Lecture 7
Physics-based modelling of cell electrochemistry and ageing

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TRA 445

Advanced Battery Modelling and Control

Outline

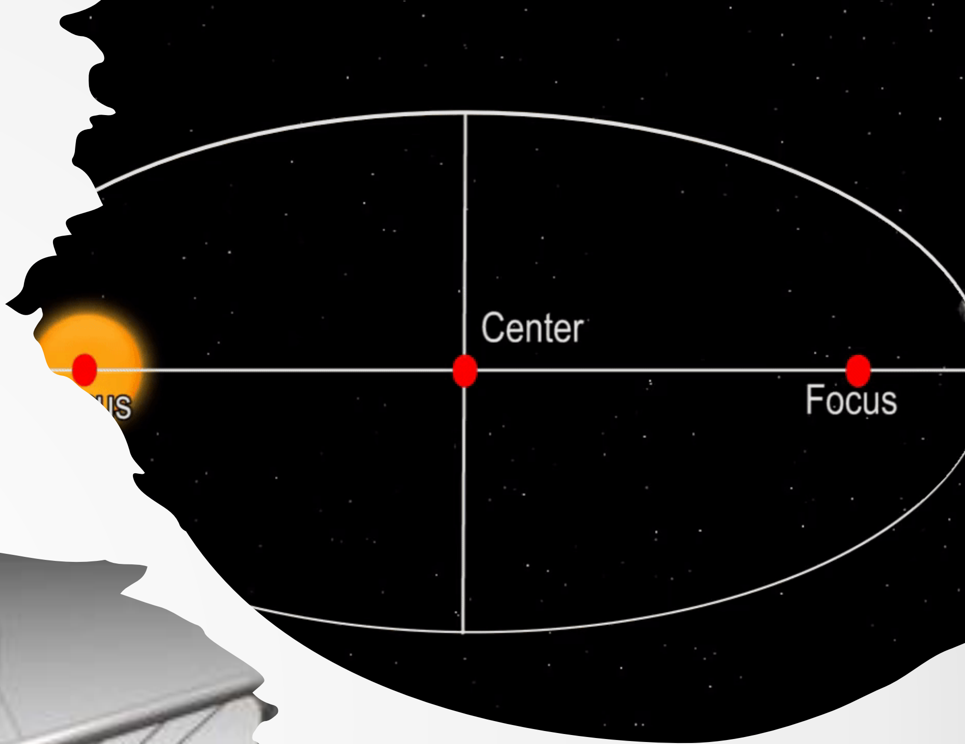
- Overview of physics-based modelling
- Working principles of electrochemical cells
- Survey of commercial/open-source tools
- Challenges of physics-based models
- Single particle model (SPM)
    - Solid-state diffusion
    - Ion exchange kinetics
    - Ageing
- Reduced order modelling
    - Numerical methods
    - Single bucket model

