

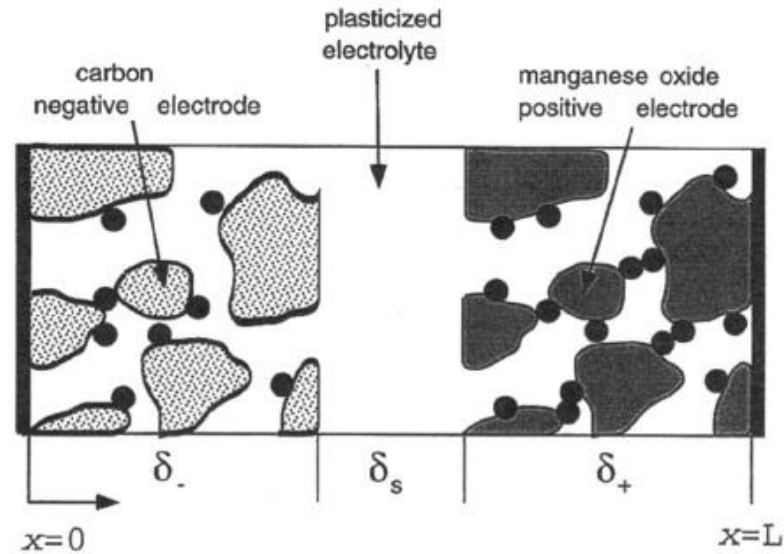
# **Li- ion modeling** physics-based

Dongmyung Suh

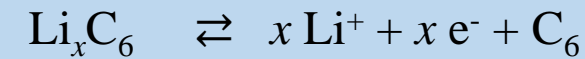
# Design of Li ion battery simulation Model

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

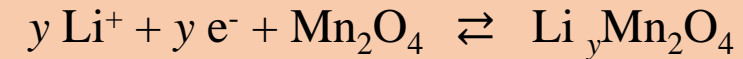


## Negative Electrode



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

## Positive Electrode



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

# Physics Based Model of Li-ion battery

- in Electrode (Negative/Positive)

- Conservation of Charge

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

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

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

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

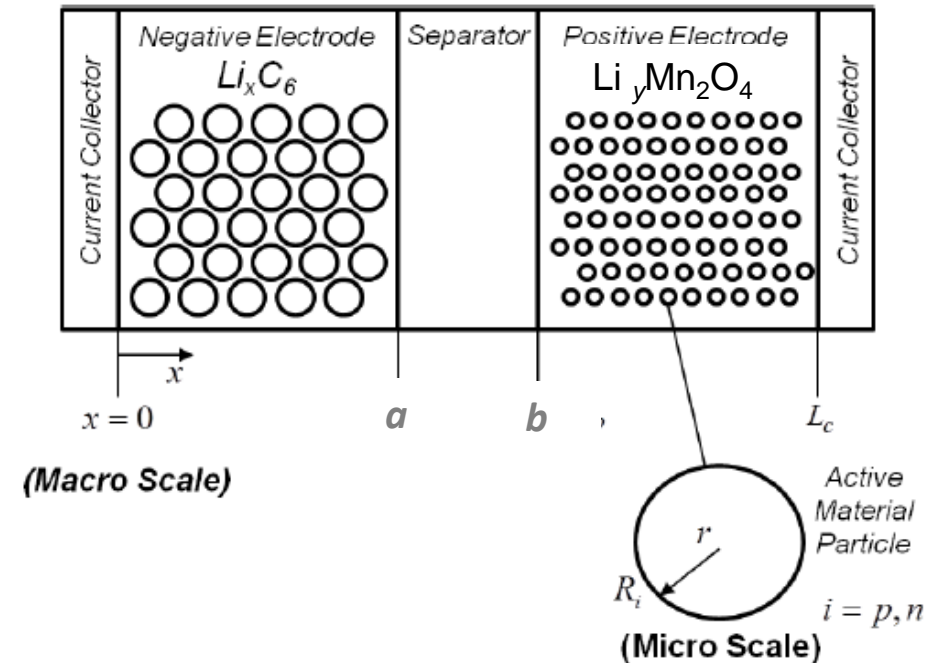
- Conservation of Mass

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

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

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

$a_s$  : specific area per unit volume



## - in Electrolyte

### - Conservation of Charge

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

$$\left. \frac{\partial \varphi_e}{\partial x} \right|_{x=0} = \left. \frac{\partial \varphi_e}{\partial x} \right|_{x=L} = 0$$

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

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

### - Conservation of Mass

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

$$\left. \frac{\partial C_e}{\partial x} \right|_{x=0} = \left. \frac{\partial C_e}{\partial x} \right|_{x=L} = 0$$

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

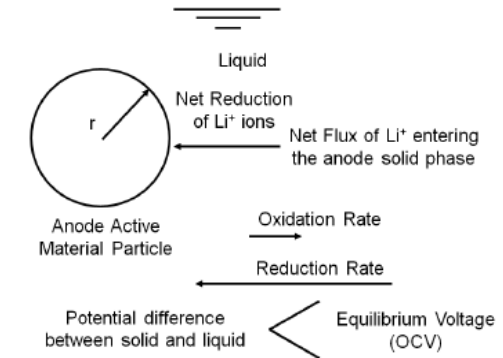
# Electrochemical Reaction

## Butler-Volmer Kinetic Equation

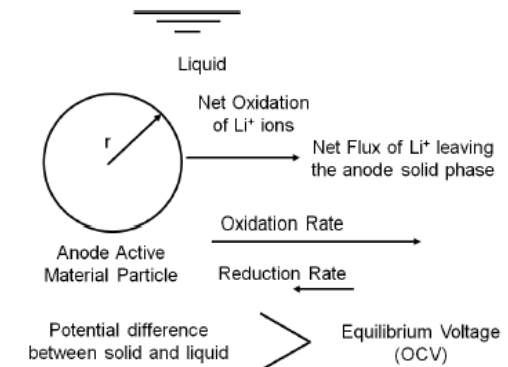
$$j_{Li} = a_s i_o \left[ \exp \left\{ \frac{\alpha_a F}{RT} \left( \eta - \frac{R_{SEI}}{a_s} j_{Li} \right) \right\} - \exp \left\{ - \frac{\alpha_c F}{RT} \left( \eta - \frac{R_{SEI}}{a_s} j_{Li} \right) \right\} \right]$$

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

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



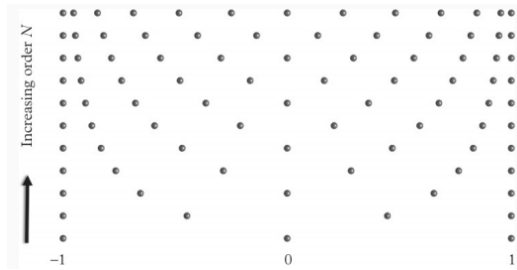
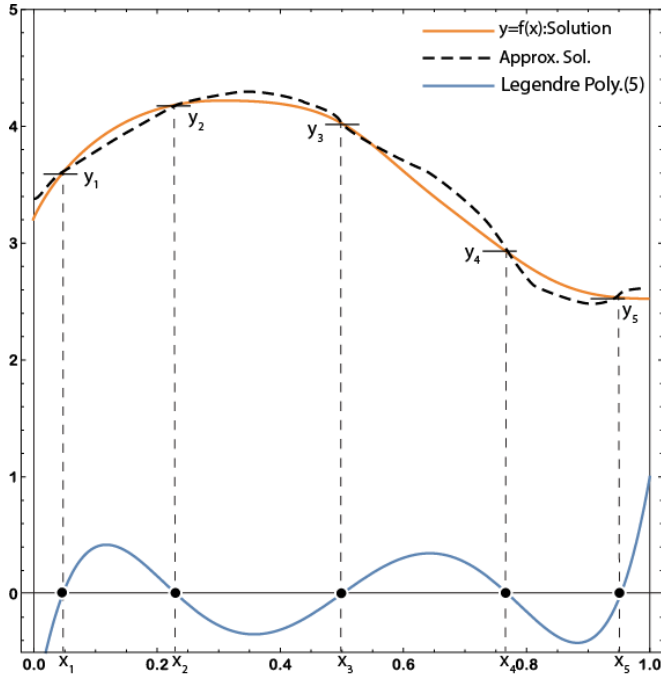
(a) Charging



(a) Discharging

# Spectral Element Method (SEM)

- High-Order FEM
- Lagrange polynomials as interpolating functions.
- Combined with interpolation scheme based on the Gauss-Lobatto-Legendre (GLL) collocation points
- High Accuracy, Fast Converging and easy to parallelizing.



### Collocation Points $[x_i]$

- Roots of  $N^{\text{th}}$  order Legendre Polynomials
- More densely placed at boundary
- Avoid overshooting at boundary
- Boundary Condition considered accurately

$$y(x) = \sum_i y_i \cdot I_i^N(x)$$

Lagrange Polynomials:  $I_i^N(x) = \prod_{j \neq i}^{N+1} \frac{(x-x_j)}{(x_i-x_j)}$   $I_i^N(x_j) = \delta_{ij}$

$$y'(x) = \frac{dy}{dx} = \sum_i y_i \cdot \frac{d}{dx} I_i^N(x) \quad y'_j = y'(x_j) = \sum_i y_i \cdot \frac{d}{dx} I_i^N(x) \Big|_{x=x_j}$$

$$D \text{ (5th Order)} = \begin{bmatrix} 8.5000 & -10.4721 & 2.8944 & -1.5279 & 1.1056 & -0.5000 \\ 2.6180 & -1.1708 & -2.0000 & 0.8944 & -0.6180 & 0.2764 \\ -0.7236 & 2.0000 & -0.1708 & -1.6180 & 0.8944 & -0.3820 \\ 0.3820 & -0.8944 & 1.6180 & 0.1708 & -2.0000 & 0.7236 \\ -0.2764 & 0.6180 & -0.8944 & 2.0000 & 1.1708 & -2.6180 \\ 0.5000 & -1.1056 & 1.5279 & -2.8944 & 10.4721 & -8.5000 \end{bmatrix} = D \begin{bmatrix} y_1 \\ y_2 \\ \vdots \\ y_N \end{bmatrix} = D Y$$

$$y''(x) = \sum_i y''_i \cdot I_i^N(x) \quad y''_j = y''(x_j) = \sum_i y_i \cdot \frac{d^2}{dx^2} I_i^N(x) \Big|_{x=x_j} = D^2 Y$$

