Argonne National Laboratory Seminar: An adjoint of nucleation in All-solid-state batteries

Tuan Vo

RWTH Aachen University × Forschungszentrum Jülich

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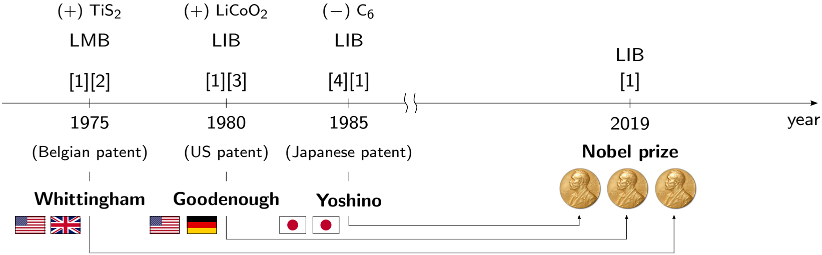
  1. Bachelor thesis at BOSCH Germany
  2. Master thesis at BOSCH Germany

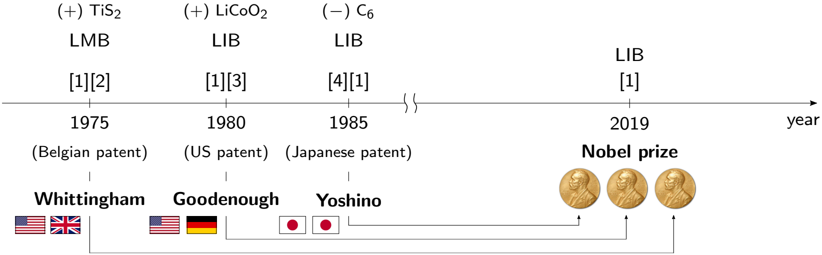
I-1. Motivation: Lithium-ion battery (LIB) is useful



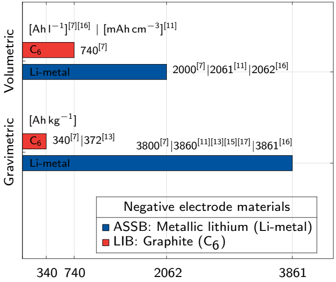
..and LIB has been widely used in various applications, such as

- Electric vehicle (EV)
- Portable electronic device (PED)
- Energy storage system (ESS)

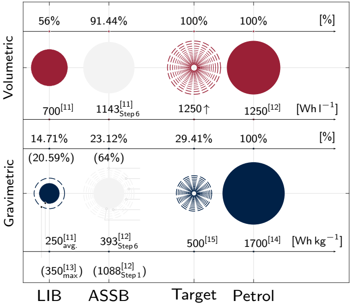
I-1. Motivation: But LIB exists limited energy density



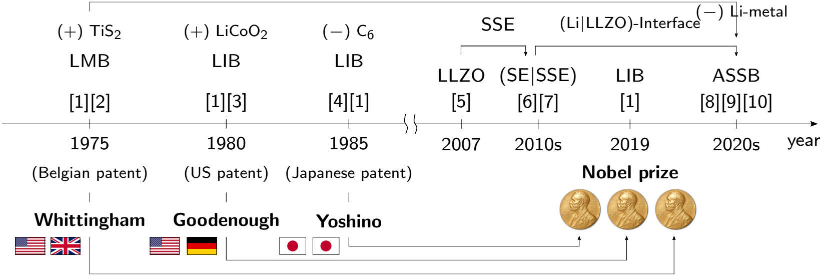
Theoretical capacity of charge:
pure metallic lithium (Li-metal) versus Graphite (C_6)

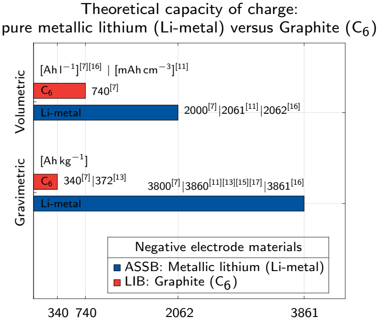


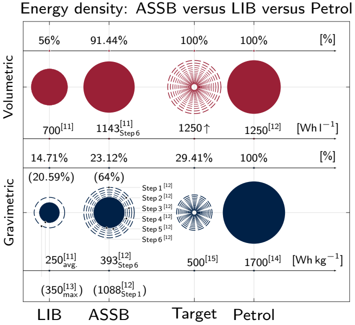
Energy density: ASSB versus LIB versus Petrol



I-1. Motivation: All-solid-state battery (ASSB) is promising







I-1. Motivation: Still, ASSB has drawbacks itself

Problem:

1. LIB is useful, but generally limited by its energy density.
2. ASSB is promising with its energy density, but has drawbacks.
3. ASSB drawbacks: **nucleation**, **dendrite growth**, **interface**.

