On the Representativity of Electrode Microstructure Parameters and Their Electrochemical Response for Lithium Ion Batteries (A02-0443)

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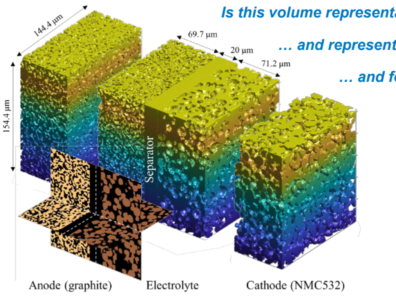
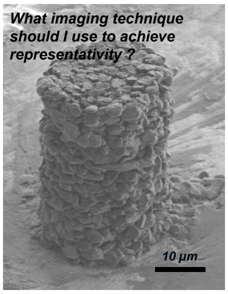
Why does representativity analysis matter ?



Representativity
⇩
predictive model
(representativity analysis
~ error analysis)
Otherwise, only qualitative results



Representativity analysis is essential

- RVE analysis enables model to be **predictive.** RVE analysis provides **imaging requirements** for FOV.

Representativity analysis must be carefully defined

- RVE is **aspect ratio dependent.** For electrodes: representative section area (RSA) x electrode thickness. RVE is **property-specific:** $\mathrm{RVE} = \max(\mathrm{RVE_p})$ considering all properties *p* relevant for the model.
- RVE is **field of view (FOV) dependent**. RVE convergence with FOV must be determined to conclude on representativity, otherwise: risk of underestimation.

Microstructure representativity ≠ performance representativity

- Error/representativity **propagation from microstructure parameters to electrochemical performances.** eRVE are increasing with C-rate: **larger volumes are required to model electrodes at fast charge rate.**
- For C-rate ≤2.5, 154x144 µm^2 is large enough to verify electrochemical performances representativity with a 5% threshold. For higher charge rates, RVE analysis is not conclusive as FOV is not large enough to confirm convergence.

How to calculate Representative Volume Element (RVE) size ?

Definition

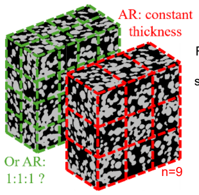
if $p(V_i) \approx p(V_j)\ \forall i \neq j$

with $\begin{cases} \Omega = \Omega_{V_i} = \Omega_{V_i} & \textbf{Same size } \Omega \\ \text{and} \\ V_i \cap V_j = \emptyset & \textbf{Independent volumes} \end{cases}$

then Ω is a representative volume for property p: $RVE_p = \Omega$

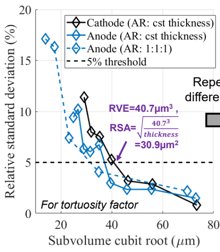
Volume V_i of size Ω_{V_i} is representative of the property *p*, if *p* calculated on other independent volumes V_j of same size is similar

Calculate $p(V_i)$ on n subvolumes, and calculate relative standard deviation to check $p(V_i) \approx p(V_j)$

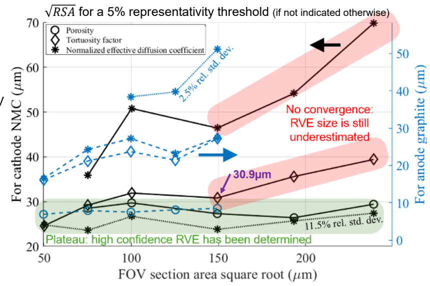


How to cut subvolumes *V* ?
(Ω = 1x1x1e^6 = 100x100x100 = 1e^6 µm3)
For batteries: **we are looking for the representative section area (RSA).**

Repeat for different subvolume size



Repeat for different FOV

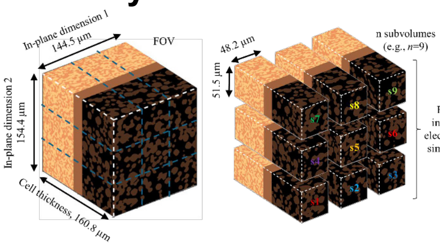


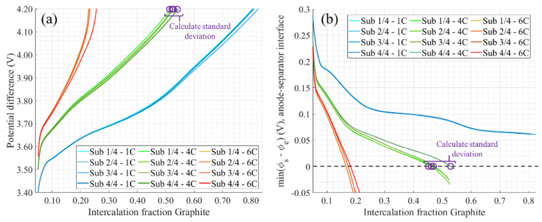
RVE is aspect ratio-dependent, property-specific, and FOV-dependent

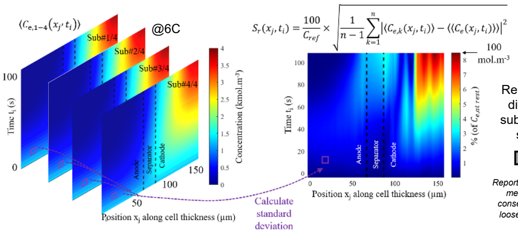
RVE analysis can be automated with NREL Microstructure Analysis Toolbox (MATBOX, Usseglio et al, SoftwareX, 2022)

Dynamic electrochemical RVE (eRVE)

Error propagation:
x% error on microstructure parameter is not x% error on electrochemical performances, and likewise for representativity threshold.