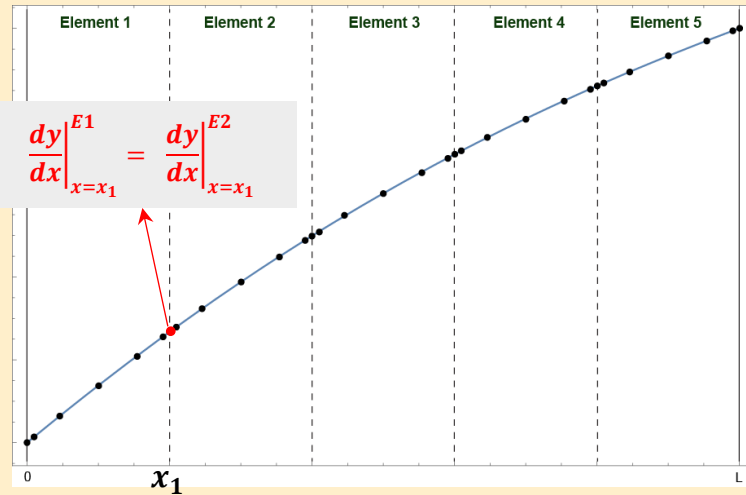
### Differential Equation $\Rightarrow$ Algebraic Equation

$$\alpha \frac{d^2 y}{dx^2} + \beta \frac{dy}{dx} + \gamma y = (\alpha D^2 + \beta D + \gamma I) Y \Rightarrow M Y$$



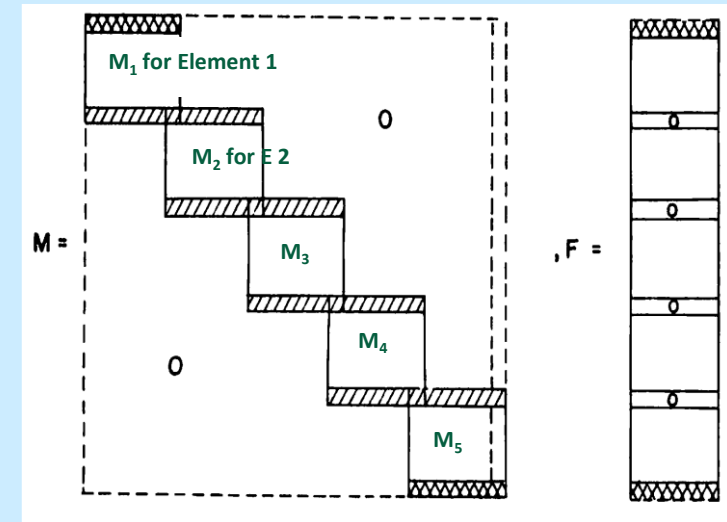
# Global Matrix ( $G$ ) in SEM

Assemble each element's Matrix( $M$ ) into a global Matrix ( $G$ ) using continuity at boundaries between elements



Spectral elements and collocation points

$G =$



Matrix Structure for SEM

# Solving the system of Non-linear Algebraic Equations

Linear Differential Equations

$$\alpha \frac{d^2 y}{dx^2} + \beta \frac{dy}{dx} + \gamma y = (\alpha \mathbf{D}^2 + \beta \mathbf{D} + \gamma \mathbf{I}) \mathbf{Y} = \mathbf{M} \mathbf{Y} = \mathbf{Constants}$$

`numpy.linalg.solve(M, Constants)`

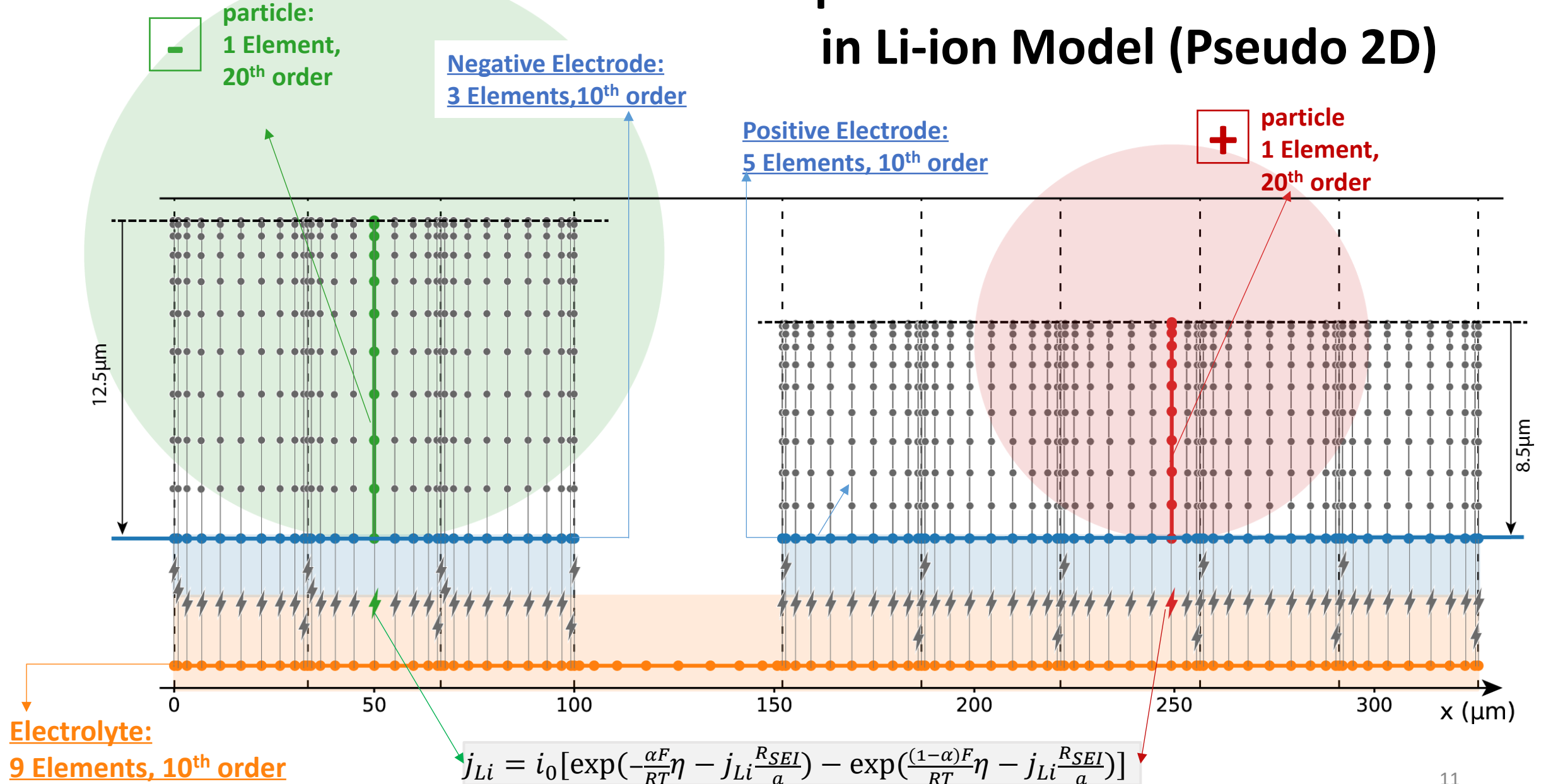
Non-Linear Differential Equations

$$\alpha \frac{d^2 y}{dx^2} + \beta \frac{dy}{dx} + \gamma y = (\alpha \mathbf{D}^2 + \beta \mathbf{D} + \gamma \mathbf{I}) \mathbf{Y} = \mathbf{M} \mathbf{Y} = \mathbf{f}(\mathbf{Y})$$

`scipy.optimize.root( fPM6a, yAll, method="hybr")`

❑ Spectral Element Method & Non-linear Solver were implemented in Li-ion simulation code (in Python)

# Spectral Elements and Nodes in Li-ion Model (Pseudo 2D)



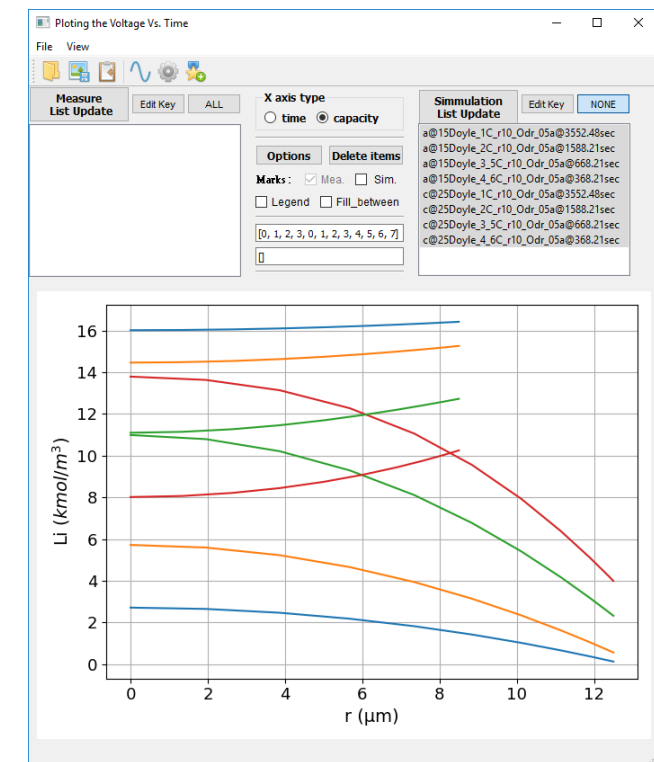
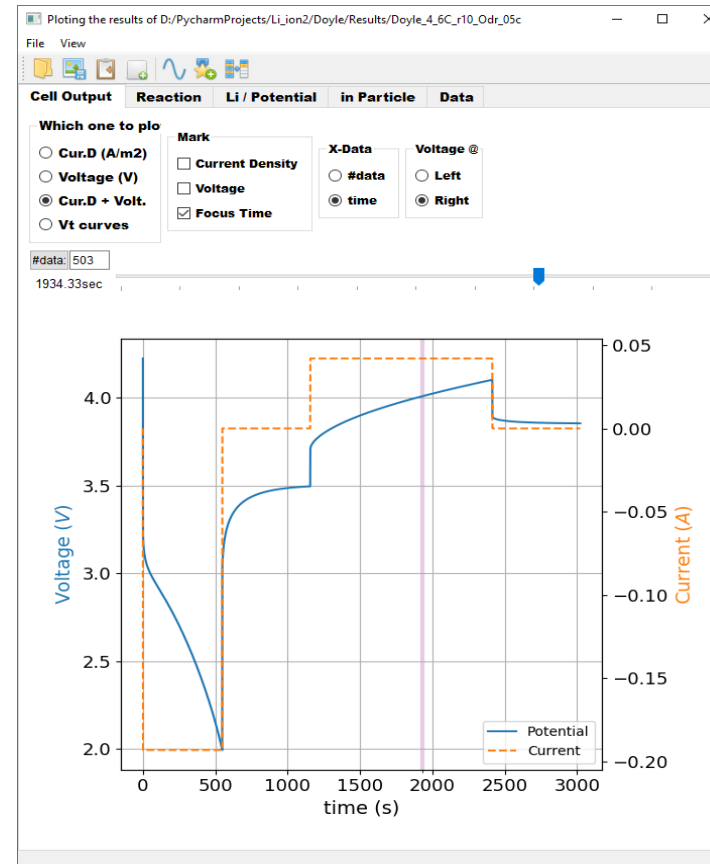
# Li-ion battery Simulator & its Postprocessor

