems. The vacancy diffusion...
and atom rearrangement dominate the charge transfer process. In contrast, due to the crystalline and high solvation towards Li\(^+\) by polymer chains, the Li\(^+\) transport in polymer electrolyte is sluggish between the available solvation sites.\([127]\) The ionic conductivities are generally lower than that of the inorganic ones (e.g., oxide and sulfide SSEs). Besides, both cations and anions diffuse in polymer matrices simultaneously in a polymer electrolyte. Taking lithium bis(fluorosulfonyl)imide (LiTFSI) as example, diffusion coefficient \(D_{\text{TFSI}}\) is higher than the cation one \(D_{\text{Li}^+}\).\([128]\) The transference number of Li\(^+\) (\(t^+\)) can only reach a low value of \(\approx 0.3-0.4\) in routine polymer electrolytes.\([129]\) A balance is still difficult to negotiate between an Li\(^+\)/vacancy diffusion in electrode and the Li\(^+\) transport in electrolyte at working interfaces. The poor ionic conduction dominates the interfacial failure. The poor mass transport of a polymer electrolyte induces a concentration gradient at a high current density, which can induce the tendency on dendrite formation. Improving the Li\(^+\) diffusion in polymer electrolyte is a feasible effective route based on the theoretical mechanisms.

Because of the rapid transport of Li\(^+\), the accumulation of Li\(^0\) results in the dendrite formation in inorganic SSEs. The accumulation of vacancies leads to contact loss, which will further concentrate the Li\(^+\)/vacancy fluxes. On the contrary, the ionic diffusion in SSEs dominates the interfacial stability in polymer SSEs. Intrinsically, the mismatch among diffusion fluxes of Li\(^+\), Li\(^0\), and corresponding vacancies simultaneously determine the CCD value and the interfacial morphological stability. In essence, a higher CCD represents on realizing the Li\(^+\)/vacancy-Li\(^0\) balance with high interfacial fluxes. Ameliorating the diffusion issues in electrode or electrolyte is an important breakthrough point.

### 3.6. Pressure

Pressure is also considered as an important external factor for SSBs. The physical and mechanical properties include the elastic plastic and creep mechanical features. The good ductility of Li metal enables their deformations by an external force. Especially, there is obvious creep applied to a wide range of applied stress at a high operation temperature. Predicting the influences derived from the deformation of Li metal is essential to realize the implementation of the Li metal anode in SSBs. Masias et al. systematically measured the Young’s modulus, shear modulus, time-dependent deformation (creep), and stress dependent deformation.\([130]\) The elastic and plastic properties are directly related to the solid–solid contacts. The deformed Li gradually flows to the side boundary of batteries without a hydrostatic pressure, which finally induces the short circuit. The prestressed system constrains the undesirable flow of Li metal. The deformation of Li metal also imports microstructural evolutions, which significantly reduce the interfacial troubles and enhance the CCD values. Because of the pressure-dependent deformation of Li metal, the ascending pressure helps to increase the interfacial contacts. Owing to the interfacial asperities, the load bearing contact area is much smaller than the actual area of electrodes in most routine situations. The contact spots will generally transfer into contact areas after implementing the hydrostatic pressure, which is induced by the plastic deformation. The pre-pressed lithium can also avoid the subsequent creep induced short circuits.\([130]\) Li metal is softer than most inorganic solid-state electrolytes in Li metal based SSBs. The deformation of Li metal dominates the deformation-dependent impedance reduction. Taking the resistive layer into consideration, the interfacial impedance is summarized in following formula:

\[
R_{\text{int}} = \frac{\rho}{2} \sqrt{\frac{\pi H}{2 F}} = \frac{1}{2\\sigma_{\text{Li}}^0} \sqrt{\frac{\pi H_{\text{Li}^+}}{F}}
\]

\(R_{\text{int}}\) is the interfacial impedance, \(\sigma_{\text{Li}}^0\) is the ionic conductivity of SSE, \(H_{\text{Li}^+}\) is the Vickers hardness of Li metal, and \(F\) is the external pressure. It is concluded that the \(R_{\text{int}}\) is proportional to the \(F^{-1/2}\). According to Equation (12), an extremely high pressure can significantly eliminate the interfacial impedance (Figure 17a). The Equation (12) is based on the ideal planar model with circular point contacts, ignoring the microscale surficial asperities of SSEs. The pressure-dependent deformation of Li metal will overcome the influence of the roughness on the electrolyte (Figure 17b). After practical experimentation, Krauskopf et al. achieved an areal impedance of 0 Ω cm\(^2\) after operating the pressure for hundreds of megapascals.\([32]\) The pressure can also improve the surface adhesion between an Li metal and SSE. It is concluded that the interfacial strength is relative to the interfacial impedance. This is a new visual angle on the advantage of the high external pressure.\([31]\) Not only that, the pressure induced Li creep can also play vital roles. As displayed in Section 3.5, the creep induced Li atom flux (\(j_{\text{creep}}\)) can compensate the insufficiency of the ionic flux at a high current density, which can improve the vacancy diffusion.\([42,132]\) Hence the \(R_{\text{int}}\) remains stable after the Li stripping (Figure 17c). Wang et al. put forward a concept of “critical pressure”. This research is also based on an LLZO system.\([133]\) The critical pressure means that the pressure induced \(j_{\text{creep}}\) is insufficient to avoid the void formation below the critical pressure. The voids at the interface can be fully eliminated after conducting the pressure over critical pressure.\([133]\) A critical pressure \(\sigma_{\text{Li}}^0\) is an emerging standard for stable Li kinetics (Figure 17d). In sulfide SSE system, the critical stripping current also exhibits a pressure-dependent character. The creep behavior of lithium metal is emphasized as a dominated factor.\([132]\)

