

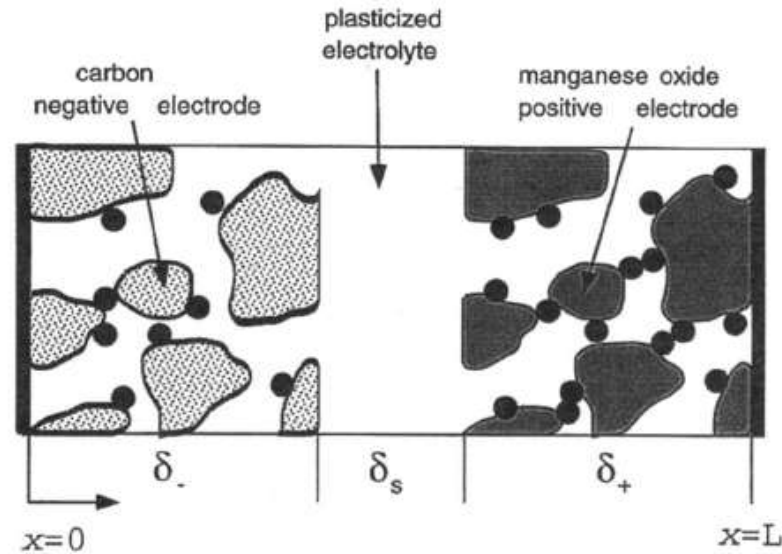
Li- ion modeling physics-based

Dongmyung Suh

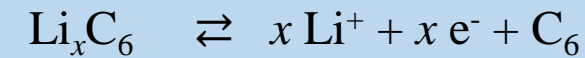
Design of Li ion battery simulation Model

- **Physics based Li-ion cell model** requires considering thermodynamics, mass/charge transfer, electrochemical reaction
- **Spectral Element Method** as numerical method (high numerical accuracy and stability)
- **Powell hybrid method** is applied to solving the system of **non-linear** algebraic equations.
- Simulation should be **transient** following charging/discharging cycle.
- Calculation time step size is **self- adjustable**.
- **Post-processing** module to analyze calculation results is also needed.
- **Simulation package** will be used freely without the concerns of license fee.

Li-ion battery ($\text{Li}_x\text{C}_6 \mid \text{Li}_y\text{Mn}_2\text{O}_4$)

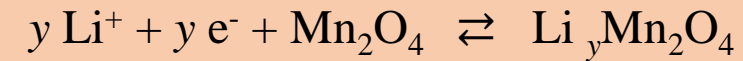


Negative Electrode



$$U_-(x) = -0.16 + 1.32 * \text{np.exp}(-3.0 * x) + 10.0 * \text{np.exp}(-2000.0 * x)$$

Positive Electrode



$$\begin{aligned} U_+(y) = & 4.1983 + 0.056566 * \tanh(-14.5546 * y + 8.60942) \\ & - 0.0275479 * ((1.0 - y)^{-0.492465} - 1.90) \\ & - 0.157123 * \exp(-0.04738 * y^8) \\ & + 0.810239 * \exp(-40 * (y - 0.133875)) \end{aligned}$$

Physics Based Model of Li-ion battery

- in Electrode (Negative/Positive)

- Conservation of Charge

$$\frac{\partial}{\partial x} (\sigma_{eff} \nabla \varphi_s) = j_{Li}$$

$$\varphi(x = 0) = 0 \text{ V}$$

$$\sigma_{eff} \frac{\partial \varphi}{\partial x} \Big|_{x=a,b} = 0$$

$$\sigma_{eff} \frac{\partial \varphi}{\partial x} \Big|_{x=L} = J = \frac{I}{A}$$

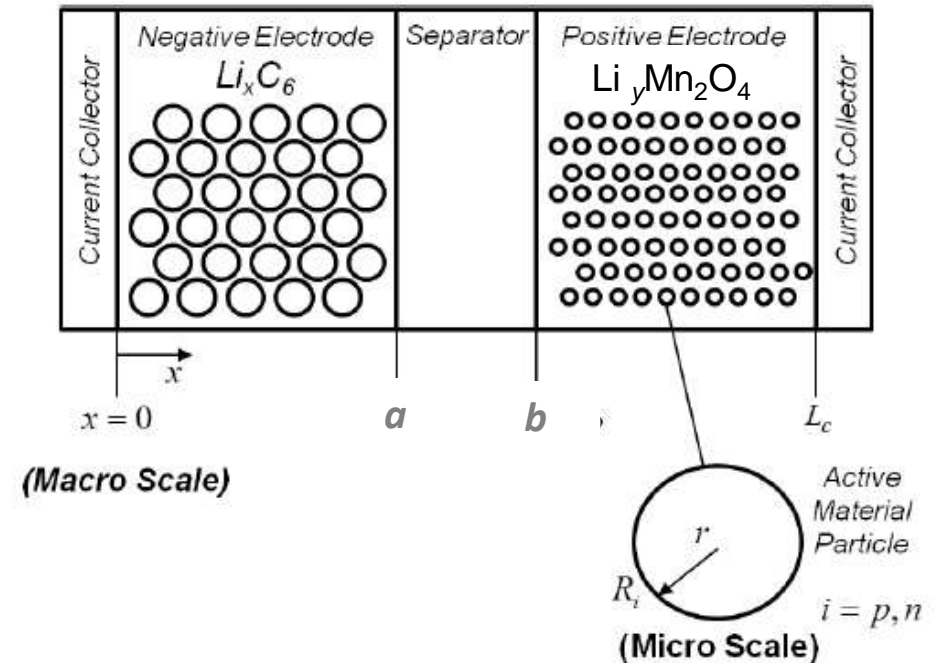
- Conservation of Mass

$$\frac{\partial C_s}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_s}{\partial r} \right)$$

$$\frac{\partial C_s}{\partial r} \Big|_{r=0} = 0$$

$$-D_s \frac{\partial C_s}{\partial r} \Big|_{r=R} = \frac{j_{Li}}{a_s F}$$

a_s : specific area per unit volume



- in Electrolyte

- Conservation of Charge

$$\frac{\partial}{\partial x} \left(\kappa^{eff} \frac{\partial \varphi_e}{\partial x} \right) + \frac{\partial}{\partial x} \left(\kappa_d^{eff} \frac{\partial}{\partial x} (\ln C_e) \right) = -j_{li}$$

$$\frac{\partial \varphi_e}{\partial x} \Big|_{x=0} = \frac{\partial \varphi_e}{\partial x} \Big|_{x=L} = 0$$

$$\kappa^{eff} = \kappa \varepsilon_e^p$$

$$\kappa_d^{eff} = \frac{2RT\kappa^{eff}}{F} (t_+ - 1) \left(1 + \frac{\partial \ln f}{\partial \ln C_e} \right)$$

- Conservation of Mass

$$\frac{\partial}{\partial t} (\varepsilon_e C_e) = \frac{\partial}{\partial x} (D_e^{eff} \nabla C_e) + \frac{1-t_+}{F} j_{li}$$

$$\frac{\partial C_e}{\partial x} \Big|_{x=0} = \frac{\partial C_e}{\partial x} \Big|_{x=L} = 0$$

$$D_e^{eff} = \varepsilon_e^p D_e$$

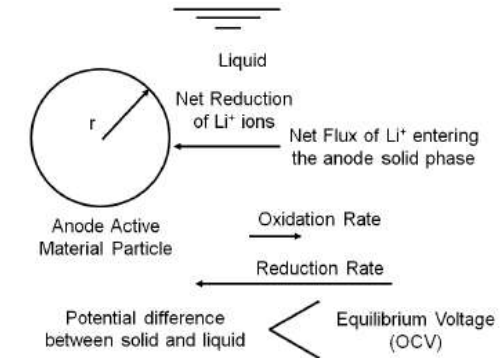
Electrochemical Reaction

Butler-Volmer Kinetic Equation

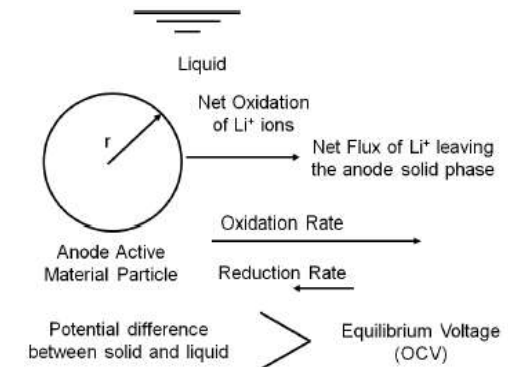
$$j_{Li} = a_s i_o \left[\exp \left\{ \frac{\alpha_a F}{RT} \left(\eta - \frac{R_{SEI}}{a_s} j_{Li} \right) \right\} - \exp \left\{ - \frac{\alpha_c F}{RT} \left(\eta - \frac{R_{SEI}}{a_s} j_{Li} \right) \right\} \right]$$

$$\eta = \varphi_s - \varphi_e - U$$

$$i_o = k_o C_e^{\alpha_a} (C_{s,max} - C_{s,surface})^{\alpha_a} C_{s,surface}^{\alpha_c}$$

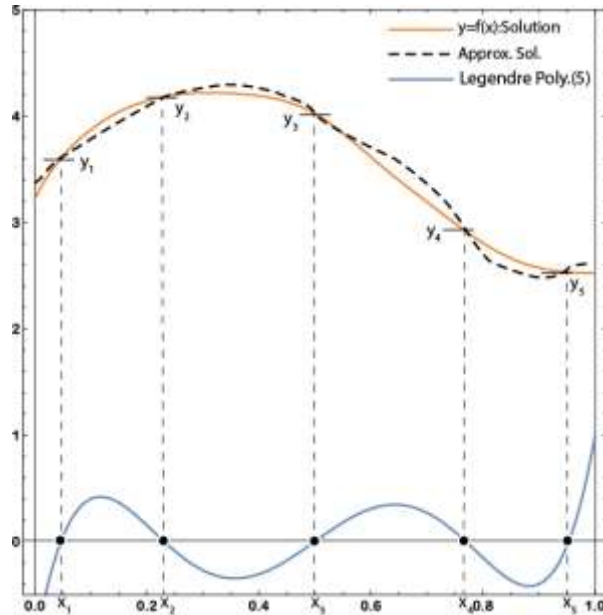


(a) Charging



(a) Discharging

Spectral Element Method (SEM)



$$y = f(x) = \sum_{i=1}^N a_i y_i(x) \quad y_j = \sum_{i=1}^N a_i y_i(x_j)$$

high order Lagrange polynomials, $y_i(x)$
with **node points of Legendre roots.**

$$y_j = \sum_{i=1}^{N+2} d_i x_j^{i-1}$$

$$y = Qd, \quad \frac{dy}{dx} = C Q^{-1} y, \quad \frac{d^2 y}{dx^2} = D Q^{-1} y$$

$$\text{where, } Q_{j,i} = x_j^{i-1}, C_{j,i} = (i-1)x_j^{i-2}, D_{j,i} = (i-1)(i-2)x_j^{i-3}$$

