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A Thermal Tanks-in-Series Model for Capacity Fade Studies in Lithium-Ion Batteries

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Talk Outline

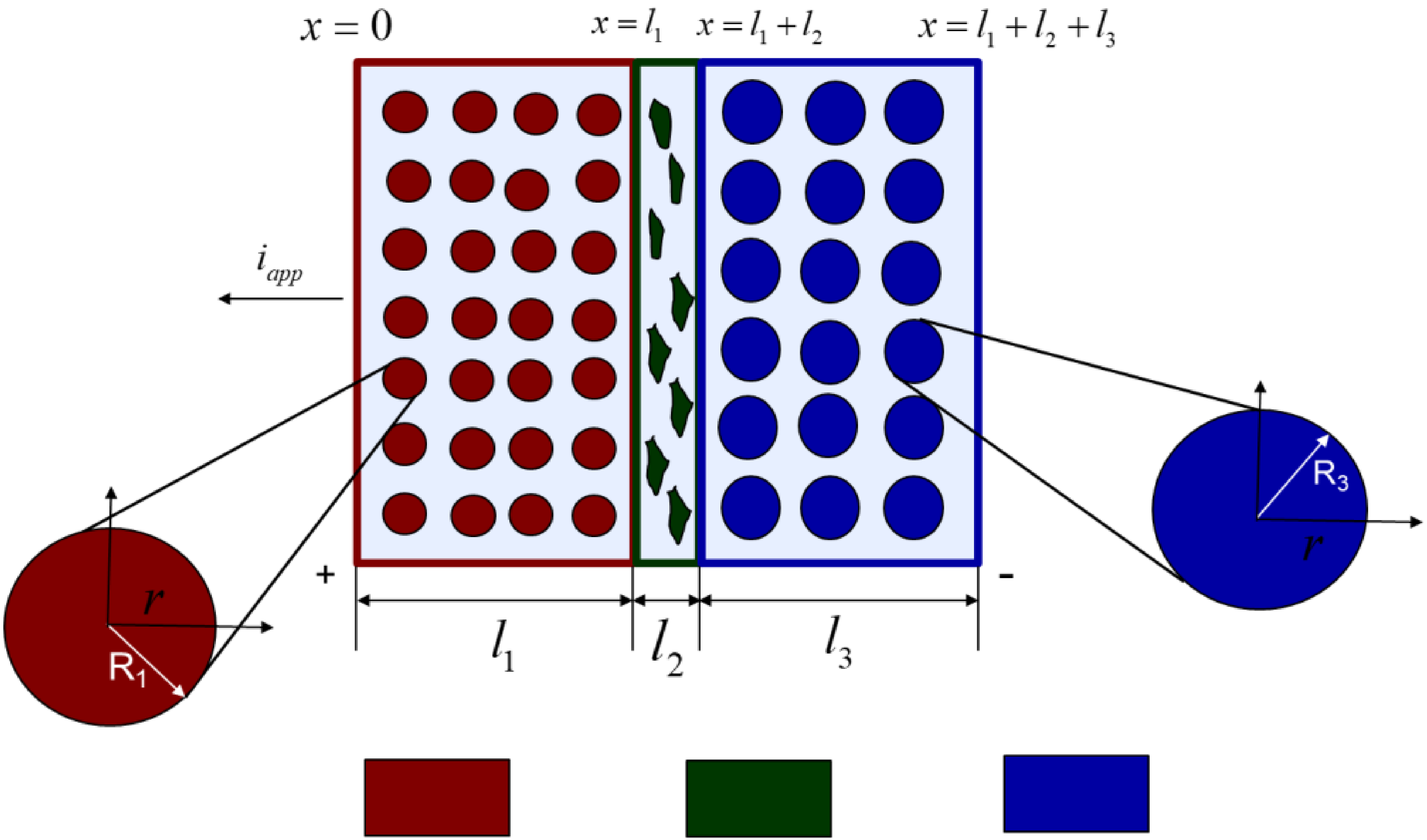
- Lithium-ion Battery models
  - P2D model
  - SPM model

- Tanks-In-Series model
  - Development
  - Extension to Thermal Tanks-In-Series

- Capacity fade due to SEI layer
  - Modeling the SEI layer

- Results

The P2D Model For Lithium-ion Batteries



Positive [Region 1]

Separator [Region 2]

Negative [Region 3]

The P2D Li-ion Battery Model

- ## Coupled Conservation Laws :

Electronic Charge :

$$\sigma_{\mathrm{eff,p}} \frac{\partial^2 \Phi_1}{\partial x^2} = a_{\mathrm{p}} F j_{\mathrm{p}}; \quad \Phi_1 \text{ is the solid-phase potential}$$

Electrolyte Mass:

$$\varepsilon_{\mathrm{p}} \frac{\partial c}{\partial t} = D_{\mathrm{eff,p}} \frac{\partial^2 c}{\partial x^2} + a_{\mathrm{p}} \left(1 - t_+\right) j_{\mathrm{p}};$$

c is the electrolyte concentration

Solid Phase Mass:

$$\frac{\partial c_p^s}{\partial t} = D_{\mathrm{s,p}} \left(\frac{\partial^2 c_p^s}{\partial r^2} + \frac{2}{\mathrm{r}} \frac{\partial c_p^s}{\partial r} \right); \quad c_p^s \text{ is the solid phase concentration}$$

Overall Charge :

$$-\sigma_{\mathrm{eff,p}} \frac{\partial \Phi_1}{\partial x} - \kappa_{\mathrm{eff,p}} \frac{\partial \Phi_2}{\partial x} + \frac{2\kappa_{\mathrm{eff,p}} RT}{F} \left(1 - t_+\right) \frac{\partial \ln c}{\partial x} = I;$$

Φ_2 is the liquid phase potential

Parameters and Constitutive Equations

$$\kappa_{\mathrm{eff,p}} = \varepsilon_{\mathrm{p}}^{\mathrm{brugg_p}} \kappa = 0.01775 \times \begin{pmatrix} 4.1253 \times 10^{-2} + 5.007 \times 10^{-1} c - 4.7212 \times 10^{-1} c^2 \\ +1.5094 \times 10^{-1} c^3 - 1.6018 \times 10^{-2} c^4 \end{pmatrix}$$

