Supplementary Information: Bridging the Gap Between Microstructurally Resolved Computed Tomography-Based and Homogenised Doyle-Fuller-Newman Models for Lithium-Ion Batteries

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Doyle-Fuller-Newman Model Framework

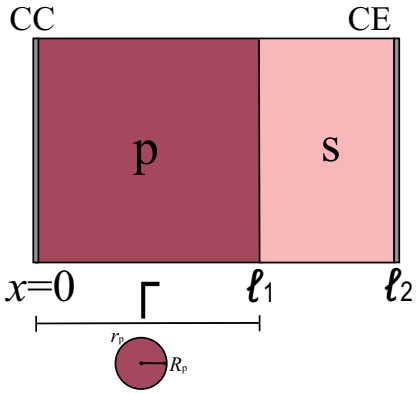


Figure S1: The model half cell battery domain. The separator, s, and positive cathode compartment, p, is shown. The cathode domain, Γ, that excludes the separator, current collector (CC) and lithium metal plate counter electrode (LMP) are shown. ℓ_1 is the thickness of the cathode and ℓ_2 is the thickness of the entire half cell.

The model equations[1] are shown below and other auxiliary functions including $\kappa_{\text{e,bulk}}$, $D_{\text{e,bulk}}$ and the open circuit potentials (OCP) are shown within the open-source code and elsewhere.[2] The DFN equations are shown, on the domain Γ, except for the separator, $I_{\text{sign}} = -1$ for discharge, and $t > 0$:

$$\frac{\partial c_{\text{s,p}}}{\partial t} = \frac{1}{r_{\text{p}}^2}\frac{\partial}{\partial r_{\text{p}}}\left(r_{\text{p}}^2\, D_{\text{s,p}}\frac{\partial c_{\text{s,p}}}{\partial r_{\text{p}}}\right), 0 < r_{\text{p}} < R_{\text{p}}, \tag{S1a}$$

$$-\frac{\partial}{\partial x}\left(-\sigma_{\text{s,p}}\frac{\partial \phi_{\text{s,p}}}{\partial x}\right) = a_{\text{p}}\, i_{\text{BV}}, \tag{S1b}$$

$$\varepsilon_{\text{e,p}}\frac{\partial c_{\text{e,p}}}{\partial t} = -\frac{\partial}{\partial x}\left(-D_{\text{e,p}}\frac{\partial c_{\text{e,p}}}{\partial x}\right) + \frac{\left(1-t^{+}\right)\, a_{\text{p}}\, i_{\text{BV}}}{F}, \tag{S1c}$$

$$\varepsilon_{\text{e,s}}\frac{\partial c_{\text{e,s}}}{\partial t} = -\frac{\partial}{\partial x}\left(-D_{\text{e,s}}\frac{\partial c_{\text{e,s}}}{\partial x}\right), \ell_1 < x < \ell_2, \tag{S1d}$$

$$\frac{\partial}{\partial x}\left[\kappa_{\text{e,p}}\left(-\frac{\partial \phi_{\text{e,p}}}{\partial x} + \omega\,\frac{\partial(\ln(c_{\text{e,p}}))}{\partial x}\right)\right] = a_{\text{p}}\, i_{\text{BV}}, \tag{S1e}$$

$$\frac{\partial}{\partial x}\left[\kappa_{\text{e,s}}\left(-\frac{\partial \phi_{\text{e,s}}}{\partial x} + \omega\,\frac{\partial(\ln(c_{\text{e,s}}))}{\partial x}\right)\right] = 0, \quad \ell_1 < x < \ell_2, \tag{S1f}$$

$$\omega = \frac{2\, g\, \left(1-t^{+}\right)\, R\, T}{F}, \tag{S1g}$$

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with boundary conditions as follows:

$$\left.\frac{\partial c_{\mathrm{s,p}}}{\partial r_{\mathrm{p}}}\right|_{r_{\mathrm{p}}=0} = 0, \tag{S2a}$$

$$-D_{\mathrm{s,p}}\left.\frac{\partial c_{\mathrm{s,p}}}{\partial r_{\mathrm{p}}}\right|_{r_{\mathrm{k}}=R_{\mathrm{p}}} = \frac{i_{\mathrm{BV}}(R_{\mathrm{p}},x,t)}{F}, \tag{S2b}$$

