Mathematical modeling for all-solid-state battery: Coordinate-free structural tensor

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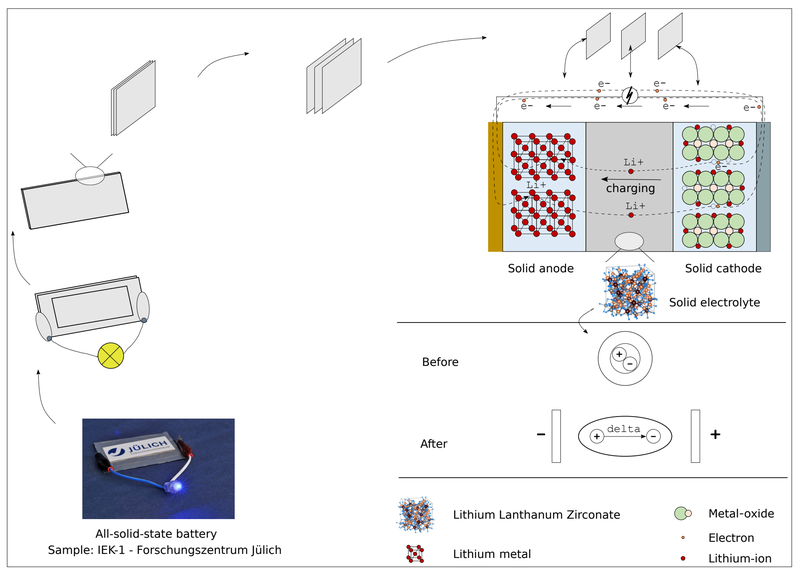
All-solid-state battery

Rechargeable Lithium-ion battery (LIB) stays at the heart of every energy storage system and electric vehicle. Undoubtedly, LIB benefits human life efficiently as well as friendly-environment. Besides, a more advanced LIB, so-called **all-solid-state battery** (ASSB), is introduced recently as ASSB is expected with non-inflammation and non-explosion as seen in common LIBs. Yet, defect due to polarization is one natural phenomenon of **solid electrolyte** (SE) to be tackled.

This poster is aimed to model the polarized SE with the use of **structural tensor**.



A sample of a typical all-solid-state battery and its non-scale hierarchical insight into structural layers.

A typical LIB includes three main components: cathode, anode and electrolyte. Different types of LIB have a variation of constitutive material composed of battery. An ASSB means that the three main components are **all made of solid material**.

Modeling goal

Two main goals to model the solid electrolyte part of the all-solid-state battery is as follows:

1. To capture the **preferred direction** behavior of the solid electrolyte due to electric potential.
2. To satisfy **thermodynamic consistency**:
   - Conservation of mass, linear & angular momentum and energy for the solid electrolyte.
   - Entropy inequality is guaranteed with sharper conditions, which lead to constitutive equation.

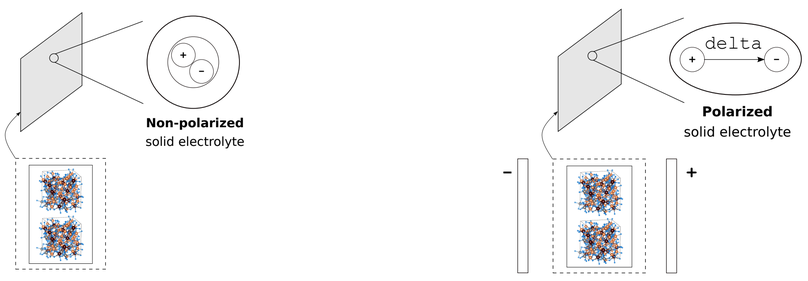
Continuum physics kinematic

Green-Lagrange strain tensor $\boldsymbol{E}$ with respect to **small** displacement $\partial \boldsymbol{u}/\partial \boldsymbol{\xi} = \mathcal{O}(\epsilon),\ \epsilon \ll 1$:

$$\boldsymbol{E} = \frac{1}{2}(\boldsymbol{F}^\top \boldsymbol{F} - \boldsymbol{I}) = \frac{1}{2}\left(\frac{\partial \boldsymbol{u}}{\partial \boldsymbol{\xi}} + \left(\frac{\partial \boldsymbol{u}}{\partial \boldsymbol{\xi}}\right)^\top + \underbrace{\left(\frac{\partial \boldsymbol{u}}{\partial \boldsymbol{\xi}}\right)^\top \left(\frac{\partial \boldsymbol{u}}{\partial \boldsymbol{\xi}}\right)}_{\text{Neglected}}\right) \rightarrow\ \boldsymbol{\varepsilon} := \frac{1}{2}\left(\frac{\partial \boldsymbol{u}}{\partial \boldsymbol{\xi}} + \left(\frac{\partial \boldsymbol{u}}{\partial \boldsymbol{\xi}}\right)^\top\right)$$

Polarization phenomenon

Due to a source of electric potential pointing from cathode $(+)$ to anode $(-)$ pole, a uniform electric field created has suppressed on the SE occupied between these two poles. Consequently, SE yields to a **preferred direction** under external deformations such as mechanical loading forces.



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Mathematical model

Constitutive equation is first derived from considering local balance laws and enforcing sharper conditions to entropy inequality.

