Quantitative Microstructure Characterization of a NMC Electrode

François L.E. Usseglio-Viretta
Kandler Smith

a National Renewable Energy Laboratory

Presented at the 231st ECS Meeting
New Orleans, Louisiana
May 30, 2017

NREL/PR-5400-68741
Outline

Characterization of NMC (already segmented) microstructures with a focus on numerical methods, bias/assumption, RVE size, and voxel size dependence

- Introducing original “level of details” parameters
- Volume fractions and connectivity
- Particle size
  - Calendaring effect
  - Correlate RVE size with standard deviation
  - Results from different methods compared
- Tortuosity factor
  - Voxel size and RVE analysis (including isotropy)
  - Introducing original two-step homogenization method
  - Calendaring effect
  - Spatial variation along electrode thickness.

Surface area results are in the annexes slides
Microstructures investigated

- **Un-calendared (UC) & Calendared (C) positive NMC**
  \(\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2\) electrode, with different composition of active material (wt 90%, 92%, 94%, and 96%).

Raw (X-ray tomographic microscopy) and binarized image available online (open-source data) on the ETH (Swiss Federal Institute of Technology Zurich) website.


- Secondary phase has not been identified (considered as pore)

- Total of **16 Volumes**

  Analyzed domain size: \(328.9 \times 328.9 \times A \ \mu m^3\)

  Equivalent domain size: \(B \times B \times B \ \mu m^3\)

<table>
<thead>
<tr>
<th>Composition of the active material (%)</th>
<th>Un-calendared electrode</th>
<th>Calendared electrode (300 bar)</th>
<th>Calendared electrode (600 bar)</th>
<th>Calendared electrode (2,000 bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>50.3 (176)</td>
<td>52.2 (178)</td>
<td>47.7 (173)</td>
<td>57.0 (183)</td>
</tr>
<tr>
<td>92</td>
<td>45.9 (171)</td>
<td>77.3 (203)</td>
<td>58.8 (185)</td>
<td>61.1 (188)</td>
</tr>
<tr>
<td>94</td>
<td>65.9 (192)</td>
<td>78.8 (204)</td>
<td>74.0 (200)</td>
<td>64.8 (191)</td>
</tr>
<tr>
<td>96</td>
<td>98.1 (220)</td>
<td>94.7 (217)</td>
<td>101.0 (222)</td>
<td>87.7 (212)</td>
</tr>
</tbody>
</table>

Voxel size: \(370 \times 370 \times 370 \ nm^3\)
Introducing parameters dedicated to evaluate the image quality

\[
\text{Edge volume ratio} = \begin{cases} 
1 - \frac{\text{Edge "volume"}}{\text{Phase volume}} \\
1 - \frac{\sum \bullet}{\sum \bullet + \sum \square}
\end{cases}
\]

Will increase if smooth interface

- Based upon edge detection
- Easy to interpretate: values ranges from 0 (poor) to 1 (ideal)
- Ideal to compare different data set image quality and different obs. techniques
Level of details of a microstructure

Introducing parameters dedicated to evaluate the image quality

Edge volume ratio

\[
\text{Edge volume ratio} = \left\{ \frac{1 - \text{Edge "volume"}}{\text{Phase volume}} \right\} \leq \frac{\sum \text{●} - \sum \text{● + □}}{1 - \sum \text{● + □}}
\]

One voxel particle volume ratio

\[
\text{One voxel particle volume ratio} = 1 - \frac{\text{Volume(\text{particle described by 1 voxel})}}{\text{Phase volume}}
\]

Will increase if smooth interface

Based upon edge detection
- Easy to interpretate: values ranges from 0 (poor) to 1 (ideal)
- Ideal to compare different data set image quality and different obs. techniques

- As expected, level of details are degrading monotonously with image resolution.
- High level of details have been achieved by Ebner group.
- Both phases exhibits similar values (2-phase data-set).
Results obtained on the 16 volumes (4 calendaring X 4 active material composition)

Porosity is ↘ when active material composition is ↗ (because secondary phase has been identified as pore) and when calendaring pressure is ↗