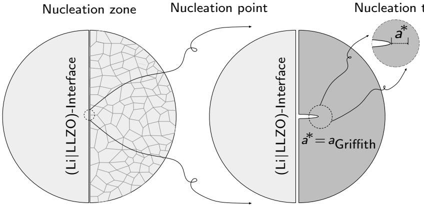
Aim:

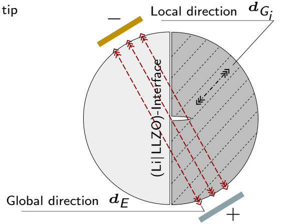
1. Tackle the **adjoint nucleation** at the ASSB interface stability.

Study:

1. Outline the **nucleation criterion** into a mathematical model.
2. Develop a numerical method to **visualise** the nucleation.
3. Examine the results with **relevant material** candidates.

I-2. Mathematical model in summary (1/3)

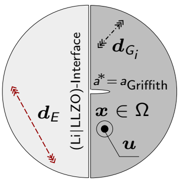




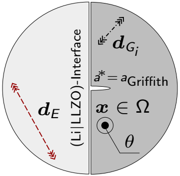
Space-charge layer
Dendrite growth

Griffith criterion a^*
Cracking nucleation

Misorientation $\boldsymbol{M} = \boldsymbol{d} \otimes \boldsymbol{d}$
Global direction: Uniform electric field $\boldsymbol{d}_E$
Local direction: Crystallographical orientation $\boldsymbol{d}_{G_i}$



Displacement field $\boldsymbol{u}$



Temperature field θ

1. **Coupled fields** include **deformation** and **temperature**.
2. **Misorientation** tensors present **grain disorder structure**.
3. **Thermodynamic consistency** is satisfied, **closure** problem is fulfilled.

I-2. Mathematical model in summary (2/3)

Coupled fields are Deformation field $\boldsymbol{u}$ and Temperature field θ:

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

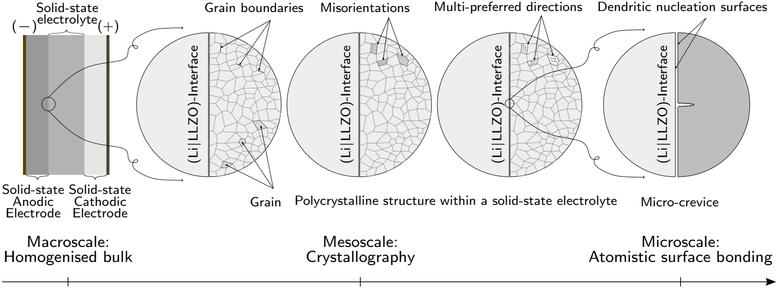
Governing conservation equation takes the form

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

which accounts for mass balance, linear and angular momentum, and energy conservation.

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

I-2. Mathematical model in summary (3/3)



Find a such that the following optimisation problem $\forall\, a \in \mathcal{V}$ hold:

$$\rho\,\frac{D^2\boldsymbol{U}}{Dt^2} - \nabla\cdot\left(\mathbb{C}^{T_f\,\phi}_{(\lambda,\mu)} : \nabla \boldsymbol{U}^{(s)}\right) + \rho\, V_E = \boldsymbol{0}, \tag{1}$$

$$\text{s.t.}\quad a^{\text{generalised}}_{\text{Griffith}} := a^* = \arg\min_{a\in\mathcal{V}} \left\{ \iiint_\Omega f\left(a, \boldsymbol{u}, \theta, c^{m|\mathrm{Li}^+|n}; \lambda, \mu, \boldsymbol{d}_{G_j} \otimes \boldsymbol{d}_{G_j}\right) d\Omega - \iint_\Gamma f(a;\gamma)\, d\Gamma \right\} \tag{2}$$

