Next-generation all-solid-state battery (#ASSB)

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Mathematical modelling for the next-generation All-solid-state batteries: Nucleation (SE|SSE)$^{(*)}$-interface

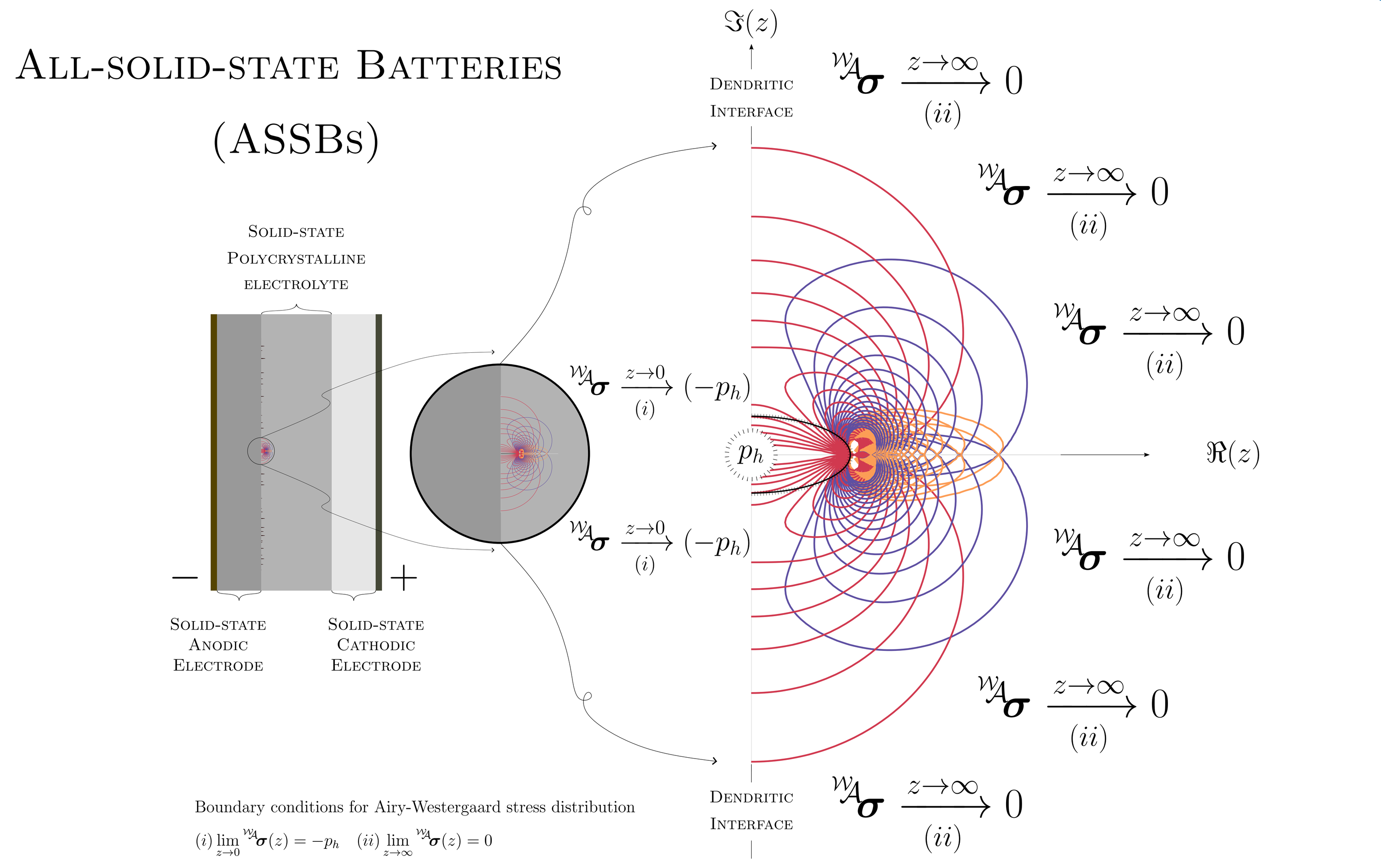
Rechargeable Lithium-ion battery (LIB) is at the heart of every electric vehicle (EV), portable electronic device, and energy storage system [1]. Nowadays, LIBs enable human life more efficient and help to solve global environment issues thanks to EVs' zero emission. However, conventional LIB (c-LIB) is sensible to temperature and pressure, hence, flammable and explosive, which is undesirable. This bottleneck is mainly due to liquid-based electrolyte found in c-LIBs.

