REDUCED-ORDER 3D MODELS OF LITHIUM-ION CELLS

Robert Timms
University of Oxford

BMWS
06 July 2021

PART 0: MOTIVATION

3D battery modelling

Distributed quantities are important

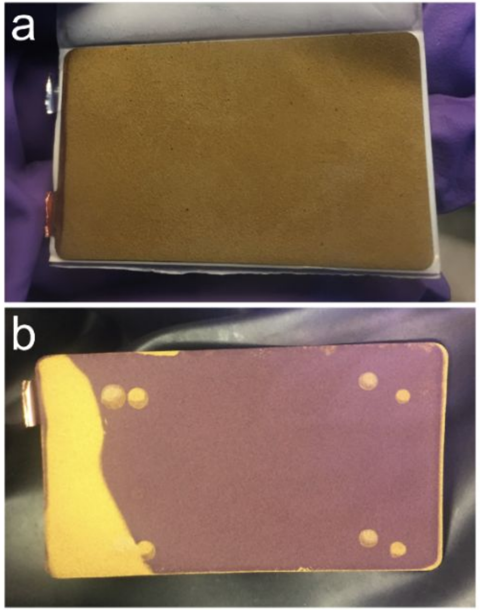
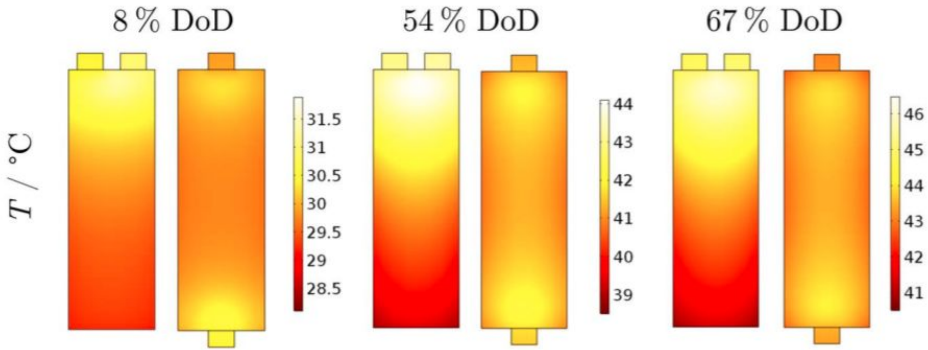
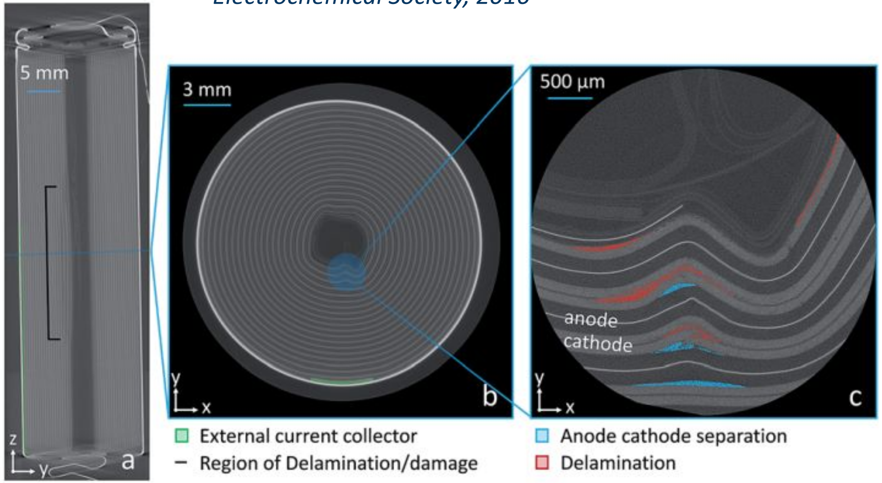


Fig. 2. Graphite negative electrodes extracted from a fully charged Kokam pouch cell; a) uniformly lithiated, b) non-uniformly lithiated.

Degradation diagnostics for lithium ion cells,
C.R. Birkl, M.R. Roberts, E. McTurk, P.G. Bruce, and D.A. Howey, Journal of Power Sources, 2017



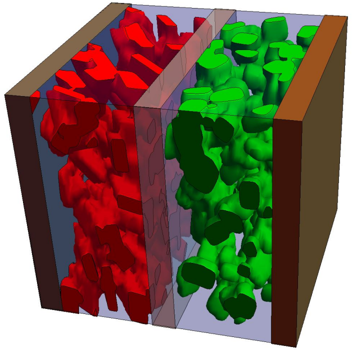
Multi-dimensional modeling of the influence of cell design on temperature, displacement and stress inhomogeneity in large-format lithium-ion cells,
B. Rieger, S.V. Erhard, S. Kosch, M. Venator, A. Rheinfeld, and A. Jossen, Journal of The Electrochemical Society, 2016

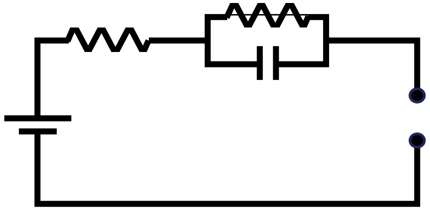


Virtual unrolling of spirally-wound lithium-ion cells for correlative degradation studies and predictive fault detection,
Kok et al., Sustainable Energy Fuels, 2019

How to model batteries?

Physics-based vs. empirical





Physics-based (PDEs)

- ✓ Gain insight
- ✓ Predict internal dynamics
- ✓ Wide range of validity

- × Lots of parameters
- × Computationally expensive
- × Comparatively difficult to formulate

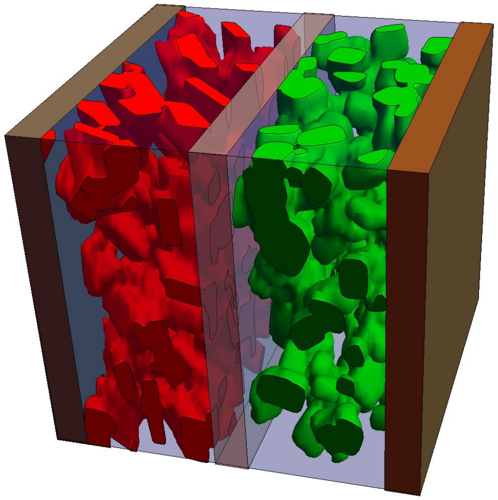
Equivalent Circuit Models (ECMs)

- ✓ Computationally cheap
- ✓ Simple
- ✓ Not many parameters

- × Limited physical insight
- × No internal dynamics
- × Only good for interpolating

Physics-based model

Microscale model



$$\nabla \cdot \boldsymbol{i}^{\pm} = 0$$

$$\frac{\partial c^{\pm}}{\partial t} + \nabla \cdot \boldsymbol{N}^{\pm} = 0$$

$$\boldsymbol{i}^{\pm} = -\sigma^{\pm} \nabla \phi^{\pm}$$

$$\boldsymbol{N}^{\pm} = -D^{\pm} \nabla c^{\pm}$$

$$c_{e+} = c_{e-} = c_e$$

$$\nabla \cdot \boldsymbol{i}_e = 0$$

$$\frac{\partial c_e}{\partial t} + \nabla \cdot \boldsymbol{N}_e = 0$$

$$\boldsymbol{i}_e = -\sigma_e \left(\nabla \phi_e - \frac{2}{F}(1 - t^+) \nabla \mu_e \right)$$

$$\nabla \mu_e \approx RT \nabla \log c_e$$

$$\boldsymbol{N}_e = -D_e \nabla c_e + \frac{t^+}{F} \boldsymbol{i}_e$$

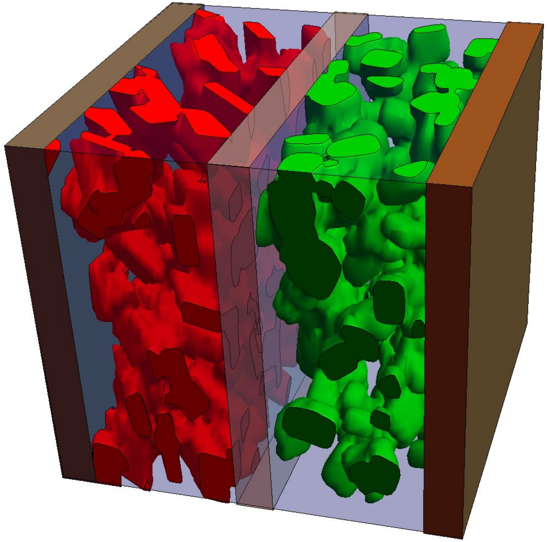
$$\boldsymbol{N}^{\pm} \cdot \boldsymbol{n} = -\boldsymbol{N_e} \cdot \boldsymbol{n} = \frac{j^{\pm}}{F}$$

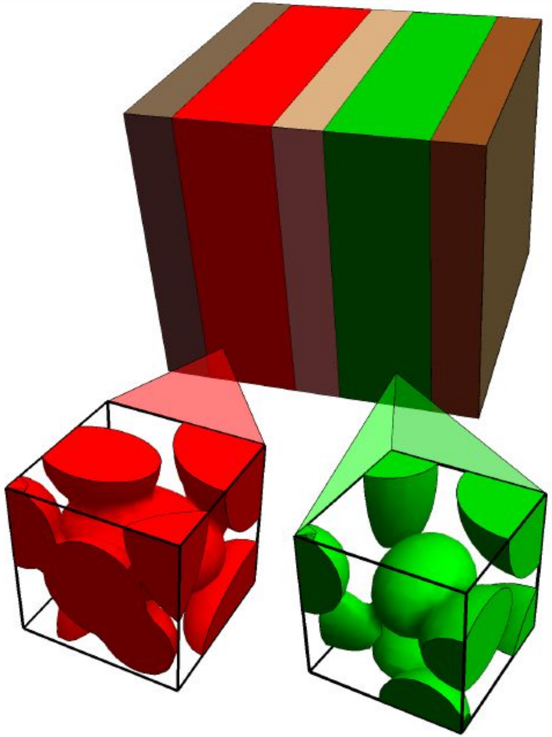
$$j^{\pm} = j_0^{\pm} \sinh \left(\frac{F}{2RT} \left(\phi^{\pm} - \phi_e - U(c^{\pm}) \right) \right)$$

$$j_0^{\pm} = F k^{\pm} \left(\frac{c_e}{c_{e0}} \right)^{1/2} \left(\frac{c^{\pm}}{c^{\pm}_{\max}} \right)^{1/2} \left(\frac{c^{\pm}_{\max} - c^{\pm}}{c^{\pm}_{\max}} \right)^{1/2}$$

Physics-based model

Porous electrode theory





Derivation of an effective thermal electrochemical model for porous electrode batteries using asymptotic homogenisation*, M. J. Hunt, F. Brosa Planella, F. Theil, and W. D. Widanage, Journal of Engineering Mathematics, 2020*

Porous electrode theory

Macroscale model

$$\nabla \cdot \boldsymbol{i}^{\pm} = -a^{\pm} j^{\pm}, \quad \boldsymbol{i}^{\pm} = -\sigma_{\mathrm{eff}}^{\pm} \nabla \phi^{\pm}$$

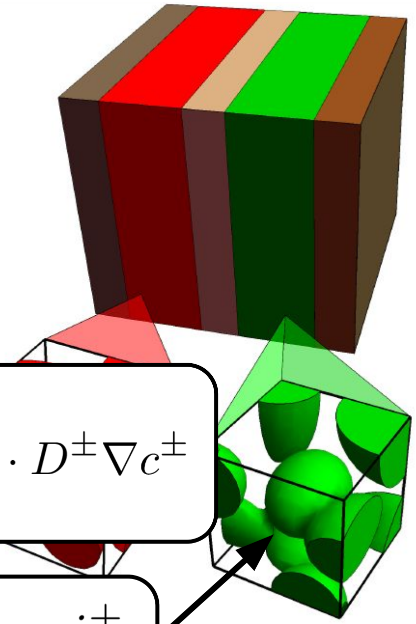
$$\nabla \cdot \boldsymbol{i}_e = a^{\pm} j^{\pm},$$

$$\boldsymbol{i}_e = \sigma_e^{\pm} \varepsilon^{1.5} \left(-\nabla \phi^{\pm} + 2(1 - t^{+}) \frac{RT}{F} \nabla \log(c_e) \right)$$

$$\varepsilon \frac{\partial c_e}{\partial t} = \nabla \cdot \left(D_e \varepsilon^{1.5} \nabla c_e \right) + \frac{1 - t+}{F} \nabla \cdot \boldsymbol{i}_e$$

$$j^{\pm} = j_0^{\pm} \sinh \left(\frac{F}{2RT} \left(\phi^{\pm} - \phi_e - U(c^{\pm}) \right) \right)$$

$$j_0^{\pm} = F k^{\pm} \left(\frac{c_e}{c_{e0}} \right)^{1/2} \left(\frac{c^{\pm}}{c_{\max}^{\pm}} \right)^{1/2} \left(\frac{c_{\max}^{\pm} - c^{\pm}}{c_{\max}^{\pm}} \right)^{1/2}$$