Volume fraction & connectivity

Pore

~50μm < RVE ε < ~100μm

NMC

~40μm < RVE ε < ~90μm

Each point (16) is a different volume.
Volume fraction & connectivity

Results obtained on the 16 volumes (4 calendaring X 4 active material composition)

Pore
\(~50\mu m < \text{RVE } \varepsilon < ~100\mu m\)

NMC
\(~40\mu m < \text{RVE } \varepsilon < ~90\mu m\)

Porosity is \(\downarrow\) when active material composition is \(\uparrow\) (because secondary phase has been identified as pore) and when calendaring pressure is \(\uparrow\)

Each point (16) is a different volume.

Pore

NMC

Very high connectivity (percolation) is achieved. Solid particles have a better connectivity when calendaring pressure is \(\uparrow\) and when active material composition is \(\uparrow\)

Results obtained on the 16 volumes (4 calendaring X 4 active material composition)
Volume fraction & connectivity

Edge effect induce a loss of percolation on small domains, especially for NMC

Unknown clusters are accumulating on subdomains → global amount of unknown voxel is increasing.

Volume fraction & connectivity

Edge effect induce a loss of percolation on small domains, especially for NMC

**Illustrated on NMC, 90 wt, 0 bar**

- Unknown clusters are replacing the main cluster
- Loss of percolation on small subdomains
- NMC small subdomains suffer from loss of percolation due to this edge effect. Pore is untouched.

Unknown clusters are accumulating on subdomains → global amount of unknown voxel is increasing.
This edge affects mainly the solid phase when calendaring pressure is not applied, as a result RVE for the connectivity is much more higher for the NMC.

Pore exhibits excellent connectivity even for small volume (RVE is < 45 μm for all volumes)

On the contrary, NMC need a larger volume to get connected. High calendaring pressure and active material composition reduce the RVE.
Particle size: spherical assumption (C-PSD)

Voxels are attributed to the largest sphere that contains them.

Underestimation of the size distribution is expected due to this particle shape assumption

Calendaring pressure significantly reduces the pore size. Slight effect on the NMC

Reduction of the pore size
Wide size distribution
Particle size: Representative volume element (RVE) size

Correlating RVE size of $d_{50}$ with particle size: $d_{50} \& \text{std}(d)$

NMC (RVE $D_{50}$) normalized with $d_{50}$

Each point (16) is a different volume.

Correlating RVE size of $d_{50}$ with particle size: $d_{50}$ & $\text{std}(d)$

RVE, by definition, must catch all heterogeneities of the medium → the more heterogeneous the medium is, the larger the RVE will be.

Simple rule $\text{RVE} = 14 \times d_{50}$ * is not enough for medium with a wide size distribution.

**Statistical approach**

- Based upon a **two-point correlation (covariance)** function.
- **Spherical assumption is no more used.** But less detail are available (no size distribution)
- Refinement added to the classic method to improve the determination of the mean particle and pore size.

**Alternative methods to avoid particle size underestimation**

Detailed in the back-up slides to save presentation time, and in the upcoming ECTS article.
Particle size: statistical approach & watershed method

Alternative methods to avoid particle size underestimation

**Statistical approach**

- Based upon a two-point correlation (covariance) function.
- **Spherical assumption is no more used.** But less detail are available (no size distribution)
- **Refinement added to the classic method to improve the determination of the mean particle and pore size.**

**Watershed method**

- Based upon an immersion approach, with a refinement to handle over-segmentation
- Distinct particles are identified without any shape assumption.

Detailed in the back-up slides to save presentation time, and in the upcoming ECTS article
Particle size: all three methods compared

Particle size difference illustrated on the 90 wt electrode with different compression level

C-PSD < statistical approach < watershed
Particle size: all three methods compared

Particle size difference illustrated on the 90 wt electrode with different compression level

All methods describe $D_{50}$ ↘ for the pore with compression

C-PSD < statistical approach < watershed

Ratio is quite high, but expected
~2.8 found be L. Holzer et al. JPS 196 (2011) 7076-7089

Ratio is higher for Pore than for NMC → Pore are less spherical than NMC particles. NMC are not so spherical.
Summary of RVE size