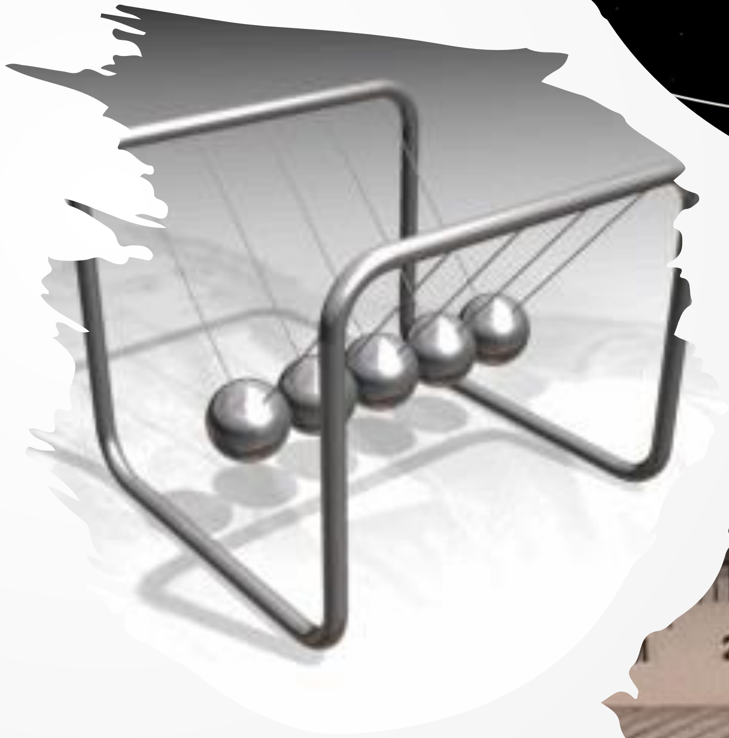
Lecture 5 v.s. lecture 7

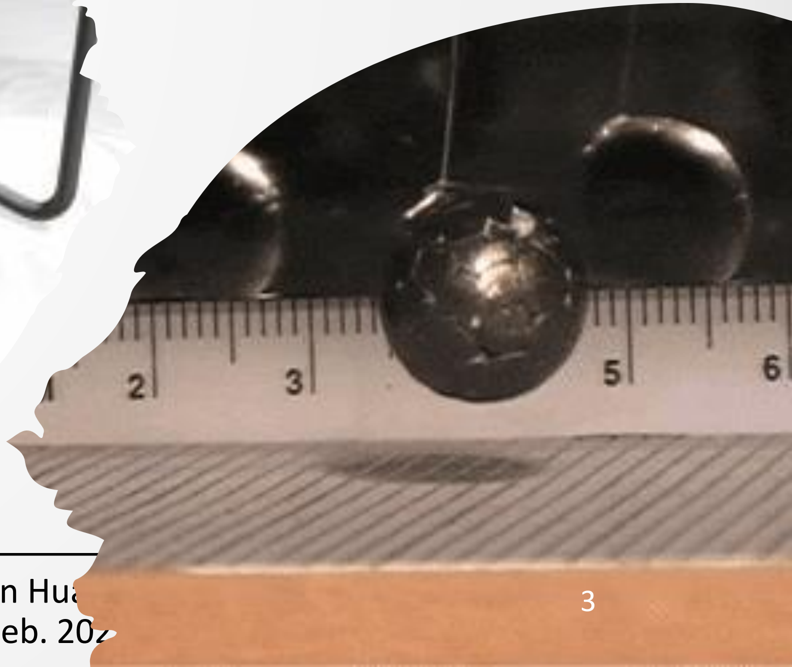
- Data-driven v.s. first-principle

- Two approaches to discovering physical models

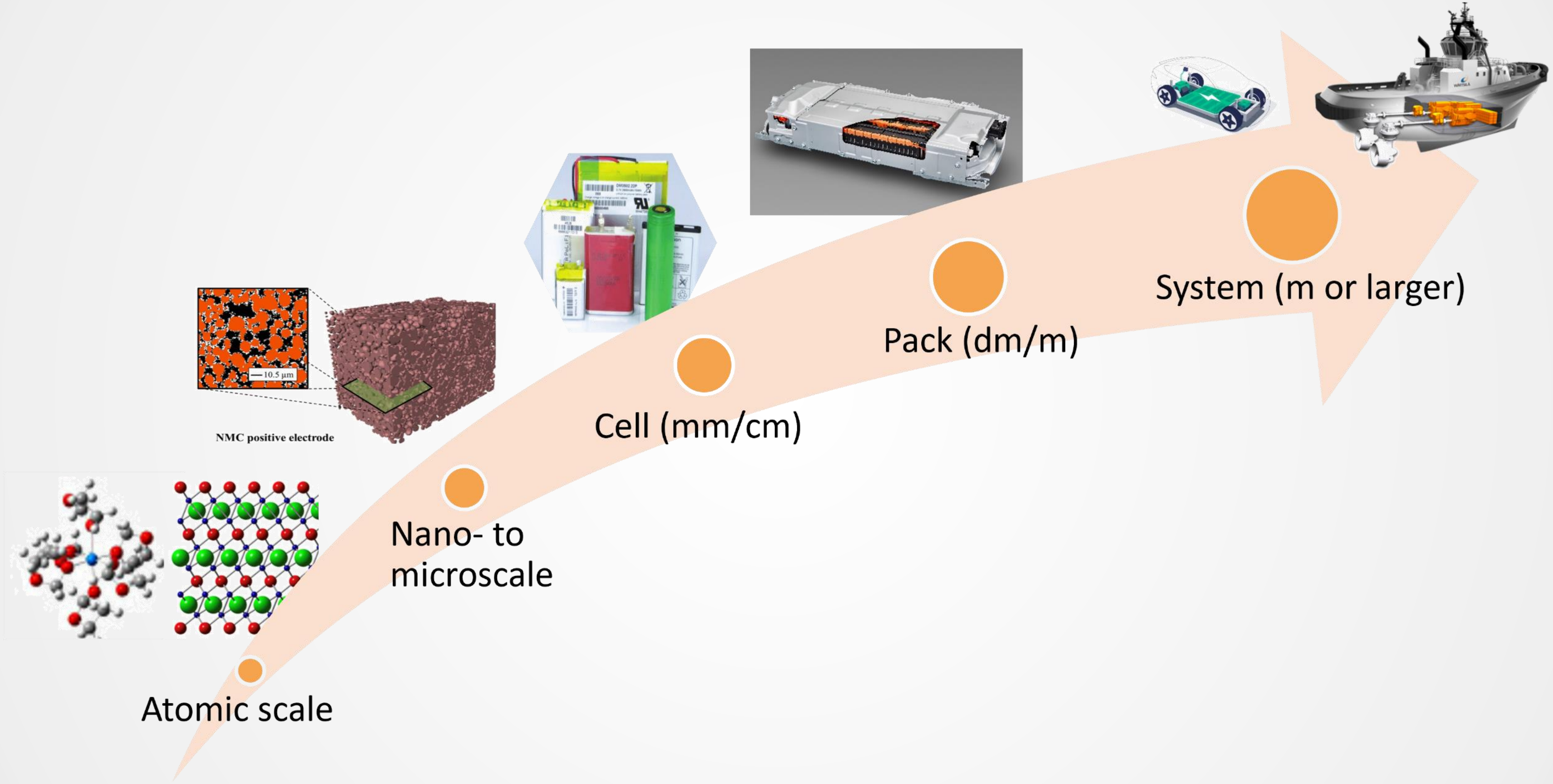
1. **Data-driven**
    - Kepler's law of planetary motion
    - Coulomb's law
    - Ohm's law
    - Ideal gas law
    - Butler-Volmer
2. **First-principle**
    - Fourier Diffusion
    - Principle of least action
    - Coupled ion-electron transfer (CIET) theory







Physics-based modelling: broad area of research



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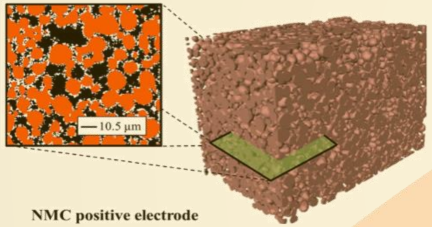
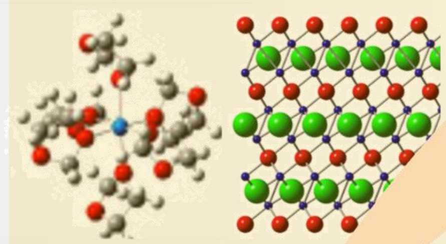
Physics-based modelling: broad area of research

Materials Science

SEI growth
Li plating
Mechanical aging

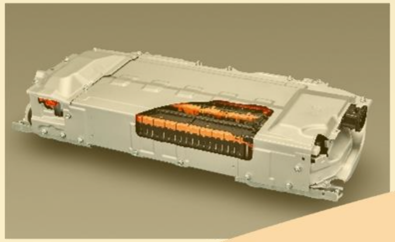




Nano- to microscale

Atomic scale

Electrical potential
Diffusion
Charge transfer



Cell (mm/cm)

Cell modelling
Cell control
SoX estimation
Capacity fade
Resistance rise
EIS

Pack (dm/m)

Cell balancing
Thermal gradient
Cooling system
Pack modelling

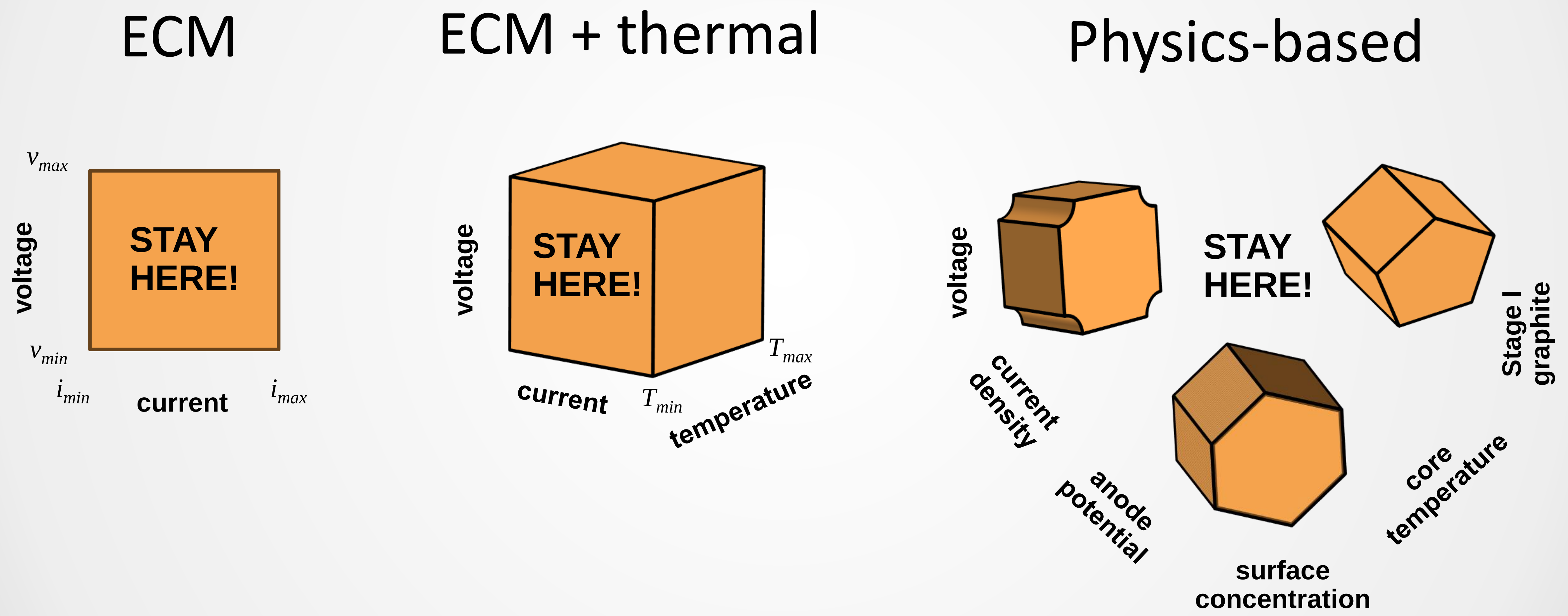
Automatic Control

System (m or larger)

Efficiency
Safety
User habits
V2X
Interaction with environment

Industrial focus

Where does physics-based cell modelling fit into BMS?