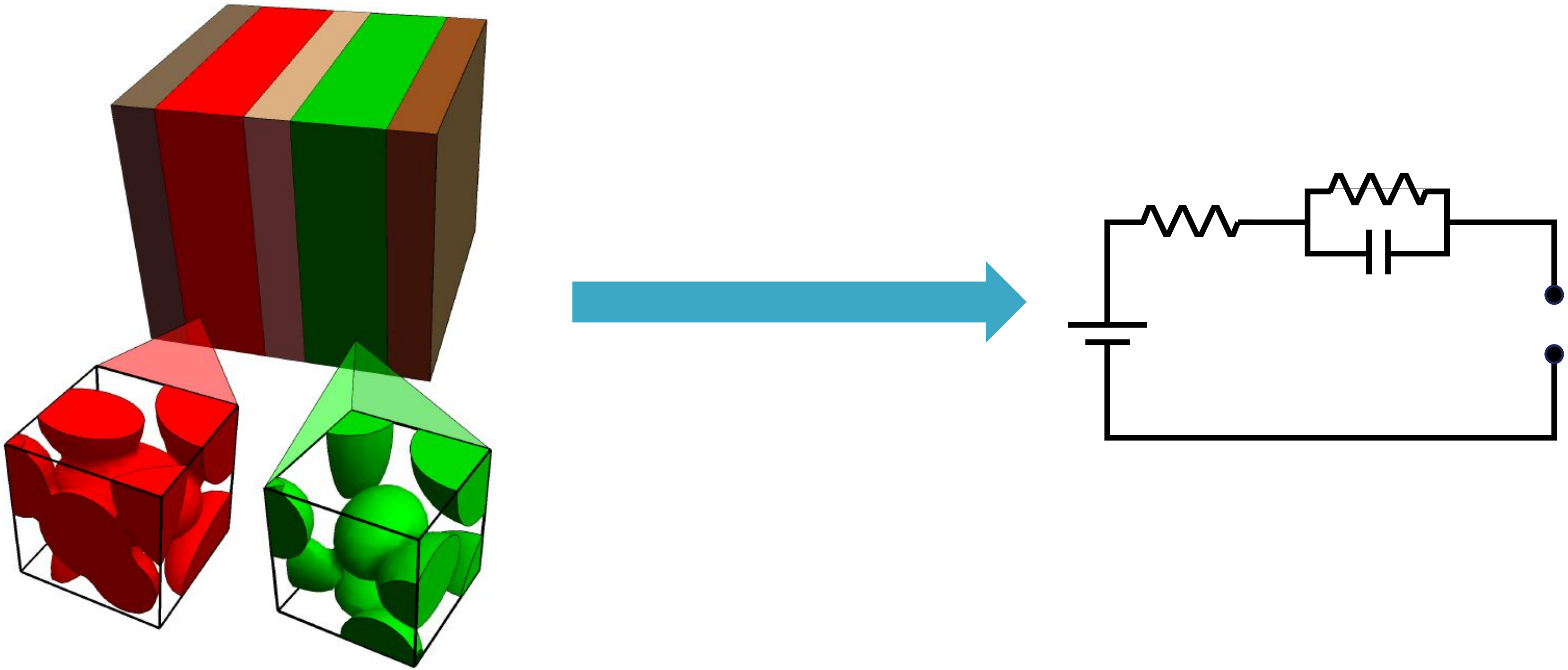


$$\frac{\partial c^{\pm}}{\partial t} = \nabla \cdot D^{\pm} \nabla c^{\pm}$$

$$-D^{\pm} \frac{\partial c^{\pm}}{\partial n} = \frac{j^{\pm}}{F}$$

Bridging the gap

Can we develop models whose complexity is comparable to an equivalent circuit model, but with the fidelity of a physics-based model?



PART 1: POUCH CELLS

Collaborators: *S.G. Marquis, V. Sulzer, C.P. Please, S.J. Chapman*

How to simplify?

Timescales:

$$\tau_d = \frac{F c^-_{\max} V}{I}$$

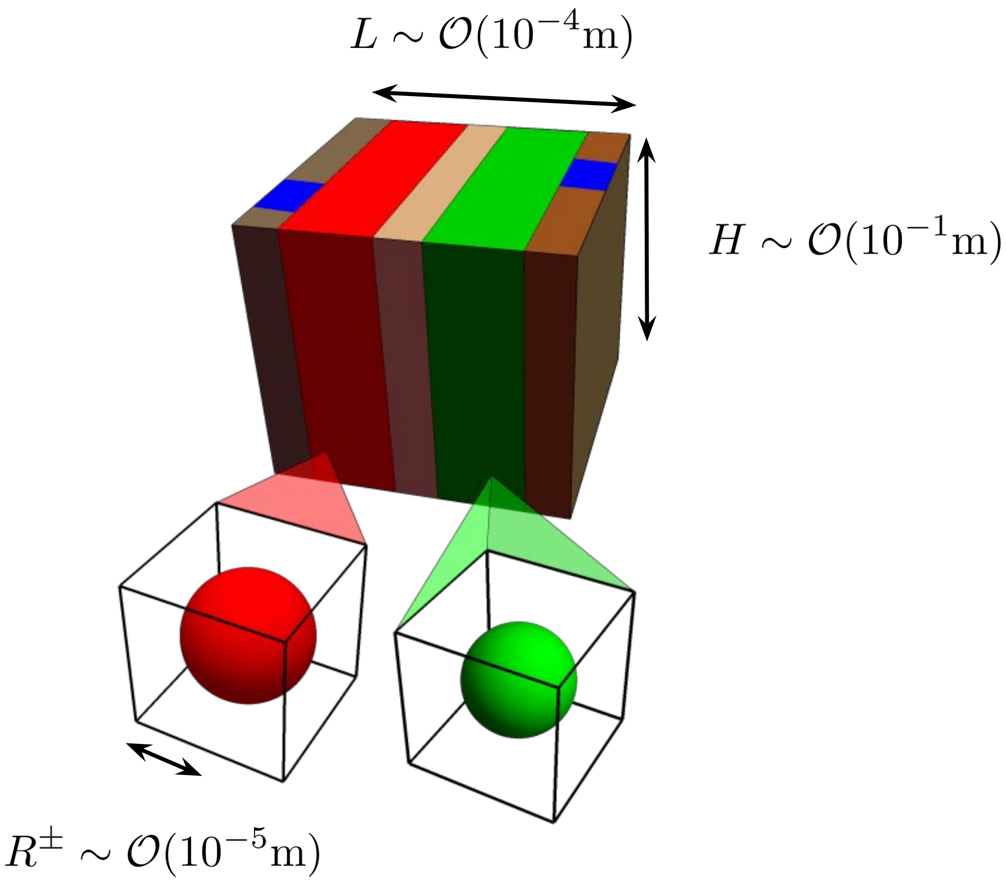
$$\tau_e = \frac{L^2}{D_e}$$

$$\tau_s^\pm = \frac{(R^\pm)^2}{D^\pm}$$

Resistances:

$$\sigma_{cc} \gg \sigma^\pm$$

$$H \gg L$$

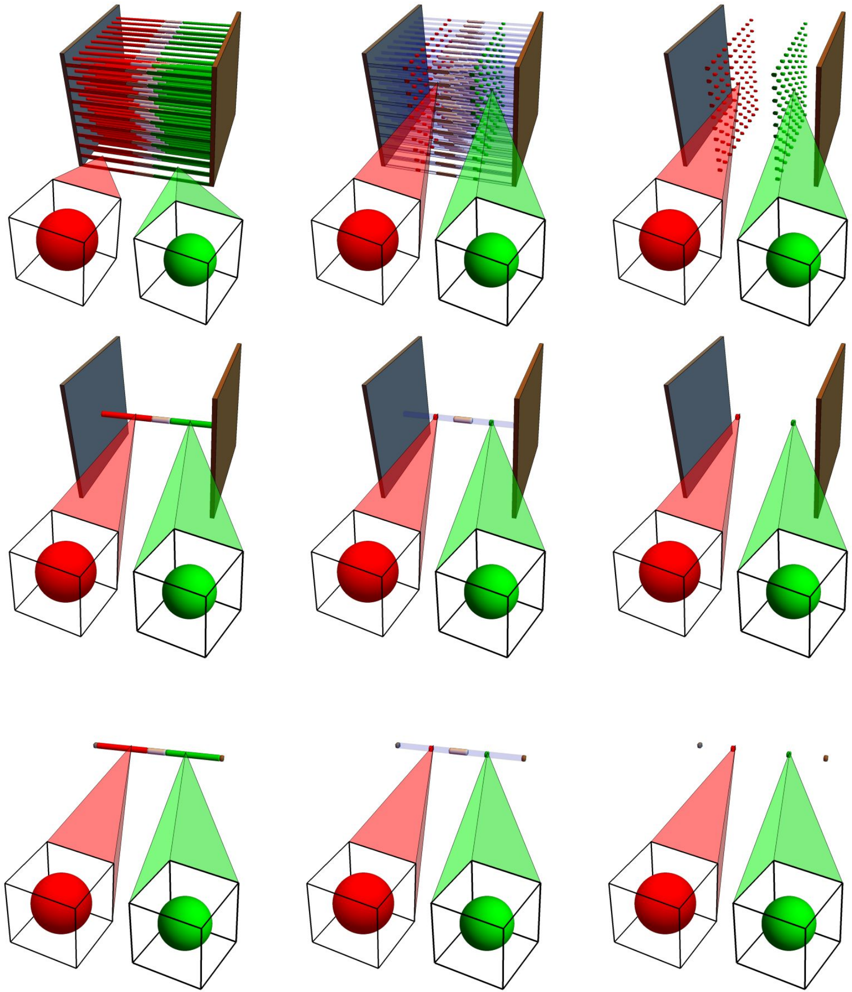


How to simplify?

https://batterymodel.ox.ac.uk/#Videos

- Simplifications to through-cell and transverse behaviour can be combined

- Can include different microscale problems to give even more models



Asymptotic reduction of a lithium-ion pouch cell model, *R. Timms, S.G. Marquis, V. Sulzer, C.P. Please, S.J. Chapman, SIAM Journal on Applied Mathematics, 2021*

A suite of reduced-order models of a single-layer lithium-ion pouch cell, *S.G. Marquis, R. Timms, V. Sulzer, C.P. Please, S.J. Chapman, Journal of the Electrochemical Society, 2020*

“2+1D” model

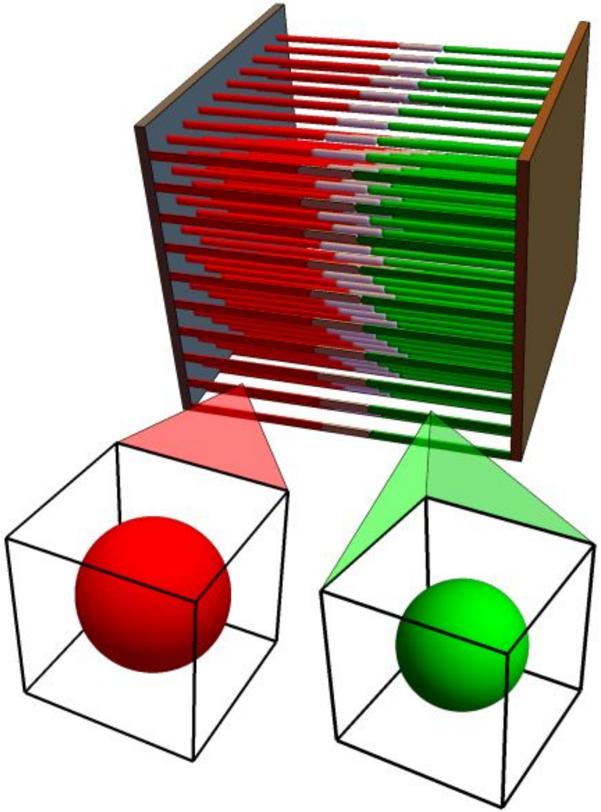
Small aspect ratio:

$$\delta = \frac{L}{H} \ll 1$$

Large current collector conductance:

$$\frac{I_{\text{app}} F}{L_{cc} \sigma_{cc} R T} \sim 1$$

$$V_T = \frac{RT}{F} \approx 25\,\text{mV}$$



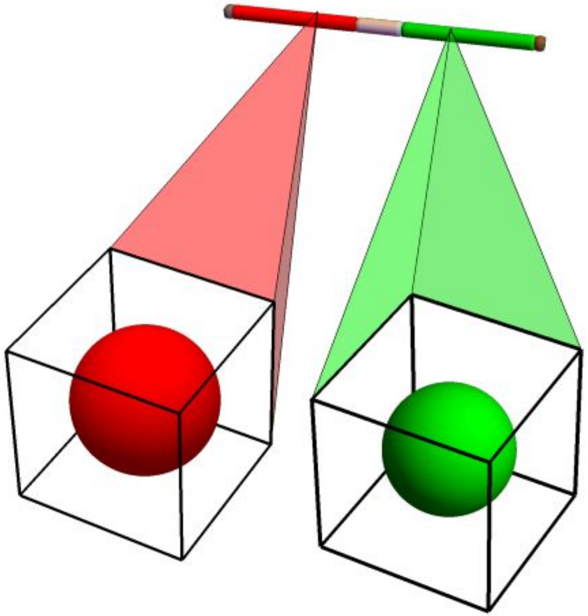
Asymptotic reduction of a lithium-ion pouch cell model, *R. Timms, S.G. Marquis, V. Sulzer, C.P. Please, S.J. Chapman, SIAM Journal on Applied Mathematics, 2021*

