

# **Li- ion modeling**

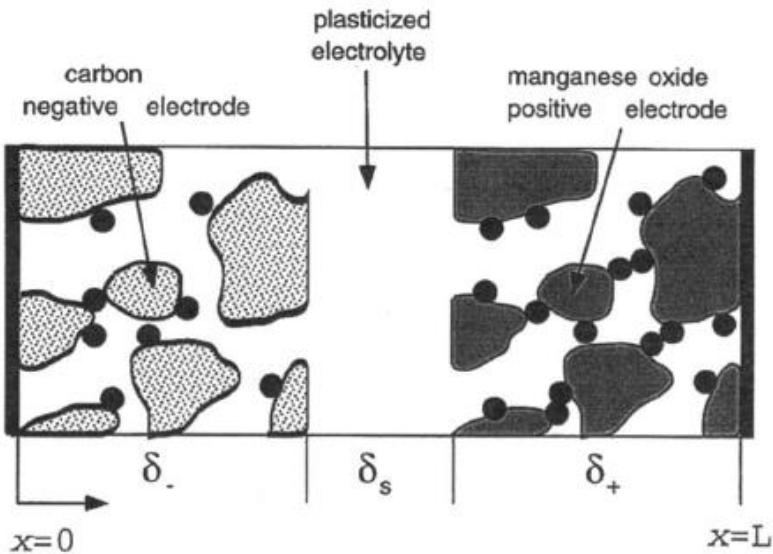
## **physics-based**

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)

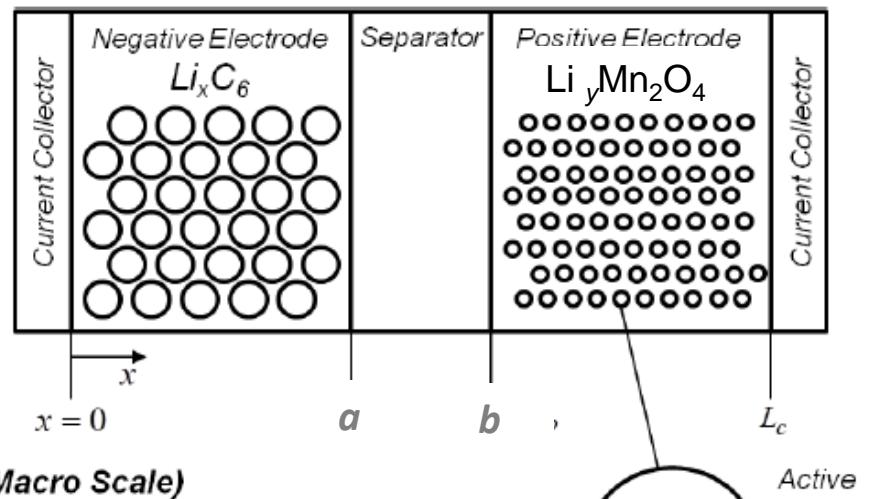
- Conservation of Charge

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

$$\varphi(x=0) = 0 V$$

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

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



- 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

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

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

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

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

### - Conservation of Mass

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

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

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

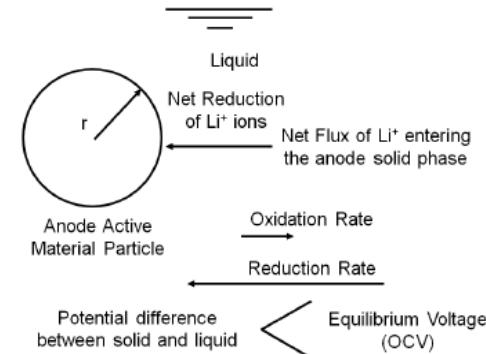
# Electrochemical Reaction

## Butler-Volmer Kinetic Equation

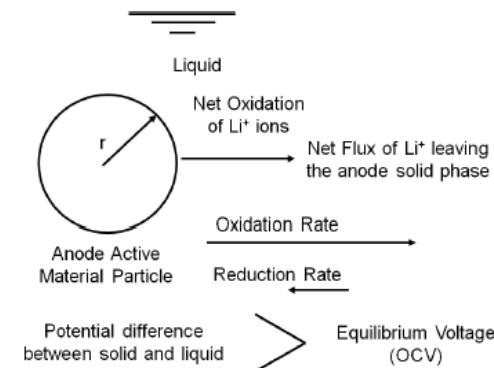
$$j_{Li} = a_s i_o \left[ \exp \left\{ \frac{\alpha_a F}{RT} \left( \eta - \frac{R_{SEI}}{a_s} j_{Li} \right) \right\} - \exp \left\{ - \frac{\alpha_c F}{RT} \left( \eta - \frac{R_{SEI}}{a_s} j_{Li} \right) \right\} \right]$$

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

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



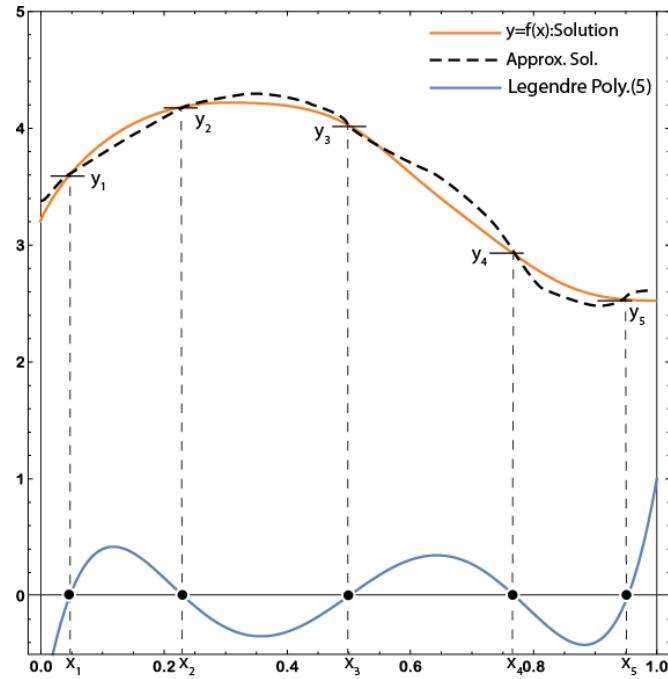
(a) Charging



(a) Discharging

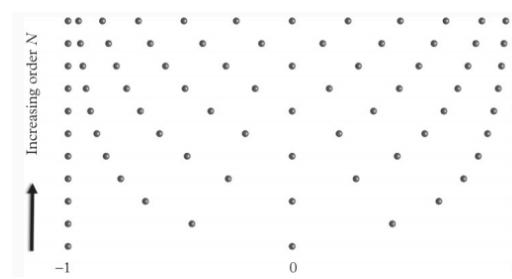
# Spectral Element Method (SEM)

- 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<sup>th</sup> order Legendre Polynomials
- More densely placed at boundary
- Avoid overshooting at boundary
- Boundary Condition considered accurately



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

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

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

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

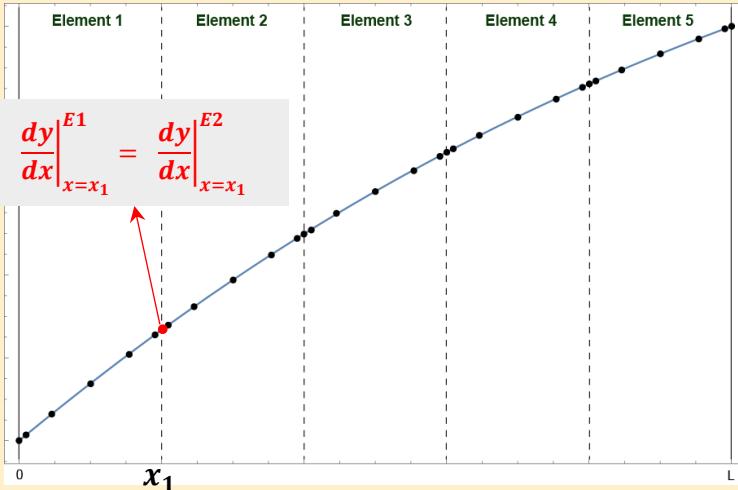
$$y''(x) = \sum_i y''_i \cdot I_i^N(x) \quad y''_j = y''(x_j) = \sum_i y_i \cdot \frac{d^2}{dx^2} I_i^N(x) \Big|_{x=x_j} = D^2 Y$$

