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HAL Authorization

Characterization and quantification of lithiation heterogeneities in graphite electrodes

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Context

Transport limitations

Graphite electrode in Li-ion batteries suffers from **low power capabilities**, that limits the charging time

Electronic

High porosity → **poor percolation**

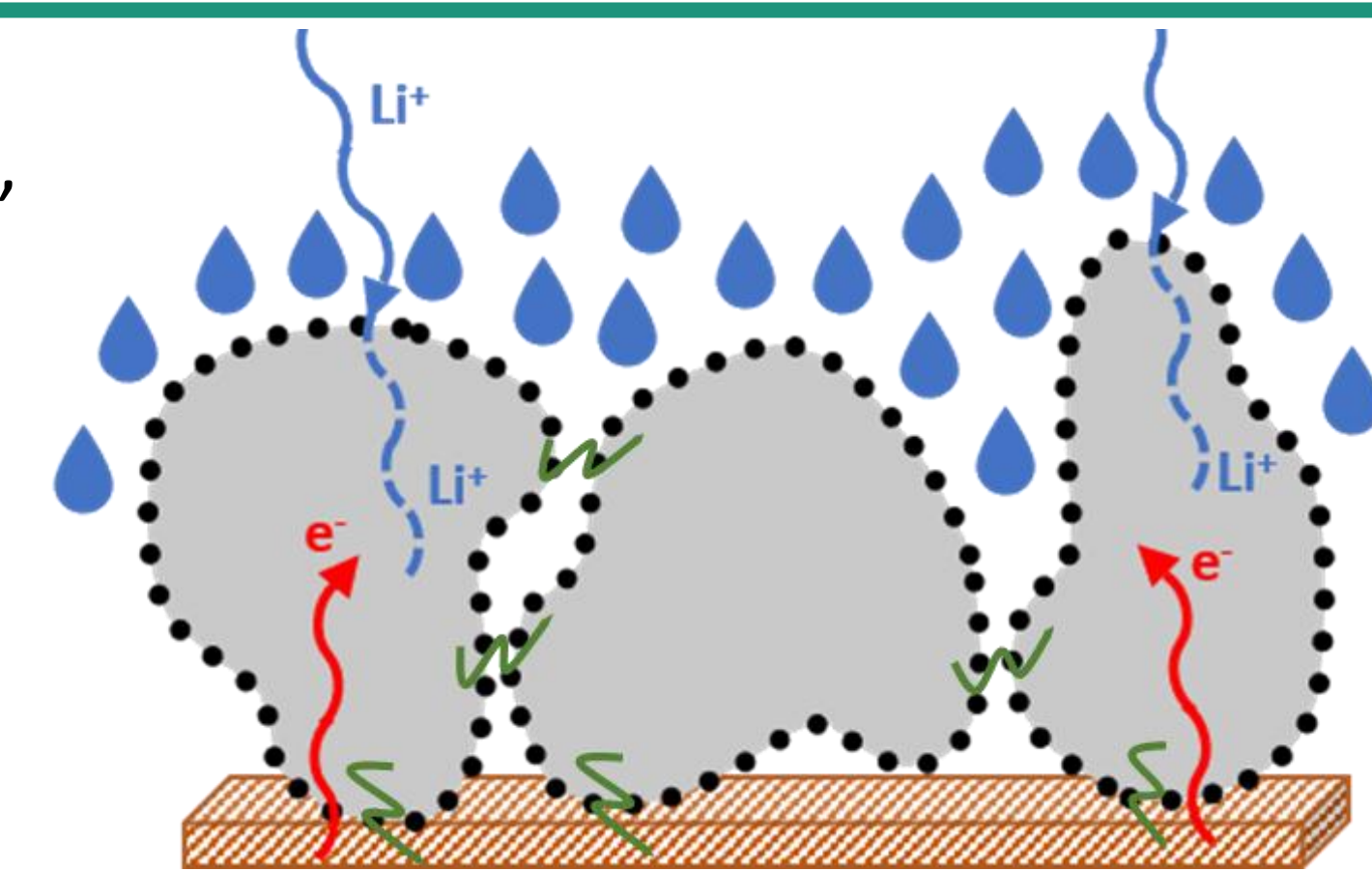
Ionic transport of lithium (electrolyte)

