1. Introduction

Solid electrolytes (SEs), and the resulting solid-state batteries, are one of the most pursued directions in the battery field.[1–3] The strong interest in solid-state batteries stems principally from the significantly improved safety, higher energy densities enabled by new electrode materials, and better low-temperature performance as compared to conventional liquid-based batteries. Nonflammable solid electrolytes are expected to improve the safety over flammable commercial liquid electrolytes. Moreover, solid electrolytes are compatible with several high-energy-density electrode materials that cannot be implemented in liquid-electrolyte-based configurations.[4–7] Solid electrolytes also maintain better low-temperature ionic conductivity than liquid electrolytes.[8–10] These advantages make solid-state batteries the most promising technology for the next generation electric-vehicle market.

Among the families of solid electrolytes, sulfides retain the highest ionic conductivity.[10–14] Sulfide glass solid electrolytes[15,16] and glass-ceramic solid electrolytes[17–19] have demonstrated ionic conductivities on the order of 0.1 – 1 mS cm⁻¹ and above 1 mS cm⁻¹, respectively. The ceramic-sulfide electrolytes, most notably Li₉GeP₂S₁₂ (LGPS) and Li₁₀SiP₂S₁₂ (LSPS), are particularly promising as they maintain exceptionally high ionic conductivities. LGPS was one of the first solid electrolytes to reach ionic conductivities comparable with liquid electrolytes[20] at 12 mS cm⁻¹, only to then be displaced by LSPS[10] which achieved the highest reported ionic conductivity of 25 mS cm⁻¹. However, despite these superior ionic conductivities, the ceramic-sulfide family has been plagued by reports of narrow electrochemical stability windows[11,13,21] and interfacial reactions with common electrode materials.[6,11,22]

Moreover, the reported electrochemical stability windows of ceramic-sulfides suffer from substantial inconsistencies. Several works, both computational and experimental, have shown that the ceramic-sulfides are only stable in the narrow voltage window on the order of 1.7-2.1 V versus lithium,[11–13,21] which is the correct general thermodynamic prediction. Many others, however, have experimentally found that the upper voltage limit can reach in excess of 4.6 V versus lithium.[10,20,23,24] A consolidated understanding of these findings is needed in order to establish design principles for practical ceramic-sulfide batteries.

In this work, we develop a generalized thermodynamic theory that unifies these disparate findings and, hence, provides the unique design principle through mechno-electrochemical effect for ceramic-sulfide-based solid-state batteries. Expanding upon our previous work,[25] in which core–shell morphologies were used to widen the voltage window of LSPS, we derive a generalized strain stabilization model that indicates at which voltages strain-induced stabilization can lead to metastability of the ceramic-sulfide phases. A mean-field solution to our generalized strain model recovers our previous model[25] and is shown to provide a greater capability for stabilization. Note that our current and previous[25] understanding forms a general theoretical framework for the design of ceramic electrolyte with widened voltage stability, which is not limited to any particular design strategy, such as the core–shell morphology of...
LGPS particle demonstrated in experiment in this work. Other design strategies, on material or battery cell level, guided by the mechanano-electrochemical effect induced metastability can also in principle stabilize the solid-state battery system.

Four points of experimental validation of our theoretical framework are provided. First, we use electron microscopy to visualize LGPS after partial decay, confirming that the post-decay morphology is in fact the predicted inclusion morphology. We then show that LGPS can be stabilized by the application of a thin-shell (thickness ≈0.1 times the core radius) as compared to the thick-shell of ref [25] (thickness approximately equal to core radius). The ability of the thin-shell to stabilize at a level comparable to the prior thick-shell, as predicted by the inclusion model, indicates that a thin shell can effectively work for stabilization and, hence, a thick shell is not necessary. Solid-state batteries with both an Li4Ti5O12 (LTO) cathode versus a lithium metal anode and with an LiCoO2 (LCO) cathode versus a LTO anode are demonstrated to have strong cyclability using constrained LGPS. Lastly, we show that our model predicts that upon oxidation, ceramic-sulfides will form lithium metal dendrites locally, rather than deposit lithium ions to the anode, consistent with previous experiments.[26–28]

2. Theory

2.1. The Physical Picture

The mechanism by which strain can expand the LGPS stability window is depicted in Figure 1. Consider the decomposition of LGPS to some arbitrary set of decomposed products, denoted “D” (LGPS → D), at standard temperature and pressure. The Gibbs energy of the system as a function of the fraction of LGPS that has decomposed (xD) is given by the dashed orange line in Figure 1 and analytically in Equation (1)

\[ G(x_D) = (1-x_D)G_{LGPS} + x_DG_D \]  

(1)

The lowest Gibbs energy state is xD = 1 (all decomposed) and the initial state is xD = 0 (pristine LGPS). Accordingly, the reaction energy is ΔG° = G°(1) - G°(0) = G_D - G_{LGPS}. This system is inherently unstable. That is, \( \partial_{x_D}G^0 \) is negative for all values of xD. Hence, for any initial value of xD, the system will move to decrease G° by increasing xD, ultimately ending at the final state xD = 1.

Next, consider the application of a mechanical system that constrains the LGPS particle. Given that LGPS tends to expand during decay, any mechanical constraint will require the decomposition to induce a strain in the surrounding neighborhood. Such a constraining system could be either material-level (i.e., a core–shell microstructure) or systems-level (i.e., a pressurized battery cell) or a combination of the two. Ultimately, this mechanical system can only induce a finite strain before failing. The maximum energy the system can withstand is denoted \( G_{fracture} \).

Prior to the actual failing of the constraining mechanism, any decomposition of the LGPS must lead to an increase in strain energy. The solid line in Figure 1 plots the constrained Gibbs energy (\( G' \)) in terms of the unconstrained Gibbs (\( G^0 \)) and the constraint induced strain term (G\_strain). The gray highlighted curve indicates the decomposition pathway of the LGPS.