## Differential Equation $\Rightarrow$ Algebraic Equation

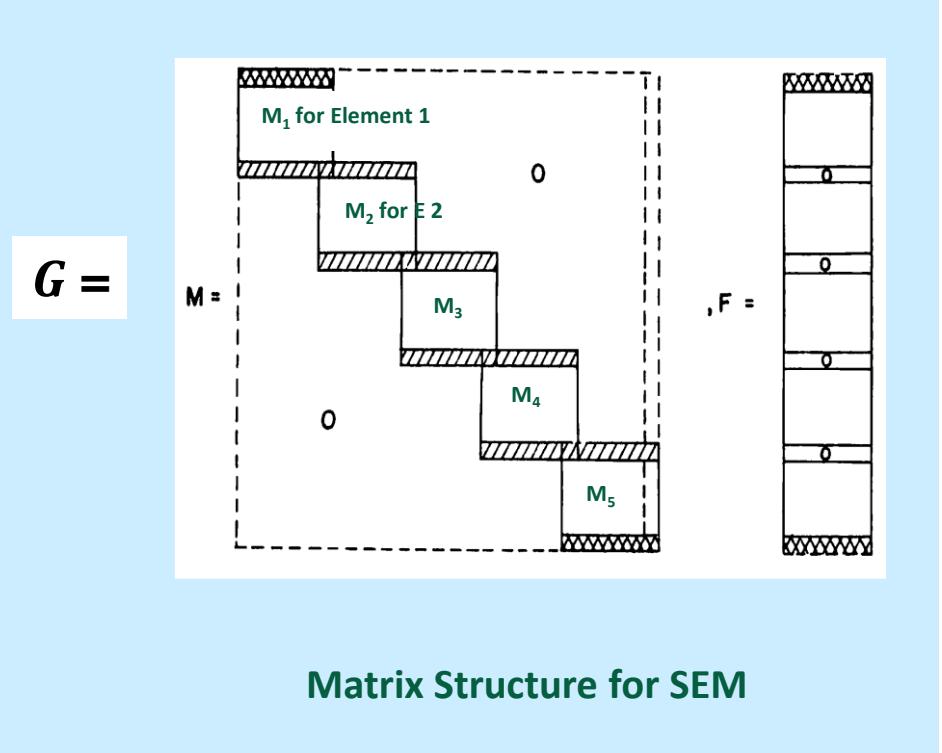
$$\alpha \frac{d^2y}{dx^2} + \beta \frac{dy}{dx} + \gamma y = (\alpha D^2 + \beta D + \gamma I) Y \Rightarrow M Y$$

# 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



# Solving the system of Non-linear Algebraic Equations

Linear Differential Equations

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

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

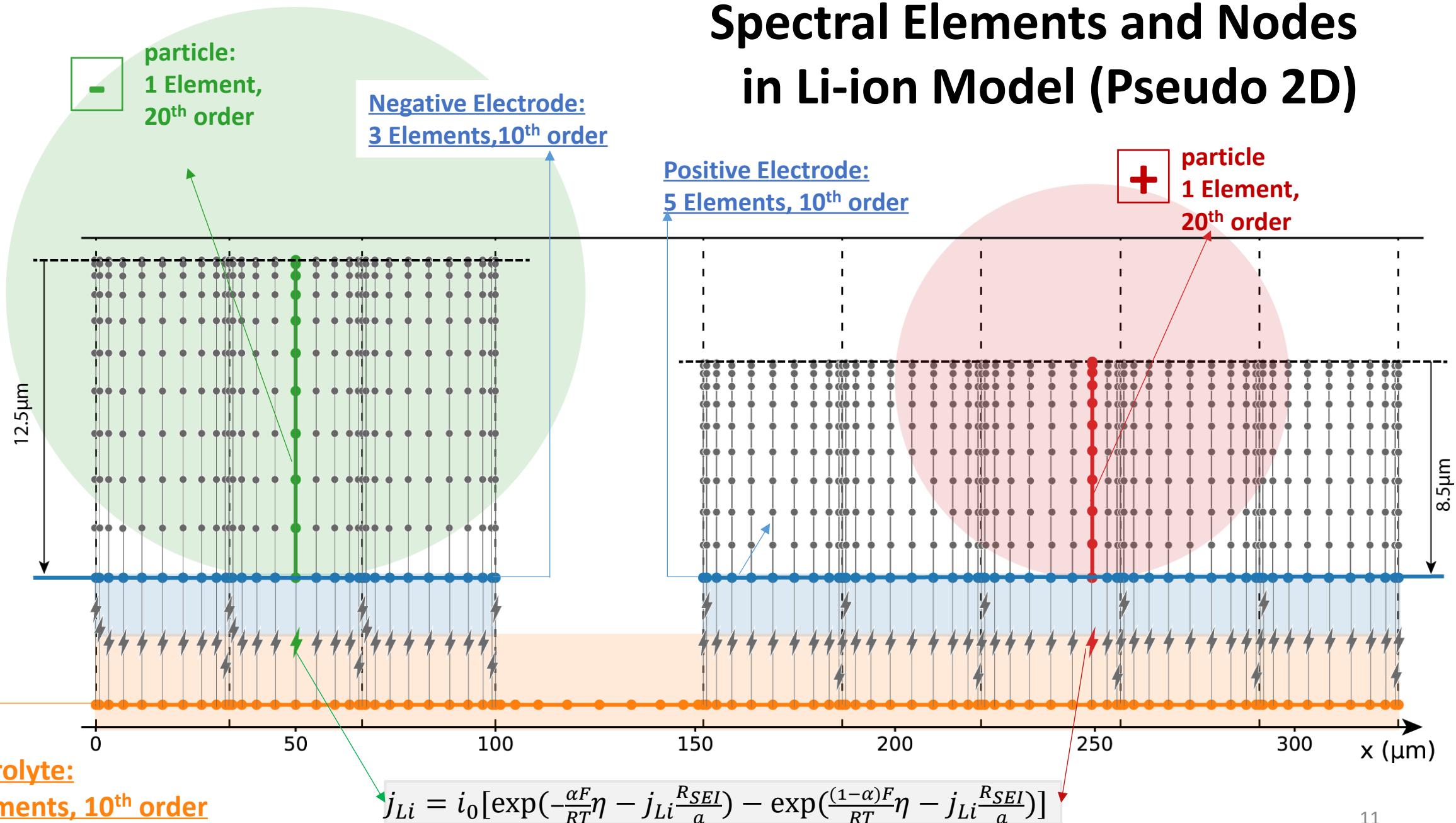
Non-Linear Differential Equations

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

`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)

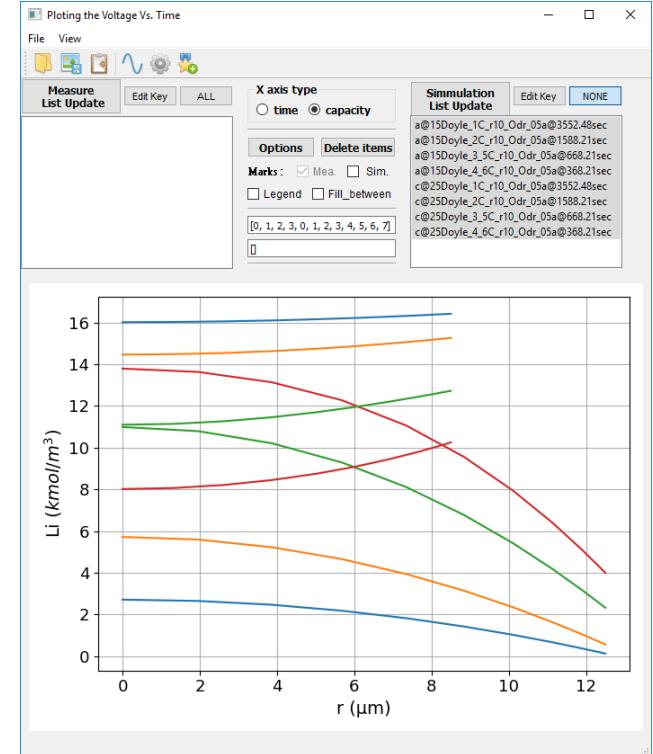
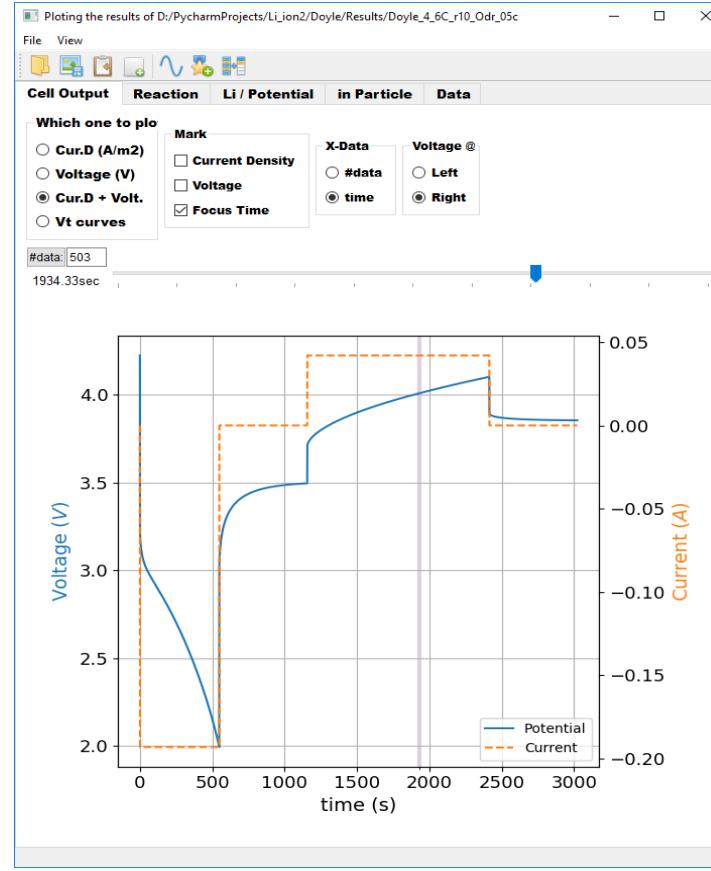
The screenshot shows the Visual Studio Code interface with several tabs open. The main tab contains Python code for a Li-ion battery simulation, specifically for a Doyle cell. The code includes logic for initializing stages, calculating current density, and managing discharge cycles. The terminal tab shows the execution of the script, displaying simulation output like step times and current values.

```
File Edit Selection View Go Run Terminal Help
Lion_V19_cycle.py - Doyle - Visual Studio Code
Lion_V19_cycle.py > Lion_V18.py Doyle_4_6C_r10_Odr_05a.py Doyle_4C_r10_Odr_05a.py Doyle_5C_r ...
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:
```