This conclusion is based on the rigid inorganic SSEs (e.g., ceramics). At once considering the yield strength of SSEs, the influence of the external stress should be reconsidered. The deformation of elastic polymer SSEs will import new effects.\([134]\) The sulfide SSEs prepared by cold pressing also exhibit poor yield stress. The SSE particles only adhere with each other. The Li creeps at a high stack pressure can be passively emerged into the SSE and subsequently short the batteries. As elucidated by Doux et al., a stack pressure of 5 MPa delivered a prolonged cycling of 1000 h (Figure 17e).\([135]\) Hence, considering the mechanical endurance capability of SSEs, only a moderate external stack pressure can balance the replenishing towards interfacial fluctuations, voids elimination, and the cycling stability at a high current density. The performance of pouch cells can be regulated more obviously by the altered external pressure.\([136]\) Virtually, a specific pressure can only impose a specific creep regulation at anodic interfaces. There are competitions among Li plating, stripping, and creep. If the morphological
evolution can’t be annihilated, continuous cycling at high current density can also destroy the interfaces. The external pressure displays more positive effects. However, the internal stress will occur and import a hidden danger in the dynamic processes of the battery operation. The internal stress can emerge with following processes. The electrochemical process can also render additional internal pressure for an Li metal anode. It has been demonstrated that in Section 3.2 that the surficial defects will lead to SSE degradations. Virtually, most SSB cells are assembled with an external stack pressure. The Li metal anode is restrained in rigid boundaries by solid-state electrolyte. The plated Li can deposit freely without boundary constraint. The plated Li metal is compressed with rigid boundaries, inducing the creep effects of the original Li. After plating the Li metal, the unit time $dt$ is corresponding to the plated Li with the height of $dh$. The strain rate is significantly related to the current density. As calculated, the power-law creep dominates the deformation of Li metal at high current densities (Figure 17f). An extremely high stress will accumulate at these areas at the cracks or the tips of the Li filament, which will split off the robust SSEs. This proves the internal stress is inevitable. The parasitic reactions with lithium metal will induce the volume expansion in SSE systems, which produces the excessive internal stress. This phenomenon can be treated as another reason for the mechanical damages. As displayed by McDowell and co-workers, the internal cracks are gradually discovered and interconnected after continuous plating and stripping, leading the chemomechanical failure. A higher current density and high real capacity can also result in the internal stress, accelerating the degradation of a working cell.

### 3.7. Disagreement for CCD Results

Although many experiments have been conducted with similar or same SSE compositions and Li metal anodes, the acquired CCD results are not in agreement. The CCD is not an...
evaluation for a single material, but a comprehensive evaluation for battery systems, including the interfaces, electrolytes, electrodes, external factors (e.g., pressure, temperature etc.), and cycling protocols. The influence factors are listed as follows: 1) the interfacial discrepancies in different experiments. The CCD results are highly related to the interfacial status including the surface homogeneities. Removing the surficial contaminations (e.g., Li$_2$CO$_3$ on LLZO) contributes to improving the performances. In comparison, the intrinsic rough surface and contaminated surface of same materials cannot realize a same performance; 2) the discrepancies on SSEs qualities. The interface and internal defects will exhibit discrepancies. The internal defects in SSEs will not only influence the internal Li$^+$ flux but also provide spaces for dendrite penetration, which is carefully discussed in Section 3.2; 3) discrepancies on external factors. Many solid-state batteries are measured in different battery types, such as coin cells, mold type Swagelok cells, or tube cells. The adopted pressures and the intrinsic discrepancies for different battery types will obviously influence the CCD results; and 4) measurement protocols. The precise evaluation for CCD is a systematic work, which requires standardized measurement protocols and accurately-controlled experimental details.

