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

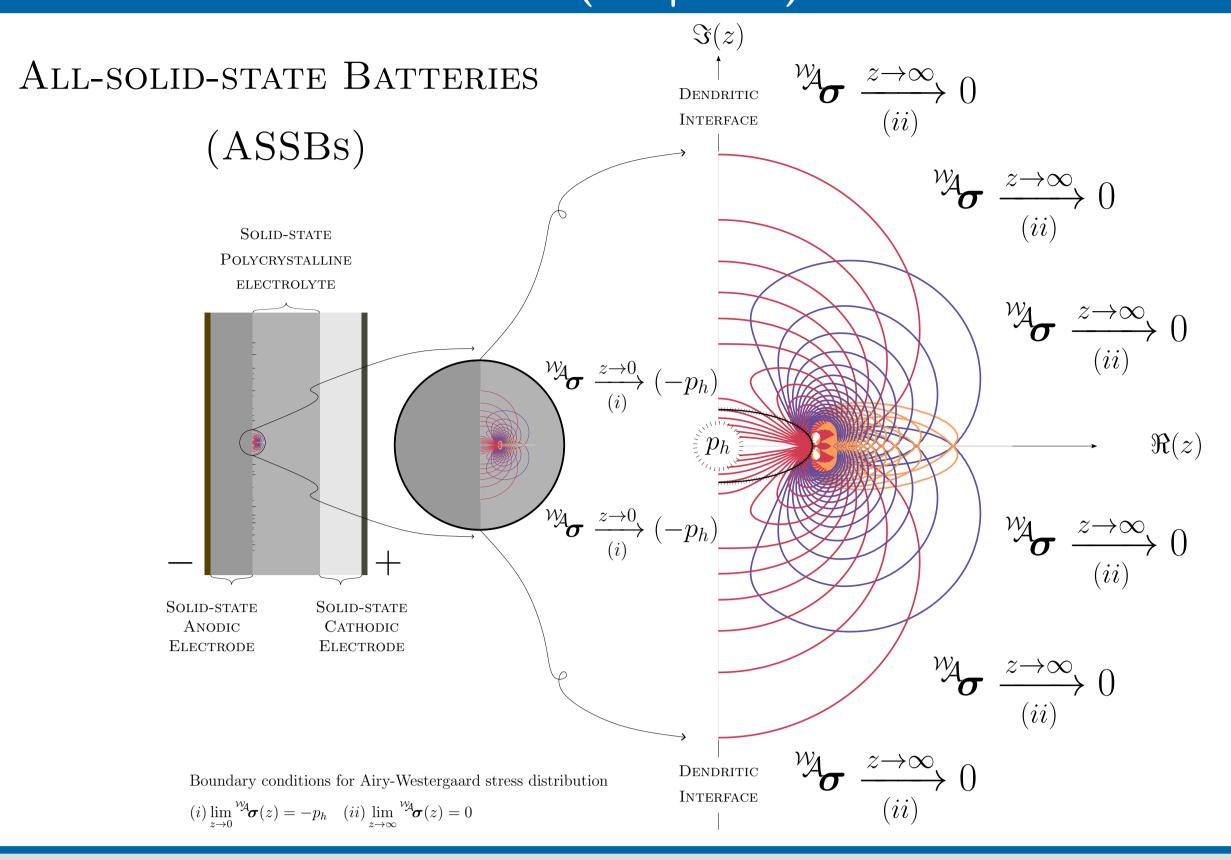
Rechargeable Lithium-ion battery (LIB) is at the heart of every electric vehicle (EV), portable electronic device, and energy storage system [1]. Nowadays, LIBs enable human life more efficient and help to solve global environment issues thanks to EVs' zero emission. However, conventional LIB (c-LIB) 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, Limetal 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

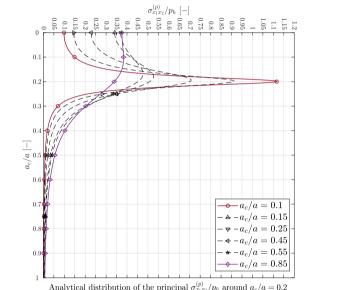
$$a_{ ext{Griffith}} := a^* = \arg\min_{a \in \mathbb{R}} \left. \iint_{\Omega} f(a, \boldsymbol{u}, \theta; \lambda, \mu, \boldsymbol{d}^R \otimes \boldsymbol{d}^R) \, d\Omega - \left. \iint_{\Gamma} f(a; \gamma) \, d\Gamma \right|_{\boldsymbol{u}^{(s)}}$$