OUTPUT DEBUG CONSOLE PROBLEMS TERMINAL

```
3: Python
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

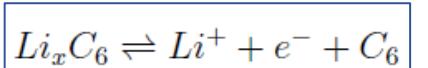


# Properties and Parameters

- 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 μm
$\delta_c$	Cathode width	174 μm
$\delta_s$	Separator width	52 μm
$\varepsilon_a$	Anode porosity	0.357
$\varepsilon_c$	Cathode porosity	0.444



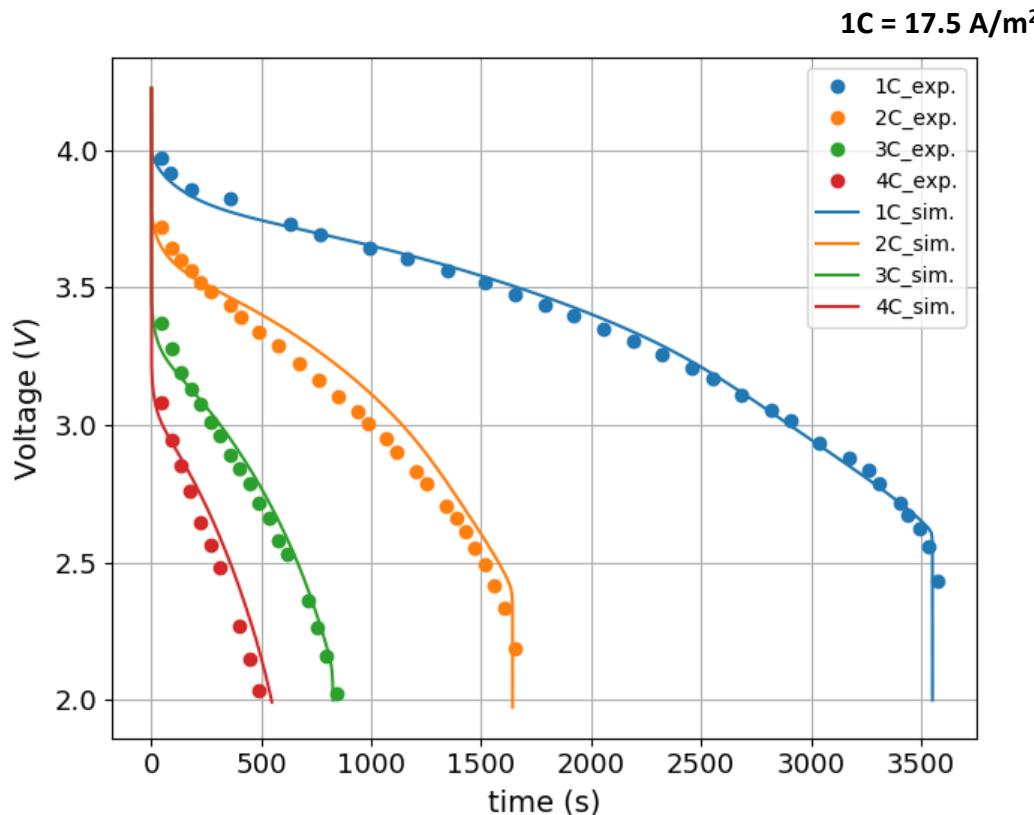
$$U_-(x) = -0.16 + 1.32 * np.exp(-3.0 * x) + 10.0 * np.exp(-2000.0 * x)$$



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

<i>Kinetic, thermodynamic and transport parameters</i>		
$C_T^a$	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 μm