Doyle-Fuller-Newman Model

“Pseudo two-dimensional” model

- Limit of very high conductivity
- Current collector potentials are uniform

$$\phi_{cn} = 0, \quad \phi_{cp} = V$$



***Modeling of galvanostatic charge and discharge of the lithium/polymer/insertion cell**, M. Doyle, T. F. Fuller, and J. Newman, Journal of the Electrochemical Society, 1993*

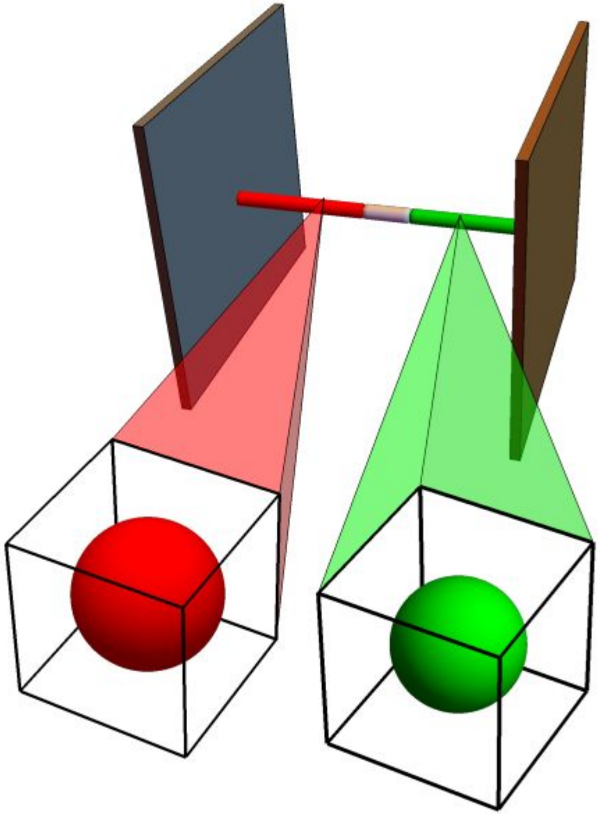
"CC" model

Small aspect ratio:

$$\delta = \frac{L}{H} \ll 1$$

Very large current collector conductance:

$$\frac{I_{\mathrm{app}} F}{L_{cc} \sigma_{cc} R T} \ll 1$$



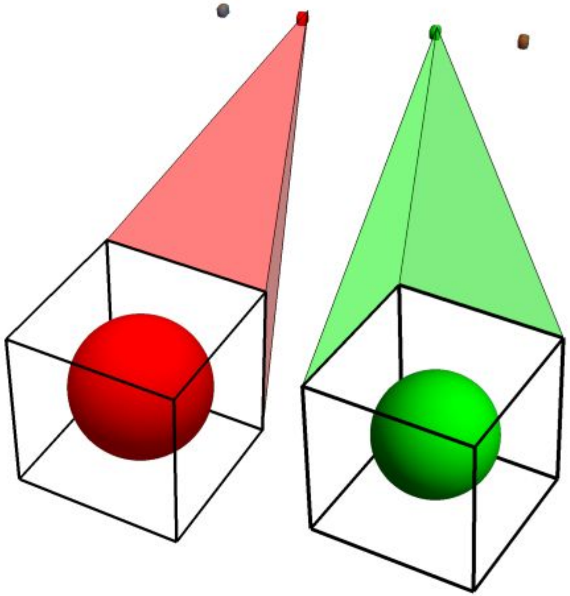
Asymptotic reduction of a lithium-ion pouch cell model, *R. Timms, S.G. Marquis, V. Sulzer, C.P. Please, S.J. Chapman, SIAM Journal on Applied Mathematics, 2021*

The Single Particle Model (SPM)

- Electrolyte diffusion time much shorter than typical discharge time:

$$\tau_e \ll \tau_d$$

- Uniform electrolyte concentration
- All particles behave in the same way
- ≈100 times faster to solve than the DFN



An asymptotic derivation of a single particle model with electrolyte, *S.G. Marquis, V. Sulzer, R. Timms, C.P. Please, S.J. Chapman, Journal of the Electrochemical Society, 2020*

The Single Particle Model with electrolyte (SPMe)

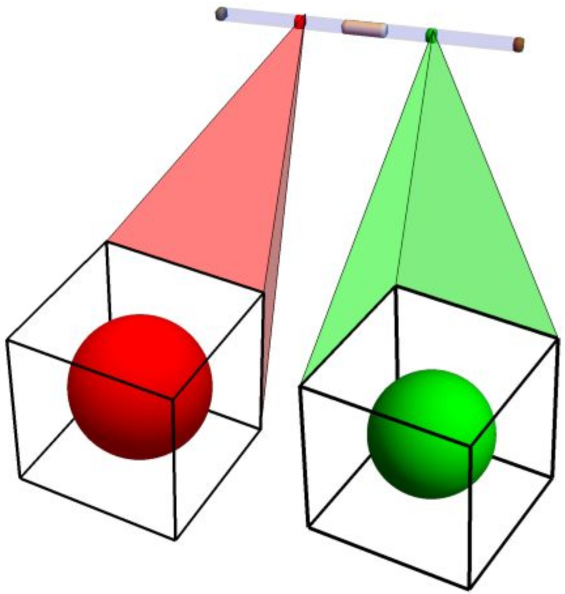
- Electrolyte diffusion time much shorter than typical discharge time:

$$\tau_e \ll \tau_d$$

- Capture concentration gradients in electrolyte

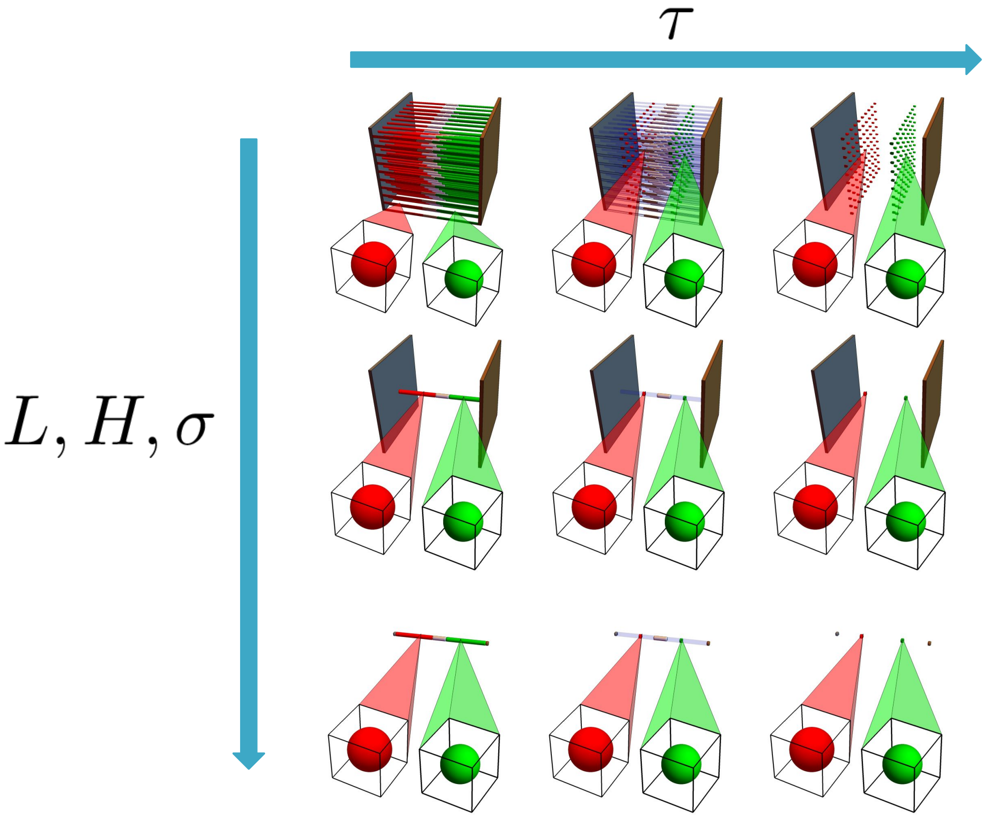
- All particles still behave in the same way

- ≈50 times faster to solve than the DFN



An asymptotic derivation of a single particle model with electrolyte, *S.G. Marquis, V. Sulzer, R. Timms, C.P. Please, S.J. Chapman, Journal of the Electrochemical Society, 2020*

Which model should I pick?



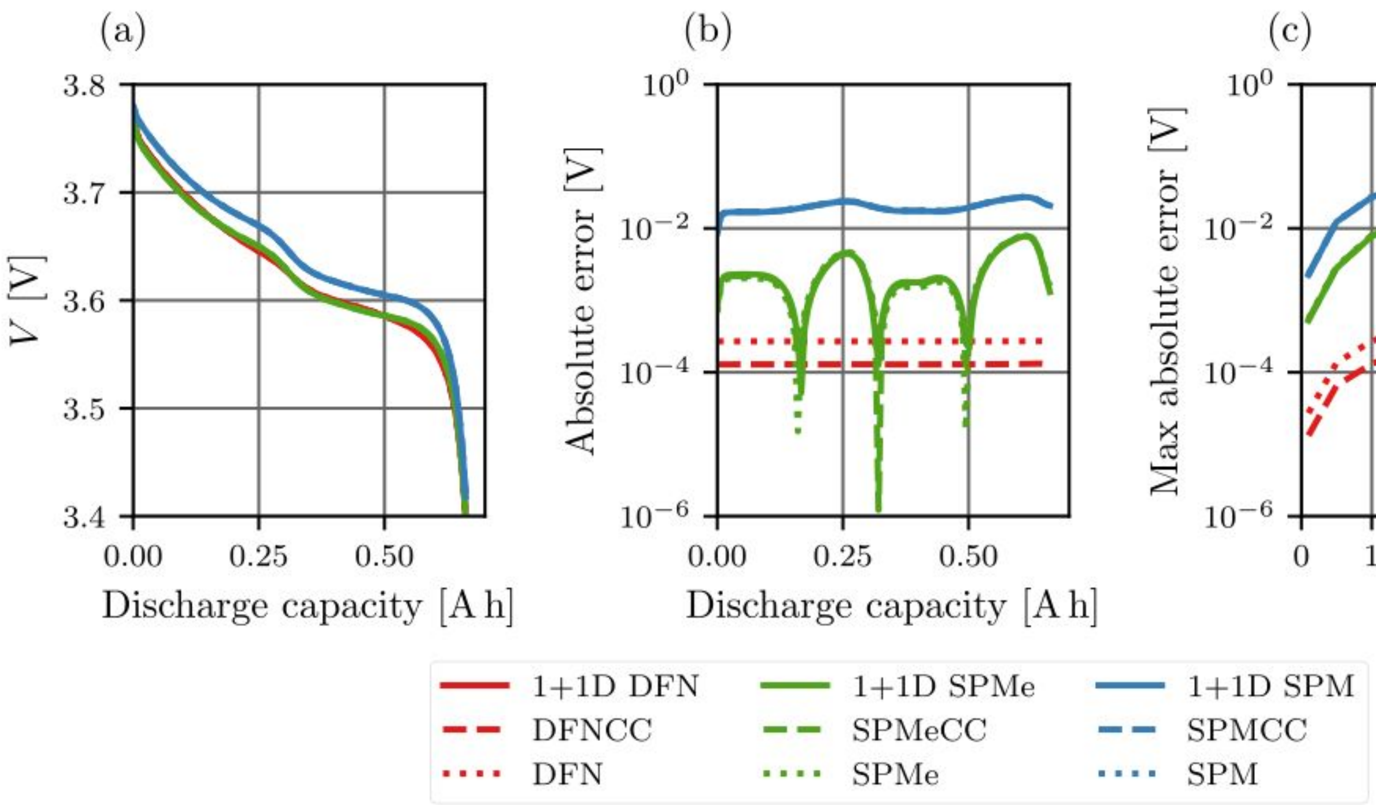
Is it better to use lots of simple through-cell models...