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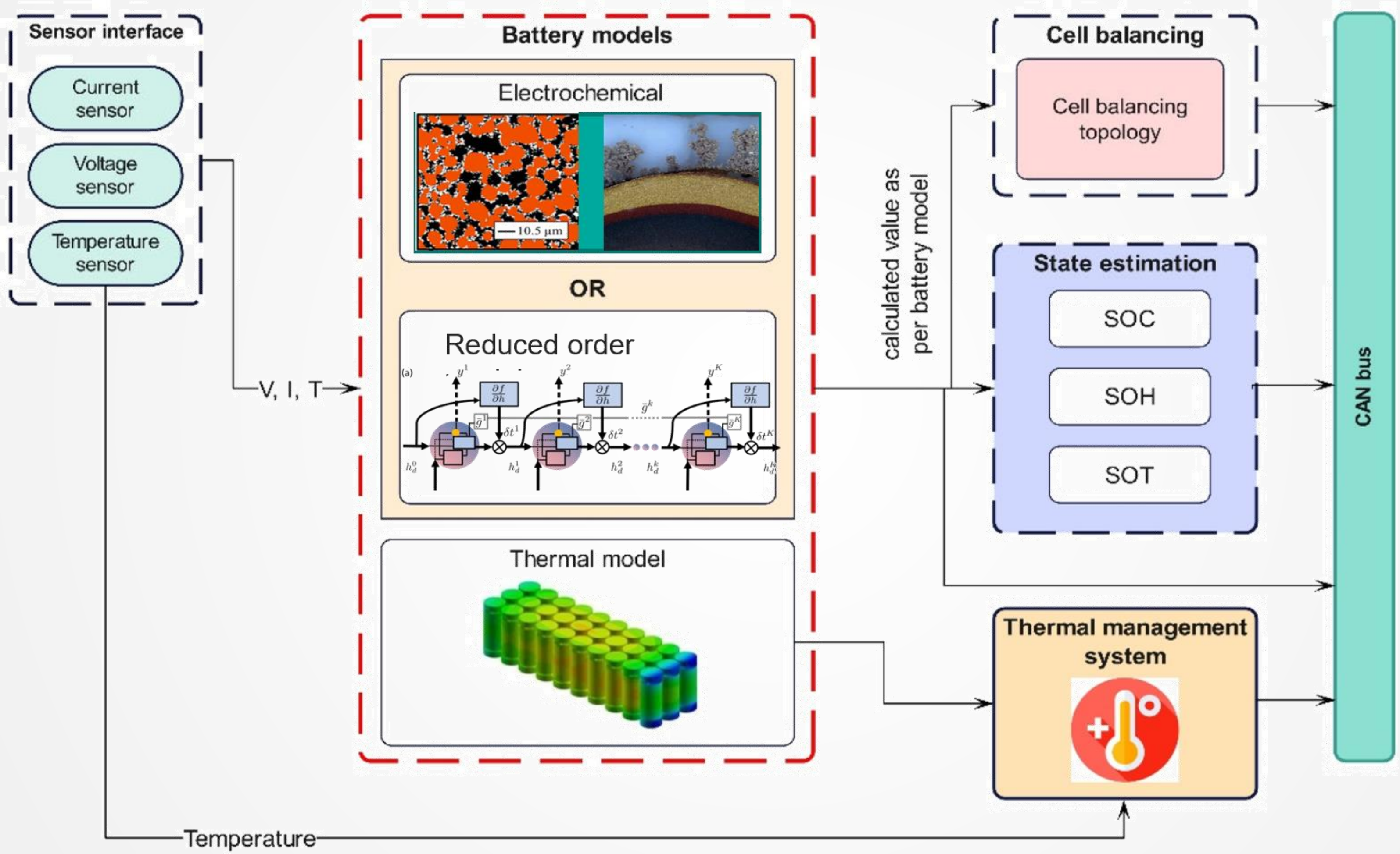
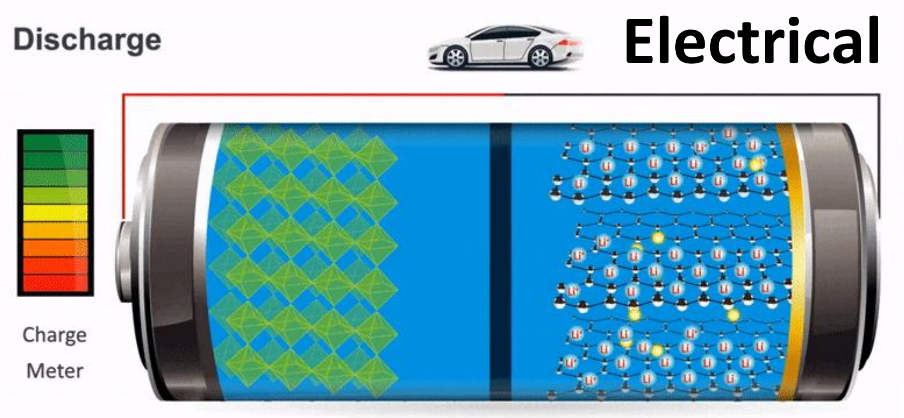
Where does physics-based cell modelling fit into BMS?



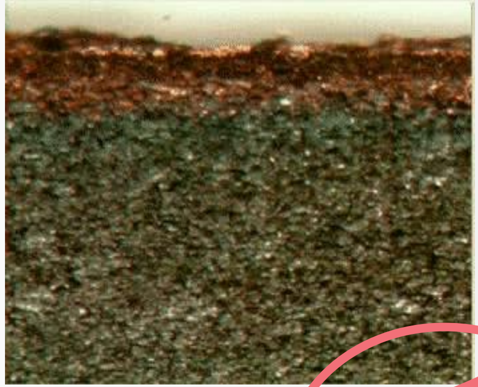
Battery models: Multiphysics

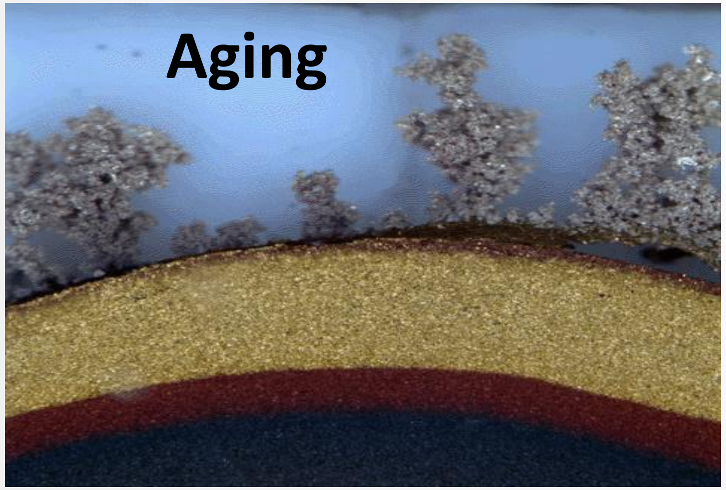
- Multiphysics are commonly dynamically coupled inside a battery cell, maybe in different timescales.



Lecture 7

Electrochemical





Harris et al. (2010). Chem. Phys Letter.

Mechanical & Thermal

Lecture 8

[Zou, C., Manzie, C., & Nešić, D. IEEE Transactions on Control Systems Technology, 2016]

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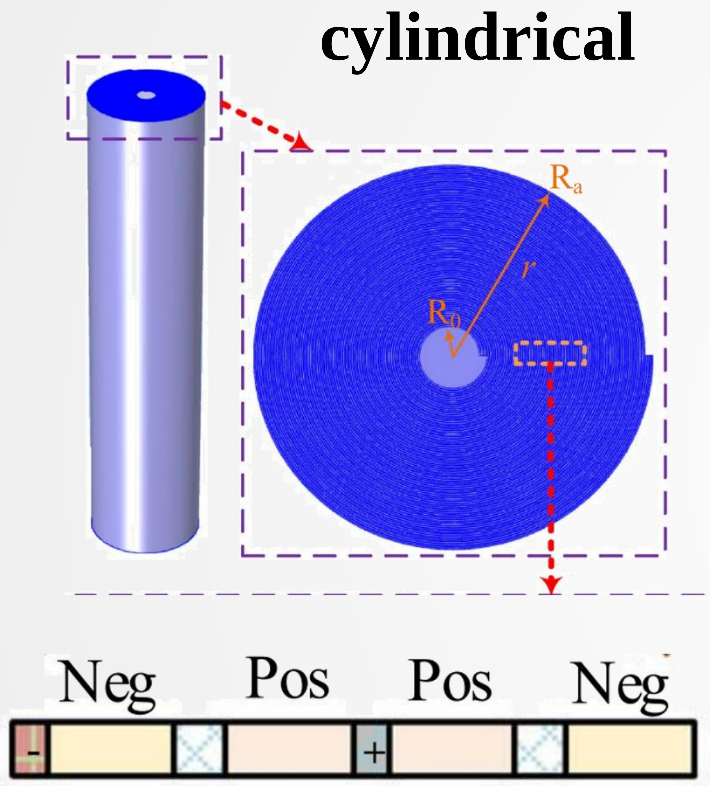
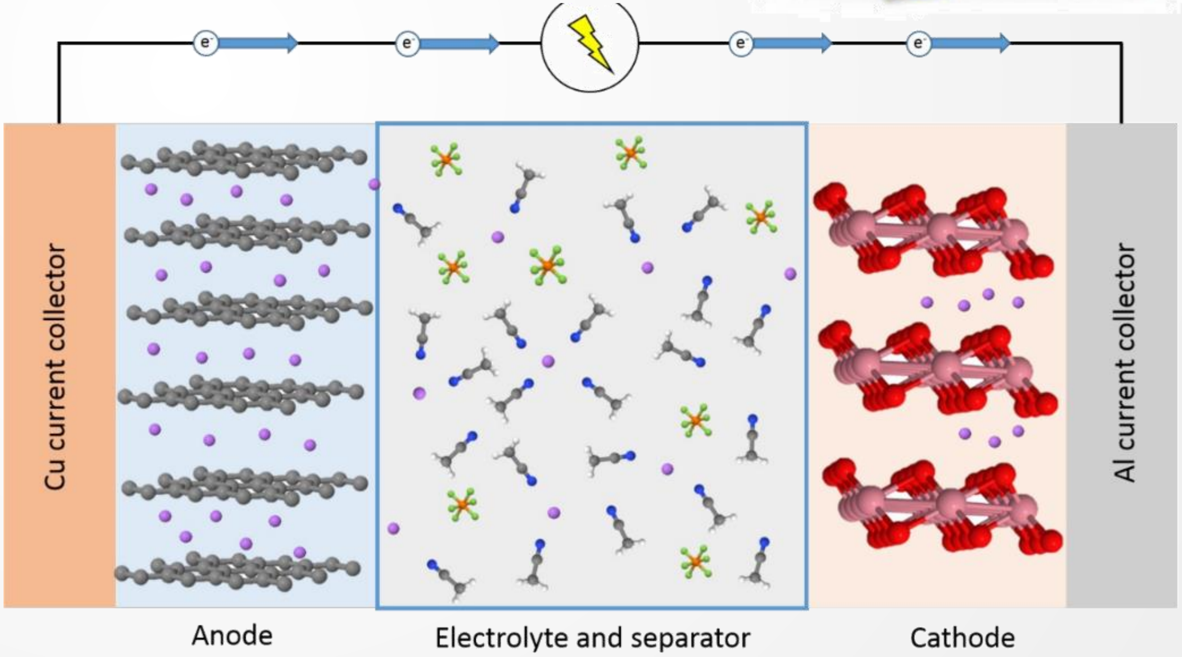
Working principles of electrochemical cells: materials