Limiting at **low porosity**

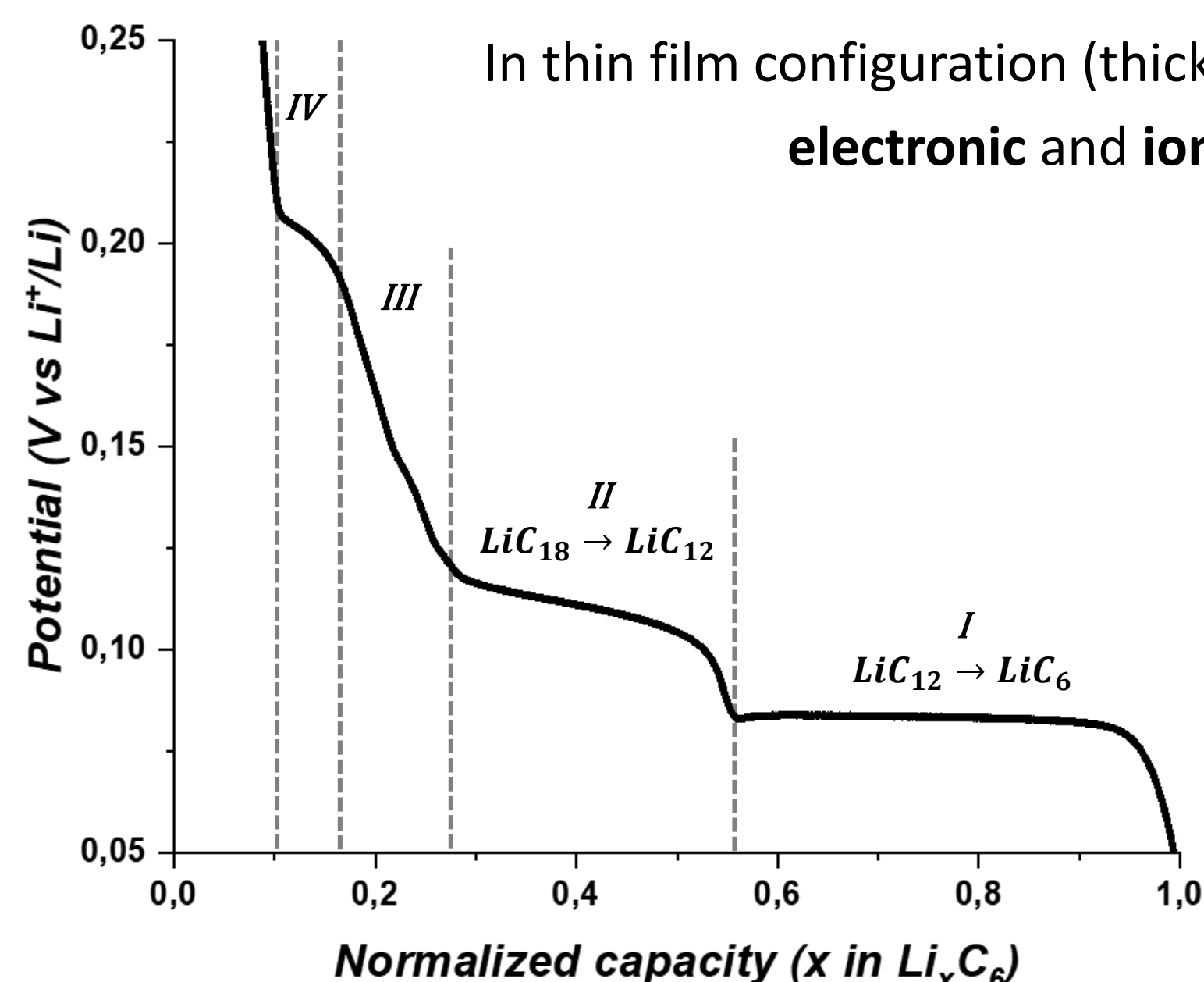
Solid state transport of lithium (graphite)

Limiting at **high cycling rate**

❖ Which processes are limiting the system regarding power capabilities?



