Heterogeneous Reinforcements to Mitigate Li Penetration through Solid Electrolytes in All-Solid-State Batteries

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Dendrite growth is one of the leading factors that cause cycling deterioration for all-solid-state batteries (ASSBs). However, using a single dominant material to form the solid electrolyte has encountered several setbacks due to the intrinsically competing factors in mechanics and electrochemistry. Inspired by the “brick-and-mortar” structure, a strategy of embedding heterogeneous blocks (HBs) within the solid electrolyte (SE) is proposed to mitigate and suppress dendrite growth-induced internal short circuits (ISCs). A phase-field-based multiphysics model is established to describe the dendrite growth behavior. Results reveal that the characteristic length ratio \( e \) between the HBs and SE is the governing factor that dominates the dendrite growth path. The results show that a single long HB and multiple HBs in medium length with specific layouts can suppress and divert dendrite growth and avoid ISCs completely. For short HB cases, HBs can delay the ISC to a certain extent. The results imply that adding an appropriately designed heterogeneous layer into the SE will effectively block dendrites, and also define desired mechanical property domains. This work provides a multiphysics mechanistic understanding of the dendrite growth and SE cracking and opens new perspectives for the material selection and structural design of SEs for long lifecycle ASSBs.

1. Introduction

All-solid-state batteries (ASSBs) are considered promising next-generation batteries due to their high energy density enabled by lithium metal anode and the much-improved safety performance by the nonflammable inorganic solid electrolyte (SE).

High energy density and thermal instability make ASSBs superior substitutions to conventional lithium-ion batteries (LIBs) with liquid electrolyte. However, the dendritic issue is the responsible reason to cause the poor cycle life of ASSBs, thus preventing further commercialization.

The dendrite growth problem in SE has been widely investigated from various aspects, including experimental characterization, theoretical analysis, and computational modeling. The dendrite usually initiates from the inevitable interfacial defect, void, impurity, and grain boundary due to the focused current density. Dendrite can also be directly generated inside electrolyte due to the excess surface electrons and local electronic structure of the electrode. Once formed, dendrites grow and penetrates through the SE, causing crack propagation and finally resulting in internal short circuits. Dendrite growth may also cause the formation of dead lithium to reduce the Coulombic efficiency. The dendrite initiation (and Li plating) and growth are basically understood; however, strategies to suppress dendrite, especially to prevent dendrite growth-induced short circuit, mainly focus on the material selection and fabrication perspective with little progress.

Early research efforts have been conducted to provide possible solutions to mitigate dendrite growth, mainly from mechanics, structural design, and material science perspectives. From the mechanical side, previous theoretical work has proven that SE with shear modulus two times higher than that of the polymer-based separator enables the capability of dendrite suppression. With various characterization techniques, e.g., SEM, TEM, and synchrotron X-ray CT, one may observe that dendrites still penetrate the SE even with the ultrahigh modulus (e.g., \( \approx 150 \) GPa for \( \text{Li}_7\text{La}_{3}\text{Zr}_2\text{O}_{12} \) (LLZO) electrolyte) to short the batteries. This finding reveals the fact that other dominating factors also actively promote the Li dendrite growth to penetrate into the SEs.

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from recent computational models demonstrate that the properties of the grain boundary region should be enhanced to mitigate/avoid dendrite growth, and increasing fracture toughness of SE is beneficial to alleviate dendrite growth and crack propagation as well.

On the other hand, the strategy of structural design to suppress dendrite mainly focuses on how to accommodate lithium deposition to prevent the formation of dendrite. Micropores were introduced to anode current collector to serve as the preferential place for lithium plating, which demonstrates that a porous current collector may be a promising method. It is further discovered that lithium can reversibly plate and strip within the parallel hollow tubules made of a mixed ionic-electronic conductor, dominated by Coble creep, to effectively relieve the stress and maintain stable interfacial contact. Other research work designed a conductive and lithiophilic porous scaffold with a high specific area to function as the stable host structure for repeated lithium plating and striping. The reported structures show promising effects in dendrite mitigation, but these structures require elaborate design and a sophisticated fabrication process. Another good structural design is the multilayer electrolyte design with less stable electrolyte sandwiched by the more stable electrolyte to prevent possible dendrite growth, leveraging an expansion-screw-like effect. Multilayer electrolyte with a reducible Ti-Li4Zr2La4Zr15Toy2O12 (LLZTO) layer contacting Li–metal and the LLZTO layer contacting cathode was reported to realize a long-term capacity of 3 mAh cm−2 without a short circuit.