4. Strategies to Improve CCD

The strategies towards improving CCD are derived from solving the intrinsic kinetic problems and regulating the key factors. Considering the possible main rate-determining steps for CCD, the present strategies are still mainly concentrated on solving some specific issues such as active areas or stabilizing the interfacial chemistry. The strategies include constructing a lithiophilic interface, optimizing solid-state electrolytes, and lean liquid therapy. Some emerging strategies concentrated on ameliorating interfacial diffusion are gradually getting attention. Herein, we summarized the reported strategies with acquired CCD values in Table 2. Key measurement parameters including real areal capacity, temperature, and duration time are also listed for comparison. The mind map on guiding the strategies is shown in Figure 18. The strategies are mainly classified by charge transfer, ionic transport, and dynamic stability. The active areas determine the effective areas for charge transfer. Then the mass transport includes the interfacial ionic transport and Li atom transport. The ionic transport and Li atom transport contributes to the dynamic interfacial stability. The interfacial contact can be improved by lithiophilic modification, utilizing a 3D host, and adopting moderate external factors. The ionic transport can be enhanced by constructing a stable interface to eliminate the electronically conductive MCI. The dynamic stability can be improved by enhancing chemical diffusion or introducing liquid-phase therapy in Li metal anodes.

4.1. Increasing Active Areas

4.1.1. Improving Interfacial Contact

(1) Constructing lithiophilic interfaces

Due to the interfacial lithiophobic contaminants, molten lithium metal cannot be directly filled into the surficial asperities, which reduce the active interfacial areas.\cite{[140], [141]}

Constructing a lithiophilic interface is strongly requested to improve the interfacial contacts.\cite{[142], [143]}

Many lithiophilic materials (e.g., Au, Al, Si, graphite, etc.) and eliminating lithiophobic contaminates such as Li$_2$CO$_3$ has been proved as effective choices for reducing the interfacial impedance in garnet electrolytes.\cite{[144]– [146]}

The Li$_2$CO$_3$ can be removed by carbon reduction at high temperature (Li$_2$CO$_3$ + C = Li$_2$O + 2CO), acid pre-treatment (2H$^+$ + Li$_2$CO$_3$ = 2Li$^+$ + CO$_2$ + H$_2$O), and mechanical polishing.\cite{[147]– [149]}

The lithiophilic transitions are common strategies in LLZO based SSLMBs, and the improved CCD value can reach from 0.3–1.5 mA cm$^{-2}$.\cite{[150]– [152]}

(2) External pressure

Considering the chemical instability of Li metal against sulfide SSEs, cold pressing or even isostatic pressing are the most adopted methods to fulfill the anodic interfacial contacts.\cite{[153]}

As described in Section 3.6, external-pressure-induced lithium creep can improve the interfacial contacts. However, the initial good contact cannot guarantee a stable cycling because of the contact loss during high volume changes at a high capacity. Hence more strategies are also in urgent need for practical applications.

4.1.2. Enhancing Interfacial Stability

As demonstrated in Section 3.1, the interfacial instabilities are mainly caused by physical contact loss and chemical parasitic reactions. Hence physical structural design for lithium hosts and interfacial chemical regulations are important guidance. The lithium hosts can be classified as the artificial hosts and natural hosts. The chemical regulation is concentrated on SEI regulation.

(1) Artificial 3D anodic hosts

Considering the expansion volume and high local current densities, constructing an ionic conductive host provides new opportunities to settle the anodic trouble. The 3D structure of SSEs can improve the active interfacial areas, reduce the local area current density, and work as supporting skeletons for lithium metal.\cite{[154]}

Hu et al. designed a 3D structural garnet framework by tape casting slurry with mixed LLZO powder, pore former (e.g., polymethyl methacrylate (PMMA)), and a binder (Figure 19a).\cite{[155]}

Porous structures are acquired by de-binding and sintering the casted precursor tapes. The porous LLZO can be prepared as a sandwich structure as a porous-dense-porous one (Figure 19b). The porous structures contribute to ameliorating the volume expansion of Li metal and dense structures possessing high ionic conductivity.\cite{[156]}

Continuous plating and stripping behaviors can be achieved in these ionic conductive hosts. The lithium can be completely deposited into the 3D structures (Figure 19c).\cite{[157]}

Although the porous structures of mixed conductive hosts are similar with the ones of pure ionic conductive 3D hosts, the mixed conductors guide the lithium deposition in the host directly due to their intrinsic...
Table 2. The state-of-the-art CCD values with cycling protocols.