1. The particle begins as pristine LGPS (xD = 0) with an unfractured constraint mechanism.
2. As the particle begins to decompose (xD: 0 → δxD), the constraint mechanism requires an increase in G\_strain. The strain term is assumed to be a function of xD that goes to zero as xD goes to zero.
3. Once the Gibbs energy of the constrained system (G'(xD)) exceeds the Gibbs energy of the fractured system (G'(xD) + G\_fracture), the constraining mechanism will fail. This occurs at the fracture point xD = xfracture.
4. Once xD > xfracture, the system will proceed to completely decompose as \( \partial_{x_D}(G' + G_{fracture}) < 0 \).

It is worth emphasizing that if the constraint induced strain term (G\_strain) is sufficiently steep, the slope of the total Gibbs at xD < xfracture will be positive (as depicted in Figure 1). In this case, the LGPS will be metastable about the pristine state (xD = 0). In this work, we focus on the quantification of constraining systems such that \( \partial_{x_D}G' > 0 \) at xD = 0, allowing metastable ceramic sulfide electrolytes to exist in a widened voltage range. Note that this picture is universal, which can be realized by various strategies in applications, as long as such local energy minimum is effectively created.

2.2. The Gibbs Differential

As discussed in our previous work,[25] the presence of G\_strain as a function of xD stems from the nature of LGPS to expand upon...
decomposition. Depending on the set of decomposed products, as determined by the applied voltage, this volume expansion can well exceed 20%. As such, the process of LGPS decomposition is one that can include significant stress-free strain—that is, strain that is the result of decomposition and not an applied stress. Anticipating the consideration of inclusions, we adopt the notation used by Eshelby.\(^{[29]}\)

The stress and strain tensors are separated into the compression and distortion terms via the use of deviatoric tensors as defined in Equation (2). Using Einstein summation notation, the pressure is generalized in terms of the stress matrix \(p = -\frac{1}{2} \text{tr} (\sigma) = -\frac{1}{2} \sigma_{\delta \delta} \) and volume strain is introduced in terms of the reference [undeformed] state \((V_0^d)\ v \equiv (V - V_0^d)/V_0^d:\)

\[
\sigma_{\delta \delta} = \sigma_{\delta \delta} + p \delta_{\delta \delta} \\
\varepsilon_{\delta \delta} = \varepsilon_{\delta \delta} - \frac{1}{3} \delta_{\delta \delta}
\]

Using these definitions, the differential work can be separated into one term that only includes compression and one term that only includes deformation:

\[
\delta W = V^d \sigma_{\delta \delta} \delta \varepsilon_{\delta \delta} = V^d \left( \sigma_{\delta \delta} \delta \varepsilon_{\delta \delta} - p \delta \varepsilon_{\delta \delta} \right)
\]

Thus, for a homogenous volume of the material, the energy can be expressed by Equation (4). For nonhomogeneous materials, Equation (4) is integrated over all homogenous subsystems:

\[
\delta E = T \delta S + \mu_o \delta N_a - p \delta V + V^d \sigma_{\delta \delta} \delta \varepsilon_{\delta \delta}
\]

Transforming to the Gibbs energy (Equation (5)) yields the differential Gibbs form (Equation (6)):

\[
G = E - TS + pV - V^d \sigma_{\delta \delta} \varepsilon_{\delta \delta} = \mu_o N_a
\]

\[
\delta G = -S \delta T + \mu_o \delta N_a + V \delta p - V^d \sigma_{\delta \delta} \delta \varepsilon_{\delta \delta}
\]

At constant temperature, Equation (7) gives the differential form of \(G'(x_0)\) in terms of the chemical terms (\(\delta G^0 = \mu_o \delta N_a\)) and the strain term (\(\delta G_{\text{strain}} = V \delta p - V^d \sigma_{\delta \delta} \delta \varepsilon_{\delta \delta}\)):

\[
\partial_{x_0} G' = \mu_o \partial_{x_0} N_a + V \partial_{x_0} p - V^d \varepsilon_{\delta \delta} \partial_{x_0} \sigma_{\delta \delta} + \partial_{x_0} G^0 + \partial_{x_0} G_{\text{strain}}
\]

\[
\partial_{x_0} G^0 = G_0 - G_{\text{LGPS}} \rightarrow \partial_{x_0} G' = G_0 - G_{\text{LGPS}} + \partial_{x_0} G_{\text{strain}}
\]

Accordingly, the case for metastability about the pristine LGPS case (\(\partial_{x_0} G'(x_0 = 0) = 0\)) is satisfied at any voltage where the strain term is sufficiently steep \(\partial_{x_0} G_{\text{strain}}(x_0 = 0) > G_{\text{LGPS}} - G_0\).

In the following discussion we consider two limiting cases for \(G_{\text{strain}}\) as a function of \(x_0\). The first case is that of an LGPS particle that decomposes homogenously and is a mean field approximation. The fraction of decomposed LGPS is assumed to be uniform throughout the particle \((x_0(\vec{r}) = x_0 \text{ for all } \vec{r})\). The second limiting case is that of spherically symmetric inclusions, where LGPS is completely decomposed within a spherical region of radius \(R_i (x_0(\vec{r}) = 1: r \leq R_i)\) and pristine outside this region \((x_0(\vec{r}) = 0: r > R_i)\). As is shown below, the homogenous case yields a lower value for \(\partial_{x_0} G_{\text{strain}}\), whereas the inclusion model shows how this value could, in practice, be much higher. In both cases, we will use the simplified model that both the LGPS and the decay products are isotropic with moduli values given by the polycrystalline averages.

### 2.3. Hydrostatic Limit/Mean Field Theory

The local stress \(\sigma(\vec{r})\) experienced by a subsection of an LGPS particle is directly a function of the decomposition profile \(x_0(\vec{r})\) as well as the mechanical properties of the particle and, if applied, the mechanically constraining system. In the homogenous approximation, the local stress is taken to be hydrostatic throughout the particle \((\sigma_{\delta \delta}(\vec{r}) = -p \delta_{\delta \delta})\). In the mean field approximation, the same is said for the decomposed fraction \((x_0(\vec{r}) = x_0)\). Given the one-to-one relation between \(\sigma(\vec{r})\) and \(x_0(\vec{r})\), these two approximations are equivalent.