$$-\sigma_{\mathrm{s,p}}\left.\frac{\partial \phi_{\mathrm{s,p}}}{\partial x}\right|_{x=0} = I\ I_{\mathrm{sign}}, \tag{S3a}$$

$$\left.\frac{\partial \phi_{\mathrm{s,p}}}{\partial x}\right|_{x=\ell_1} = 0, \tag{S3b}$$

$$\left.\frac{\partial c_{\mathrm{e,p}}}{\partial x}\right|_{x=0} = 0, \tag{S4a}$$

$$c_{\mathrm{e,p}}(\ell_1,t) = c_{\mathrm{e,s}}(\ell_1,t), \tag{S4b}$$

$$-D_{\mathrm{e,s}}\left.\frac{\partial c_{\mathrm{e,s}}}{\partial x}\right|_{x=\ell_1} = -D_{\mathrm{e,p}}\left.\frac{\partial c_{\mathrm{e,p}}}{\partial x}\right|_{x=\ell_1}, \tag{S4c}$$

$$-D_{\mathrm{e,s}}\left.\frac{\partial c_{\mathrm{e,s}}}{\partial x}\right|_{x=\ell_2} = \frac{\left(1-t^{+}\right)\ I\ I_{\mathrm{sign}}}{F}. \tag{S4d}$$

$$\left.\frac{\partial \phi_{\mathrm{e,p}}}{\partial x}\right|_{x=0} = 0, \tag{S5a}$$

$$\phi_{\mathrm{e,p}}(\ell_1,t) = \phi_{\mathrm{e,s}}(\ell_1,t), \tag{S5b}$$

$$\kappa_{\mathrm{e,s}}\left.\frac{\partial \phi_{\mathrm{e,s}}}{\partial x}\right|_{x=\ell_1} = \kappa_{\mathrm{e,s}}\ \omega\ \left.\frac{\partial(\ln(c_{\mathrm{e,s}}))}{\partial x}\right|_{x=\ell_1} - I\ I_{\mathrm{sign}}, \tag{S5c}$$

$$\text{Reference Potential:} \phi_{\mathrm{e,s}}(\ell_2,t) = 0, \tag{S5d}$$

$$\tag{S5e}$$

and initial conditions:

$$c_{\mathrm{s,p}}(r_{\mathrm{p}},0) = c_{\mathrm{s,p,0}}, \tag{S6a}$$

$$\phi_{\mathrm{s,p}}(x,0) = U_{\mathrm{k}}, \tag{S6b}$$

$$c_{\mathrm{e,k}}(x,0) = c_{\mathrm{e0}},\ \ \mathrm{k} \in \{\mathrm{p,s}\}, \tag{S6c}$$

$$\phi_{\mathrm{e,k}}(x,0) = 0,\ \ \mathrm{k} \in \{\mathrm{p,s}\}, \tag{S6d}$$

and auxiliary equations:

$$a_{\mathrm{p}} = \frac{3\ (1-\varepsilon_{\mathrm{e,p}}-\varepsilon_{\mathrm{CBD,p}})}{R_{\mathrm{p}}}, \tag{S7a}$$

$$i_{\mathrm{BV}} = 2\ i_0\ \sinh\left(\frac{F\ \eta_{\mathrm{p}}}{2\ R\ T}\right), \tag{S7b}$$

$$i_0 = k_{\mathrm{p}}\ F\ \sqrt{c_{\mathrm{e,p}}\ c_{\mathrm{s,p}}\left(c_{\mathrm{s,p,max}}-c_{\mathrm{s,p}}\right)}\Big|_{r_{\mathrm{p}}=R_{\mathrm{p}}}, \tag{S7c}$$

$$\eta_{\mathrm{p}} = \phi_{\mathrm{s,p}} - \phi_{\mathrm{e,p}} - U_{\mathrm{p}}|_{r_{\mathrm{p}}=R_{\mathrm{p}}}, \tag{S7d}$$

$$D_{\mathrm{e,k}} = D_{\mathrm{e,bulk}}\ {\varepsilon_{\mathrm{e,k}}}^{b_{\mathrm{k}}},\ \ \mathrm{k} \in \{\mathrm{p,s}\}, \tag{S7e}$$

$$\kappa_{\mathrm{e,k}} = \kappa_{\mathrm{e,bulk}}\ {\varepsilon_{\mathrm{e,k}}}^{b_{\mathrm{k}}},\ \ \mathrm{k} \in \{\mathrm{p,s}\}, \tag{S7f}$$

$$V = \phi_{\mathrm{s,p}}(0,t) + R_{\mathrm{c}}\ I\ I_{\mathrm{sign}}, \tag{S7g}$$

where $D_{\mathrm{e,bulk}}(c_e)$ and $\kappa_{\mathrm{e,bulk}}(c_e)$, and solved variables are shown in Table S1.