$R_p^c$	Radius of the active material sphere in the cathode	8.5 μm
$t_+^o$	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>
<i>Description</i>		<i>Formula</i>
<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	$1 - \varepsilon^c - 0.259$

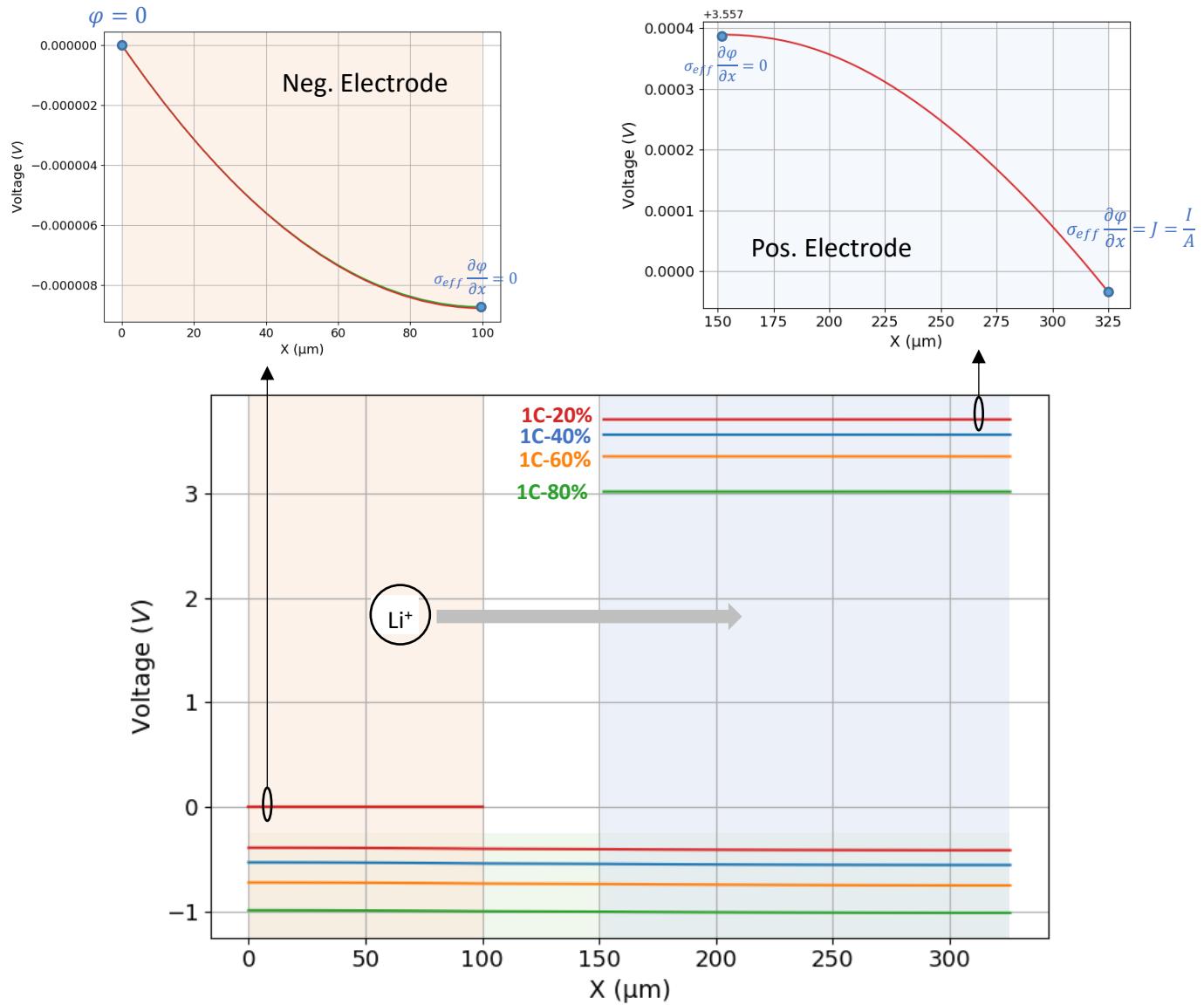
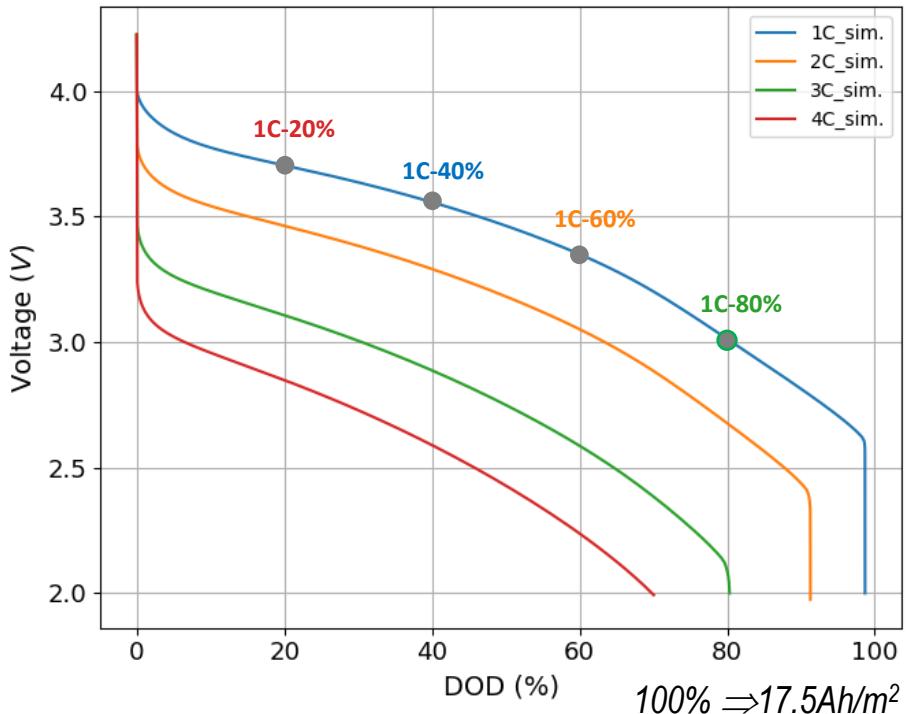
# Comparison Simulation Results with Experiments



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

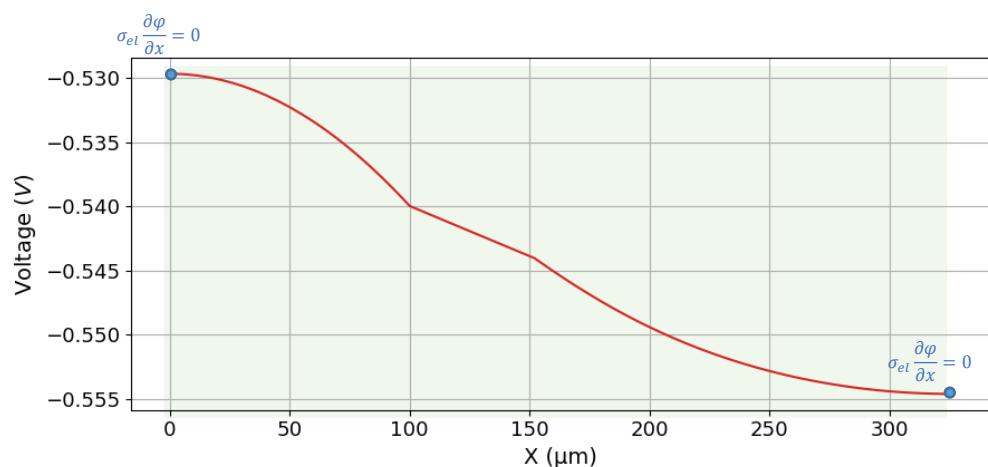
\* exp. data from Doyle, M., & Newman, J. (1996). Comparison of the modeling predictions with experimental data from plastic lithium ion cells. *Journal of the Electrochemical Society*, 143(6), 1890