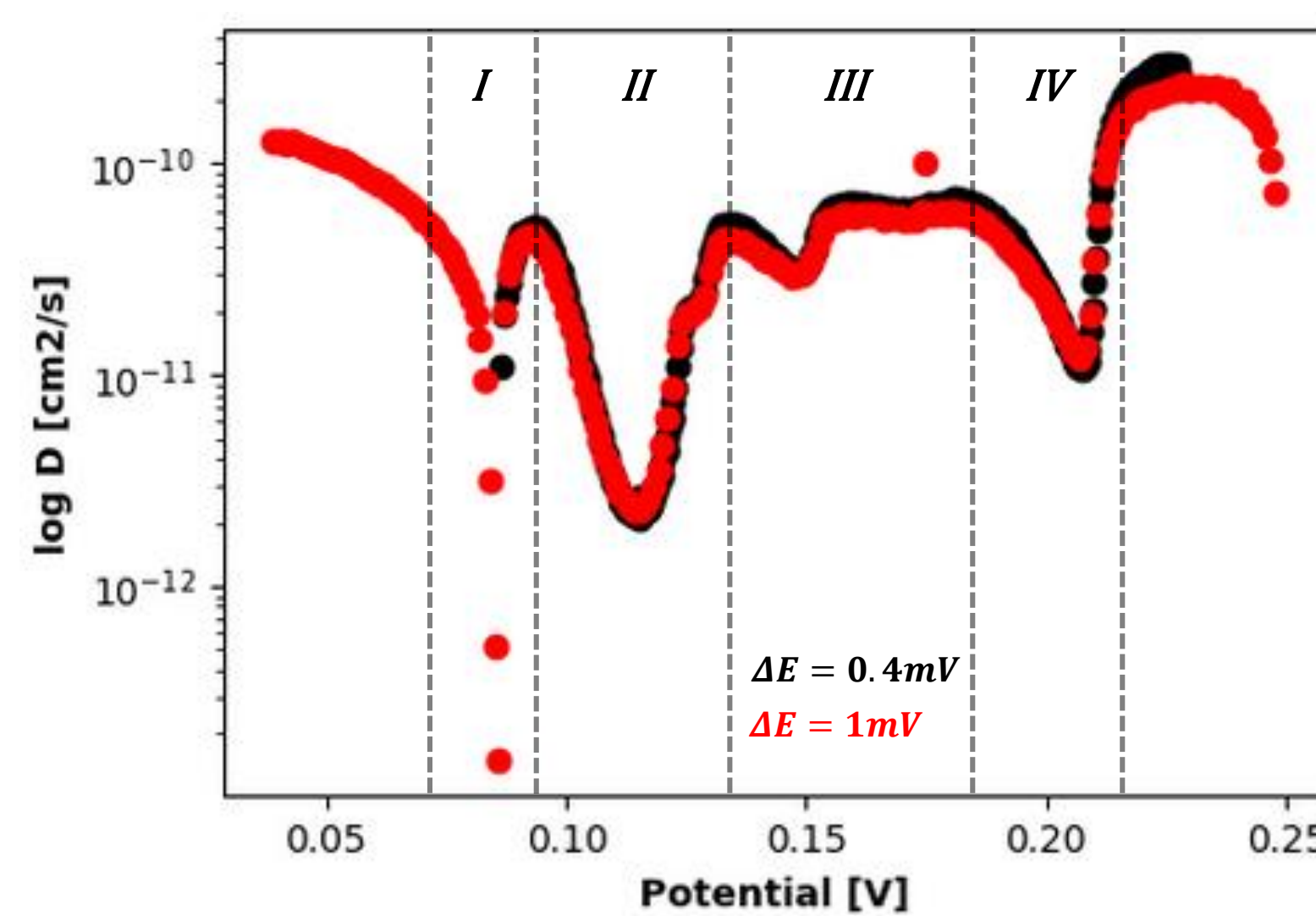
"Thermodynamic" insight – Thin film



In thin film configuration (thickness ≈ particle size), no issue regarding **electronic and ionic transports** are expected

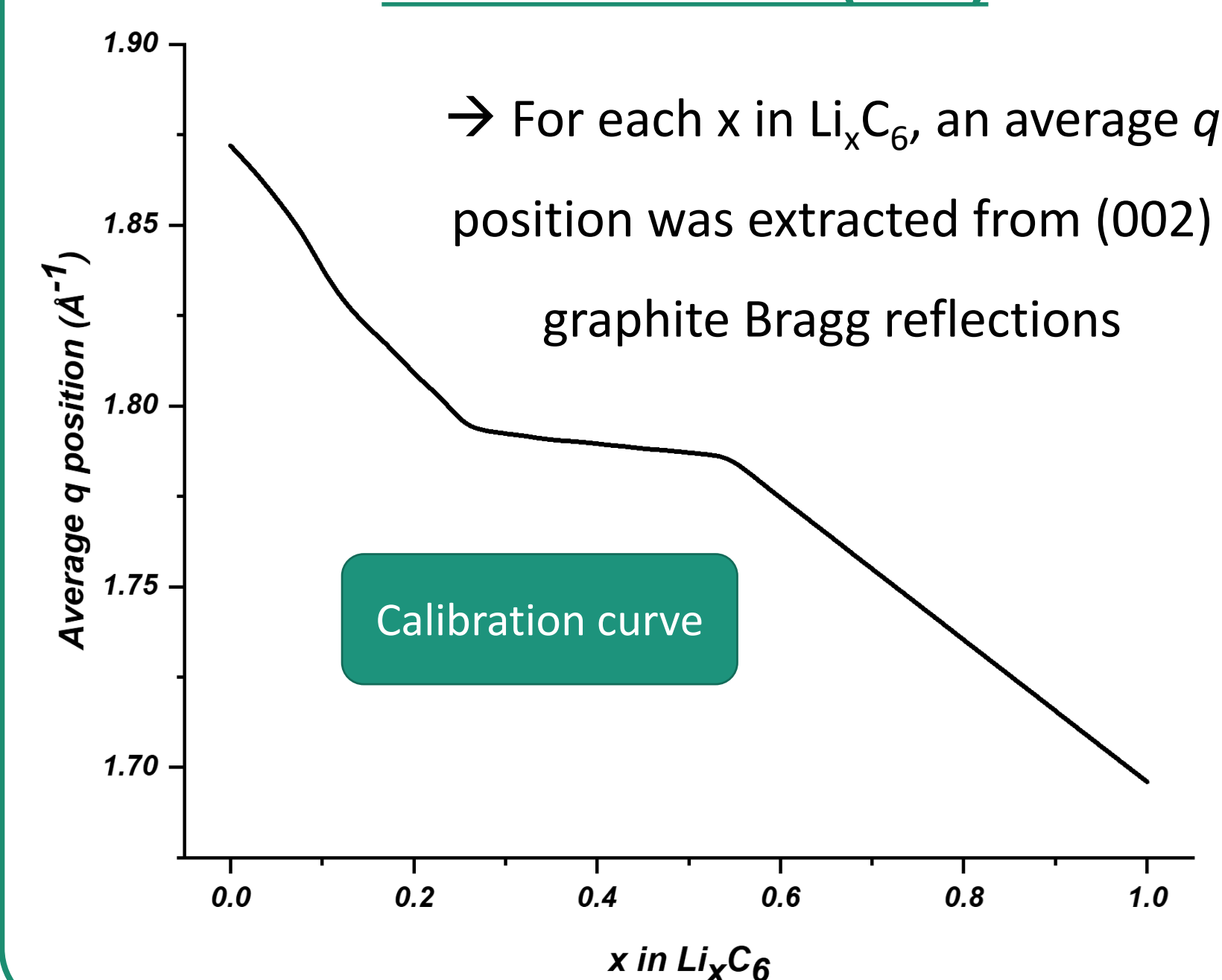
Solid state transport of lithium is limiting