We restrict our focus to the limit as \(x_0 \rightarrow 0\) to evaluate the metastability of LGPS about the pristine state. If \(\partial_{x_0} G'(x_0 = 0) > 0\), then the particle is known to be at least metastable with total stability being determined by the magnitude of \(G_{\text{Fracture}}\). The relationship between the pressure and decomposed fraction was shown in previous work\(^{[25]}\) to be, in the hydrostatic limit, \(p(x_0) = x_0 K_{\text{eff}} \varepsilon_{\text{XXN}}\), where \(K_{\text{eff}}\) is the effective bulk modulus of the system, accounting for both the compressibility of the material and the applied mechanical constraint, and \(\varepsilon_{\text{XXN}}\) is the reaction strain describing the tendency of LGPS to expand upon decomposition. The reaction strain is given by the volumes of the decomposed products \((V_{\text{LGPS}})\) and the pristine LGPS \((V_{\text{LGPS}})\) as \(\varepsilon_{\text{XXN}} = (V_0 - V_{\text{LGPS}})/V_{\text{LGPS}}\).

The differential strain Gibbs is solved assuming a homogenous hydrostatic pressure as shown in Equation (8) and (9):

\[
\partial_{x_0} G_{\text{strain}} = V \partial_{x_0} p
\]

\[
\partial_{x_0} G_{\text{strain}} = V \varepsilon_{\text{XXN}} K_{\text{eff}}
\]

Combining Equation (7) and (9) with the metastability condition \(\partial_{x_0} G'(x_0 = 0) > 0\), it is found that fluid-like LGPS will be stabilized whenever Equation (10) is satisfied:

\[
\varepsilon_{\text{XXN}} K_{\text{eff}} > (G_{\text{LGPS}} - G_0)/V
\]

Equation (10) is solved in Figure 2 for the case of a "core–shell" constriction mechanism with a core comprised of LGPS and a shell of an arbitrary rigid material. In Figure 2a, Equation (10) is evaluated for all of the decomposition reactions that are predicted for LGPS in the unconstrained case. The value of the effective bulk modulus is given by \(K_{\text{eff}} = K_{\text{LGPS}} + K_{\text{sys}}\), where \(K_{\text{LGPS}}\) is the actual bulk modulus of LGPS and \(K_{\text{sys}}\) is the inverse of the constraint's effective compressibility \((K_{\text{sys}} = 1/\beta_{\text{shell}})\).\(^{[25]}\)

When the system is under isovolumetric conditions, \(\beta_{\text{shell}} = 0\) and \(K_{\text{eff}} = K_{\text{LGPS}}\). On the other hand, if the system is isobaric, \(\beta_{\text{shell}} = \infty\) and \(K_{\text{eff}} = 0\). As shown in Figure 2a, the isovolumetric condition leads to significant voltage widening.
Figure 2b expands upon these results, showing the derivative \( \partial G_x \). In contrast with the method depicted in Figure 2a, which focuses on those decomposition reactions known to be problematic in the absence of constraint, Figure 2b finds the set of decomposition products that minimize \( \partial G_x \) (i.e., thermodynamic worst case). The effective bulk modulus is swept from 0 GPa (no constraint) to 20 GPa. When LGPS is metastable, the set of decomposed products that minimize \( \partial G_x \) is that of no decay (i.e., LGPS \( \rightarrow \) LGPS), in which case \( \partial G_x \) is identically 0. Hence, in practice, the computationally determined value for \( \partial G_x \) will never be strictly positive. Instead it will be either negative when the material is unstable or zero when the material is metastable.

2.4. Spherical Inclusion Limit

The maximally localized decomposition mechanism is that of a spherical inclusion as illustrated in Figure 3a. In this model, an LGPS particle of outer radius \( R_o \) undergoes a decomposition at its center. The decomposed region corresponds to the material that was initially within a radius of \( R_i \). The new reference state is of higher volume than the pristine state as the material has decomposed to a larger volume given by \( \frac{4}{3}\pi R_o^3 = \frac{4}{3}\pi R_i^3 (1 + \epsilon_{\text{RXN}}) \). The decomposed fraction is no longer a constant in the particle as it was in the hydrostatic case. Instead, \( x_0 (\hat{r}) = 1 \) for all material that was initially (prior to decomposition) within the region \( r < R_i \) and \( x_0 (\hat{r}) = 0 \) for all material initially outside this region, \( r > R_i \). The total decomposed fraction is denoted \( x_D \) and is given by the average value of \( x_0 (\hat{r}) \) over all \( \hat{r} \).

To fit the decomposed reference state of radius \( R_D \) into the void of radius \( R_i \), both the decomposed sphere and the remaining LGPS must become strained as shown in Figures 3a-iii,iv. Thus, solving for the stress in terms of the decomposed fraction \( x_D \) becomes the problem of a thick-walled spherical pressure vessel compressing a solid sphere. The pressure-vessel has reference states of inner and outer radii given by \( R_i \) and \( R_o \), and the spherical particle has an undeformed radius of \( R_D = (1 + \epsilon_{\text{RXN}})^{1/3} R_i \).

In terms of the displacement vector of the decomposed and pristine materials, \( \mathbf{u}^D (\hat{r}) \) and \( \mathbf{u}^P (\hat{r}) \), and the radial stress components, \( \sigma_{rr}^D (\hat{r}) \) and \( \sigma_{rr}^P (\hat{r}) \), the boundary conditions are:
1. Continuity between the decomposed and pristine products: 
\[ R_o + u^t(R^t) = R_i + u^l(R) \]
Where vector notation has been dropped to reflect the radial symmetry of the system.

2. Continuity between the radial components of stress for those materials at the interface between the decomposed and pristine products, which is defined as the compressive pressure:
\[-p^0 = \sigma_{rr}^p (R_o) = \sigma_{rr}^p (R_i) \]

For a spherically symmetric stress in an isotropic material, the displacement vector is known to be of the form \( u(t) = Ar + Br^2 \) (again, vector notation has been removed to reflect symmetry). The stress induced in an isotropic compressed sphere under condition 2 \((p^0 = -\sigma_{rr}^p (R_o)) \) has an effective pressure \( p = p^0 \) and a zero deviatoric component \( (\sigma^d = 0) \). For a thick-walled spherical pressure vessel of isotropic material under condition 2, and the additional constraint that because \( R_i \ll R_o \) in the \( R_o \to 0 \) limit, the outer surface does not move \( (\mu^p (R_o) = 0) \), the compressive pressure is found to be \( p = \pi_o p^0 (1 + v)/(1 - 2v) \) where \( v \) is the Poisson’s ratio of the material. For a typical value, \( v = 0.2 \), the compressive pressure is \( p = \pi_o p^0 \).