- Developing the numerical algorithm
- Coding simulation & post-processing programs with Python (PyQt5)

```
File Edit Selection View Go Run Terminal Help Li-ion_V19_cycle.py - Doyle - Visual Studio Code
Li-ion_V19_cycle.py x Li-ion_V18.py Doyle_4_6C_r10_Odr_05a.py Doyle_4C_r10_Odr_05a.py Doyle_5C_r10_Odr_05a.py
Li-ion_V19_cycle.py > ...
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.initTN) ** 2
1197     CH = False
1198
1199     if InitN == Li.initTN:
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.ConUpNum:
1211             dTime *= 1.25
1212             if dTime > Li.dTmax:
1213                 dTime = Li.dTmax
1214             NumUP = 0
1215             NumDown = 0
1216         elif NumRoot > Li.DownNum:
```

```
0E-01, Cur = (-1.9320E-01, 1.9320E-01)
Step = 4, StepTime = 57.1172, Adj_dTime = 10.0000, dTime = 2.2737, Cnt = (1253,17,17), Cell Vol = 2.9887E+00, Cell Cur = -1.932
0E-01, Cur = (-1.9320E-01, 1.9320E-01)
Step = 4, StepTime = 59.3909, Adj_dTime = 10.0000, dTime = 2.2737, Cnt = (1253,17,17), Cell Vol = 2.9851E+00, Cell Cur = -1.932
0E-01, Cur = (-1.9320E-01, 1.9320E-01)
Step = 4, StepTime = 61.6646, Adj_dTime = 10.0000, dTime = 2.2737, Cnt = (1253,17,17), Cell Vol = 2.9815E+00, Cell Cur = -1.932
0E-01, Cur = (-1.9320E-01, 1.9320E-01)
Step = 4, StepTime = 63.9384, Adj_dTime = 10.0000, dTime = 2.2737, Cnt = (1253,17,17), Cell Vol = 2.9780E+00, Cell Cur = -1.932
0E-01, Cur = (-1.9320E-01, 1.9320E-01)
```

Python 3.7.4 64-bit (ProgramData\virtualenv) 0 0 Ln 1198, Col 1 Spaces: 4 UTF-8 CRLF Python

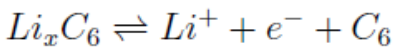


# Properties and Parameters

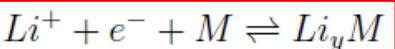
- from Doyle and Newman(1996)

*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 <sup>2</sup>
$T$	Temperature	298 K
<i>Design variables</i>		
$C_{e,0}$	Initial concentration of LiPF <sub>6</sub> in the electrolyte	2000 mol/m <sup>3</sup>
$C_{sa,0}$	Initial concentration of Li ions in the anode	14,870 mol/m <sup>3</sup>
$C_{sc,0}$	Initial concentration of Li ions in the cathode	3900 mol/m <sup>3</sup>
$\delta_a$	Anode width	100 $\mu$ m
$\delta_c$	Cathode width	174 $\mu$ m
$\delta_s$	Separator width	52 $\mu$ m
$\varepsilon_a$	Anode porosity	0.357
$\varepsilon_c$	Cathode porosity	0.444



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



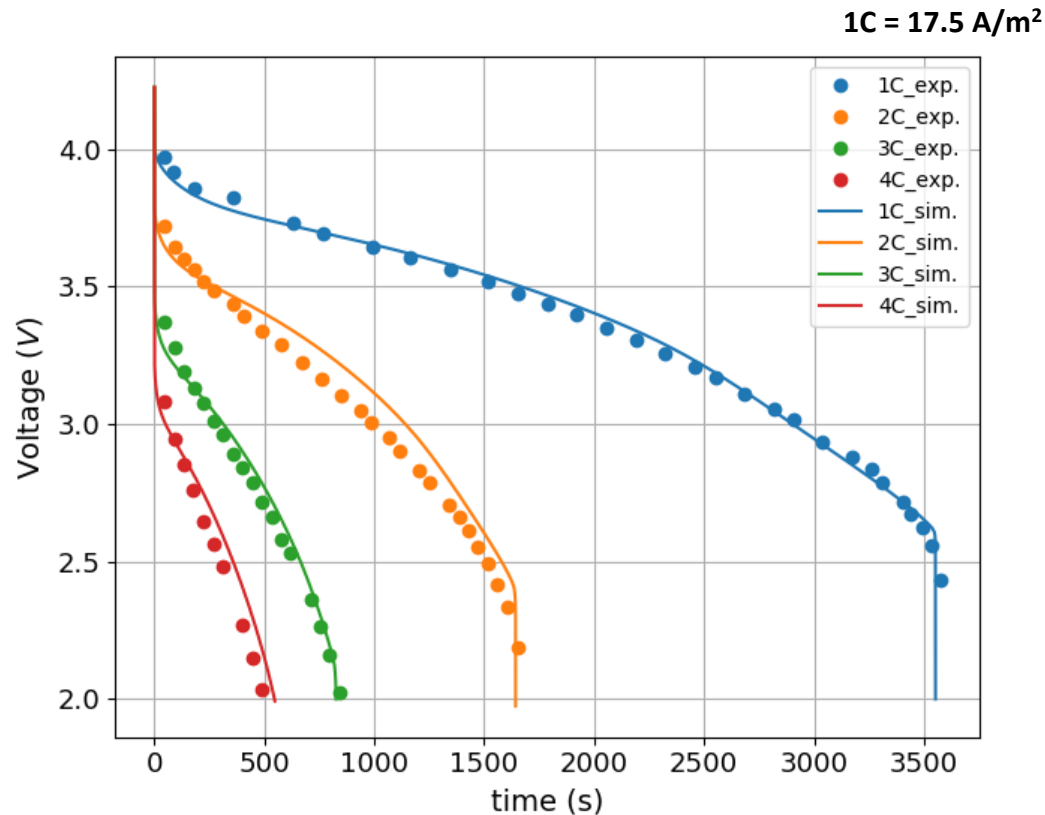
$$U_+(y) = 4.1983 + 0.056566 * \tanh(-14.5546 * y + 8.60942) - 0.0275479 * ((1.0 - y)^{-0.492465} - 1.90) - 0.157123 * \exp(-0.04738 * y^8) + 0.810239 * \exp(-40 * (y - 0.133875))$$

*Kinetic, thermodynamic and transport parameters*

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

	Description	Formula
<i>Calculated parameters</i>		
$a^{a,c}$	Specific area of the electrodes (m <sup>2</sup> /m <sup>3</sup> )	$3 \frac{\varepsilon_s}{R_p}$
$\varepsilon_s^a$	Volume fraction of the solid phase in the anode	$1 - \varepsilon^a - 0.172$
$\varepsilon_s^c$	Volume fraction of the solid phase in the cathode	$1 - \varepsilon^c - 0.259$