Diffusion coefficients of lithium in graphite can be extracted through Potential Intermittent Titration Technique (PITT)



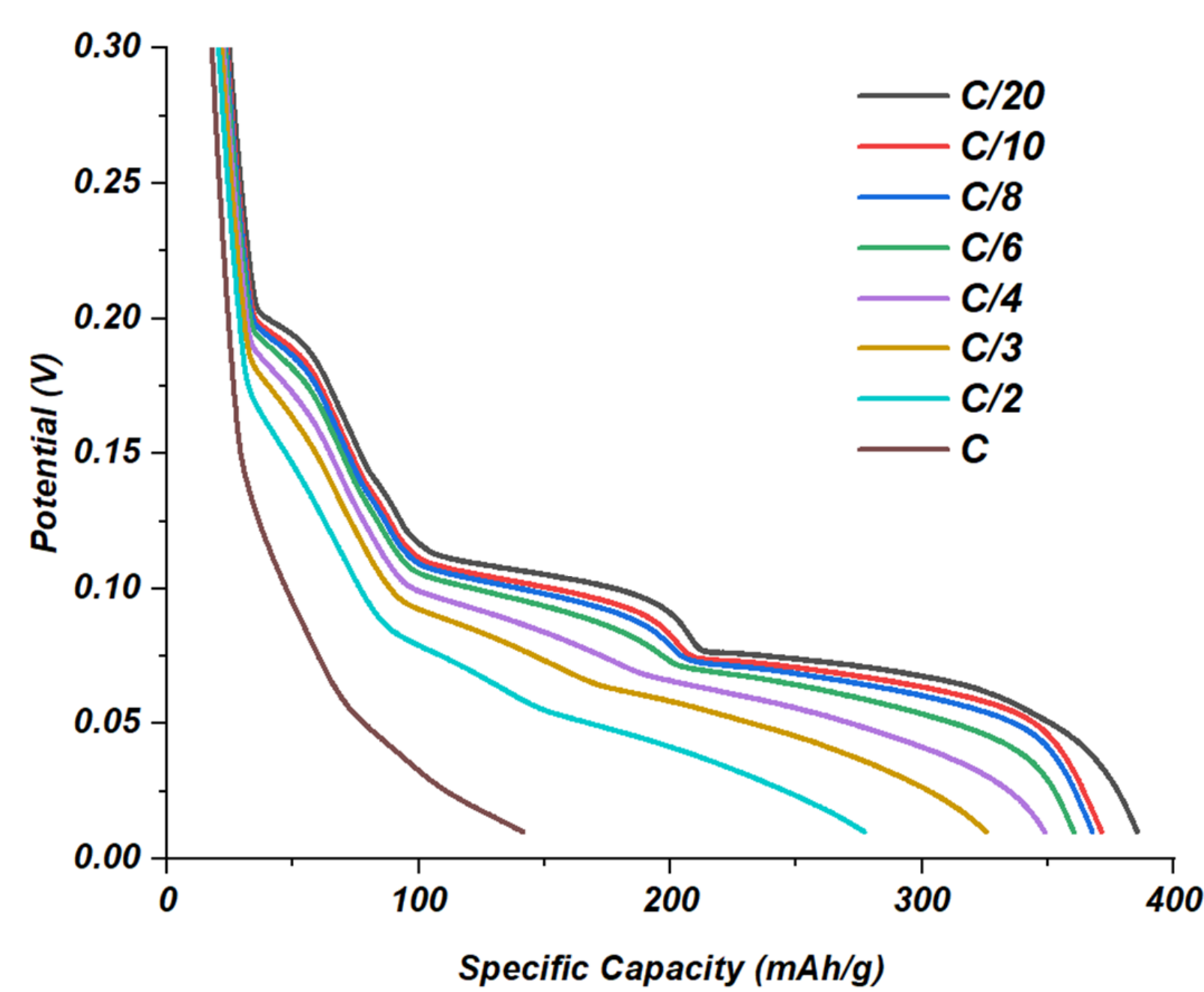
Diffusion is slower for **biphasic mechanisms** (stages IV, II and I)

