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

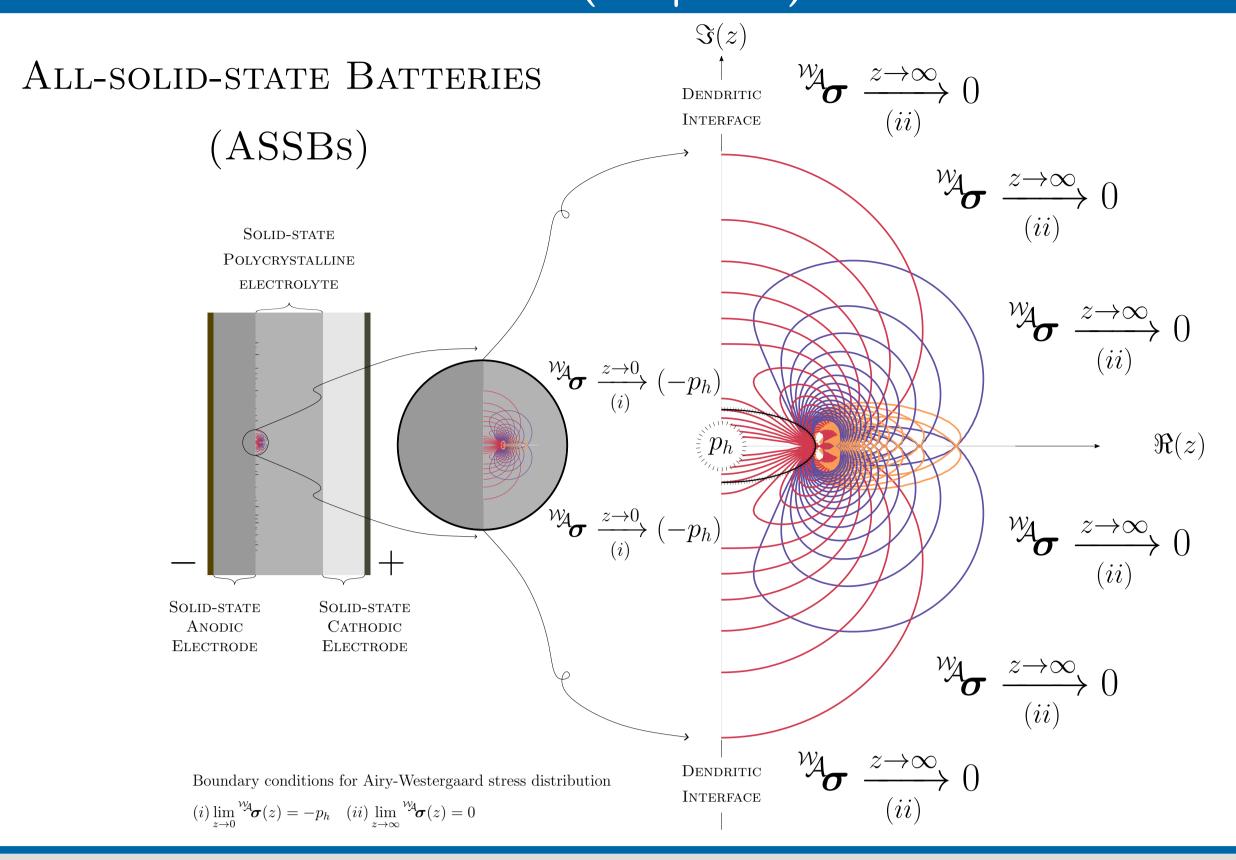
Rechargeable Lithium-ion battery (LIB) is at the heart of every electric vehicle (EV), portable electronic device, and energy storage system [1]. Nowadays, LIBs enable human life more efficient and help to solve global environment issues thanks to EVs' zero emission. However, conventional LIB (c-LIB)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

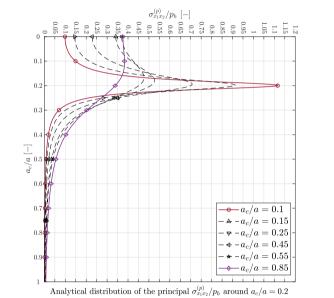
$$a_{ ext{Griffith}} := a^* = \arg\min_{a \in \mathbb{R}} \left. \iint_{\Omega} f(a, oldsymbol{u}, heta; \lambda, \mu, oldsymbol{d}^R \otimes oldsymbol{d}^R) d\Omega - \iint_{\Gamma} f(a; \gamma) d\Gamma
ight|_{oldsymbol{u}^{(s)}}$$

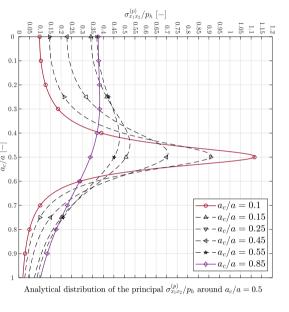
where \boldsymbol{u} displacement field, θ temperature field, a crevice length, λ, μ Lamé constants, $\boldsymbol{d}^R \otimes \boldsymbol{d}^R$ embedded misorientation structural tensor, and γ cracking-surface energy density, can help to improve ASSB performance.