CT Image-based Model Framework

Fick's first and second laws, ion conduction and conservation of current associated with lithium-ion transport are given as follows

$$J_{\mathrm{e}} = -D_{\mathrm{e,p}}\nabla c_{\mathrm{e,p}} + \frac{i_{\mathrm{e}}t^{+}}{F}, \tag{S8a}$$

$$\frac{\partial c_{\mathrm{e,p}}}{\partial t} + \nabla\cdot J_{\mathrm{e}} = 0, \tag{S8b}$$

$$i_{\mathrm{e}} = -\kappa_{\mathrm{e,p}}\nabla\phi_{\mathrm{e,p}} + \frac{2g\kappa_{\mathrm{e,p}}RT}{F}(1-t^{+})\nabla\ln c_{\mathrm{e,p}}, \tag{S8c}$$

$$\nabla\cdot i_{\mathrm{e}} = 0. \tag{S8d}$$

Table S1: Variables of the DFN model, where k $\in$ {p,s}, for positive and separator compartments.

Parameter	Description	Unit
a_{p}	Reaction surface area per volume	1/m
$c_{\mathrm{e,k}}$	Concentration of lithium in the liquid electrolyte	mol/m^3
$c_{\mathrm{s,p}}$	Concentration of lithium in the solid particles	mol/m^3
$D_{\mathrm{e,k}}$	Diffusivity function in the electrolyte	m^2/s
$D_{\mathrm{e,bulk}}$	Bulk diffusivity function in the electrolyte	m^2/s
i_{BV}	Butler-Volmer reaction density	A/m^2
i_0	Exchange current density	A/m^2
r_{p}	Particle radius	m
t	Time	s
U_{p}	Open circuit potential (OCP)	V
V	Voltage	V
x	Direction through cell	m
$\kappa_{\mathrm{e,k}}$	Ionic conductivity function in the electrolyte	S/m
$\kappa_{\mathrm{e,bulk}}$	Bulk ionic conductivity function in the electrolyte	S/m
η_{p}	Local overpotential	V
$\phi_{\mathrm{s,p}}$	Potential in the solid particles	V
$\phi_{\mathrm{e,k}}$	Potential in the liquid electrolyte	V

Fick's first and second laws for solid lithium transport and Ohm's law with charge conservation for electronic conduction in the active material

$$J_{\mathrm{p}} = -D_{\mathrm{s,p}} \nabla c_{\mathrm{s,p}}, \tag{S9a}$$

$$\frac{\partial c_{\mathrm{s,p}}}{\partial t} + \nabla \cdot J_{\mathrm{p}} = 0, \tag{S9b}$$

$$i_{\mathrm{p}} = -\sigma_{\mathrm{s,p}} \nabla \phi_{\mathrm{s,p}}, \tag{S9c}$$

$$\nabla \cdot i_{\mathrm{p}} = 0. \tag{S9d}$$

Ohm's law and charge conservation for electronic conduction in the carbon binder domain are given as follows for NMC. For LFP, the carbon-binder and electrolyte domains are homogenised using Bruggeman exponents with equations similar to the DFN model.

$$i_{\mathrm{c}} = -\sigma_{\mathrm{CBD}} \nabla \phi_{\mathrm{c}}, \tag{S10a}$$

$$\nabla \cdot i_{\mathrm{c}} = 0. \tag{S10b}$$

The boundary conditions are as follows, related to Fig. 2

$$\mathbf{i}_{\mathrm{c}} \cdot \mathbf{n}_{\mathrm{cc}} = i_{\mathrm{in}}|_{z=0}, \tag{S11a}$$

$$\mathbf{J}_{\mathrm{e}} \cdot \mathbf{n}_{\mathrm{e}} = \left.\frac{i_{\mathrm{in}}}{F}\right|_{z=t_{\mathrm{cc}}+L+t_{\mathrm{sep}}}, \tag{S11b}$$

