# Mathematical modelling for all-solid-state battery: (SE|SSE)-Interface

Tuan Vo[a,b †], Claas Hüter[b], Stefanie Braun[a], Manuel Torrilhon[a]

[a]Department of Mathematics, Applied and Computational Mathematics (ACoM), RWTH Aachen University, Schinkelstraße 02, 52062 Aachen, Germany
[b]Institute of Energy and Climate Research (IEK-2), Forschungszentrum Jülich, Wilhelm-Johnen-Straße, 52428 Jülich, Germany

## 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.

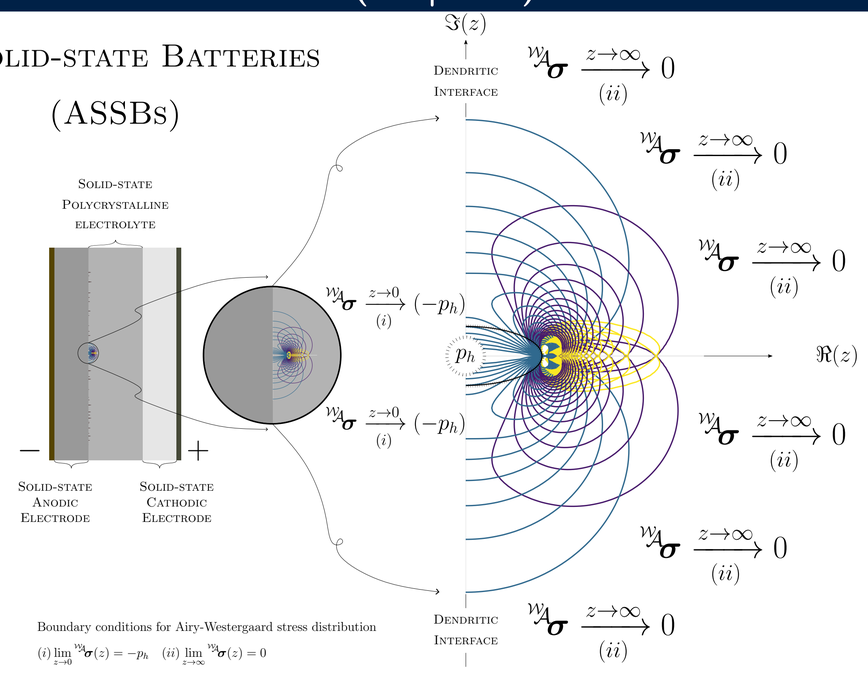
**All-solid-state battery** (ASSB) is one of promising candidates to overcome bottlenecks of c-LIBs. Thanks to solid-state electrolyte (SSE), ASSB is highly stable towards temperature and pressure. Nevertheless, Li-metal dendrite triggered at (SE|SSE)-interface [5] is the main drawback of ASSB since 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

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

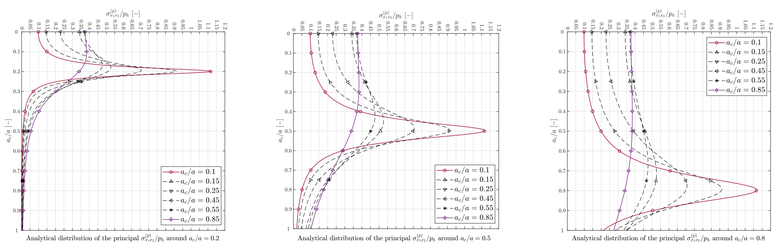
where $\boldsymbol{u}$ displacement field, $\theta$ temperature field, $a$ crevice length, $\lambda,\mu$ Lamé constants, $\boldsymbol{d}^{(\star)}\otimes\boldsymbol{d}^{(\star)}$ embedded misorientation structural tensor, and $\gamma$ cracking-surface energy density, can help to improve ASSB performance.

### All-solid-state Batteries (ASSBs)




## (SE|SSE)-Interface Analysis

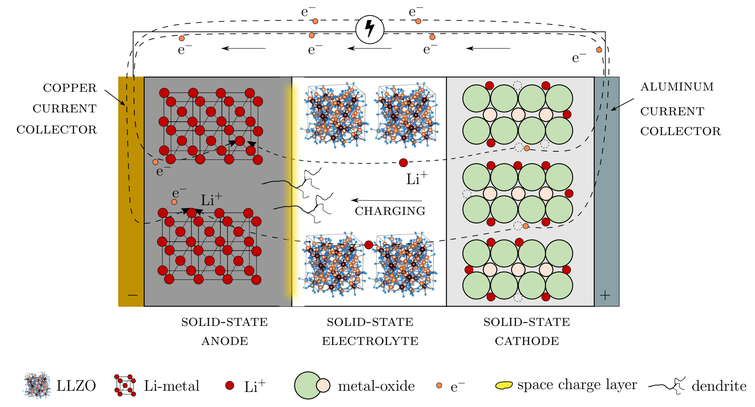
**Interface** between solid electrode and solid-state electrolyte (SE|SSE) taking place at space charge layer (SCL) [2] found in ASSBs critically exhibits mechanical and electrochemical instability [3]. This evidence points directly to the fact that the soft metallic li anode is erroneously prone to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