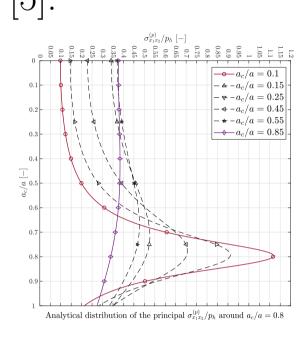


Interface Analysis

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].



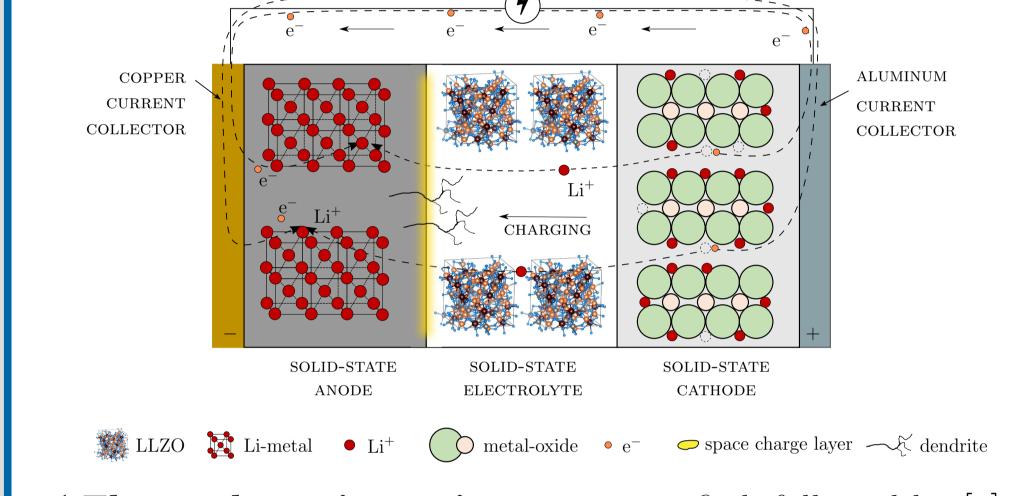




<u>Distribution</u>: ana. max. shear stress ${}^{\mathcal{W}}\!\!\sigma_{x_1x_2}^{\Pi}$ around crack tip a_c .

Next-generation All-solid-state battery

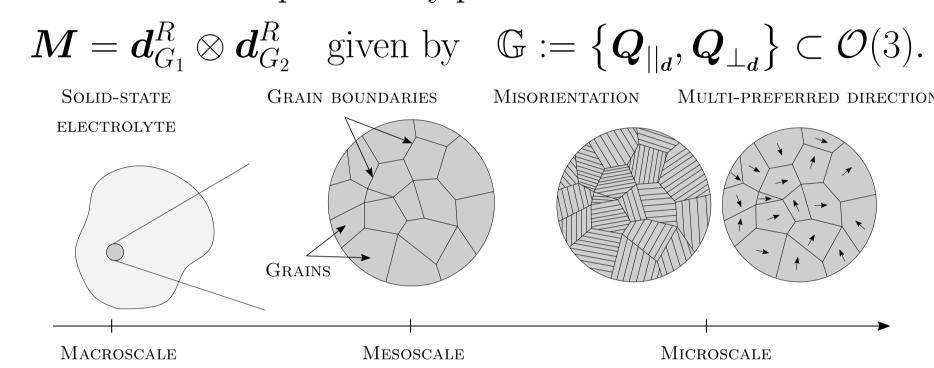
Nucleation criterion governs the instable (SE|SSE)-interface [3]



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 u and temperature field θ ; structural tensor M

$$oxed{m{u}:egin{array}{c} \Omega imes\mathbb{R}_+
ightarrow \mathbb{R}^3, \ (m{x},t)\mapsto m{u}(m{x},t), \end{array}} m{ heta}:egin{array}{c} \Omega imes\mathbb{R}_+
ightarrow \mathbb{R}, \ (m{x},t)\mapsto m{ heta}(m{x},t), \end{array}} m{m{M}}_{i=1,...,N}^{\{RR,RE\}}:egin{array}{c} m{d}_{ ext{Grain i}}^R\otimes m{d}_{ ext{Grain i}}^R\otimes m{d}^E \end{array}$$

Governing conservation equations

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

 $\rho(\boldsymbol{x},t)$ 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

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

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 uniform electric potential applied globally on ASSB.