From the perspective of material fabrication, surface modification and improvement of electrolyte properties are the main measures to suppress Li dendrite. Composite electrolyte consisting of ceramic- and polymer–electrolytes has attracted increasingly heated research focus because it takes the combined advantages of high ionic conductivity from the ceramic-based electrolyte and good flexibility from polymer-based electrolyte. In the meantime, such a design also improves the contact between SE and lithium anode and provides a better dendrite suppression capability.

According to the experiment results, the relative density ρLZ0 of LLZO electrolyte greatly affects its Young’s modulus ELLZO, fracture toughness KLLZO, and ionic conductivity κLLZO. As ρLZ0 increases from 85% to 98%, ELLZO increases from ≈135 to ≈140 GPa, KLLZO reduces from 2.37 to 0.97 MPa m0.5, and κLLZO varies from 0.0094 to 0.34 mS cm−1. To reduce the battery internal resistance and achieve better electrochemical performance, the electrolyte with larger ionic conductivity has the priority, and in this case, the electrolyte fracture toughness is relatively small, then the dendrite can easily penetrate the electrolyte, causing a short circuit. On the other hand, using LLZO electrolyte with higher mechanical strength may block the dendrite, but such electrolyte with low conductivity will increase the internal resistance and sacrifice the battery performance.

Thus, it requires us to conduct material selection, and structural design of SE with higher robustness against dendrite propagation with the consideration of electrochemo-mechanics coupled factors. To this end, inspired by the nacre-like brick-and-mortar structure, we propose the strategy of embedding heterogeneous blocks (HBs) into the solid electrolyte to reduce the short-circuit risk induced by dendrite growth through taking the advantage of mechanical mismatch. To understand the fundamental mechanism, we assume the main body of the electrolyte is LLZO with high conductivity to guarantee low cell resistance, and the HBs are LLZO with enhanced mechanical properties. The governing factors to control the dendrite mitigation effect are comprehensively investigated to provide insights and guidance on the design of dendrite-suppression electrolytes.

2. Results and Discussion

2.1. Dendrite Propagation

The baseline case is dendrite growth from an interfacial defect at the lithium anode side that grows along the x-axis. Upon reaching the cathode, the dendrite bridges the SE, and electron transport between the anode and cathode triggers an internal short circuit (ISC) (Figure S1, Supporting Information). The aim of this study is to investigate possible mitigation mechanisms where this type of dendrite growth-induced short circuit is slowed/stopped by diverting dendrite propagation away from the x-axis direction.

To determine the dominant properties of HBs that are capable of blocking a dendrite, we conduct parametric studies of Young’s modulus EHB, ionic conductivity κHB, and fracture toughness KHB. The computational results indicate that adjusting EHB from 100 to 200 GPa or κHB from 9 × 10−3 to 4.43 mS cm−1 is incapable of mitigating dendrite growth (Figure S2a,b, Supporting Information). However, the dendrite growth behavior (i.e., growing speed, dendrite angle, and length) is highly dependent on KHB. There are a variety of possible factors that may promote dendrite penetration within the solid electrolyte, such as cracks, voids, grain boundaries, local electronic structure, and electron segregation at surfaces and interfaces. The relative contributions of these phenomena are currently not well understood and thus it is difficult to incorporate all of these factors in the model in a meaningful way. Recent experiments provide direct evidence that dendrite growth in some inorganic solid electrolyte can be coupled with the crack propagation, where dendrite penetration drives crack propagation, and the newly formed crack then provides further space for dendrite growth. The model employed in this study is based on this type of behavior, where internal pressure in the Li-filled filaments drives fracture, and crack extension provides space for further Li metal penetration. Herein, the lithium filaments are mechanically constrained by the surrounding solid electrolyte, and their continuous growth is then driven by electrochemical deposition that exerts pressure on the neighboring electrolyte. The resulting strain energy in the SE is subsequently relaxed by fracture of the SE which then provides more growth space.

In the model (governing equations in Table S1, Supporting Information), the internal stress Sext(x,t) is calculated from the overpotential η(x,t) in the electrochemical model, and imposed at the lithium–electrolyte interface, based on Sext(x,t) = −∂Fη(x,t)/∂ξ. This relationship assumes that the Li filaments are highly constrained, such that full pressurization occurs quickly and reaches the maximum hydrostatic stress Sext(x,t) that is thermodynamically possible for a given electrochemical driving force η(x,t) (i.e., the overpotential at the lithium–electrolyte interface). This assumption gives an upper
bound on the pressure. Lower stresses are predicted in more detailed models that includes more realistic descriptions of the crack opening displacements and Li plasticity near the base of the crack. However, these effects are neglected here, where the focus is on dendrite growth/crack propagation paths in SEs with heterogeneous mechanical properties over macroscopic time scales. The formulation used here also overestimates the Li flux into the sides of the Li filament, however, this is also a secondary factor since most of the flux enters at or near the dendrite tip. To demonstrate this, additional simulations were conducted with variations in the exchange current density, the applied current density (i.e., faster interface kinetics) and the SE ionic conductivity values. These effects alter the Li-ion flux into the flaw, and in all of these cases the predicted dendrite growth is similar to the baseline case (Figure S3, Supporting Information). This further justifies the effectiveness of the modeling approach in this study.