Quadratic polynomial surface fit on RVE size

<table>
<thead>
<tr>
<th>Pore RVE (µm)</th>
<th>Mean</th>
<th>Max</th>
<th>Std</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume fraction ε</td>
<td>63,9</td>
<td>97,1</td>
<td>13,7</td>
</tr>
<tr>
<td>Connectivity δ</td>
<td>38,9</td>
<td>44,3</td>
<td>3,4</td>
</tr>
<tr>
<td>Mean particle size $D_{50}$</td>
<td>73,2</td>
<td>123,1</td>
<td>20,3</td>
</tr>
<tr>
<td>Specific surface area $S_p$</td>
<td>79,5</td>
<td>123,3</td>
<td>20,9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>NMC RVE (µm)</th>
<th>Mean</th>
<th>Max</th>
<th>Std</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume fraction ε</td>
<td>62,1</td>
<td>88,4</td>
<td>16,6</td>
</tr>
<tr>
<td>Connectivity δ</td>
<td>50,9</td>
<td>90,6</td>
<td>17,6</td>
</tr>
<tr>
<td>Mean particle size $D_{50}$</td>
<td>69,6</td>
<td>105,8</td>
<td>13,4</td>
</tr>
<tr>
<td>Specific surface area $S_p$</td>
<td>78,3</td>
<td>123,7</td>
<td>19,3</td>
</tr>
</tbody>
</table>

RVE is property dependent
Factor of tortuosity: voxel size dependence analysis

- Both methods (FEM & neighbors difference) are converging to the same value.
- FEniCS has been used since it allows applying different boundary conditions.
- Save CPU time and memory: FEniCS with a linear interpolation and a voxel size of 740 nm.

Voxel size analyze performed on a pore subdomain (~185 × 185 × 50 μm³) of the 90 wt un-calendared electrode.

- **Tau factor** (open source) iteratively solves the Laplace equation, using a neighbors difference, with Dirichlet Boundary conditions and a great emphasis on speed convergence. [S.J. Cooper et al., Software X 5 (2016) 203-210]

- **FEniCS** (open source) solves steady-state Laplace equation with the finite elements method. Dirichlet BC used in this figure.
Concentration field calculated on the 96 wt calendared (2,000 bar) electrode, within the pore with mixed boundary condition.

$328.9 \times 328.9 \times 87.7 \, \mu m^3$

Voxel size: 740 nm
8,909,443 voxels & 13,026,509 degree of freedom for the pore.

CPU time: ~245 seconds (HPC)

Achieved with FEniCS open source software (Finite element method)
Factor of tortuosity: Representative volume element analysis

• **RVE analysis on** $\tau_{\text{through-plane dir.}}$ **with mixed BC (i.e. Dirichlet-Neumann)**

Illustrated on 90 wt, UC and C (2,000 bar) for both phases

For which domain’s size $\tau_{\text{through-plane dir.}}$ is stable?

---

Tortuosity table (the RVE are written in parentheses)

<table>
<thead>
<tr>
<th></th>
<th>Pore</th>
<th>NMC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tau_{\text{through-plane dir.}}$</td>
<td>$\tau_{\text{through-plane dir.}}$</td>
</tr>
<tr>
<td>UC</td>
<td>1.322 ($&lt;35.2 \mu m$)</td>
<td>5.379 (&gt;110.7 $\mu m$, std--15%)</td>
</tr>
<tr>
<td>90 wt UC</td>
<td>1.593 (42.2 $\mu m$)</td>
<td>3.597 (&gt;115.4 $\mu m$, std--10%)</td>
</tr>
</tbody>
</table>

RVE pore $<$ RVE solid &

$\tau \nearrow \Rightarrow \text{RVE} \nearrow$

Mean value subdomains $\neq$ value whole domain
Factor of tortuosity: Representative volume element analysis

- **RVE analysis on τ anisotropy with mixed BC**
  Illustrated on 90 wt, UC and C (2,000 bar) for both phases

  \[ \tau_{anisotropy} \approx RVE \tau_{through-plane dir} \]
  (While being inferior for the NMC)

<table>
<thead>
<tr>
<th></th>
<th>Pore</th>
<th>NMC</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \tau_{max} - \tau_{min} )</td>
<td>( UC )</td>
<td>( C ) (2000 bar)</td>
</tr>
<tr>
<td></td>
<td>0.030 (54.7 ( \mu )m)</td>
<td>0.091 (39.0 ( \mu )m)</td>
</tr>
</tbody>
</table>

Isotropy is expected since solid phase is made of quasi-spherical spheres with a random space distribution.