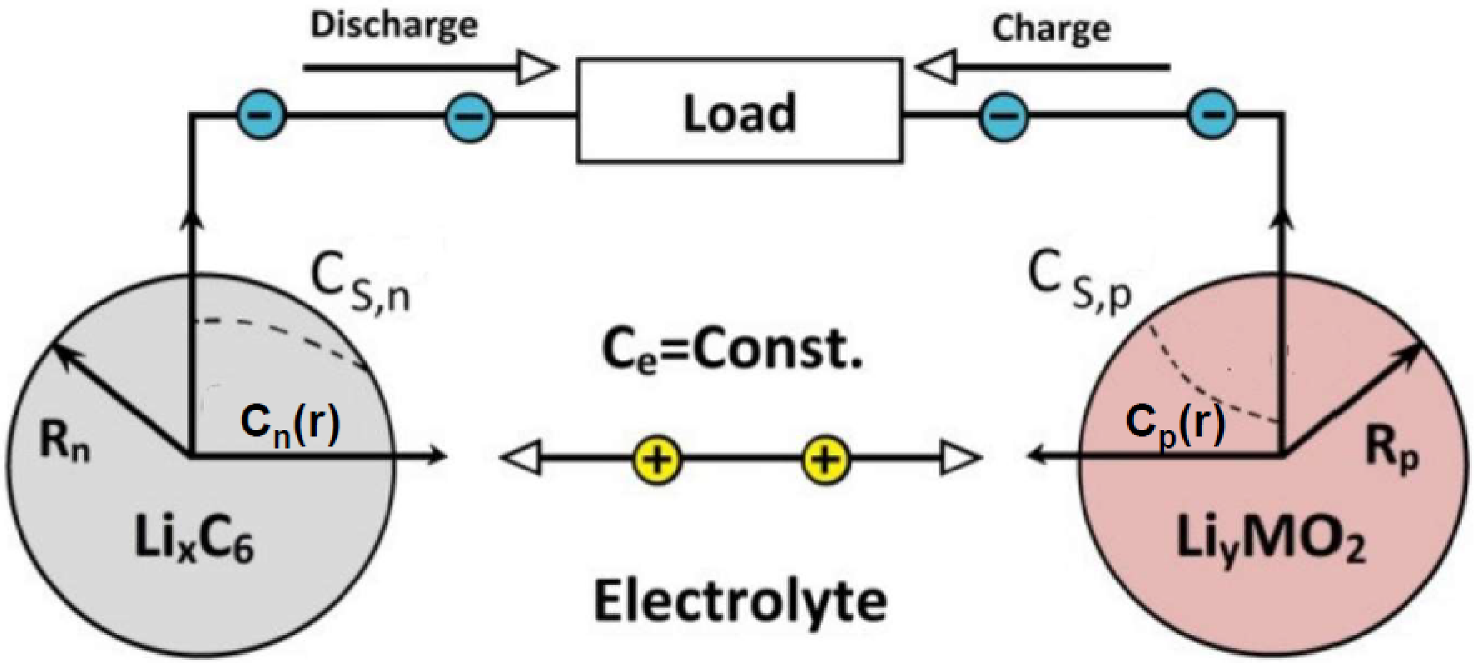
$$j_{\mathrm{p}} = 2k_{\mathrm{p}} \left(c_{\mathrm{s,max,p}} - c_p^s \right)^{0.5} c_p^{s\,0.5} c^{0.5} \sinh\left[\frac{0.5F}{RT} \left(\Phi_1 - \Phi_2 - U_{\mathrm{p}} \right) \right]$$

$$U_{\mathrm{p}} = f(SOC)$$

Computational Complexity has spurred active investigation of different simplification and reformulation techniques

[J. S. Newman+, (1993-2012)]

The Single Particle Model



Negative electrode

Positive electrode

R_i : Radius of the electrode
$C_i(r)$: Solid phase concentration of Li in the electrode
$C_{S,i}$: Solid phase concentration of Li at the surface of the electrode
i : n (Negative) or p (Positive)

Ref: Al-Gabalawy+, *Batteries*, 2020

The Single Particle Model

Neglect Electrolyte Effects:

$$\frac{\partial c_1^s}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_1^s \frac{\partial c_1^s}{\partial r} \right)$$

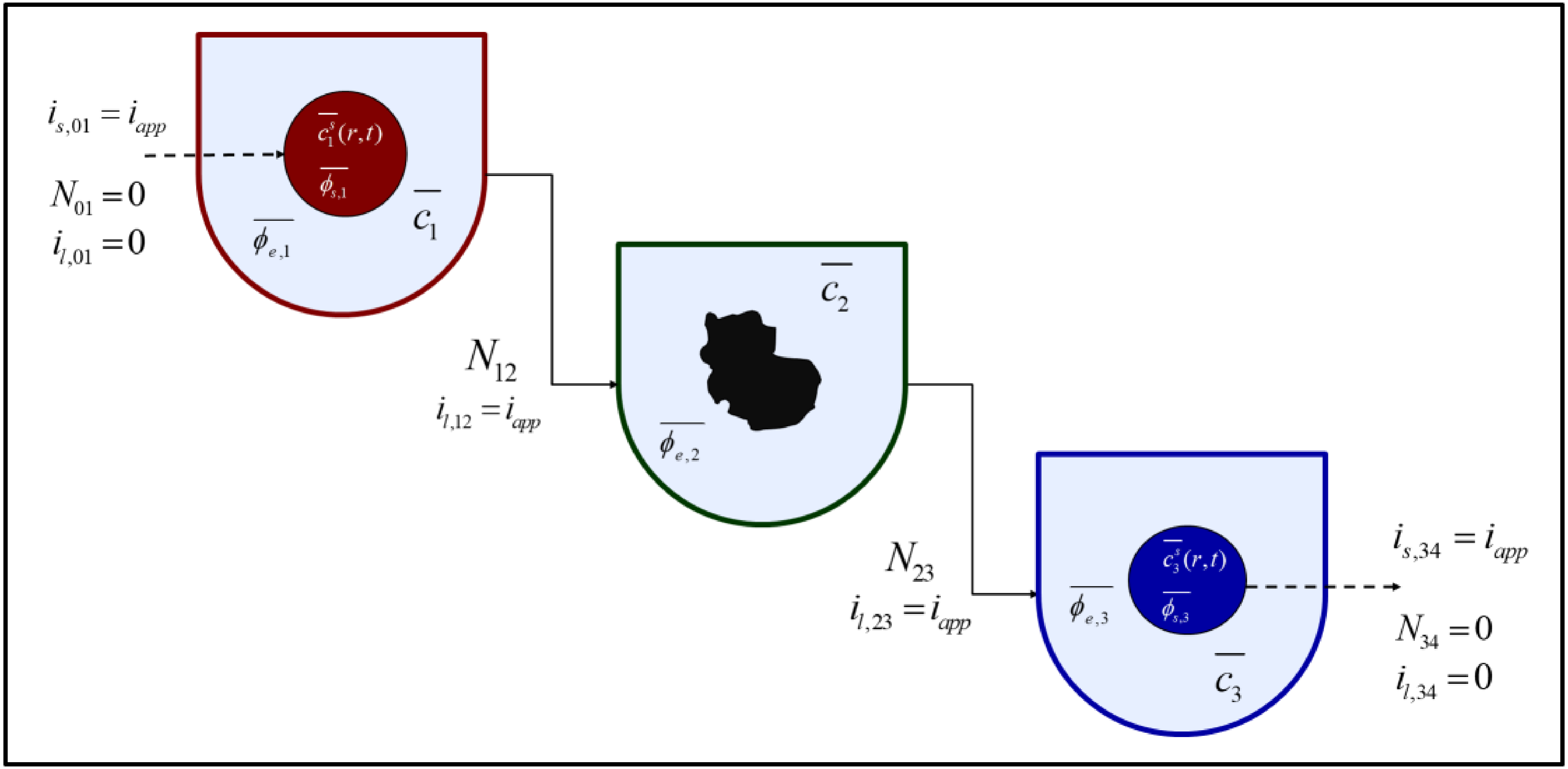
$$\frac{\partial \int_{x=0}^{x=l_1} c_1^s \, dx}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_1^s \frac{\partial \int_{x=0}^{x=l_1} c_1^s \, dx}{\partial r} \right)$$