All-solid-state battery (ASSB) is one of promising candidates to overcome bottlenecks of c-LIBs. Thanks to solid-state electrolyte (SSE), ASSB is highly stable towards temperature and pressure. Nevertheless, Li-metal dendrite triggered at (SE|SSE)-interface [5] is the main drawback of ASSB since these dendritic threads extrapolate into SSE grain boundary network, causing crevice, degradation of ionic conductivity, and the probability of short-circuit, which is unfavorable.

Next-generation All-solid-state battery (ng-ASSB) with a consideration of nucleation criterion defined by

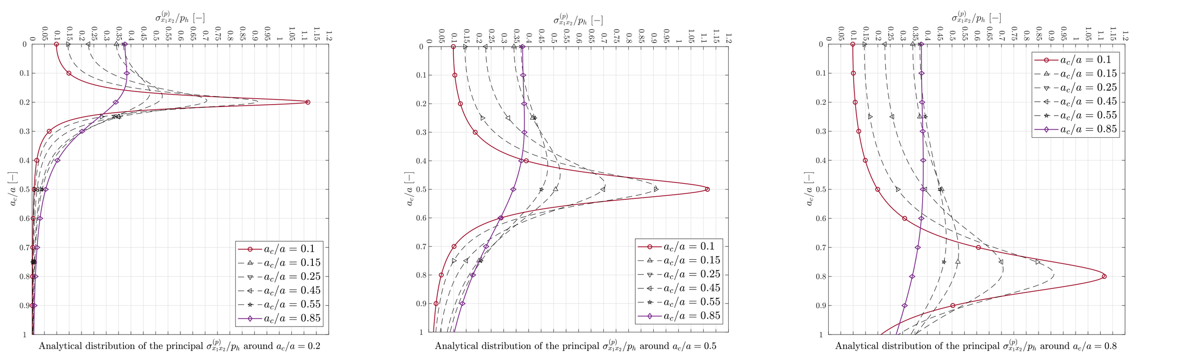
$$a_{\text{Griffith}} := a^* = \arg\min_{a\in\mathbb{R}} \iiint_\Omega f(a, \boldsymbol{u}, \theta; \lambda, \mu, \boldsymbol{d}^R \otimes \boldsymbol{d}^R)\, d\Omega - \iint_\Gamma f(a;\gamma)\, d\Gamma \Big|_{\boldsymbol{u}^{(s)}}$$

where $\boldsymbol{u}$ displacement field, θ temperature field, a crevice length, λ, μ Lamé constants, $\boldsymbol{d}^R \otimes \boldsymbol{d}^R$ embedded misorientation structural tensor, and γ cracking-surface energy density, can help to improve ASSB performance.



Interface Analysis

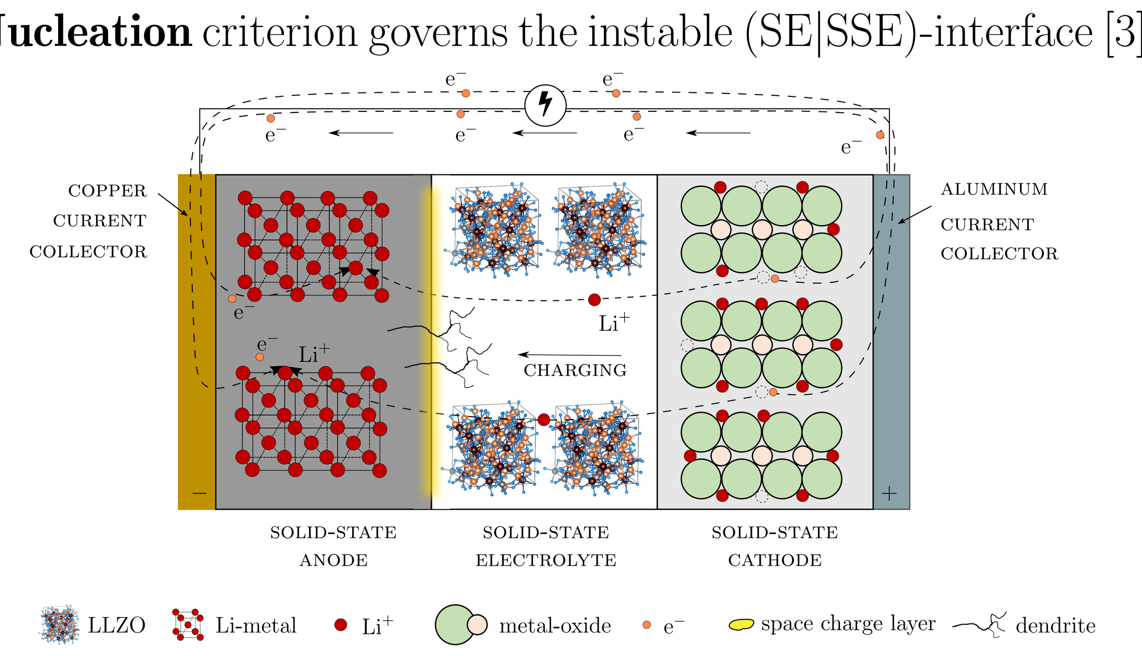
Interface between solid electrode and solid-state electrolyte (SE|SSE) taking place at space charge layer (SCL) [2] found in ASSBs critically exhibits mechanical and electrochemical instability [3]. This evidence points directly to the fact that the soft metallic li anode is erroneously prone to triggering dendrites, under cycles of electric charge & discharge [5].