Structural model (XRD)



→ For each x in Li_xC₆, an average q position was extracted from (002) graphite Bragg reflections

Power limited system – Thick & porous electrode



In thick porous electrode, **electronic and ionic transports** become significant

Determination of the limiting process

1st strategy: *electrochemical insight*

- Reduction of the electrode porosity
From 50% to 30%
- Decrease of the salt concentration
From 1M to 0.35M

Porosity reduction:

- Improves electronic percolation but degrades ionic transport (τ increases)
- Salt concentration decrease:**
Decreases ionic conductivity and slow down intercalation kinetics

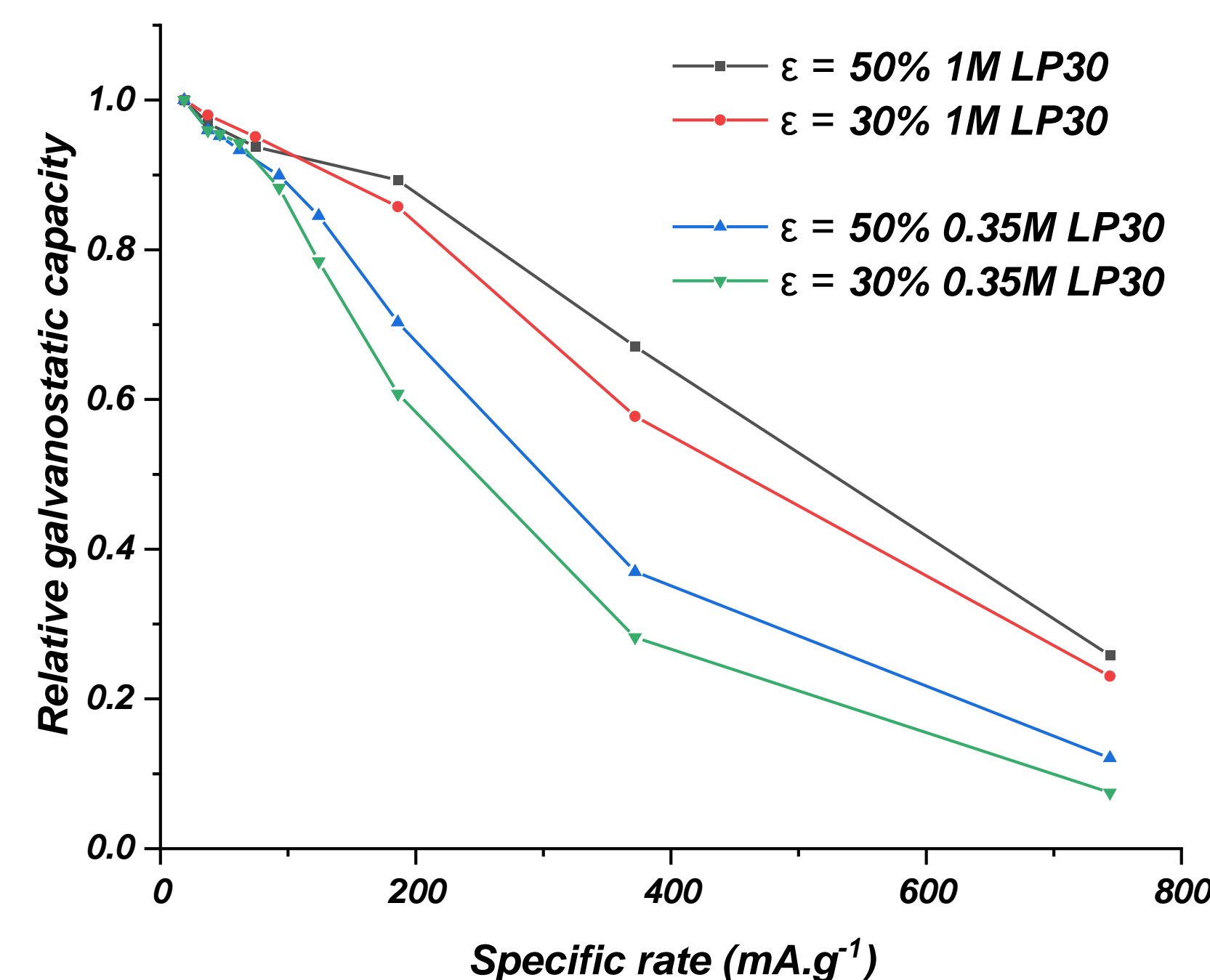
Observations

- Porosity and concentration decrease:**
Detrimental effect on power capabilities

Hypothesis

- ❖ **Ionic transport of lithium** is limiting?