An increase in the amount of the total decomposed fraction \((x_o \to x_o + \delta x_o)\) corresponds to a decomposition of the material initially between \( R_i \) and \( R_i + \delta R_i \). In the nearly pristine limit \((x_o = 0)\), the material at this location experiences a change of pressure from \( \pi_o p^0 (1 + v)/(1 - 2v) \approx 0 \) to \( p^0 \) as \( x_o (R) \) changes from 0 to 1. Thus, the pressure derivative is \( \partial_{x_o} p = p^0 \) and the metastability condition becomes

\[ p^0 > (G_{LGPS} - G_o)/V \]  \hspace{1cm} (11)

Note that the metastability conditions described in Equations (10) and (11) and the condition of \( \partial_{x_o} \sigma' (x_o = 0) > 0 \), used to generate Figure 2, are a general theoretical understanding, which is not limited to any particular realization strategy. However, we will use a core–shell morphology on the electrolyte material’s level to demonstrate this idea in the following discussions.

2.5. Model Comparison

Solving Equation (11) requires an expression for \( p^0 \) as a function of reaction strain \( (\epsilon_{XXX}) \). For the inclusion decay illustrated in Figure 3a, the mechanics leading to \( p^0 \) are equivalent to that of the core–shell structure solved in the hydrostatic case.\(^{[25]}\) That is, the inclusion decay consists of a core of decomposed products embedded in a constricting shell of pristine LGPS. In the limit \( x_o \to 0 \), the nucleated site is much smaller than the embedding LGPS, hence the mechanics is that of a shell thickness that trends toward infinity. Figure 3b plots the pressure resulting from such an inclusion decay as well as two hydrostatic core–shell models. The hydrostatic core–shell models are either thin-shell, where the shell thickness \( (t) \) is \( \approx 10\% \) of the core radius \( (r) \), or thick-shell, where the shell thickness is equal to the core radius. As expected, the inclusion decay, with an approximately infinite shell thickness, is seen to have a higher pressure than either of the hydrostatic alternatives.

In short, inclusion decay is, in the \( R_o \to 0 \) limit, equivalent to the case of a hydrostatic core–shell with a shell thickness \( (t) \) much larger than the core. Since \( R_o = R_i + t \), this is termed the “infinitely thick” shell as \( R_i/R_o \) tends to zero. Thus, the inclusion decay is seen to be most susceptible to mechanically induced stability. As will be discussed in following sections, this allows for the use of a much less intrusive microstructure than would be required if the system were to decay hydrostatically.

2.6. Passivation Layer Theory and Local Lithium Dendrite Formation

Electrolytes, either liquid or solid, are likely to react with electrodes when the electrode potential is outside the electrolyte stability window.\(^{[30]}\) To address this, it is suggested that electrolytes be chosen such that they form a passivating solid-electrolyte interface (SEI) that is at least kinetically stable at the electrode potential. Previous works have suggested that such stabilizing passivation layers can be formed for sulfide solid electrolytes by using an electronically insulating coating layer. In this section, we show that an electronically insulating layer does in fact improve the stability of ceramic-sulfide, conditional that the LGPS already be mechanically constrained. This is due to the electronically insulating layer maximizing the number of retained lithium ions and, hence, maximizing the reaction strain. This retention of lithium ions predicts that upon oxidation, ceramic-sulfides will form lithium metal dendrites locally, rather than deposit lithium ions to the anode. Such understanding can explain why dendrites form even more readily in solid-state batteries than in conventional liquid-electrolyte cells,\(^{[26,28,31]}\) suggesting the importance of the design taking into account the mechnano-electrochemical interactions.

As a reference, Figure 4a gives the thermodynamic equilibrium state for the most basic battery half-cell model. A cathode is separated from lithium metal by an electrically insulating and ionically conducting material \((\sigma = 0, \kappa \neq 0)\), where \( \sigma, \kappa \) are the electronic and ionic conductivities, respectively and a voltage \( \phi \) is applied to the cathode relative to the lithium metal. The voltage of the lithium metal is defined to be the zero point. In terms of the number of electrons \( (n) \), the number of lithium ions \( (N) \), the Fermi level \( (\phi) \) and the lithium ion chemical potential \( (\mu_{Li}) \), the differential Gibbs energy can be written as Equation (12) (superscripts \( a, c \) differentiate the anode from the cathode)

\[ \delta G = \mu_{Li}^c + \delta N^c \sigma_{Li}^c + (\mu_{Li}^a + \phi) e \delta N^a + e \delta n^a + (\mu_{Li}^c - e \phi) \delta n^c \]  \hspace{1cm} (12)

Applying conservation \( \delta N^c = -\delta N^a, \delta n^a = -\delta n^c \) gives the well-known equilibrium conditions

\[ \delta G = (\mu_{Li}^c + e \phi - \mu_{Li}^a) \delta N^a + (e \phi) \delta n^a \]

\[ \rightarrow \mu_{Li}^c + e \phi = \mu_{Li}^a \]

\[ e \phi = E_\phi \]  \hspace{1cm} (13)
Or, in other words, the electrochemical potential \( \eta = \mu + z e \phi \) of both the electrons and the lithium ions must be constant everywhere within the cell. As a result, the lithium metal potential \( \eta_{Li^+} = \eta_{Li} + z e \phi \) also remains constant throughout the cell. The band diagrams found in Figure 4a illustrate how the chemical potential of each species, as well as the voltage, varies throughout the cell while the electrochemical potential remains constant.

