Purpose of the research: understand and quantify impact of simplifications in macrohomogeneous models by comparison to structure-resolving microheterogeneous models

Content
- introduction to macrohomogeneous and microheterogeneous approaches
- code to code comparison – systematic and results
- key messages and outlook
Macrohomogenous pseudo 2D approach (BDS)

- **1D solid (spherical):** $r \sim 5\mu m$
  - **Li-Ion flux:** electrolyte $\leftrightarrow$ solid

- **1D electrolyte:** $x \sim 130\mu m$

**Disambiguation:**
- Properties of material composite (solid + pore/electrolyte) are homogenized ("effective properties")
- Domains (electrodes, separator) subdivided (discretized) into control volumes with effective, macroscopic composite properties.
Microheterogenous 3D approach (OpelLib)

disambiguation:
• structure (solid and pore morphology) spatially resolved in 3D computational domain
• transport equations solved separately in solid (active material) and pore (electrolyte) phases (interface coupling by Butler-Volmer)
• bulk properties instead of effective properties used (exception: separator)

transport in solid (active particles):
\[
\frac{\partial c_s}{\partial t} = \nabla \cdot \left( D_s \nabla c_s \right)
\]
\[
0 = \nabla \cdot \left( \kappa_s \nabla \phi_s \right)
\]

transport in pore (electrolyte):
\[
\frac{\partial c_e}{\partial t} = \nabla \cdot \left( D_e \nabla c_e - \frac{I}{F} \right)
\]
\[
0 = \nabla \cdot \left( \kappa_e \nabla \phi_e + \kappa_e \left( \frac{I_T - 1}{F} \right) \left( 1 + \frac{\partial \log f}{\partial \log c} \right) \nabla (\log c) \right)
\]

coupling at solid/electrolyte interface (Butler-Volmer):
\[
i_{se} = k c^{\alpha_a} c_s^{\alpha_s} (c_{s, max} - c_s)^{\nu_c} \left( e^{\frac{-a_F}{RT} \eta} - e^{\frac{-a_F}{RT} \eta_s} \right)
\]

isothermal battery model; reference: A. Latz, J. Zausch, Thermodynamic consistent transport theory of Li-ion batteries, J. Power Sources 196 (2011) 3296-3302
 Parameter Set used for code to code comparison

<table>
<thead>
<tr>
<th>domain</th>
<th>parameter</th>
<th>value</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>positive electrode</td>
<td>Range of Stoichiometry</td>
<td>0.405 ... ~1</td>
<td>representative value for technical application</td>
</tr>
<tr>
<td></td>
<td>Li diffusion coefficient</td>
<td>$1.10^{-9}$ cm²/s</td>
<td>Jeong et al., J. Power Sources 102 (2001)</td>
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<td>electron conductivity</td>
<td>0.038 S/cm</td>
<td>Doyle et al., J. Electrochem. Soc. 143 (1996)</td>
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<td>reaction rate constant</td>
<td>$0.2$ (A/cm²)/(mol/cm³)^1.5</td>
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<td>negative electrode</td>
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<td>~0 ... 0.64</td>
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<td>Li diffusion coefficient</td>
<td>$3.9\cdot10^{-10}$ cm²/s</td>
<td>Wen et al., J. Electrochem. Soc. 126 (1979)</td>
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<tr>
<td></td>
<td>electron conductivity</td>
<td>1 S/cm</td>
<td>Doyle et al., J. Electrochem. Soc. 143 (1996)</td>
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<tr>
<td></td>
<td>reaction rate constant</td>
<td>$0.2$ (A/cm²)/(mol/cm³)^1.5</td>
<td>representative value for technical application</td>
</tr>
<tr>
<td>electrolyte</td>
<td>initial salt concentration</td>
<td>$1000\cdot10^{-6}$ mol/cm³</td>
<td>representative value for technical application</td>
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<td></td>
<td>activity term</td>
<td>1</td>
<td>Simplification for model comparison</td>
</tr>
<tr>
<td></td>
<td>ion conductivity</td>
<td>f (c)</td>
<td>Albertus et al., J. Electrochem. Soc. 156 (2009)</td>
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<tr>
<td></td>
<td>Li diffusion coefficient</td>
<td>$7.5\cdot10^{-6}$ cm²/s</td>
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<tr>
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<td>transference number</td>
<td>0.363</td>
<td>Doyle et al., J. Electrochem. Soc. 143 (1996)</td>
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<tr>
<td>separator</td>
<td>MacMullin number</td>
<td>4.4432</td>
<td>(1/(porosity)^1.5)</td>
</tr>
</tbody>
</table>

**macrohomogenous model requires structure related geometrical data:**
- diffusion length solid / surface area solid / porosity / tortuosity
Systematic of macrohomogeneous vs. microheterogeneous code to code comparison

- **Starting point**: pseudo 2D approach utilizes porous media theory which assumes that particles are small relative to material thickness (homogeneity assumption): \( d_{\text{particle}} \ll l_{\text{electrode}} \)
- **Approach**: compare results from macrohomogeneous and microheterogeneous simulations for consistent case set-up
- **Systematic**: increase electrode structure complexity from simple generic (pearl necklace arrangement of spherical active particles reflecting pseudo 2D approach) to complex realistic (random arrangement of non-spherical primary particles)