FDM:



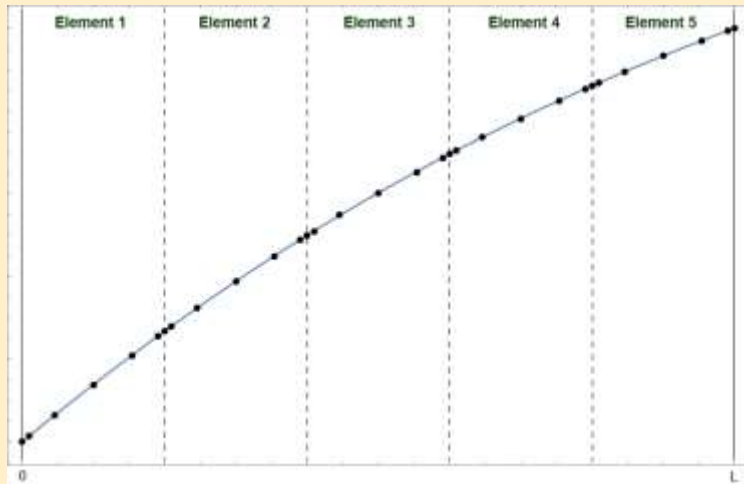
SEM:



Differential Equation \Rightarrow Algebraic Equation

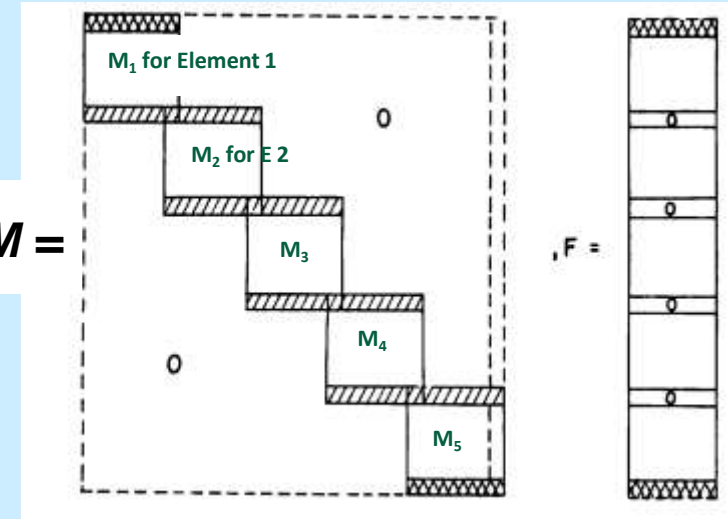
$$\alpha \frac{d^2 y}{dx^2} + \beta \frac{dy}{dx} + \gamma y = (\alpha D Q^{-1} + \beta C Q^{-1} + \gamma) y \Rightarrow M y_j$$

Differentiation Matrix(M) in SEM



Spectral elements and collocation points

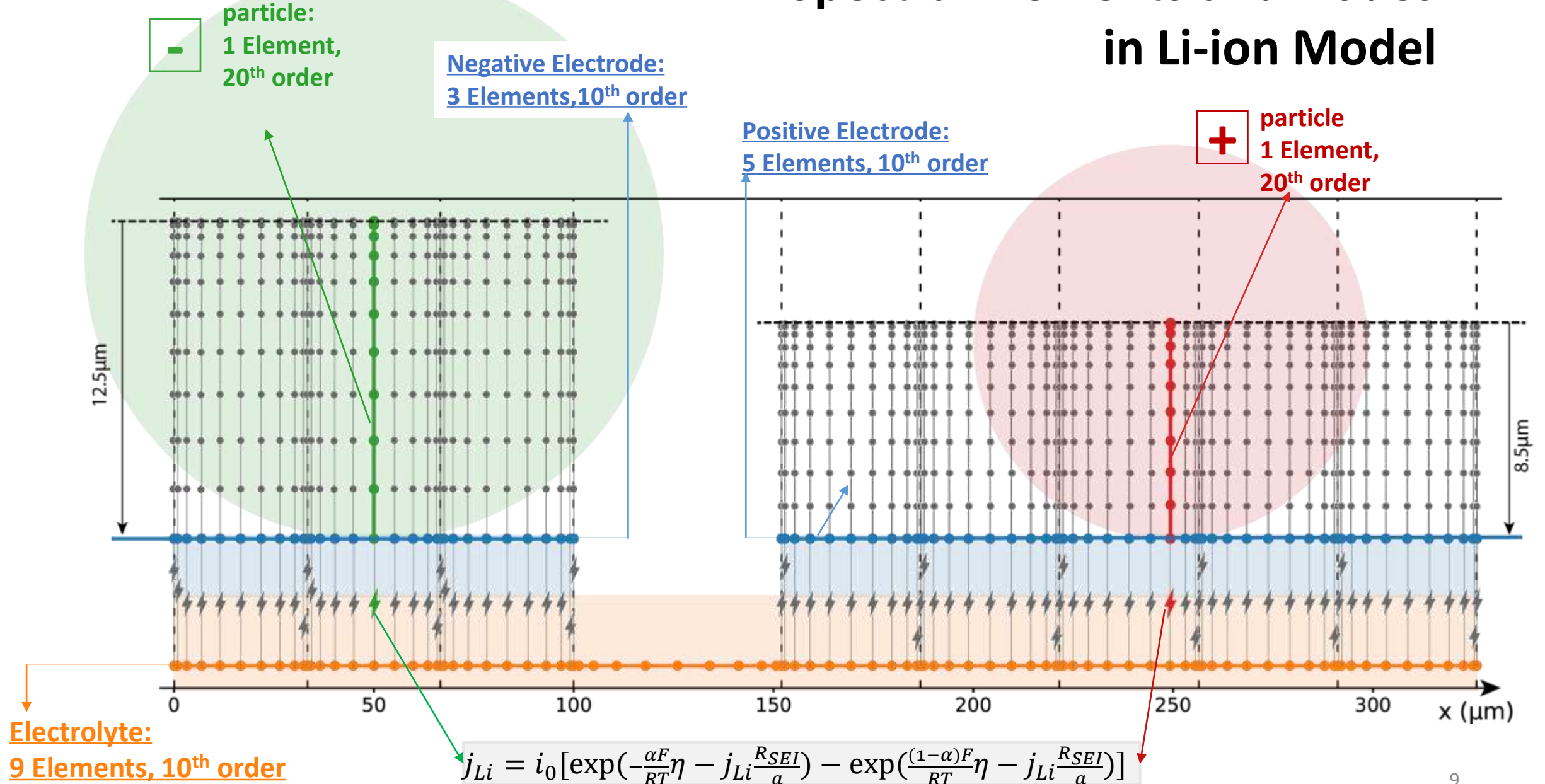
$$\frac{d}{dx} = M =$$



Matrix Structure for SEM

$$M \text{ (5th Order)} = \begin{bmatrix} 8.5000 & -10.4721 & 2.8944 & -1.5279 & 1.1056 & -0.5000 \\ 2.6180 & -1.1708 & -2.0000 & 0.8944 & -0.6180 & 0.2764 \\ -0.7236 & 2.0000 & -0.1708 & -1.6180 & 0.8944 & -0.3820 \\ 0.3820 & -0.8944 & 1.6180 & 0.1708 & -2.0000 & 0.7236 \\ -0.2764 & 0.6180 & -0.8944 & 2.0000 & 1.1708 & -2.6180 \\ 0.5000 & -1.1056 & 1.5279 & -2.8944 & 10.4721 & -8.5000 \end{bmatrix}$$

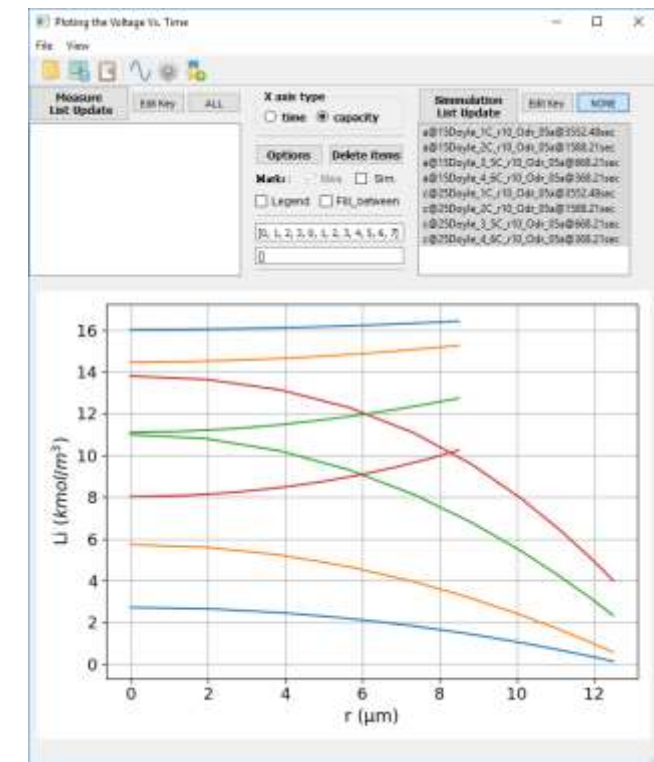
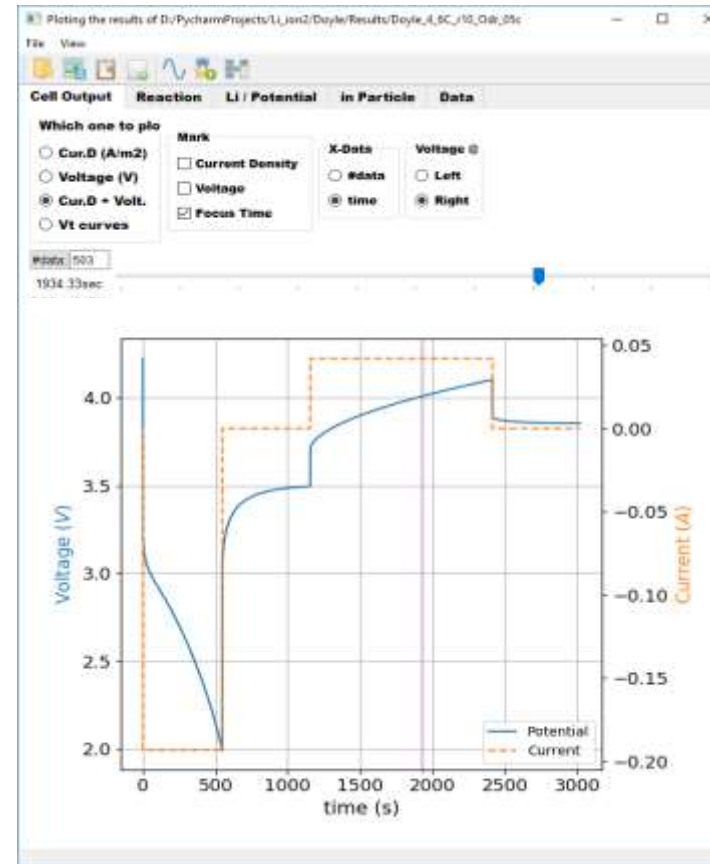
Spectral Elements and Nodes in Li-ion Model