I-3 Adjoint Griffith nucleation criterion (1/4)

Adjoint Griffith nucleation criterion in terms of **critical length** has two forms:

$a^{generalised}_{Griffith}$	$a^{simplified}_{Griffith}$
• Surface energy	• Surface energy
• Strain energy	• Strain energy
• Grain disorder structure	• $\times$

Observations:

1. **Generalised** Griffith criterion is an optimisation problem, considering **surface energy**, **strain energy**, and **grain disorder structure**.
2. **Simplified** Griffith criterion requires **surface energy** and **strain energy**.
3. **Simplified** Griffith criterion in terms of **critical length** takes the form

$$\boxed{a^{simplified}_{Griffith} = \frac{2E\gamma_s}{\pi\sigma^2}} \Leftrightarrow \boxed{\sigma_{Griffith} = \sqrt{\frac{2E\gamma_s}{\pi a}}}$$

where σ is the Cauchy stress, E Young's modulus, and γ_s surface energy.

I-3 Adjoint Griffith nucleation criterion (2/4)

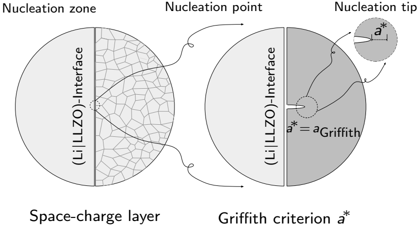
Adjoint Griffith nucleation criterion in terms of **critical length** has two forms:

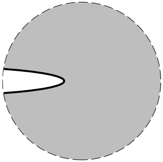
$a^{generalised}_{Griffith}$	$a^{simplified}_{Griffith}$
• Surface energy (DFT)	• Surface energy (DFT)
• Strain energy (Continuum)	• Strain energy (Continuum)
• Grain disorder structure (FEM)	• $\times$

Approaches:

1. **Surface energy** is computed using **DFT calculations**.
2. **Strain energy** is computed using deformation problems in **Continuum**.
3. Simplified Griffith nucleation may require **FEM** or **FVM**, along with **DFT**.
4. Generalised Griffith nucleation may require **FEM** and **DFT**.
5. **Grain disorder structure** is a 4th order tensor, and computed using **FEM**.
6. Study **25**$Ta^{\bullet}_{Zr}$-LLZO, **50**$Ta^{\bullet}_{Zr}$-LLZO, **28**$Al^{\bullet\bullet}_{Li}$-LLZO, **36**$Al^{\bullet\bullet}_{Li}$-LLZO.
7. The results are visualised in the following figures.

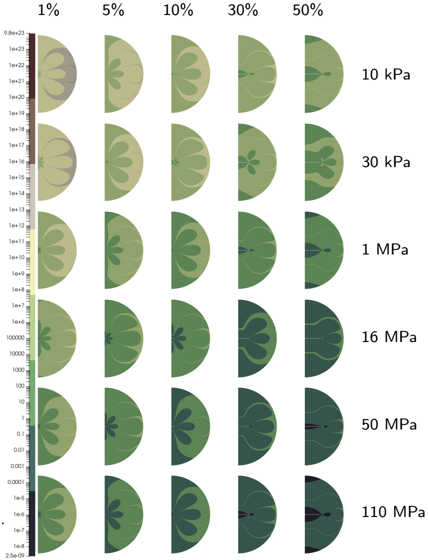
I-3 Adjoint Griffith nucleation criterion (3/4)





Nucleation tip

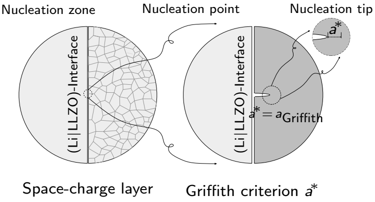
- Horizontal axis: Crevice length.
- Vertical axis: Stacking pressure.
- OpenFOAM **solidDisplacementFoam.C** solver is developed.
- Nucleation criterion is shown using **logarithmic scale**.