- Local balance laws governing the infinitesimal elasticity embedded structural tensor:

Balance of mass	$\dot{\rho} + \rho\ \mathrm{div}\boldsymbol{v} = 0$
Balance of linear momentum	$\rho\dot{\boldsymbol{v}} = \mathrm{div}\boldsymbol{\pi} + \rho\boldsymbol{b}$
Balance of angular momentum	$\boldsymbol{\pi}^\top = \boldsymbol{\pi}$
Balance of energy	$\rho\dot{e} = \boldsymbol{\pi} : \dot{\boldsymbol{\varepsilon}} + \rho r - \mathrm{div}\boldsymbol{q}$

- Entropy inequality

$$\rho\mathcal{D} := \boldsymbol{\pi} : \dot{\boldsymbol{\varepsilon}} - \rho\eta\dot{\theta} - \rho\dot{\Psi} - \frac{1}{\theta}\boldsymbol{q}\cdot\nabla\theta \geq 0$$

- Mathematical model:

PDE	$\pi_{ij,j} + \rho b_i = 0$
Kinematic relation	$\varepsilon_{kl} = \frac{1}{2}\left(\frac{\partial u_k}{\partial x_l} + \frac{\partial u_l}{\partial x_k}\right)$
Constitutive relation	$\pi_{ij} = \mathbb{C}_{ijkl}\ \varepsilon_{kl}$
Dirichlet BC	$u_i = \bar{u}_i$ on $\partial\Omega_{u_i}$
Neumann BC	$\pi_{ij}n_j = t_i$ on $\partial\Omega_{t_i}$

where

$$\begin{aligned}\mathbb{C}_{ijkl} &= \lambda\delta_{ij}\delta_{kl} + 2\mu_T\mathbb{I}_{ijkl} \\ &\quad + \alpha(\delta_{ij}M_{kl} + M_{ij}\delta_{kl}) + 2(\mu_L - \mu_T)\,[\mathbb{I}_{\boldsymbol{d}}]_{ijkl} + \beta M_{ij}M_{kl} \\ [\mathbb{I}_{\boldsymbol{d}}]_{ijkl} &= \frac{1}{2}(d_i\delta_{jl}d_k + d_i\delta_{jk}d_l + d_j\delta_{ik}d_l + d_j\delta_{il}d_k) \\ \mathbb{I}_{ijkl} &= \frac{1}{2}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\end{aligned}$$

Structural tensor

SE microstructure with structural tensor $\boldsymbol{M} = \boldsymbol{d}\otimes\boldsymbol{d}$ is defined by a symmetry group $\mathbb{G}$:

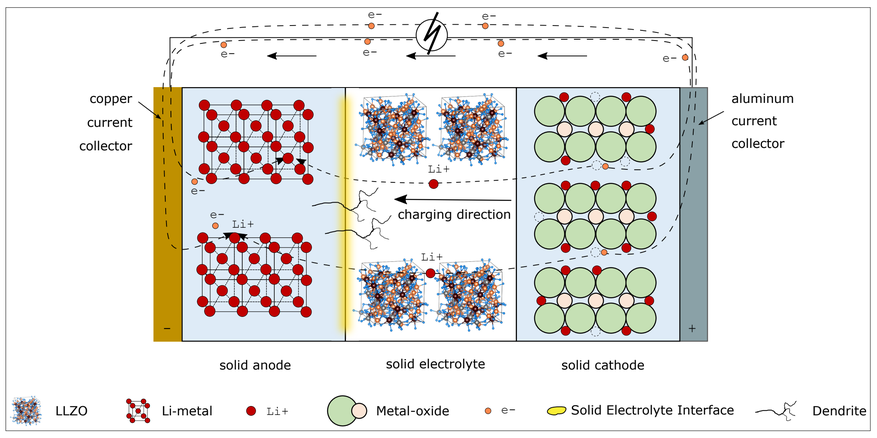
$$\mathbb{G} := \{\boldsymbol{Q}_{\|_d}, \boldsymbol{Q}_{\perp_d}\} \subset \mathcal{O}(3),$$

which leads to invariant free energy function $\hat{\Psi}$ under rotations followed by group $\mathbb{G}$:

$$\hat{\Psi}(\boldsymbol{\varepsilon}, \boldsymbol{M}) = \hat{\Psi}(\boldsymbol{Q}\boldsymbol{\varepsilon}\boldsymbol{Q}^\top, \boldsymbol{Q}\boldsymbol{M}\boldsymbol{Q}^\top) = \hat{\Psi}(\boldsymbol{\varepsilon}, \boldsymbol{M}) \quad \forall\ \boldsymbol{Q} \in \mathbb{G}.$$

Next steps and future direction

- Time-dependent implementation, numerical analysis, verification and validation.
- Explicit description of coordinate-based polarization variation.
- Bridging scale into quantum physics: Update information from quantum for continuum.
- Capture a phenomenon so-called **dendrite formation**:



Dendrite formation: After a several number of charging cycles, dendrite branches are slowly formed and developed from Solid electrolyte interface (SEI) through grain boundaries.

References

[1] Vo T. *Modeling the swelling phenomena of lithium-ion battery cells based on a numerical chemo-mechanical coupled approach*. Master thesis, 2018.

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