**Case 0 (reference):**
- pearl necklace of 5 spherical particles
- reflects pseudo 2D approach for 5 control volumes

**Case 1:**
- “rod” comprised of 10 spherical particles having 50% overlap

**Case 2:**
- pearl necklace of 10 spherical particles of different diameter
- “forces” 2 particles into one control volume

**Case 3:**
- random complex structure based on spherical base particles (“high” porosity)

**Case 4:**
- random complex structure with non-spherical base particle (low porosity)
Microheterogenous 3D-model based on macrohomogenous Pseudo-2D approach

geometrical parameter (case 0)

- footprint: 10 x 10 µm²
- radius particle: 5 µm
- thickness active material: 50 µm

for n = 5 → one particle / control volume

homogenized properties:
- porosity = 1 – volume sphere / control volume
- surface active material = surface sphere
- tortuosity = 1 / porosity^{0.5} (Bruggeman)

screenshot OpelLib

- one electrode
- 0.25µm voxel resolution
- no homogenized properties
- tortuosity is a result

Li-Ion flux: electrolyte ↔ solid

Collector n = 5 homogenized properties anode Separator homogenized properties cathode Collector n = 5

x
Microheterogenous 3D-model based on macrohomogenous Pseudo-2D approach

results (case 0) for 1C:

absolute values

- the results of OpelLib and BDS are in good agreement

difference in voltage between models

- the different resolutions of OpelLib (800,000 control volumes) and BDS (1D electrolyte: 15 nodes, 1D solid: 5 nodes) correspond with the computational effort (hours vs. seconds)
Influence of Discretization on macrohomogenous Pseudo-2D approach

expectation: discretization affects result

results (case 0) for 1C: absolute values

observations
- numerically: a refinement of the grid does not influence the results with the given parameter set
- physical: no parameter adjustment necessary to account for the “too small” volume

1D electrolyte: volume fitted to sphere

1D electrolyte: volume to small for sphere
Microheterogenous 3D-model based on macrohomogenous Pseudo-2D approach

**case 1**
- electrode
- 10 particles with r = 5µm

**case 2**
- 5 particles with r = 3.5µm
- 5 particles with r = 1.5µm

**results for 1C**
- Absolute values
- Difference in voltage between models
Macrohomogenous Pseudo-2D Model based on microheterogenous 3D approach

case 3
OpelLib structure:
non-overlapping spherical particles
4 µm diameter
random arrangement
derived from structure:
- porosity (59.1%)
- specific surface area
used as input for BDS

case 0 to 3:
good agreement between OpelLib and BDS
best match for case 1 (overlapping spheres),
with lowest „fraction“ of microstructural heterogeneity

absolute values
difference in voltage

1C

10C
Macrohomogenous Pseudo-2D Model based on microheterogenous 3D approach

case 4
OpelLib structure:
overlapping planar pentahedral particles
2 µm thick, 5µm “radius”
random arrangement

derived from structure:
- porosity (30.3%)
- specific surface area
- particle size distribution
used as input for BDS

most realistic case in terms of morphology and porosity yields worst agreement between OpelLib and BDS

absolute values

difference in voltage
Calibration of macrohomogeneous model to microheterogeneous results

- hypothesis: complex pore/particle structure not well represented in macrohomogeneous model → calibrate macrohomogeneous model with structure parameters

<table>
<thead>
<tr>
<th>BDS ref</th>
<th>calibration</th>
</tr>
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<tbody>
<tr>
<td>a) specific surface</td>
<td>OpelLib</td>
</tr>
<tr>
<td>b) diffusion length</td>
<td>OpelLib (PSD)</td>
</tr>
<tr>
<td>c) tortuosity = 1/porosity^n</td>
<td>n = 0.5, n = 2.1</td>
</tr>
</tbody>
</table>

- observation: comparable improvements can be achieved by either calibrating diffusion length (1D solid) or tortuosity (1D electrolyte) → ambiguity undesired for predictive simulation
Parameterization of macrohomogeneous model with microheterogeneous results

Tortuosity of pore structure can be derived as input for BDS diagrams. These diagrams show the results when applying the equivalent exponent (n=1.9) in BDS.

**Hypothesis:**
Effective lithium ion transport resistance depends on rate and SOC (local and global). This cannot be captured by a rigid parameterization of a simplified structure model (e.g., spheres).
Next steps

**Next steps:**
- DoE of transport parameters and analysis of local conditions needed to quantify structure contribution to macro/micro discrepancy
- Experimental validation of models ("comparison is not verification is not validation")

Preliminary results of microheterogeneous simulation suggest transport limitations at high charge/discharge rates may cause early performance drop.
Key Messages

- simple model structures and “low” charge/discharge rates
  → macrohomogeneous and microheterogeneous approaches match well
- complex model structures and “high” charge/discharge rates
  → discrepancy of macrohomogeneous and microheterogeneous approaches
  → calibration w/ macrohomogeneous model parameters ambiguous
- microheterogeneous simulation results may provide sophisticated
  parameterization of macrohomogeneous model and maintain overall predictive
  capability
- challenge:
  appropriately derive macrohomogeneous parameters (e.g. specific surface,
  diffusion length) from μ-simulation results (e.g. PSD)
- outlook:
  consistently predictive process chain utilizing CPU-consuming
  microheterogeneous simulation to parameterize fast macrohomogeneous models
  for productive simulation runs