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

## Next-generation All-solid-state battery

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

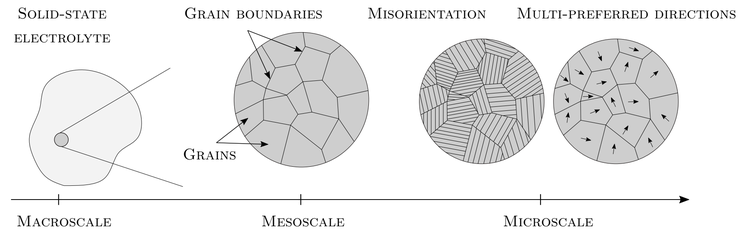



✓ **Thermodynamic consistency** is satisfied, followed by [2].
✓ **Closure** $\bar{\Omega}$ is fulfilled by 15 moments, followed by [4].

## 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.

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




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

## Nucleation interface: Taking place at the critically dendritic (SE|SSE)-interface

Coupled fields: Displacement field $\boldsymbol{u}$ and temperature field $\theta$; structural tensor $\boldsymbol{M}$

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

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) for the thermodynamically consistent coupled problem with deformation field $\boldsymbol{u}$ as its variable takes the form

$$\partial_t\boldsymbol{u} + \nabla\cdot\left(\overset{4}{\mathbb{C}}{}^{f_{\text{alocation}}(\lambda,\mu,\boldsymbol{d}^R_{G_i,i=1,\dots,N},\boldsymbol{d}^E;\boldsymbol{x})} : \nabla\boldsymbol{u}^{(s)}\right) + \rho\boldsymbol{b} = -\rho\nabla V_e,$$

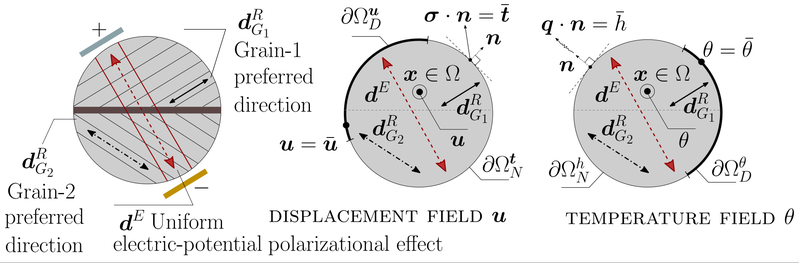
where $V_e:\mathbb{R}^3\to\mathbb{R}$ is the electric potential applied globally on ASSB. Due to nature setting of ASSB taking the form (SE|SSE|SE) the electric potential becomes uniform.

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

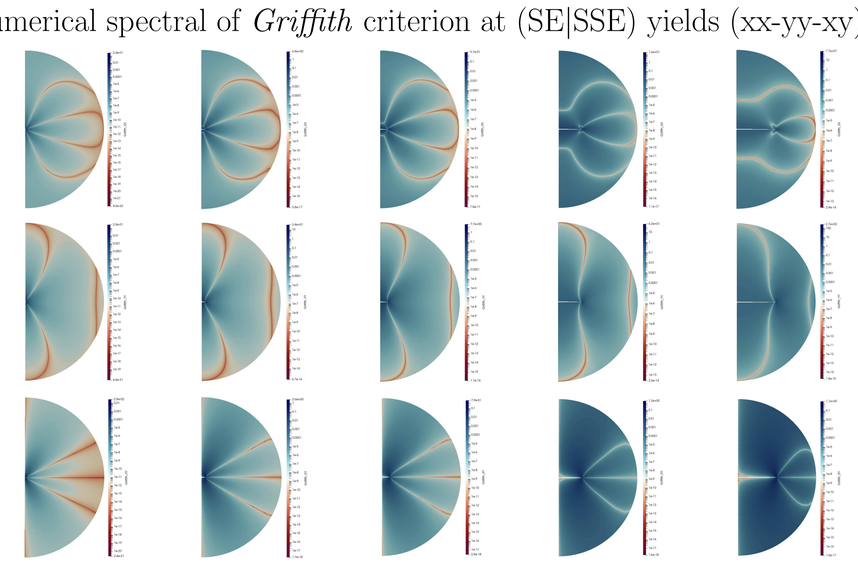
$${}^{\mathcal{W}}\mathcal{A}: \begin{cases}\mathbb{C}\to\mathbb{C},\\ z\mapsto {}^{\mathcal{W}}\mathcal{A}(z) := \Re(\iint_\Gamma \mathcal{K}^{(\star)}\,dz) + x_2\,\Im(\oint_\Gamma \mathcal{K}^{(\star)}\,dz),\end{cases} \quad \mathcal{K}^{(\star)}: \begin{cases}\mathbb{C}\to\mathbb{C},\\ z\mapsto \mathcal{K}^{(\star)}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