...or fewer more complicated through-cell models?

***A suite of reduced-order models of a single-layer lithium-ion pouch cell**, S.G. Marquis, R. Timms, V. Sulzer, C.P. Please, S.J. Chapman, Journal of the Electrochemical Society, 2020*

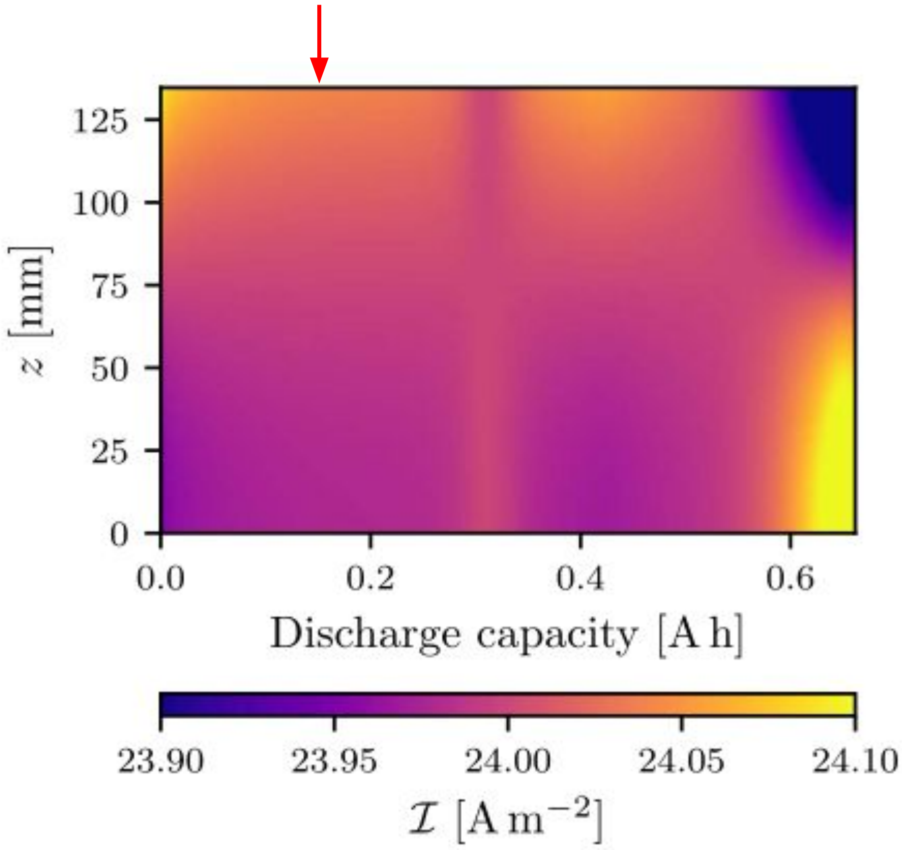
Pouch cell modelling (1+1D)

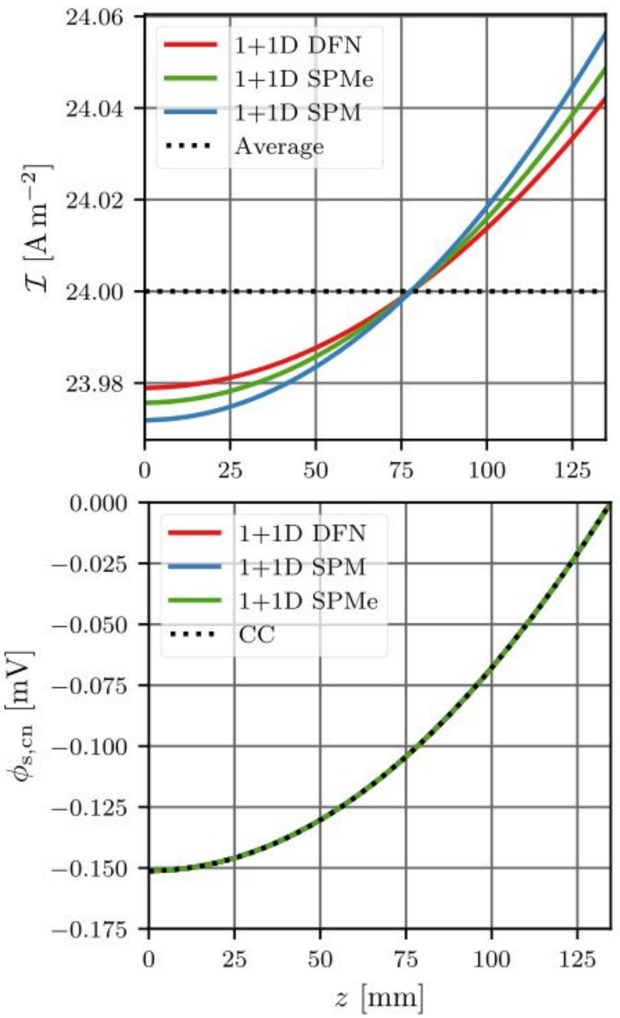
1C discharge, uniform cooling



Pouch cell modelling (1+1D)

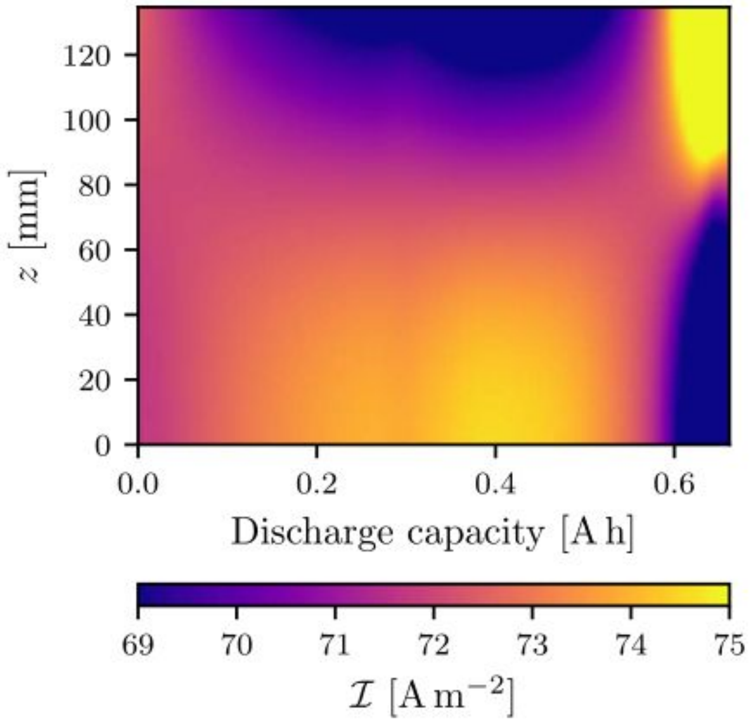
1C discharge, uniform cooling

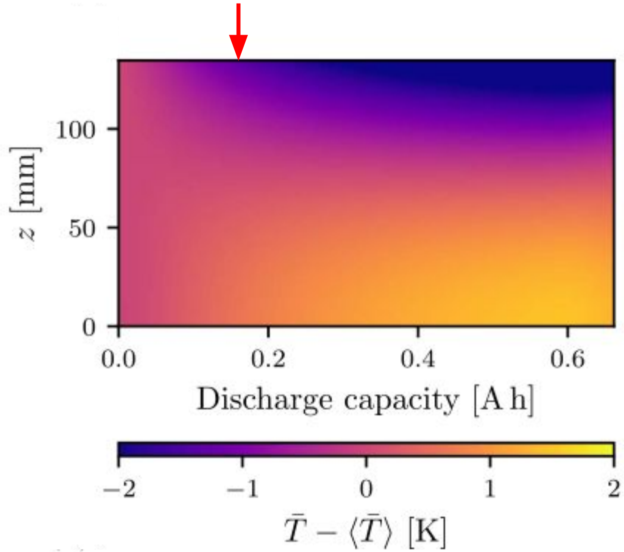


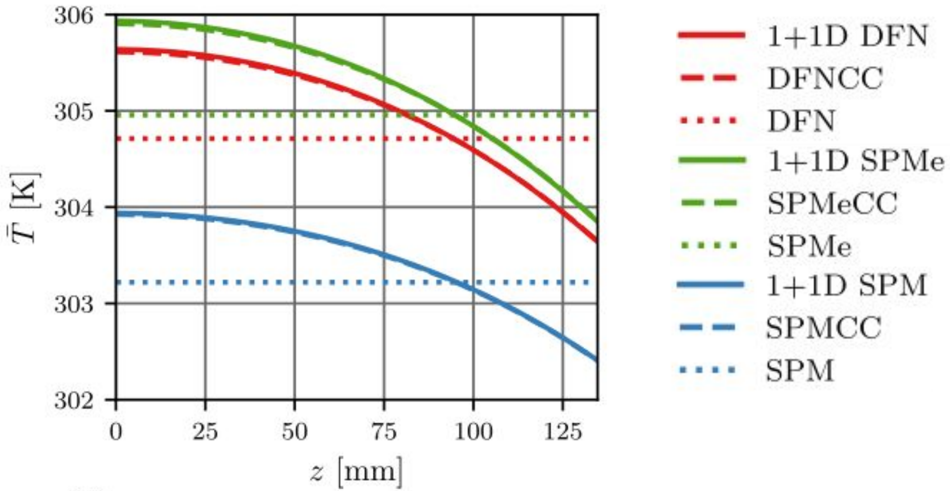


Pouch cell modelling (1+1D)

3C discharge, tab cooling

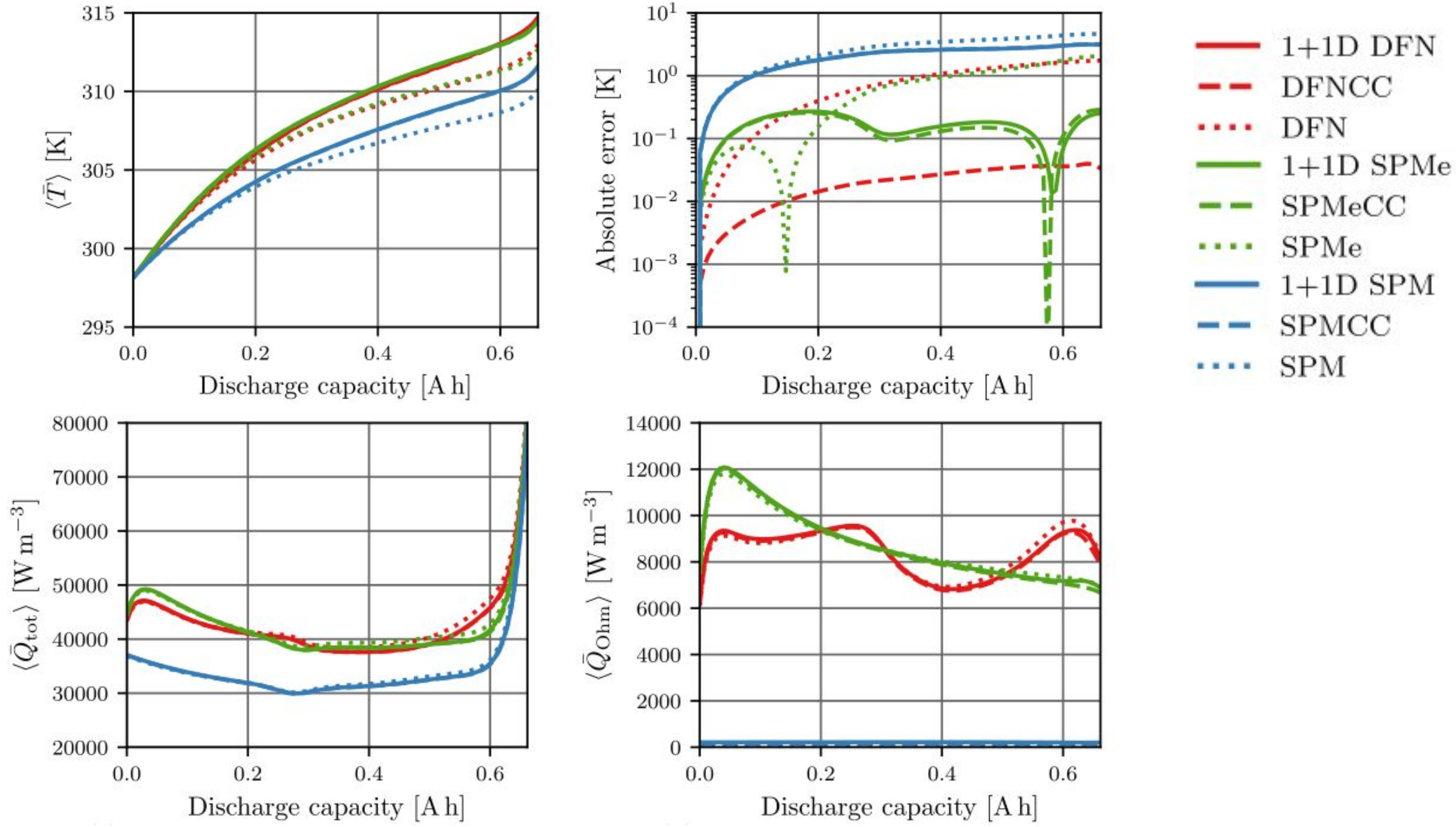






Pouch cell modelling (1+1D)

3C discharge, tab cooling



Pouch cell modelling (1+1D)

Table IV. Qualitative evaluation of model. In the variables, we employed the traffic light system described in Table V. For the final set of columns (current dependence), we make use of the results in Fig. 2c with the following traffic light system for the maximum absolute errors: <1 × 10^{-3} V (green), <1 × 10^{-1} V (orange), <1 V (red).

