A computational model for examining the role of externally applied stress on dendrite growth pattern in solid state Lithium-ion batteries

Sachin Poudel [1, *]

Anna Timofiejczuk [1]

Nele Moelans [2]

Anil Kunwar [1]

Promoters

* sachin.poudel@polsl.pl

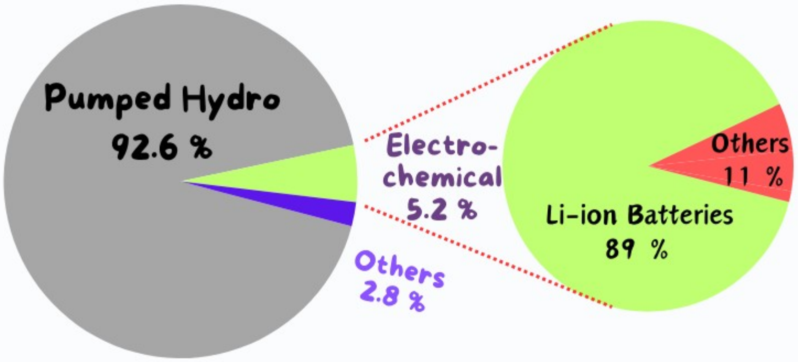
1 Politechnika Śląska

2 KU LEUVEN

May 22 | 2024

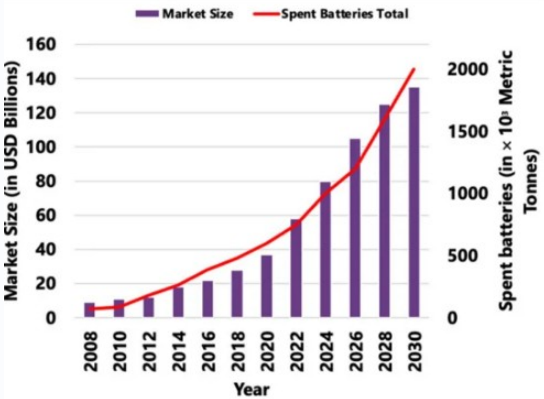
1. Energy Storage: Why Li-ion Batteries ?

High demand of energy storage devices



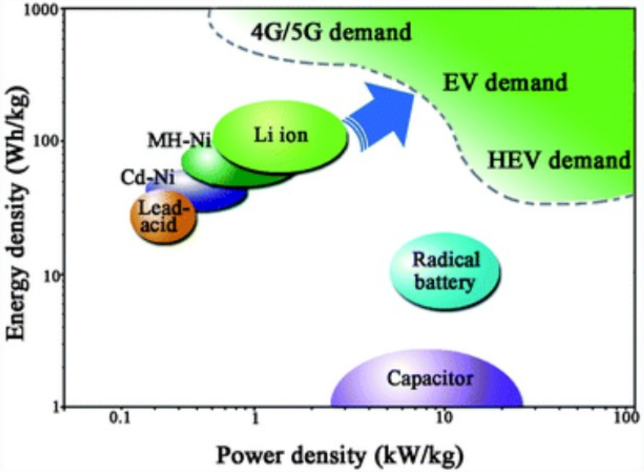
Global total operational energy storage

http://en.cnesa.org/latest-news/2020/5/28/cnesa-global-energy-storage-market-analysis-2020q1-summary