Li-ion battery Simulator & its Postprocessor

- Developing the numerical algorithm
- Coding simulation & post-processing programs with Python

```
Li-ion_V19_cycapy > ...
1188 StepInCycle = 3
1189 continue
1190
1191 elif StepInCycle == 3: # Initializing Stage before discharging
1192
1193     InitN += 1
1194     dTime = Li.dTime0
1195
1196     OutCurDen = DchCurDensity * (Float(InitN) / Li.InitN) ** 2
1197     Ch = False
1198
1199     if InitN == Li.InitN:
1200         StepInCycle = 4
1201
1202 elif StepInCycle == 4: # Discharging Stage
1203
1204     OutCurDen = DchCurDensity
1205     Ch = False
1206
1207     # Discharging Stage
1208     if NumRoot < Li.UpNum:
1209         NumUp += 1
1210         if NumUp > Li.ContNum:
1211             dTime *= 1.25
1212             if dTime > Li.dTime:
1213                 dTime = Li.dTime
1214             NumUp = 0
1215             NumDown = 0
1216         elif NumRoot > Li.DownNum:
```

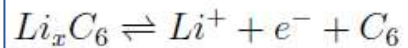


Properties and Parameters

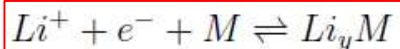
- from Doyle and Newman(1996)

Journal of the Electrochemical Society, 143(6), 1890

Parameters	Description	Value
<i>Operation variables</i>		
I	Discharge current (1.0 C)	17.5 A/m ²
T	Temperature	298 K
<i>Design variables</i>		
$C_{e,0}$	Initial concentration of LiPF ₆ in the electrolyte	2000 mol/m ³
$C_{sa,0}$	Initial concentration of Li ions in the anode	14,870 mol/m ³
$C_{sc,0}$	Initial concentration of Li ions in the cathode	3900 mol/m ³
δ_a	Anode width	100 μ m
δ_c	Cathode width	174 μ m
δ_s	Separator width	52 μ m
ε_a	Anode porosity	0.357
ε_c	Cathode porosity	0.444



$$U_-(x) = -0.16 + 1.32 * \text{np.exp}(-3.0 * x) + 10.0 * \text{np.exp}(-2000.0 * x)$$



$$U_+(y) = 4.1983 + 0.056566 * \tanh(-14.5546 * y + 8.60942) - 0.0275479 * ((1.0 - y)^{-0.492465} - 1.90) - 0.157123 * \exp(-0.04738 * y^8) + 0.810239 * \exp(-40 * (y - 0.133875))$$

Kinetic, thermodynamic and transport parameters

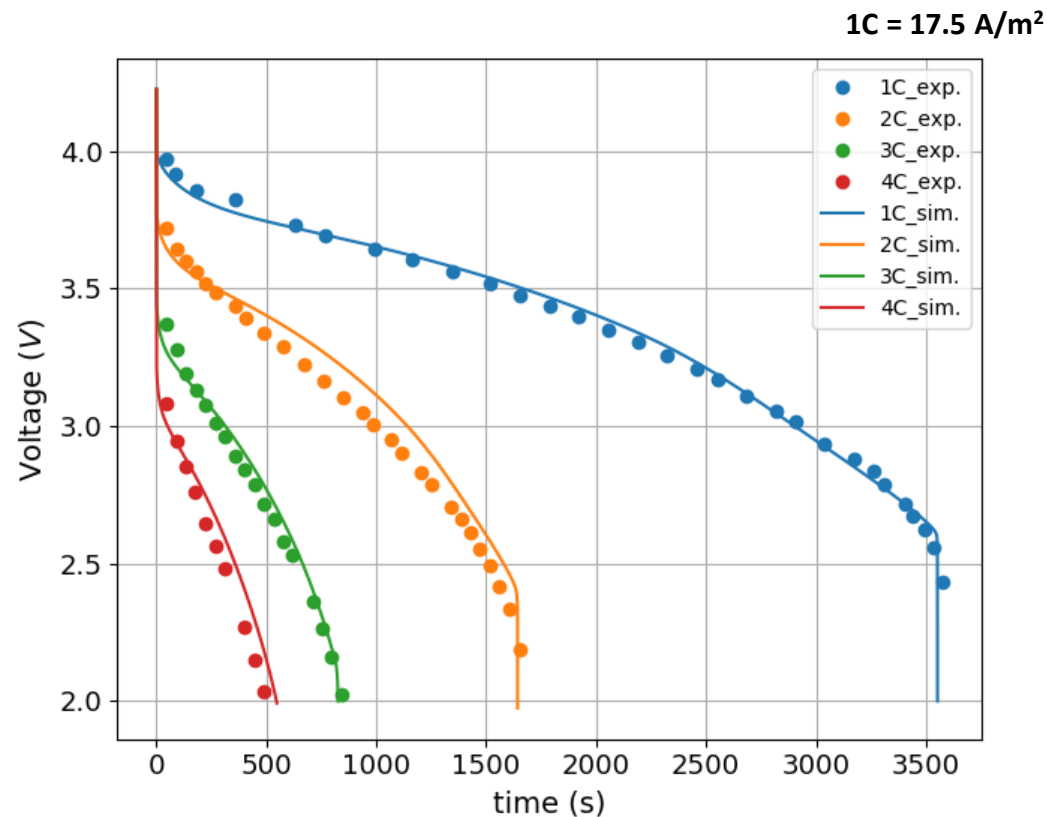
C_T^a	Max. conc. of Li ions in the anode	26,390 mol/m ³
C_T^c	Max. conc. of Li ions in the cathode	22,860 mol/m ³
D_s^a	Particle diffusivity coefficient in the anode	3.9×10^{-14} m ² /s
D_s^c	Particle diffusivity coefficient in the cathode	1.0×10^{-13} m ² /s
D	Electrolyte diffusivity coefficient	7.5×10^{-11} m ² /s
R_p^a	Radius of the active material sphere in the anode	12.5 μ m
R_p^c	Radius of the active material sphere in the cathode	8.5 μ m
t_+^o	Transport number	0.363
σ^a	Conductivity in the anode	100 S/m ²
σ^c	Conductivity in the cathode	3.8 S/m ²

Description	Formula
-------------	---------

Calculated parameters

$a^{a,c}$	Specific area of the electrodes (m ² /m ³)	$3 \frac{\varepsilon_s}{R_p}$
ε_s^a	Volume fraction of the solid phase in the anode	$1 - \varepsilon^a - 0.172$
ε_s^c	Volume fraction of the solid phase in the cathode	$1 - \varepsilon^c - 0.259$