Model	Solve time [ms]	States	1 C			3 C	V		
			$\mathcal{I}$	$\phi_{\mathrm{s,cn}}$	$\bar{c}_{\mathrm{s,n}}$	$\langle \bar{T} \rangle$	$I_{\mathrm{app}} < 1\,\mathrm{C}$	$1\,\mathrm{C} < I_{\mathrm{app}} < 4\,\mathrm{C}$	$I_{\mathrm{app}} > 4C$
1+1D DFN	8377	49561	🟢	🟢	🟢	🟢	🟢	🟢	🟢
1+1D SPMe	1519	3961	🟢	🟢	🟢	🟠	🟠	🟠	🔴
1+1D SPM	102	1261	🟠	🟠	🟠	🔴	🟠	🔴	🔴
DFNCC	248	1651	🔴	🟠	🔴	🟢	🟢	🟢	🟢
SPMeCC	10	131	🔴	🟠	🔴	🟠	🟠	🟠	🔴
SPMCC	5	41	🔴	🟠	🔴	🔴	🟠	🔴	🔴
DFN	248	1651	🔴	🔴	🔴	🔴	🟢	🟢	🟢
SPMe	10	131	🔴	🔴	🔴	🔴	🟠	🟠	🔴
SPM	5	41	🔴	🔴	🔴	🔴	🟠	🔴	🔴

Summary

- Homogenisation can be used to formally derive porous electrode theory
- Various parameter regimes can be explored to develop a suite of battery models
- Choice of model depends on application
- Extra physics can be included (SEI, mechanics, …)
- Can scale up further from electrode-scale to cell-scale (multi-layer pouch)
- Test it out in PyBaMM!

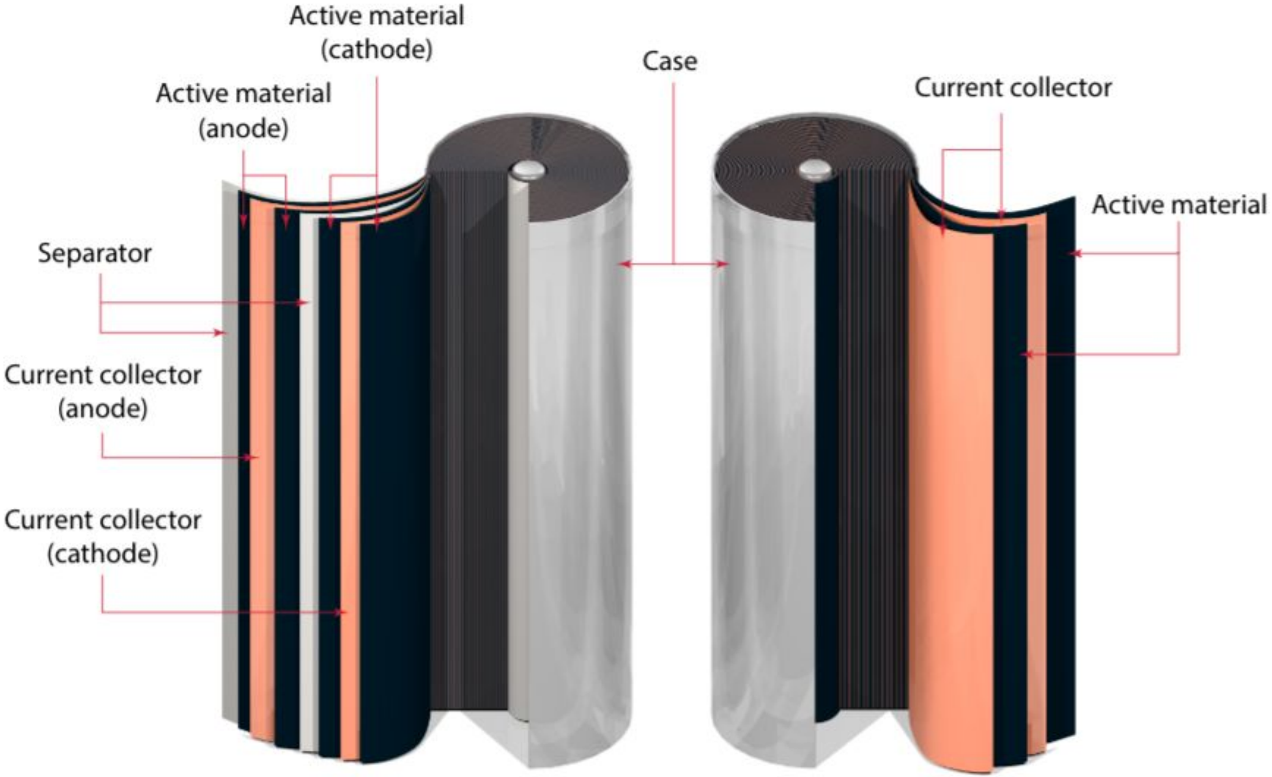
www.pybamm.org

PART 2: CYLINDRICAL CELLS

Collaborators: *T.G. Tranter, T. Heenan, S.G. Marquis, V. Sulzer, A. Jnawali, M.D.R. Kok, C.P. Please, S.J. Chapman, P.R. Shearing, S. Psaltis*

Jelly-roll cell

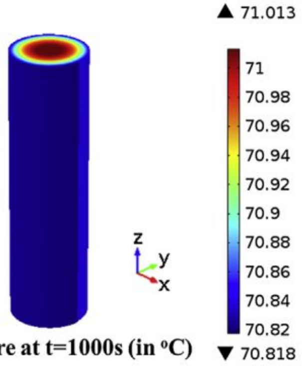
How to model this?



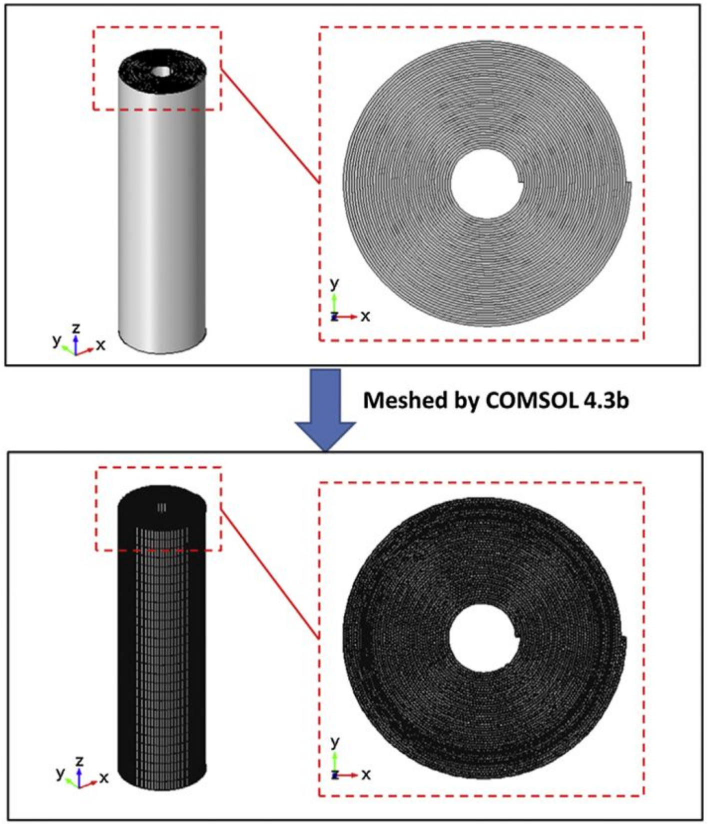
Jelly-roll cell

Direct numerical simulation

- 18650-type jelly-roll
- Large number of mesh elements
- Computationally expensive



Temperature at t=1000s (in °C)

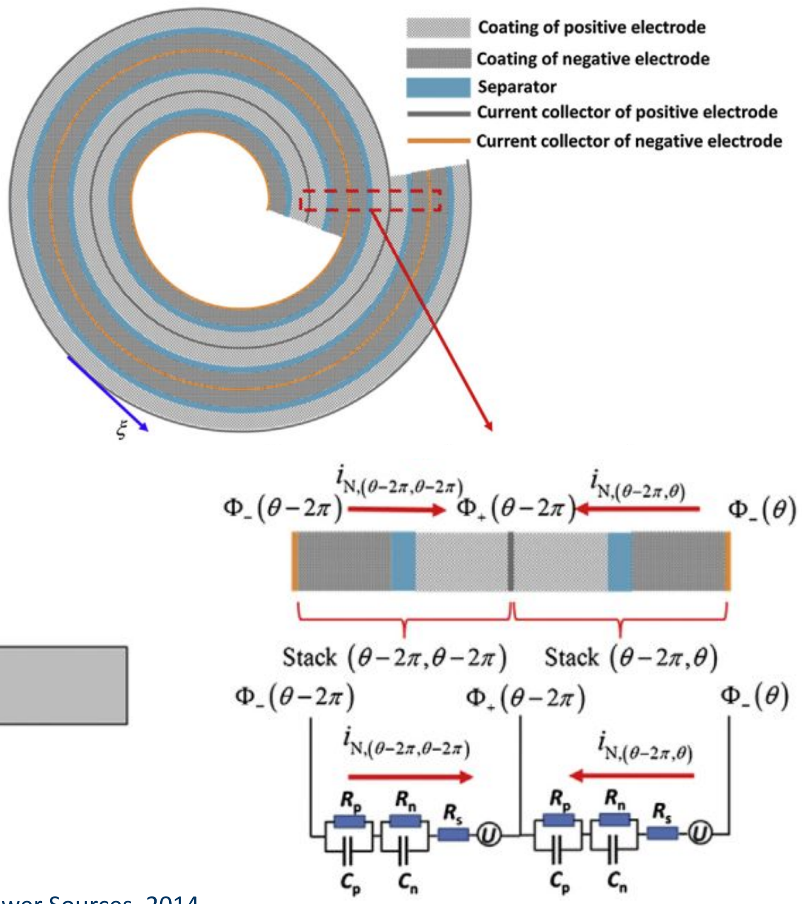


Mathematical model for a spirally-wound lithium-ion cell, Guo & White, Journal of Power Sources, 2014

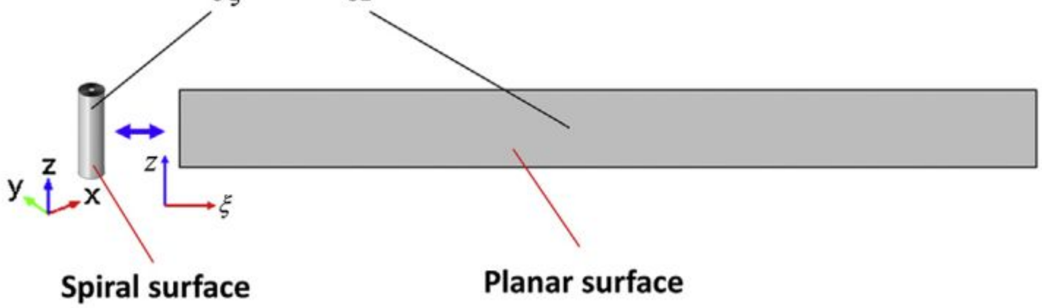
Jelly-roll cell

The "unwinding" method

- Solve electrochemistry and heat generation on planar domain
- Solve heat transport on cylindrical domain