Demand for Li-ion batteries over years

Energies 2023, 16(3), 1365



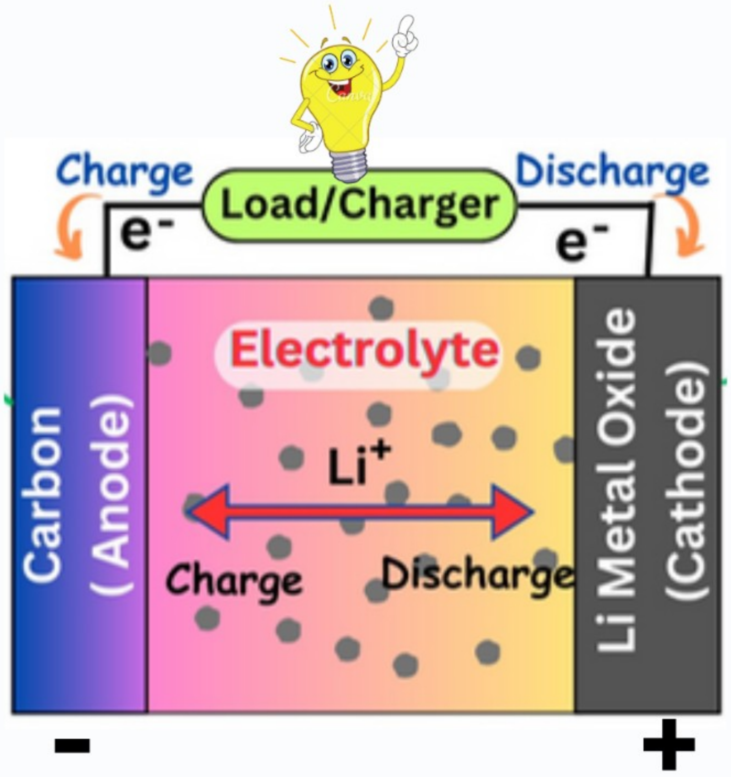
Energy and power densities of rechargeable batteries.

Energy Environ. Sci., 2010,3, 174-189

- High specific energy and load capabilities.
- Long cycle life
- High capacity, low internal resistance
- Simple charge algorithms.
- Low self-discharge rates

2. Li-ion battery: Challenges

National Science Centre Poland



Extra Li+ accumulate on the anode surface and cannot be absorbed in time.

Challenges in Liquid Electrolyte

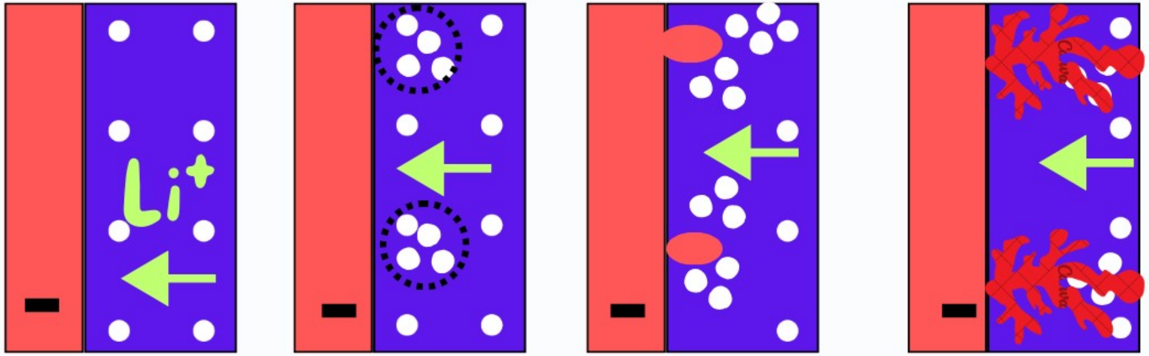
- solid-electrolyte interphase (SEI),
- electrode dissolution
- corrosion
- electrolyte flammability.

Benefits of Solid State electrolyte (SSE)

- Non-volatilization
- High-temperature resistance
- No corrosion
- No explosion risk
- Low reaction activity w/ Li

Dendrite growth

During Charging



Ion accumulation

3. Phase field Model Formulations

ButlerVolmer equation

$$R_{elec} = -L_\eta h_{int}\left\{\exp\left[\frac{(1-a)zF\xi}{RT}\right] - \frac{c_{Li^+}}{c_{oLi^+}}\exp\left[-\frac{azF\xi}{RT}\right]\right\}$$

Parameters		Value
Interfacial mobility	L_σ	$2.5 \times 10^{-6}\ \mathrm{m^3/(J \times s)}$
Kinetic coefficient	L_η	$1\ /\mathrm{s}$
Interfacial energy	σ	$0.5\ \mathrm{J/m^2}$
Interface thickness	δ	$1\ \mu\mathrm{m}$
Transfer coefficient	a	0.5

Li+ Diffusivity:

Electrode	D_{ms}	$3.197 \times 10^{-13}\ \mathrm{m^2/s}$
Electrolyte	D_{yt}	$3.197 \times 10^{-10}\ \mathrm{m^2/s}$

Site Density:

Electrode	C_{ms}	$7.64 \times 10^4\ \mathrm{mol/m^3}$
Electrolyte	C_{yt}	$1.44 \times 10^4\ \mathrm{mol/m^3}$
Bulk Conc.	C_o	$10^3\ \mathrm{mol/m^3}$