For which domain’s size \( \max\{\text{abs}(\tau_i - \tau_j)\} \) is stable?

For the un-calendared electrode, subdomains are anisotropic while whole domain is isotropic: isotropy emerges only for large volume.

Calendaring affects isotropy.

RVE on boundary conditions has been also evaluated (back-up slides)
Why factor of tortuosity obtained on subdomains differs from the whole domain?

Loss of percolation on small subdomains should increase tortuosity by creating local bottleneck at the edges…but we see the opposite.

That’s because taking the mean value (thus performed a **rule of mixture**) is a poor idea…it is true only when the subdomains are assembled in parallel with the flux (details in the annexes slides)
Factor of tortuosity: two-step homogenization numerical scheme

How to avoid using the mean value: two-step homogenization numerical scheme

Each subdomain is represented with a dense anisotropic coarse mesh

For each subdomain, $D_{x}^{\text{sub}}, D_{y}^{\text{sub}}$ and $D_{z}^{\text{sub}}$ are calculated (1\text{st} homogenization calculation)

$D_{z}^{\text{eff}}$ is calculated (2\text{nd} homogenization calculation)
Factor of tortuosity: two-step homogenization numerical scheme

How to avoid using the mean value: two-step homogenization numerical scheme

Whole domain

For each subdomain, $D_{x}^{\text{sub}}, D_{y}^{\text{sub}}$ and $D_{z}^{\text{sub}}$ are calculated (1st homogenization calculation)

Each subdomain is represented with a dense anisotropic coarse mesh

$D_{z}^{\text{eff}}$ is calculated (2nd homogenization calculation)

Even though this method suits better highly connected structure, it still gives a better estimation than the mean value.

Two-step homogenization: overestimation due to percolation loss
Mean value: underestimation due to misuse of rule of mixture
Factor of tortuosity: calendaring effect

Calendaring induce a general increase of the tortuosity, due to the decrease of the connected porosity (Bruggeman exponent 0.65) & a slight anisotropy between in-plane directions and through-plane direction (could be induced by a change of NMC particle shape)
Factor of tortuosity: along electrode thickness

Un-calendared electrode 90 wt, Pore, **cut in 6 slices**

Each individual thick slice has conserved its connectivity (edge effect insignificant)

Effective diff coefficient ranges from ~0.42 to 0.5.

Difference on tortuosity can be explained by porosity (Bruggeman exponent 0.73)

1D-macromodel could use such $\tau_z = f(z)$
Conclusions 1/2: numerical aspects

• RVE
  ➢ Are property-dependent
  ➢ Simple rule such as RVE size = x times mean particle size doesn’t stand for structure with wide size distribution. RVE size increases with heterogeneity (i.e. standard deviation of parameters)

• Particle size and surface area (annexes)
  ➢ Dependent on the voxel size.
  ➢ The product $S_p \times d_{50}$ is less sensitive to the voxel size and exhibits more similar values compared with $S_p$ and $d_{50}$ taken individually: it is thus a better identifier of the microstructure.

• Bias & assumption
  ➢ Connectivity suffers from a border effect. It should be monitored on small domains.
  ➢ Particle size depends a lot on the chosen method. One should not rely on a unique approach.
  ➢ Spherical assumption is incorrect both for Pore and NMC. Shown for particle size: pore are less spherical than NMC, which are themselves not really spherical. Results obtained on the product $S_p \times d_{50}$ goes to the same direction (annexes)
Conclusions 2/2: practical information

• **Microstructure observation**
  - Image quality of the segmented data set can be evaluated with the image level of detail parameters.
  - Consider standard deviation of the particle size when choosing your field of view.