$$\mathbf{i}_{\mathrm{e}} \cdot \mathbf{n}_{\mathrm{e}} = -i_{\mathrm{in}}|_{z=t_{\mathrm{cc}}+L+t_{\mathrm{sep}}}, \tag{S11c}$$

$$\phi_{\mathrm{e,p}} = 0|_{z=t_{\mathrm{cc}}+L+t_{\mathrm{sep}}}, \tag{S11d}$$

$$\mathbf{i}_{\mathrm{c}} \cdot \mathbf{n}_{\mathrm{se}} = 0|_{z=t_{\mathrm{cc}}+L}, \tag{S11e}$$

$$\mathbf{i}_{\mathrm{p}} \cdot \mathbf{n}_{\mathrm{se}} = 0|_{z=t_{\mathrm{cc}}+L}, \tag{S11f}$$

$$\mathbf{J}_{\mathrm{e}} \cdot \mathbf{n}_{\mathrm{pe}} = \frac{-i_{\mathrm{BV}}}{F}, \tag{S11g}$$

$$\mathbf{J}_{\mathrm{s}} \cdot \mathbf{n}_{\mathrm{pe}} = \left.\frac{-i_{\mathrm{BV}}}{F}\right|_{r=R_{\mathrm{p}}}, \tag{S11h}$$

$$\mathbf{i}_{\mathrm{e}} \cdot \mathbf{n}_{\mathrm{pe}} = -i_{\mathrm{BV}}, \tag{S11i}$$

$$\mathbf{i}_{\mathrm{p}} \cdot \mathbf{n}_{\mathrm{pe}} = i_{\mathrm{BV}}|_{r=R_{\mathrm{p}}}. \tag{S11j}$$

The charge transfer reaction is represented using the Butler-Volmer equation with an exchange current density as described in equations (S7b) to (S7d), voltage and electrolyte functions as described in equations (S7e) to (S7g) and initial conditions the same as equations S6.