Figure 4b depicts the expected equilibrium state in the case of a solid-electrolyte cathode, where the cathode material is imbedded in a matrix of solid electrolyte. For cathode materials that typically delithiate at voltages of \( \approx 4 \) V, compared to LGPS at 2.1 V, the lower (i.e., more-negative) Li ion chemical potential of the cathode material relative to the electrolyte causes charge separation that results in an interface voltage drop \( \chi_i \). Analogous to the procedure following Equation (12), it can be shown that the...
equilibrium points now include the anode (a), cathode (c) and the solid electrolyte (SE)

\[
\begin{align*}
\mu_{i_a}^{SE} + e\phi &= \mu_{i_a}^\ast + \mu_{i_a}^{SE} + e\phi, \\
\epsilon_i^{SE} - e\phi &= \epsilon_i^\ast, \\
\epsilon_i - e\phi &= \epsilon_i^\ast.
\end{align*}
\] (14)

Like Equation (13), Equation (14) leads to the condition that the lithium metal potential remains constant throughout the cell.

When a solid-electrolyte particle is coated by an electronically insulating passivation layer, Figure 4c depicts the electrochemical state prior to any lithium ion migration out of the insulated electrolyte particle. Since the external circuitry does not directly contact the solid electrolyte and there is no electron conducting pathway, the number of electrons within the solid electrolyte is fixed. Hence the Fermi energy cannot equilibrate via electron flow. This effect in principle could be utilized to allow a deviation of the lithium metal potential within the solid electrolyte relative to the electrodes, leading to a wider operational voltage window. The band diagrams of Figure 4c illustrate how the electron electrochemical potential can experience a local maximum (or minimum) in the solid electrolyte due to a lack of electron conduction. This local maximum (or minimum) is carried over to the lithium metal potential.

However, small amounts of lithium ion capacity always exist in the sulfide solid electrolyte even with a passivated coating layer. Therefore, effective electron conduction can occur due to the lithium holes that are created when a lithium ion migrates out of the insulated region, leaving behind the corresponding electrons. The term “lithium holes” is used here to refer to the lithium vacancies that migrate as the lithium ions conduct—in effect creating a negative charge carrier for conduction. The differental Gibbs energy of this system is represented by adding a solid-electrolyte term to Equation (12) (denoted by superscript SE)

\[
\delta G = \mu_{i_a} - \mu_{i_a}^{SE} + \mu_{i_a}^{SE} + e\phi \delta N_i^+ + (\mu_{i_a}^{SE} + e\phi)^{SE} \delta N_i^{SE} \\
+ \epsilon_i^{SE} - e\phi \delta n_i^- + (\epsilon_i^{SE} - e\phi)^{SE} \delta n_i^{SE}.
\] (15)

The excess electron and lithium constraints are now:

1. \( \delta n_i^{SE} = -\delta N_i^+ \): For each lithium ion removed from the SE, the SE gains one excess electron in the form of a lithium hole.
2. \( \delta n_i = \delta n_i^+ + \delta N_i^{SE} \): Gaining a lithium ion, but not the corresponding electron, at the anode reduces the number of excess electrons at the anode.
3. \( \delta N_i^+ = -\delta N_i^- - \delta N_i^{SE} \): Conservation of total lithium.

Constraints 1 and 2 represent the tethering of the electron and lithium density in the case of an insulated particle. Unlike the system governed by Equation (12), the Fermi level of the solid electrolyte is not fixed by an external voltage. The result is that by lowering the number of atoms within the solid electrolyte from extracting lithium ions, and hence increasing the number of electrons per atom within the insulated region, the number of excess electrons increases. In effect, this is equivalent to the conduction of electrons by way of lithium holes. Solving Equation (15) for the equilibrium points given the above constraints lead to those of Equation (14) between the anode/cathode as well as the following relation between the anode and solid electrolyte

\[
\rightarrow \mu_{i_a}^{SE} + e\phi^{SE} = \mu_{i_a}^\ast, \\
\epsilon_i^{SE} - e\phi^{SE} = \epsilon_i^\ast.
\] (16)

Equation (16) implies that lithium ion/hole migration is sufficient to equilibize the electron electrochemical potential between the solid electrolyte and the anode. The system illustrated in Figure 4c thus does not satisfy these equilibrium conditions and will hence relax to an equilibrium state. Such an equilibrium state is depicted in Figure 4d, where lithium ions have migrated from the solid electrolyte to the anode. The charge separation of the migrated lithium ions from the corresponding electrons causes a charge separation voltage. In other words, if prior to lithium migration the voltage in the solid electrolyte was \( \phi^{SE} = \phi^\ast \), then after the migration the voltage within the solid electrolyte is \( \phi^{SE} = \phi^\ast - V_S \) where \( V_S \) is the voltage due to the charge separation. This charge separation voltage acts as a degree of freedom and will vary until Equation (16) is satisfied. In this case, because the charge separation has made the electron electrochemical potential constant throughout the cell, so too is the lithium metal potential. The ultimate result of this voltage relaxation within the electronically insulated region is depicted in Figure 4e. Given the effective electron transport via lithium hole conduction, negatively charged lithium metal can form locally within the electrolyte particle once the applied voltage exceeds the intrinsic stability of the solid electrolyte. The negative charge is due to the lithium ions that have left the insulated region to equilibize the lithium metal potential. As such, the local (i.e., within the insulated region) lithium metal is expected to have an interface voltage \( \chi_I \) with the remaining solid electrolyte. The voltage must be equal to the voltage between the anode lithium and the solid electrolyte \( \chi_I = \phi^{SE} \). In short, from a thermodynamic perspective, applying a voltage \( \phi^{SE} \) to an electronically insulated solid-electrolyte particle relative to a lithium metal anode is equivalent to applying a charged lithium metal directly in contact with the solid electrolyte.