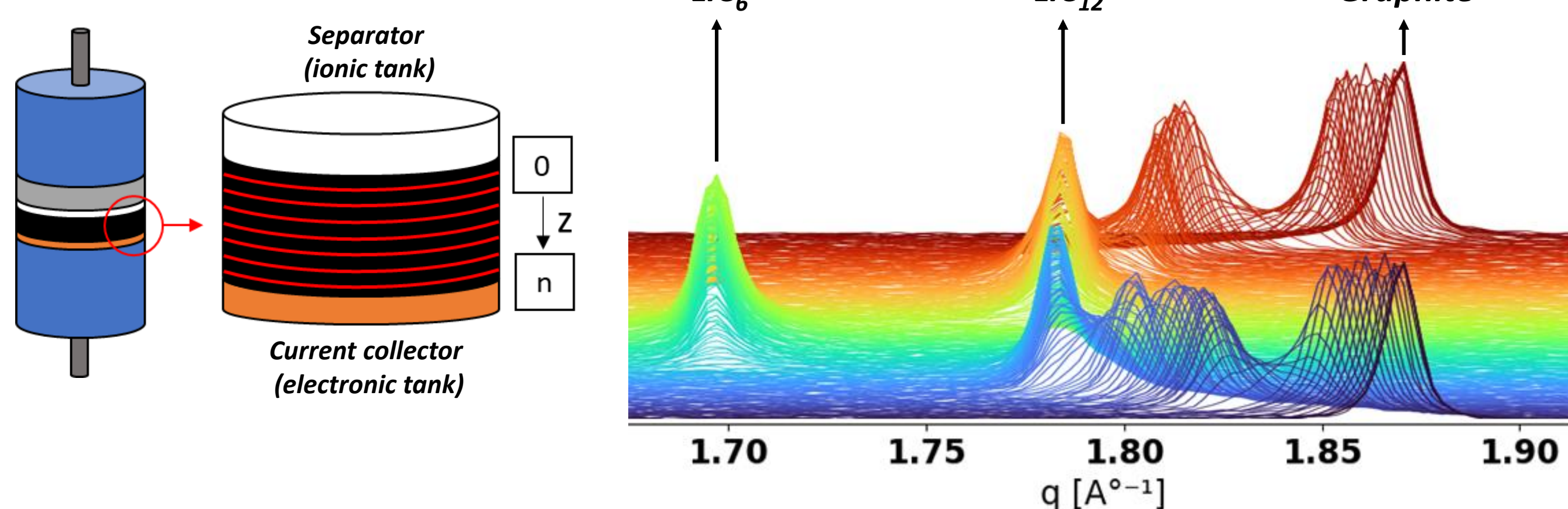
2nd strategy: *structural characterization*



Structural characterization of lithiation heterogeneities

ID31, ESRF – HIGH SPATIAL (5μm) & TEMPORAL (<1s) RESOLUTION

- Operando measurement** at C/4 cycling rate for 50% and 30% porosity
- Scanning in the **electrode thickness** with several z positions