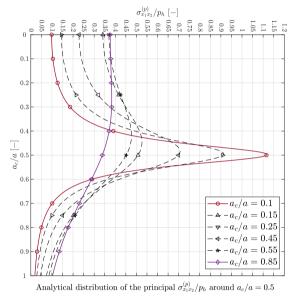
where \boldsymbol{u} displacement field, θ temperature field, a crevice length, λ, μ Lamé constants, $\boldsymbol{d}^R \otimes \boldsymbol{d}^R$ embedded misorientation structural tensor, and γ cracking-surface energy density, can help to improve ASSB performance.

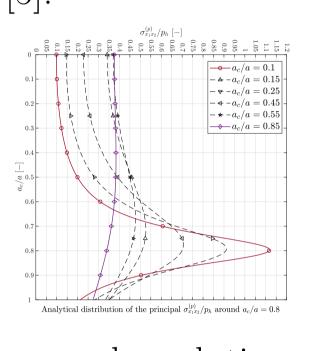


Interface Analysis

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].



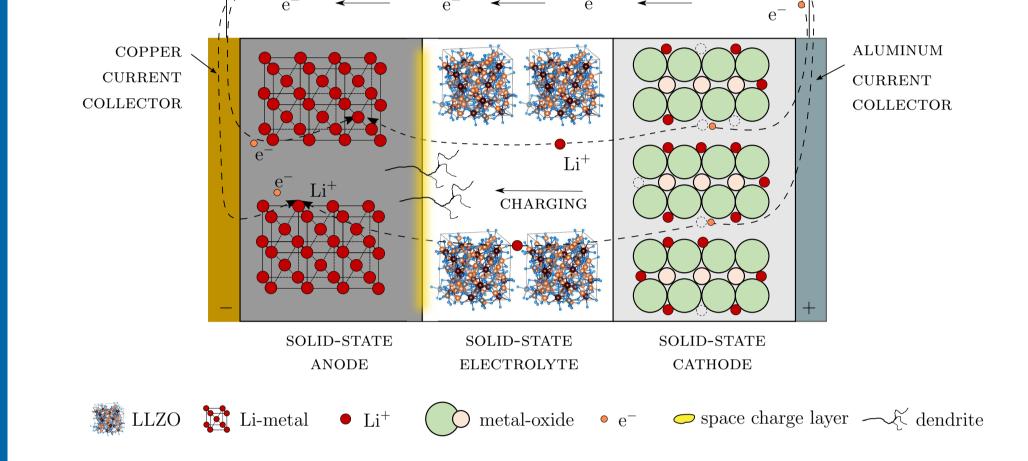




<u>Distribution</u>: ana. max. shear stress ${}^{\mathcal{V}}\!\!\sigma_{x_1x_2}^{\Pi}$ around crack tip a_c .

Next-generation All-solid-state battery

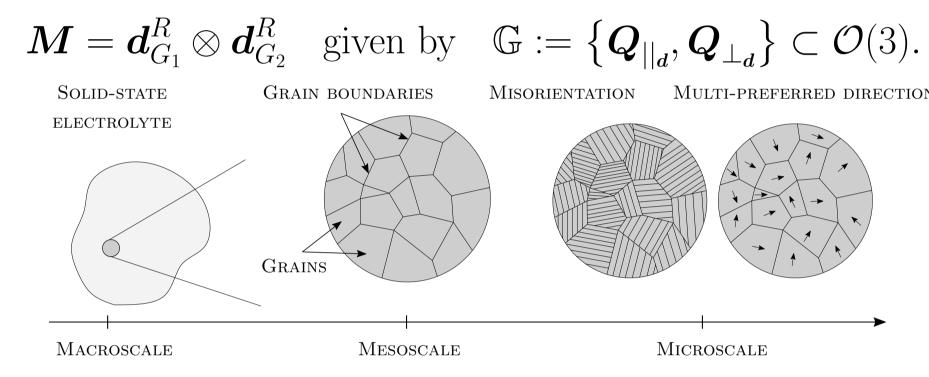
Nucleation criterion governs the instable (SE|SSE)-interface [3]



✓ **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.