The model defines the path for Li dendrite penetration by energy minimization. It is thus consistent with a crack propagation mechanism, where the resistance of the material to crack propagation (i.e., described here by the fracture toughness $K_c$) reflects its resistance to dendrite penetration. $K_{cHB} = 0.98 \text{ MPa m}^{0.5}$ is used as the baseline value, below and above which a series of $K_c$ values (i.e., 0.78, 0.98, 1.47, 1.96) are studied (Figure S2c, Supporting Information). The dendrite initially grows along the x-axis through material with small value of $K_c$ (i.e., low dendrite penetration resistance), but the growth direction is diverted to the y-axis by HB with high $K_{cHB}$, i.e., $K_{cHB} = 1.96 \text{ MPa m}^{0.5}$. This doubling corresponds to a fourfold increase in the fracture resistance, which is sufficient to prevent dendrite growth into the HB (Figure S2c, Supporting Information). The crack propagation/dendrite growth here is described by the phase-field method which employs energy conservation, where changes in the strain energy density serve as the driving force. The phase-field model employs continuous property variations across the interface between the two regions, in contrast to the sharp interfaces that are considered in conventional fracture mechanics analyses of crack deflection at bimaterial interfaces.[28] The latter is based on the fracture resistance of the interface, which is not specifically defined in our case. However, the results of these two approaches are generally similar, with deflection induced by a relatively high fracture toughness in the HB layer. Note that when the dendrite deflects along the LLZO-HB interface ($t = 70 \text{ s}$, Figure S4, Supporting Information), the stress components $\sigma_{xx}$ and $\sigma_{yy}$ correspond to mixed-mode loading (i.e., a combination of Mode-I in-plane tension and Mode-II in-plane shear). In the phase-field method, this overall effect is generally reflected in the strain energy density, i.e., the concentrated energy density at the dendrite tip (e.g., see $t = 80 \text{ s}$ in Figure S4, Supporting Information).

Furthermore, the different dendrite growth behavior and mitigation effect are less obvious for the HBs with different $E_{HB}$ and $K_{cHB}$ compared to the fracture toughness $K_{cHB}$ (Figure S5, Supporting Information). To summarize the general trend based on the above trial computational results, $K_{cHB}$ (dendrite penetration resistance) is the primary HB property that alters dendrite propagation, and in general, HBs with higher $K_{cHB}$ can be used to block dendrite growth. Therefore, in the following study, we define HBs with large enough fracture toughness $K_{cHB} = 1.96 \text{ MPa m}^{0.5}$ to deflect dendrites (Figure S2c, Supporting Information), and the other material properties are set to be the same as those of the main-body LLZO electrolyte.

### 2.2. Dendrite Mitigation Effect with Single HB

The risk associated with a dendrite growth-induced short circuit can be evaluated by calculating the time that it takes for the dendrite to reach the cathode side, i.e., the short-circuit risk is high if dendrite grows to the cathode side within a very short time, while the short-circuit risk is low if it takes a long time for dendrite to reach the cathode, and the risk can be reduced to zero if the dendrite is prevented from reaching the cathode (i.e., the short-circuit time is infinite). To understand the dendrite mitigation effect using HBs, we first embed a single HB and focus on the individual HB’s size effect from a structural design perspective. Different cell lengths $L_{cell}$ (i.e., 50 and 100 $\mu$m) and normalized HB length $\epsilon = L_{HB}/L_{cell}$ from 0.05 to 0.2 are considered. Note that adding HB ($K_{cHB} = 0.009 \text{ mS/cm}$, $K_{cHB} = 1.96 \text{ MPa m}^{0.5}$) into the LLZO electrolyte ($K_{cEB} = 0.443 \text{ mS cm}^{-1}$, $K_{cHB} = 0.98 \text{ MPa m}^{0.5}$) has little influence over the total effective electrolyte conductivity $\kappa_{eff}$ (e.g., the $\kappa_{eff}$ is only reduced 0.49% from 0.443 to 0.4408 $\text{mS cm}^{-1}$ when adding 10 $\mu$m long HB to 50 $\mu$m long electrolyte). The ionic conductivity $\kappa_{SE}$ is defined individually for the main-body of the electrolyte, the heterogeneous block, and the lithium metal domains. Meanwhile, $\kappa_{SE}$ will change as the dendrite evolves.[39] The electrolyte conductivity directly determines battery internal resistance which can then influence the electrical potential distribution according to the Ohm’s law in the governing equations of Table S1 of the Supporting Information. Furthermore, the electrolyte potential $\phi$ distribution is similar for the electrolyte with and without HB (Figure 1a), thus demonstrating that the HB has little adverse influence on the overall electrochemical behavior. The potential drop over the heterogeneous block is $\approx 0.00109 \text{ V}$ (Figure 1a), which is several orders of magnitude smaller than $\phi(\approx 0.16 \text{ V})$. Thus, the influence of the additional resistance caused by the additional block is negligible. Note that, a significantly lower conductivity in HB compared to the surrounding electrolyte will have a nontrivial impact on the local electrical potential distribution (i.e., by increasing the potential drop within HB domain).