• **Calendaring pressure**
  - Increases solid phase connectivity
  - Reduces the pore size
  - General increase of the tortuosity + slight anisotropy that hinder the diffusion in the through-plane direction (likely due to particle rearrangement and/or change of particle shape), something we would prefer to avoid.

• **Modeling**
  - 1D-model could take advantage of spatially varying parameter along the electrode thickness (as illustrated for tortuosity).

• **Tortuosity determination for large domain**
  - Consider using the two-step homogenization method to analyze if your domain is too big (or if you don’t have access to an HPC). It’s better than relying on a rule of mixture.
Thank you for your attention

Any questions?
Annexes: RVE
Determination of the RVE based upon subdomains

Representative volume element analysis illustrated on volume fractions $\varepsilon$

Step 1

Property is calculated on independent subdomains

27 independent (i.e. non overlapping) subdomains

Whole domain
Determination of the RVE based upon subdomains

Representative volume element analysis illustrated on volume fractions $\varepsilon$

Standard deviation obtained on subdomains is expressed in % of the mean value

When the std is lower than a critical value (5%) then the volume is large enough to be representative: it is the RVE size
Determination of the RVE based upon subdomains

Representative volume element analysis illustrated on volume fractions $\varepsilon$

The RVE size obtained on each microstructure (16 volumes) are plotted as a function of the calendaring pressure and of the active material composition.

Similar analysis have been performed for the other properties

$\sim 50 \mu m < \text{RVE } \varepsilon \text{ Pore } < \sim 100 \mu m$

$\sim 40 \mu m < \text{RVE } \varepsilon \text{ NMC } < \sim 90 \mu m$

Calendering pressure $\uparrow$ RVE $\varepsilon$ NMC $\downarrow$
Annexes: Surface area
Specific surface area

• Based upon a **direct counting method** (overestimation corrected with a $2/3$ factor that uses a spherical assumption)

\[ S_{\text{discretized}} \approx 6 \times \pi \times R^2 \]
\[ S_{\text{ideal sphere}} = 4 \times \pi \times R^2 \]

• Alternative method based upon the **geometrical covariogram** $K$ that gives the exact value without overestimation, but requires an isotropic assumption.

\[ K(V, \bar{h}) = \text{Mes}(V \cap V_{\bar{h}}) \]

Surface area = $-4 \times \frac{d(K(V, h))}{dh} \bigg|_{h=0}$


Less voxel per sphere diameter are required to get the actual specific surface area with the geometric covariogram method.
Specific surface area, geometric covariogram

\[ K(V, \vec{h}) = \text{Mes}(V \cap \overline{V}) = \iiint_{V(h)} k(x, y, z) \times k(x + h_1, y + h_2, z + h_3) \times dV \]

\[ A = -4 \times \left. \frac{d(K(V, h))}{dh} \right|_{h=0} \]

if \( V \) isotropic

with

\[ k(x, y, z) = \begin{cases} 1 & \text{if } (x, y, z) \in V \\ 0 & \text{if } (x, y, z) \notin V \end{cases} \]

\[ \vec{h} = h_1 \vec{e}_x + h_2 \vec{e}_y + h_3 \vec{e}_z \]

\[ S_p(V) = \frac{\delta V}{\text{mes}(V)} = -4 \times \left. \frac{dK(V, h, \infty)}{dh} \right|_{h=0} \]

if \( V \) isotropic

No overestimation since the function is based upon a volume calculation. Volume does not depend on the medium discretization

Specific surface area, results compared between methods

\[ 1.028 \leq \frac{S_p \text{ Geometric covariogram}}{S_p \text{ direct method} \times \frac{2}{3}} \leq 1.094 \]

Once the corrective factor 2/3 is applied to the direct method, both methods provides very similar results. (difference <10%)

\[ S_p \text{ Pore} \uparrow \text{ with calendaring pressure. NMC stays quasi constant (from 0.55 to 0.61 } \mu m^{-1}) \]
Both properties exhibit **opposite** voxel size dependence trend.