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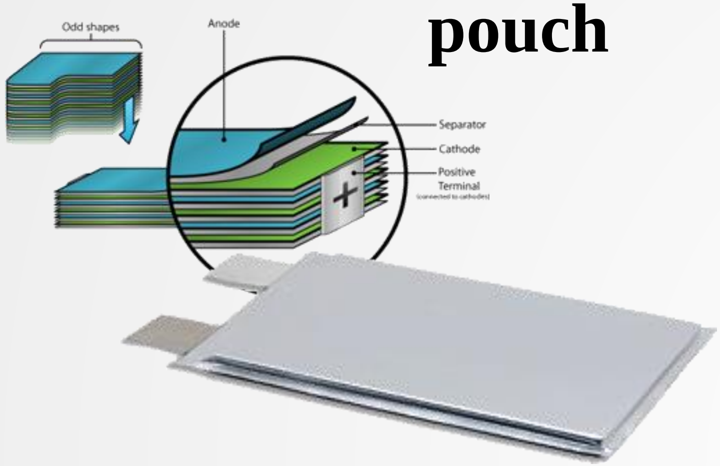
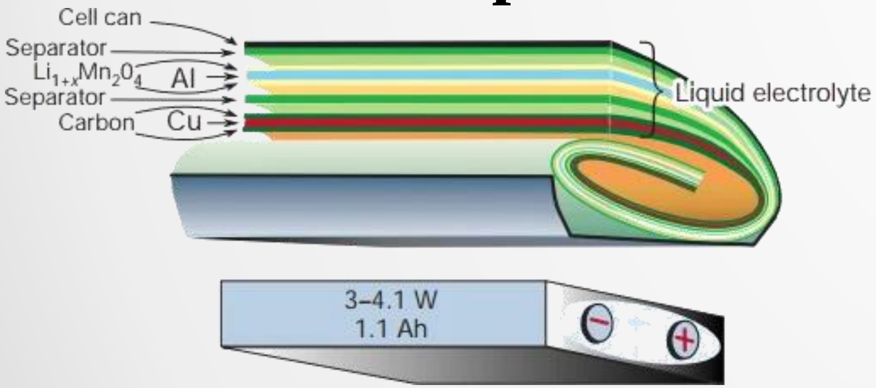
Working principles of electrochemical cells: materials

pouch

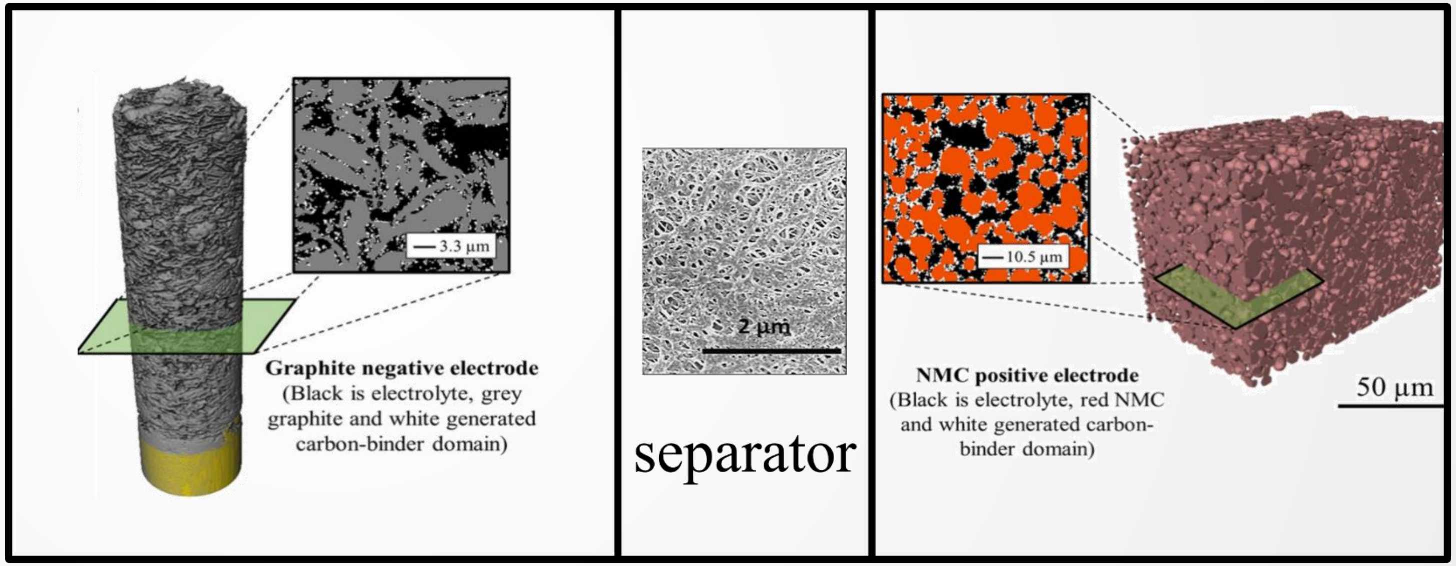


prismatic



anode

cathode



Working principles of electrochemical cells:

- **Forward Reaction (Intercalation)**:

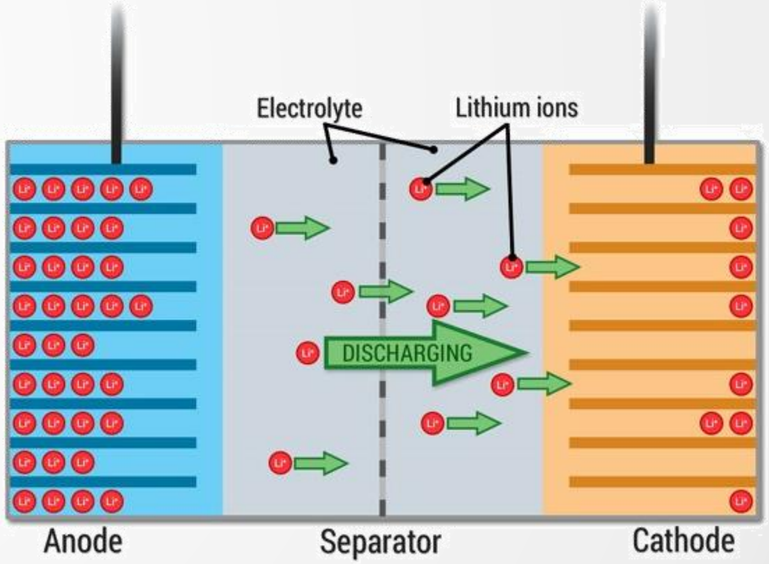
$$\mathrm{Li}^{+}_{(\text{electrolyte})} + \mathrm{e}^{-} + \mathrm{Host}_{(\text{electrode})} \longrightarrow \mathrm{Li{-}Host}_{(\text{electrode})}$$

  Lithium ions (Li^{+}) from the electrolyte, along with electrons (e^{-}), are inserted into the host material (Host) in the electrode.