# Potential Distribution in Discharging

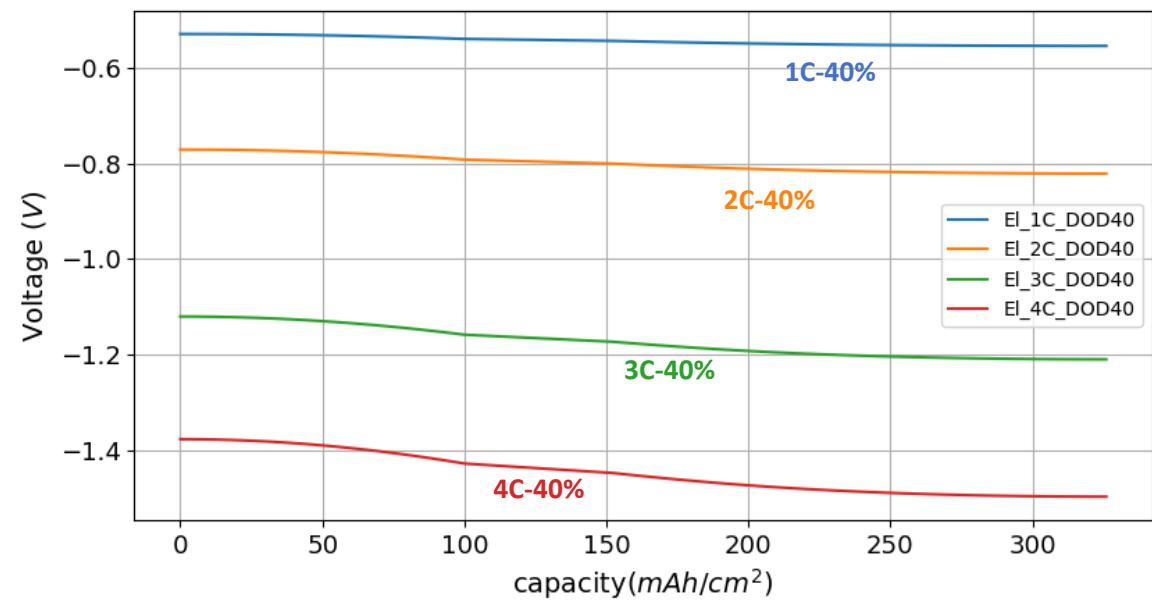


Potential evolution in the cell  
in discharging at 1C rate

# Potential Distribution in Electrolyte



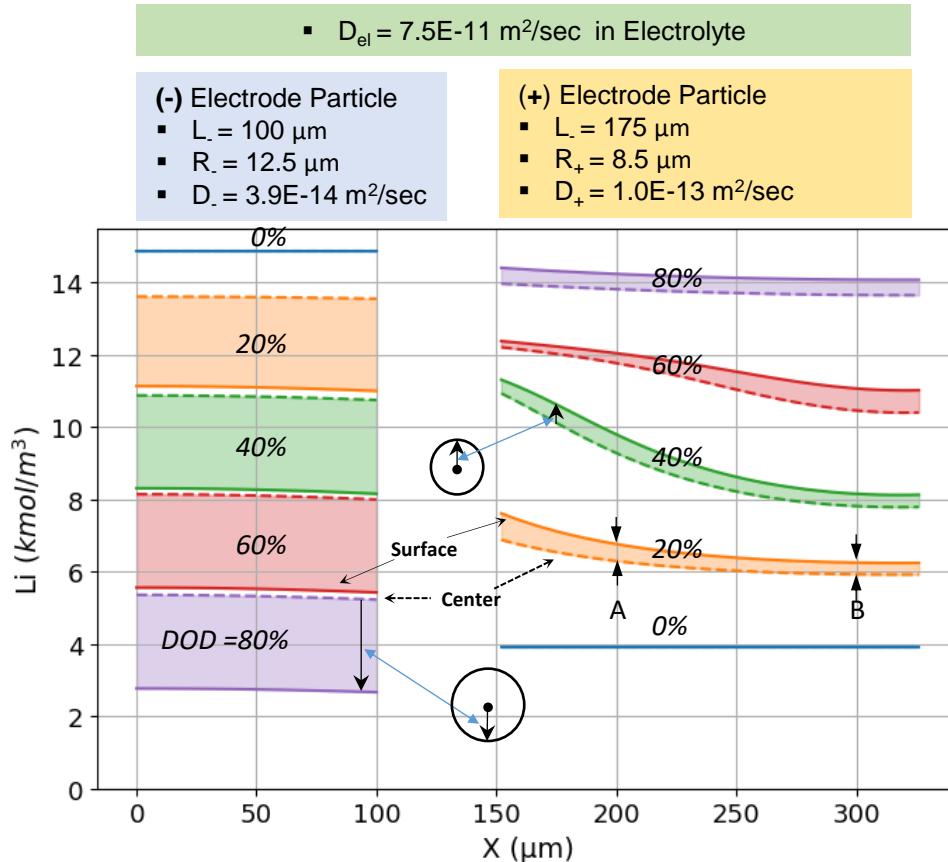
1C discharging at DOD = 20%



Potential distribution

# Li concentration distribution ( 1C discharging)

A



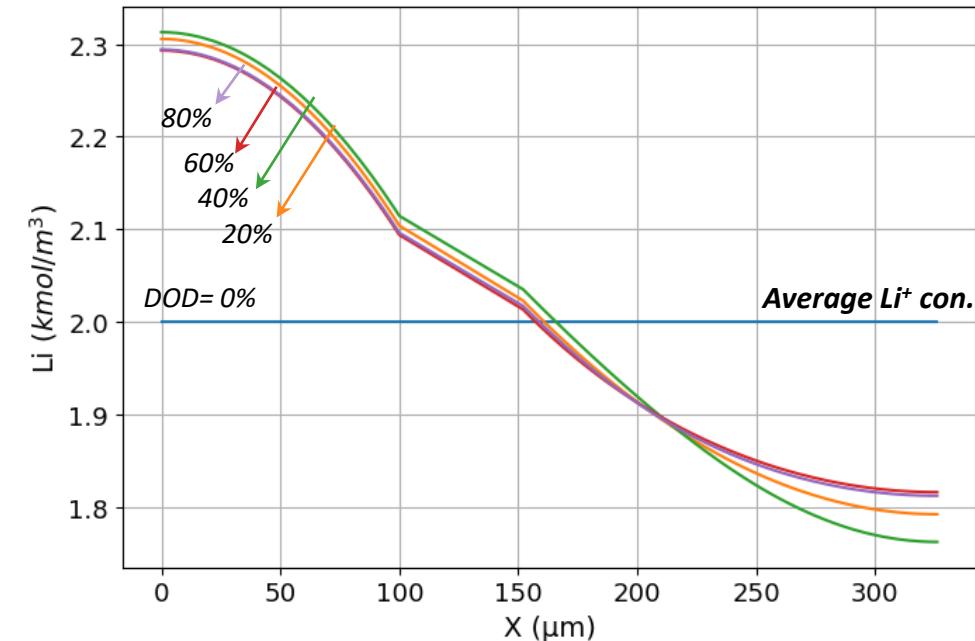
Li concentration distribution in Electrode Particles

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

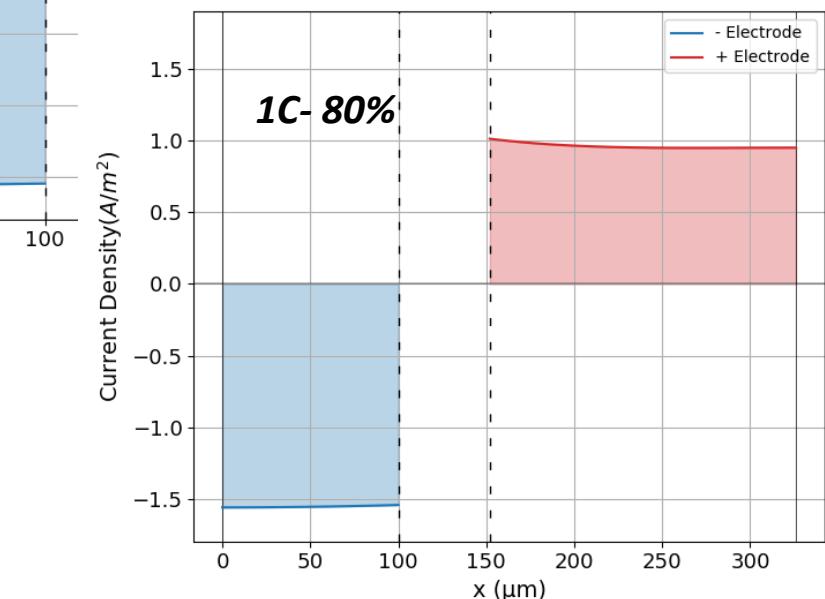
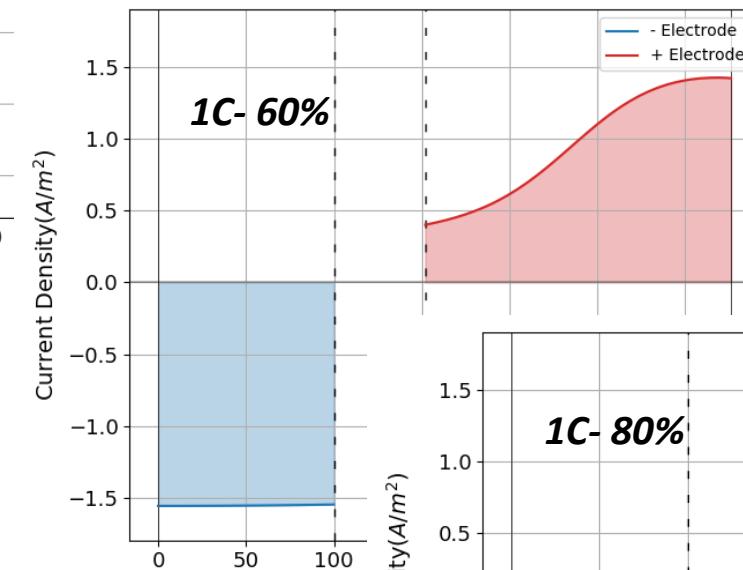
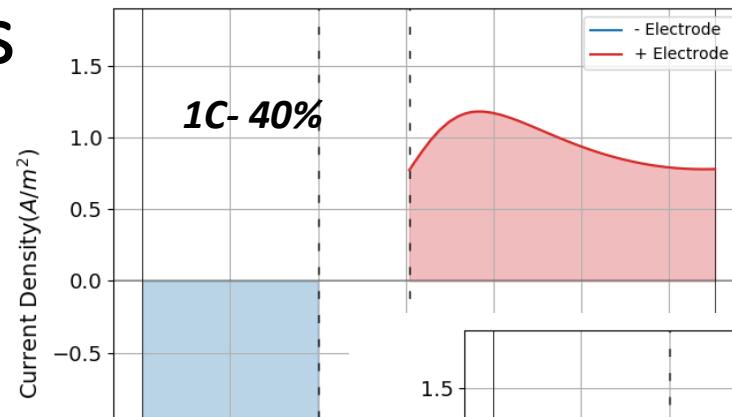
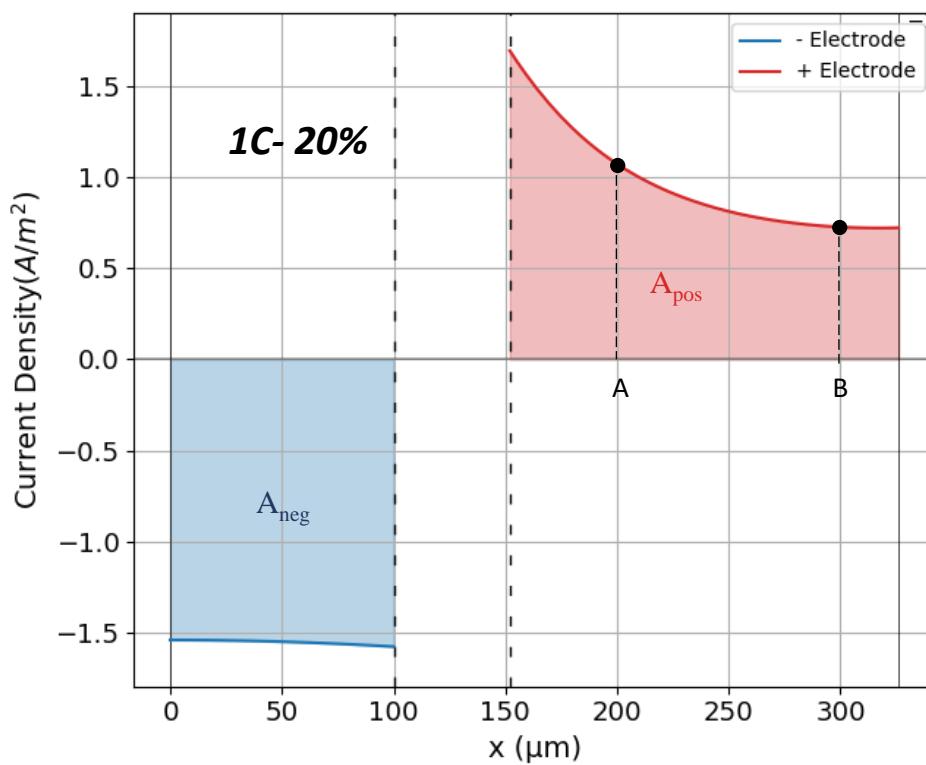


Li concentration in Electrolyte