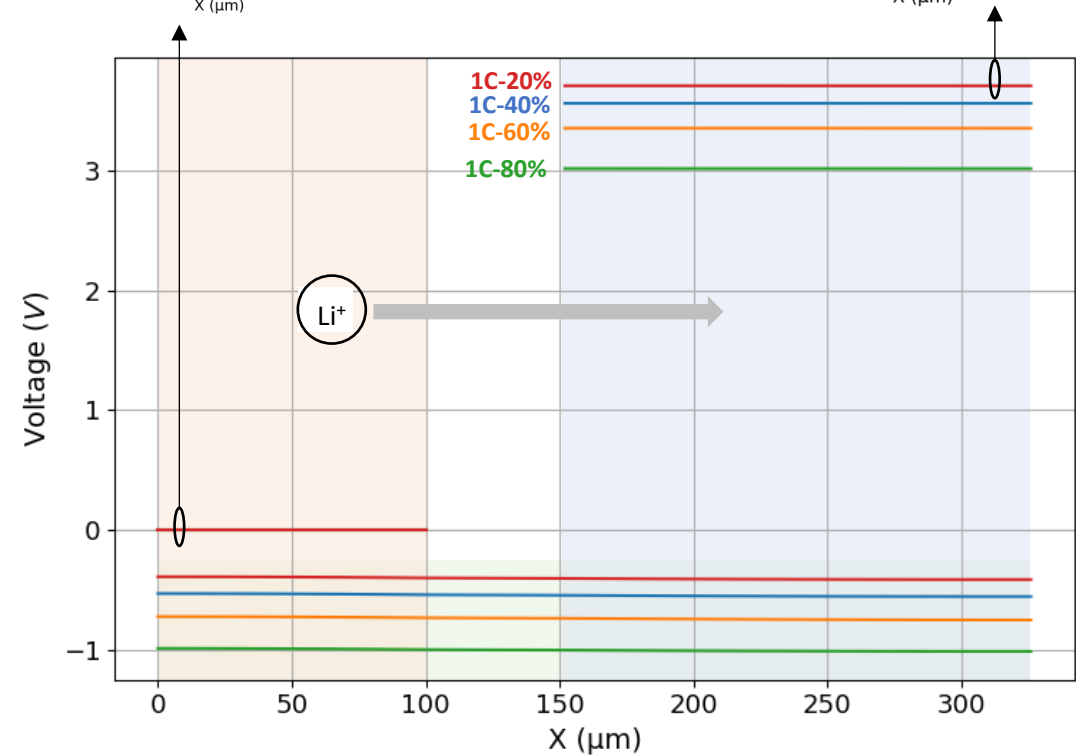
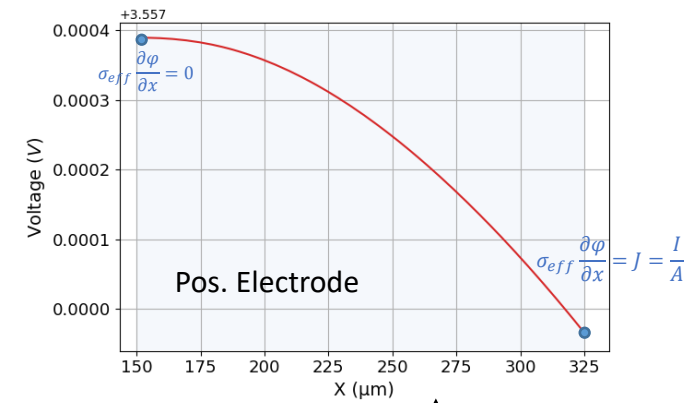
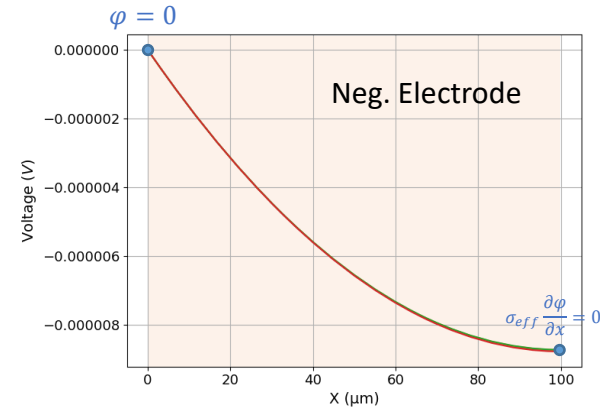
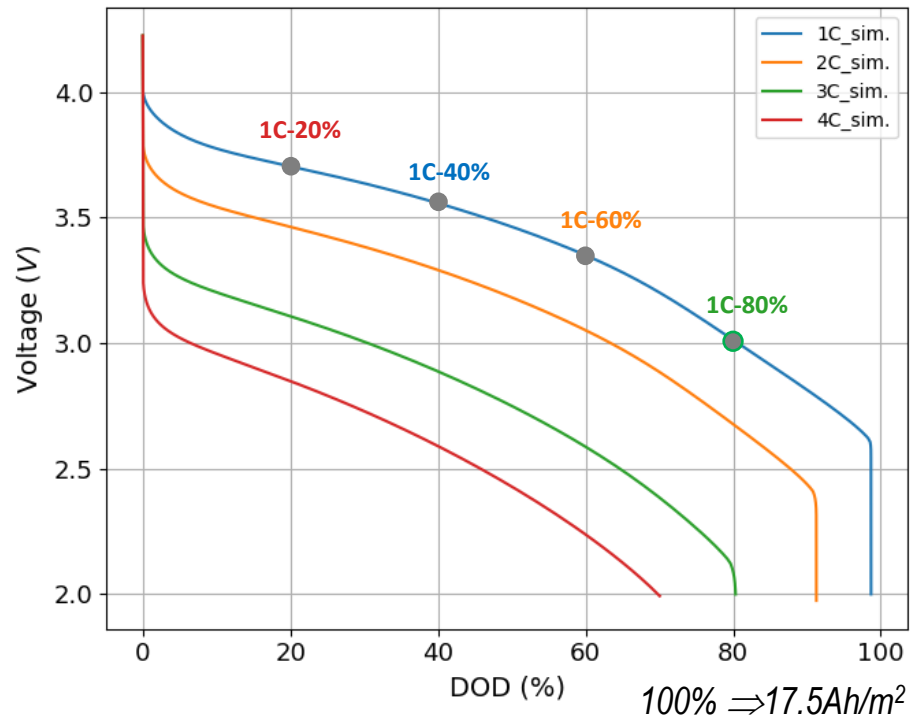
# Comparison Simulation Results with Experiments



Simulating conducted with this model shows a close agreement with test data Doyle & Newman got from Li-Mn<sub>2</sub>O<sub>4</sub> battery cell

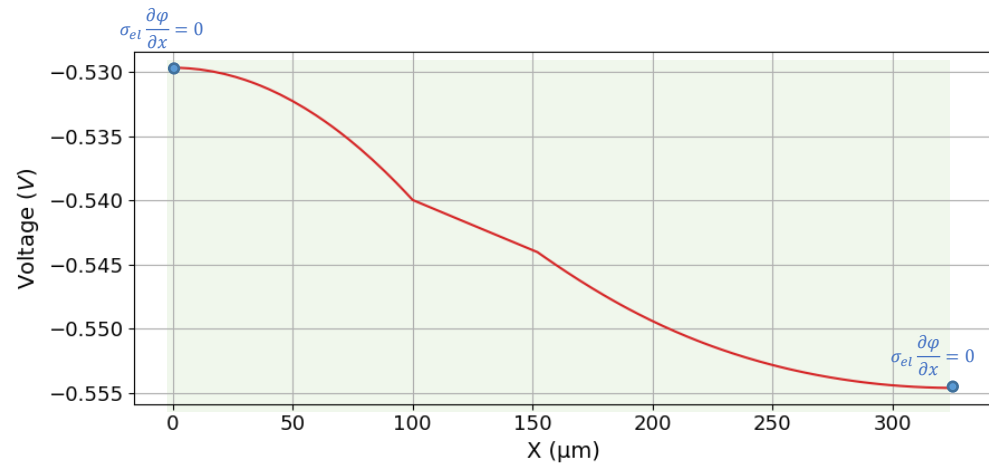
\* exp. data from Doyle, M., & Newman, J. (1996). Comparison of the modeling predictions with experimental data from plastic lithium ion cells. *Journal of the Electrochemical Society*, 143(6), 1890

