Supporting Information for:

Mesoscale Effects in the Extraction of Solid-State Lithium Diffusion Coefficient Value of Battery Active Materials: Physical Insights from 3D Modeling

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1. Experimental Section

a. Electrode Formulation

LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (NMC111) was supplied by Umicore. C-NERGY$^\text{TM}$ super C65 carbon black (CB) was supplied by IMERYS. Solef$^\text{TM}$ Polyvinylidene fluoride (PVdF) was purchased from Solvay and N-methylpyrrolidone (NMP) from BASF. All the other reagents were battery grade and were used without further purification.

The slurry solid components NMC111, CB and PVdF were premixed with a soft blender, with a composition in weight of 96:2:2, respectively. Afterwards, NMP was added until reaching the desired ratio between solid components and solvent (69:31, in weight). The mixture was performed in a Dispermat CV3-PLUS high-shear mixer for 2 h in a water-bath cooled recipient at 25 $^\circ$C. The slurry was coated over a 22 $\mu$m thick aluminum current collector using a comma-coater prototype-grade machine. For minimizing porous electrode effects, the thickness and porosity of the cathode were adjusted to 29.2 $\pm$ 0.8 $\mu$m and 0.29, respectively, by calendering.

The electrochemical experiments were conducted in a galvanostat/potentiostat (BioLogic, France). The half cell was assembled in a glove box using a Li foil as both counter and reference electrode and LP30 as electrolyte. After three formation cycles at C/10, the GITT was performed by stepping the current (between 3.0 and 4.4 V) at C/10 for 30 min followed by a resting period of 6 h in both charge and discharge.

b. Representative Radius

As stated in Cui et al.\textsuperscript{(1)} taking the average value of the radius distribution to extract the diffusion coefficient would introduce errors. The chosen radius value should be representative of the overall volume and surface of particles, so the radius should be $R = \frac{R_3}{R_2}$ . Particle size
distribution of the AM was obtained by in house experiments and it is shown in Figure S1. With this particle size distribution of NMC111 comes $R = 3.94 \, \mu m$.

*Figure S1.* NMC111 SEM image (A) and particle size distribution (B) used in the CGMD simulations.
2. Computational Details

a. GITT Current Pulse

The full GITT cycle was modelled in two separate simulations, one for the charge and one for the discharge. As the GITT conditions should allow reaching the thermodynamic equilibrium at each step, having two separate simulations should not impact the final results. The complexity of a 3D GITT simulation with explicit CBD relies on the dramatic changes in current applied to a complex system. To smoothen these current variations, exponential functions were used before (Eq. (S1)) and after (Eq. (S2)) the pulse to shift gradually the current value from zero to the pulse value. It mitigates the stiff variations while having a minor impact on the pulse shape.

\[ i_{\text{pulse}} = \frac{e^{x-1}}{e-1-1} \quad \text{(Eq. S1)} \]

\[ i_{\text{pulse}} = \frac{e^{1-x-1}}{e-1-1} \quad \text{(Eq. S2)} \]

In addition, it was observed when the resting time between two pulses was too long that the simulation would at some point ignore the following pulses. In that case, the current was kept constant and equal to zero for the rest of the simulation time. To avoid such behavior, the resting time was decreased from 6 hours (experimental) to 1 hour in the simulation. It is assumed 1 hour of resting time is long enough for the system to reach the equilibrium.

The same issue was encountered when the current during the resting time was equal to zero. A current density of 6 mA.m\(^2\) was applied during rest which corresponds approximately to a C-rate of C/6600. It is assumed this C-rate is negligible when applied for an hour.

b. Ohmic Drop Correction
Figure S2. Simulated OCV for blocking CBD during charge and discharge with the ohmic drop (ΔIR) corrected OCV.

