Asymptotic Model Reduction

Why Mathematicians Have An Important Role in Electrochemistry

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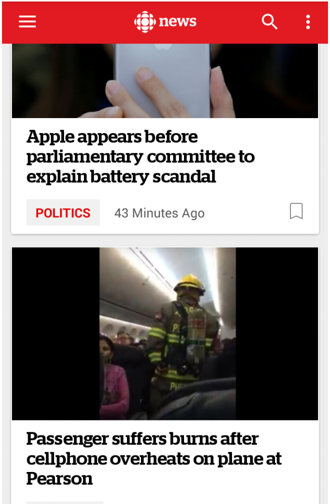
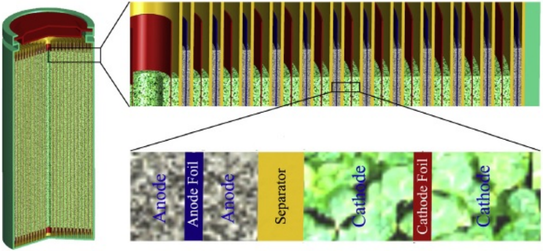
Introduction



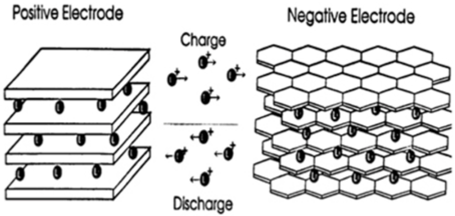
- Lithium-ion batteries power many of today's electronic devices
- Expected to play a key role in emerging technologies
- Advantages include long lifetime, high energy density, low self-discharge rates
- Unfortunately have been at the center of several controversies

What is an LiB?



- A battery is composed of two electrodes and an electrolyte
- **P**ositive electrode (cathode on discharge)
- **S**eparator - non-conductive region filled with electrolyte
- **N**egative electrode (anode on discharge)

What is an LiB?



Electrodes:

$$\mathrm{ILi} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} \mathrm{I} + \mathrm{Li}^{+} + \mathrm{e}^{-}$$

Electrolyte:

$$\mathrm{LiA} \rightleftharpoons \mathrm{Li}^{+} + \mathrm{A}^{-}$$

Modelling Strategies

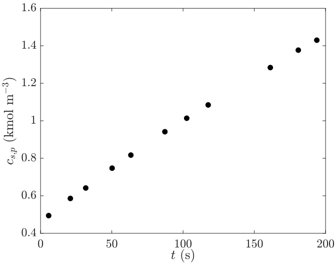
Two types of models are typically used:

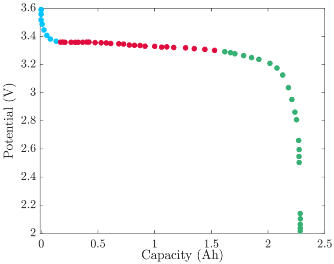
- Equivalent circuit models (fast but not robust)
- Detailed electrochemical models (robust but not fast)

Can we use best of both worlds? Yes, asymptotic reduction!

- Exploit small parameters to extract dominant terms and reduce equation complexity

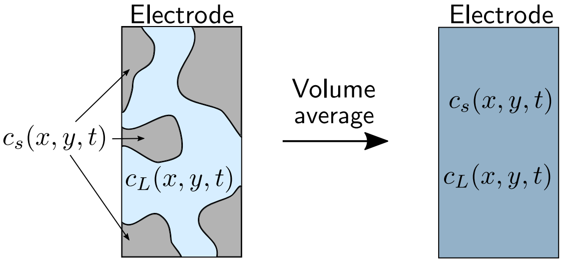
Data





Model Approach

We use a volume averaging approach



Conserve mass, charge and factor in electrochemistry

What is an LIB?