# Electrochemical Reactions

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

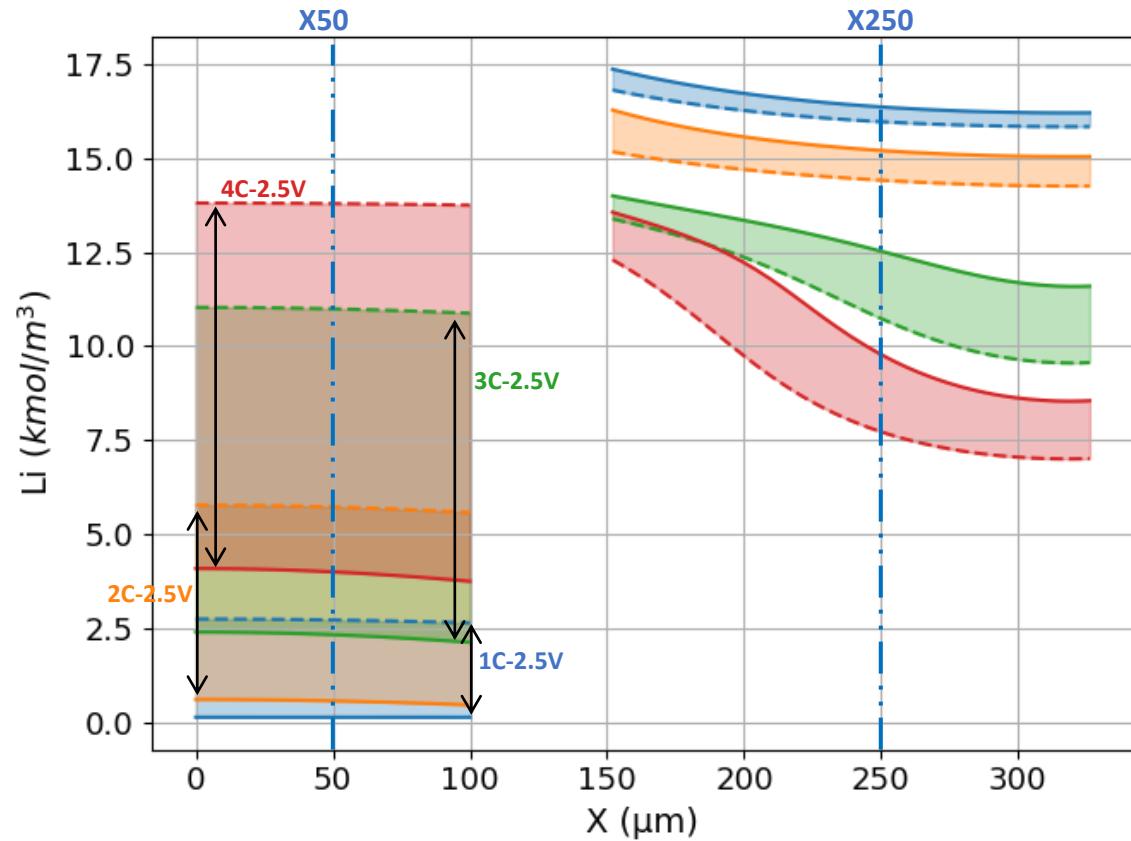
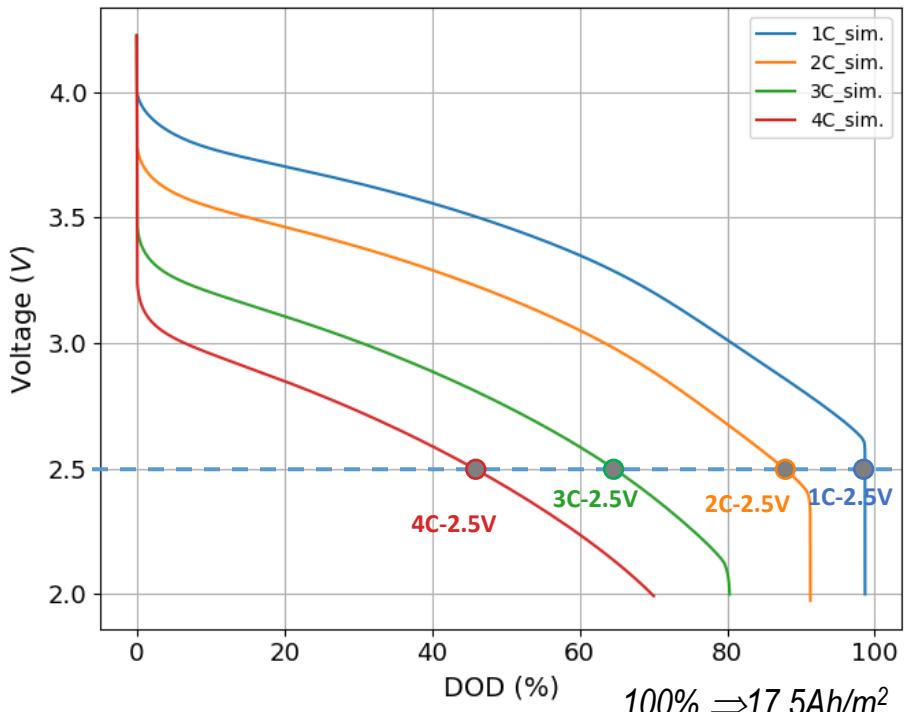
$$i_0 = k_0 (C_e (C_{s,max} - C_s) (C_s - C_{s,min}))^{0.5}$$



## Conservation of Charge

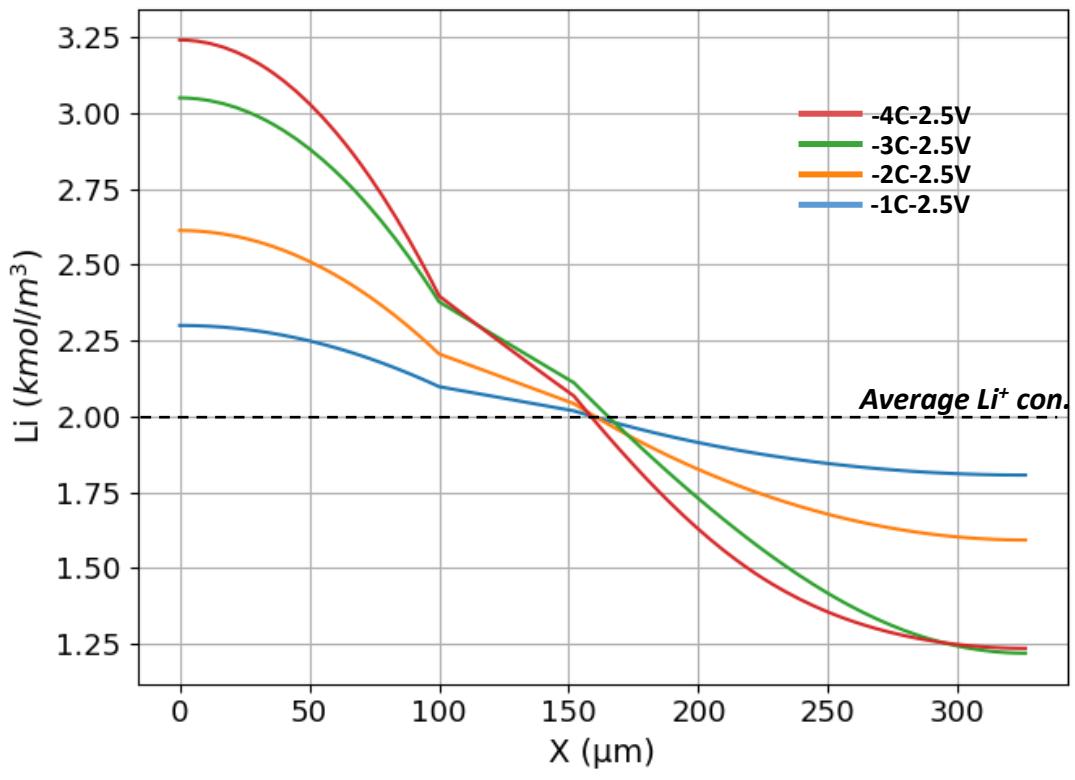
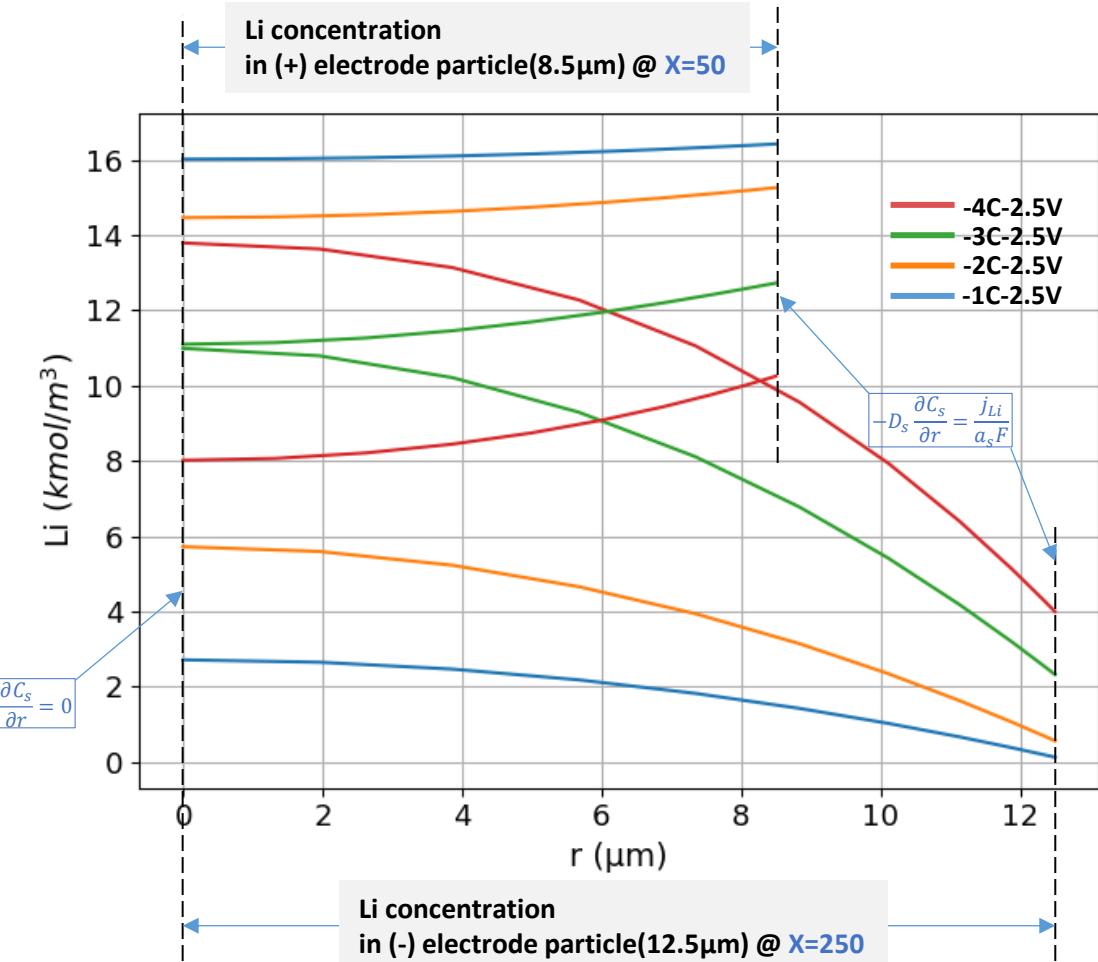
$$\frac{3(1 - \varepsilon_-)}{R_-} A_{neg} = \frac{3(1 - \varepsilon_+)}{R_+} A_{pos} = J$$

# $\text{Li}^+$ 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 ( $C_{\text{sur}}$ ) has reached its minimum( $\approx 0$ ) at surface. Due to depletion of  $\text{Li}^+$ , 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.



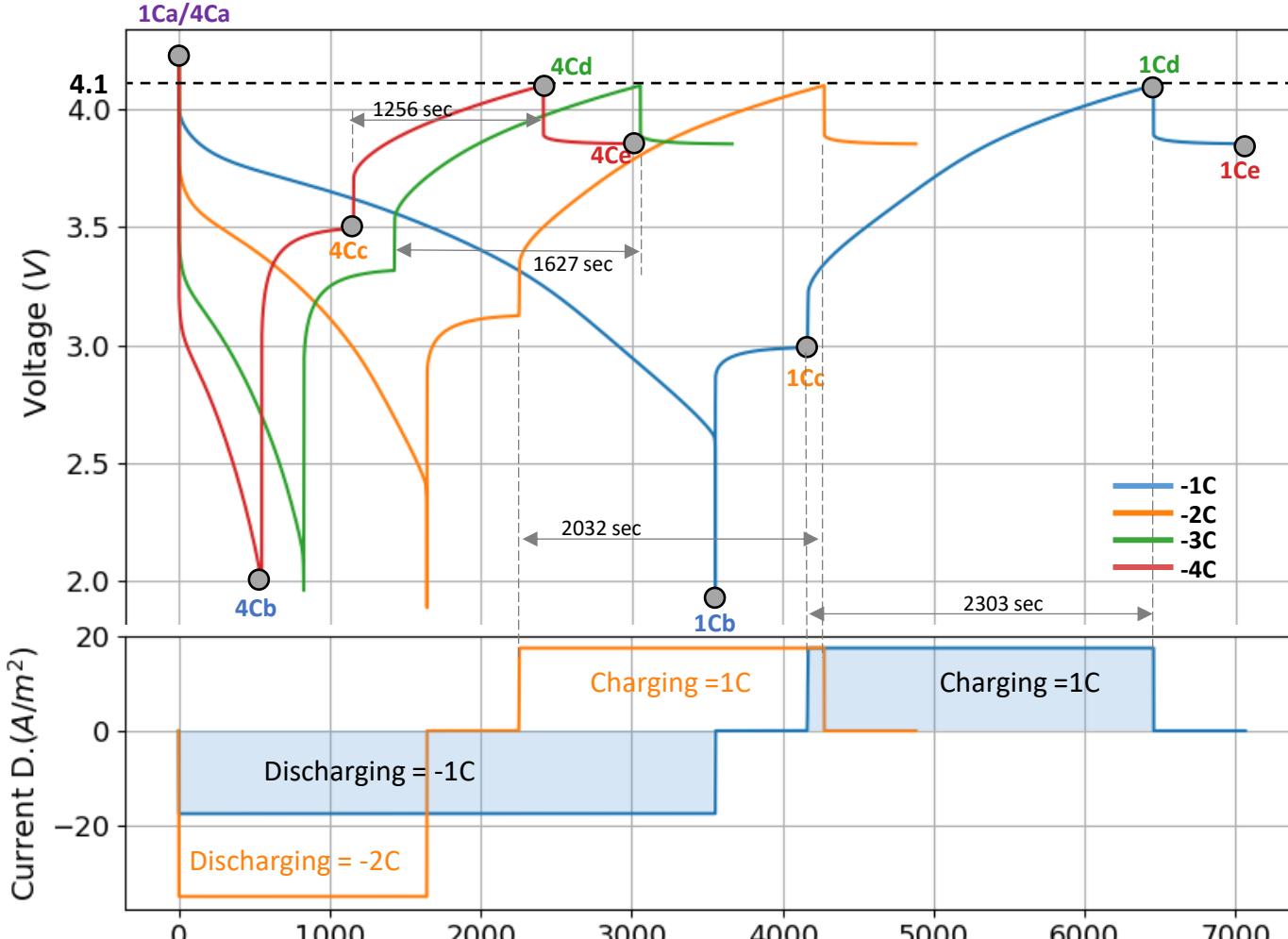