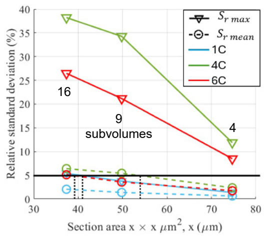




$$S_r(x_j, t_i) = \frac{100}{C_{ref}} \times \sqrt{\frac{1}{n-1}\sum_{k=1}^{n}\left|\langle C_{e,k}(x_j,t_i)\rangle - \langle\langle C_e(x_j,t_i)\rangle\rangle\right|^2}$$

Repeat for different subvolume sizes

Report maximum or mean (resp., conservative and loose approach)



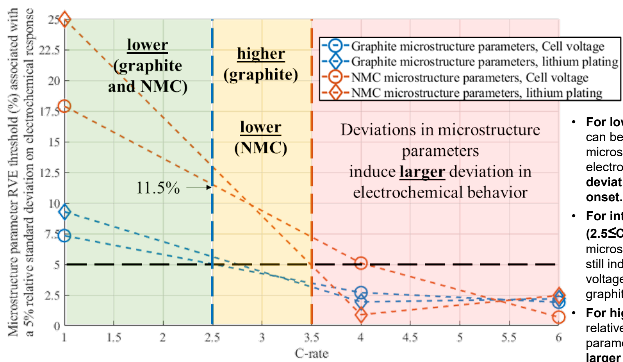
For instance, electrolyte concentration relative std between independent subvolumes can be calculated, and then compared with microstructure parameter representativity

eRVE can be calculated for a variety of metrics: e.g.: anode intercalation fraction reached at cell voltage limit or lithium plating

Static RVE and dynamic eRVE comparison and representativity propagation

For a 5% representativity threshold. (some values are underestimated due to RVE non-convergence with FOV).		Representative section area $x \times x\ \mu m^2, x\ (\mu m)$				
		Static RVE		Dynamic eRVE		
	Domain / Parameters	SLC1506T2	NMC532	Full cell SLC1506T2-NMC532 1C	4C	6C
Static RVE	Normalized effective diffusion coefficient	27.4	46.4	n/a		
	Tortuosity factor	27.2	30.9	n/a		
	Volume fractions	8.5	27.9	n/a		
	Specific surface area	<7.5	22.1	n/a		
	Mean particle size	12.9	21.1	n/a		
Dynamic RVE	Cell voltage cut-off	n/a	n/a	18.1**	45.7	83.5**
	Potential for lithium plating	n/a	n/a	13.8*,**	81.7**	68.1
	Electrolyte concentration profile (conservative, $S_{r\ max}$)	n/a	n/a	40.4	82.4**	81.6**
	Electrolyte concentration profile (loose, $S_{r\ mean}$)	n/a	n/a	-	53.2	38.3

* No plating were predicted at 1C. Standard deviation has been calculated for the end time shared among the different subvolumes.
** Extrapolated to the representativity threshold.



* Threshold for the electrolyte normalized effective diffusion coefficient, as this parameter has the largest RVE among the microstructure parameters.

Propagation analysis: for a 5% std on cell voltage or lithium plating, what should be the %std for microstructure parameters* (y-axis) for a given C-rate (x-axis) ?

- **For low C-rate (≤2.5)**, a higher threshold can be used: relative deviations in microstructure parameters for both electrodes induce **lower relative deviations in cell voltage and plating onset.**
- **For intermediate charge rate (2.5≤C≤3.5)** relative deviations in microstructure parameters for the NMC still induce lower relative deviations in cell voltage and plating onset, while for the graphite they induce higher deviations.
- **For higher charge rate (≥3.5-4C)**, relative deviations in microstructure parameters for both electrodes induce **larger relative deviations in cell voltage and plating onset.**

F. L. E. Usseglio-Viretta, P. patel, E. Bernhardt, A. Mistry, P. P. Mukherjee, J. Allen, S. J. Cooper, J. Laurencin, and K. Smith, *MATBOX: An Open-source Microstructure Analysis Toolbox for microstructure generation, segmentation, characterization, visualization, correlation, and meshing*, SoftwareX, 2022
F. L. E. Usseglio-Viretta, A. M. Colclasure, J. M. Allen, D. P. Finegan, P. Graf, and K. Smith, Microstructure Scale Lithium-ion Battery Modeling, Part II: on the representativity of microstructure parameters and electrochemical response, in redaction

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