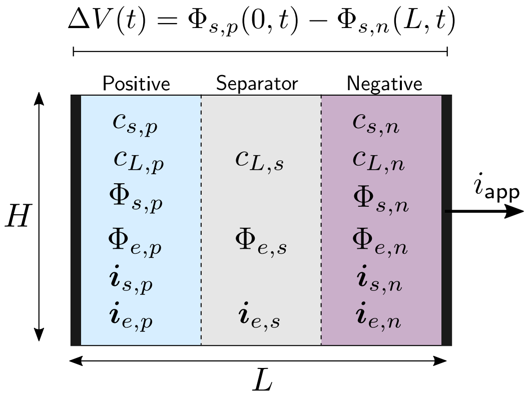


Figure: c concentration; Φ electric potential; $\mathbf{i}$ current density; i_{app} discharge current; ΔV voltage drop across cell

Model Equations

$$
\begin{aligned}
\frac{\partial}{\partial t}(\phi_{a,\mathsf{i}} c_{a,\mathsf{i}}) =& \nabla \cdot (\phi_{a,\mathsf{i}} D_{a,\mathsf{i}} \nabla c_{a,\mathsf{i}}) + \frac{1}{F} \nabla \cdot (\phi_{a,\mathsf{i}} \mathbf{i}_{a,\mathsf{i}}),\\
\mathbf{i}_{a,\mathsf{i}} =& -\sigma_{a,\mathsf{i}} \nabla \Phi_{a,\mathsf{i}},\\
\nabla \cdot (\phi_{a,\mathsf{i}} \mathbf{i}_{a,\mathsf{i}}) =& -a_{\mathsf{i}} \left(\bar{g}_{\mathsf{i}} + C_{\Gamma,\mathsf{i}} \frac{\partial}{\partial t} (\Phi_{a,\mathsf{i}} - \Phi_{e,\mathsf{i}}) \right),\\
\frac{\partial}{\partial t}(\phi_{e,\mathsf{i}} c_{L,\mathsf{i}}) =& \nabla \cdot (\phi_{e,\mathsf{i}} D_{L,\mathsf{i}} \nabla c_{L,\mathsf{i}} + \phi_{e,\mathsf{i}} \mu_L F c_{L,\mathsf{i}} \nabla \Phi_{e,\mathsf{i}}) + \frac{1}{F} \nabla \cdot (\phi_{e,\mathsf{i}} \mathbf{i}_{e,\mathsf{i}}),\\
\mathbf{i}_{e,\mathsf{i}} =& F(\mathbf{N}_{L,\mathsf{i}} - \mathbf{N}_{A,\mathsf{i}}),\\
\nabla \cdot (\phi_{e,\mathsf{i}} \mathbf{i}_{e,\mathsf{i}}) =& a_{\mathsf{i}} \left(\bar{g}_{\mathsf{i}} + C_{\Gamma,\mathsf{i}} \frac{\partial}{\partial t} (\Phi_s - \Phi_e) \right),\\
\frac{\partial}{\partial t}(\phi_{e,\mathsf{s}} c_{L,\mathsf{s}}) =& \nabla \cdot (\phi_{e,\mathsf{s}} D_{L,\mathsf{s}} \nabla c_{L,\mathsf{s}} + \phi_{e,\mathsf{s}} \mu_L F c_{L,\mathsf{s}} \nabla \Phi_{e,\mathsf{s}}),\\
\mathbf{i}_{e,\mathsf{s}} =& F(\mathbf{N}_{L,\mathsf{s}} - \mathbf{N}_{A,\mathsf{s}}),\\
\nabla \cdot (\phi_{e,\mathsf{s}} \mathbf{i}_{e,\mathsf{s}}) =& 0.
\end{aligned}
$$

Reaction Kinetics

Chemical reaction $r = k_{a,\mathrm{i}} c_{a,\mathrm{i}} - k_{L,\mathrm{i}} c_{L,\mathrm{i}} \left(\frac{c_{a,\mathrm{i}}^{\mathrm{max}} - c_{a,\mathrm{i}}}{c_{a,\mathrm{i}}^{\mathrm{max}}} \right)$

Butler-Volmer:

$$\bar{g}_\mathrm{i} = j_{0,\mathrm{i}}(c_{a,\mathrm{i}}, c_{L,\mathrm{i}}) \left(\exp\left[\frac{(1-\beta_\mathrm{i})F}{RT} \eta_\mathrm{i} \right] - \exp\left[\frac{-\beta_\mathrm{i} F}{RT} \eta_\mathrm{i} \right] \right),$$

$$\eta_\mathrm{i} = \Phi_{a,\mathrm{i}} - \Phi_{e,\mathrm{i}} - \frac{RT_a}{F} U_\mathrm{i},$$