<table>
<thead>
<tr>
<th>Method-electrolyte</th>
<th>CCD value [mA cm⁻²]</th>
<th>Areal capacity [mAh cm⁻²]</th>
<th>Duration time (per cycle)</th>
<th>Temperature [°C]</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxide electrolyte and interfacial treatment</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au sputtered LLZO</td>
<td>0.8</td>
<td>0.4</td>
<td>30 min</td>
<td>50</td>
<td>[144]</td>
</tr>
<tr>
<td>Li₂CO₃ free LLZO</td>
<td>0.9</td>
<td>0.45</td>
<td>30 min</td>
<td>60</td>
<td>[147]</td>
</tr>
<tr>
<td>Li-Mg alloy LLZO</td>
<td>2</td>
<td>2</td>
<td>1 h</td>
<td>25</td>
<td>[126]</td>
</tr>
<tr>
<td>Si CVD LLZO</td>
<td>0.2</td>
<td>0.0167</td>
<td>5 min</td>
<td>25</td>
<td>[145]</td>
</tr>
<tr>
<td>Pencil drawing interface LLZO</td>
<td>0.3</td>
<td>0.3</td>
<td>1 h</td>
<td>25</td>
<td>[203]</td>
</tr>
<tr>
<td>Li-Al alloy LLZO</td>
<td>1.2</td>
<td>0.2</td>
<td>10 min</td>
<td>25</td>
<td>[88]</td>
</tr>
<tr>
<td></td>
<td>2.3</td>
<td>0.4</td>
<td>10 min</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>ALD Al₂O₃ LLZO</td>
<td>0.2</td>
<td>0.1</td>
<td>30 min</td>
<td>25</td>
<td>[204]</td>
</tr>
<tr>
<td>ALD ZnO LLZO</td>
<td>0.1</td>
<td>&lt;0.01</td>
<td>–</td>
<td>–</td>
<td>[205]</td>
</tr>
<tr>
<td>Thermal treatment LLZO</td>
<td>0.3</td>
<td>0.15</td>
<td>30 min</td>
<td>25</td>
<td>[41]</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.2</td>
<td>1 h</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Li-C₃N₄-LLZO</td>
<td>1.5</td>
<td>0.25</td>
<td>10 min</td>
<td>25</td>
<td>[152]</td>
</tr>
<tr>
<td>Li-ITO-LLZO</td>
<td>1.05</td>
<td>=0.8</td>
<td>=45 min</td>
<td>30</td>
<td>[206]</td>
</tr>
<tr>
<td>Evaporated Li on LLZO</td>
<td>7</td>
<td>0.2</td>
<td>–</td>
<td>100</td>
<td>[42]</td>
</tr>
<tr>
<td></td>
<td>0.93</td>
<td></td>
<td></td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>H₃PO₄ treatment on LLZO</td>
<td>0.8</td>
<td>0.4</td>
<td>30 min</td>
<td>25</td>
<td>[149]</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.25</td>
<td>30 min</td>
<td></td>
<td>[207]</td>
</tr>
<tr>
<td>Li-Ag coated LLZO</td>
<td>0.75</td>
<td>1.5</td>
<td>2 h</td>
<td>25</td>
<td>[207]</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.25</td>
<td>30 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li LLZO</td>
<td>13.3</td>
<td>0.36</td>
<td>–</td>
<td>25</td>
<td>[208]</td>
</tr>
<tr>
<td>Sputtered Li on LLZO</td>
<td>20</td>
<td>10</td>
<td>30 min</td>
<td>160</td>
<td>[51]</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>1.75</td>
<td></td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>Heat treating/Au coated LLZO</td>
<td>6</td>
<td>–</td>
<td>–</td>
<td>60</td>
<td>[209]</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>3</td>
<td>3 h</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li₂OCl coating LLZO</td>
<td>0.05</td>
<td>0.05</td>
<td>1 h</td>
<td>25</td>
<td>[210]</td>
</tr>
<tr>
<td>Li-Na-LLZO</td>
<td>1.5</td>
<td>0.05</td>
<td>–</td>
<td>25</td>
<td>[211]</td>
</tr>
<tr>
<td>TVD-carbon-LLZO</td>
<td>1.2</td>
<td>0.6</td>
<td>30 min</td>
<td>25</td>
<td>[36]</td>
</tr>
<tr>
<td>COF coating LLZO</td>
<td>3</td>
<td>–</td>
<td>–</td>
<td>25</td>
<td>[212]</td>
</tr>
<tr>
<td><strong>Modified electrolyte</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No mother powder densified LLZO</td>
<td>1.15</td>
<td>0.58</td>
<td>30 min</td>
<td>25</td>
<td>[202]</td>
</tr>
<tr>
<td>MgO densified LLZO</td>
<td>0.95</td>
<td>0.498</td>
<td>30 min</td>
<td>25</td>
<td>[118]</td>
</tr>
<tr>
<td>LiAlO₂ modified LLZO</td>
<td>0.75</td>
<td>0.375</td>
<td>30 min</td>
<td>25</td>
<td>[173]</td>
</tr>
<tr>
<td>Li₃PO₄ densified LLZO</td>
<td>0.6</td>
<td>0.3</td>
<td>30 min</td>
<td>25</td>
<td>[174]</td>
</tr>
<tr>
<td>3D LLZO host</td>
<td>10</td>
<td>2.5</td>
<td>15 min</td>
<td>25</td>
<td>[157]</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td></td>
<td>45 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3D C-LLZO host</td>
<td>1</td>
<td>3</td>
<td>3 h</td>
<td>25</td>
<td>[158]</td>
</tr>
<tr>
<td><strong>Sulfide electrolyte</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li-LiH₂PO₄ LGPS</td>
<td>0.1</td>
<td>0.1</td>
<td>1 h</td>
<td>25</td>
<td>[171]</td>
</tr>
<tr>
<td>Li incorporation Li₂S-P₂S₅</td>
<td>3.9</td>
<td>3.9</td>
<td>1 h</td>
<td>100</td>
<td>[167]</td>
</tr>
<tr>
<td>LiF-Li₃PS₄</td>
<td>&gt;2</td>
<td>–</td>
<td>1 h</td>
<td>25</td>
<td>[166]</td>
</tr>
<tr>
<td>LiF/LiI-Li₃PS₄</td>
<td>0.1</td>
<td>0.1</td>
<td>1 h</td>
<td>25</td>
<td>[168]</td>
</tr>
<tr>
<td>Li₃PS₄-Br₂</td>
<td>0.45</td>
<td>0.225</td>
<td>30 min</td>
<td>25</td>
<td>[213]</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0.2</td>
<td>30 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li₃PS₄-B₂O₅</td>
<td>0.5</td>
<td>0.5</td>
<td>1 h</td>
<td>25</td>
<td>[22]</td>
</tr>
<tr>
<td>Li₃S-S₄</td>
<td>1.5</td>
<td>1.5</td>
<td>1 h</td>
<td>25</td>
<td>[214]</td>
</tr>
</tbody>
</table>
electric conductivity (Figure 19d). Hence batteries with porous SSEs can realize a much higher CCD (>1.0 mA cm\(^{-2}\)) even 10 mA cm\(^{-2}\) with a high areal capacity (>1.0 mAh cm\(^{-2}\)) than that with conventional planar SSE and electrodes.\(^{[157,158]}\) A 3D electrode can also help to ameliorate volume expansion during lithium plating. Li et al. analyzed the lithium plating behavior in a 3D Ti electrode, and concluded the superiority of 3D structures on improving the lithium deposition in SSLMBs.\(^{[159]}\) Nevertheless, building 3D SSE structures will not only increase the complexity on battery manufacture, the fragilities of 3D porous frameworks will also hinder their practical usage.