Strain energy: Deformation of solidelectrolyte due to dendrite formation at (SE|SSE)-interface

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

Surface energy: Opening crevice at (SE|SSE)-interface influenced by prescribed pressure caused by dendrite

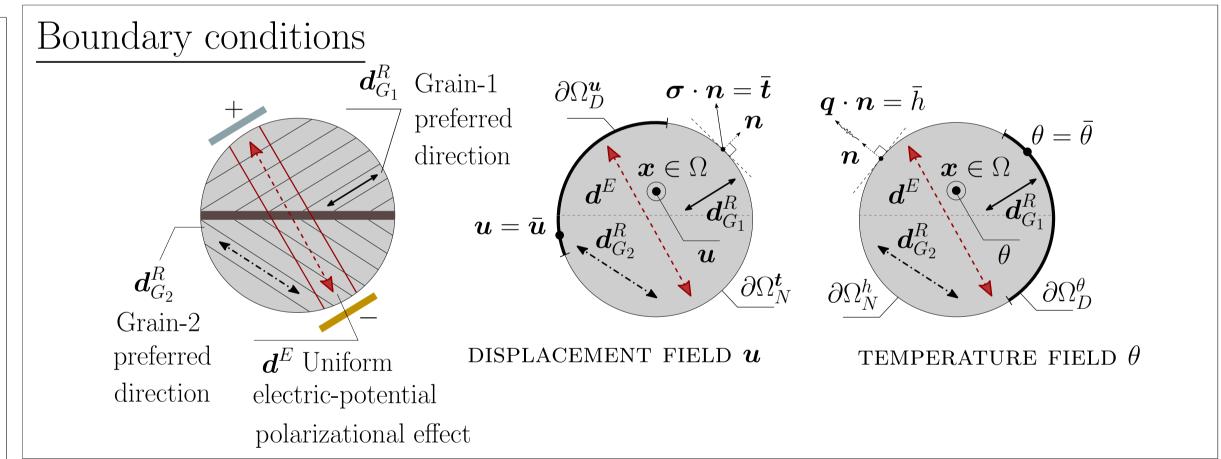
$$\iint_{\Gamma} f(a;\gamma) \, d\Gamma$$

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

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

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) Case 1 (b) Case 2 (c) Case 3 (d) Case 4 (e) Case 5 $a_{\text{crevice}} = 0.01$ $a_{\text{crevice}} = 0.1$ $a_{\text{crevice}} = 0.05$ $a_{\text{crevice}} = 0.3$

Strain solution takes the following form $a_{\text{crevice}} = 0.5$ $\frac{1}{2} \sum_{\alpha=1}^{\mathcal{N}_{\text{node}}^{\Omega^e}} \left(\sum_{L=1}^{\mathcal{N}_{\text{dof}}^{\Omega^{\text{node}}}} N_{,\xi_L}^{\alpha} \xi_{L,x_k} u_k^{\alpha} + \sum_{K=1}^{\mathcal{N}_{\text{dof}}^{\Omega^{\text{node}}}} N_{,\xi_K}^{\alpha} \xi_{K,x_l} u_l^{\alpha} \right)$ where a sample of 5 cases with various prescribed crevice length is studied. Analysis: Airy-Westergaard function used for stress analysis: (i) max. shear stress and (ii) principal stresses

 $\mathcal{E}_{ ext{strain}} := rac{1}{2} \sum_{i,j} \sigma_{ij} \, arepsilon_{ij}$

FEM: Strain energy density

Partial differential equation (PDE)

 $abla \cdot \left(\overset{4}{\mathbb{C}} f^{\mathbb{D}(\Omega)}_{(\lambda,\mu)} \,
abla^{(s)} oldsymbol{u}
ight) +
ho \, oldsymbol{b} = oldsymbol{0}$

Displacement vector field solution

Strain tensor

Stress tensor

 $\mathbf{u_i} \leftarrow \mathbf{u} = \mathbf{K}^{-1} \mathbf{f}$

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

 $\sigma_{ij} = \sum_{k,l} \overset{4}{\mathbb{C}}_{ijkl}^{f_{(\lambda,\mu)}^{(i,l)}} \, arepsilon_{kl}$

Strain energy density

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

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

Numerics \rightarrow FEM: element matrix \mathbf{K}^e approx. by Gauss quadrature; indices imply 4+2=6 for-loop: $K_{ik}^{e^{lphaeta}} = \int_{\Omega^{\epsilon}} \left(\mathcal{L}_{1}^{lpha} \, \, \mathbb{C}_{i1k1}^{fGL}(oldsymbol{x}) \, \, \mathcal{R}_{1}^{eta} + \mathcal{L}_{1}^{lpha} \, \, \mathbb{C}_{i1k2}^{fGL}(oldsymbol{x}) \, \, \mathcal{R}_{2}^{eta} + \mathcal{L}_{2}^{lpha} \, \, \mathbb{C}_{i2k1}^{fGL}(oldsymbol{x}) \, \, \mathcal{R}_{1}^{eta} + \mathcal{L}_{2}^{lpha} \, \, \mathbb{C}_{i2k2}^{fGL}(oldsymbol{x}) \, \, \mathcal{R}_{2}^{eta}
ight) \det(oldsymbol{J}) \, \, d\Omega^{\xi}$

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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