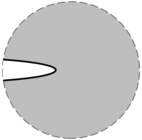


Nucleation at the adjoint interfaces in (100Li)-**50**$Ta^{\bullet}_{Zr}$-LLZO

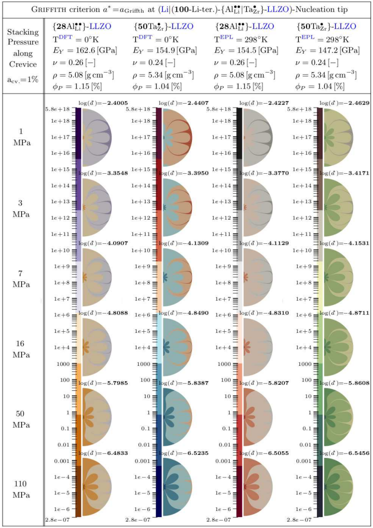
I-3 Adjoint Griffith nucleation criterion (4/4)

Further studies





Nucleation tip



Observations:

- Stacking pressure influences nucleation.
- Pre-existing crevice presents grain boundary.
- Griffith criterion is observed on log-scale.

I-4 Summary

Conclusion:

1. A **generalised** Griffith criterion is developed for nucleation adjoint in ASSB.
2. Both **DFT** and **Continuum** methods are used for nucleation criterion.
3. DFT calculation results for **LLZO-surfaces** are obtained using literature [6].
4. Continuum calculations have been studied and presented in [1][2][3][4].
5. **Griffith** criterion has been studied and presented in [5].
6. **Simplified** Griffith criterion is used to study LLZO adjoint nucleation.

Outlook:

1. Would metallic Li **anode-less** ASSB be a solution eventually?

Literature:

1 **T.Vo**, *C.Hüter, S.Braun, Poster, BOSCH Spring School on AI in Industry, Robert Bosch GmbH*, **2024**.

2 **T.Vo**, *C.Hüter, S.Braun, M.Torrilhon, Poster, Oxford Battery Modelling Symp., University of Oxford*, **2023**.

3 **T.Vo**, *C.Hüter, S.Braun, M.Torrilhon, Next-gen ASSB Poster, SIAM Conference on Comp. Sci. Eng.*, **2023**.

4 **T.Vo**, *NUMAP-FOAM Summer School, OpenFOAM Pres., Maxwell Centre, University of Cambridge*, **2022**.

5 **T.Vo**, *C.Hüter, S.Braun, R.Spatschek, ASSB Griffith, IEK Doc. Pres., Forschungszentrum Jülich*, **2020**.

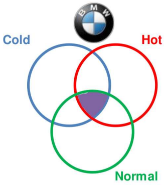
6 **P.Barai**, *A.Ngo, B.Narayanan, K.Higa, L.Curtiss, V.Srinivasan, LLZO, J. of the electrochemical soc.*, **2020**.

7 **C.Hüter**, *S.Fu, M.Finsterbusch, E.Figgemeier, L.Wells, R.Spatschek, E-E interface, AIMS Mat. Sci.*, **2017**.

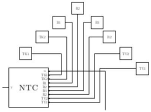
8 **S.Braun**, *C.Yada, A.Latz, Space-charge layer ASSB, J. Physical Chem. C, 119, 22281-22288*, **2015**.

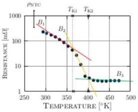
II-1. Other relevant experience: BOSCH Bachelor thesis

Semiconductor[I]



Application: Start/Stop-System in Starter.
Use-case: BMW B47 (-25°C, 0°C, 120°C).
Optimisation: Pareto @BoschForschung.
(Multi-objective optimisation framework)





Nd/Gd Negative-Temperature Coefficient (NTC) semiconductor model validated [7].

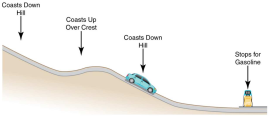


Figure 1.2.: Coasting function of St/St Starter [14].

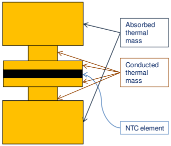


Figure 5.1.: Symmetry model of a NTC component.

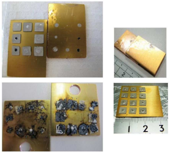
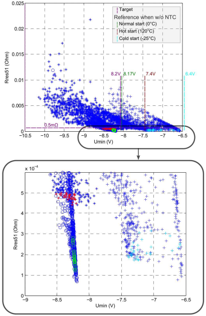


Table 6.4.: Testing conditions and Requirements of BMW B47 4 Cylinders Engine.