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 \boldsymbol{u} and temperature field $\boldsymbol{\theta}$; structural tensor \boldsymbol{M}

$$\boldsymbol{u}: \begin{cases} \Omega \times \mathbb{R}_{+} \to \mathbb{R}^{3}, \\ (\boldsymbol{x},t) \mapsto \boldsymbol{u}(\boldsymbol{x},t), \end{cases} \quad \theta: \begin{cases} \Omega \times \mathbb{R}_{+} \to \mathbb{R}, \\ (\boldsymbol{x},t) \mapsto \theta(\boldsymbol{x},t), \end{cases} \quad \boldsymbol{M}_{i=1,\dots,N}^{\{RR,RE\}}: \begin{cases} \boldsymbol{d}_{\text{Grain i}}^{R} \otimes \boldsymbol{d}_{\text{Grain i}}^{R} \\ \boldsymbol{d}_{\text{Grain i}}^{R} \otimes \boldsymbol{d}^{E} \end{cases}$$

Governing conservation equations

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

used to describe balance of mass, conservation of linear momentum, conservation of angular momentum, and conservation of energy with $\rho(\boldsymbol{x},t)$ 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. Then, the governing partial differential equation (PDE) of deformation takes the form

$$\partial_t oldsymbol{u} +
abla \cdot \left(\overset{4}{\mathbb{C}}^{f_{ ext{alocation}}(\lambda, \mu, oldsymbol{d}_{G_i, i=1,...,N}^R, oldsymbol{d}^E; oldsymbol{x})} :
abla oldsymbol{u}^{(s)}
ight) +
ho oldsymbol{b} = -
ho
abla V_e,$$

where $V_e : \mathbb{R}^3 \to \mathbb{R}$ is the electric potential applied globally on ASSB. Due to nature setting of ASSB taking the form (SE|SSE|SE) the electric potential becomes uniform.

Strain energy is based on the deformation of SSE due to dendrite formation at (SE|SSE)-interface

tion at (SE|SSE)-interface $\iiint_{\Omega} f(a, \boldsymbol{u}; \lambda, \mu, \boldsymbol{d} \otimes \boldsymbol{d}) \, d\Omega$

Surface energy is analysized based on the open crevice cracking at (SE|SSE)-interface affected by prescribed pressure

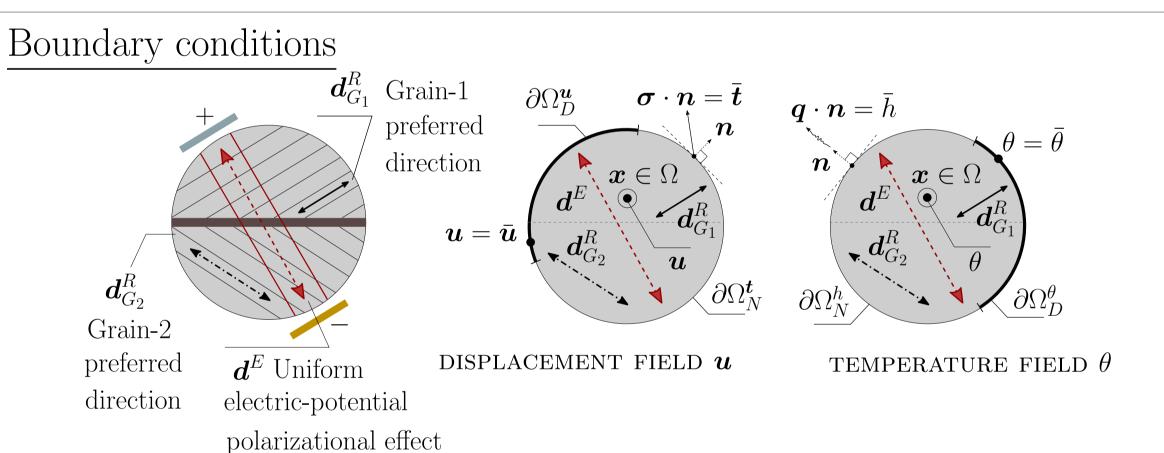
$$\iint_{\Gamma} f(a;\gamma) \, d\Gamma$$