# Potential Distribution in Discharging

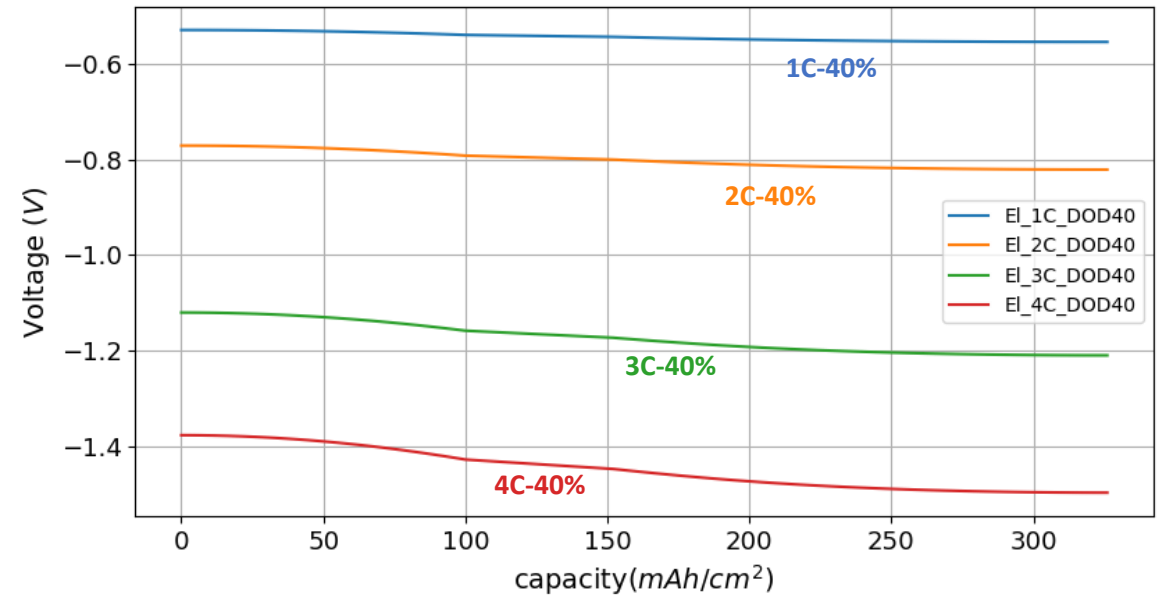


Potential evolution in the cell  
in discharging at 1C rate

# Potential Distribution in Electrolyte



1C discharging at DOD = 20%

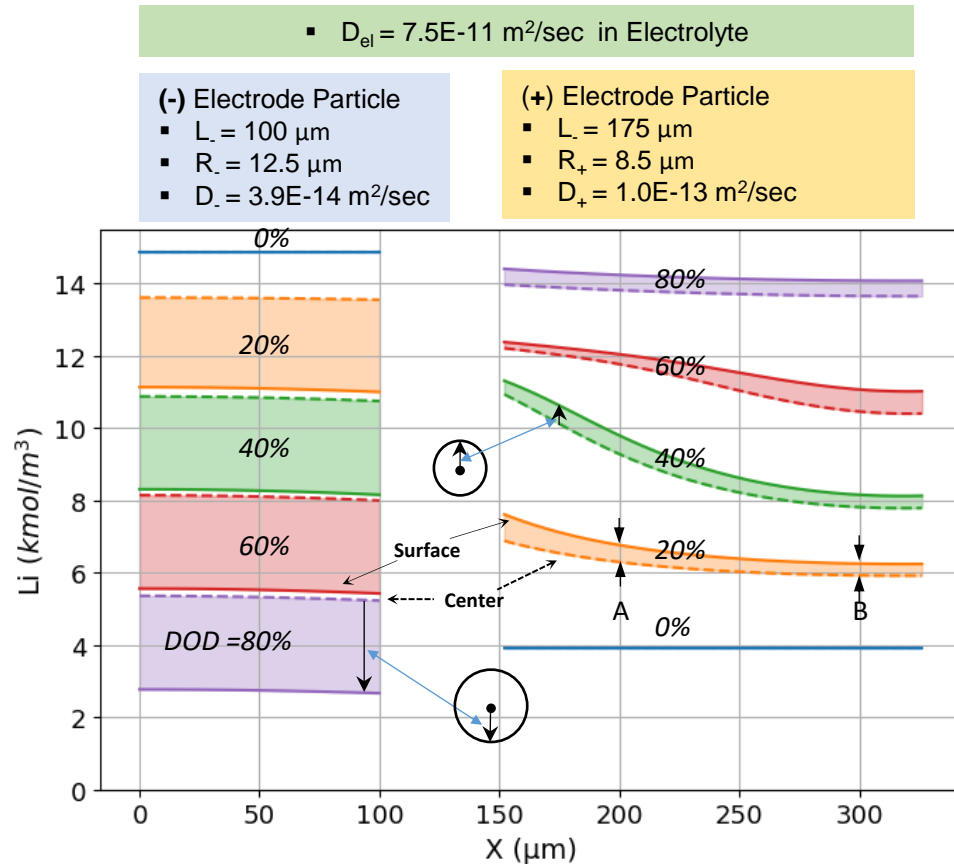


Potential distribution



# Li concentration distribution ( 1C discharging)

A



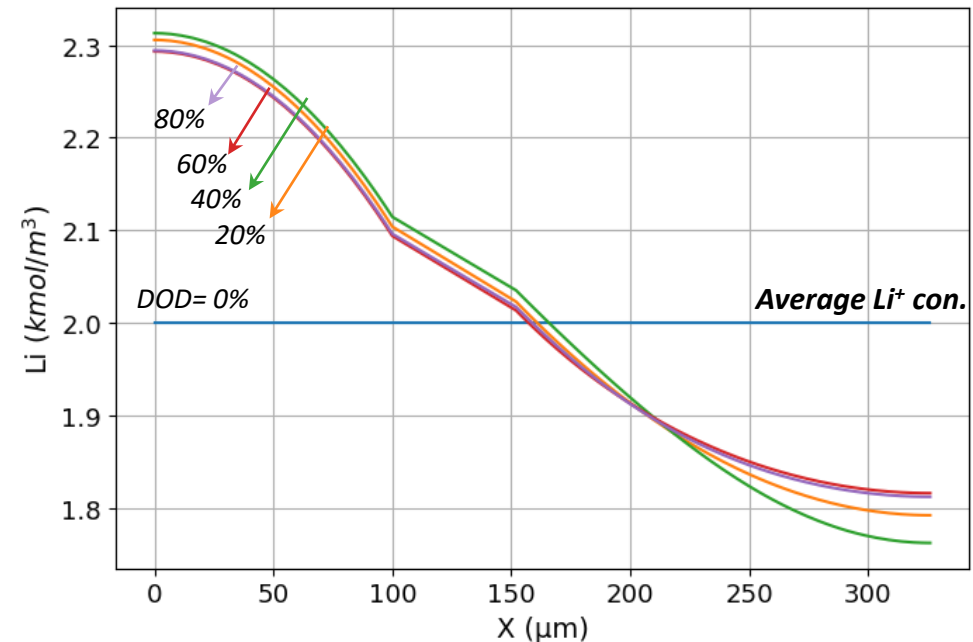
Li concentration distribution in Electrode Particles

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,  $2 \text{ kmol/m}^3$ .

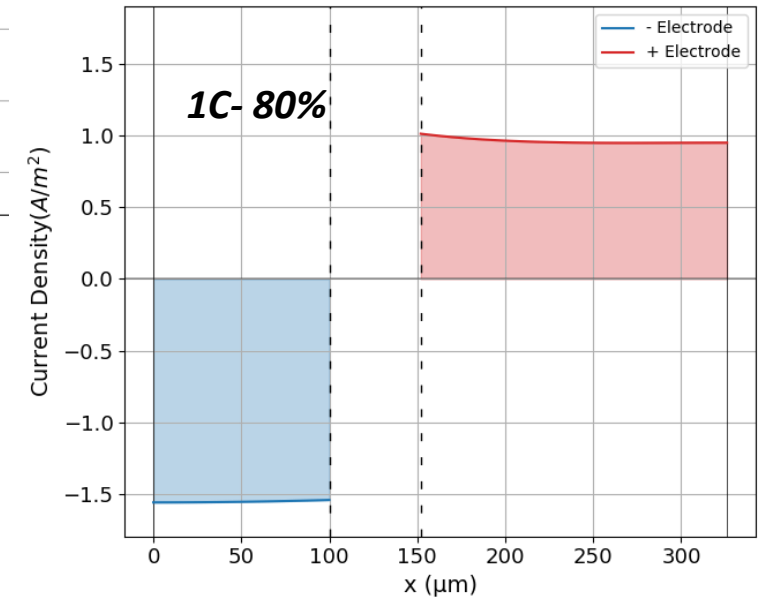
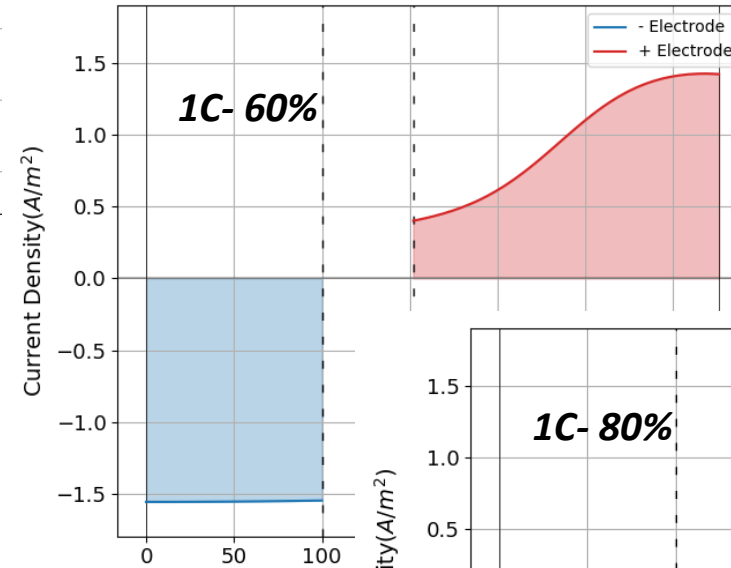
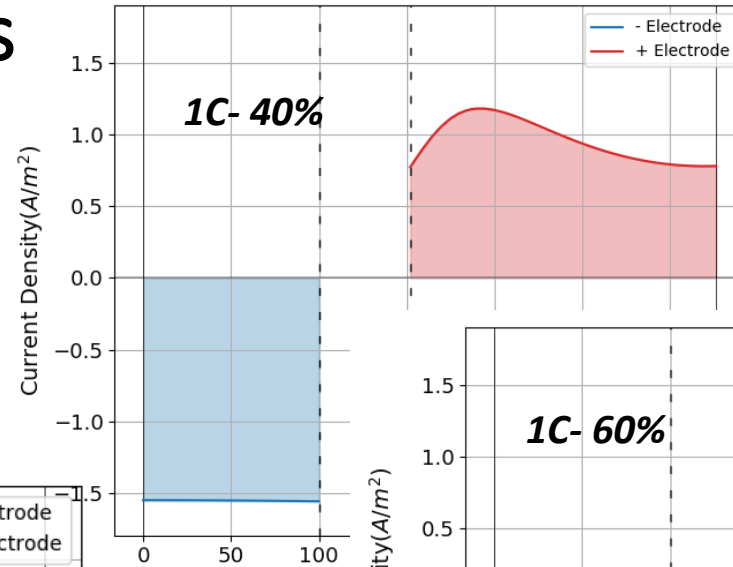
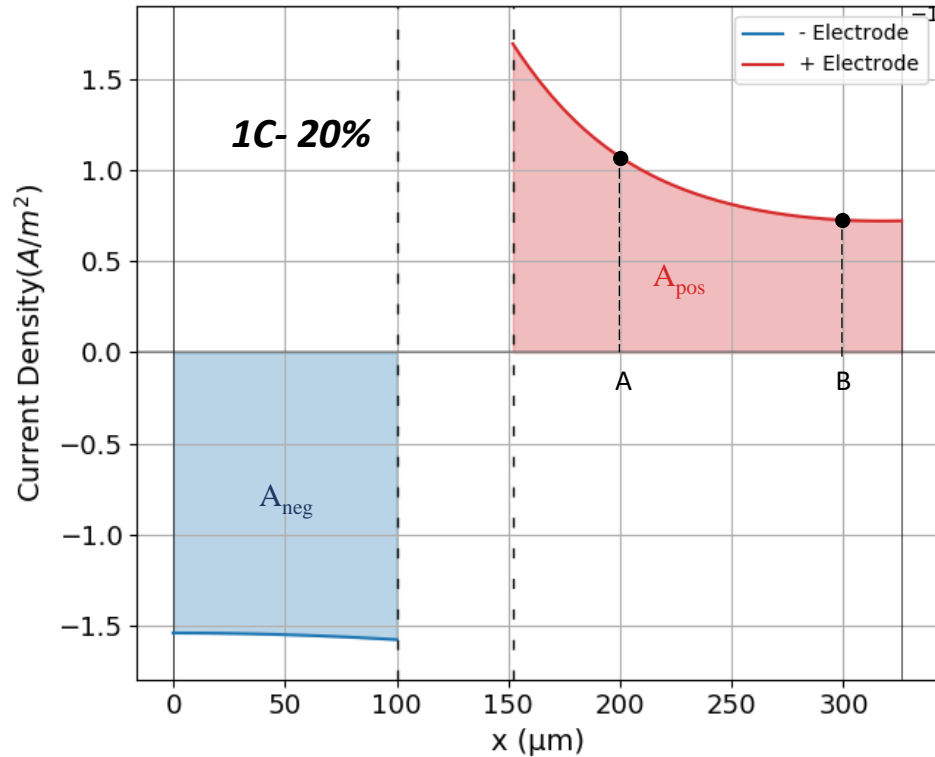