Li Particle Concentration for LFP

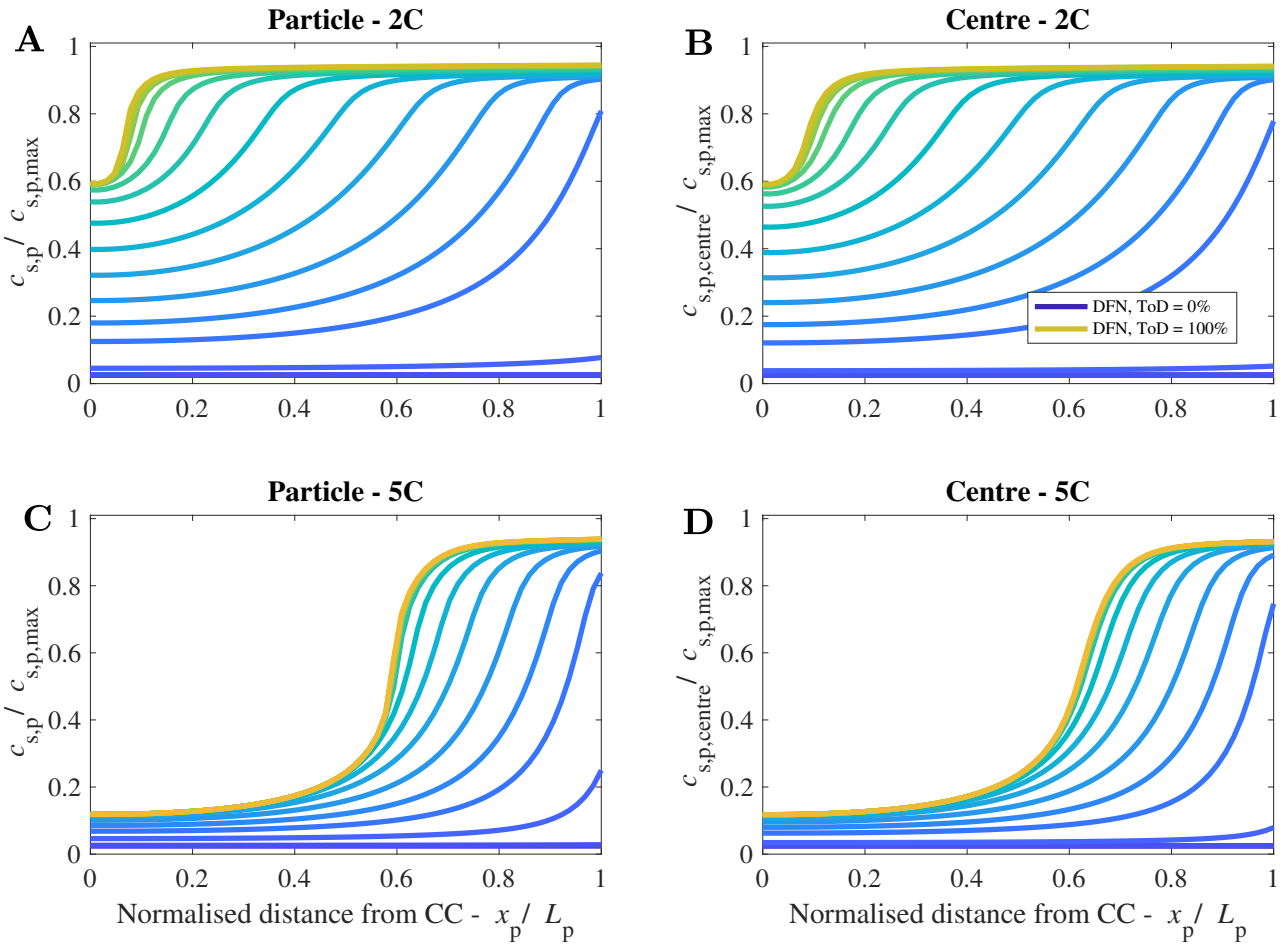


Figure S2: 2C (A, B) and 5C (C, D) 90 μm for LFP. The normalised Li solid particle concentration ($c_{s,p}/c_{s,p,max}$) is shown integrated over the particle (A,C), and at the centre of the particle ($c_{s,p,centre}/c_{s,p,max}$) (B,D). The current collector (CC) is on the left and separator on the right of each subfigure.

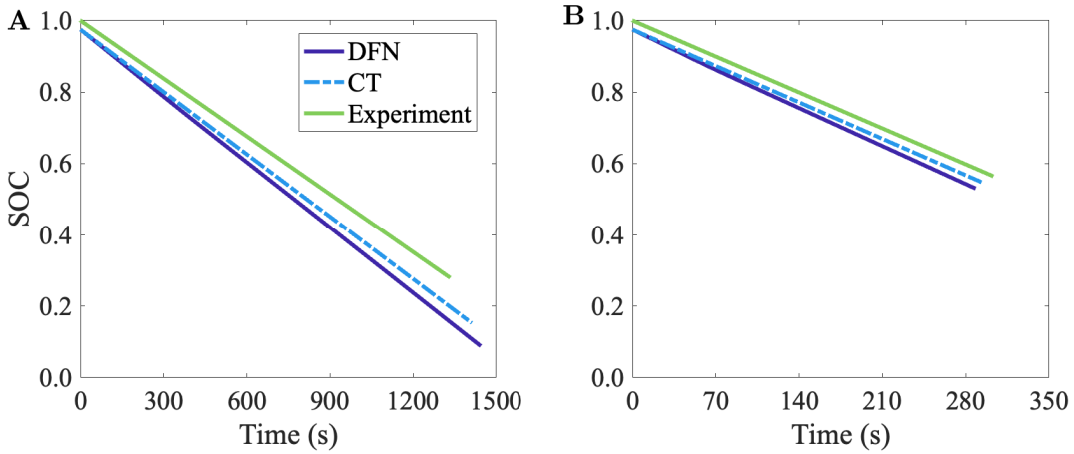


Figure S3: The LFP state-of-charge (SOC) with time, where the SOC is the solid particle concentration integrated over the particle radius and cathode, at (A) 2C and (B) 5C, where $\text{SOC}(t) = \frac{3}{L_p R_p^3} \int_0^{L_p} \int_0^{R_p} r_p^2 \left(1 - c_{s,p}(r_p, x_p, t)/c_{s,p,max}\right) dr_p dx_p$.

References

[1] M. Doyle, T. F. Fuller, and J. Newman, "Modeling of galvanostatic charge and discharge of the lithium/polymer/insertion cell," *Journal of the Electrochemical society*, vol. 140, no. 6, p. 1526, 1993.

[2] E. C. Tredenick, S. Wheeler, R. Drummond, S. R. Duncan, and P. S. Grant, "A multilayer Doyle-Fuller-Newman model (M-DFN) to optimise the rate performance of bi-layer cathodes for Li-ion batteries," 2023.