- **Backward Reaction (Deintercalation)**:

$$\mathrm{Li{-}Host}_{(\text{electrode})} \longrightarrow \mathrm{Li}^{+}_{(\text{electrolyte})} + \mathrm{e}^{-} + \mathrm{Host}_{(\text{electrode})}$$

  Lithium ions (Li^{+}) are released from the host material (Li−Host) back into the electrolyte, and electrons (e^{-}) are returned to the external circuit.



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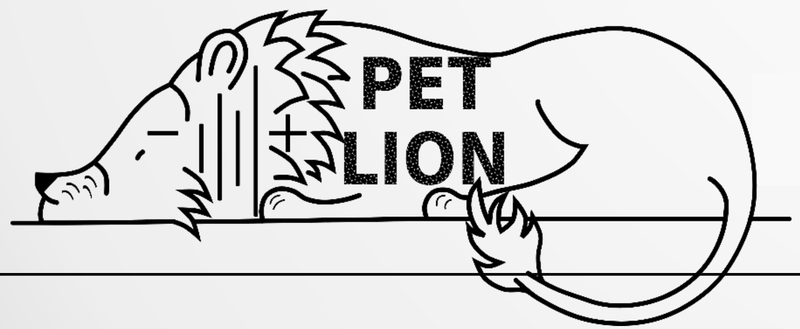
Physics-based modelling packages: survey

20+ packages

- Propiriatary
- Open-source

Economics

- languages
- Developing team
- Eco-system



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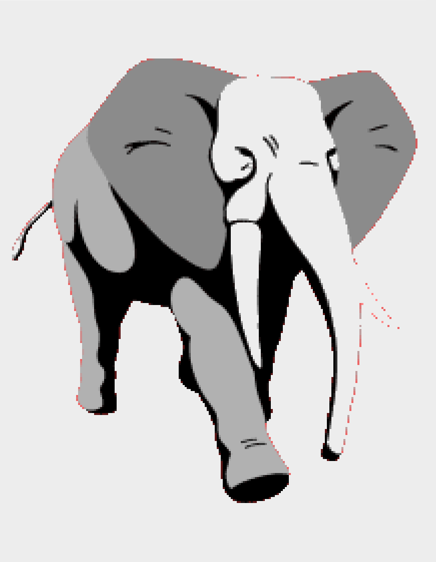
Challenge 1: parameterisation

- Accurate parameterization ensures that the model predictions align with experimental data

    E.g., an incorrect diffusion coefficient would lead to errors in predicting lithium concentration profiles

- However, it is difficult to capture real-world variability

    1. temperature-dependent parameters
    2. ageing-related parameters
    3. parameter variation due to assumptions

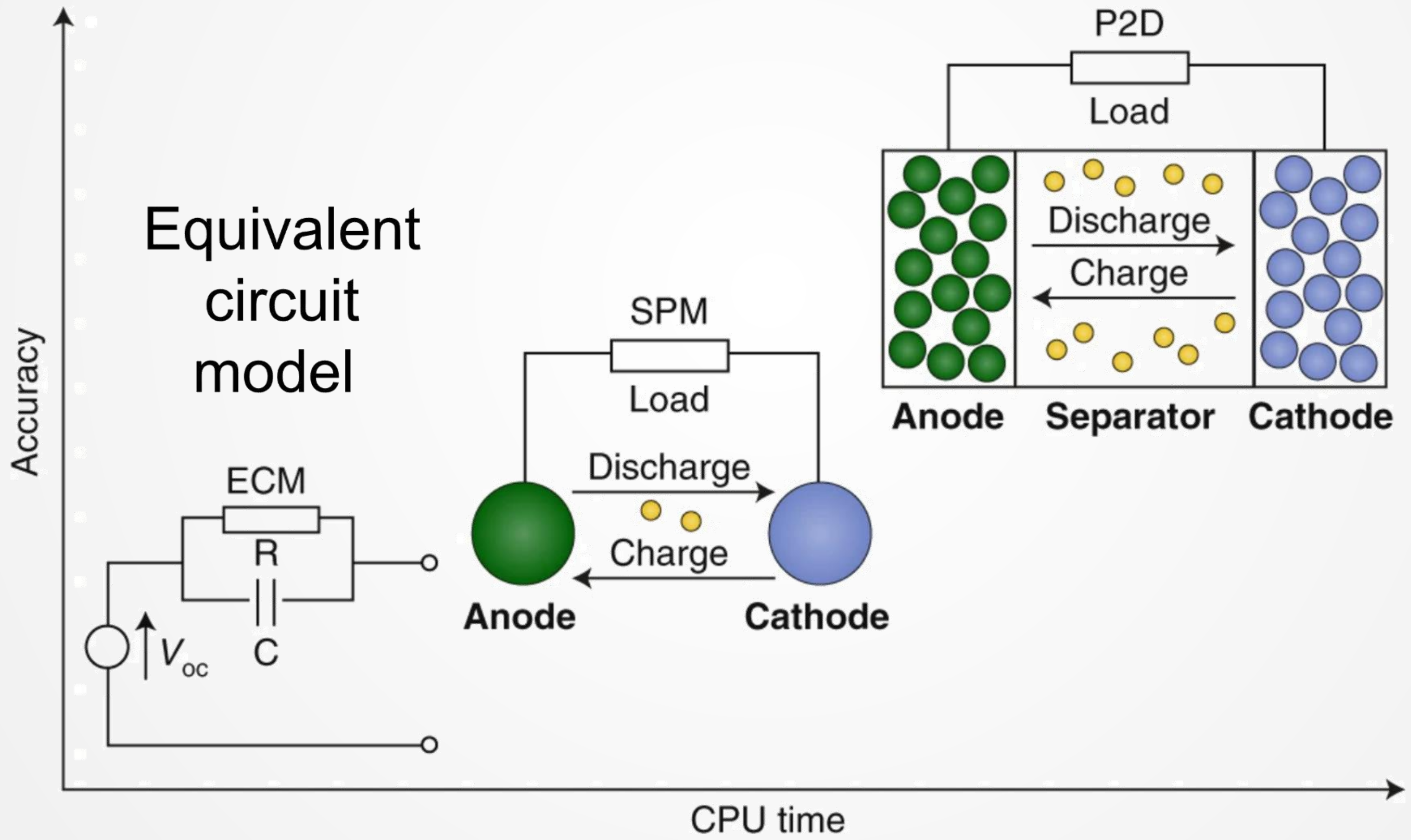


“With four parameters I can fit an elephant.”

- John von Neumann

Challenge 2: computational complexity

In terms of model order



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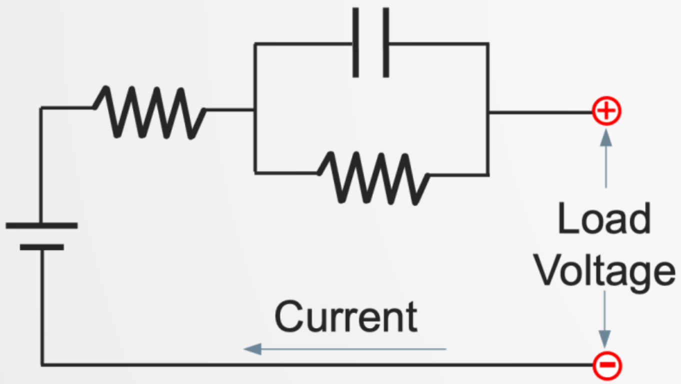
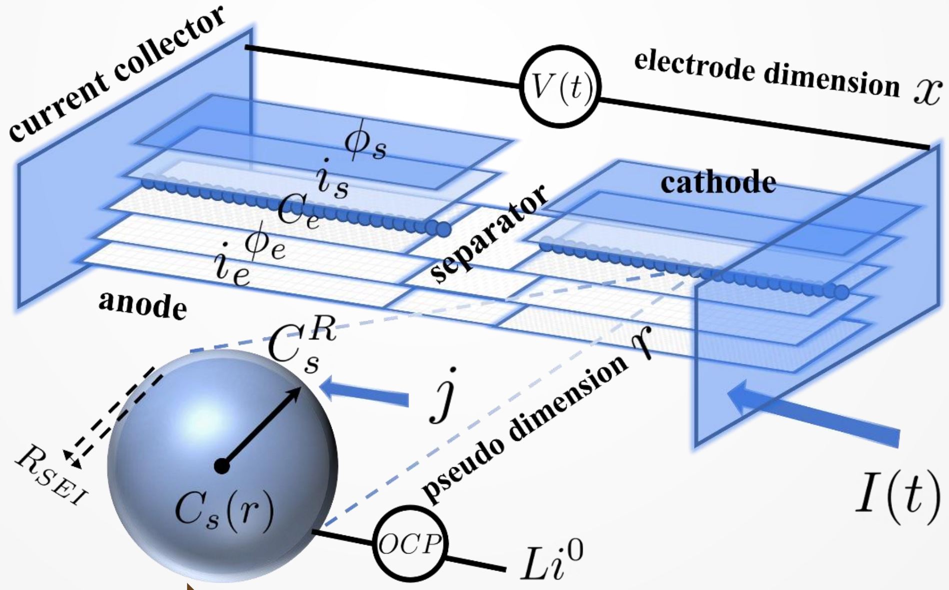
Challenge 2: computational complexity