Interestingly, we discover that dendrite growth exhibits different modes when $\epsilon = 0.05$, 0.1, and 0.2 (Figure 1b) (where $L_{cell} = 50 \mu$m, and the corresponding HB length $L_{HB}$ are 2.5, 5, 10 $\mu$m, respectively). For $\epsilon = 0.05$ case, the dendrite first grows along the x-axis, then bypasses the HB, and finally approaches the cathode side along the y-axis. This has no effect in preventing the ISC, but it delays the ISC triggering time. For the $\epsilon = 0.1$ case, after encountering the HB, the dendrite splits into two parts, i.e., the bottom dendrite branch diverges its direction toward the y-axis (no ISC risk anymore). The top branch bypasses the HB and continuously grows along the direction with an angle $\theta = 45^\circ$ to the x-axis (Figure 1b), greatly reducing the safety risk by prolonging the dendrite growth path. For $\epsilon = 0.2$ case, the two dendrite branches both divert their growth direction from the x- to y-axis, eliminating short-circuit risk since the dendrite growth along the y-axis will not cause direct...
contact between anode and cathode. Similar results also apply to the case of \( L_{\text{Cell}} = 100 \, \mu m \) with the same \( e \) values (Figure 1c) (Video S1, Supporting Information).

To illustrate the underlying mechanism, the stress state \( \sigma_{ij} \) \((i, j = x, y)\) is extracted at the moment when the dendrite growth first extends beyond the right side of the HB. The stress state
here varies with $e$ (Figure 1d): 1) for $e = 0.05$, the $\sigma_{xx} (2.88 \text{ GPa})$ at dendrite tip highlighted in the red dashed circle is larger and more concentrated than $\sigma_{xx} (1.125 \text{ GPa})$ and $\sigma_{yy} (1.038 \text{ GPa})$, which drives dendritic growth along the $x$-axis; 2) for $e = 0.1$, the $\sigma_{xx} (2.6 \text{ GPa})$ and $\sigma_{yy} (1.16 \text{ GPa})$ are more concentrated at the dendrite tip, with promotes the dendrite branches along the $y$-axis, and the direction $45^\circ$ with the $x$-axis, respectively; 3) for $e = 0.2$, the $\sigma_{xx} (2.6 \text{ GPa})$ at both dendrite tips is larger and more concentrated than $\sigma_{xx} (1.5 \text{ GPa})$ and $\sigma_{yy} (1.12 \text{ GPa})$, which explains the dendrite growth preferentially along the $y$-direction. Both $x$- and $y$-axis dendrite growth can eventually damage the cell, i.e., in the $x$-axis direction it electrically short circuits the cell, and in the $y$-axis direction it mechanically splits the solid electrolyte (note that here we do not consider the possible growth toward z-direction). However, the SE sample is usually a cylindrical pellet and the thickness of SE ($x$ direction) is at least 1–2 orders of magnitude less than its diameter ($y$ direction)[25c,29] and experimental characterizations revealed that dendrite prefers to grow toward the other electrode (i.e., along $x$ direction).[17,30] As such, the focus of this study is to suppress the $x$-axis dendrite growth, but attention should also be paid to the $y$-axis dendrite growth when long-time cycling is included.