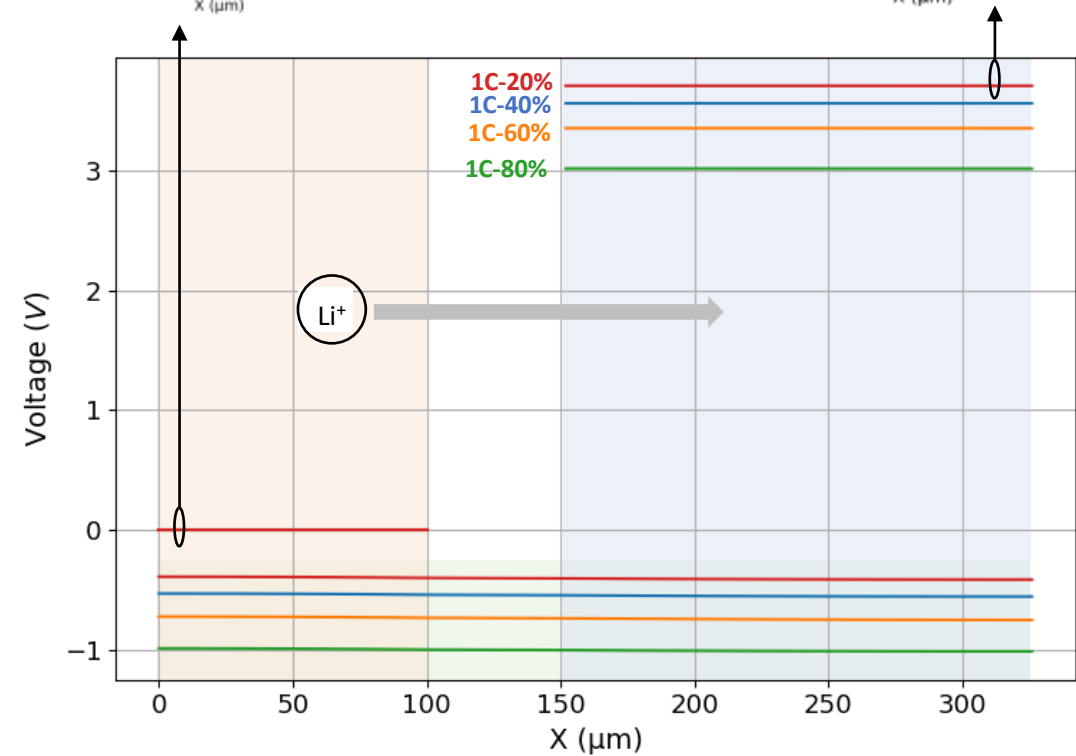
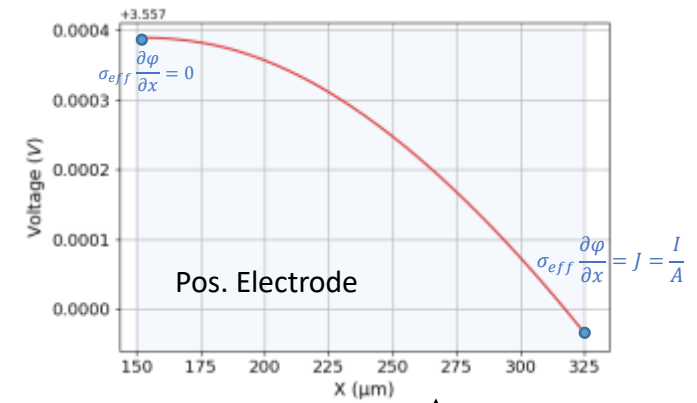
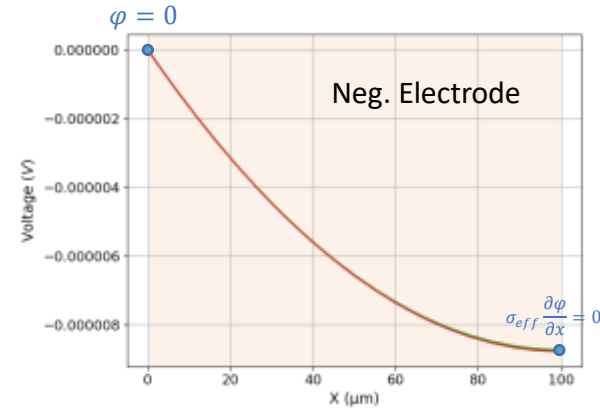
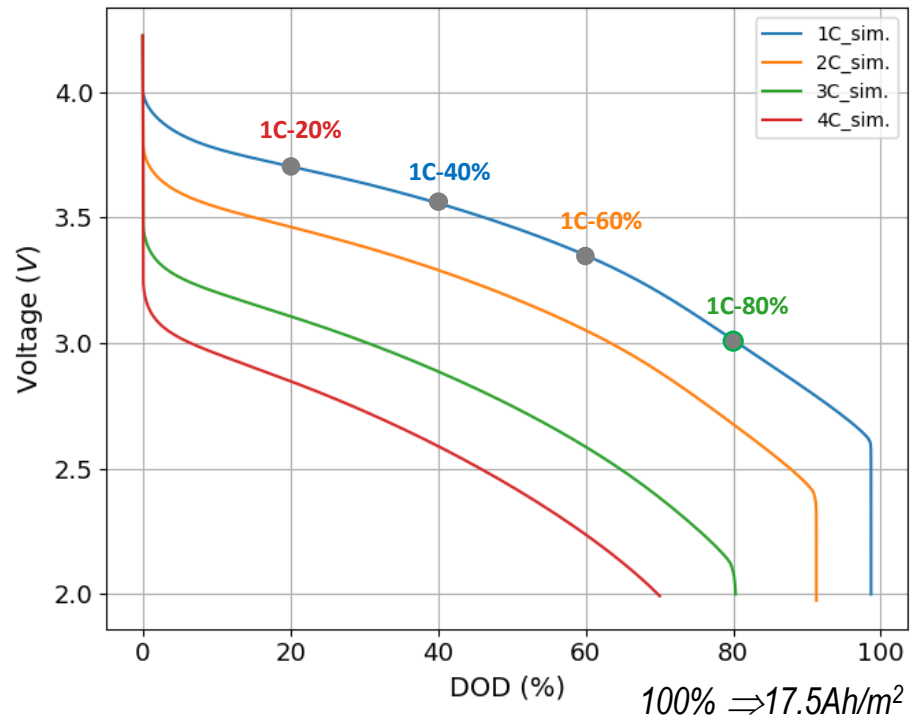
Comparison Simulation Results with Experiments



Simulating conducted with this model shows a close agreement with test data Doyle & Newman got from Li-Mn₂O₄ battery cell

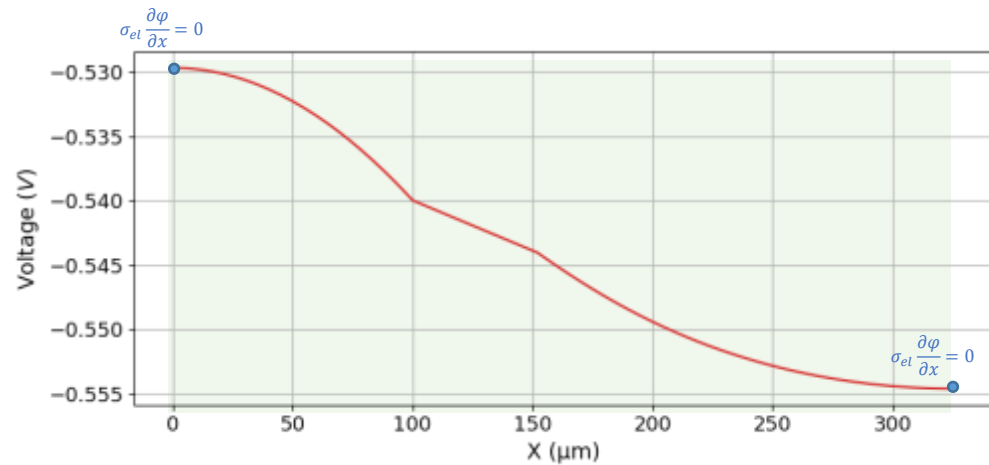
* exp. data from Doyle, M., & Newman, J. (1996). Comparison of the modeling predictions with experimental data from plastic lithium ion cells. *Journal of the Electrochemical Society*, 143(6), 1890

Potential Distribution in Discharging

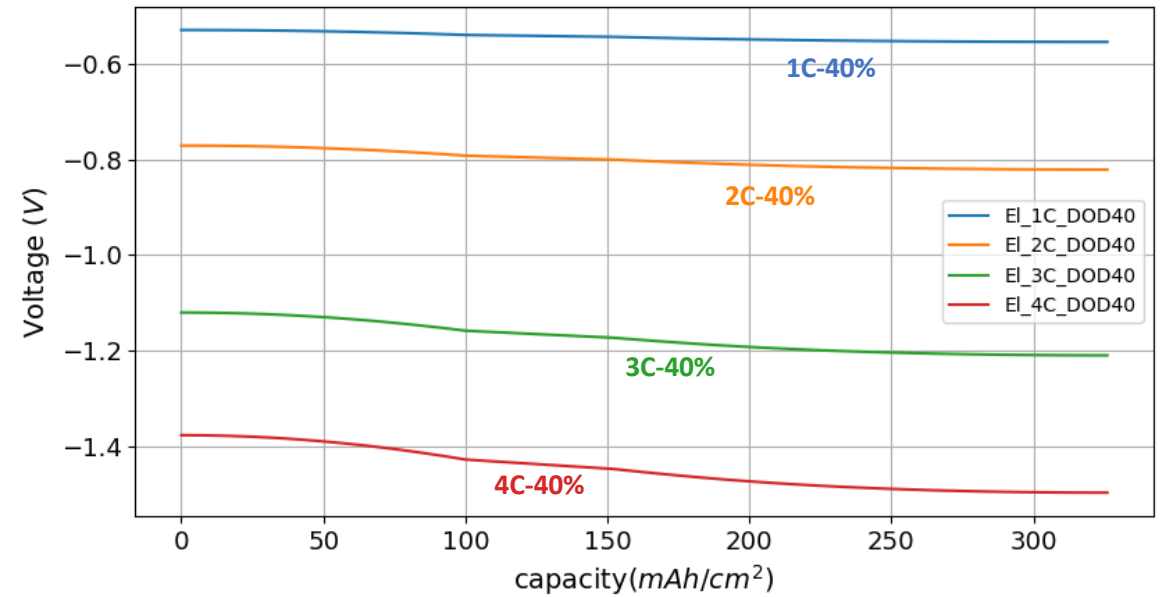


Potential evolution in the cell
in discharging at 1C rate

Potential Distribution in Electrolyte



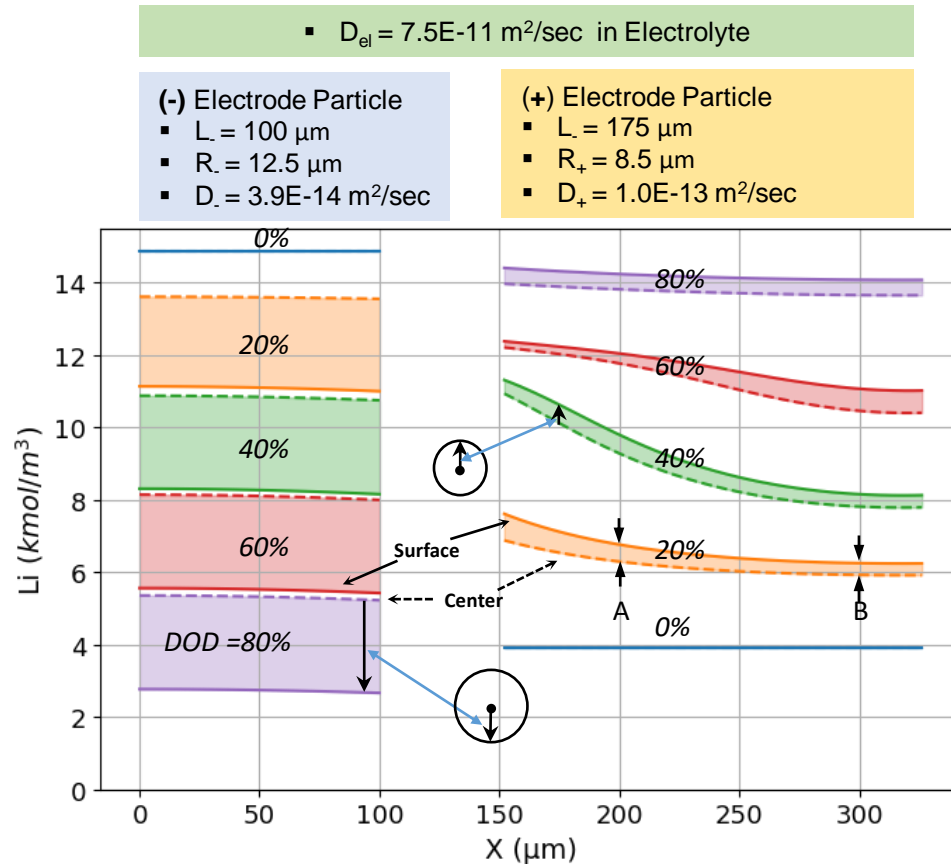
1C discharging at DOD = 20%



Potential distribution

Li concentration distribution (1C discharging)