1. Is ionic transport limiting power capabilities?

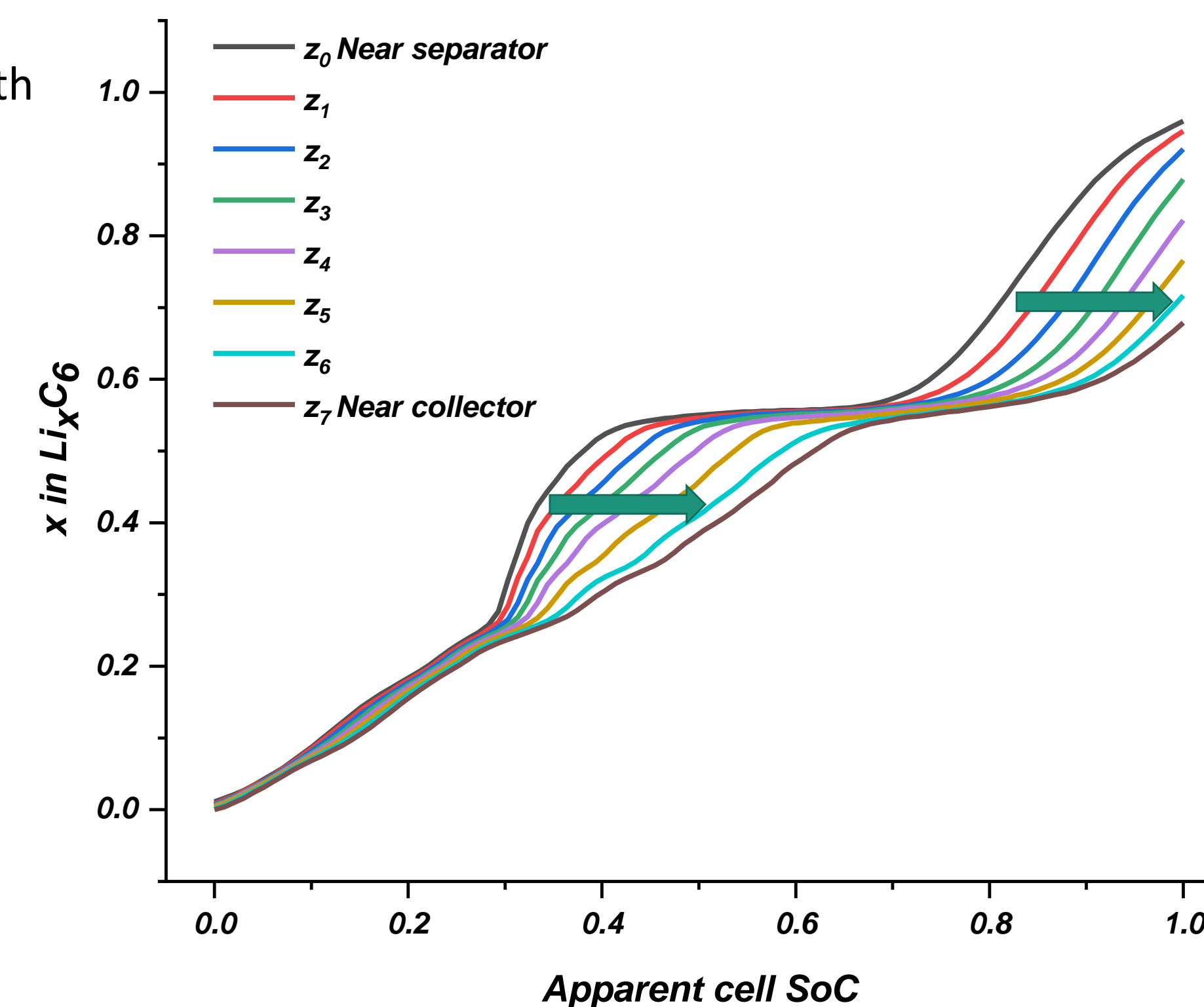
Extraction of x_{Li} (SoC) for each z positions with the cell capacity (apparent SoC)

Lithiation gradient:

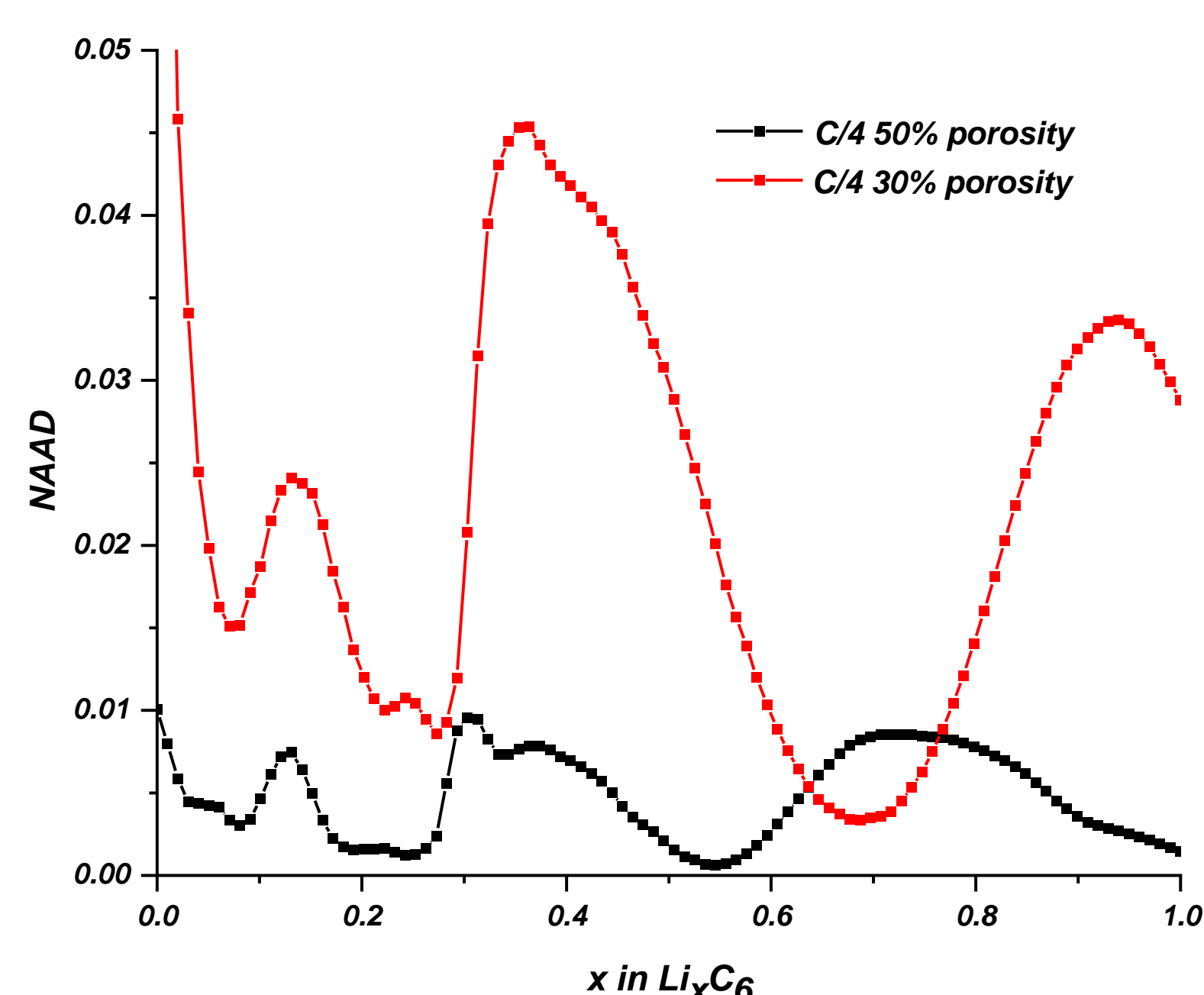
Established from separator toward current collector
→ **YES: Ionic transport of lithium** limits the power capabilities