$$\frac{\partial \overline{c_1^s}}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_1^s \frac{\partial \overline{c_1^s}}{\partial r} \right)$$

- **Features**
  - **Large reduction in number of equations compared to P2D**
  - **Neglects potential and concentration variations in electrolyte**
  - **Applicable in low to moderate C rates where polarization is not significant**
  - **Poor low temperature performance due to sluggish kinetics causing higher polarization**

Restricted to moderate current scenarios, where liquid phase polarizations aren't significant

Lithium-ion Battery as Tanks in Series



Can we incorporate average electrolyte dynamics by a similar volume-averaging approach?

Generating the Tank Model

Example Conservation Equation in Electrolyte:

$$\varepsilon_1 \frac{\partial c_1}{\partial t} = -\frac{\partial N_1}{\partial x} + a_1\left(1 - t_+^0\right) j_1$$

$$\overline{c_1} = \frac{d\int_{V_1} c_1 dV}{\int_{V_1} c_1 dV}$$

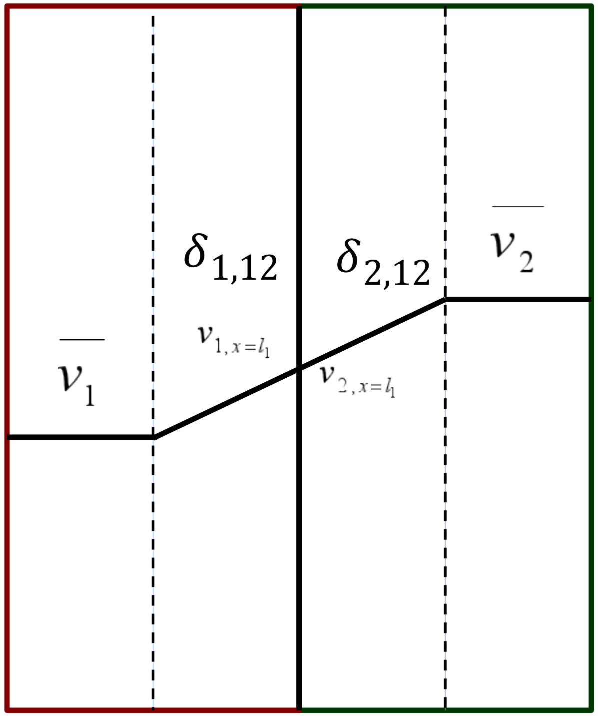
$$dV = Adx$$

Volume averaging involves integrating the variable w.r.t the volume of the region

$$\frac{d\int_{V_1} \varepsilon_1 c_1 dV}{dt} = -\int_{V_1} \frac{\partial N_1}{\partial x} dV + \int_{V_1} a_1\left(1 - t_+^0\right) j_1 dV$$

$$\varepsilon_1 \frac{d\overline{c_1}}{dt} = -\frac{\int\limits_{x=0}^{x=l_1} \frac{\partial N_1}{\partial x} dx}{l_1} + a_1\left(1 - t_+\right)\overline{j_1} = \boxed{\frac{N_{1,x=0} - N_{1,x=l_1}}{l_1}} + a_1\left(1 - t_+\right)\overline{j_1}$$