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

Boundary conditions applied on a solid-state object




Numerical spectral of *Griffith* criterion at (SE|SSE) yields (xx-yy-xy)



(a) Case 1 $a_{\text{crevice}} = 0.01$ (b) Case 2 $a_{\text{crevice}} = 0.05$ (c) Case 3 $a_{\text{crevice}} = 0.1$ (d) Case 4 $a_{\text{crevice}} = 0.3$ (e) Case 5 $a_{\text{crevice}} = 0.5$

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

FEM: Strain energy density

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

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

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

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

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

Strain solution takes the following form
$\frac{1}{2}\sum_{\alpha=1}^{\mathcal{N}^e_{\text{node}}}(\sum_{L=1}^{\mathcal{N}^{\text{node}}_{\text{dof}}}N^\alpha_{,\xi_L}\xi_{L,x_k}u^\alpha_k + \sum_{K=1}^{\mathcal{N}^{\text{node}}_{\text{dof}}}N^\alpha_{,\xi_K}\xi_{K,x_l}u^\alpha_l)$
where displacement field $\boldsymbol{u}$ is known, numerically computed from the PDE above.

**Strain energy** is based on the deformation of SSE 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** 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

$$\partial_t\bar{\boldsymbol{u}} + \nabla\cdot\left(\overset{4}{\mathbb{C}}{}^{f_{\text{alocation}}(\lambda,\mu,\boldsymbol{d}^R_{G_i,i=1,\dots,N},\boldsymbol{d}^E;\boldsymbol{x})} : \nabla\boldsymbol{u}^{(s)}\right) + \rho\boldsymbol{b} = -\rho\nabla V_e, \quad (1)$$

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

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

*Griffith*-based critical stress
$$\sigma_{\text{Griffith}} = \sqrt{\frac{2\,\gamma\,E}{\pi\,a_{\text{crevice}}}}$$
governs nucleation interface.

## Contact

Tuan Vo
vo@acom.rwth-aachen.de

Scan me

## References

[1] **T.Vo**, *Modeling the swelling phenomena of li-ion batt. cells based on a numerical chemo-mech. coupled approach.* MA, Robert Bosch Battery Systems GmbH, **2018**.

[2] **S.Braun**, C.Yada, and A.Latz, *Thermodynamically consistent model for Space-Charge-Layer formation in a solid electrolyte.* Jr. Phys. Chem., 119, 22281-22288, **2015**.

[3] **C.Hüter**, S.Fu, M.Finsterbusch, E.Figgemeier, L.Wells, and R.Spatschek, *Electrode-electrolyte interface stability in solid state electrolyte system: influence of coating thickness under varying residual stresses.* AIMS Materials Science, 4(4):867-877, **2017**.

[4] **M.Torrilhon**. *Modeling nonequilibrium gas flow based on moment equations.* Annual Review of Fluid Mechanics, 48(1):429-458, **2016**.

[5] **S.Kim**, J.S.Kim, L.Miara, Y.Wang, S.K.Jung, S.Y.Park, Z.Song, H.King, M.Badding, J.M.Chang, V.Roev, G.Yoon, R.Kim, J.H.Kim, K.Yoon, D.Im, and K.Kang, *High-energy and durable li metal batt. using garnet-type solid electrolytes with tailored li-metal compatibility.* Nature Communications, 13(1):1883, **2022**.

OXFORD BATTERY MODELLING SYMPOSIUM
IN-PERSON MEETING, HOSTED AT PEMBROKE COLLEGE, UNIVERSITY OF OXFORD, ENGLAND
27TH AND 28TH MARCH 2023

#OBMS2023