A



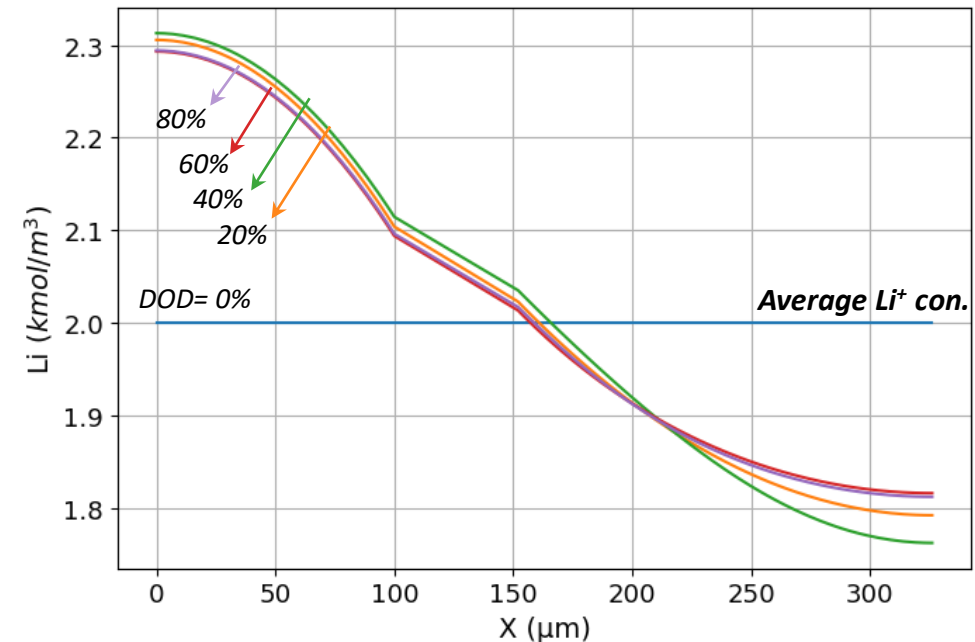
Li concentration distribution in Electrode Particles

In the left figure,

- At each DOD condition, Li concentration range is wider in (-) electrode particle than (+) particle.
- Along X-direction (the electrode thickness direction), Li concentrations at (+) particle's surface and center change more than the concentrations of (-) particle.
- The reason is because Li ion diffusivity in (-) particle is smaller, but its radius is larger. Also, thickness (L) of (-) electrode is smaller than that of (+) electrode.
- Electrochemical reaction rate changes along X-direction(See the next page).

In the right figure,

- Li ion concentration distribution in the electrolyte doesn't much change with depth of discharge(DOD), if it is discharged under the same rate, here 1C
- The average concentration of Li in electrolyte is maintained at the initial value, 2 kmol/m^3 .

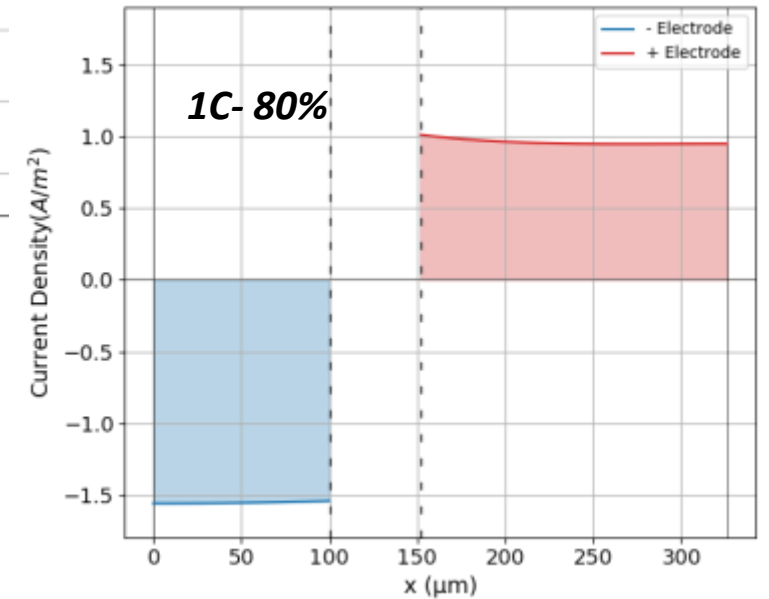
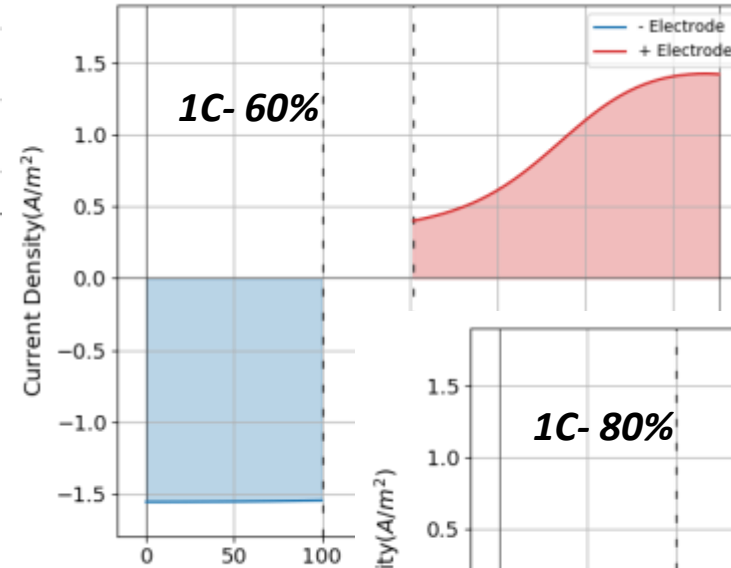
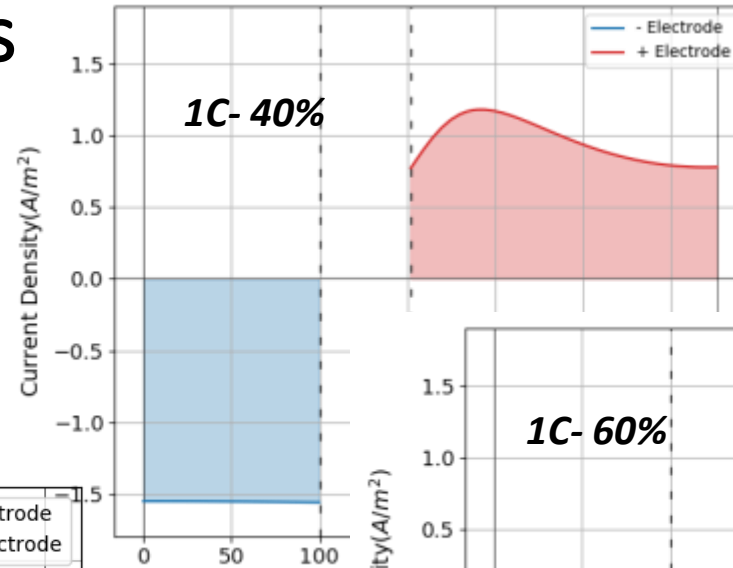
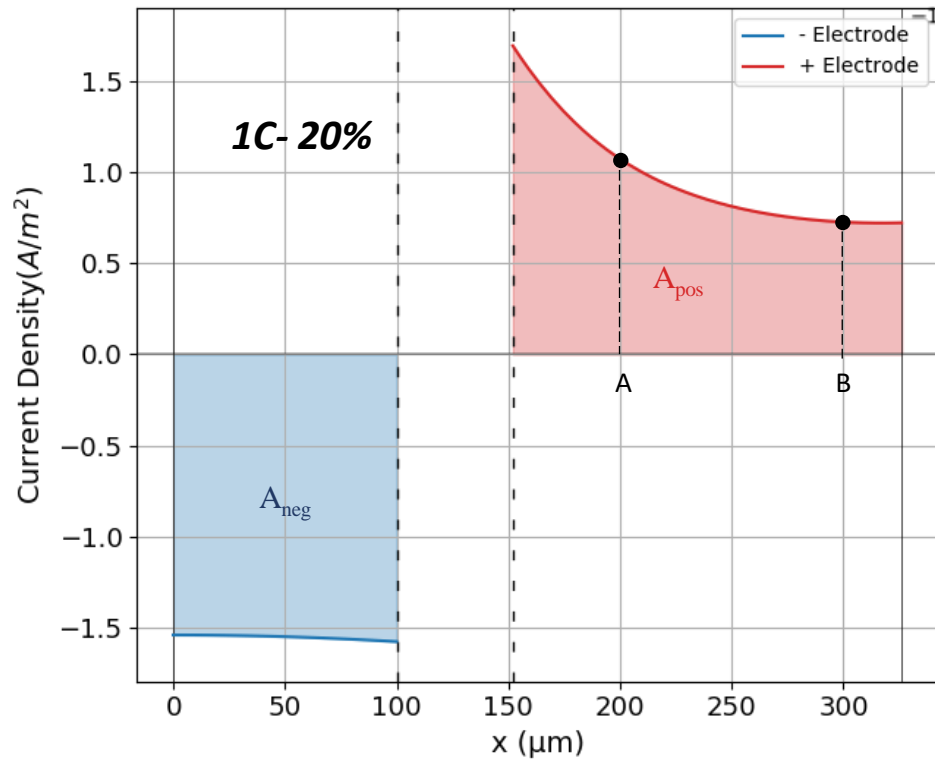


Li concentration in Electrolyte

Electrochemical Reactions

$$j_{Li} = i_0 [\exp(\frac{\alpha F}{RT} \eta) - \exp(\frac{-\alpha F}{RT} \eta)]$$