To quantitatively evaluate the short-circuit risk $R$ under HB with varied $e$, the normalized dendrite-growth time $t_d/t_0$ is adopted, based on the dendrite tip reaching the distance $X_d = 35 \mu m$ (on the right of single HB), where $t_0 = 80 s$ is the baseline time without any HB (Figure S1, Supporting Information), and $t_d$ is the dendrite growth time with the HB. $R$ here is defined to be linear with $t_d/t_0$, i.e., $R = 100\%$ when $t_d/t_0 = 1$ since the dendrite growth is not delayed nor blocked, and $R = 0$ when $t_d/t_0 = 0$ as the dendrite is completely prevented from growing toward the cathode side. According to the dendrite growth mitigation effect under different $e$ values, three categories are classified based on the short-circuit risk, i.e., small $e$ ($0 < e < 0.1$), medium $e$ ($0.1 < e < 0.18$), and large $e$ ($0.18 < e < 1.0$) (Figure 2). The single HB with small $e$ has little effect in dendrite mitigation and can only elongate the dendrite growth path to delay the ISC time, and the ISC risk is above 80%. The single HB in medium $e$ can partially change the dendrite growth direction to reduce the short-circuit risk below 70%, which may need further modulation in multiple HBs to realize the full mitigation effect. The single HB with large $e$ can change dendrite growth direction from $x$ to $y$-axis, which is then capable of preventing the dendrite growth-induced ISC completely.

### 2.3. Dendrite Mitigation Effect with Multiple HBs in Small $e$

A single HB with large $e$ can lead to full elimination of the ISC risk (i.e., the dendrite grows along the $y$-axis), while in cases with small/medium $e$, the HB cannot fully stop the dendrite growth toward the cathode. As such, we naturally speculate that multiple HBs in small/medium $e$ cases may be able to block dendrite propagation.

Two HB arrangements are considered here, i.e., aligned (A1 type) and staggered (A2 type) (Figure 3a). The two governing geometric parameters are the gap $G$ between adjacent HBs in the same column and the distance $D$ between two neighboring columns. Due to the synergic enhancing effect from neighboring HBs, different dendrite growth mitigation behaviors are observed. As for multiple small-$e$ HBs ($L_{HB} = G = D = 4 \mu m$, Figure 3a), at $t = 70 s$, the dendrite reaches the first-column HBs in both A1 and A2, then it changes growth direction to bypass HB (Figure 3b). In A1, when the dendrite grows to bypass the HB in the first column, it continues to grow along the $x$-axis, and the dendrite tip faces the gap in the second column (since the two columns are aligned) ($t = 96 s$, Figure 3b). In this case, the second column plays no role in blocking the dendrite growth. In A2, since there is an offset distance between the neighboring columns, the dendrite tip faces the HB in the second column after it crawls across the first column via the gap. In this case, the dendrite growth direction is altered due to the HB in the second column ($t = 96 s$, Figure 3b), which elongates the dendrite growth path. Finally, dendrites in both A1 and A2 cases grow to bypass the second column HBs and toward the cathode side (Video S2, Supporting Information).

The dendrite in A2 is farther to the cathode than that in A1 case due to the extended dendrite growth path ($t = 120 s$, Figure 3b), delaying the ISC time. In short, by properly designing the staggering space, the dendrite growth path can be significantly extended, and the growth angle may also be diverted away from...
the cathode side. Besides, the total effective electrolyte conductivity $\kappa_{\text{eff}}$ decreases from 0.443 to 0.4343 mS cm$^{-1}$ by only 1.96% when A1 or A2 is adopted, and the electrolyte potential is seldomly affected (Figure S6, Supporting Information).

The applied current density $i$ dictates the internal electrochemical reaction kinetics of the cell, which further affects the dendrite growth behavior. Here various current density values are selected to explore its influence, i.e., $i = 0.4795$, 0.959, 1.4385, and 1.918 mA cm$^{-2}$. At low current density ($i \leq 0.959$ mA cm$^{-2}$), dendrite growth occurs along the $y$-axis without short-circuit risk (Figure 3c). However, when $i \geq 0.959$ mA cm$^{-2}$, the dendrite penetrates the electrolyte and grows toward the cathode. Furthermore, the dendrite reaches the right edge of the 2nd-column HB earlier with both the A1 and A2 arrangement methods at $i = 1.918$ mA cm$^{-2}$ than it does with the $i = 1.4385$ mA cm$^{-2}$ (Figure 3c), indicating faster dendrite growth at higher current density. Increased current density and simultaneous dendrite suppression are critical requirements for ASSB commercialization, thus $i = 1.918$ mA cm$^{-2}$ is selected in this study to explore dendrite mitigation strategies with practically relevant current densities.

2.4. Dendrite Mitigation Effect with Multiple HBs in Medium $\varepsilon$

Again, the HB structures are classified into two categories, the same as in the small-$\varepsilon$ cases (i.e., A3 and A4 for aligned and staggered lineups, respectively). In the A3 case, after the dendrite grows through the gaps in the first column, it continuously grows along the direction $45^\circ$ to the $x$-axis. Once the dendrite meets one of the HBs in the second column, the growth angle further changes along the $y$-axis for further growth (which turns $90^\circ$ compared to its original growth path, Figure 4a). In this way, the dendrite growth-induced ISC can be completely prevented. On the other hand, in A4 cases, the dendrite penetrates through the gap in the first column and extends diagonally, then it reaches the gap in the second column, which provides an accessible opportunity for the growth path (Figure 4a).
this case, ISC cannot be entirely avoided, though the dendrite growth path is extended (Video S3, Supporting Information).