Distribution: ana. max. shear stress ${}^{\mathcal{W}}\!\sigma^{\Pi}_{x_1x_2}$ around crack tip a_c.

Next-generation All-solid-state battery

Nucleation criterion governs the instable (SE|SSE)-interface [3]

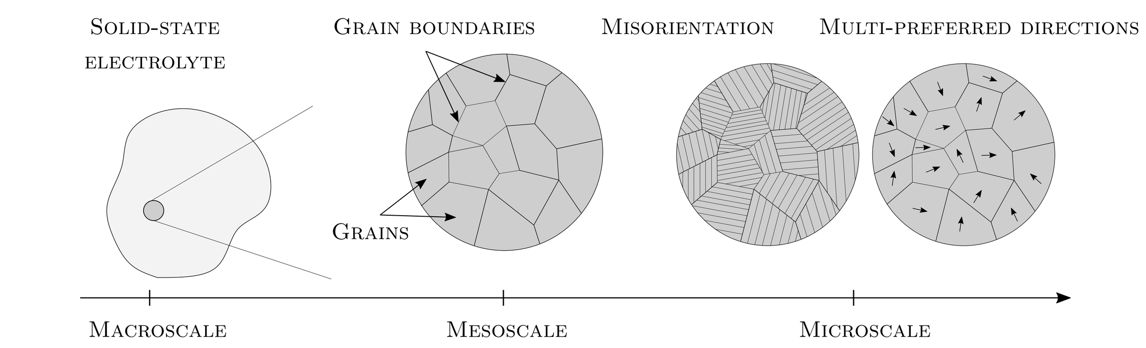


✓ **Thermodynamic consistency** is satisfied, followed by [2].
✓ **Closure** $\bar{\Omega}$ is fulfilled by 15 moments, followed by [4].

Embedded structural-tensor in SSE

Polycrystalline garnet-type SSE [5] such as LLZO exhibit grain boundary network, and grains with variation of {size, shape} under microscopic observation. Hence, this microstructure is potentially prone to nuances of destruction.

$$\boldsymbol{M} = \boldsymbol{d}^R_{G_1} \otimes \boldsymbol{d}^R_{G_2} \quad \text{given by} \quad \mathbb{G} := \left\{\boldsymbol{Q}_{||_d}, \boldsymbol{Q}_{\perp_d}\right\} \subset \mathcal{O}(3).$$



Consequentially, dendrites contribute to degradation of ionic conductivity and tiny-cracks tracing along grain boundaries.

Nucleation interface: Taking place at the critical dendritic interface

Coupled fields: Displacement field and temperature field; structural tensor

$$\boldsymbol{u}: \begin{cases} \Omega\times\mathbb{R}_+ \to \mathbb{R}^3, \\ (\boldsymbol{x},t)\mapsto \boldsymbol{u}(\boldsymbol{x},t), \end{cases} \quad \theta: \begin{cases} \Omega\times\mathbb{R}_+ \to \mathbb{R}, \\ (\boldsymbol{x},t)\mapsto \theta(\boldsymbol{x},t), \end{cases} \quad \boldsymbol{M}: \begin{cases} \Omega\times\mathbb{R}_+ \to \mathbb{R}, \\ (\boldsymbol{x},t)\mapsto \theta(\boldsymbol{x},t), \end{cases}$$

Governing conservation equations

$$\frac{d}{dt}\int_\Omega (\cdot)\, d\Omega = \int_\Omega (\cdot)^{\text{action}}\, d\Omega + \int_{\partial\Omega} (\cdot)^{\text{action}}\, d\partial\Omega + \int_\Omega (\cdot)^{\text{production/source/sink}}\, d\Omega$$