(2) Natural 3D host

Li-rich alloy can be seen as a natural mixed conductive host. After high-capacity lithium stripping, the porous alloy skeleton remains at the interfaces, which guarantees the anodic contacts at the Li-lean stage. Hence, an alloy anode can realize a high CCD with a high operational real capacity with a planar electrode and electrolyte. The alloy anodes avoid complicated design and material preparation, and the rational design for

**Figure 18.** Strategies towards improving CCD in SSLMBs.
alloy components is promising for full batteries. The alloy also possesses an improved Li diffusion coefficient, which will be discussed subsequently.

(3) Artificial SEI

The parasitic reactions between Li metal and SSEs can induce morphological breakdown and the uneven ionic conductive interfaces, which are unfavorable for uniform lithium plating. Similar to the modification towards Li metal anodes in routine liquid electrolytes, an artificial SEI is constructed to reduce the side reactions and works as robust shields to resist the dendrite penetration.

Typical sulfide SSE and many oxide SSEs possess an obvious potential gap against Li metal according to the theoretical calculation.[160] The relative chemical potential of the interface (\(\mu_{\text{int}}\)) should be the intermediate value between that of the Li metal (\(\mu_{\text{Li}}\)) and the SSEs (\(\mu_{\text{SSE}}\), which can suppress the subsequent decomposition of the solid-state electrolyte and the electrode materials.[161–163] Besides, an ideal artificial layer should possess very small electronic conductivity and high ionic conductivity. The side reactions are perfectly suppressed, and the high ionic conductivity can avoid the interfacial polarization and lithium accumulation. Examples such as boron nitride for Li-Li\(_{1+x}\)Al\(_x\)Ge\(_{2-x}\)(PO\(_4\))\(_x\)=0.3–0.5 (LATP) interface, [164] and Ge for Li-Li\(_{1+x}\)Ge\(_{2-x}\)(PO\(_4\))\(_x\)=0.3–0.5 (LAGP) SSEs,[165] both following the aforementioned design principles. Au,[74] LiF,[166] and LiI[110,167,168] have been proved as effective SEI components for sulfide SSE systems. The LiF modification can realize the CCD of 2.0 mA cm\(^{-2}\).[166] The organic polymer and lithium salts construct protective layer between Li metal and Li\(_{10}\)Ge\(_2\)P\(_2\)S\(_{12}\) (LGPS) SSEs, enabling a stable operation for over 3000 h.[169] The Li\(_3\)PO\(_4\) has been selected as a robust SEI component to suppress dendrite growth and parasitic reactions,[170] which can also play similar roles in solid-state system such as garnet SSE[149] or sulfide SSE.[171] These results powerfully validate the improved chemical stability can help to ameliorate electrochemical performances.