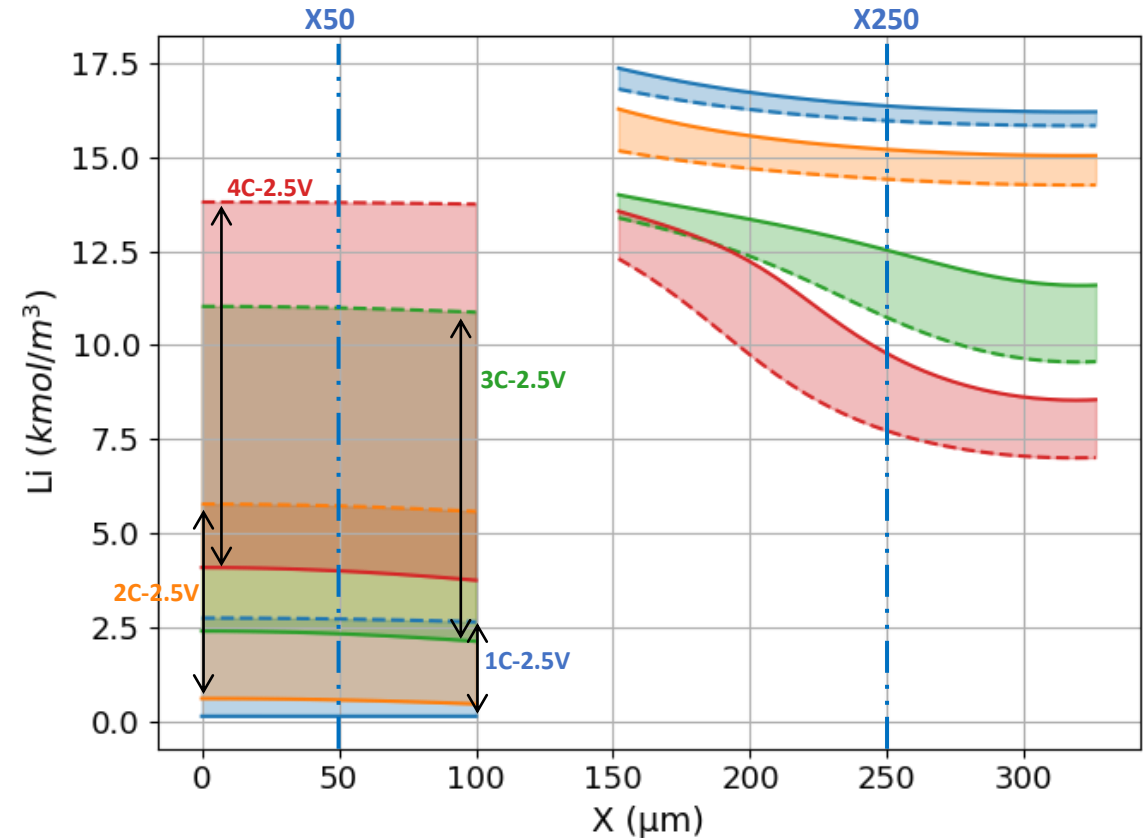
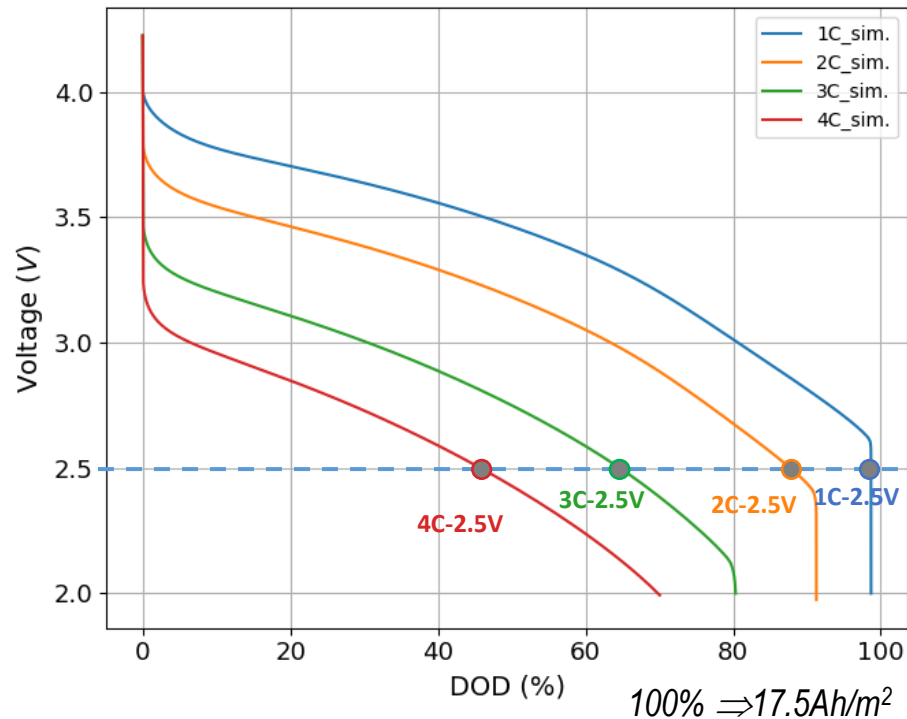
$$i_0 = k_0 (C_e(C_{s,max} - C_s)(C_s - C_{s,min}))^{0.5}$$



Conservation of Charge

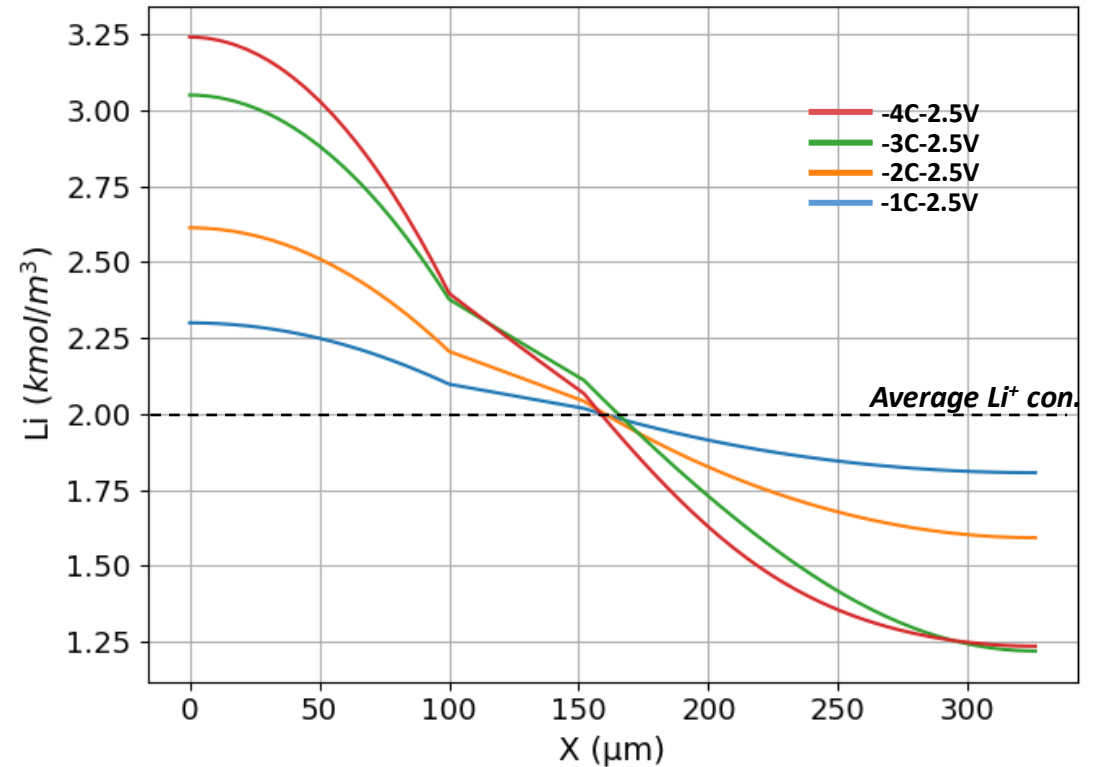
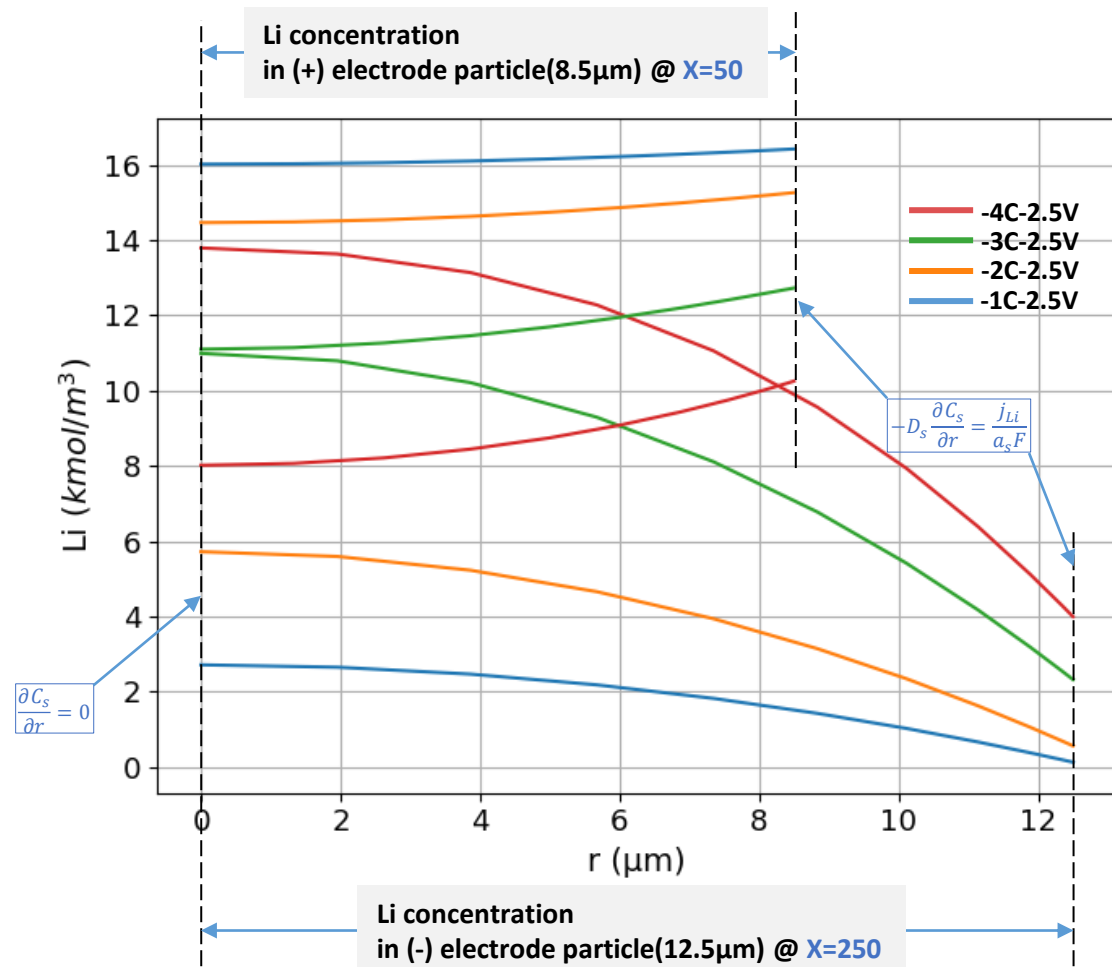
$$\frac{3(1 - \varepsilon_-)}{R_-} A_{neg} = \frac{3(1 - \varepsilon_+)}{R_+} A_{pos} = J$$