The potentials on Figure 3b were corrected because of an ohmic resistance introduced by the model. The ohmic drop was calculated with the average gap between the two OCV curves in charge and discharge as seen Figure S2.

c. **Computational Details**

The simulations were carried out using an Intel® Core™ i7-6700 CPU @ 3.4 GHz with 32 GB of RAM and an Intel® Core™ i7-8700 CPU @ 3.2 GHz with 32 GB of RAM. Each simulation took approximately between 15 h.

d. **Information Related to the Meshed Structure**
The 96:4 (AM:CBD weight composition) meshed electrode has 29406 nodes, 54570 faces and 147683 elements. The electrode is $35.30 \times 35.30 \times 38.80 \, \mu m^3$, the separator is 6 \, \mu m high and the Li foil is 2 \, \mu m high.

e. 4D-Resolved Electrochemical Model Parameters

The parameters listed here below (Table S1) were obtained from literature, experimental measurements and optimization and sensitivity analysis. The CBD electronic conductivity of 700 S.m$^{-1}$ adopted in this work is within the same order of magnitude compared to the value reported in the literature (760 S.m$^{-1}$).\textsuperscript{(2,3)}

Table S1. 4D-resolved electrochemical model parameters.

| Name                                      | Symbol  | Value/Definition |
|-------------------------------------------|---------|------------------|
| Anodic charge transfer coefficient of NMC | $\alpha_a$ | 0.5              |
| Cathodic charge transfer coefficient of Li foil | $\alpha_c$ | 0.5              |
| Anodic charge transfer coefficient of NMC | $\beta_a$ | 0.5              |
| Cathodic charge transfer coefficient of Li foil | $\beta_c$ | 0.5              |
| Porosity of the separator                 | $\varepsilon_{sep}$ | 0.6              |
| Over potential                            | $\eta$ (V) | $\Phi_{AM} - \Phi_{E-U}$ |
| Electronic conductivity of AM             | $\sigma_{AM}$ | 1 S.m$^{-1}$    |
| Electronic conductivity of CBD            | $\sigma_{CBD}$ | 700 S.m$^{-1}$  |
| Ionic conductivity of the electrolyte$^{(4)}$ | $\sigma_e$ (S.m$^{-1}$) | $0.00158 \times C_e \times \exp(-5.363 \times 10^{-5} \times (C_e/C_0)^{1.4})$ |
| Density of AM                             | $\rho_{AM}$ | $4.65 \times 10^6$ g. m$^{-3}$ |
| AM potential                              | $\Phi_{AM}$ (V) |                  |
| CBD potential                             | $\Phi_{CBD}$ (V) |                  |
| Electrolyte potential | $\Phi_e$ (V) |
|----------------------|-------------|
| **Standard concentration in the electrolyte** | $C_0$ | 1000 mol.m$^{-3}$ |
| **Li$^+$ concentration** | $C_e$ (mol.m$^{-3}$) |
| **Initial Li$^+$ concentration in the electrolyte** | $C_{e,moy}$ | 1000 mol.m$^{-3}$ |
| **Li concentration in the AM** | $C_s$ (mol.m$^{-3}$) |
| **Maximal Li concentration in AM** | $C_{s,max}$ | 32286 mol.m$^{-3}$ |
| **Theoretical Capacity of NMC** | $\text{Cap}_\text{Th}$ (Ah/g) | 0.28 |
| **Capacity** | $\text{Cap}$ (Ah) | $\text{Cap}_\text{Th} \times \rho_{AM} \times V_{AM}$ |
| **Diffusion coefficient of Li$^+$ in the electrolyte** | $D_e$ | $2.72 \times 10^{-10}$ m$^2$.s$^{-1}$ |
| **Li diffusion coefficient in AM** | $D_{AM}$ | From GITT |
| **Li$^+$ diffusion coefficient in CBD (fully open)** | $D_{s,CBD}$ | $2.72 \times 10^{-10}$ m$^2$.s$^{-1}$ |
| **Li$^+$ diffusion coefficient in CBD (partially open)** | $D_{s,CBD}$ | $2 \times 10^{-15}$ m$^2$.s$^{-1}$ |
| **Faraday constant** | $F$ | 96485 C.mol$^{-1}$ |
| **Initial constant exchange current** | $i_{00}$ | $6.06 \times 10^{-6}$ A.m$^{-2}$ |
| **Current density pulse value at the current collector** | $J_{CC}$ (A.m$^{-2}$) | $\text{Cap} \times C_{int} / S_{CC}$ |
| **Reduction kinetic constant** | $k_{Li}$ | $1.99 \times 10^{-3}$ mol.m$^{-2}$.s$^{-1}$ |
| **Oxidation kinetic constant** | $k_{Li^-}$ | $6 \times 10^{-7}$ mol.m$^{-2}$.s$^{-1}$ |
| **Bruggeman exponent coefficient for the electrolyte** | $p_{electrolyte}$ | 0 |
| **Bruggeman exponent coefficient for the separator** | $p_{sep}$ | 1.5 |
| **Ideal gas constant** | $R$ | 8.314 J.mol$^{-1}$.K$^{-1}$ |
| **Surface area of solid in contact with the current collector** | $S_{CC}$ (m$^2$) | $984.7 \times 10^{-12}$ m$^2$ |
| **Reference temperature** | $T_{ref}$ | 298 K |
| **Li transference number** | $t_+$ | 0.363 |
### Open-Circuit Voltage