4.1.3. Electrolyte Optimization

(I) Ultra-fine surface and densified SSEs

The surficial fluctuation should be eliminated to reduce the interfacial differences for uniform ionic conduction. These ultra-fine surface achieved by careful polishing can deliver improved performances.[172] Grain boundary strength is useful to reduce the tendency of the dendrite penetration along the grain boundaries. Virtually, rational densification of the oxide SSEs can reduce the defects, which help to enhance CCD. Densified SSEs realize the improved ionic conductivity, providing sufficient ionic flux. La\(_2\)Zr\(_2\)O\(_7\) densified LLZO SSEs can achieve an ionic conductivity to \(10^{-3}\) S cm\(^{-1}\).[88,173] Densified grain boundaries also improve the CCD performance. Yamada et al. investigated the influence of LiOH and Li\(_2\)CO\(_3\) to manipulate the grain boundaries, which realize a CCD of 0.6 mA cm\(^{-2}\).[174] The grain boundary modified by MgO[118] and LiAlO\(_2\)[175] fulfilled an increase of a range from 0.75–0.95 mA cm\(^{-2}\) in CCD values. The high intrinsic quality of SSEs realizes a slight improvement for CCD. If more chemical decoration is involved, the interface and bulk properties can be ameliorated simultaneously.

(2) Additives for SSEs

Adding beneficial additives in SSEs aims at dealing with interfacial instability or digesting the formed dendrite by chemical reactions, which help to mitigate the dendrite issues. Both Li\(_3\)PO\(_4\) in LLZO powder before sintering can react with the penetrated lithium dendrites.[176] In sulfide SSEs, Xu et al. added methoxyperfluorobutane (HFE) in sulfide SSEs to convert the internal active dendrites into inert LiF.[168] The additives also help to stabilize the interfaces. Tatsumisago et al. added...
LiI in Li$_3$PS$_4$ SSEs to reduce the interfacial parasitic reaction and volume expansion, realizing a high current density of 1.5 mA cm$^{-2}$ with the real capacity of 7.5 mAh cm$^{-2}$ at 100 °C.[110] Han et al. also conducted similar strategy. After LiI incorporation, the CCD value can be improved to 3.9 mA cm$^{-2}$ at 100 °C.[167] Zhao et al. designed doped Li$_6$PS$_5$Cl$_{1-x}$F$_x$ electrolyte, which can form LiF-based interface, realizing an amazing current density of 6.37 mA cm$^{-2}$, with an areal capacity of 5.0 mAh cm$^{-2}$.[177]

4.1.4. Limitations for Improving Active Areas

Basic solutions for improving active areas dominate the Li metal researches. These strategies are very effective at the initial stage. However, these solutions are gradually approaching the intrinsic bottlenecks. These methods can guarantee the initial active areas but cannot overcome the voids accumulation during the continuous dynamic processes such as Li stripping. The common planar structure of SSLMBs will be significantly restrained by the interfacial voids and they are hard to recover due to the uncontrollable Li surficial adatom diffusion. The present strategies can mostly realize an interfacial impedance of <10 Ω cm$^2$. Hence these rate determining steps of the initial interfacial contact have been partly overcome. The voids accumulations induced by high current density and high capacity can hardly be solved. It seems that although an artificial host can address the voids dilemmas, the complicated fabrication processes may weaken the practical value. Improving the active area is insufficient to break the bottlenecks. The mass transport issue must be considered to realize a breakthrough.

4.2. Mass Transport Balance View

4.2.1. Improving the Vacancy and Li$^0$ Diffusion in Anodes

As mentioned in Section 3.5, the vacancy accumulation results in contact loss and Li$^0$ accumulation at interfaces, leading to the dendrite growth. Due to the rapid diffusive speed of Li$^+$ in SSEs, vacancy and Li$^0$ diffusion are main issues to realize the interfacial balances. The Li atom and the diffusion on Li voids are ensured as the rate determining steps in inorganic systems. Virtually, the Li–In alloy have been widely applied in sulfide bases SSLMBs, which can easily realize stable cycling with the current density of >1 mA cm$^{-2}$. However, the real mechanisms have not been proved. The understanding on the specific properties of Li alloys in SSLMBs has drawn attention previously. Basically, Wang et al. proved that the Li-alloy skeleton remains at the interfaces after high-capacity lithium stripping, reducing the influence of contact loss (Figure 20a). The lithium alloy can also promote fast Li diffusion. Krauskopf et al. used LLZO system to probe the influence of Li alloy on improving the anodic performances (Figure 20b).[77] The diffusion co-efficiencies in an Li-Mg alloy can be increased from $0.8 \times 10^{-11}$ to $2.3 \times 10^{-11}$ cm$^2$ s$^{-1}$. This can be attributed to the altering on diffusion mode in Li alloy. The diffusion of Li$^0$ in an alloy obeys the 1D chemical diffusion model by the Fick’s second law, which breaks the limitation on Li diffusion. As expected, the alloy anode can realize a high CCD value over 2 mA cm$^{-2}$.[88,126] The depletion of active Li can also be significantly delayed due to the improved diffusion capability and the elimination of interfacial voids. Although the temperature and external pressure can both improve the diffusion of Li$^0$ or vacancies improving the intrinsic diffusion can reduce the dependence on external factors. However, the corresponding research for the diffusion balance is extremely insufficient and should be underlined.

