Computational homogenization of the electro-chemically coupled multi-scale transport of Li-ions in structural battery electrolytes

Vinh Tu1,∗, Fredrik Larsson1, Kenneth Runesson1, and Ralf Jänicke1
1 Chalmers University of Technology, Division of Material and Computational Mechanics
Chalmersplatsen 4, 412 96 Göteborg

The structural battery electrolyte (SBE) is a crucial component for the structural battery, which is an innovative energy storage device. While the SBE must allow for ion transport, it must also contribute to the structural integrity of the battery. In this contribution, we study the electro-chemical properties of the SBE using finite element analysis. For the governing equations, we use Ampere’s law in terms of a balance equation, and also the mass continuity equation of ions, which in the end results in a fully coupled transient multiphysics problem. Due to the strong heterogeneities in the SBE microstructure, a multi-scale approach is adopted.

1 Structural battery electrolyte

The structural battery is a new multifunctional material with simultaneous load bearing and energy storage functionality. This material can be realized by utilizing carbon fibers as structural reinforcement materials and electrode components [1, 2]. The motivation behind using such a material is that large weight and volume savings can be achieved when different needs are addressed by a single multifunctional material instead of separate subsystems [2].

In this contribution, we will focus on the structural battery electrolyte (SBE), which is a crucial component for the structural battery. The SBE must be electrically insulating, but ioniically conductive, and at the same time be able to carry mechanical loads. In this case, the SBE is a highly porous solid polymer matrix, where the pores are interconnected and form a complex channel system that contains liquid electrolyte [3]. The aim of this contribution is to study the SBE using finite element analysis.

2 Governing equations

The ions in the structural electrolyte are affected by the electrical fields that are present in the structural power composite, but they also undergo diffusion due to concentration gradients. Clearly, such interactions correspond to an electro-chemically coupled multiphysics problem. We formulate Ampere’s law in terms of a balance equation and the mass continuity equation of the ions

\[ (\dot{d} + i) \cdot \nabla = 0 \quad \text{in} \quad \Omega_i, \]  
\[ \dot{c}_\alpha + j_\alpha \cdot \nabla = 0 \quad \text{in} \quad \Omega_l, \]  
\[ d \cdot \nabla = 0 \quad \text{in} \quad \Omega_s, \]  

where the index \( \alpha = 1, 2, ..., N_\alpha \) refers to different ion species. The corresponding constitutive relations entail the electric flux density \( d := \epsilon \cdot E \), electric field \( E[\varphi] := -\nabla \varphi \), current density \( i := \sum_{\alpha=1}^{N_\alpha} z_\alpha \cdot \dot{j}_\alpha \), ion mass flux \( j_\alpha := -M_\alpha \cdot (\nabla \mu_\alpha + z_\alpha \nabla \varphi) \), and linearized ion concentration \( c \approx \frac{\dot{c}_\alpha}{\mu_\alpha} \). The symbols \( \varphi \), \( \mu \), \( \epsilon \), \( z_\alpha \) and \( M_\alpha \) correspond to the electric potential, chemical potential, electric permittivity, electric charge of ion, and mobility of ion respectively.

It can be seen that the full domain is split into two parts \( \Omega = \Omega_l \cup \Omega_s \); the liquid domain \( \Omega_l \) and the solid domain \( \Omega_s \). Since we assume that no ion transport can occur in the solid phase, we restrict the mass continuity equation to the liquid domain. However, we still allow for the electric field to penetrate through all medium. Thus, (1) corresponds to Ampere’s law for the liquid domain, and (2) is the mass continuity equation of ions in the liquid domain. Equation (3), which represents Ampere’s law in the solid domain, collapses into the homogeneous Gauss’s law since there is no ion transport.