- $j_{0,\mathrm{i}}$ - exchange current density
- U_i - Open Circuit Potential

Reduction Approach

- Non-dimensionalise
- Several dimensionless numbers appear
  - $L/H \ll 1$: problem can be reduced to one dimension
  - $D_{s,\mathsf{i}}/D_L \ll 1$: solid concentration spatially uniform
  - $(i_{\mathsf{app}}LF)/(RT_a\sigma_{\mathsf{i}}) \ll 1$: electric potentials spatially uniform
- Some small numbers are important
  - Capacitance $\mathcal{C}_{\mathsf{i}}$
  - Concentration gradients $\gamma = \Delta c/c_{L0}$
- Liquid problem reaches an $\mathcal{O}(1)$ steady state in $\mathcal{O}(1)$ time

Composite Reduced Model

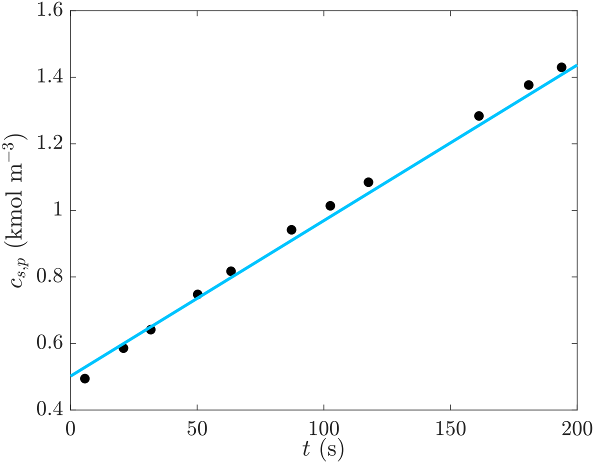
$$c_{a,\mathsf{n}} = c_{a,\mathsf{n}}^0 - \frac{\int_0^t i_{\mathrm{app}}(\tau)\,\mathrm{d}\tau}{F\phi_{a,\mathsf{n}}(L - X_n)}, \qquad c_{a,\mathsf{p}} = c_{a,\mathsf{p}}^0 + \frac{\int_0^t i_{\mathrm{app}}(\tau)\,\mathrm{d}\tau}{F\phi_{a,\mathsf{p}}X_p}$$

Single ODE for potential in each electrode

$$C_n \frac{\mathrm{d}\Phi_{a,\mathsf{n}}}{\mathrm{d}t} + \bar{g}_{\mathsf{n}}(\Phi_{a,\mathsf{n}}, c_{a,\mathsf{n}}) = \frac{i_{\mathrm{app}}}{a_n(L - X_n)}, \quad \Phi_{a,\mathsf{n}}(0) = U_n(c_{a,\mathsf{n}}^0 / c_{a,\mathsf{n}}^{\mathsf{max}}),$$

$$C_p \frac{\mathrm{d}\Phi_{a,\mathsf{p}}}{\mathrm{d}t} + \bar{g}_{\mathsf{p}}(\Phi_{a,\mathsf{p}}, c_{a,\mathsf{p}}) = -\frac{i_{\mathrm{app}}}{a_p X_p}, \quad \Phi_{a,\mathsf{p}}(0) = U_p(c_{a,\mathsf{p}}^0 / c_{a,\mathsf{p}}^{\mathsf{max}})$$

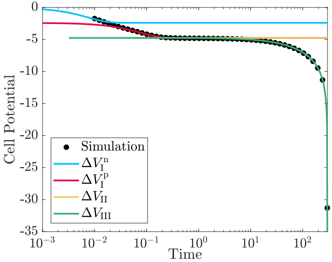
Electrode- “Data”