As an additional step to obtain comprehensive knowledge about the modulation of the HB arrangement to completely block dendrite growth, a further parametric study is carried out following the effective arrangement method in A3. The dominant geometric parameters are: 1) the HB length $L$, 2) the gap $G$ between HBs in the same column, and 3) the distance $D$ between two adjacent columns. To make it more generalized, the normalized gap ratio $G/L$ and distance $D/L$ are used to quantitatively characterize the geometric information. Within the range of medium $e$, four values are selected, i.e., $e = 0.1, 0.12, 0.14, 0.16$. Furthermore, since the large gap and distance provide additional possible space for dendrite growth resulting in poor performance in mitigating dendrite (Figure S7, Supporting Information), the $G/L$ and $D/L$ values are limited within 1.

Similarly, the normalized time $t_0/t_x$ is adopted to evaluate the dendrite growth induced short-circuit risk $R$. Here $t_x$ is the time when dendrite grows to the right edge of the second-column HBs in each specific arrangement, and $t_0$ is the corresponding baseline time without any HB. Based on the mitigation effect of HB lineups, we classify the effects into two categories: Group 0 for completely preventing dendrite from growing toward the cathode (safe region, blue area in Figure 4b), Group 1 for dendrite still growing to cause a short circuit (dangerous region, nonblue area in Figure 4b). The region of $G/L$ close to 0 is safe, which is much close to the scenario with large $e$. For $e = 0.1$, the dangerous regions in Group 1 are: Region 1 ($0.1 < G/L < 0.4$), and Region 2 ($0.6 < G/L < 1, 0 < D/L < 0.6$). As $e$ increases to 0.12, the dangerous Regions 1 and 2 are both split into two small regions, one of which further disappears in $e = 0.14$. When it comes to $e = 0.16$, only a small portion of Region 2 ($0.9 < G/L < 1, 0 < D/L < 0.3$) remains and the high-risk red area ($R$ close to 100%) nearly disappears, indicating a promising dendrite mitigation effect. Thus, for multiple HBs in medium $e$, the dendrite can be completely suppressed with specific combination of gap and distance ratios. The overall trend discovered with larger medium $e$, is the larger safe Group 0 area and the smaller high-risk red region in dangerous Group 1, thus demonstrating better dendrite mitigation.

### 2.5. Multilayer Electrolyte Design to Mitigate Dendrite

In extreme cases, HB arrangement with gap $G = 0$ becomes a new layer of electrolyte. As such, a multilayer electrolyte structure consisting of a main-body electrolyte and an embedded layer (EL) is formed (Figure 5), combining the mechanical advantage from HB (high fracture toughness) and electrochemical advantage from baseline electrolyte (high conductivity). To leverage the mechanical stiffness gradient and mismatch, we assign different Young’s moduli to the embedded layer and the main body of the electrolyte to improve the overall dendrite mitigation effect of the multilayer electrolyte.

The main-body electrolyte is LLZO with Young’s modulus $150$ GPa. Here four different Young’s modulus $E_{EL}$ (i.e., 50, 100, 150 (baseline), 200 GPa) are considered to investigate the dendrite mitigation effect for the 10 µm thick embedded layer.

Note here that the energy release rate at fracture $G_c = \frac{(1-v^2)K_c^2}{E}$
describes the fracture resistance. To study the effect of Young’s modulus, the fracture toughness $K_c$ of the embedded layer is first held constant as 0.98 MPa m$^{0.5}$, which is same as the main-body electrolyte. As the dendrite grows into the embedded layer, the stress tensor component $\sigma_{yy}$ at the dendrite tip is $-1.436$ GPa for $E_{EL} = 50$ GPa, smaller and less concentrated than the other cases ($\sigma_{yy} = -1.938$, $-2.39$, $-2.28$ GPa for $E_{EL} = 100$, 150, 200 GPa, respectively) (Figure 5a). Accordingly, the short-circuit time is 276, 235, 225, 234 s for $E_{EL} = 50$, 100, 150, and 200 GPa, respectively, and $G_c$ increases with decreasing $E_{EL}$, which implies that smaller Young’s modulus $E_{EL} = 50$ GPa improves dendrite mitigation. As a second case, we set the $G_c$ of the embedded layer to be the same as that of the electrolyte (i.e., $G_c = 3.02 \, \text{J m}^{-2}$) and vary $E_{EL}$. Similarly, $E_{EL} = 50$ GPa leads to better dendrite mitigation and can even keep the dendrite growth within the embedded layer (Figure S8, Supporting Information). Thus, we observe a continuous dendrite growth along the initial dendrite direction (Figure 5b–d). The farthest dendrite growth distance $X_d$ (from the leftmost base to the rightmost tip) is used to intuitively indicate the degree of dendrite mitigation since larger $X_d$ implies earlier short circuit, and smaller $X_d$ represents a better mitigation effect and lower short-circuit risk. For all cases in Figure 5, the dendrite initiates from the predefect area and grows toward the cathode side. At $t = 55$ s, the dendrite reaches the left edge of the embedded layer in all the scenarios, then penetrates into the embedded layer and continues to grow along the x-axis. At $t = 120$ s, the dendrite reaches the right edge of the embedded layer in Scenario 1 with $X_d = 35$ µm, meanwhile the $X_d = 37.3$ µm, 39.2 µm for Scenarios 2 and 3, respectively. Later, the dendrite penetrates through all the embedded layers and re-enters the main-body electrolyte as the charging process continues. At $t = 160$ s, $X_d = 49.8$, 43.8, 57.5 µm for Scenarios 1,
Figure 6. Overview of the ISC risk as a function of length ratio $\epsilon$, quantity and arrangement of HB, and quantity and Young's modulus of the embedded layer.