|               | U (V) | From GITT |
|---------------|-------|-----------|
| **Volume of AM** | $V_{AM}$ (m³) |           |

### 4D-Resolved Electrochemical Model Equations

The model described below is a 3D extension of the 1D model developed by Newman and collaborators, with the addition of new physics in order to take into account the explicit representation of all the phases.

**Table S2.** 4D-resolved electrochemical model equations.

| **Lithium foil electrode** |  |
|-----------------------------|---|
| Lithium foil current       | $J_{Li} = F k_a^{a_c k_c} \frac{C_e}{C_0}^{a_a} \left[ \exp \left( \frac{a_a \eta F}{RT} \right) - \exp \left( \frac{-a_c \eta F}{RT} \right) \right]$ |
| Electrolyte-lithium foil boundary conditions | $D_e^{eff} \nabla C_e = \frac{J_{Li} t^+_e}{F}$ |
|                             | $\phi_e = 0$ |

| **Active material** |  |
|---------------------|---|
| Material balance    | $\frac{\partial C_s}{\partial t} = -\nabla (-D_{AM} \nabla C_s)$ |
| Lithium insertion equation | $J_{AM} = i_0 \left[ \exp \left( \frac{\beta_a \eta F}{RT} \right) - \exp \left( \frac{-\beta_c \eta F}{RT} \right) \right]$ |
|                     | $i_0 = F k_a^{\beta_c k_c} \frac{C_e}{C_0}^{\beta_a} c_s^{\beta_c (C_{s,max} - C_s)^{\beta_a}}$ |
|                     | $\eta = \phi_{AM} - \phi_e - U$ |
| Particle-electrolyte boundary conditions | $D_{AM} \frac{\partial C_s}{\partial r} \bigg|_{r=R_i} = \frac{J_{AM} t^+_e}{F}$ |
| Charge balance       | $\nabla \cdot (\sigma_{AM} \nabla \phi_{AM}) = 0$ |
Particle-current collector boundary condition
\[ |J_{CC}| = \sigma_{AM} \nabla \phi_{AM} \]

Overpotential
\[ \eta = \phi_{AM} - \phi_e - U \]

**Electrolyte**

Material Balance
\[ \frac{\partial (\varepsilon_i C_e)}{\partial t} = \nabla \left( D_{e,eff} \nabla C_e + \frac{t+J_e}{F} \right) \]

\[ D_{e,eff} = D_{e,i}^{n_i} \quad i = \text{separator, electrolyte} \]

Charge Balance
\[ \nabla \cdot J_e = 0 \]

\[ J_e = -\sigma_{e,i}^{eff} \nabla \phi_e - k_{De} \nabla \ln C_e \]

\[ k_{De} = \frac{2RT \sigma_{e,i}^{eff}}{F} (1 - t_+) \]

\[ \sigma_{e,i}^{eff} = \sigma_{e,i}^{n_i} \quad i = \text{separator, electrolyte} \]

Electrolyte-current collector boundary conditions
\[ D_{e,eff} \nabla C_e = 0 \]

\[ \nabla \phi_e = 0 \]

**Carbon-binder domain**

Charge balance
\[ \nabla \cdot \left( -\sigma_{CBD}^{eff} \nabla \phi_{CBD} \right) = 0 \]
3. References

(1) Cui, S.; Wei, Y.; Liu, T.; Deng, W.; Hu, Z.; Su, Y.; Li, H.; Li, M.; Guo, H.; Duan, Y.; et al. Optimized Temperature Effect of Li-Ion Diffusion with Layer Distance in Li(NixMnyCoz)O2 Cathode Materials for High Performance Li-Ion Battery. *Adv. Energy Mater.* 2016, 6 (4), 1–9.

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