Approximating Interfacial Fluxes



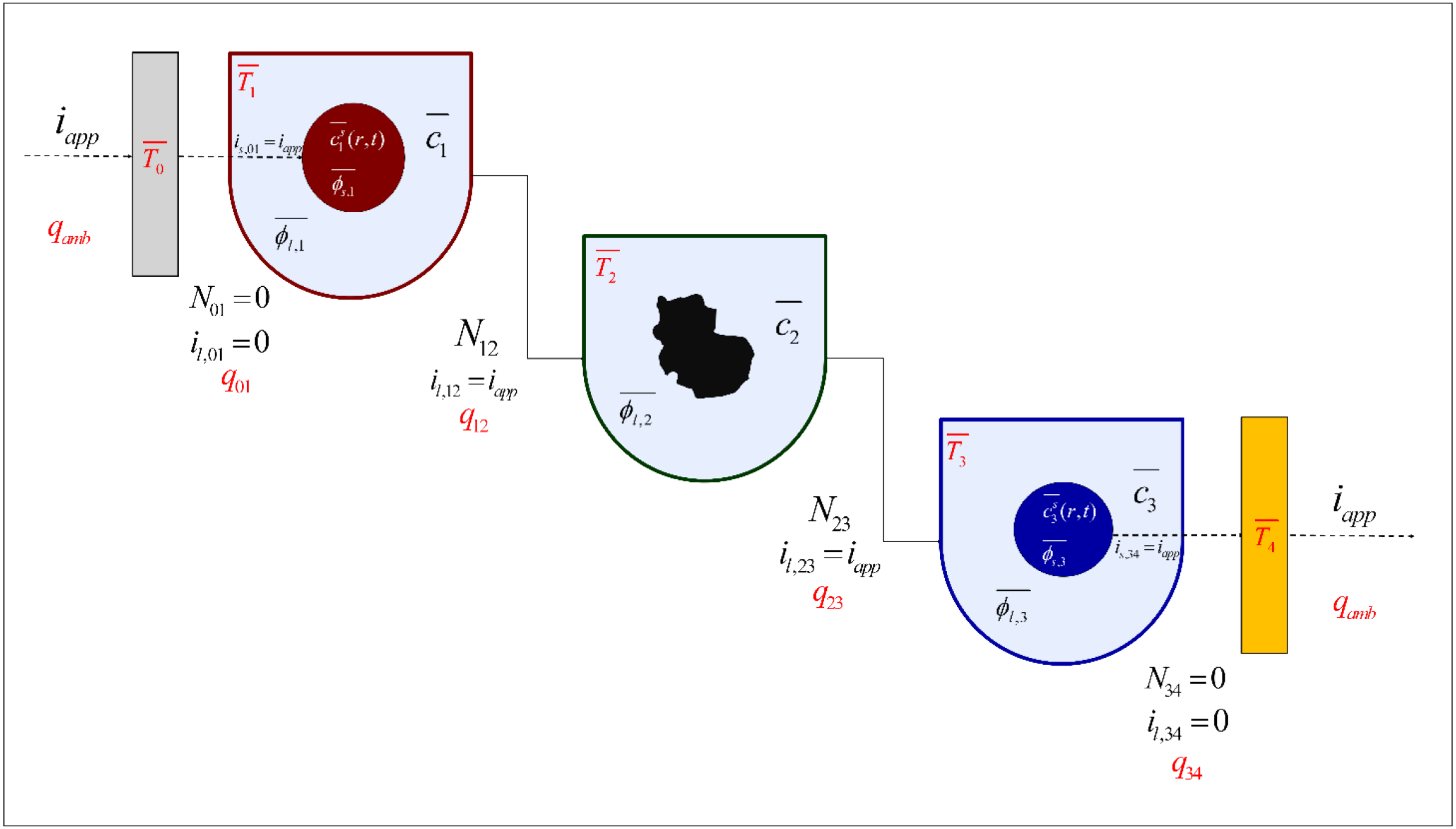
$$N_{1,x=l_1} = -D(c_{1,x=l_1})\varepsilon_1^{b_1}\frac{\partial c_1}{\partial x}_{x=l_1} \approx D(c_{1,x=l_1})\varepsilon_1^{b_1}\left(\frac{\Delta c_1}{\delta_{1,12}}\right) = D(c_{1,x=l_1})\varepsilon_1^{b_1}\left(\frac{\overline{c}_1 - c_{1,x=l_1}}{\frac{l_1}{2}}\right)$$

$$N_{2,x=l_1} = -D(c_{2,x=l_1})\varepsilon_2^{b_2}\frac{\partial c_2}{\partial x}_{x=l_2} \approx D(c_{2,x=l_1})\varepsilon_2^{b_2}\left(\frac{\Delta c_2}{\delta_{2,12}}\right) = D(c_{2,x=l_1})\varepsilon_2^{b_2}\left(\frac{-\overline{c}_2 + c_{2,x=l_1}}{\frac{l_2}{2}}\right)$$

$$D(c_{1,x=l_1})\varepsilon_1^{b_1}\left(\frac{\overline{c}_1 - c_{1,x=l_1}}{\frac{l_1}{2}}\right) = D(c_{2,x=l_1})\varepsilon_2^{b_2}\left(\frac{-\overline{c}_2 + c_{2,x=l_1}}{\frac{l_2}{2}}\right)$$

Naive assumptions of ‘film thickness’, can be regarded an adjustable parameter

Extensions to Thermal Effects



Apply methodology for Energy Conservation equations

[A. Subramaniam+, JES,2020]

Generating the Thermal Tank Model

Conservation Equation:

$$\rho_1 C_{p1} \frac{\partial T_1}{\partial t} = -\frac{\partial q_1}{\partial x} + Fa_1 j_1 (\phi_{s,1} - \phi_{l,1} - U(c_1^{s,surf})) + Fa_1 j_1 T_1 \frac{\partial U(c_1^{s,surf})}{\partial T_1} - i_{s,1} \frac{\partial \phi_{s,1}}{\partial x} - i_{l,1} \frac{\partial \phi_{l,1}}{\partial x}$$

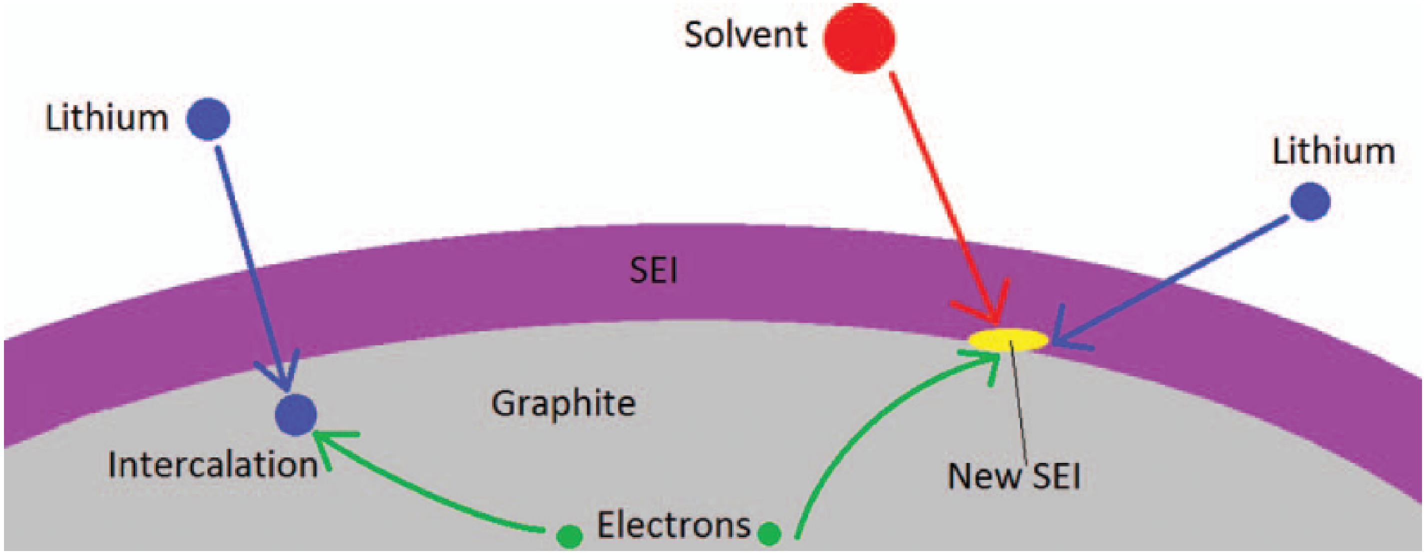
$$\frac{\partial \int_{V_1} \rho_1 C_{p1} T_1 dV}{\partial t} = -\int_{V_1} \frac{\partial q_1}{\partial x} dV + \int_{V_1} Fa_1 j_1 (\phi_{s,1} - \phi_{l,1} - U(c_1^{s,surf})) dV + \int_{V_1} Fa_1 j_1 T_1 \frac{\partial U(c_1^{s,surf})}{\partial T_1} dV - \int_{V_1} i_{s,1} \frac{\partial \phi_{s,1}}{\partial x} dV - \int_{V_1} i_{l,1} \frac{\partial \phi_{l,1}}{\partial x} dV$$