Left figure shows the Li ion concentration in (+)/(-) particle at x=50 and x=250 position

- 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,

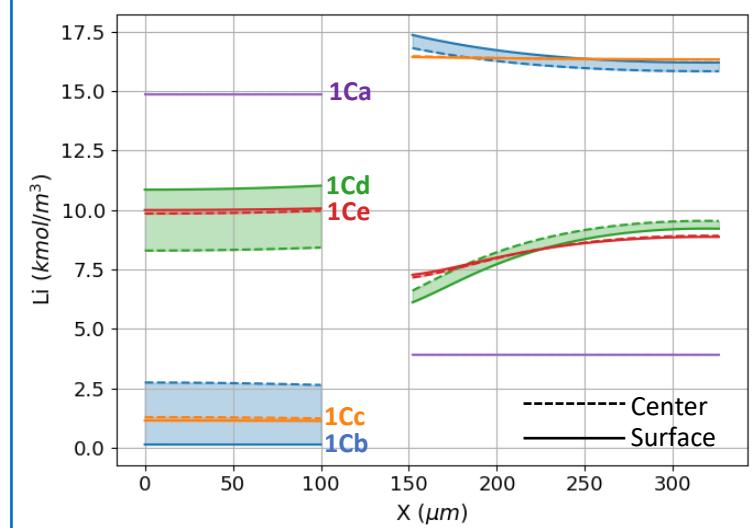
- As the discharging rate increases, more Li ion transfer through electrolyte from (-) to (+) electrode. And It causes the concentration gradient of Li ion to increase.
- However, the average concentration of Li ion is maintained at the initial concentration,  $2 \text{ kmol}/\text{m}^3$ .

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

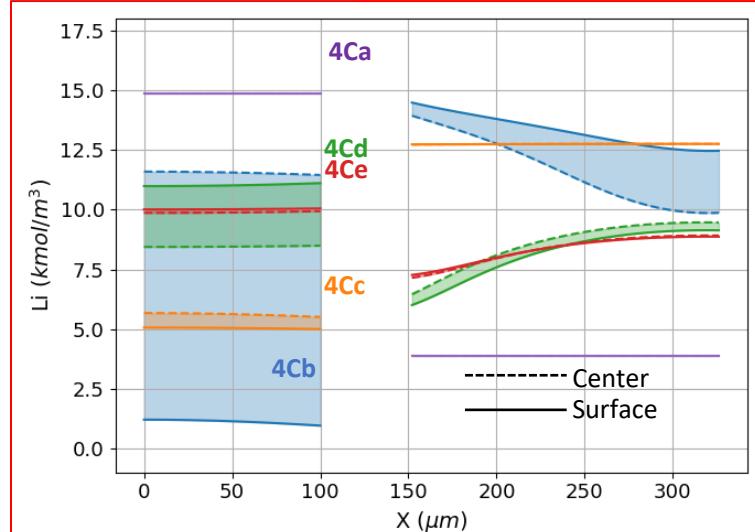


- During charging/discharging period, Li concentration distribution in the electrode particles widens as shown in the right figures.