In terms of number of parameters

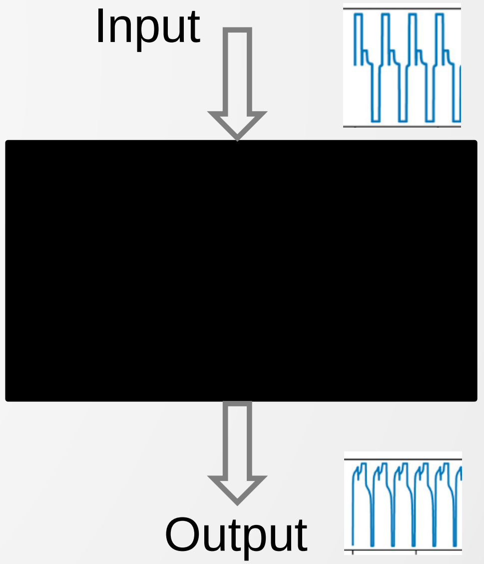
Grey-Box Model
(e.g., n^{th} order RC model)



White-Box Model
(e.g., P2D model)



Black-Box Model
(e.g., ANN model)



number of parameters

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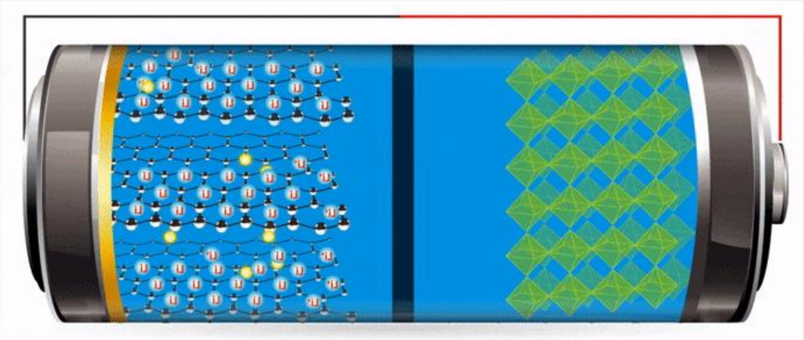
Single particle model

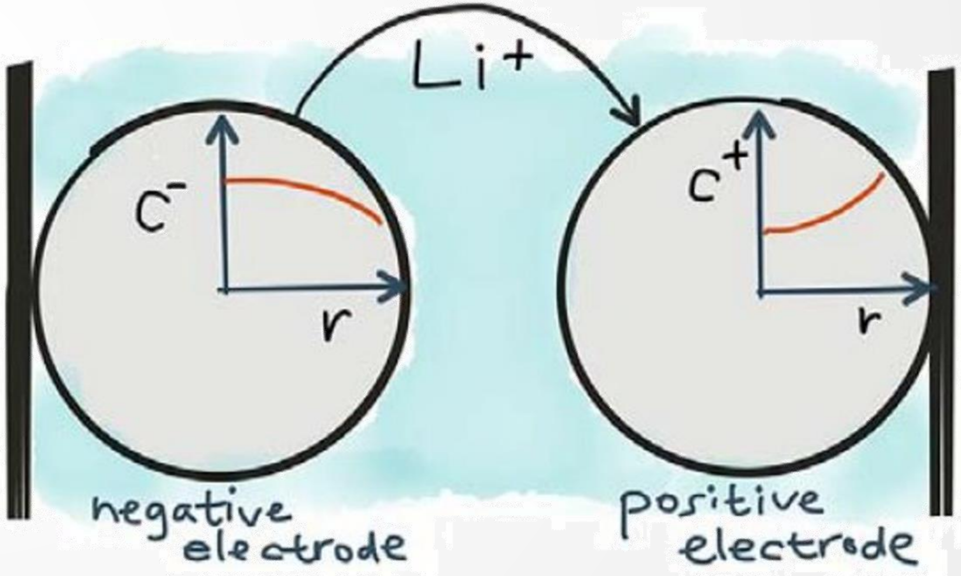


Two key physics

- Solid phase diffusion
- Ion exchange at the electrolyte-particle interface

Key differences v.s. ECM

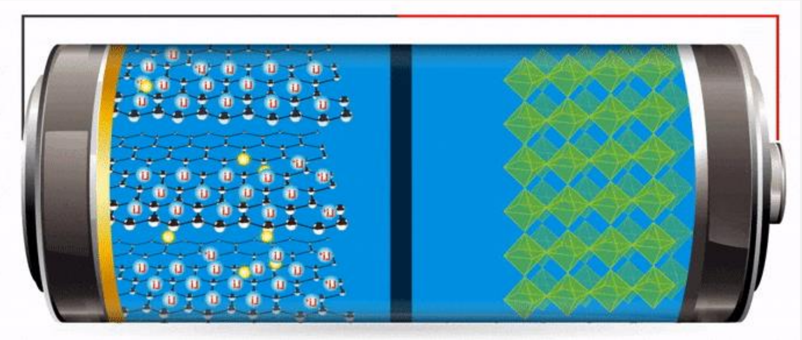
- Describe by PDEs with BCs and algebraic equations
- Fixed parameters with no SOC dependence
- Consider the two electrodes separately
- OCP as opposed to OCV

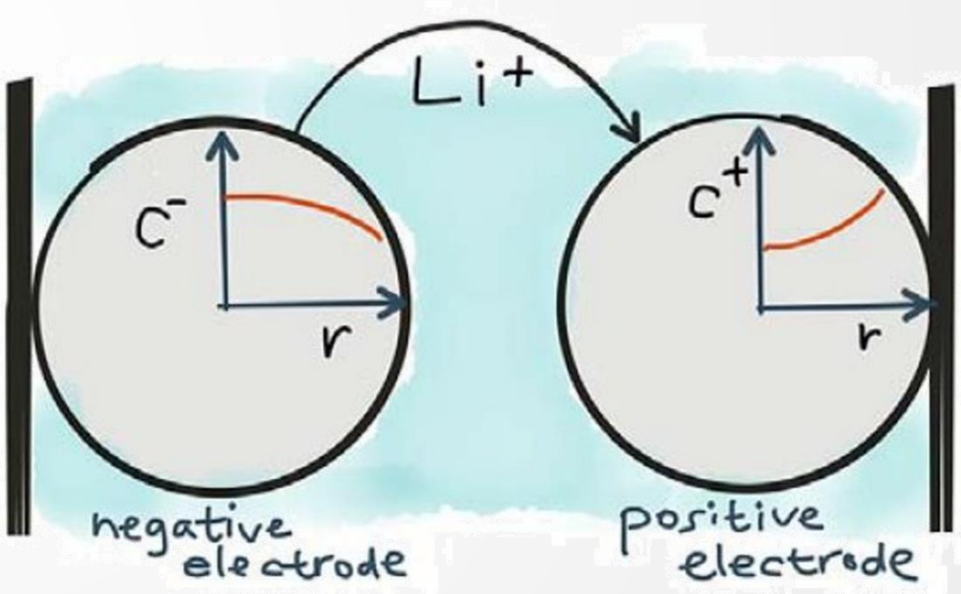


Single particle model

Key assumptions (in addition to P2D assumptions)

- Single spherical particle representation approximating the porous structure of the electrode material.
- Transport of lithium ion in the electrolyte is fast compared to solid-phase transport, thus neglecting electrolyte diffusion and migration.
- Uniform reaction rate, simplifying the interaction between the particle and the electrolyte (decoupled).