Conductivity:

Electrode	λ_{ms}	$10^7\ \mathrm{S/m}$
Electrolyte	λ_{yt}	$1.19\ \mathrm{S/m}$

1. Non-conserved order parameters

$$\frac{\partial \eta_\tau}{\partial t} = -L_{int}\left(\frac{\partial f_{\mathrm{bulk}}}{\partial \eta_\tau} + \frac{\partial f_{\mathrm{el}}}{\partial \eta_\tau} + \frac{\partial f_o}{\partial \eta_\tau} - \nabla \cdot \frac{\partial f_{\mathrm{grad}}}{\partial(\nabla \eta_\tau)}\right) + \underbrace{R_{elec}}_{\text{ElectroChemical Reaction rate}}$$

Moelans, Acta Materialia 59 (3), 1077-1086

Chen et. al., 2015, Journal of Power Sources, 376-385

2. Concentration field

Li- atoms is immobile without diffusion. ElectroChemical reaction serves as a source term driving the evolution of Li+ cations

Nernst-Plank Equation:

$$\frac{\partial c_{\mathrm{Li}}}{\partial t} = \nabla \cdot \left(D_{\mathrm{i}}^{\mathrm{eff}}\,\nabla c_{\mathrm{Li}} + \frac{D_{\mathrm{i}}^{\mathrm{eff}}}{RT} zFc_{\mathrm{Li}}\,\nabla\Phi\right) - \underbrace{\frac{C_{ms}}{C_o}\frac{\partial \eta}{\partial t}}_{\text{Ion consumption rate}}$$

Hu, S. Y., et al. Calphad 31.2 (2007): 303-312.

3. Electric potential

Poisson Equation:

$$\nabla \cdot \lambda_{\mathrm{eff}}\,\nabla\phi\,(r,t) = \underbrace{nFC_{\mathrm{ms}}}_{\text{Source Term}}\frac{\partial \eta}{\partial t}$$

4. Numerical implementations

National Science Centre Poland

Phase Field

MOOSE

An open-source, parallel FEM framework

Mesh adaptivity:

Mesh size:	6 μm
h-refinement:	2

Time adaptivity:

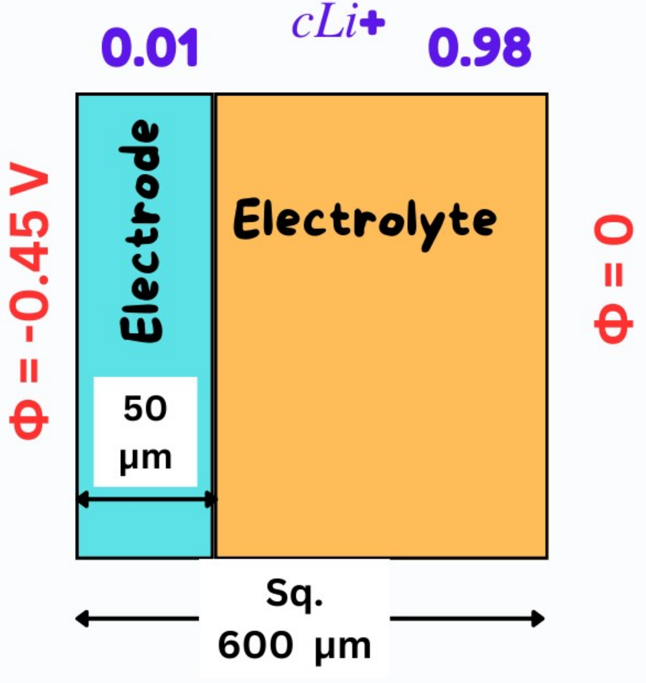
dt:	1 ms
growth factor:	1.1
cutback factor:	0.8