$$\rho_1 C_{p1} \frac{d\overline{T_1}}{dt} = \frac{q_{1,x=0} - q_{1,x=l_1}}{l_1} + Fa_1 \overline{j_1} (\overline{\phi_{s,1}} - \overline{\phi_{l,1}} - U(\overline{c_1^{s,surf}})) + Fa_1 \overline{j_1} \overline{T_1} \overline{\frac{\partial U(c_1^{s,surf})}{\partial T_1}} - i_{app} \left(\frac{\overline{\phi_{l,1}} - \phi_{l,1,x=l_1}}{l_1} \right)$$

$$\overline{T_1} = \frac{d\int_{V_1} T_1 dV}{\int_{V_1} dV}$$

$$dV = Adx$$

Solid Electrolyte Interphase (SEI) Layer

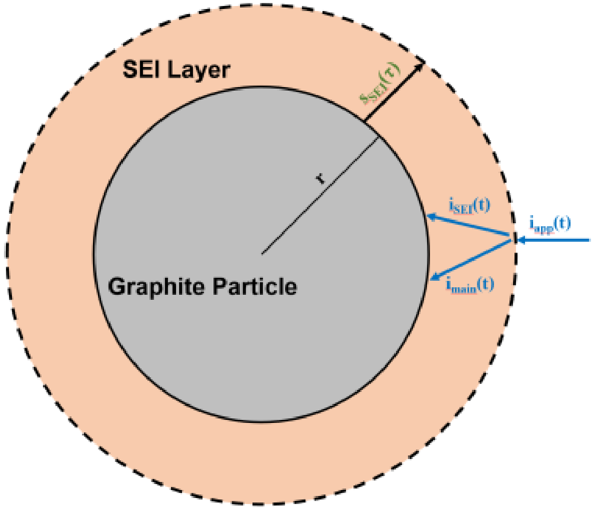


- Formation of a passivation layer on the surface of the anode particle.
- Electrolyte solvent is reduced at the surface with Li^+ ions and electrons.
- The SEI layer grows due to diffusion through the SEI, increased surface area, plating, transition metal deposition, etc.

$$2\,C_3H_4O_3\,(l) + 2\,e^- + 2\,Li^+ \rightleftharpoons (CH_2OCO_2Li)_2\,(s) + C_2H_4\,(g)$$

Image reproduced from M. B. Pinson and M. Z. Bazant, J. Electrochem. Soc., 160, 2–9 (2013).

Modeling the SEI Layer



Growth of the SEI Layer:

$$\frac{ds_{SEI}(t)}{dt} = \frac{i_{SEI}(t)M_{SEI}}{2F\rho_{SEI}}$$

SEI Kinetics (Tafel Equation)

$$i_{SEI}(t) = k_{SEI}c_{EC}\exp\left[\frac{-Ea_{sei}}{R\left(T - T_{ref}\right)}\right]\exp\left[\frac{-\alpha_{SEI}F}{RT}\left(\underbrace{\phi_n - \phi_l - U_{SEI} - \frac{s_{SEI}(t)i_{app}(t)}{\kappa_{SEI}}}_{\text{Overpotential}}\right)\right]$$

$$i_{app}(t) = i_{int}(t) + i_{SEI}(t)$$

Note:

$\frac{s_{SEI}(t)}{\kappa_{SEI}}$ is the resistance from the SEI layer.

- **Assumptions**
  - **Uniform thickness of SEI layer**
  - **SEI is made of a single component**
  - **Same mechanism of formation across a large temperature range**

Simulation Results

- **Simulation protocol for 1 cycle**
  - **1C CC-CV Charge till 4.2V**
  - **1C Discharge till 2.8V**

- **$LiCoO_2$ – Graphite chemistry**
  - **Parameter values taken from literature**