$\rho(\boldsymbol{x},t)$ is mass density per unit volume (puv); $\boldsymbol{b}(\boldsymbol{x},t)$ body force puv; $\boldsymbol{v}(\boldsymbol{x},t)$ velocity; $e(\boldsymbol{x},t)$ internal energy puv; $\boldsymbol{q}(\boldsymbol{x},t)$ heat flux; $r(\boldsymbol{x},t)$ heat source puv; $\boldsymbol{\sigma}$ Cauchy stress and $\boldsymbol{\varepsilon}$ infinitesimal strain. Helmholtz energy functional

$$a_{\text{Griffith}} := a^* = \arg\min_{a\in\mathbb{R}} \iiint_\Omega f(a, \boldsymbol{u}; \lambda, \mu, \boldsymbol{d}\otimes\boldsymbol{d})\, d\Omega - \iint_\Gamma f(a;\gamma)\, d\Gamma \Big|_{\boldsymbol{u}^{(s)}}$$

Governing PDE

$$a_{\text{Griffith}} := a^* = \arg\min_{a\in\mathbb{R}} \iiint_\Omega f(a, \boldsymbol{u}; \lambda, \mu, \boldsymbol{d}\otimes\boldsymbol{d})\, d\Omega - \iint_\Gamma f(a;\gamma)\, d\Gamma \Big|_{\boldsymbol{u}^{(s)}}$$

abc

Strain energy: Interface between solid electrode and solid-state electrolyte (SE|SSE) taking place at space charge

$$\iiint_\Omega f(a, \boldsymbol{u}; \lambda, \mu, \boldsymbol{d}\otimes\boldsymbol{d})\, d\Omega$$

Surface energy: Interface between solid electrode and solid-state electrolyte (SE|SSE) taking place

$$\iint_\Gamma f(a;\gamma)\, d\Gamma$$

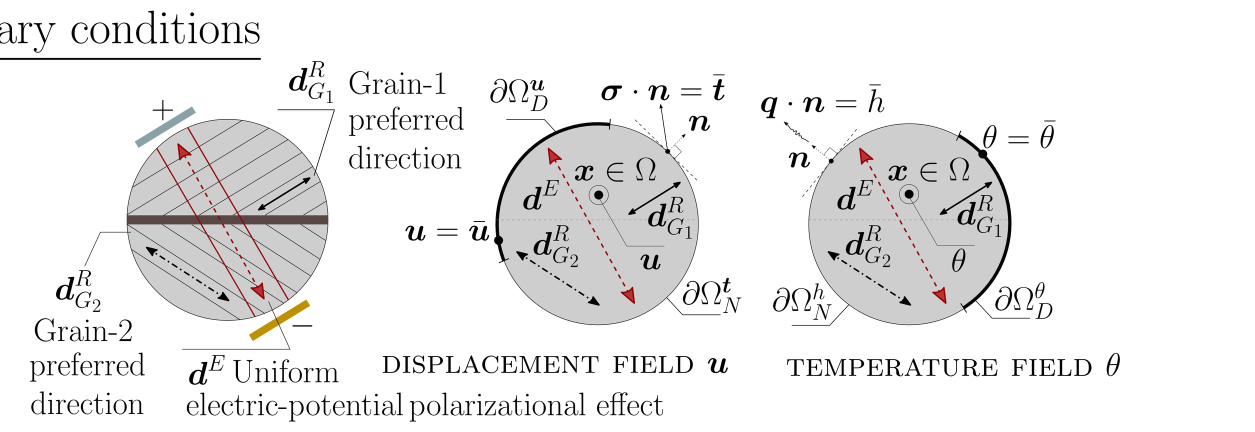
Therefore, the governing problem of dendritic nucleation at (SE|SSE) takes the form

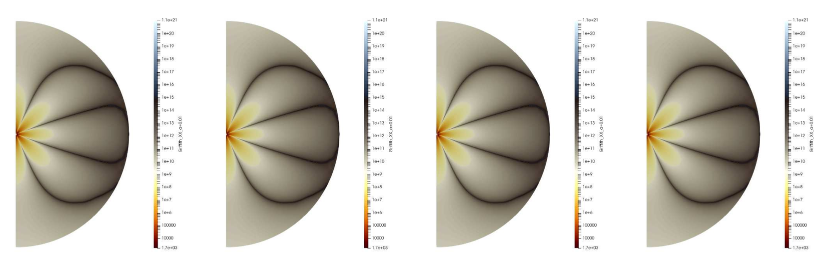
$$\rho\,\partial^2_{t^2}\boldsymbol{u}^{(s)} + \nabla\cdot\left(\overset{4}{\mathbb{C}}{}^{f^{\mathbb{D}(\Omega)}_{(\lambda,\mu)}} : \nabla\boldsymbol{u}^{(s)}\right) + \rho\nabla V_e = \boldsymbol{0},$$

$$\text{s.t.} \quad a_{\text{Griffith}} := a^* = \arg\min_{a\in\mathbb{R}} \iiint_\Omega f(a, \boldsymbol{u}; \lambda, \mu, \boldsymbol{d}\otimes\boldsymbol{d})\, d\Omega - \iint_\Gamma f(a;\gamma)\, d\Gamma \Big|_{\boldsymbol{u}^{(s)}}$$