- Ideally, particle & pore size will converge but surface area will keep increasing (fractal property)

How to correlate them?
Specific surface area as a function of $1/d_{50}$

- The range of value for the pore is very large, both for $S_p$ and $d_{50}$ while it’s basically the same microstructure.

- Linear correlation between $S_p$ and $1/d_{50}$.

- Let’s consider the slope $S_p \times d_{50}$ as a better identifier of the microstructure, instead of $S_p$ or $d_{50}$ alone.

Product $S_p \times d_{50}$ voxel is less dependent with voxel size than $S_p$ or $d_{50}$ alone. Thus, the product better identifies a specific microstructure.

$$\Delta \approx 0.25 \ (88\%)$$

$$\Delta \approx 0.4 \ (19\%)$$

Pore are less spherical than NMC particles. NMC are not so spherical.
If they are intrinsically correlated, then they should share the same RVE size

RVE size of all 16 volumes, for $S_p$ and $D_{50}$

As expected, Representative Volume Element sizes are very similar between $S_p$ and $D_{50}$

NMC: $\langle RVE S_p \rangle \approx 1.12 \times \langle RVE D_{50} \rangle$

Pore: $\langle RVE S_p \rangle \approx 1.09 \times \langle RVE D_{50} \rangle$
Annexes: Particle size
Particle size: statistical approach

Using the conditional probability:
$$C(V,h) = P\{\bar{x} + h \in V | \bar{x} \in V\} \times P\{\bar{x} \in V\}$$

The zero correlation (stage c in the figure) is reached for different value of $h$ for particles of different size. The total loss of correlation (and thus the asymptotic value $\varepsilon^2$) is only achieved when all voxels have lost their correlation from their initial position: **thus it indicates the largest particle size and not the mean particle size.**
Particle size: statistical approach

Using the conditional probability:

\[ C(V, \bar{h}) = P\{\bar{x} + \bar{h} \in V | \bar{x} \in V\} \times P\{\bar{x} \in V\} \]

\[ P\{x + \bar{h} \in V | x \in V\} = P\{A\} + P\{B\} \]

with

\[ \{A\} = \{x + \bar{h} \text{ belongs to the initial sphere on which } x \text{ belongs}\} \]

\[ \{B\} = \{x + \bar{h} \text{ belongs to another sphere of same diameter}\} \]

\[ V_S = \frac{\pi}{6} \times D^3 \]

\[ V_{IS} = \begin{cases} 
\frac{1}{12} \times \pi \times (2 \times D + h) \times (D - h)^2 & \text{if } h < d \\
0 & \text{otherwise}
\end{cases} \]

The events A and B are contained within the volume \(V_S\) of a sphere of diameter \(D\). The ratio of voxels \(x + \bar{h}\) that will be tested for the event A is \(V_{IS}/V_S\), and it is sure they all belong to the phase \(V\) (since they are still in the initial particle). The ratio of voxels \(x + \bar{h}\) that will be tested for the event B is \((V_S - V_{IS})/V_S\) and the probability they belong to the phase \(V\) is the volume fraction of \(V\) (since they are outside the initial particle). Then:

\[ P\{A\} = \frac{V_{IS}}{V_S} \times 1 \]

\[ P\{B\} = \left(\frac{V_S - V_{IS}}{V_S}\right) \times \varepsilon \]

Fitting the diameter \(h\) of the theoretical covariance
Particle size: watershed method

(a) Euclidean distance transform (EDT) of the pores calculated on a two-dimensional subset of a positive electrode. Values are scaled with the color: from dark blue to red (maximum distance).

(b) One-dimensional schematic of the immersion watershed process, from left to right. Three catchment basins (i.e. distinct particles) have been identified. The smallest one appears to be an artifact due to the local noise gradient. (c) Original addition to the algorithm: Voxels in the smallest distinct particle are considered to be irrelevant since their local size verifies \( D^{PSD}_{D}(x) < D^{PSD}_{C}(x) \). The red circle illustrates \( D^{PSD}_{C}(x) \) while one unique color is attributed to \( D^{PSD}_{D}(x) \).