Li concentration in Electrolyte

# Electrochemical Reactions

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

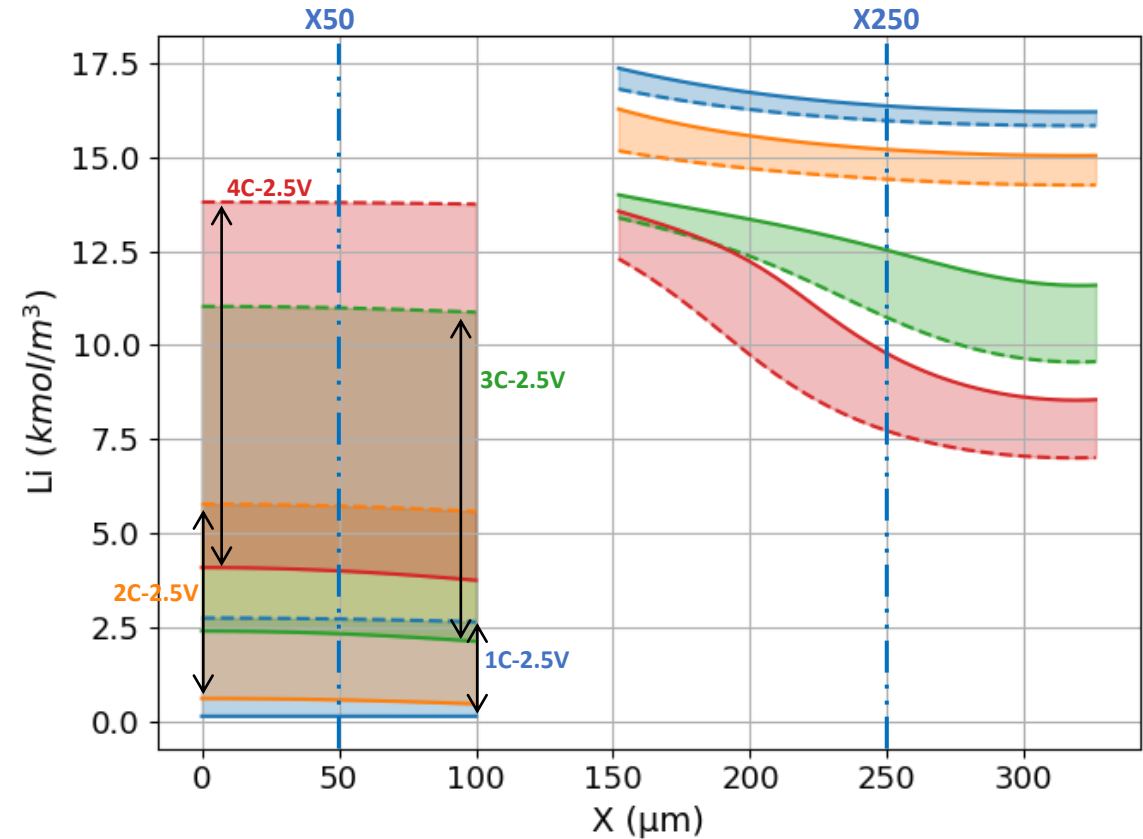
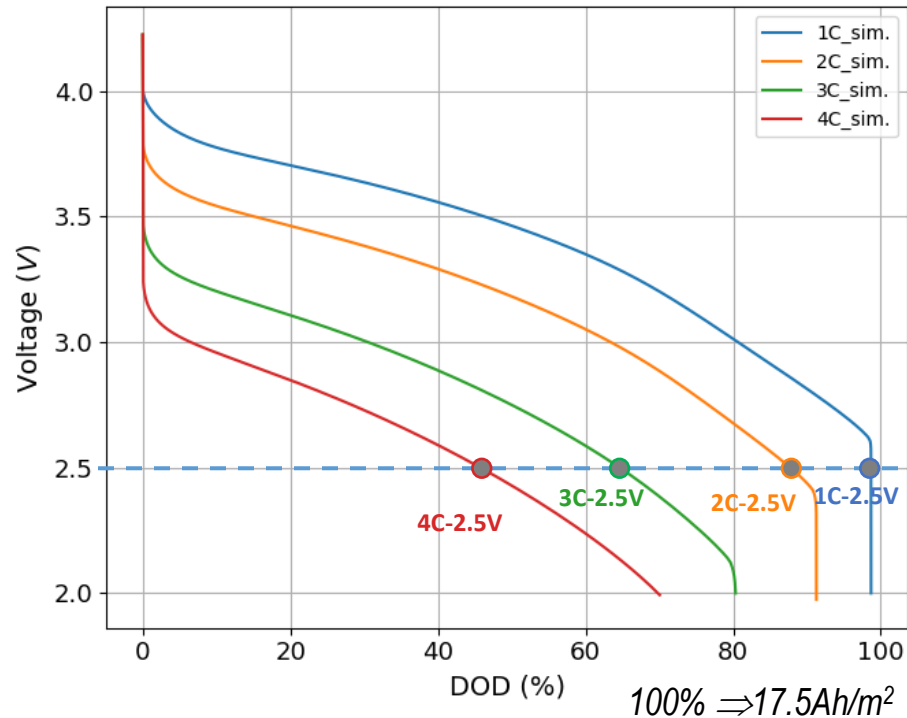
$$i_0 = k_0 \left( C_e (C_{s,max} - C_s) (C_s - C_{s,min}) \right)^{0.5}$$



## Conservation of Charge

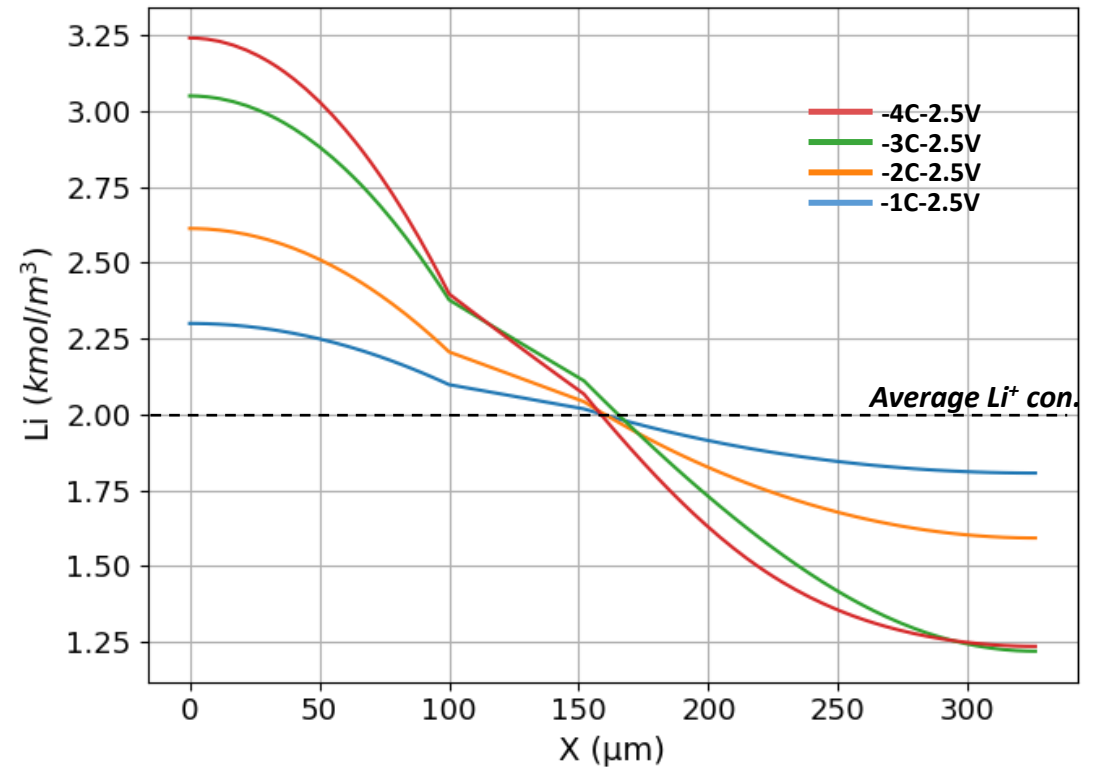
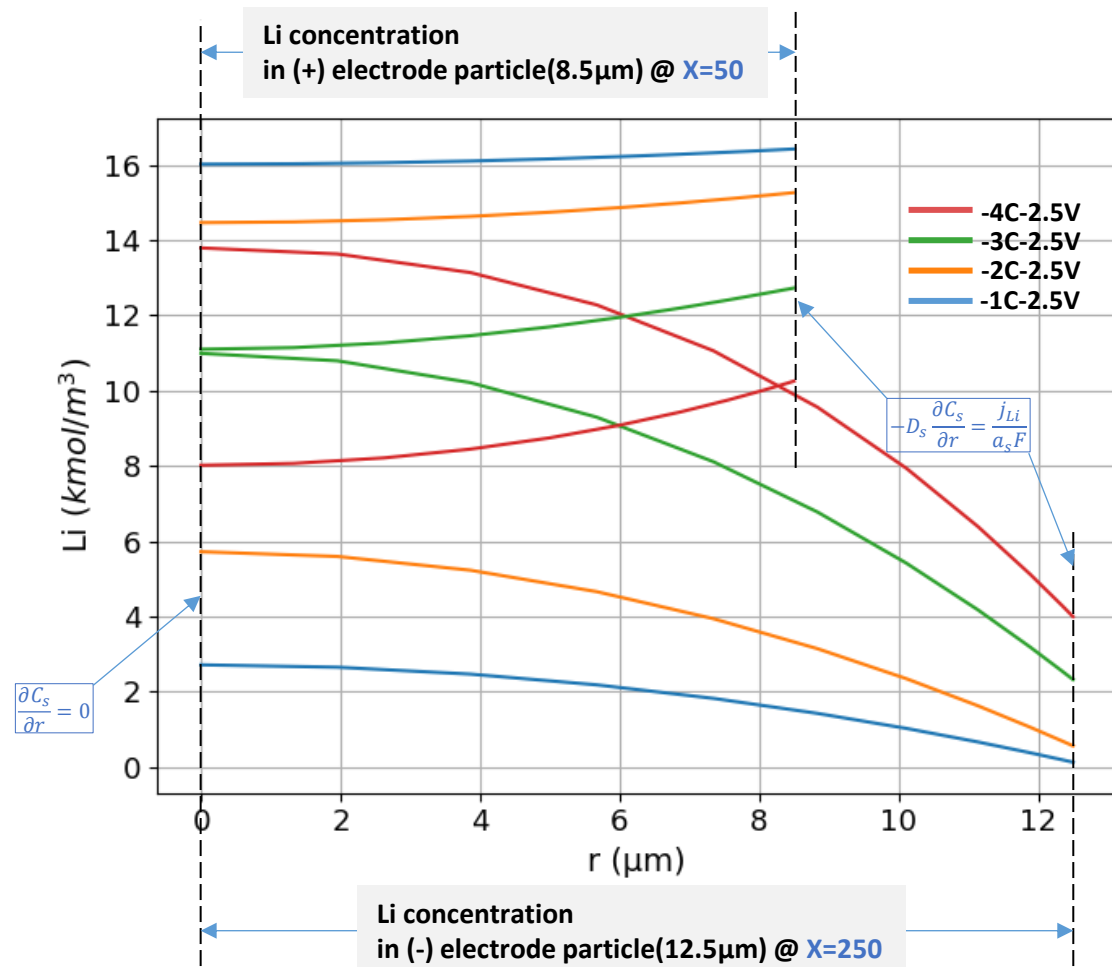
$$\frac{3(1 - \varepsilon_-)}{R_-} A_{neg} = \frac{3(1 - \varepsilon_+)}{R_+} A_{pos} = J$$