Li⁺ transfer in Electrodes, when cell is discharged to $V_{\text{out}} = 2.5\text{V}$



As shown in the right figure,

- At 1C-2.5V, Li concentration at surface (C_{sur}) has reached its minimum (≈ 0) at surface. Due to depletion of Li⁺, electrochemical reaction is limited and cell output voltage drops quickly.
- As discharging get faster than 1C, C_{sur} is higher at $V_{\text{out}} = 2.5\text{V}$. But voltage drop quickly by internal resistance.
- At higher discharging rate condition, C_{Li} range in the electrode particle, $|C_{\text{sur}} - C_{\text{cen}}|$, becomes wider at both +/- electrodes.
- The range of (+) electrode is narrower than that of (-), because the diffusivity and the particle radius of (+) particle are higher and smaller than (-) electrode.



Li ion concentration in electrolyte at $V_{out} = 2.5V$

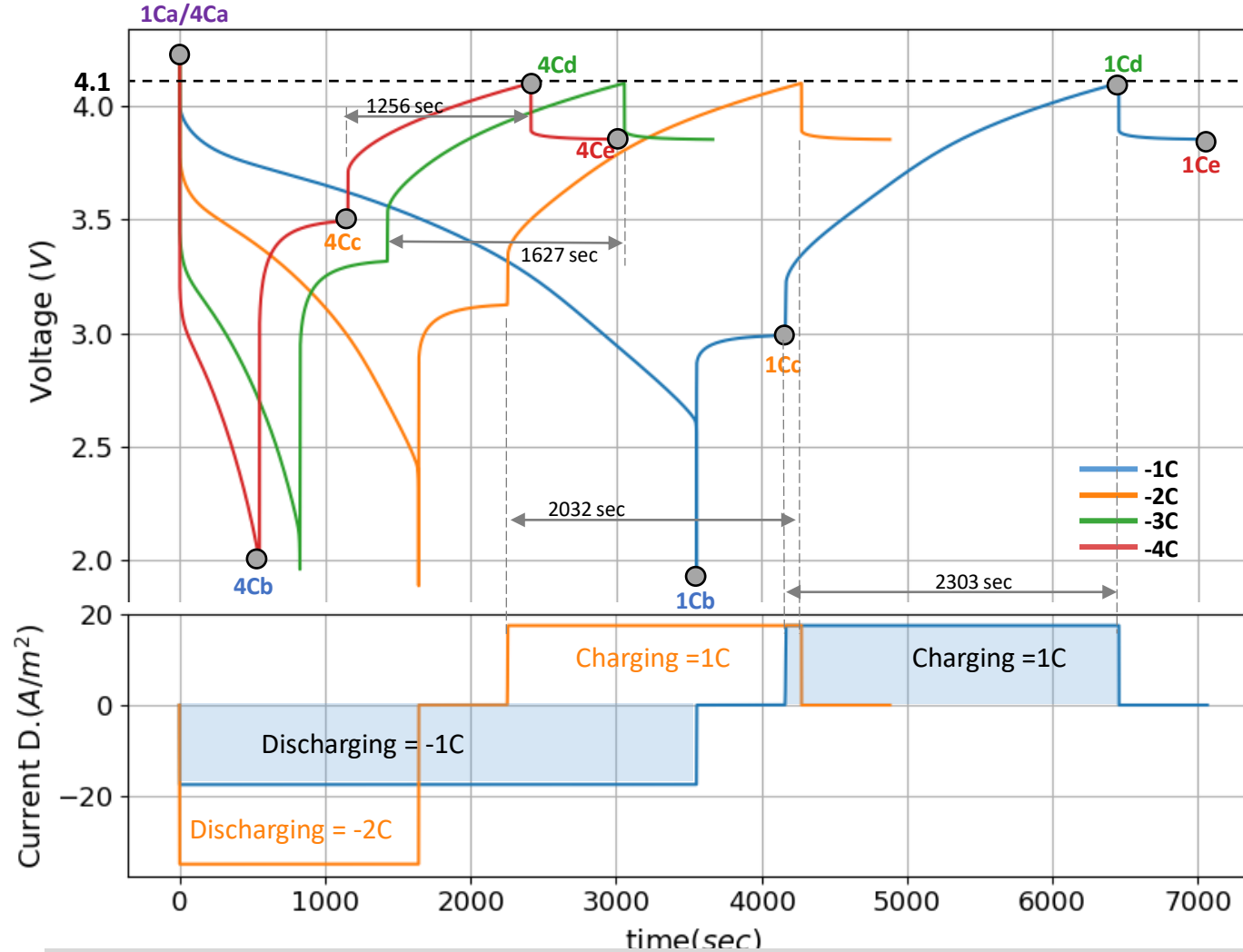
Left figure shows the Li ion concentration in (+)/(-) particle at x=50 and x=250 position

- In (+) electrode particle which has smaller size and higher diffusivity, Li concentration range is smaller than in (-) electrode.
- The concentration range expands with higher discharging rate.
- The cell's voltage decreases from 4.2V to 2.5V as it discharges at four different rates. During discharging, Li ions in (-) electrode transfer to (+) electrode.
- The difference between Li concentration curves of (+)/(-) electrode is larger at lower C-rate (Max. at 1C). That means more Li ions transfer at slower discharging condition; higher discharge capacity.

In the right figure,

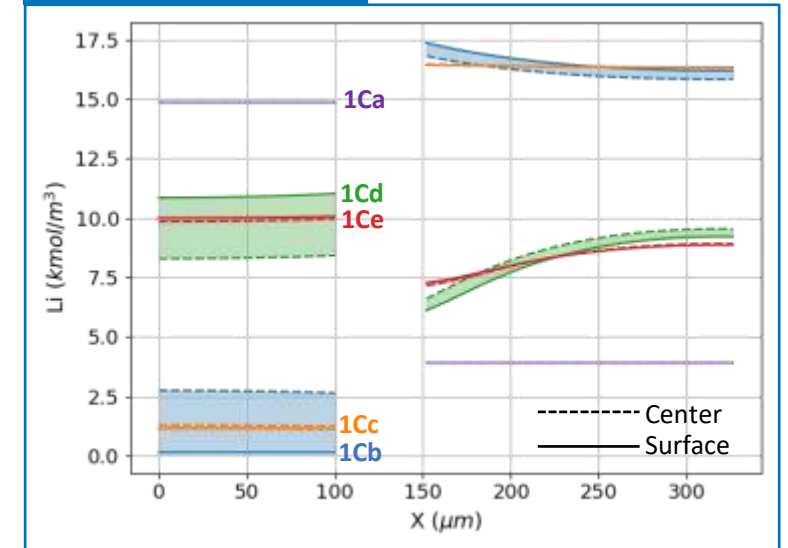
- As the discharging rate increases, more Li ion transfer through electrolyte from (-) to (+) electrode. And It causes the concentration gradient of Li ion to increase.
- However, the average concentration of Li ion is maintained at the initial concentration, 2 kmol/m³.

Discharging (1/2/3/4C) + Charging (1C)

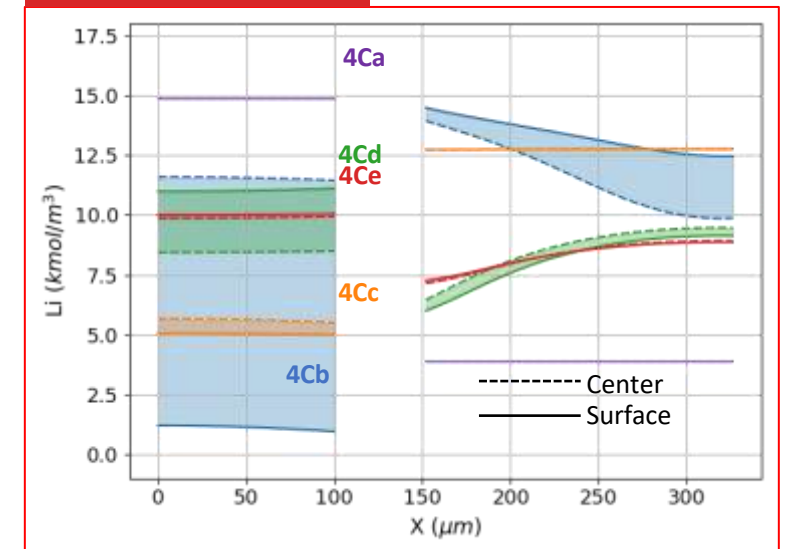


- During charging/discharging period, Li concentration distribution in the electrode particles widens as shown in the right figures.
- Its distribution range shrinks in the relaxation period.
- The expansion/shrinkage gets enhanced by increasing discharging rate from 1C to 4C.
- At higher discharging rate, the discharging capacity is reduced as well as the charging capacity