For 50% porosity, similar lithiation gradient

30% porosity @C/4



2. Lithiation heterogeneities quantification – 50% vs. 30% porosity



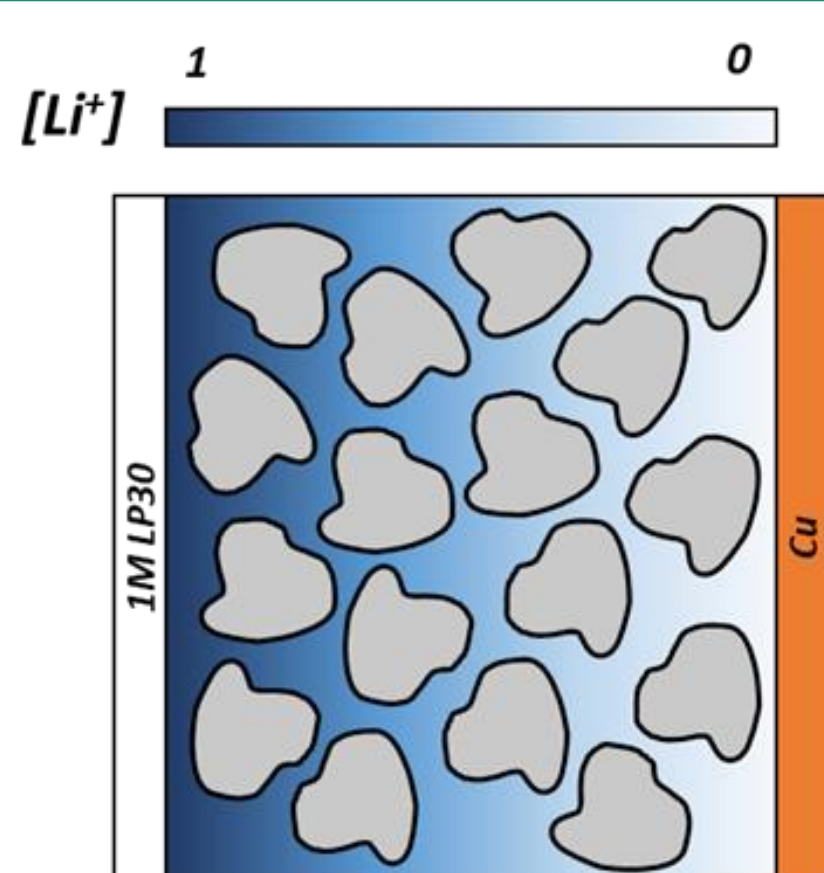
$$(1) NAAD(xLi) = \frac{1}{L} \int_{z_0}^{z_L} \frac{|x_{Li}(z) - \langle x_{Li} \rangle_z|}{\langle x_{Li} \rangle_z} dz$$

→ Quantification of **dispersion in state of charge** over the electrode thickness

❖ **Higher tortuosity for 30% porosity induces larger heterogeneities of lithiation**

Lithiation gradient decreases for solid solutions mechanism and phase transitions

Conclusion and future work



COMSOL modelling (diffusion coefficients, porosity, tortuosity)

Tortuosity measurement (nano-tomography, electrochemically)

50% porosity → 30% porosity
Calendering
Lower tortuosity → Higher tortuosity
Smaller SoC gradients → Larger SoC gradients
Better power capabilities → Lower power capabilities