# Li<sup>+</sup> 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 ( $C_{\text{sur}}$ ) has reached its minimum ( $\approx 0$ ) at surface. Due to depletion of Li<sup>+</sup>, electrochemical reaction is limited and cell output voltage drops quickly.
- As discharging get faster than 1C,  $C_{\text{sur}}$  is higher at  $V_{\text{out}}=2.5\text{V}$ . But voltage drop quickly by internal resistance.
- At higher discharging rate condition,  $C_{\text{Li}}$  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  $V_{out} = 2.5V$

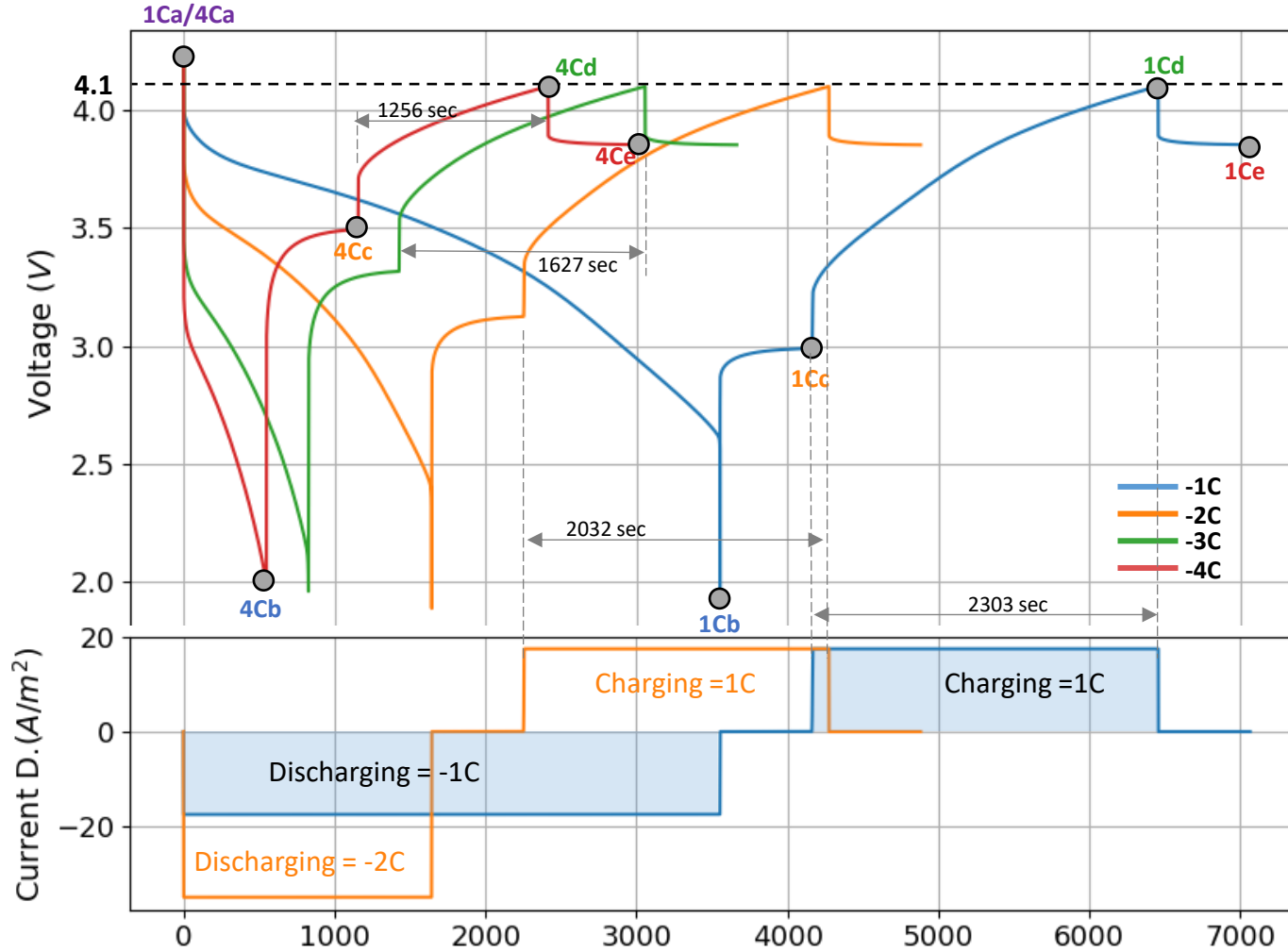
Left figure shows the Li ion concentration in (+)/(-) particle at x=50 and x=250 position

- 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,

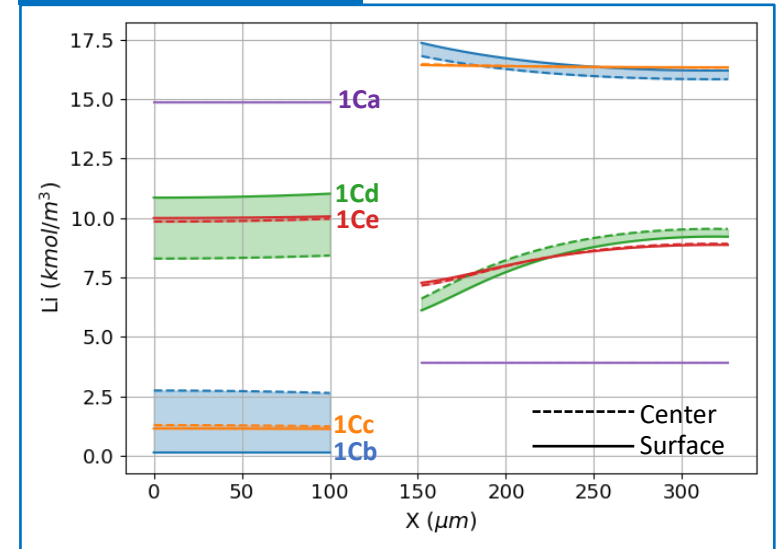
- As the discharging rate increases, more Li ion transfer through electrolyte from (-) to (+) electrode. And It causes the concentration gradient of Li ion to increase.
- However, the average concentration of Li ion is maintained at the initial concentration,  $2 \text{ kmol/m}^3$ .