4.2.2. Increasing the Transference Number of Li$^+$ in Polymer SSEs

Li$^+$ diffusion in polymer SSEs dominates the rate determining steps on dendrite propagation. Therefore, increasing the ionic transference number is employed to ameliorate the diffusion issues in polymer matrices. The anion immobilization is considered as an important thought to improve Li-ion migration in polymer SSEs. Importing strong Lewis acid to solvate the anions, adding filler to restrain the mobility of anions and regulating the chain components have all effectively improved the transference number.[178–183] Increasing the transference...
number of polymer SSE can reduce the tendency of dendrite propagation. However, the relationship between CCD and the polymer transference numbers deserves to be further developed. In addition, the CCDs of pure polymer are overall relatively poor than that in inorganic SSEs. The polymer systems are still valuable deserving to be fully developed.

4.2.3. Interfacial Therapy by Lean Liquid or Polymer

Stable lithium plating and stripping at a high current density in an all-solid-state mode is very difficult to achieve. The liquid or polymer wetting are the compromised strategies for practical batteries.\textsuperscript{[182–187]} The liquid or polymer electrolytes can immerse into the interfacial fluctuations to regulate the interfacial ionic conduction.\textsuperscript{[188]} The Li\textsuperscript{+} flux is not highly reliable to the solid–solid contact. The produced voids can also be emerged by liquid. The liquid therapy is mainly applied to ameliorate the cathodic troubles.\textsuperscript{[189]} This strategy can also significantly improve the anodic performance. As measured by Lu et al., the liquid enables the stable operation of hybrid symmetric cells of high current density (>1.0 mA cm\textsuperscript{-2}) (Figure 21).\textsuperscript{[84]} The liquid between Li-SSE alters the Li deposition style (Figure 21a1–a3). The liquid provides homogeneous Li flux which helps to reduce the inner dendrite in SSEs. The dendrite can be blocked by SSEs with improved current density from 0.1 to 1.5 mA cm\textsuperscript{-2} (Figure 21b–d). As expected, the stable cycling in asymmetric cells with liquid electrolyte at single side also remained. Li et al. designed a semi-liquid Li metal coupling with the LLZO

![Figure 21](https://www.afm-journal.de)
electrolyte. The operation current density can easily reach to 1.0 mA cm\(^{-2}\).[190] The hybrid electrolyte is usually conducted in a sandwiched structure or mixture styles.[183,191–193] The lean liquid can significantly improve the ionic conduction and interfacial contacts in practical batteries.[194] The lithium plating and stripping deliver the characters of that in liquid electrolyte.[195] In hybrid or quasi solid-state electrolyte, many conventional strategies can be transplanted to widen the thoughts. The SSEs plays as physical barriers for dendrite extension, and fire retardant to ameliorate the safety.[196–198] After cooperating with the liquid or gel polymer, the level of performance can approach that in conventional batteries, which is the shortcut for the industrial developing direction.[32]

4.2.4. Limitations of Addressing the Mass Transport Balance

The mass transport issues still need to be fully addressed to break the limitation on the intrinsic poor self-diffusion Li metal. There is still a lack of effective strategies on improving the Li atom diffusion. Li alloy is an effective method to realize improved diffusion. The Li alloy will suffer from problems such as low Li contents, volume expansions, and the loss on energy density. More new designs to improve Li diffusion or voids diffusion are in urgent need. In addition, breaking mass transport limitation requires high-quality SSEs and sufficient active areas. The poor intrinsic ionic conduction and low Li\(^+\) transference number of polymer SSEs still fall behind those of inorganic ones. Consequently, the applications of polymer electrolytes with Li metal anode will confront more challenges in high-power situations.

5. Conclusions and Outlooks

An energy-dense solid-state Li metal anode suffers from various interfacial concerns, while the batteries operated at a high current density for high-power situations will exacerbate the interfacial degradations. The high utilization of an Li metal anode is also one of the most prerequisite issues to fully utilize the energy provided by solid-state Li chemistry. Consequently, cycling under a high current density (>3 mA cm\(^{-2}\)) and high areal capacity (>3 mAh cm\(^{-2}\)) is essential for the development of SSLMBs.[43]

There is still a large gap between the targets and current SSLMB performances. CCD is not only an important criterion to evaluate the SSLMBs, but also provide chances to comprehensively understand the interfacial behaviors, failure mechanisms, and other factors influencing electrochemical performances. The relationship among basic behaviors, influence, and CCD strategies are integrated in Figure 22. The key conclusions are summarized as follows.