However, the electronically insulating coating can still improve stability by coexisting with a mechanical constraint. By allowing lithium metal to form locally within the particle, rather than in the anode, the reaction strain is maximized. That is, if the lithium ions go to the anode, they do not act to swell the particle from within. Hence it is important to note the function of the electronically insulating shell under our new picture:

1) Such an insulator itself cannot create a deviation of the lithium metal potential within the solid electrolyte relative to the electrodes, nor lead directly to a wider operational voltage window. This is because lithium ions still relax until the lithium metal chemical potential is equal everywhere (Figure 4e).
2) Unlike conventional battery models, this picture recognizes that in battery systems the components are not necessarily charge neutral. In this case, the separation of lithium ions from the corresponding electrons leads to the thermodynamic possibility of forming charged lithium metal locally.
3) The reaction strain is maximized by the formation of local lithium metal and ergo the insulating shell improves the ability of an arbitrary mechanical constraint to stabilize the system.
3. Experiment and Discussion

3.1. Structure and Composition

The impact of mechanical constriction on the stability of LGPS was studied by comparing decay metrics between LGPS and the same LGPS with an added core–shell morphology that provides a constriction mechanism. To minimize chemical changes, the constricting core–shell morphology was created using the postsynthesis ultrasonication. This core–shell LGPS (“ultra-LGPS” hereafter) was achieved by high-frequency ultrasonication that results in the conversion of the outer layer of LGPS to an amorphous material. Bright-field (BF) transmission electron microscopy (TEM) images of the LGPS particles before (Figure 5a) and after (Figure 5b) sonication show the distinct layer of an amorphous shell. Statistically analyzed energy dispersive X-ray spectroscopy (EDS) (Figure 5c,d) shows that this amorphous shell is sulfur deficient whereas the bulk regions of LGPS and ultra-LGPS maintain similar elemental distributions. EDS line-scans on significant number of different (ultra-) LGPS particles (Figures S1–S3, Supporting Information) confirm that surface layers with, on average, sulfur-deficient composition exist for ultra-LGPS particles within a wide size range, whereas no such phenomenon is observed for LGPS particles. Note that this is true for LGPS sonication in both solvents tested, dimethyl carbonate (DMC) and diethyl carbonate (DEC) (Figures S2–S4, Supporting Information). Simply soaking LGPS in DMC without sonication had no obvious effect (Figure S5, Supporting Information). This method of postsynthesis core–shell formation minimizes structural changes to the bulk of the LGPS, allowing us to evaluate the effects of the volume constriction on stability without compositional changes in the bulk. The amorphous nature of the shell, combined with the high conductivity of the total material, suggests that the shell is a glassy sulfide.\(^{[15,12–34]}\) For intrinsic LGPS, the stoichiometrically expected glassy system would be \(5 \text{LiS}_2 + \text{GeS}_2 + \text{P}_2\text{S}_5\). Based on the EDS, the shell composition should be of the form \((5 - \delta) \text{LiS}_2 + \text{GeS}_2 + \text{P}_2\text{S}_5\), with a shell modulus equal to or larger than the one without.

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Figure 5. Comparison between microstructures and chemical composition of LGPS and ultra-LGPS particles. a,b) Typical TEM bright-field images of LGPS and ultra-LGPS particles respectively, showing a distinct surface layer for ultra-LGPS particle. c,d) Statistically analyzed STEM EDS line scans performed on various LGPS and ultra-LGPS particles with different sizes, showing a uniform distribution of sulfur concentration from the surface to the bulk for LGPS particles, but a decreased sulfur concentration in the surface layer for ultra-LGPS.
sulfur deficiency, since Ge amorphous phase, just like Si,\textsuperscript{[25]} exhibits large modulus. Considering the bulk modulus of crystalline LGPS is on the order of 20–30 GPa,\textsuperscript{[25]} the amorphous shell serves as an effective mechanical constriction for the ultra-LGPS running beyond 4 V based on our prediction in Figure 2.

Figure 6. a,b) First to seventh charge–discharge profiles of LGPS-Li ion battery (LTO+LGPS+C/Glass fiber separator/Li) and ultra-LGPS-Li ion battery (LTO+ultra-LGPS+C/Glass fiber separator/Li) cycled at 0.5 C current rate in the voltage range of 1.0–2.2 V. c,d) Cyclic capacity curves and Coulombic efficiency of LGPS-Li ion battery and ultra-LGPS-Li ion battery. e) First charge and discharge performance of all-solid-state battery: LTO+LGPS+C/LGPS/LiH\textsubscript{2}PO\textsubscript{4}-coated lithium foil. The battery failed at first charge and cannot be charged above 3.6V. f) First, second, and fifth charge and discharge curves of all-solid-state battery: LTO+ultra-LGPS+C/ultra-LGPS/LiH\textsubscript{2}PO\textsubscript{4}-coated lithium foil. The battery can be charged to 4 V and cycle smoothly.
3.2. Electrochemical Stability

The electrochemical stabilities of nonstricted LGPS and constricted ultra-LGPS were demonstrated by charge–discharge curves and cycling performance of batteries cycled at 0.5 C in the voltage range of 1.0–2.2 V. For LGPS battery (LTO+LGPS+carbon black (C)/Glass fiber separator/Li) (Figure 6a), a flat voltage plateau at 1.55 V appeared for 70 cycles, which can be ascribable to the redox of titanium. However, the plateau length decreases from cycle 1 to cycle 70 by almost 85.7%, indicating a large decay of the cathode. On the other hand, ultra-LGPS (LTO+ultra-LGPS+C/Glass fiber separator/Li) battery (Figure 6b) shows the same flat voltage plateau remaining almost unchanged after 70 cycles. This increase in the cathode stability is further confirmed by the cyclic capacity curves (Figures 6c,d). For LGPS, the specific charge and discharge capacities decrease from ≈159 to ≈27 mAh g⁻¹, and ≈170 to ≈28 mAh g⁻¹, respectively, after 70 cycle. However, ultra-LGPS demonstrates a much better cyclic stability than its LGPS counterpart. After 70 cycles the discharge capacity is still as high as 160 mAh g⁻¹, with only roughly 5% of capacity loss. It is worth mentioning that the stability advantages of ultra-LGPS over LGPS can be supported by cycling performance of various battery configurations. For example, if another (ultra-)LGPS solid-electrolyte layer is inserted between cathode and glass fiber separator, the cycling performance of ultra-LGPS batteries are still obviously better than that of LGPS batteries (Figures S6 and S7, Supporting Information).

To rule out the potential influence of liquid electrolyte, all-solid-state batteries in the configuration of LTO+(ultra-)LGPS+C+PTFE/(ultra-)LGPS/Li were constructed to further prove the stability difference between LGPS and ultra-LGPS. Special treatment was performed on Li foil to form a protective layer (see Methods) so that the interfacial reaction between (ultra-)LGPS solid electrolyte and Li can be avoided. Results show that all-solid-state battery using a mixture of LTO+LGPS+C+PTFE as cathode (Figure 6e) failed at ≈3.5 V and cannot be charged above it, due to severe decomposition of LGPS at high voltage. In contrast, the ultra-LGPS counterpart can be charged to 4 V smoothly (Figure 6f), indicating the largely improved stability of constricted ultra-LGPS up to at least 4 V. In addition, the ultra-LGPS solid-state battery can be cycled well between 1 and 4 V (Figure 6f), proving again its better stability than nonstricted LGPS.