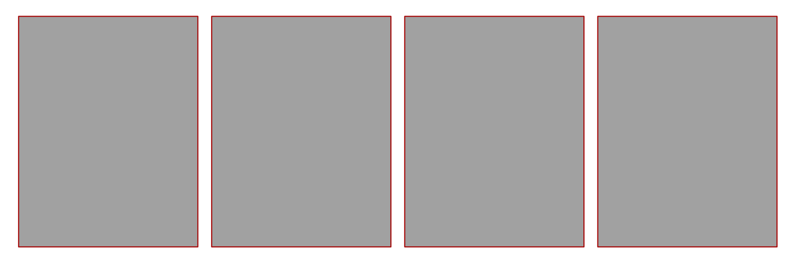
where

Boundary conditions





Comparison: Analytical vs. Numerical solutions



FEM: Strain energy density

Partial differential equation (PDE)
$\nabla\cdot\left(\overset{4}{\mathbb{C}}{}^{\mathbb{D}(\Omega)}_{(\lambda,\mu)}\,\nabla^{(s)}\boldsymbol{u}\right) + \rho\,\boldsymbol{b} = \boldsymbol{0}$

Displacement vector field solution
$u_i \leftarrow \boldsymbol{u} = \boldsymbol{K}^{-1}\boldsymbol{f}$

Strain tensor
$\varepsilon_{ij} = \frac{1}{2}\left(\partial_{x_j}u_i + \partial_{x_i}u_j\right)$

Stress tensor
$\sigma_{ij} = \sum_{k,l} \overset{4}{\mathbb{C}}{}^{f^{\mathbb{D}(\Omega)}_{(\lambda,\mu)}}_{ijkl}\,\varepsilon_{kl}$

Strain energy density
$\mathcal{E}_{\text{strain}} := \frac{1}{2}\sum_{i,j}\sigma_{ij}\,\varepsilon_{ij}$

abc
abc

Analysis: Airy-Westergaard function used for stress analysis: (i) max. shear stress and (ii) principal stresses

$${}^{\mathcal{W}}\!\mathcal{A}: \begin{cases} \mathbb{C}\to\mathbb{C}, \\ z\mapsto {}^{\mathcal{W}}\!\mathcal{A}(z) := \Re\left(\oint_\Gamma \mathcal{K}^{(*)}\, dz\right) + x_2\,\Im\left(\oint_\Gamma \mathcal{K}^{(*)}\, dz\right), \end{cases} \quad \mathcal{K}^{(*)}: \begin{cases} \mathbb{C}\to\mathbb{C}, \\ z\mapsto \mathcal{K}^{(*)} := -p_h + p_h/\sqrt{1-a^2/z^2}, \end{cases}$$

where a the crevice length, p_h pressure at the opening crevice on dendritic interface, and $\forall\,\{p_h, a\}\in\mathbb{R}_+$.

Numerics → FEM: element matrix $\boldsymbol{K}^e$ approx. by *Gauss quadrature*; indices imply $4+2=6$ *for-loop*:

$$K^{e\,\alpha\beta}_{ik} = \int_{\Omega^\xi}\left(\mathcal{L}^\alpha_1\,\mathbb{C}^{f^{GL}}_{i1k1}(\boldsymbol{x})\,\mathcal{R}^\beta_1 + \mathcal{L}^\alpha_1\,\mathbb{C}^{f^{GL}}_{i1k2}(\boldsymbol{x})\,\mathcal{R}^\beta_2 + \mathcal{L}^\alpha_2\,\mathbb{C}^{f^{GL}}_{i2k1}(\boldsymbol{x})\,\mathcal{R}^\beta_1 + \mathcal{L}^\alpha_2\,\mathbb{C}^{f^{GL}}_{i2k2}(\boldsymbol{x})\,\mathcal{R}^\beta_2\right)\det(\boldsymbol{J})\, d\Omega^\xi$$

where $\mathcal{L}^\alpha_j$ and $\mathcal{R}^\beta_l$ are gradients of basis functions at node α^{th} and β^{th}, respectively.

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