3 Multi-scale approach

Since the structural electrolyte is a highly porous solid polymer matrix with a complex pore channel system, it is computationally infeasible to fully resolve the domain, especially in a fully coupled transient 3D analysis. One way to tackle this issue is to convert the single-scale problem into a two-scale problem. By introducing a micro-scale and a macro-scale, we can first solve the governing equations for a Representative Volume Element (RVE) containing the fine features on the micro-scale, and then use computational homogenization to obtain the corresponding average macro-scale response.

The starting point for the multi-scale approach is the fully resolved single-scale weak format of the above-mentioned governing equations. We convert the single-scale problem into a two-scale problem via Variationally Consistent Homogenization.
by introducing the RVE volume averaging operator \( \langle \bullet \rangle = \frac{1}{|\Omega|} \int_{\Omega} \bullet \, d\Omega \), which we use to enforce the running average approximation \( \int_{\Omega} \bullet \, d\Omega \approx \int_{\Omega} \langle \bullet \rangle \, d\Omega \). In the next step, we separate the scales of \( \varphi \) and \( \mu \) via first-order homogenization

\[
\begin{align*}
\bullet(x) &= \bullet^M(x) + \bullet^S(x) & x & \in \Omega^M, \\
\bullet^M(x) &= \bullet + \nabla \cdot \left[ x - \bar{x} \right] & x & \in \Omega^M,
\end{align*}
\]

where the superscripts M and S represent the macro-scale and micro-scale respectively. Ultimately, we end up with a two-scale problem where \( \delta \varphi^S \in \mathbb{P}^{\beta,S} \), \( \delta \varphi \in \mathbb{P}^\beta \), \( \delta \mu^S \in \mathbb{M}^{\alpha,S} \), and \( \delta \mu_\alpha \in \mathbb{M}^\alpha \)

\[
\int_{\Omega} \langle \nabla \delta \varphi \cdot \mathbf{e} \cdot \nabla \varphi \rangle \, d\Omega + \sum_{\alpha} \left[ \int_{\Omega} \langle \nabla \delta \varphi \cdot M_\alpha \cdot \nabla \varphi \rangle \, d\Omega + z_\alpha \int_{\Omega} \langle \nabla \delta \varphi \cdot \mathbf{M}_\alpha \cdot \nabla \mu_\alpha \rangle \, d\Omega \right] = -\int_{\Gamma_N}^\alpha \delta \varphi \, h^p \, d\Gamma, \\
\int_{\Omega} \langle \delta \mu_\alpha \circ \mathbf{e}_\alpha \rangle \, d\Omega + \int_{\Omega} \langle \nabla \delta \mu_\alpha \cdot M_\alpha \cdot \nabla \varphi \rangle \, d\Omega + z_\alpha \int_{\Omega} \langle \nabla \delta \mu_\alpha \cdot \mathbf{M}_\alpha \cdot \nabla \varphi \rangle \, d\Omega = -\int_{\Gamma_N}^\alpha \delta \mu_\alpha \, j^p \, d\Gamma.
\]

Note that only the weak formats of (1) and (2) are considered here, since (3) can be handled analogously.

4 Preliminary numerical results from simulation of an SBE cross-section

We extract the micro-scale problem from (6) and (7), and then solve it for a 2D RVE that represents the SBE cross-section on the micro-scale. We use periodic boundary conditions and consider only one single species \( \alpha = 1 \). The loading condition is explicitly given by the macro-scale part of the chemical potential as \( \mu^M = \mu + \nabla \mu [x - \bar{x}] \). Here, we impose a macro-scale chemical potential unit gradient \( \nabla \mu \) in x-direction. This loading case is smoothly ramped up from \( t = 0 \) s to \( t = 10^{-9} \) s. Appropriate numerical values are used for the various material parameters, and for simplicity all units are kept dimensionless.

![Simulation of an SBE cross-section. Simulations performed using the commercial software COMSOL Multiphysics.](image)

In the plots with the homogenized quantities, we can observe a relaxation effect where the response is still on-going despite the ramping load being fully active already at \( t = 10^{-9} \) s.

References

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