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

$$\partial_{t}\boldsymbol{u} + \nabla \cdot \left(\mathbb{C}^{f_{\text{alocation}}(\lambda, \mu, \boldsymbol{d}_{G_{i}, i=1,\dots,N}^{R}, \boldsymbol{d}^{E}; \boldsymbol{x})} : \nabla \boldsymbol{u}^{(s)} \right) + \rho \boldsymbol{b} = -\rho \nabla V_{e}, \tag{1}$$

s.t.
$$a_{\text{Griffith}} := a^* = \arg\min_{a \in \mathbb{R}} \iiint_{\Omega} f(a, \boldsymbol{u}, \theta; \lambda, \mu, \boldsymbol{d} \otimes \boldsymbol{d}) d\Omega - \iint_{\Gamma} f(a; \gamma) d\Gamma \Big|_{\bar{\boldsymbol{u}}}$$
 (2)

where deformation $\bar{\boldsymbol{u}}$ is (i) based on (1), and then (ii) for Griffith-analysis in (2).



Numerical spectral of Griffith criterion in x-direction at (SE|SSE) yields a = 0.05 (SE | SSE) yields a = 0.05 (C) Case 3 (d) Case 4 (e) Case 5 a = 0.05

where a sample of 5 cases with various prescribed crevice length is studied.

FEM: Strain energy density

Partial differential equation (PDE) $\nabla \cdot \begin{pmatrix} \frac{4}{C} f^{\mathbb{D}(\Omega)}_{(\lambda,\mu)} \nabla^{(s)} \boldsymbol{u} \end{pmatrix} + \rho \, \boldsymbol{b} = \boldsymbol{0}$ Displacement vector field solution $\boldsymbol{u_i} \leftarrow \boldsymbol{u} = \boldsymbol{K}^{-1} \boldsymbol{f}$ Strain tensor $\varepsilon_{ij} = \frac{1}{2} \left(\partial_{x_j} \boldsymbol{u_i} + \partial_{x_i} \boldsymbol{u_j} \right)$ Stress tensor $\boldsymbol{\sigma_{ij}} = \sum_{k,l} \overset{4}{C}^{\mathbb{D}(\Omega)}_{(\lambda,\mu)} \varepsilon_{kl}$ Strain energy density $\mathcal{E}_{\text{strain}} := \frac{1}{2} \sum_{i,j} \boldsymbol{\sigma_{ij}} \varepsilon_{ij}$ Strain solution takes the following form $\frac{1}{2} \sum_{\alpha=1}^{N_{\text{node}}} \overset{N_{\text{opode}}}{\sum_{L=1}^{N_{\text{opode}}}} \mathcal{E}_{L,x_k} \boldsymbol{u_k}^{\alpha} + \sum_{K=1}^{N_{\text{opode}}} \mathcal{E}_{K,x_l} \boldsymbol{u_l}^{\alpha} \right)$

shear stress and (ii) principal stresse

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

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

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

 $\underline{\text{Numerics} \to \text{FEM}}: \text{ element matrix } \boldsymbol{K}^{e} \text{ approx. by } Gauss \ quadrature; \text{ indices imply } 4 + 2 = 6 \ for\text{-loop}: \\
K_{ik}^{e^{\alpha\beta}} = \int_{\Omega^{\xi}} \left(\mathcal{L}_{1}^{\alpha} \ \mathbb{C}_{i1k1}^{f^{GL}}(\boldsymbol{x}) \ \mathcal{R}_{1}^{\beta} + \mathcal{L}_{1}^{\alpha} \ \mathbb{C}_{i1k2}^{f^{GL}}(\boldsymbol{x}) \ \mathcal{R}_{2}^{\beta} + \mathcal{L}_{2}^{\alpha} \ \mathbb{C}_{i2k1}^{f^{GL}}(\boldsymbol{x}) \ \mathcal{R}_{1}^{\beta} + \mathcal{L}_{2}^{\alpha} \ \mathbb{C}_{i2k2}^{f^{GL}}(\boldsymbol{x}) \ \mathcal{R}_{2}^{\beta} \right) \det(\boldsymbol{J}) \ d\Omega^{\xi}$

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

Contact

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