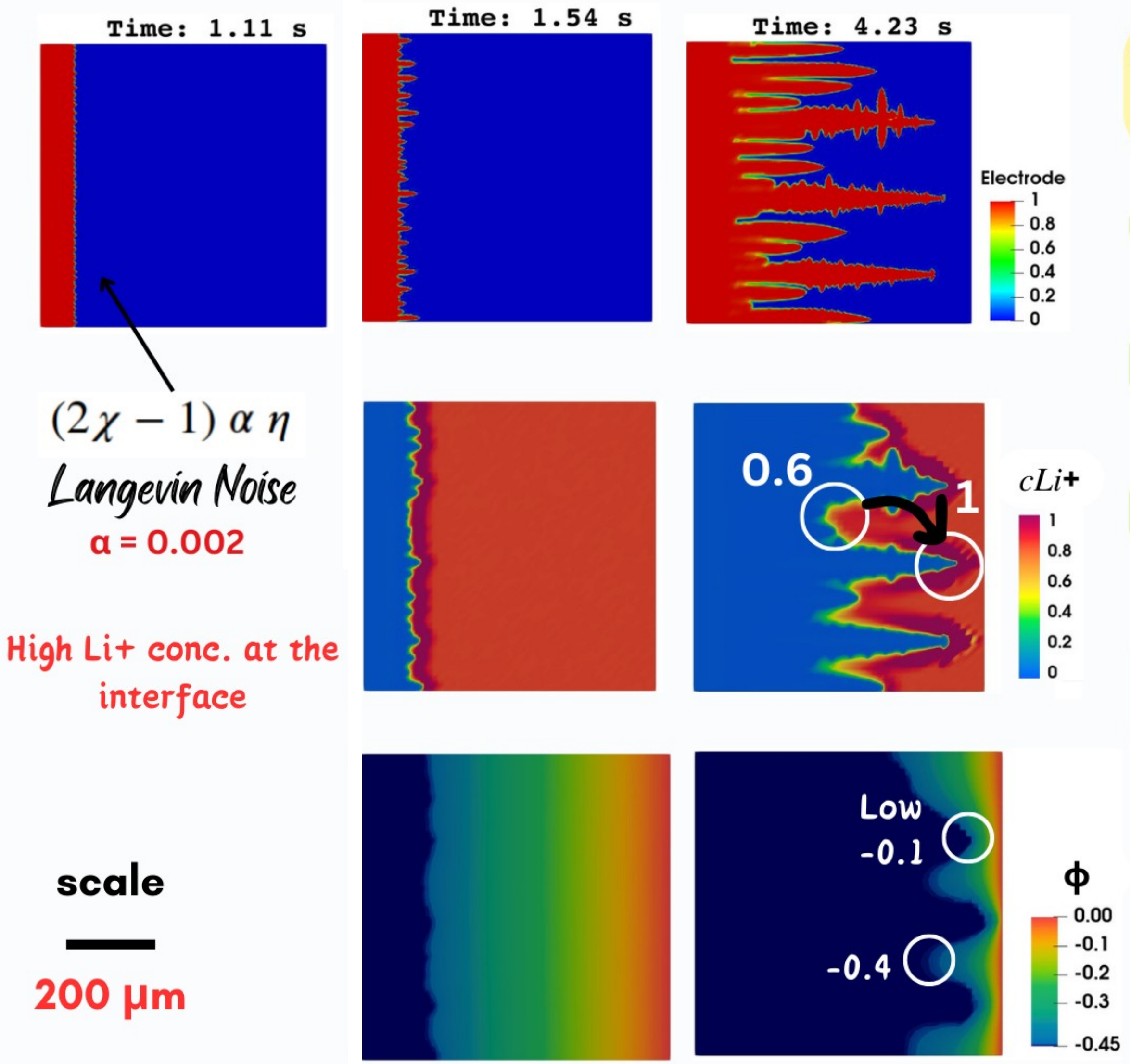
Solution method: Preconditioned JFNK

domain decomposition: The Additive Schwartz Method (ASM)

linear tolerance:	10^{-4}
nonlinear relative tolerance:	10^{-10}
nonlinear absolute tolerance:	10^{-11}

Geometry setup





5. Discussions: Fields and Driving Force (DF)

ϕ is uniform at electrode regions

The tips of deposits have larger cLi+ and ϕ gradients

At tip: Electric field towards vertical direction in addition to horizontal.