- Its distribution range shrinks in the relaxation period.
- The expansion/shrinkage gets enhanced by increasing discharging rate from 1C to 4C.
- At higher discharging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

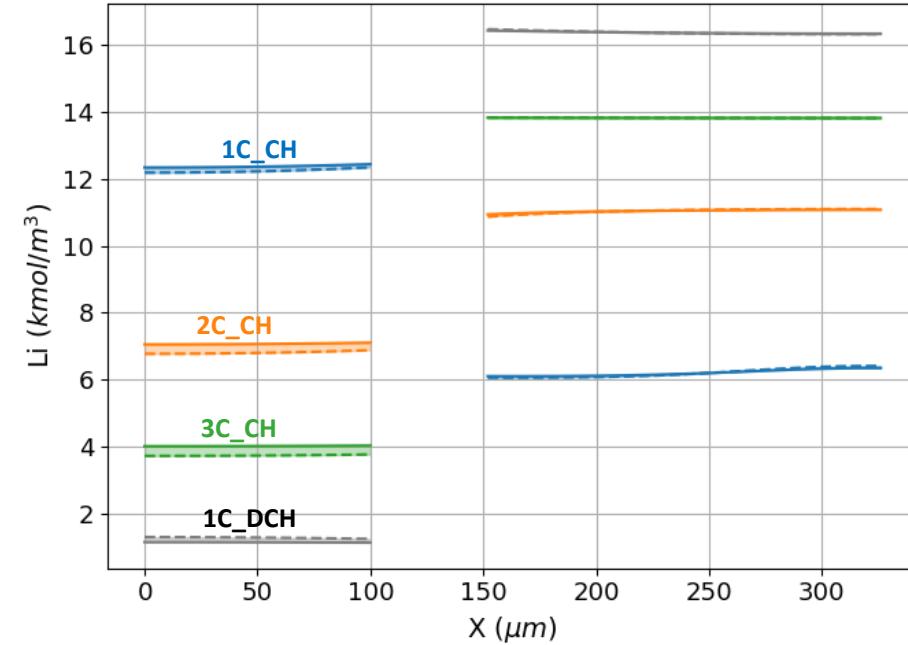
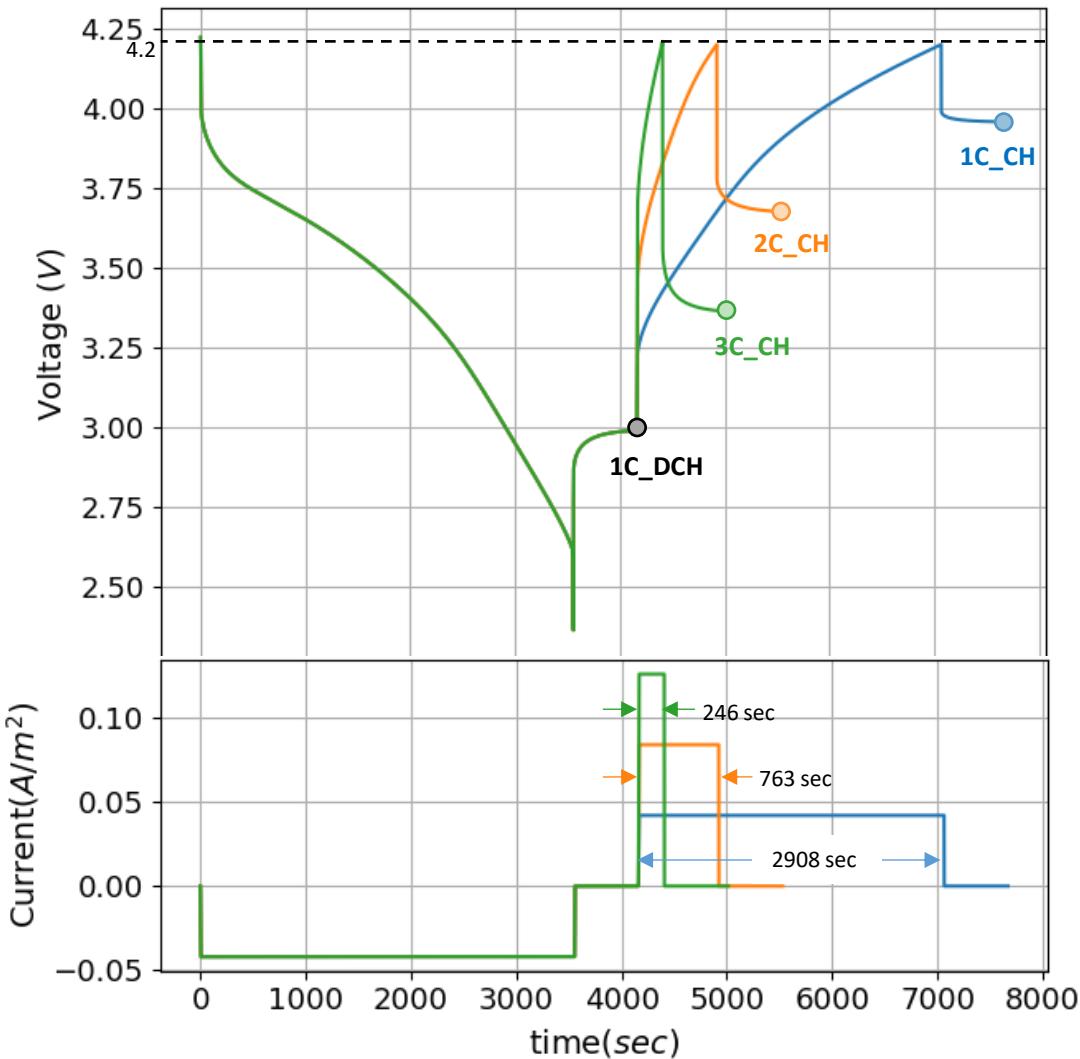
## Discharging = -1C



## Discharging = -4C

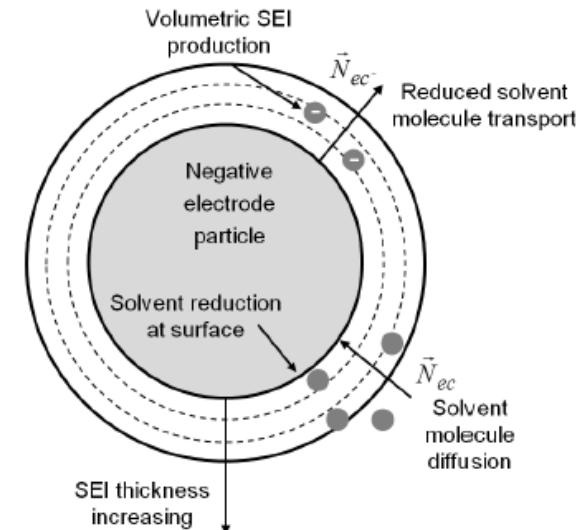
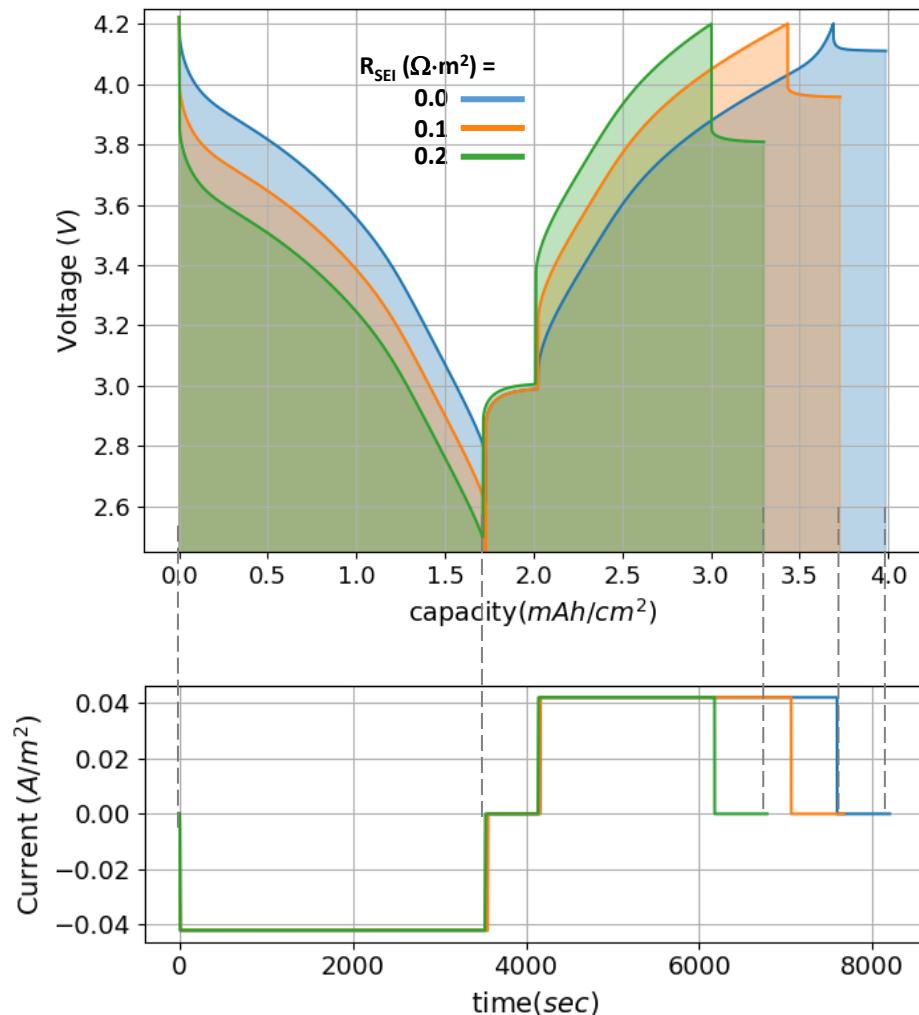


# Discharging (1C) + Charging (1/2/3C)



- The charging behavior is simulated at different charging rate. At higher charging rate,
- The cell reaches quickly the charging limit voltage ( $V_{max} = 4.2v$ ) 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