Particle size: watershed method

Illustrated on Pore, 90 wt, 600 bar

Color scaled with the particle size

Difference of size distribution between spherical assumption and watershed. Small irrelevant particles have been removed.
Annexes: Tortuosity
Factor of tortuosity

- Factor of tortuosity (homogenization method)

**Step 1:** Mean concentration at the face $F_1$

$$c_{i,1} = \int_{F_{1,i}} c \, ds / S_{i,\text{face 1}}^{\text{actual}}$$

**Step 2:** Effective surface density flux at the face $F_1$

$$\varphi_{i,1} = \int_{F_{i,1}} -k_{\text{bulk}} \times \nabla c \cdot \hat{n} \, ds / S_i^{\text{eff}}$$

**Step 3:** Deduce the effective diffusion coefficient (1D diffusion law)

$$k_i^{\text{eff}} = -\varphi_{i,1} \times \frac{\Delta L_i}{c_{i,2} - c_{i,1}}$$

**Step 4:** Deduce the factor of tortuosity

$$\tau_i = \varepsilon \times k_{\text{bulk}} / k_i^{\text{eff}} \geq 1$$

Effective section area normal to direction $i$:

$$S_i^{\text{eff}} = \Delta L_j \times \Delta L_k$$

Actual section area normal to direction $i$ at face 1:

$$S_{i,\text{face 1}}^{\text{actual}} = \int_{F_{1,i}} 1 \, ds(\text{phase})$$
• **RVE analysis on** \( \tau_{\text{through–plane dir.}} \) **with different boundary conditions**

**For which domain’s size**

\( \tau_{\text{through–plane dir.}} \) **does not depend on the chosen BC?**

---

**Tortuosity Boundary conditions table (written in brackets are the RVE):**

<table>
<thead>
<tr>
<th>( \tau_{\text{max}} - \tau_{\text{min}} )</th>
<th>Pore</th>
<th>NMC</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (110.8 , \mu m) )</td>
<td>( (115.5 , \mu m) )</td>
<td>( (&gt; 175 , \mu m) )</td>
</tr>
</tbody>
</table>

**RVE \( \tau_{\text{Boundary conditions}} > \text{RVE } \tau_{\text{Through–plane dir. Dirichlet–Neumann}}**

**RVE criterion is different:**

Instead of \( \text{std must } \rightarrow 0: \)

\[ \tau_{\text{max}} - \tau_{\text{min}} \text{ must } \rightarrow 0 \]

\( \tau_{\text{max}} - \tau_{\text{min}} \leq 5\% \text{ of } \tau_{\text{whole domain through–plane dir.}} \)

---

**To remove the boundary conditions dependence, a larger domain is required.**

**The plateau obtained for large domains indicates a convergence issue. It could be solved with a quadratic interpolation (better convergence is expected).**

---

*T. Kanit et al., Inter. J. of Solids and Structures, 40 (2003) 3647-3679*

*J. Laurencin et al., JPS, 198 (2012) 182-189*
Factor of tortuosity: rule of mixture & percolation loss

Why factor of tortuosity obtained on subdomains differs from the whole domain?

Loss of percolation on small subdomains should increase tortuosity by creating local bottleneck at the edges…but we see the opposite.

Subdomains with different “effective” diffusion coefficients
\[ k_i \in [0; 1] \]

Concentrations field
Density flux
Theoretical effective diffusion coefficient
Numerical one (FEniCS)

<table>
<thead>
<tr>
<th>Flux in series along subdomains</th>
<th>Flux in parallel along subdomains</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentrations field</td>
<td>Density flux</td>
</tr>
</tbody>
</table>

Using a rule of mixture consists of assuming flux of all the subdomains are in parallel…which is not necessary true.

\[
\frac{1}{k_{\text{series}}^{\text{eff}}} = \frac{\sum_i w_i}{\sum_i k_i} \\
= 0.441
\]

\[
k_{\text{parallel}}^{\text{eff}} = \frac{\sum_i w_i \times k_i}{\sum_i w_i} \\
= 0.543
\]

**Analytical verification of FEniCS**

**Rule of mixture**

**0.440**

**0.543**