Electrodeposition because od ionic transfer from lower cLi+ to higher cLi+. (from valley towards tips)

Overpotential (significant variable in DF) depends on cLi+ and ϕ

5. Discussions: Thermodynamic aspects

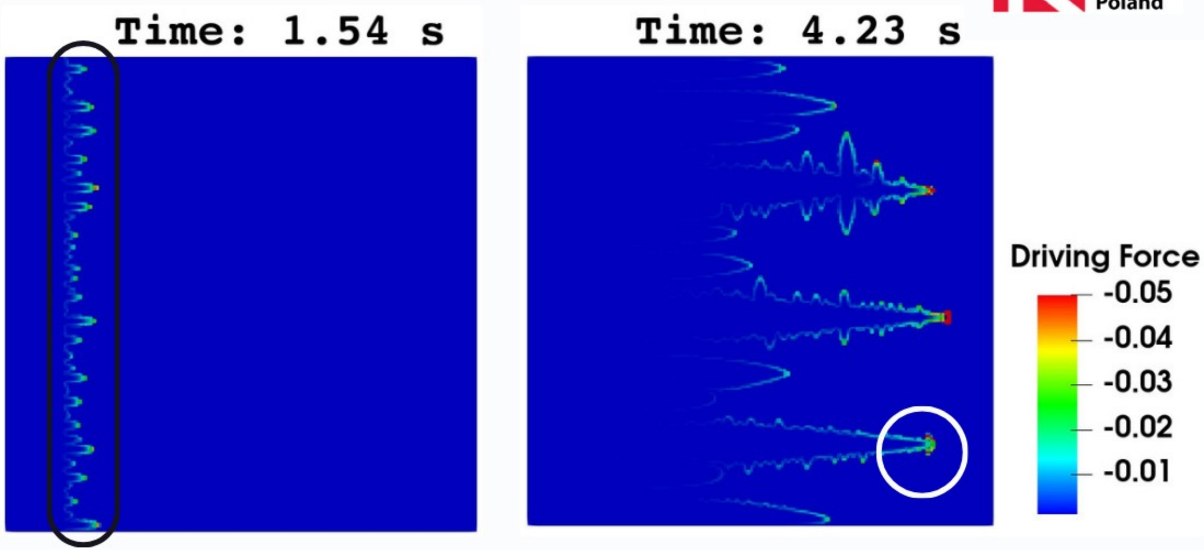
National Science Centre Poland

Bulk free energy: Double well function to describe equillibrum for electrode and electrolyte.

$$f_{\text{bulk}} = c_{Li^+}^2 \cdot (1 - c_{Li^+})^2$$

Driving Energy

- **Interfacial Thermal Energy** $\approx$ **0 for applied electrostatic field**
- **Thermodynamic DF because of electrod reaction**



Electrochemical reaction only occurs at interface

Large DF at tips compared to valley.

Nonlinear dendrite growth kinetics

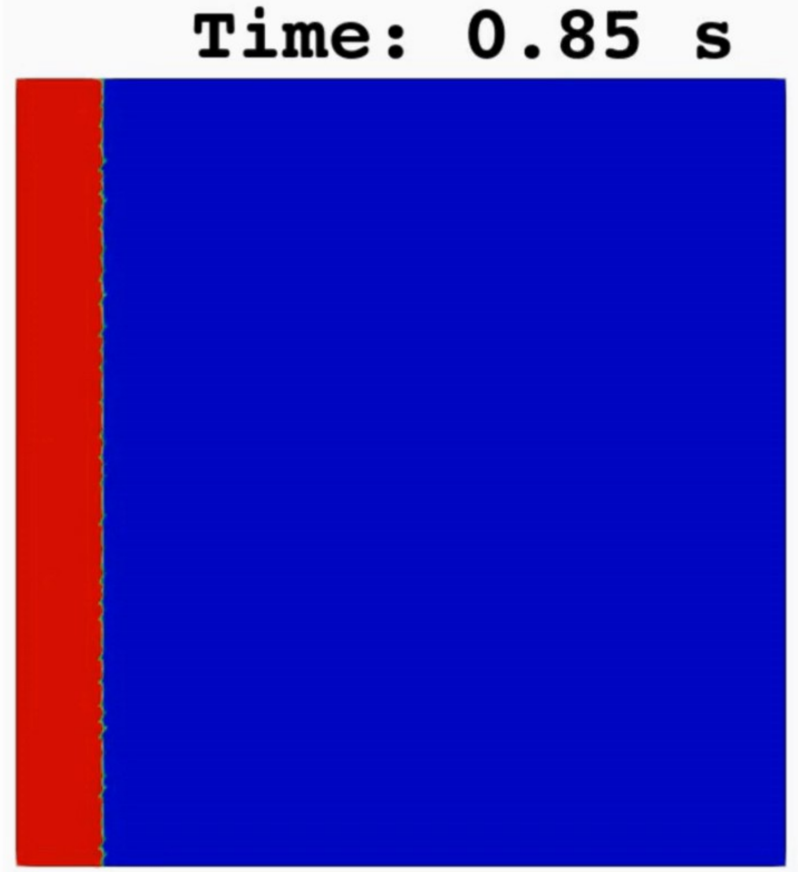
$$R_{elec} = -L_\eta h_{int}\left\{\exp\left[\frac{(1-a)zF\xi}{RT}\right] - \frac{c_{Li^+}}{c_{oLi^+}}\exp\left[-\frac{azF\xi}{RT}\right]\right\}$$