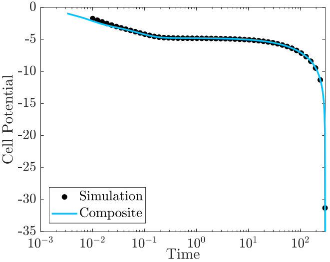


Summary of asymptotic regimes

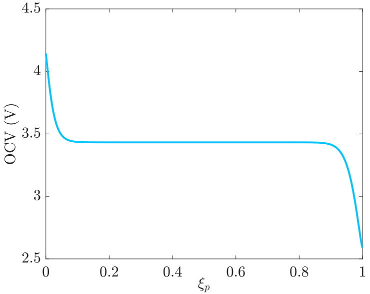
Asymptotic analysis reveals three key regimes of battery operation:

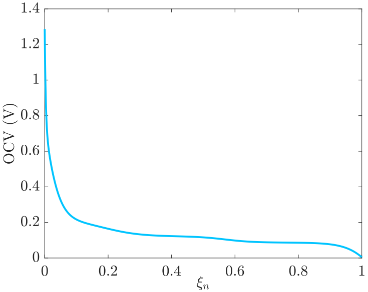
1. $t \ll 1$: Formation of double charging layers due to instantaneous application of current to cell
2. $t = O(1)$: Onset of (de)lithiation of electrodes and diffusive transport through separator
3. $t \gg 1$: Electrode saturation and depletion





Open Circuit Potential

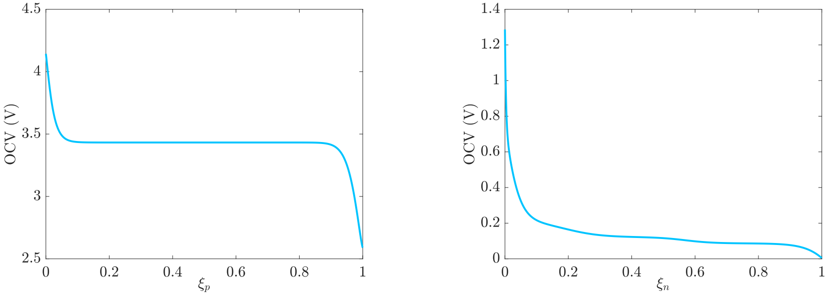




$$C_n \frac{\mathrm{d}\Phi_{a,\mathsf{n}}}{\mathrm{d}t} + \bar{g}_{\mathsf{n}}(\Phi_{a,\mathsf{n}}, c_{a,\mathsf{n}}) = \frac{i_{\text{app}}}{a_n(L - X_n)}, \quad \Phi_{a,\mathsf{n}}(0) = U_n(c^0_{a,\mathsf{n}}/c^{\mathsf{max}}_{a,\mathsf{n}}),$$

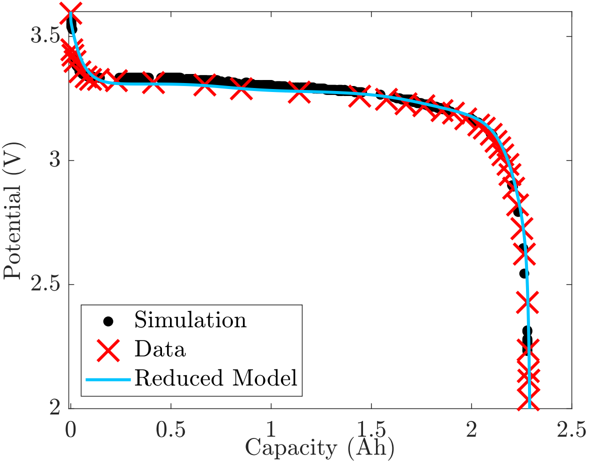
$$C_p \frac{\mathrm{d}\Phi_{a,\mathsf{p}}}{\mathrm{d}t} + \bar{g}_{\mathsf{p}}(\Phi_{a,\mathsf{p}}, c_{a,\mathsf{p}}) = -\frac{i_{\text{app}}}{a_p X_p}, \quad \Phi_{a,\mathsf{p}}(0) = U_p(c^0_{a,\mathsf{p}}/c^{\mathsf{max}}_{a,\mathsf{p}})$$