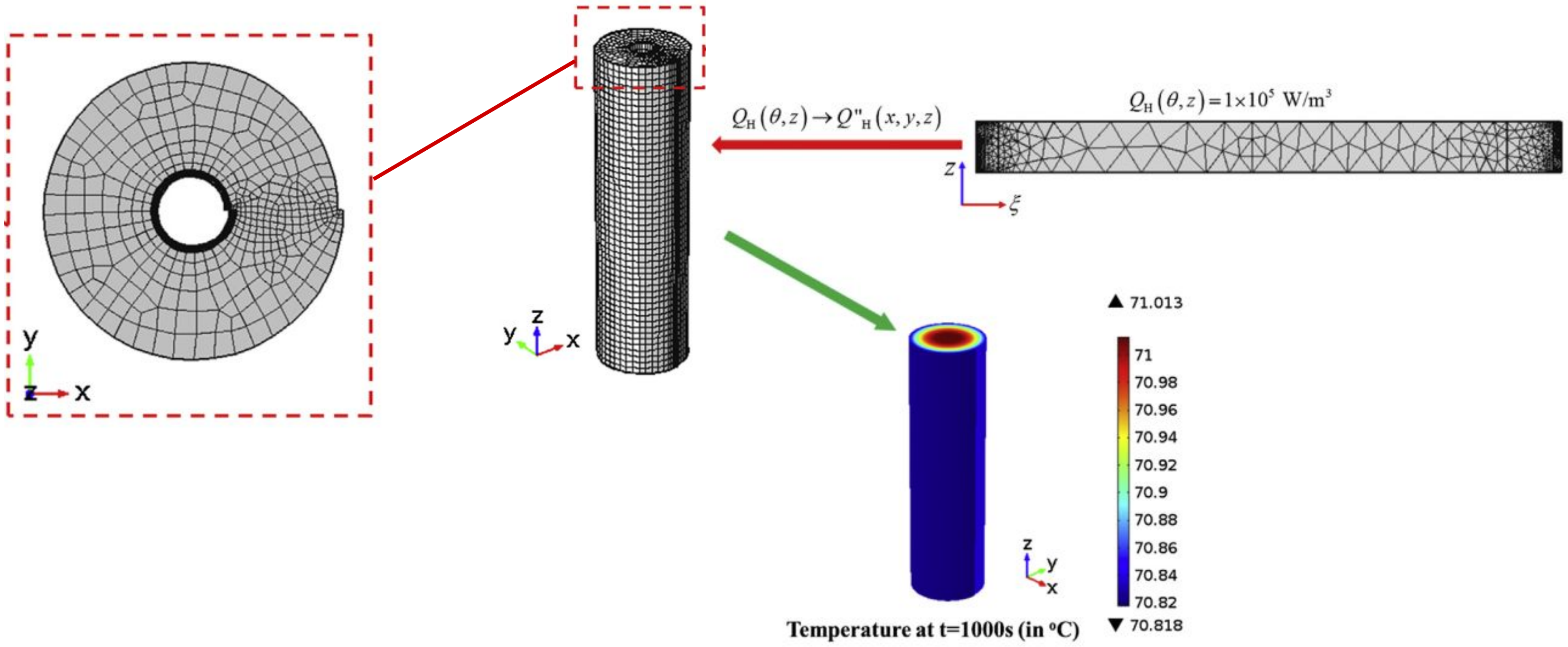
$$\sigma_j \frac{\partial^2 \Phi_j}{\partial \xi^2} + \sigma_j \frac{\partial^2 \Phi_j}{\partial z^2} + i_{v,j} = 0$$



Mathematical model for a spirally-wound lithium-ion cell, Guo & White, Journal of Power Sources, 2014

Jelly-roll cell

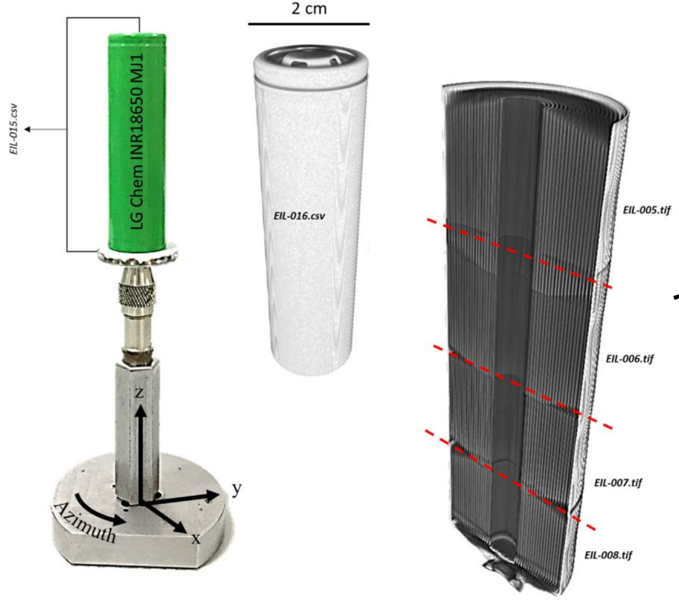
The "unwinding" method



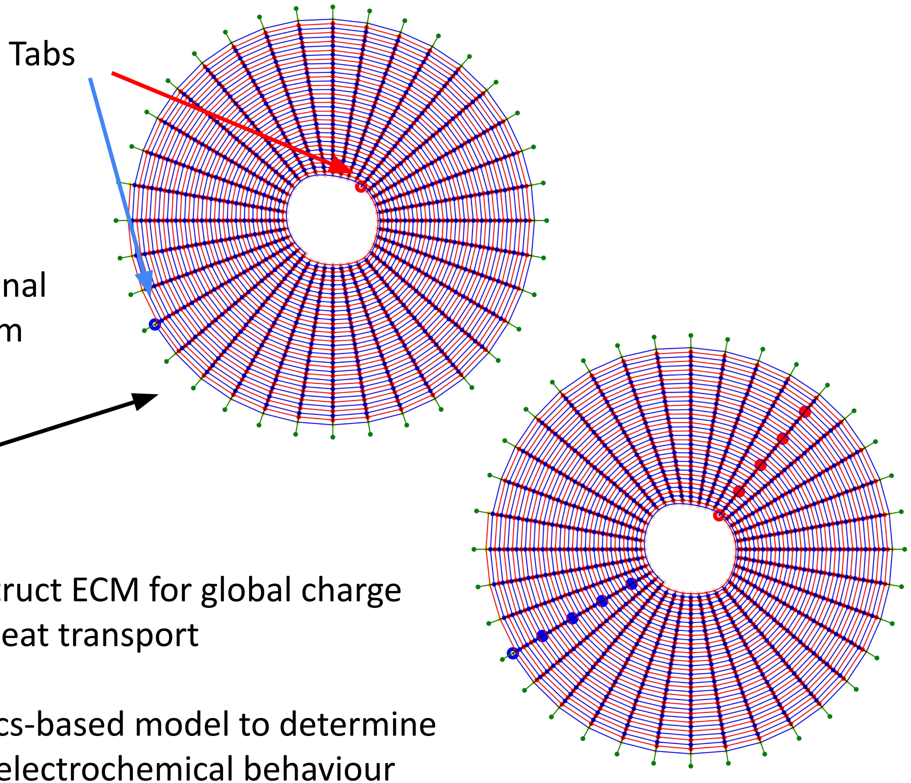
Mathematical model for a spirally-wound lithium-ion cell, Guo & White, Journal of Power Sources, 2014

Jelly-roll cell

A hybrid ECM and physics-based approach



Extract computational domain from CT scan



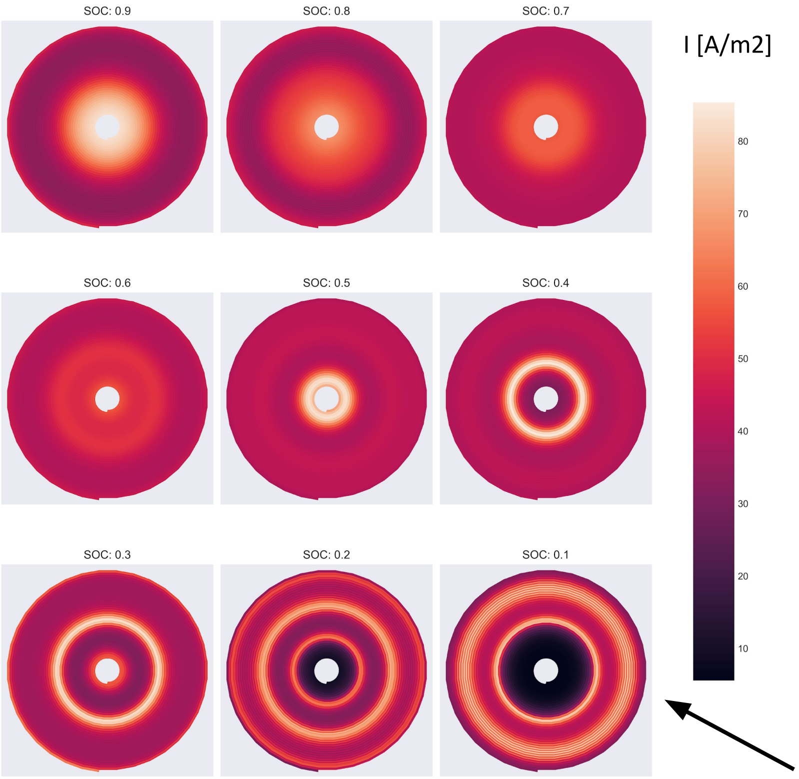
- Construct ECM for global charge and heat transport
- Physics-based model to determine local electrochemical behaviour and heat source

Probing heterogeneity in Li-ion batteries with coupled multiscale models of electrochemistry and thermal transport using tomographic domains, *T.G. Tranter, R. Timms, T. Heenan, S.G. Marquis, V. Sulzer, A. Jnawali, M.D.R. Kok, C.P. Please, S.J. Chapman, P.R. Shearing, Journal of the Electrochemical Society, 2020*

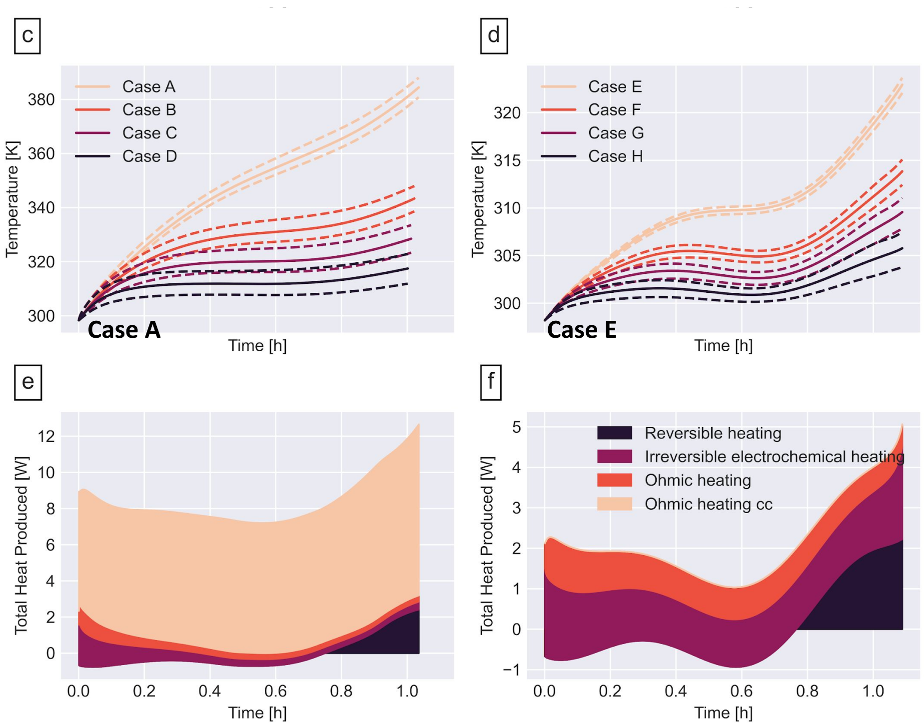
Prediction of Thermal Issues for Larger Format 4680 Cylindrical Cells and Their Mitigation with Enhanced Current Collection, *T.G. Tranter, R. Timms, P.R. Shearing, D.J.L. Brett, Journal of the Electrochemical Society, 2020*

Jelly-roll cell

A hybrid ECM and physics-based approach



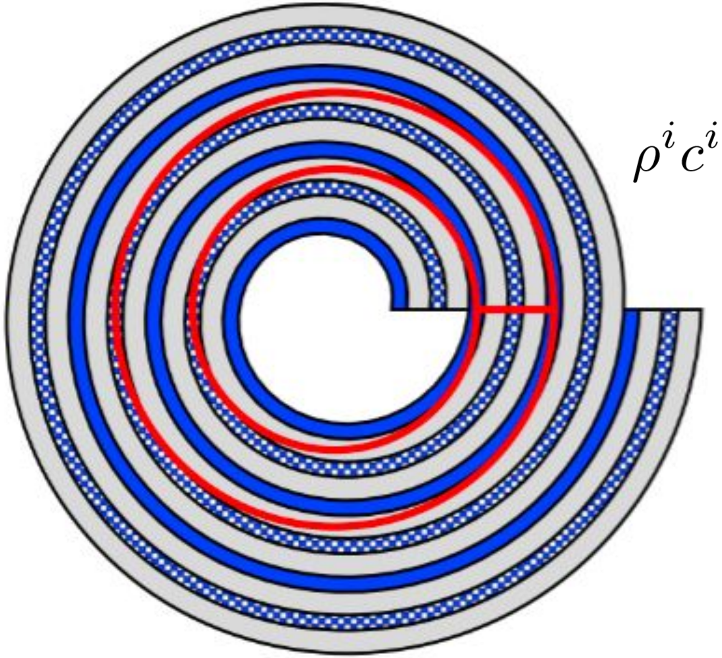
Case A



Convective heat loss [W m^{-2} K^{-1}]	Standard tabs	Tabless
10	A	E
28	B	F
50	C	G
100	D	H