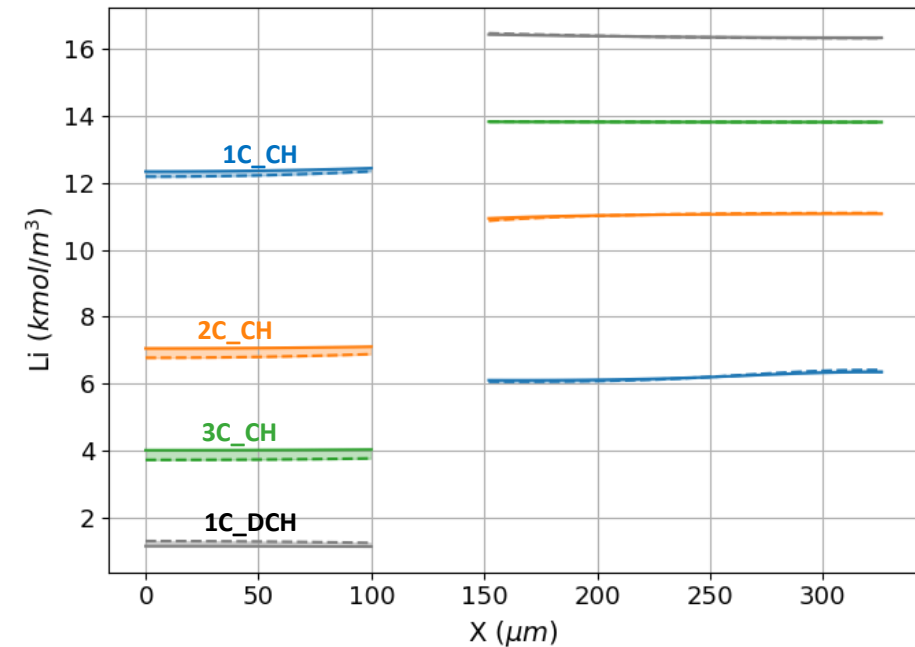
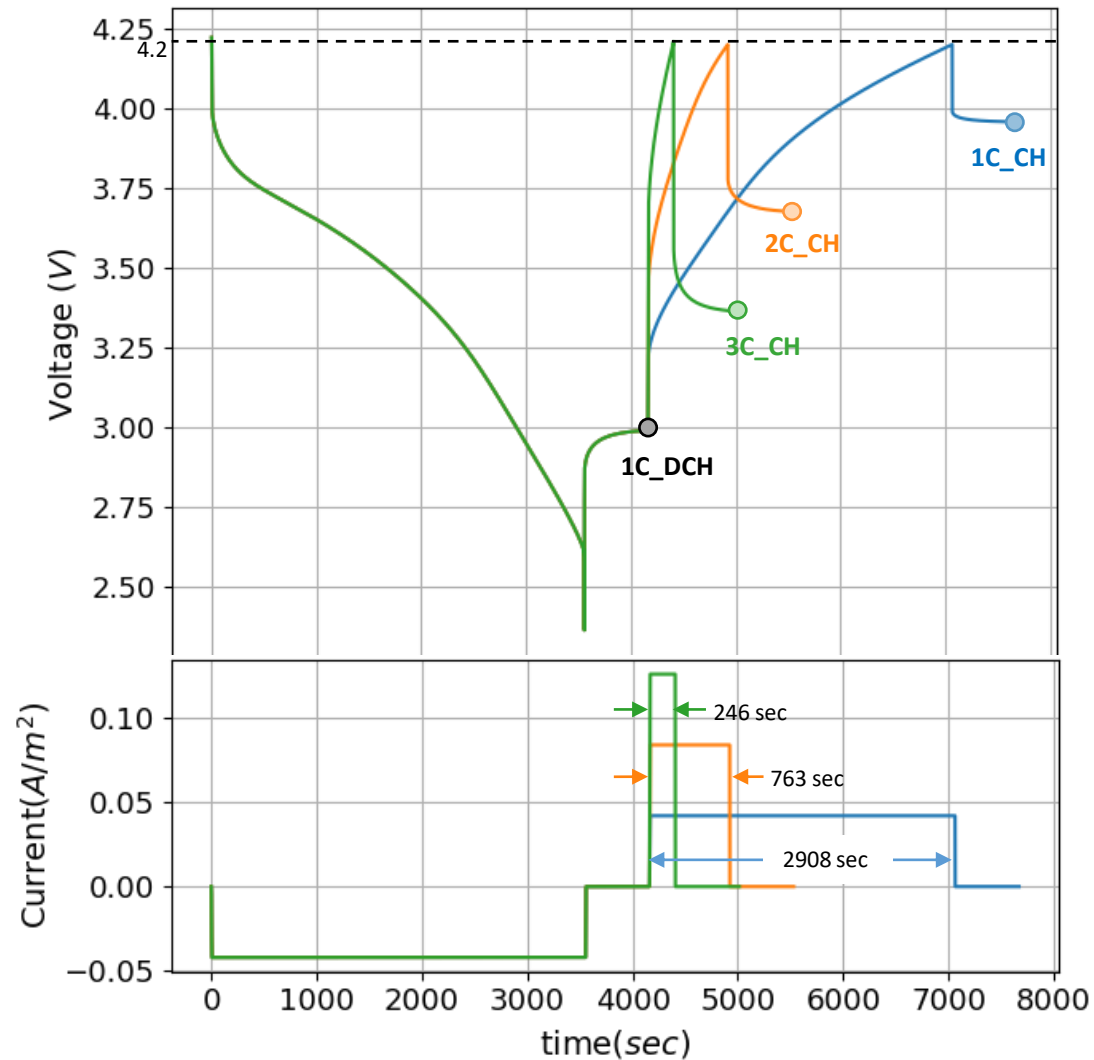
Discharging = -1C



Discharging = -4C

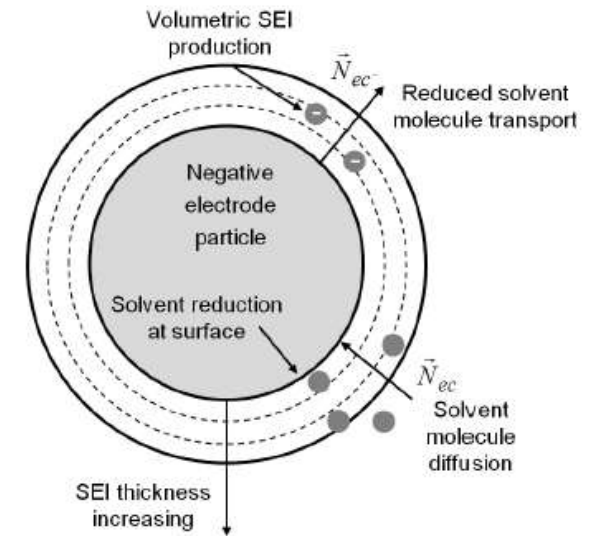
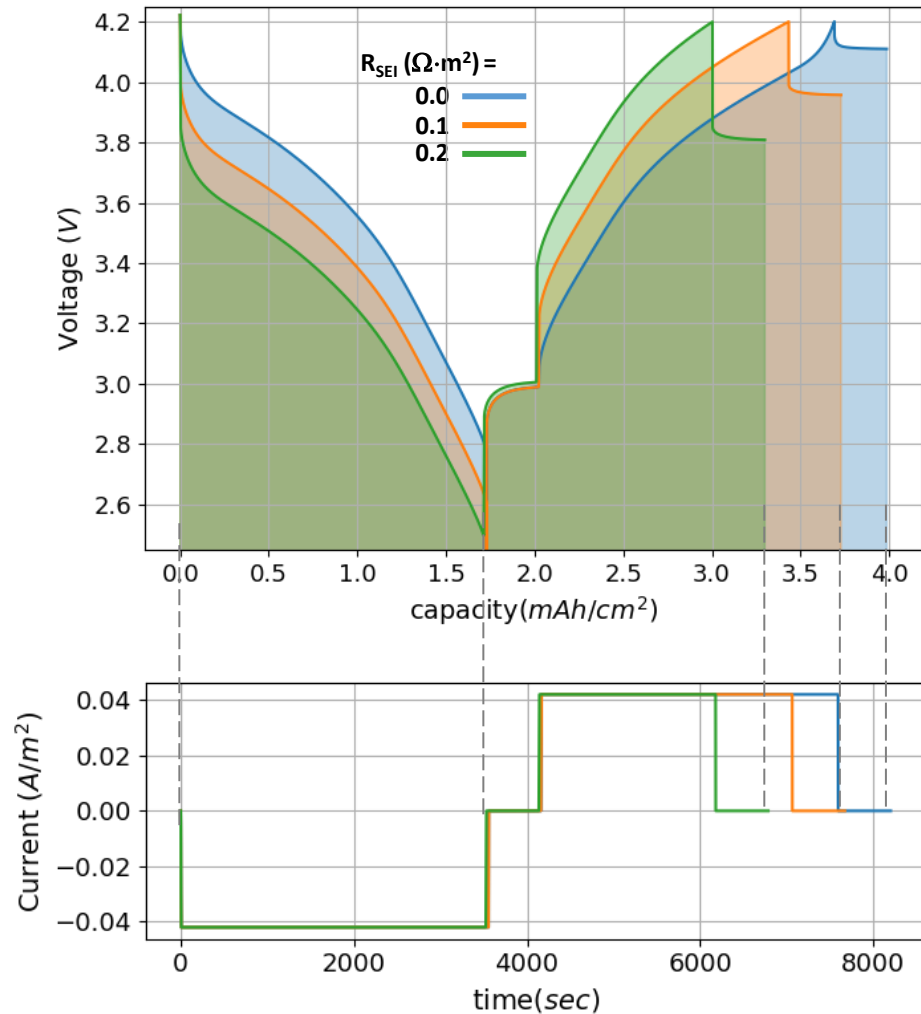


Discharging (1C) + Charging (1/2/3C)



- The charging behavior is simulated at different charging rate.
- At higher charging rate,
- The cell reaches quickly the charging limit voltage ($V_{\max} = 4.2\text{v}$) and the charging time is shortened.
- But, the amount of Li ions having transferred from cathode to anode electrode is reduced as shown in the right figure.
- The discharging capacity will be dwindled.

Effect of R_{SEI} (SEI resistance)



- The effect of SEI resistance on cell capacity is studied by simulation.
- As the solid electrolyte film layer grows, cell's internal resistance grows.
- Cell voltage change at the start of discharge/charge increases with higher SEI resistivity.
- As SEI resistivity increases, the time to reach charging limit voltage gets shorter and charging /discharging capacity is reduced..

Conclusion

- Physics based Li-ion cell model is developed successfully.
- The model is verified by comparison with test data.
- Mass and charge transfer with electrochemical reactions are well analyzed.
- The simulation model will be applied to analyzing cell performance issues such as capacity fade and impedance growth.
- The simulation tool developed is able to deploy freely to other battery engineers