1) The significance of CCD

The major target for CCD is to evaluate the Li dynamic stability with a series of current densities and capacities. It helps to ensure the endurance of an Li interface with a specific current density and capacity, which can provide references to construct SSLMBs with high power density.

2) Basic Li kinetics for CCD

The nucleation and growth kinetics of Li metal are influenced by the current density. The high current densities tend to induce small nuclei with thin and prolonged whiskers, constituting the origin of morphological instabilities. A high current density and high capacity will lead to rapid Li void accumulations, which will deteriorate the interfacial stability.
(3) Rate-determining steps for CCD

The rate-determining steps of CCD help to unravel the essence of the limitation for the instability of Li-SSE interfaces. The basic rate-determining steps are Li ion transport, charge transfer, and the Li adatom diffusion and voids diffusion. The charge transfer is controlled by active contact area. A different SSEs system will be controlled by different systems. The polymer system is limited by the mass transport of Li ion and the inorganic system is controlled by Li atom and Li voids diffusion. The rate-determining steps are derived from the ideal model for solid-state Li kinetics, which will be significantly influenced by many practical influence factors.

(4) Rational identification for CCD

The identification of CCD is based on the standardized protocols with time control, capacity control, and long cycling methods. Those measurement protocols offer various information under different practical situations. Rational identification on CCD should avoid the “fake stable” phenomena.

(5) Key influence factors for CCD

The CCD will be influenced by many internal and external factors. These factors are interfacial contact, intrinsic quality of SSEs, mass transport (diffusion) balance, pressure, and temperature.

(6) The strategies to improve CCD

The strategies towards improving CCD must concentrate on the rate-determining steps and their influence factors. The present strategies have paid much attention on the active area factors and achieved many progresses. The mass transport issues are gradually emphasized, which are major points to realize a performance breakthrough.

Elevating CCD is essential for the development of SSLMBs with brilliant prospects. More insights into the intrinsic science and engineering are of vital importance in the following areas:

(1) Enhancing fundamental understandings on solid-state electrochemistry

The solid–solid Li kinetics are involved in multiple solid-state electrochemistry phenomena. Many Li kinetics behaviors have not been fully unraveled such as the voids evolution rules, the influences of specific morphology on Li plating/stripping, and their accumulation effects. More basic theories on solid-state electrochemistry should be demonstrated in details. Some electrochemical theories in liquid electrolytes should be carefully transferred and validated in solid-state systems. All of them contribute to ensuring the accurate rate-determining factors for solid-state Li kinetics.

(2) Emphasizing the diffusion balance issues

The diffusion issues usually act as the rate-determining steps for Li kinetics. Enhancing the diffusion ability of Li⁺, V Li⁺, or Li⁺ contributes to constructing the interfacial balance of Li⁺/V Li⁺ and Li⁺ at a higher current density, postponing the local accumulation of voids, Li atoms, or concentration gradients. These issues contribute to the dynamic interfacial evolutions. The presented effective strategies on solving the diffusion issues are still insufficient.

(3) Developing non-destructive characterization techniques

Non-destructive, high-resolution and in situ characterization methods will provide more fundamental understandings about the buried interfaces in solid-state systems.

(4) Establishing computational simulations

The theoretical computational study towards Li-SSE interfaces especially adopting the critical situations can provide important references for experiments and mechanism interpretation. A rational model validated by experimental results can provide profound understandings on solid-state electrochemistry.

(5) Establishing the standard for evaluating the CCD

CCD values are measured in various methods presently. Some test protocols are far from practical conditions, and many external conditions (e.g., temperature, pressure) have not been accurately controlled. Hence, a clear standard for CCD evaluation should be built. The CCD value should be clearly related with the areal capacity, temperature, and pressure. Also, CCD should be tested under practical areal capacities and full cells, as employing a high areal capacity are essential to construct energy-dense devices.

(6) Conducting CCD evaluation in scale-up SSLMBs

Most of the CCD results are measured in coin cells or mold cells, which can provide precisely-controlled measurement conditions (e.g., pressure) with less interfacial inhomogeneity. The enlarged batteries fabricated by industry techniques with complex interfaces will expose more problems under the critical evaluation at practical levels.

Generally, realizing high current density in SSLMBs is an important issue for their practical applications. The synergism from materials, chemistry, and mechanics will inspire more progresses and in-depth understandings, shedding lights in developing next-generation high-energy and high-power batteries.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

battery failure, critical current density, dendrites, Li kinetics, Li metal anodes, solid-state batteries, standards


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