Open Circuit Potential

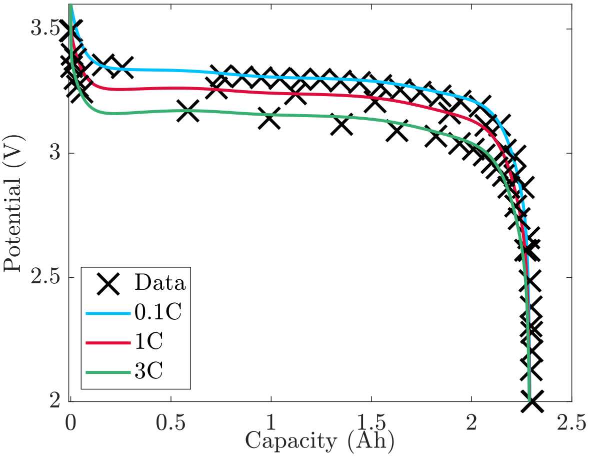


$$\frac{\mathrm{d}y}{\mathrm{d}t} = f(y,t), \qquad y(0) = y_0$$

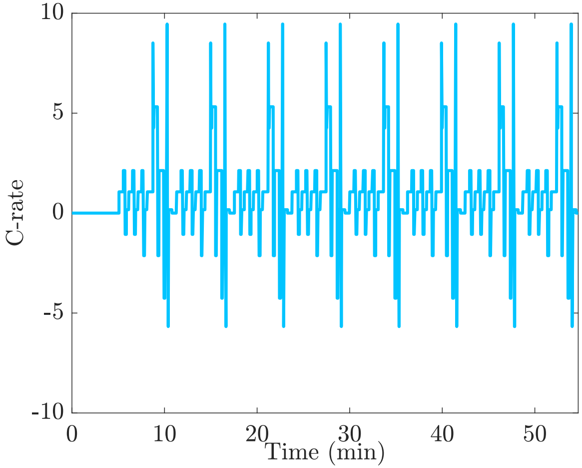
Cell Voltage-Li *et al.*



Cell Voltage-Safari and Delacourt



Non-Galvanostatic Discharge



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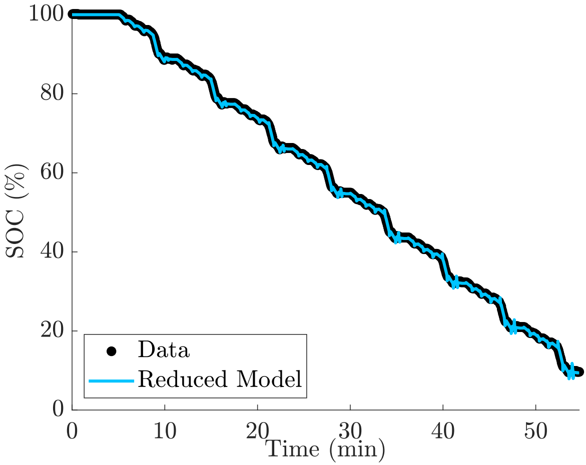
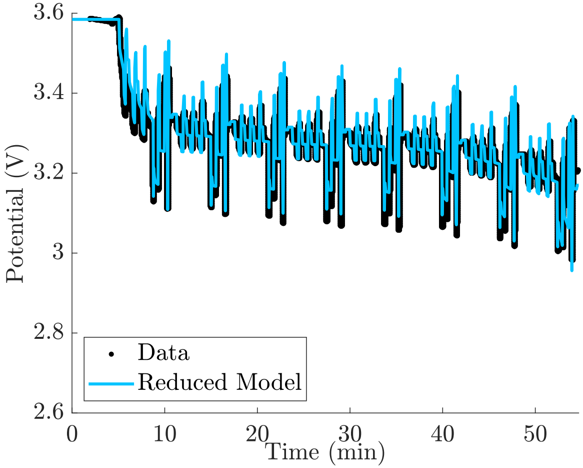


Non-Galvanostatic Discharge



Summary

- Mathematics can be used to extract important features from model
- Simpler and faster model derived
- Can also provide insight when model fails
  - May hint that the microscale is playing an important role

Future Work

- Add temperature
- Investigate breakdown of volume average approach

Questions?