In each of these results, ultra-LGPS particles with core–shell morphologies have outperformed the stability of LGPS counterparts, consistent with our above theoretical analysis. The experimental electrochemical stability data herein agrees well with this theory. Sulfur deficient amorphous shells, as seen in the case of ultra-LGPS, are expected to lower the effective compressibility of the system and hence increase the volume constraint.²⁵ Solid-state battery cycling performance demonstrates that ultra-LGPS has, in practice, improved stability over LGPS in the cases of both LGPS oxidation and reduction. A solid state full-cell battery (Figure 7) using LTO+ultra-LGPS+C+PTFE as anode and LiCoO₂+ultra-LGPS+C+PTFE as cathode shows strong cyclability after 140 cycles. The full-cell was cycled at charge–discharge rate of 0.3 C. The ultra-LGPS was found to have a bulk conductivity of 4 mS cm⁻¹ by the impedance measurement.

3.3. Decomposition Mechanism

To better understand the mechanism by which LGPS decomposes, TEM analyses were performed to study the microstructure of LTO/[ultra-LGPS interfaces after cycling of an all-solid-state battery. A focused ion beam (FIB) sample (Figure 8a), in which the composite cathode (LTO+LGPS+C) and solid-electrolyte layer (LGPS) are included, was prepared after 1 charge–discharge cycle versus a lithium metal anode. A platinum layer was deposited onto the cathode layer during FIB sample preparation for protection from ion beam milling. A transit layer exists at the cathode/solid-electrolyte interface (hereafter “LTO/LGPS primary interface), as manifested in the TEM BF images (Figure 8b, Figure S8, Supporting Information) and scanning transmission electron microscopy dark-field (STEM DF) images (Figure 8d, Figure S8, Supporting Information). The particles within the transit layer of STEM DF images show bright contrast, indicating the accumulation of heavy elements. To understand the chemical composition of this transit layer, STEM EELS (electron energy loss spectroscopy) line-scans were performed. The EELS spectra show that Li K, Ge M₄,₅ (Figure S9, Supporting Information), Ge M₃,₄ and P L₂,₃ (Figure 8e) peaks exist throughout the transit layer, but sulfur peaks (S L₂,₃, S L₁) only show up inside the brighter regions, and are absent in the darker regions (EELS spectra 12–14 in Figure 8e). This result indicates that the decomposition results in multiple phases of products. Those phases which constitute the bright regions within the transit layer are sulfur-rich, which is not only supported by the Z-contrast and EELS line-scan (Figure 8e, Figures S9 and S10, Supporting Information), but also corroborated by previous studies¹⁹ reporting that the decomposition products of LGPS include sulfur-rich phases such as S, Li₂S, P₂S₅, and GeS₂. These results also set the length scale for decomposed phases in LGPS at the order of 20 nm.

Since the composite cathode layer is composed of LTO, LGPS, and C, there will be minor LTO/LGPS interfaces (hereafter “LTO/LGPS secondary interface”) that are ubiquitous within the cathode layer. Figure 8f demonstrates the typical
STEM DF image of LTO/LGPS secondary interfaces, in which bright regions show up again. The density of such bright particles with smaller sizes is much higher, possibly due to higher carbon concentration within cathode layer and the consequently facilitated LGPS decomposition. The corresponding STEM EELS line-scan spectra (Figure 8g) show that strong $S_{L_{2,3}}$ peaks exist at the interface region, indicating that the region is sulfur-rich.

As comparison, Figure 9 shows the microstructural and compositional (S)TEM studies for ultra-LGPS half-cells. The primary LTO ula-LGPS interface after 1 charge–discharge cycle was characterized by TEM BF image (Figure 9a). A smooth
Figure 9. Microstructural and compositional (S)TEM studies of LTO/ultra-LGPS interfaces after cycling in ultra-LGPS all-solid-state Li ion battery. 
a) TEM BF image of LTO/ultra-LGPS primary interface, showing a smooth and clean interface. b) STEM EELS line-scan spectra corresponding to the red line in panel (a). c) STEM DF image of LTO/ultra-LGPS secondary interface. d) STEM EDS line scans show a continuously decreasing atomic percentage of sulfur from inner ultra-LGPS particle to secondary LTO/ultra-LGPS interface, and finally into LTO+C composite region. e) STEM EDS mapping shows that the large particle in panel (c) is LGPS particle. f) STEM EDS quantitative analyses show that the atomic percentage of sulfur inside ultra-LGPS particle is as high as ≈38%, while that of secondary LTO/ultra-LGPS interface is as low as 8%.
interface was observed between the ultra-LGPS solid-electrolyte layer and the composite cathode layer. The primary LTO/ultra-LGPS interface is clean and uniform, showing no transit layer (Figure 9b). The secondary LTO/ultra-LGPS interfaces were also investigated for comparison by STEM DF image, EDS line-scan and EDS mapping (Figures 9c,e). Results show that the atomic percentage of sulfur decreases, as the STEM EDS line-scan goes from inner ultra-LGPS particle across the secondary LTO/ultra-LGPS interface, and finally into LTO+C composite region (Figure 9d, Figure S11, Supporting Information). In other words, the sulfur-deficient-shell feature of ultra-LGPS particles is maintained after cycling, and no sulfur-rich transit layer is formed at the LTO/ultra-LGPS secondary interface. STEM EDS quantitative analyses (Figure 9f) show that the atomic percentage of sulfur inside ultra-LGPS particle is as high as ≈38%, while that of secondary LTO/ultra-LGPS interface is as low as 8%.