2, 3, respectively, while $X_e = 71.8$ $\mu$m for the baseline case without any embedded layer (Figure S1, Supporting Information). Finally, the dendrite reaches the cathode side, causing short circuits in all the scenarios, and short-circuit time $t_{\text{short}} = 276, 290, 262$ s for Scenarios 1, 2, 3, respectively. Such results demonstrate the effectiveness of the dendrite growth mitigation for the multilayer. It is also clear that a thicker embedded layer can further slow down the dendrite growth. For the same total thickness, multiple layers with gaps impose more mechanical stiffness gradient transitions on the multilayer electrolyte design, thus leading to better dendrite mitigation. The embedded layer affects dendrite growth mainly by delaying growth speed within EL, thus, the EL thickness is one dominant factor that controls the mitigation effect. EL with different thicknesses (i.e., 10, 5, and 0 $\mu$m) is considered here. The dendrite grows at the same speed until it reaches the EL region. Then, the dendrite growth speed is reduced by the EL region and the dendrite penetration distance is largest for the baseline case (Figure S9, Supporting Information). The short-circuit time is delayed at the thickest EL case (i.e., 10 $\mu$m), demonstrating that increasing the EL thickness also helps to mitigate dendrite penetration and reduces short circuit risk.

To provide a clear overview of the dendrite-induced ISC risk, we consider the main governing effects from the length ratio $\epsilon$, along with the quantity and arrangement of HBs, and the Young’s modulus of the electrolyte. The resulting map in Figure 6 for $0 < \epsilon < 1$ (regions I and II) shows combined strategies that combine the advantages of HBs’ high fracture toughness to suppress dendrite growth and LLZO’s high ionic conductivity to maintain electrochemical performance. In Region I (high ISC risk), whether single or multiple HBs are adopted, the dendrite-induced short circuit is not prevented but only delayed by the elongated growth path, for both small $\epsilon$ ($0 < \epsilon < 0.1$) area and medium $\epsilon$ ($0.1 < \epsilon < 0.18$) area using the A4 arrangement method. Nevertheless, multiple HBs in medium $\epsilon$ through the specific A3 arrangement are capable of completely suppressing dendrite growth toward the cathode (Figure 4b), and single/multiple HBs in large $\epsilon$ can prevent the dendrite-induced short circuit as well, both of which are included in Region II (zero ISC risk). At $\epsilon = 1$ (Region III), the strategy becomes a multilayer electrolyte structure consisting of main-body electrolyte and embedded layer to mitigate dendrite growth through stiffness gradient design. In this case, the electrolytes have different Young's moduli $E_{\text{EL}}$ compared to the main-body electrolyte, and their other properties are the same. Although the dendrite-induced ISC is not completely prevented in Region III, electrolytes with smaller $E_{\text{EL}}$ in more and thicker layers show promising dendrite mitigation effects to delay the short-circuit time significantly.

3. Conclusions

The dendritic growth-induced ISC safety issue is one of the main problems to be solved for the successful implementation of ASSBs. Inspired by “brick-and-mortar” toughening mechanisms, we propose the strategy of adding heterogeneous blocks into SEs. Dendrite growth mitigation is then evaluated with an established multiphysics modeling framework under practical current density. The effect of adding HBs within the electrolyte on dendrite mitigation is then comprehensively investigated by considering the HB length, arrangement method, and multilayer design. Our major findings are as follows.