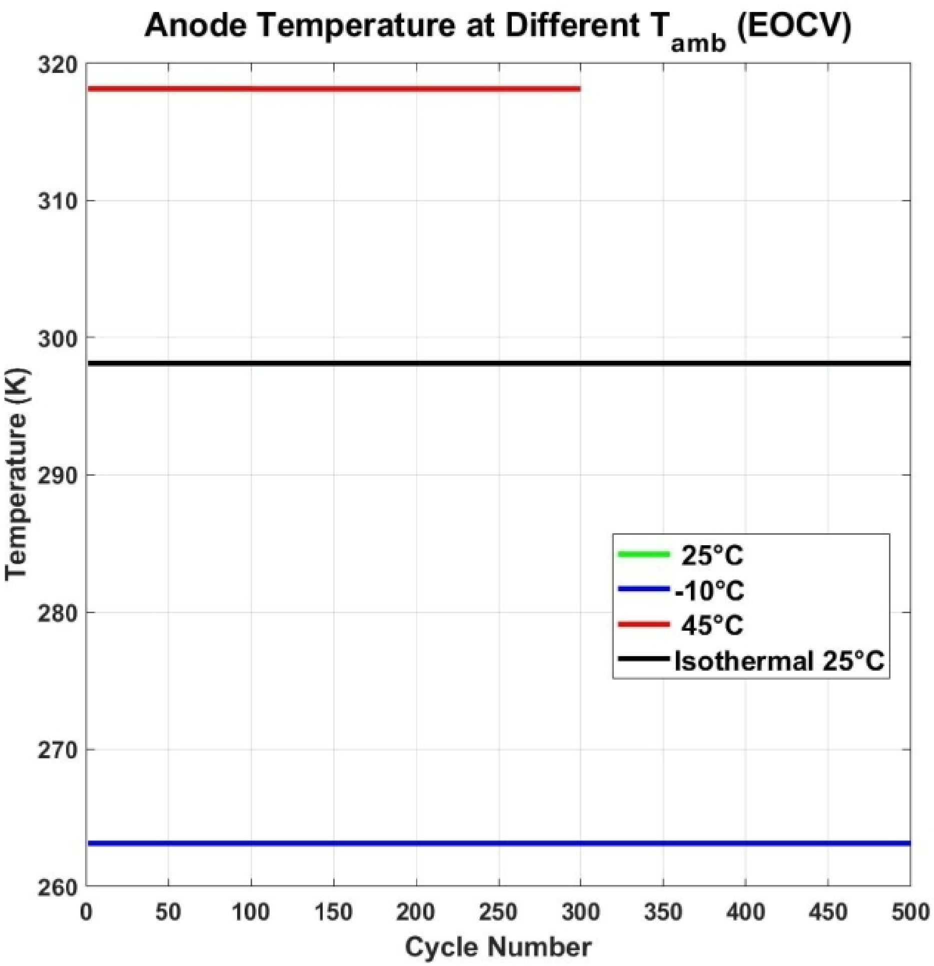
    Electrode and Separator - Northrop et al. (2011)

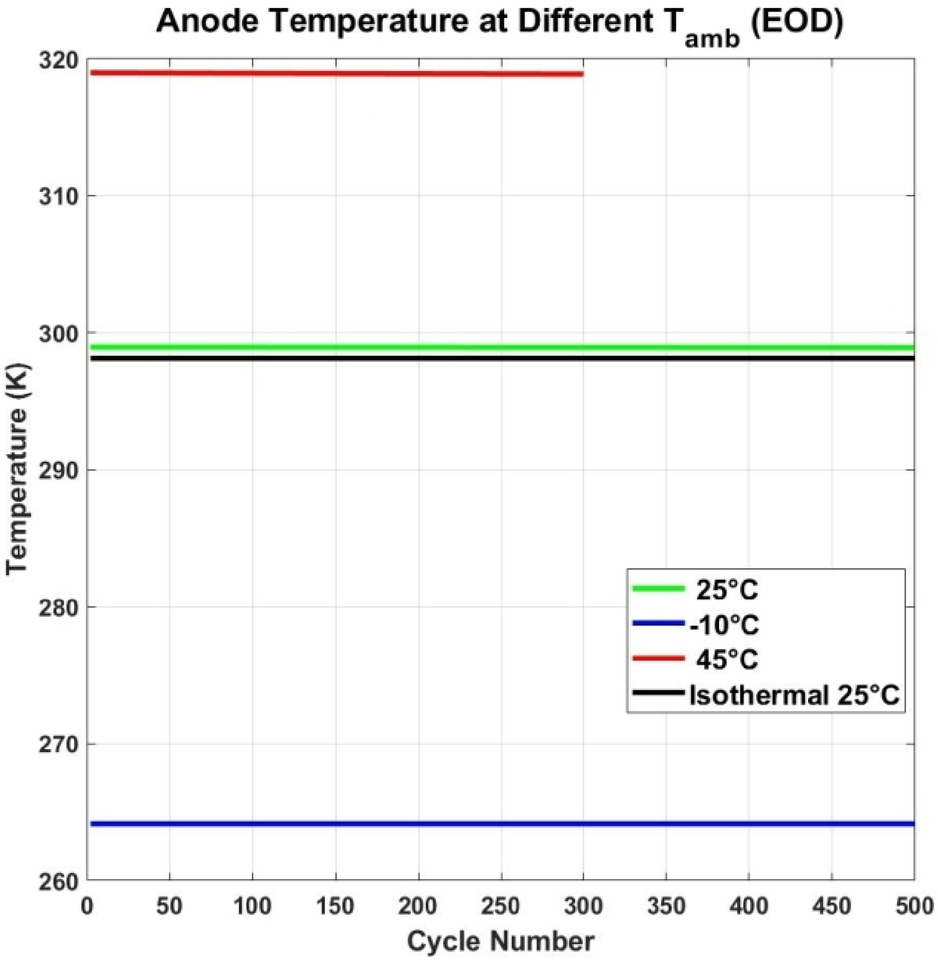
    Electrolyte - Valøen and Reimers (2005)

- **Thermal Tanks-In-Series used to simulate at an ambient temperate of**
  - **25°C**
  - **-10°C**
  - **45°C**