Snapshots of local current density at various SOCs

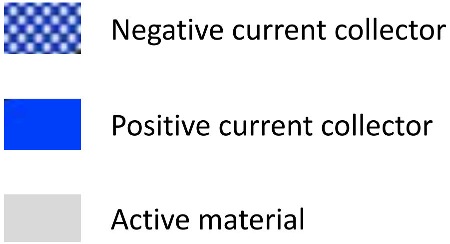
Jelly-roll model



$$0 = -\nabla \cdot (\sigma^i \nabla \phi^i), \quad i \in \{+, -\}$$

$$i^i = i^i(\phi^+ - \phi^-), \quad i \in \{a_1, a_2\}$$

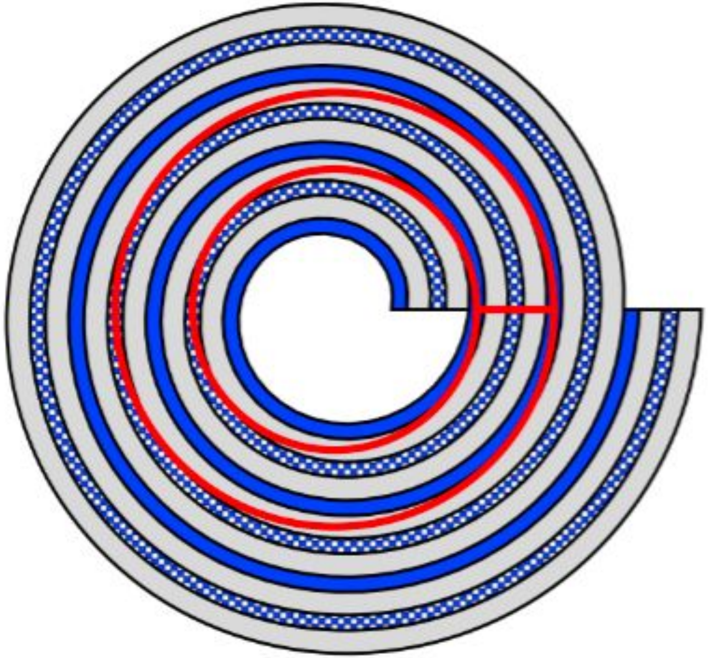
$$\rho^i c^i \frac{\partial T^i}{\partial t} = \nabla \cdot (\kappa^i \nabla T^i) + q^i, \quad i \in \{+, -, a_1, a_2\}$$



Homogenisation of spirally-wound high-contrast layered materials, Psaltis, Timms, Please, Chapman, 2021

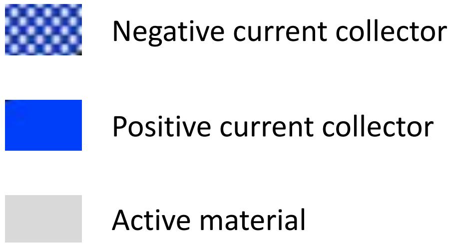
Simple jelly-roll model

Everything is a resistor...



$$-\boldsymbol{\nabla}\cdot\left(\sigma^i\boldsymbol{\nabla}\phi^i\right)=F^i(\vec{x}),$$

$$\text{in } \Omega^i, \quad i\in\{+,-,a_1,a_2\}.$$



Total sandwich thickness

Outer radius

$$h \ll L$$

Homogenisation of spirally-wound high-contrast layered materials, Psaltis, Timms, Please, Chapman, 2021

“Poorly conductive current collectors”

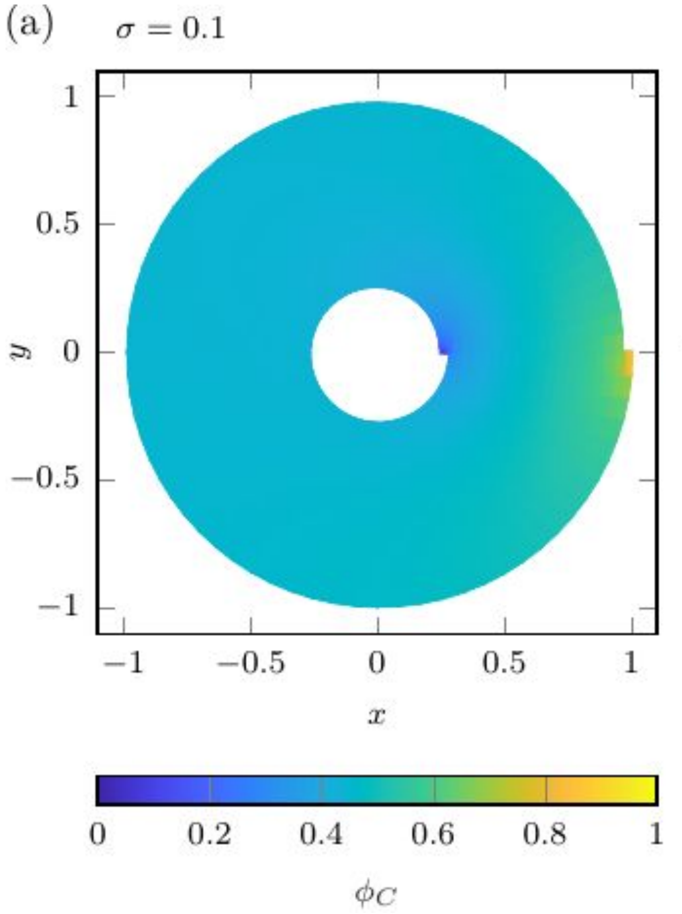
With $\sigma^+ \sim \sigma^- \sim \sigma^{a_1} \sim \sigma^{a_2},\ h \ll L$, we find

$$\frac{\sigma_N}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \phi_0}{\partial r}\right) + \frac{\sigma_T}{r^2}\frac{\partial^2 \phi_0}{\partial \theta^2} = 0,$$

where

$$\sigma_N = \frac{1}{2\delta^+/\sigma^+ + 2\delta^-/\sigma^- + \ell_1/\sigma^{a_1} + \ell_2/\sigma^{a_2}},$$
$$\sigma_T = 2\delta^+\sigma^+ + 2\delta^-\sigma^- + \ell_1\sigma^{a_1} + \ell_2\sigma^{a_2}.$$

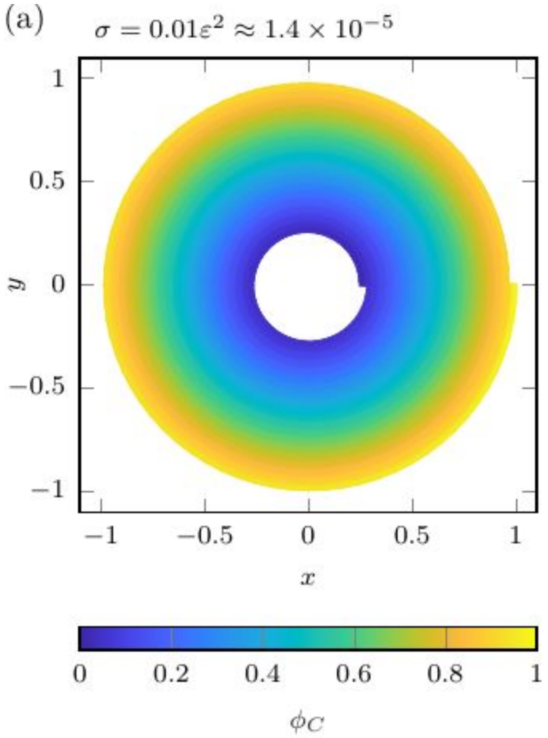
- Anisotropic conductivity tensor
- Spiral connectivity not important
- **Local anisotropy** matters, not global connectivity



“Reasonably conductive current collectors”

A limit with enhanced radial diffusion

(a)



With $L^2\sigma^{a_1} \sim L^2\sigma^{a_2} \sim h^2\sigma^+ \sim h^2\sigma^-$, $h \ll L$, we find

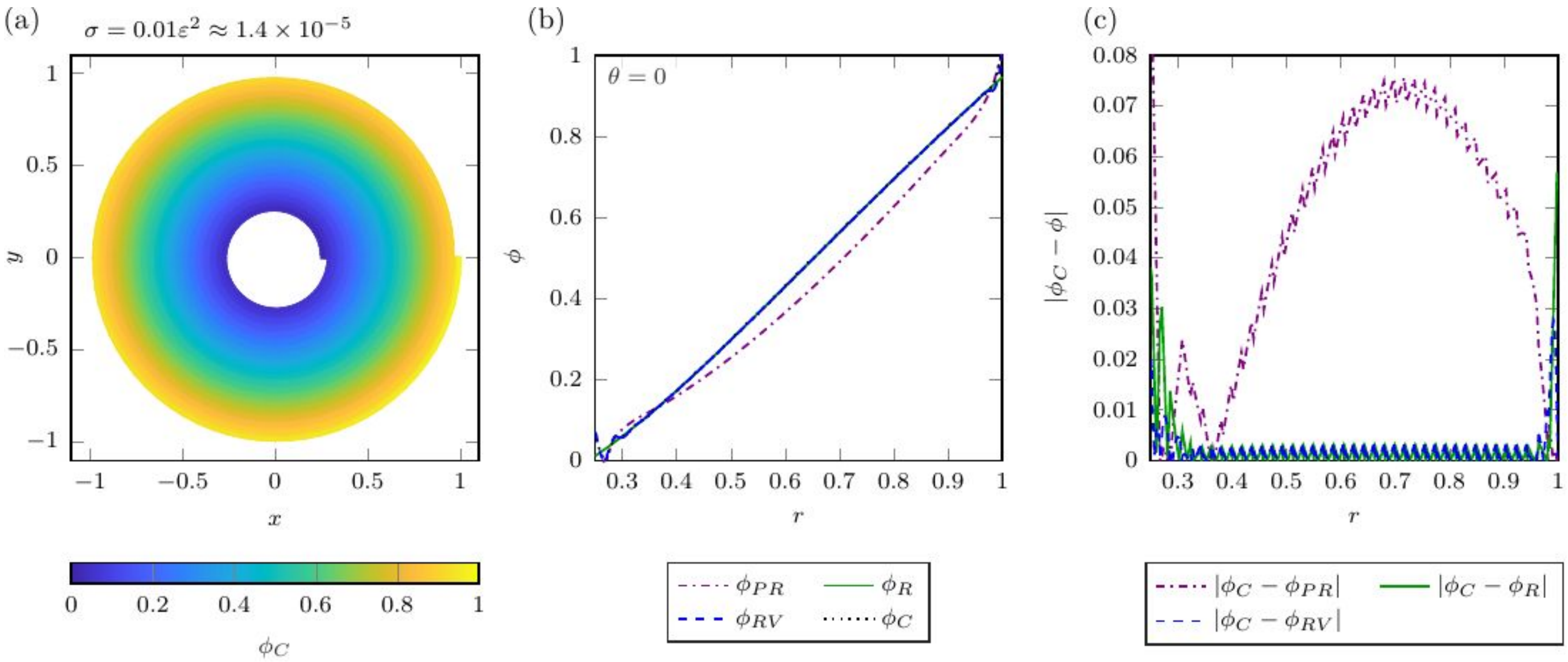
$$\frac{1}{(\ell_1/\sigma^{a_1} + \ell_2/\sigma^{a_2})}\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}\left(r\frac{\mathrm{d}\phi}{\mathrm{d}r}\right) + \frac{h^2(2\delta^+\sigma^+ + 2\delta^-\sigma^-)}{(2\pi)^2 r}\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{1}{r}\frac{\mathrm{d}\phi}{\mathrm{d}r}\right) = 0.$$

Current through the active material
(short distance, low conductivity, series)

Current through the current collectors
(long distance, high conductivity, parallel)

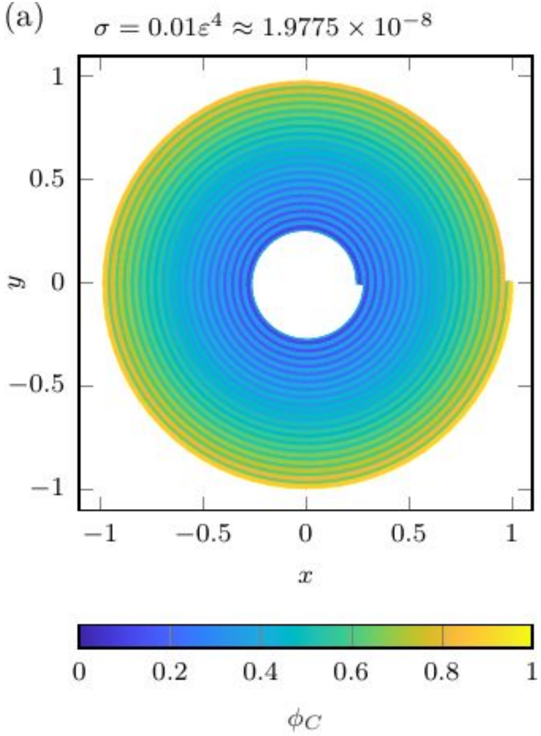
“Reasonably conductive current collectors”