- The nominal length $\epsilon$ of the HB dominates the dendrite mitigation effect with a single HB. Specifically, large $\epsilon$ ($0.18 < \epsilon < 1$) may completely change dendrite growth direction and prevent short circuit, while medium $\epsilon$ ($0.1 < \epsilon < 0.18$) can partially block dendrite growth, and small $\epsilon$ ($0 < \epsilon < 0.1$) can only mitigate dendrite growth to a limited extent.
- Multiple HBs with medium $\epsilon$, modulated by a specific arrangement method, can fully mitigate dendrite penetration, while multiple HBs with small $\epsilon$ only elongate the dendrite growth path and delay the short-circuit time.
- The multilayer SE structure shows promise for mitigating dendrites and delaying short circuits, especially when thicker
These results reveal that adding HBs with high fracture resistance is a promising approach to mitigate dendrites and reduce short-circuit risk. To implement these findings, additional consideration of actual microstructural effects is needed. Current LLZO electrolyte have a $G_c \approx 3 \text{ J m}^{-2}$ with Young's modulus 150 GPa, fracture toughness 0.985 MPa m$^{0.5}$, and Poisson's ratio 0.257. In polycrystalline ceramics varying the grain size can have some effect on Poisson's ratio $\nu = 0.257$. In polycrystalline ceramics varying the modulus $G_c$ differences. The mesoscale engineering HBs with large $G_c$ differences should be considered in most cases these effects are well below the 4:1 ratio used in the model. Differences this large can be created by varying porosity,$^{[31]}$ but this might limit overall performance of the SE in other ways. In some ceramics, large increases in $G_c$ are obtained with elongated whisker-like grain structures (e.g., Si$_3$N$_4$), and our results indicate that focused efforts to create these structures in SEs are potentially worthwhile. Ultimately, nanocomposites that employ second phases may provide a wider array of options for engineering HBs with large $G_c$ differences.$^{[32]}$ The mesoscale model with a homogenized electrolyte domain in this study focuses on the mitigation of dendrite-induced short circuit risk. In future work, this can be further improved with a multiscale approach by including the intricate polycrystalline electrolyte structure to predict the transgranular or intergranular dendrite penetration.

4. Experimental Section

The multiphysics model used here was developed to include a) the battery model to describe the electrochemical phenomena, b) mechanical model to calculate the overpotential-induced stress $\sigma$ fields, c) phase-field model to solve the evolution of dendrite growth and crack propagation (phase-field order parameter $\xi = 1$ for intact SE region, $\xi = -1$ for crack/dendrite region), and d) short-circuit model to detect the triggering of dendrite growth-induced short circuit. These four submodels were interconnected by transferring relevant physical variables, described by the governing equations (Table S1, Supporting Information).$^{[39]}$

The lithium and LiCoO$_2$ were used as the anode and the cathode, respectively (Figure 7a). The promising LLZO solid electrolyte with high Young’s modulus $E_{\text{LLZO}} = 150$ GPa and ionic conductivity $\kappa_{\text{HB}} = 0.443 \text{ mS cm}^{-1}$ was set as the main body of the electrolyte in this study. Note that due to the high hydrostatic stress developed within the vicinity of the tip of Li dendrite (Figure 1), the plasticity of Li material was not considered here. The geometry was simplified as a 2D plane to improve the computational efficiency (Figure 7b). For the dendrite growth simulation (without any heterogeneous blocks) in this study, the model was validated in three ways: 1) the cell voltage response during charging/discharging agreed with the experiment results,$^{[19]}$ 2) the predicted critical current density, i.e., the threshold value of applied current density to drive dendrite growth-induced ISC was comparable to reported values,$^{[19,33]}$ and 3) the simulation morphology of dendrite penetration and its coupled crack propagation was similar to experimental observations of transverse cracking with minimal branching.$^{[13a-c,17a,30]}$ The current density adopted in this study of 1,918 mA cm$^{-2}$ mimicked current densities used in practical ASSBs. Note that the Li dendrite initiation mechanisms, e.g., Li plating and nucleation, were not the focus of this paper. Thus, an initial defect with length 4 $\mu$m and width 2 $\mu$m was predefined to initiate dendrite growth. It is also confirmed that the initial geometry of the defect did not influence the Li dendrite growth (Figure S10, Supporting Information). An HB with length $L_{\text{HB}}$ and width $W_{\text{HB}} = 2.5$ $\mu$m were selected to demonstrate the representative result. The electrolyte and HBs were assumed to be homogeneous without voids; thus, the effect of the internal void was not considered in this study.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

C.Y.: methodology, modeling, data analysis, and writing – original draft. B.W.S.: data analysis and writing – review and editing. J.X.: conceptualization, supervision, methodology, and writing – review and editing.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.