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

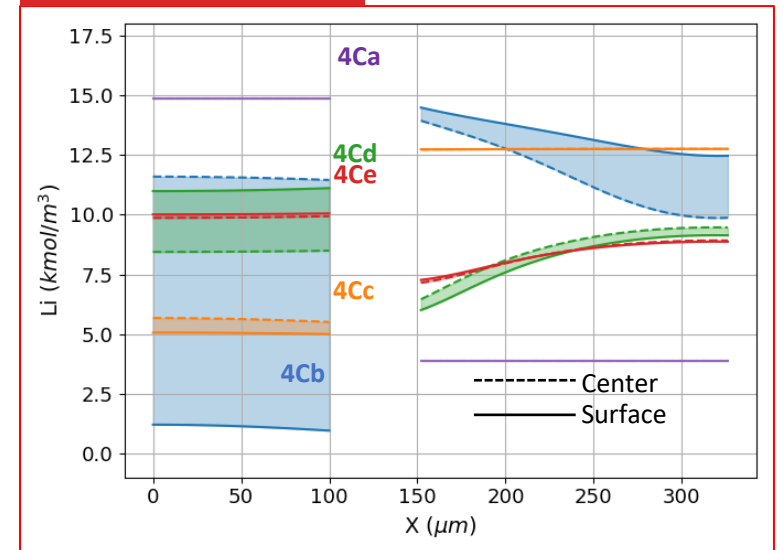


- During charging/discharging period, Li concentration distribution in the electrode particles widens as shown in the right figures.
- Its distribution range shrinks in the relaxation period.
- The expansion/shrinkage gets enhanced by increasing discharging rate from 1C to 4C.
- At higher discharging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

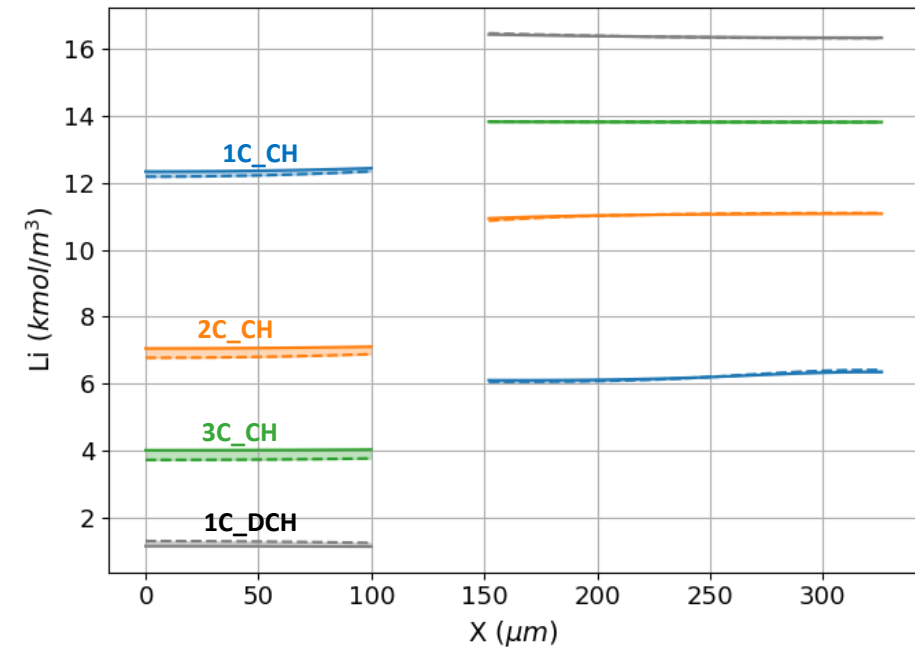
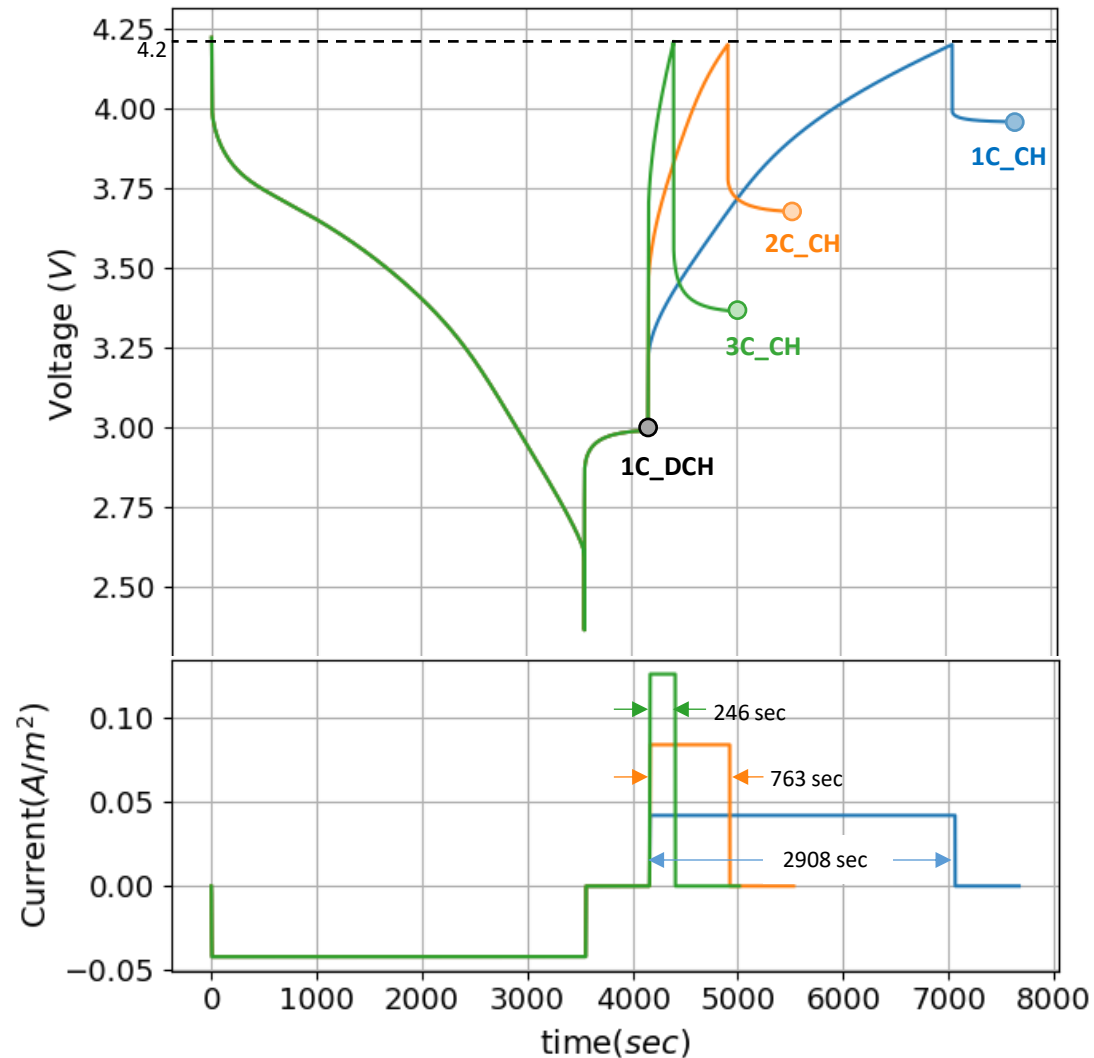
## Discharging = -1C



## Discharging = -4C

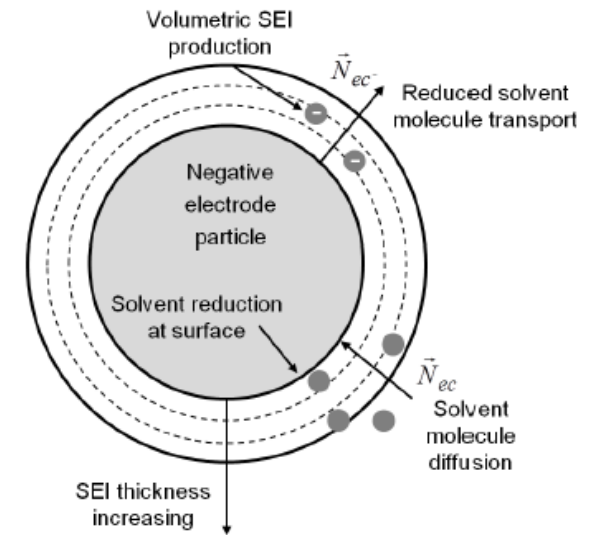
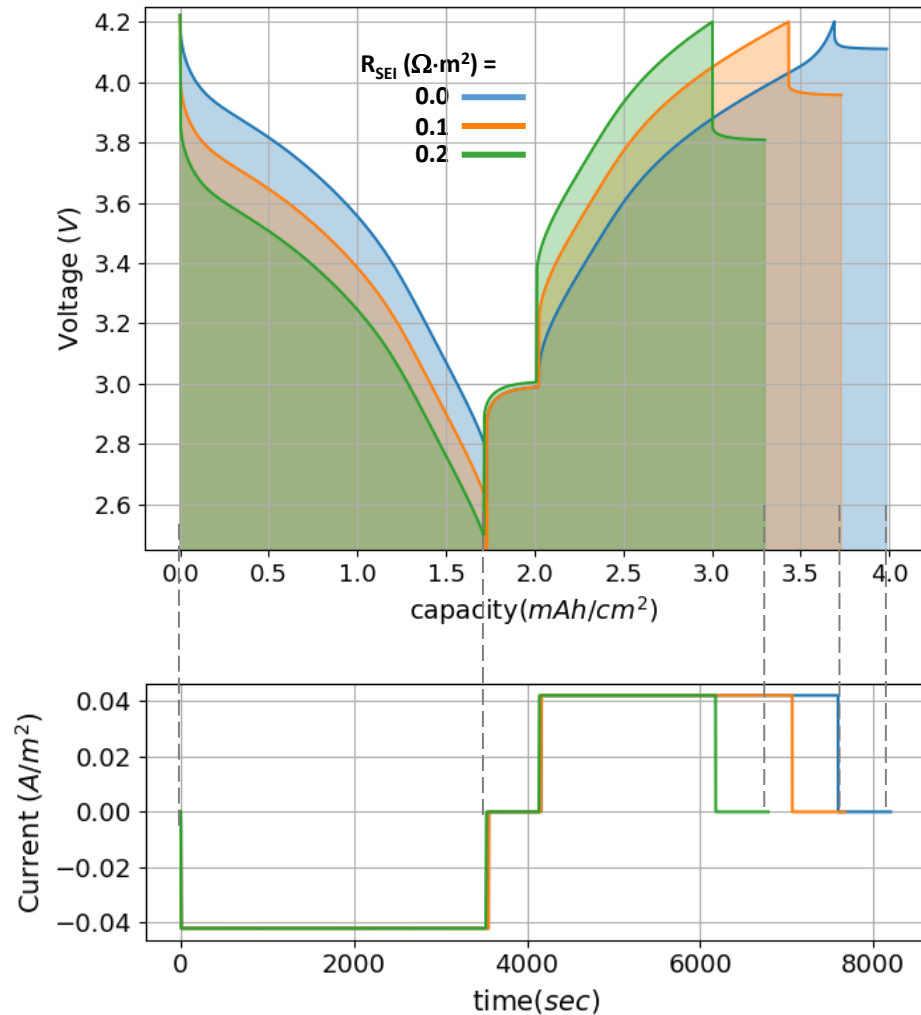


# Discharging (1C) + Charging (1/2/3C)



- 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