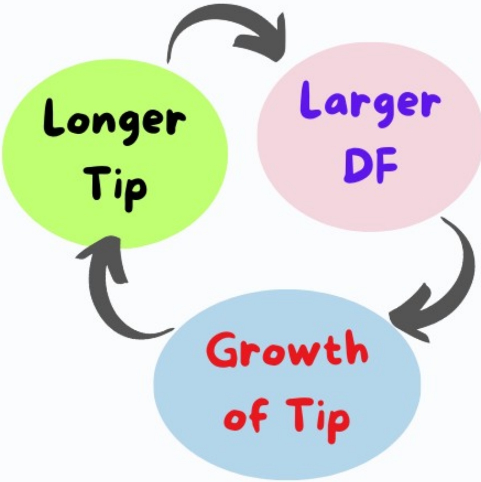
$$\xi = \Phi - \underbrace{\cancel{\Phi_{eq}}}_{0}$$

DF exponential function of Φ

National Science Centre Poland

6. Video for Spatio-temporal Description of Dendrite Growth



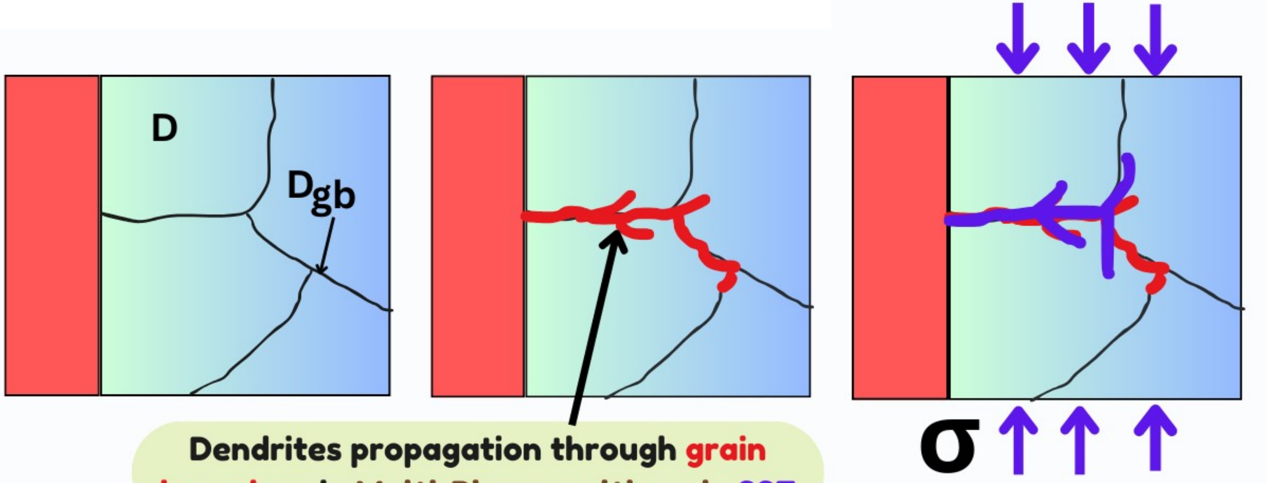


Scale

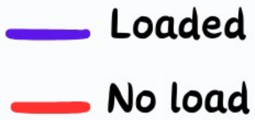
200 μm

Larger DF facilitates tip Splits

7. Work in Progress: Dendrite in Solid State Electrolyte (SSE)



Dendrites propagation through grain boundary in Multi-Phase multi-grain SSE



Dendrite deflects towards the direction of applied loads

Fincher et al., Joule 6, 2794–2809

This work is supported by National Science Centre Poland

8. Future Work

- Application of model in SSE with appropriate compressive stress
- Compare dendrite growth over different stress values.
- Modeling multi-grain SSE phase.

Thank you