Single particle model: solid phase diffusion

- The general diffusion equation in three dimensions is given by:

$$\frac{\partial c}{\partial t} = D\nabla^2 c,$$

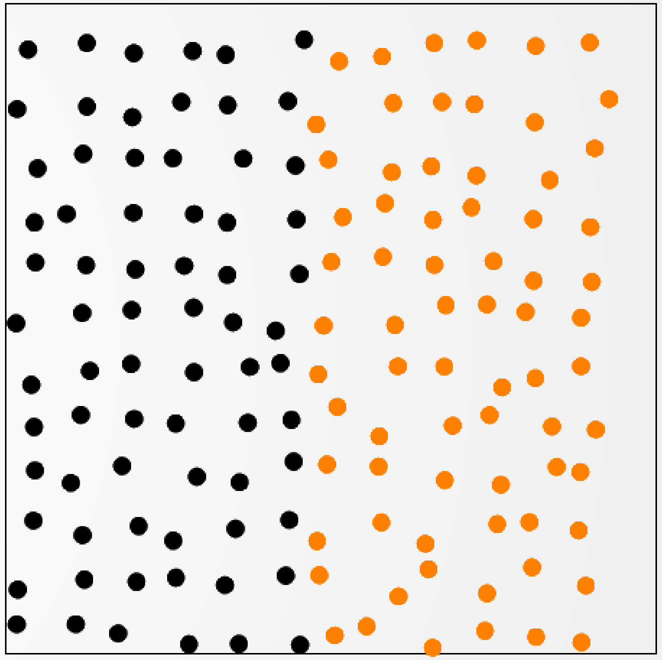
where:

  - $c(\mathbf{r}, t)$ is the concentration,
  - D is the diffusion coefficient,
  - $\nabla^2 c$ is the Laplacian of c.

- **Laplacian Definition:** In Cartesian coordinates,

$$\nabla^2 c = \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}.$$

- The Laplacian measures the divergence of the gradient, giving a sense of how the function "curves".



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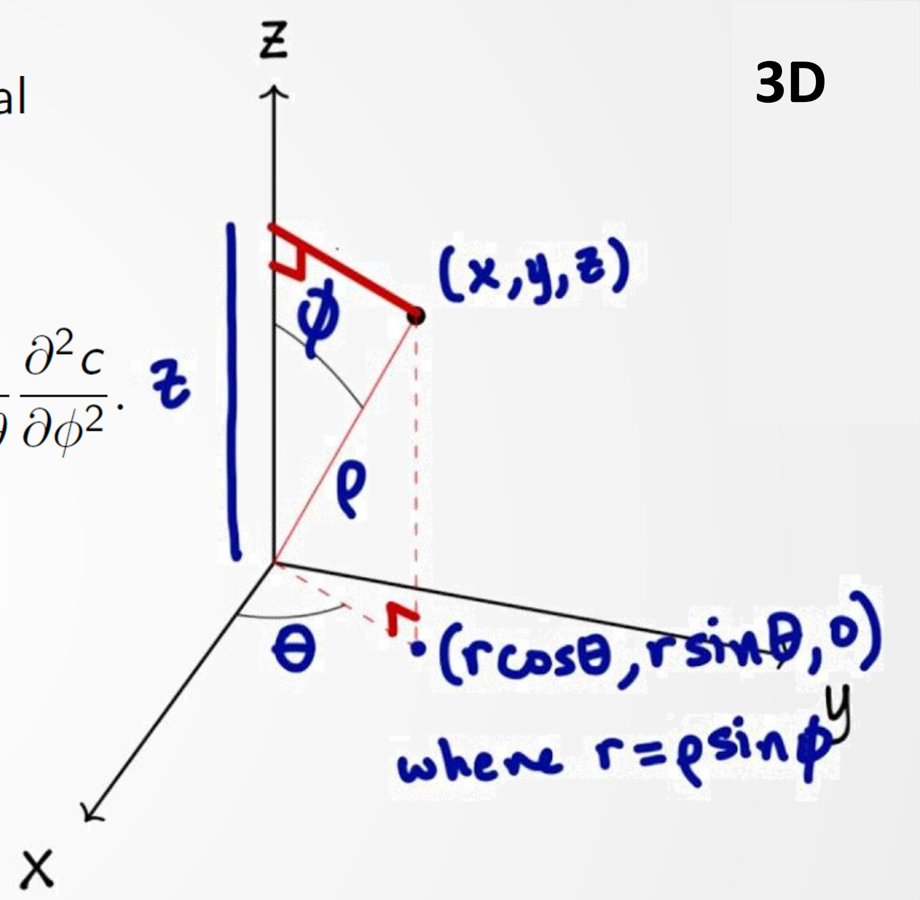
Single particle model: solid phase diffusion

- For a spherical particle, it is natural to switch to spherical coordinates (r, θ, ϕ).
- In spherical coordinates, the Laplacian becomes:

$$\nabla^2 c = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial c}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 c}{\partial \phi^2}.$$



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Single particle model: solid phase diffusion

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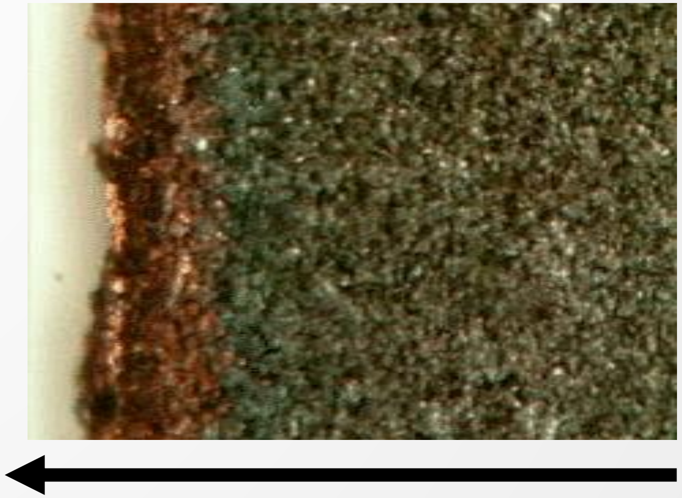
- For a radially symmetric situation (i.e., $c = c(r, t)$ only), the angular terms vanish, so:

$$\nabla^2 c = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right).$$

- Thus, the diffusion equation simplifies to:

$$\frac{\partial c}{\partial t} = D\,\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right).$$

1D



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Single particle model: solid phase diffusion

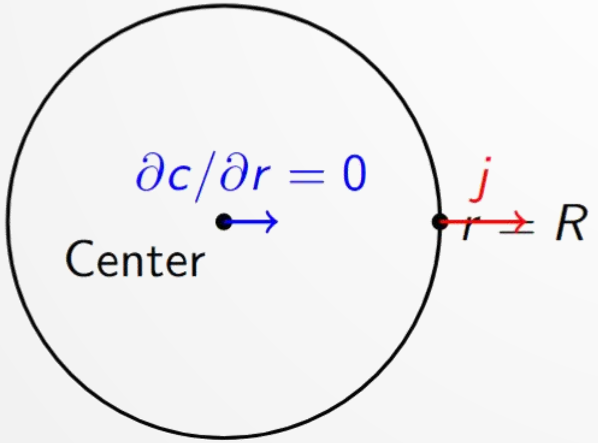
- **At** $r = 0$ (center): By symmetry,

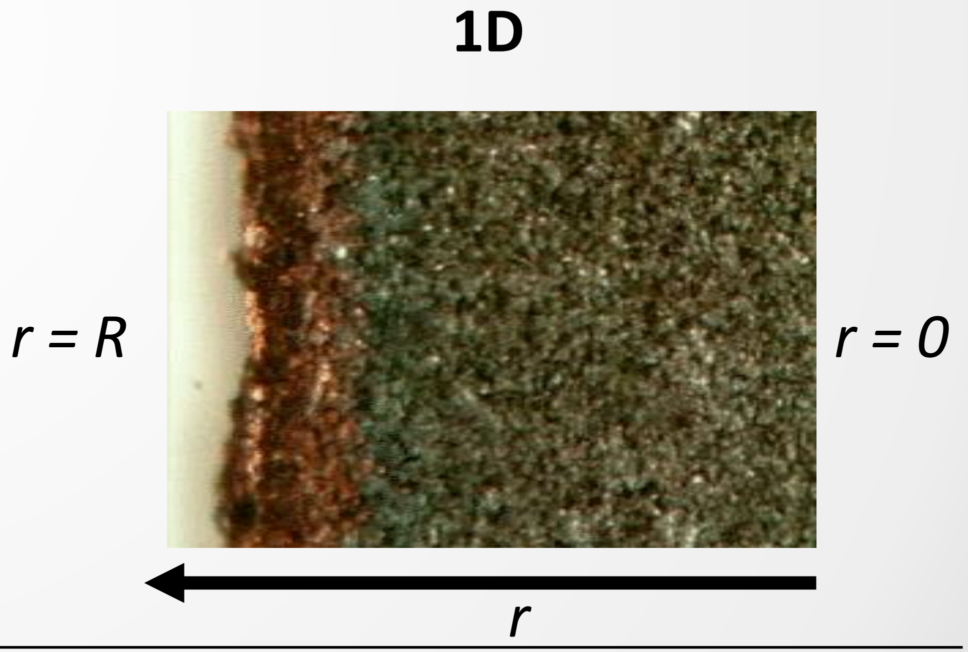
$$\left.\frac{\partial c}{\partial r}\right|_{r=0} = 0.$$

- **At** $r = R$ (particle surface): A flux boundary condition is imposed,

$$-D\left.\frac{\partial c}{\partial r}\right|_{r=R} = j \quad \text{(flux)},$$

where j is the molar flux (related to interfacial reactions).