A limit with enhanced radial diffusion



“Very conductive current collectors”

A potential pair model



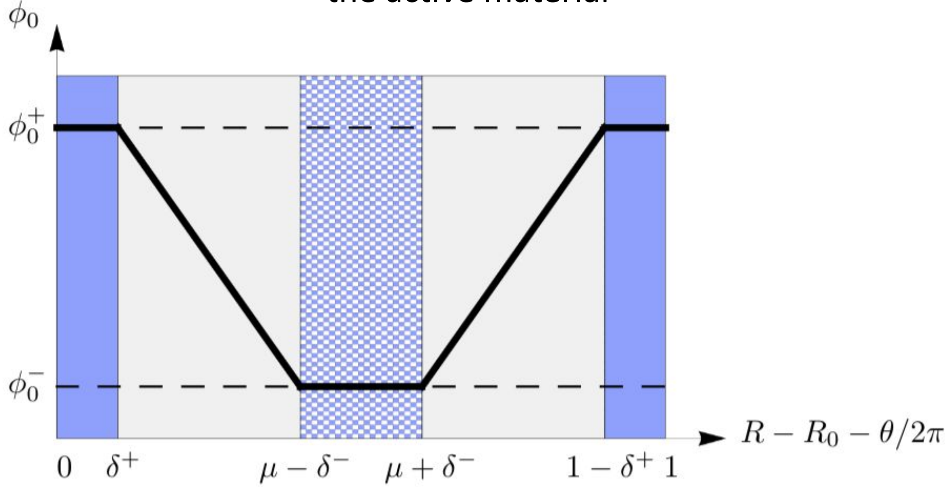
With $L^4\sigma^{a_1} \sim L^4\sigma^{a_2} \sim h^4\sigma^+ \sim h^4\sigma^-$, $h \ll L$ we find

$$\frac{h^2\delta^+\sigma^+}{2\pi^2}\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{1}{r}\frac{\mathrm{d}\phi^+}{\mathrm{d}r}\right) + \frac{\sigma^{a_1}(\phi^- - \phi^+)}{\ell_1 h^2} + \frac{\sigma^{a_2}(\phi^- - \phi^+)}{\ell_2 h^2} = 0,$$

$$\frac{h^2\delta^-\sigma^-}{2\pi^2}\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{1}{r}\frac{\mathrm{d}\phi^-}{\mathrm{d}r}\right) + \frac{\sigma^{a_2}(\phi^+ - \phi^-)}{\ell_2 h^2} + \frac{\sigma^{a_1}(\phi^+ - \phi^-)}{\ell_1 h^2} = 0.$$

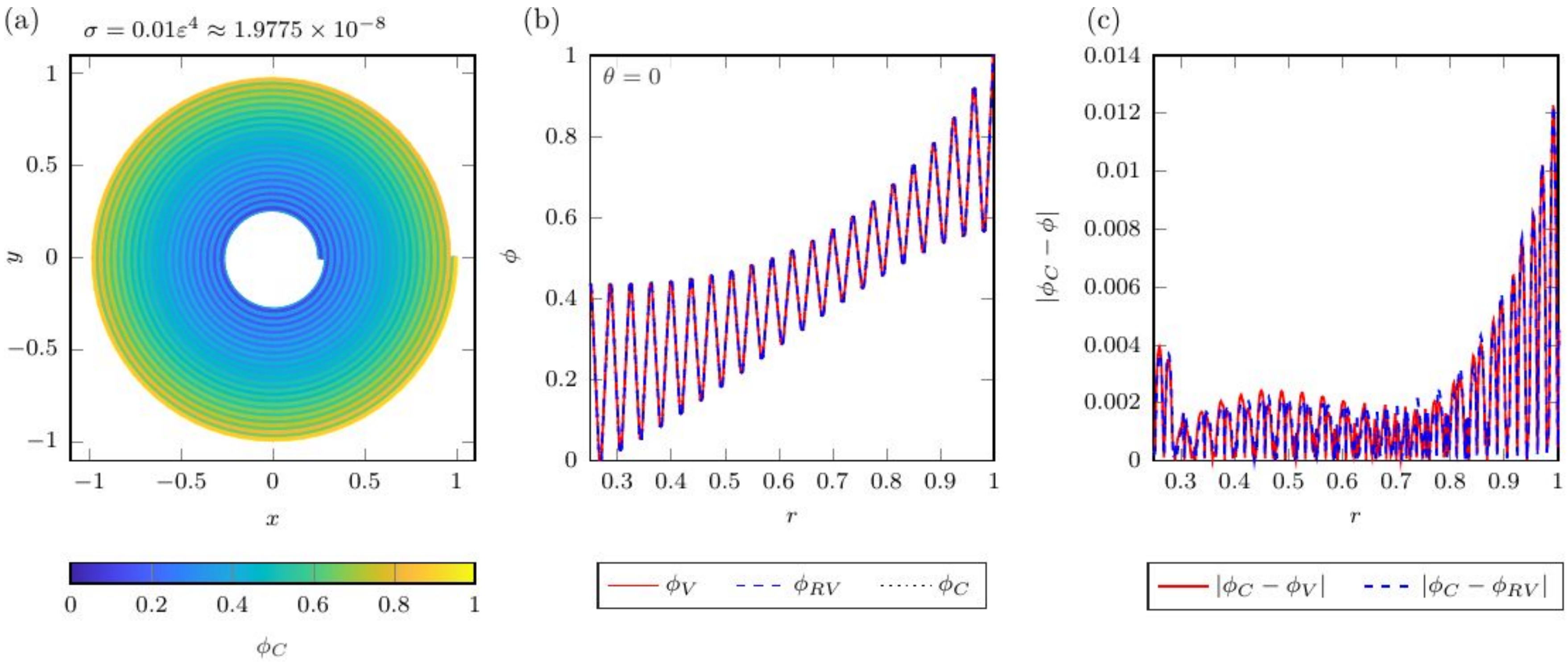
dominant path for current flow along the current collectors

potential difference drives a current through the active material



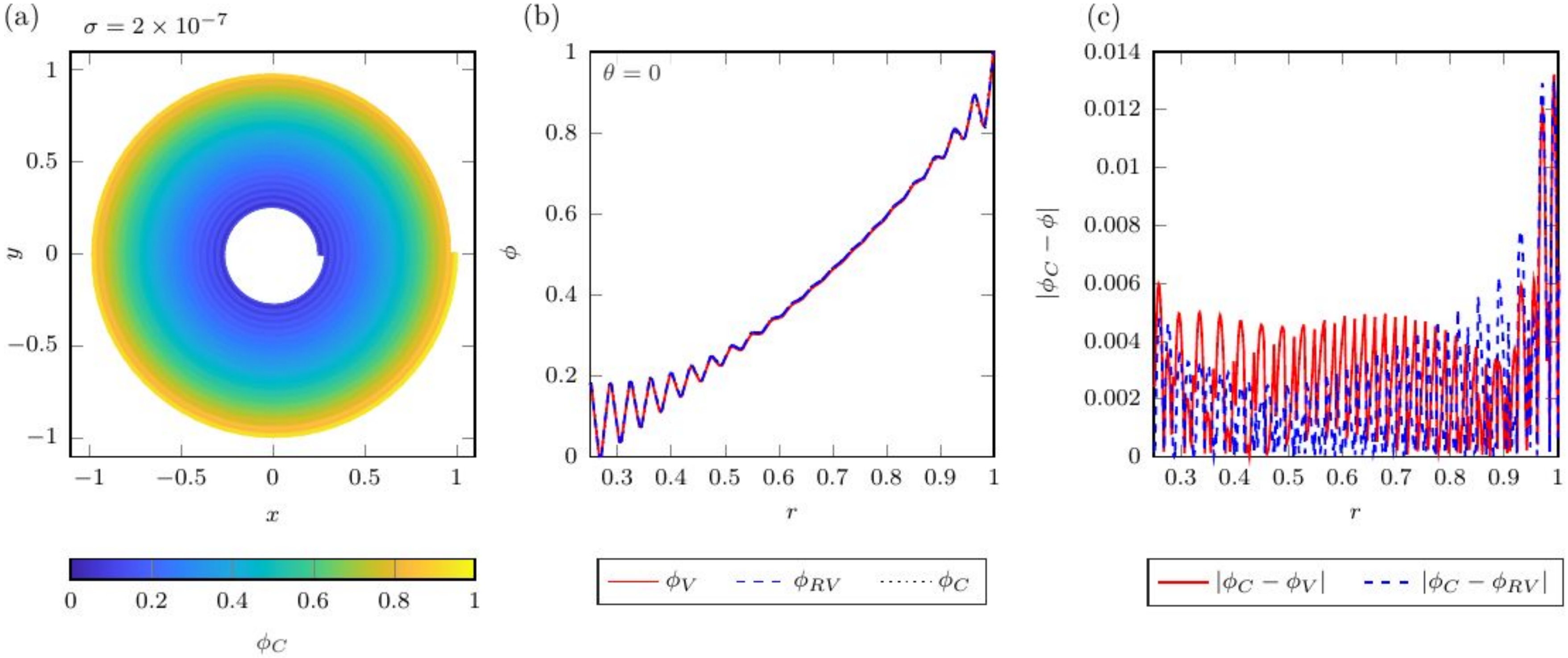
“Very conductive current collectors”

A potential pair model



Some real numbers

18650-type jelly roll



A more realistic battery model

Work in progress in PyBaMM

PyBaMM

"Very conductive" or "potential pair" model

$$\frac{h^2\delta^+\sigma^+}{2\pi^2}\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{1}{r}\frac{\mathrm{d}\phi^+}{\mathrm{d}r}\right)+\frac{2}{h}I(\phi^+-\phi^-,T)=0,$$

$$\frac{h^2\delta^-\sigma^-}{2\pi^2}\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{1}{r}\frac{\mathrm{d}\phi^-}{\mathrm{d}r}\right)-\frac{2}{h}I(\phi^+-\phi^-,T)=0,$$

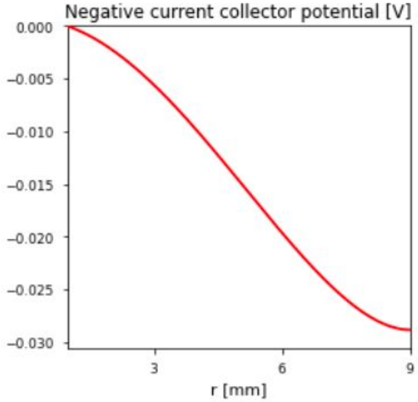
$$\phi^+-\phi^- = U^+(c^+,T)-U^-(c^-,T)+\eta^+(c^+,I,T)-\eta^-(c^-,I,T),$$

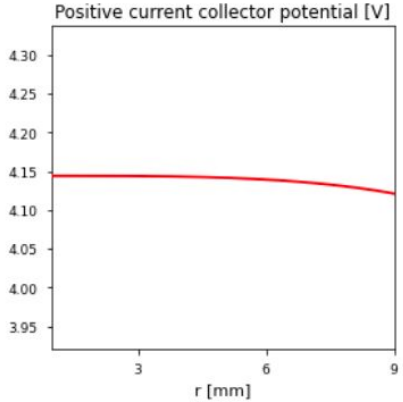
$$\rho_{\mathrm{eff}}C_{\mathrm{eff}}\frac{\partial T}{\partial t}=\frac{k_N}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right)+\frac{k_T}{r^2}\frac{\partial^2 T}{\partial\theta^2}+\bar{F}.$$

Some battery model (e.g. SPM)

Effective density & heat capacity

Anisotropic thermal conductivity





Summary

- Can use a combined ECM/physics-based approach to account for cell geometry
- Homogenisation reveals 3 interesting distinguished limits
- Models suitable for electrochemical and thermal modelling can be derived
- Computationally cheap - no need to explicitly mesh spiral structure
- Conceptually simpler - no awkward coupling between cylindrical and planar domain

Acknowledgements

UNIVERSITY OF OXFORD

http://people.maths.ox.ac.uk/chapman/battery/

PyBaMM

www.pybamm.org
https://github.com/pybamm-team/PyBaMM#contributors-

THE FARADAY INSTITUTION

The Faraday Institution
[grant number EP/S003053/1, FIRG003]

MultiScale Modelling

https://www.faraday.ac.uk/research/lithium-ion/