These results suggest that the inclusion limit discussed in the theory section is a more faithful representation of the true decay process than the hydrostatic limit. The sulfur rich particles formed in LGPS have a length scale on the order of $R_i \approx 20$ nm. In ultra-LGPS, the shell thickness is also roughly $l \approx 20$ nm. Hence if we consider the formation of such a sulfur rich particle near the core–shell boundary in ultra-LGPS, the minimum distance from the center of the sulfur rich particle to the exterior of the shell is $R_o = R_i + l \approx 40$ nm. In this case $R_i^3 = 8R_o^3$, which satisfies the condition $R_i^3 < R_o^3$ needed to apply the inclusion model. In summary, experimental results show that LGPS decays via a mechanism with inclusion of sulfur rich particles on the surface. A shell layer with a thickness close to nuclei size inhibits such decay in ultra-LGPS. These results suggest that the pristine core–shell state is at least metastable with respect to the decay toward the state with inclusion decay just below the core–shell interface.

4. Conclusion

We have developed a generalized strain model to show how mechanical constriction, given the nature of LGPS to expand upon decay, can lead to metastability in a significantly expanded voltage range. The precise level to which constriction expands the voltage window depends on the morphology of the decay. We performed a theoretical analysis of two limits of the decay morphology, i.e., the minimally and maximally localized cases. The minimally localized case consisted of a mean field theory where every part of the particle decays simultaneously, whereas the maximally localized case consisted of an inclusion decay. It was demonstrated that, while the maximally localized case was best, both cases had the potential for greatly expanding the stability window. We also developed a theory for the role of an electrically insulating passivation layer in such a strain-stabilized system. This model suggests that such passivation layers improve the voltage stability by keeping lithium ions localized within the mechanically constrained particle, maximizing the reaction strain.

Experimental evidence for the stability of LGPS before and after the formation of a constricting shell supports this theory. After the formation of shell via ultrasonication, core–shell structured LGPS demonstrated remarkably improved performance in solid-state battery performance. The post-synthesis approach of shell formation prevents the LGPS core composition from deviation, which might otherwise affect stability. The core–shell is believed to be an instance of mechanically constrained LGPS, as during any decomposition, the LGPS core will seek to expand whereas the shell will largely remain fixed. In other words, the shell provides a quasi-isovolumetric constraint on the core dependent on the biaxial modulus of the shell and the particle geometry.

Analysis of the decay morphology found in LGPS particles but not in ultra-LGPS particle suggests that the inclusion decay limit more accurately reflects the true thermodynamics. It was found that, in LGPS, inclusion sulfur-rich decay centers were embedded in the surface of the LGPS particles after cycling. In contrast, these inclusion decay centers were not found in the cycled ultra-LGPS. The ultra-LGPS maintained a shell thickness comparable to the decay sites in LGPS ($\approx 20$ nm), which was predicted to be sufficient for the high level of stabilization afforded by the inclusion decay model. These results, combined with the improved stability of ultra-LGPS, indicate that not only is strain-stabilization occurring, but that the magnitude at which it is occurring is dominated by maximally localized decay mechanism. This is a promising result as such inclusion decay has been shown to provide a larger value of $\Delta G_{\text{min}}$, opening up the door to solid-state batteries that operate at much higher voltages and thus with higher energy densities.

5. Experimental Section

Sample Preparation: LGPS powder was purchased from MSE Supplies company. Ultra-LGPS was synthesized by soaking LGPS powder into organic electrolytes, such as dimethyl carbonate (DMC) and diethyl carbonate (DEC), and then sonicated for 70 h.

Electrochemistry: For all-solid-state batteries, lithium anode was coated with a protection layer in the steps described in the previous work.[22] The cathode of the all-solid-state cell was a mixture of LTO+(ultra-) LGPS+carbon black+PTFE (68:19:10:3), and solid electrolyte was pure (ultra-)LGPS powder. The cathode thin film and solid-electrolyte powder were pressed together to form a disc-shaped pellet, which was pressed onto a freshly prepared Li-P-S amorphous layer coated Li in a Swagelok Cell to form an all-solid-state battery. Swagelok-type cells were assembled inside an argon-filled glove box. The charge-discharge behavior was tested using an ArbinBT2000 workstation (Arbin Instruments, TX, USA) at room temperature. For the semisolid batteries, a piece of glass fiber is used as separator to prevent the interfacial reaction between Li metal and LGPS solid electrolyte. For LCO-LTO full all-solid-state battery, LCO+ultra-LGPS+carbon black (70:25:5) + PTFE (extra 3%) were mixed and rolled into a thin film as the cathode. LTO+ultra-LGPS+carbon black (30:60:10) + PTFE (extra 3%) were made as the anode using the same method. Three films of LCO cathode, LTO separator, and LTO anode were pressed together and tested under 78 MPa in a homemade pressurized cell. Here, LCO was coated with 5 wt% LiNbO3 using a sol-gel method.[23] The capacity was calculated based on the mass of LTO.

Characterization: For FIB sample preparation, the cold-pressed thin film of composite cathode and (ultra-)LGPS after 1 charge–discharge cycle in (ultra-)LGPS all-solid-state battery was taken out inside an argon-filled glove box. It was then mounted onto an scanning electron microscope (SEM) stub and sealed into a plastic bag inside the same glove box. FIB sample preparation was conducted on an FEI
Helios 660 dual-beam system. The prepared FIB sample was then immediately transferred into JOEL 2010F for TEM and STEM EDS/EELS characterization.

Density Functional Theory (DFT) Calculations: All calculations were performed using the Vienna Ab initio simulation package (VASP) using the recommended Projector Augmented Wave (PAW) pseudopotentials. An energy cutoff of 520 eV with a k-point mesh of 1000 k-points per atom (kppa) was used. Compressibility values were found by discretely evaluating the average compressibility of the material between 0 and 1 GPa. Enthalpies were calculated at various pressures by applying external stresses to the stress tensor during relaxation and self-consistent field calculations. Crystal structures spanning Li-Ge-P-S phase space were obtained from the Materials Project. [36]

Thermodynamic Calculations: Unconstrained ($K_{\text{eff}} = 0$) decomposition reactions were calculated using DFT energies following previous methods. [33] Figure 2a was calculated by comparing the reaction strains and hull energies of the unconstrained decomposition reactions at $K_{\text{eff}} > 0$. Figure 2b was calculated by minimizing $\partial_{\sigma_k} G$ with respect to all possible decomposition products.

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.

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