  - **Cell is Isothermal**

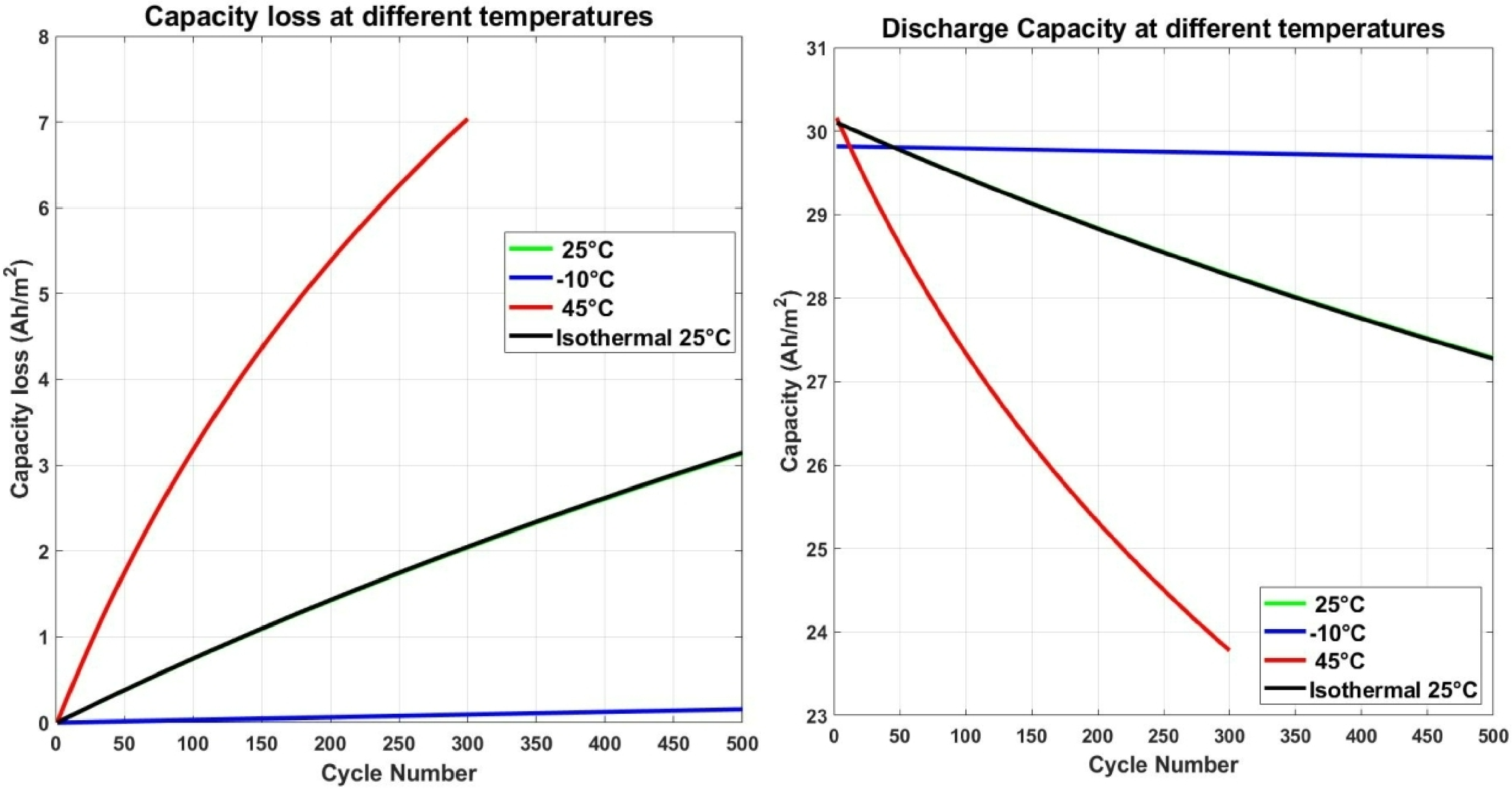
Effects of T_{amb}





No temperature increase during discharge in Isothermal case

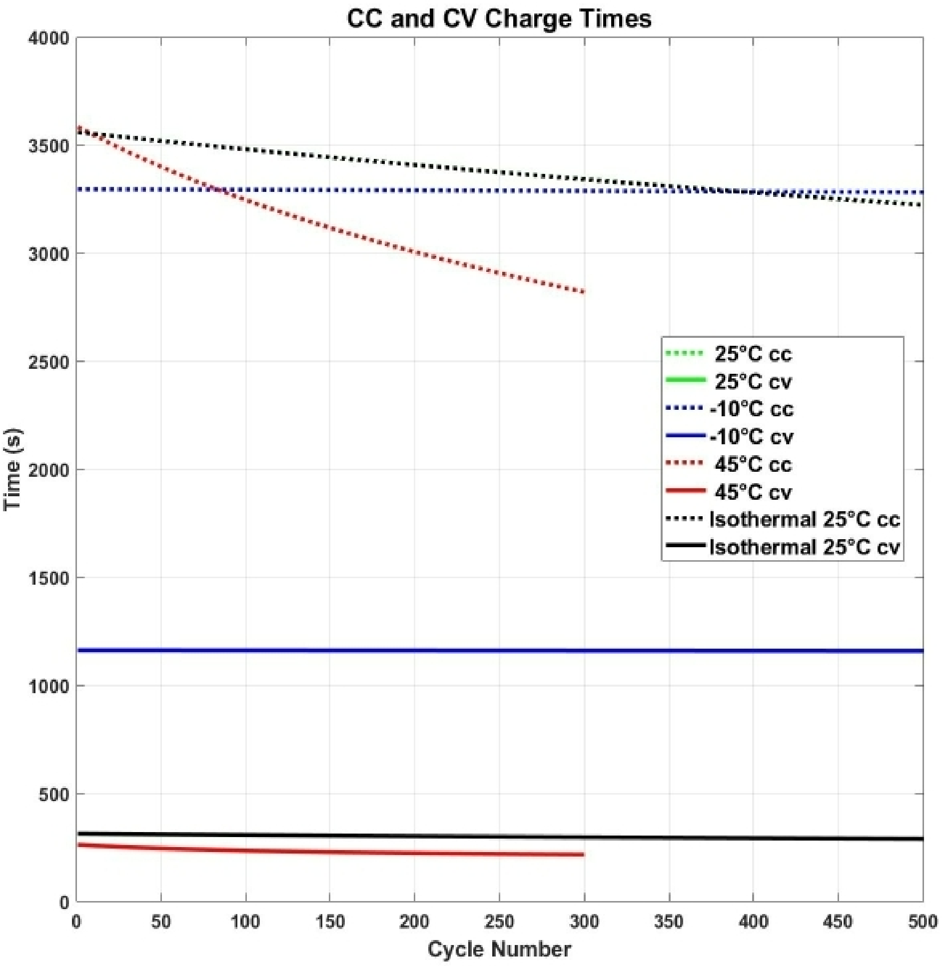
Capacity loss due to SEI layer

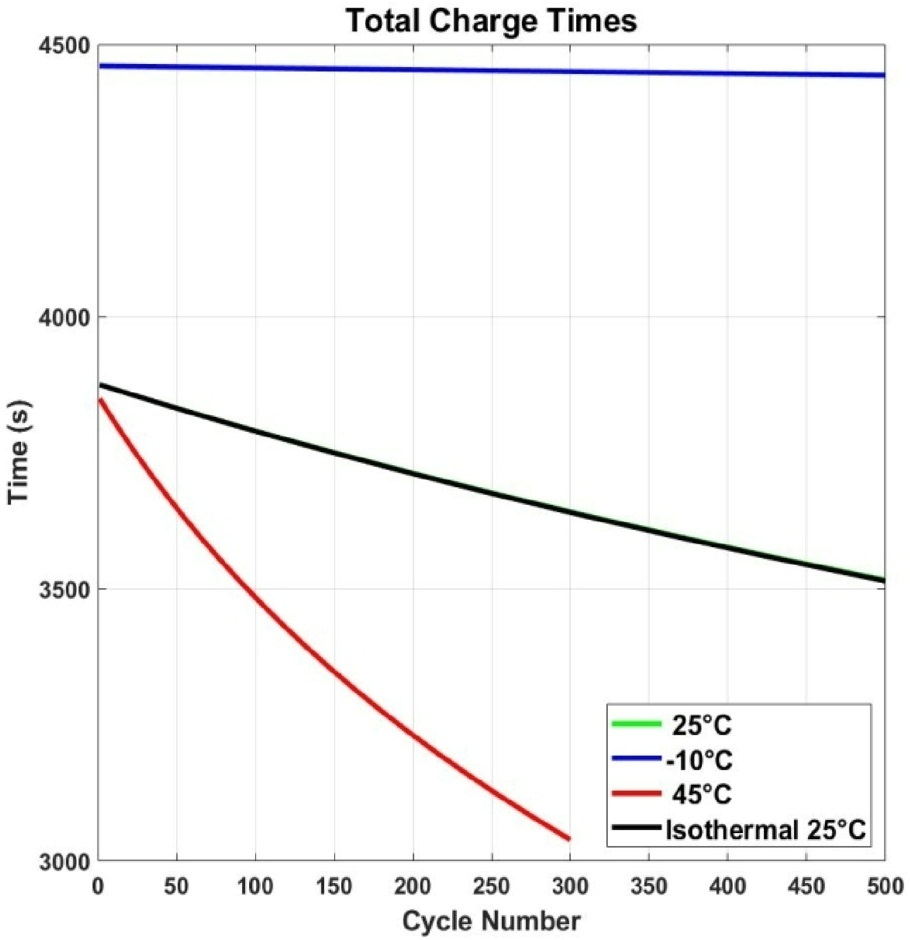


Higher fade at higher temperature due to kinetic favorability of fade reaction.
Reactions are sluggish at low temperature

Capacity fade is only due to SEI layer formation. Other mechanisms are not considered in this study

Charging times at different T



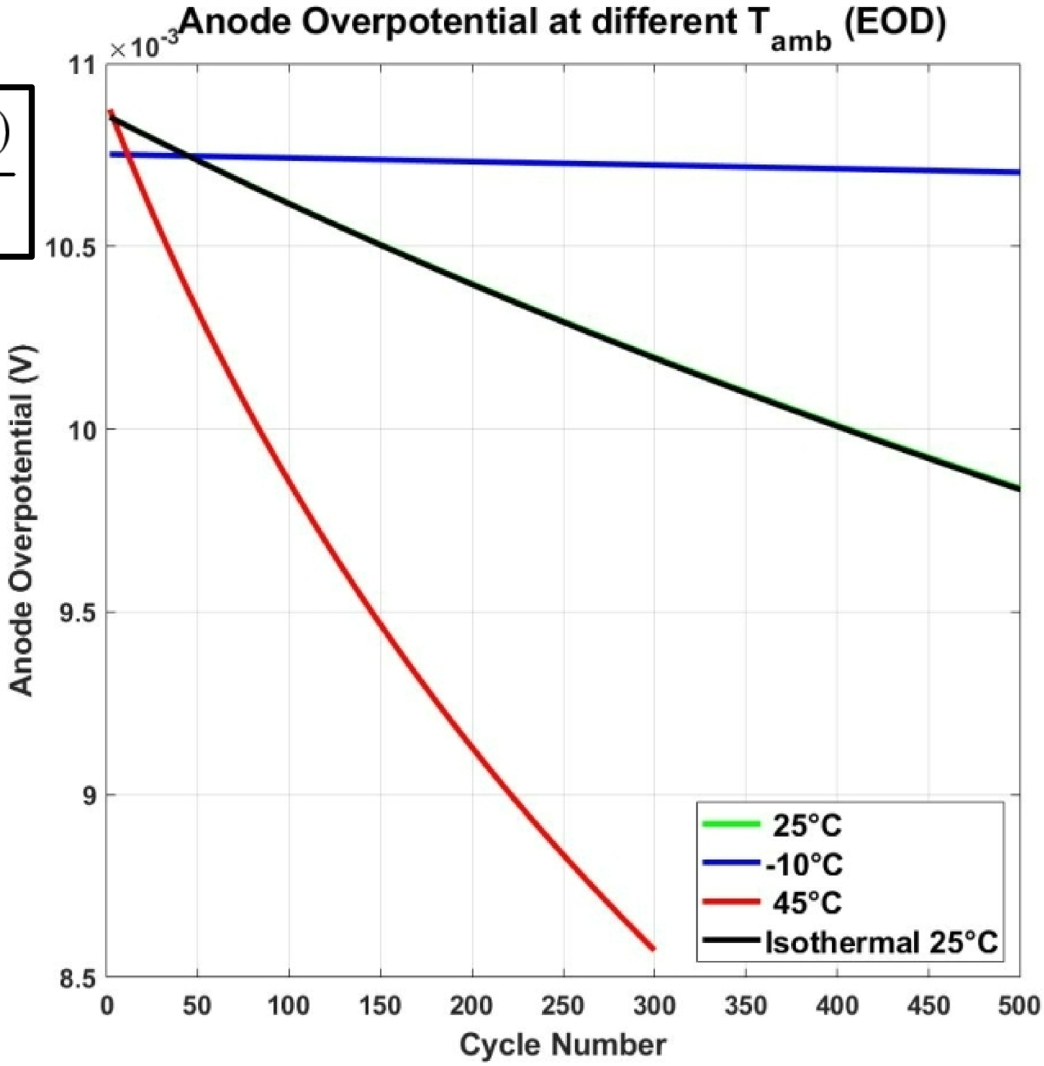


CC charging time reduces with cycling for higher temperatures as cut off voltage is reached at lower SOC values Low temperature charging times are always higher due to sluggish kinetics, SOC at end of charging is relatively unchanged with cycling

Capacity fade is only due to SEI layer formation. Other mechanisms are not considered in this study

Anode overpotentials

$$\eta = \phi_{s,1} - \phi_{l,1} - U(c_1^{s,surf}) - \frac{\delta_{SEI}(t)\, i_{app}(t)}{\kappa_{SEI}}$$



Anode overpotential decreases at high temperatures at higher temperatures, due to increase in SEI resistance

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M.A.P.L.E Lab

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Thank You!

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