Conditions	$-25°C$	$0°C$	$120°C$
U_0	$11V$	12.03	12
R_{Line}	$3.5m\Omega$	4.3	6.3
R_{Batt}	$6.0m\Omega$	5.7	5.4
M_{Last}	$116Nm$	39	35
I_{BN}	$35A$	75	75
$M_{R,Armature}$	$0.69Nm$	0.76	1.04
$J_{Armature}$	$0.0004kgm^2$	0.0004	0.0004
$c\phi_{Armature}$	$0.0095Nm/A$	0.0092	0.0078
R_{St}	$5.5m\Omega$	5.8	6.6
Requirements	$\omega = 120min^{-1}$	$U_{Kl} = 8.2V$	$U_{Kl} = 8.2V$

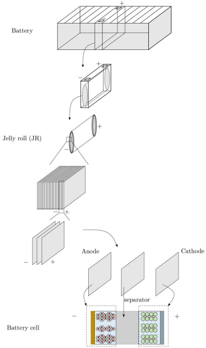


BOSCH
Invented for life

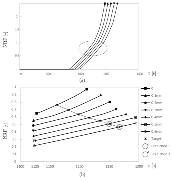
[I] **T.Vo**, *Sim. environment for NTC-based vol. drop reduction in Start/Stop appl. and its optimisation*, **2014**.

II-2. Other relevant experience: BOSCH Master thesis

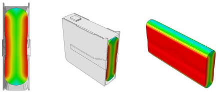
Battery[II]



Modelling: Swelling phenomena @FEM
Use-case: Bosch-48-V-Battery.

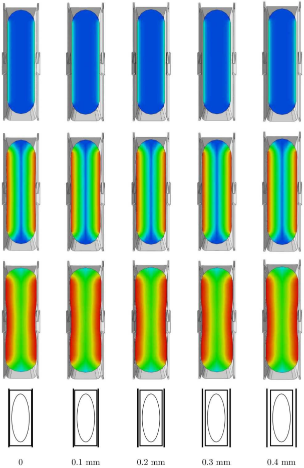


	Prediction NRF [-]	Target NRF [-]	Deviation
0.5mm	0.4968	0.5069	**2.0** %
0.6mm	0.4428	0.4753	**6.8** %



The total Helmholtz free energy then reads

$$\rho_0\hat{\Psi} = \rho_0\hat{\Psi}(\boldsymbol{C}_e, c) = R\theta\rho_0 c\left[\ln\left(\frac{\Omega\rho_0 c}{1+\Omega\rho_0 c}\right) + \chi\left(\frac{1}{1+\Omega\rho_0 c}\right)\right] + \frac{1}{2}G(\operatorname{tr}\boldsymbol{C}_e - 3) - G\ln J + \frac{1}{2}KJ_c(\ln J_e)^2$$

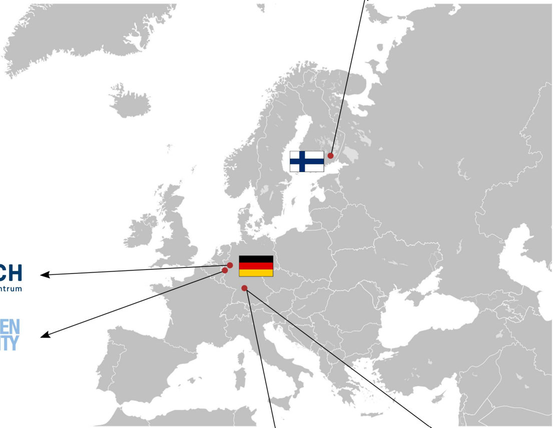


BOSCH
Invented for life

[II] **T.Vo**, *Modeling the swelling phenomena of LIB cells based on a num. chemo-mech. coupled approach*, **2018**.

II-3. Other relevant experience: Summary

Saimaan ammattikorkeakoulu (Bachelor)



JÜLICH Forschungszentrum

RWTH AACHEN UNIVERSITY

(PhD)

Universität Stuttgart

(Master)

BOSCH

(Bachelor thesis, 2014)

(PreMaster, 2015)

(Master thesis, 2018)

Thank you for your listening.