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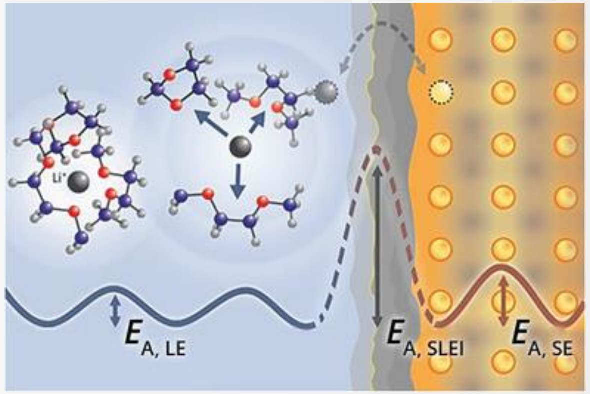
Single particle model: Butler-Volmer kinetics

Chemical Reaction:

$$\underbrace{\mathrm{Li}^{+}_{(\mathrm{electrolyte})} + e^{-} + \mathrm{Host}_{(\mathrm{electrode})}}_{\substack{\text{Reactants} \\ \text{(Oxidized state)}}} \underset{\text{Backward (De-intercalation)}}{\overset{\text{Forward (Intercalation)}}{\rightleftharpoons}} \underbrace{\mathrm{Li\text{-}Host}_{(\mathrm{electrode})}}_{\substack{\text{Product} \\ \text{(Reduced state)}}}$$

- The Butler–Volmer equation describes the net current density at an electrode as a function of the overpotential η:

$$j = i_0 \left[\exp\left(\frac{\alpha F \eta}{RT}\right) - \exp\left(-\frac{(1-\alpha) F \eta}{RT}\right) \right].$$



- **Forward Reaction Rate:** $j_{\mathrm{fwd}} = i_0 \exp\left(\frac{\alpha F \eta}{RT}\right)$.
- **Backward Reaction Rate:** $j_{\mathrm{bwd}} = i_0 \exp\left(-\frac{(1-\alpha) F \eta}{RT}\right)$.

- i_0: Exchange current density
- η: Overpotential
- α: Symmetry factors

Single particle model: Symmetric Butler-Volmer kinetics

- For symmetric kinetics, assume $\alpha = 0.5$. Then:

$$j = i_0 \left[\exp\left(\frac{F\eta}{2RT}\right) - \exp\left(-\frac{F\eta}{2RT}\right) \right].$$

- Recognize the hyperbolic sine function:

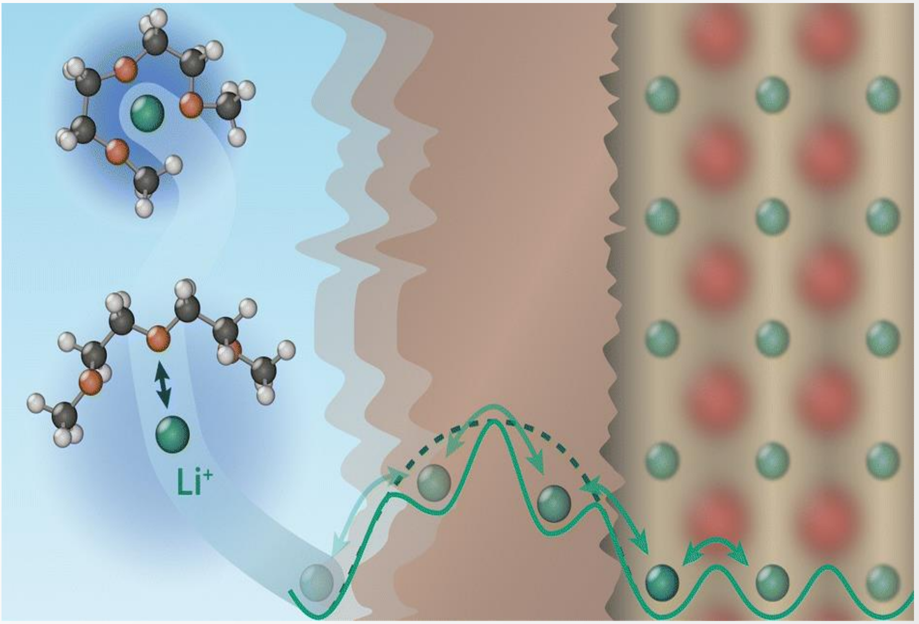
$$\sinh(x) = \frac{e^x - e^{-x}}{2}.$$

- Therefore, the Butler–Volmer equation becomes:

$$j = 2 i_0 \sinh\left(\frac{F\eta}{2RT}\right).$$

- This allows us to obtain η in SPM:

$$\eta = \frac{2RT}{F} \sinh^{-1}\left(\frac{j}{2 i_0}\right).$$



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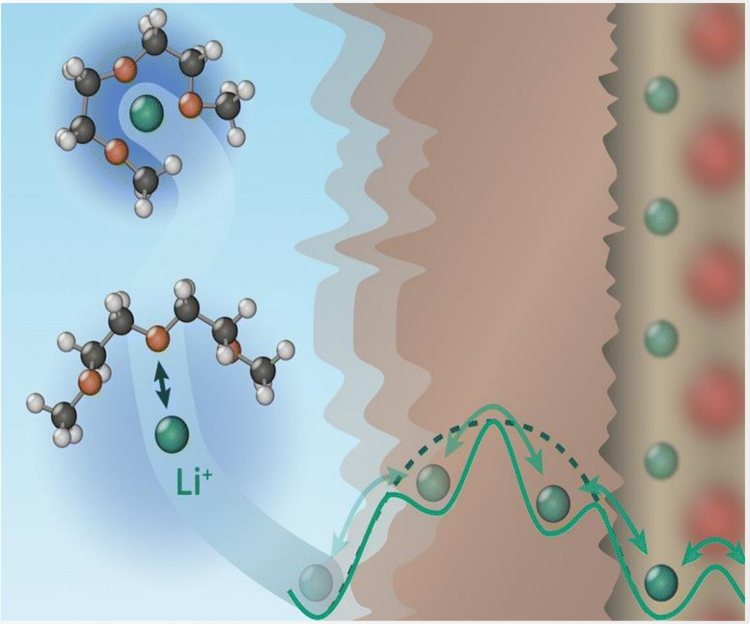
Single particle model: Exchange current density

- i_0 represents the reaction rate when there is no net current; it quantifies the ease of charge transfer.
- For a given species i, the exchange current density $i_{0,i}$ is expressed as:

$$i_0 = k_i(T)\,\mathcal{F}\,\sqrt{c_e^{\text{avg}}}\,\sqrt{c_s^{\text{surf}}}\,\sqrt{c_s^{\text{max}} - c_s^{\text{surf}}},$$

  where:
  - $k_i(T)$ is the temperature-dependent reaction rate constant for species i,
  - $\mathcal{F}$ is Faraday's constant,
  - c_e^{avg} is the average electrolyte concentration,
  - c_s^{surf} is the surface concentration of species i in the solid phase,
  - c_s^{max} is the maximum concentration of species i in the solid phase.
- Physically, a higher i_0 implies that the electrode can more readily accommodate charge transfer, leading to lower kinetic overpotentials.



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Single particle model: Voltage calculation

- The terminal voltage V_{cell} of a battery cell is determined by the difference between the cathode and anode potentials, modified by kinetic and ohmic losses.
- A common expression is:

$$V_{\text{cell}} = [U_{\text{cathode}} + \eta_{\text{cathode}}] - [U_{\text{anode}} + \eta_{\text{anode}}] - I\,R_{\text{int}},$$

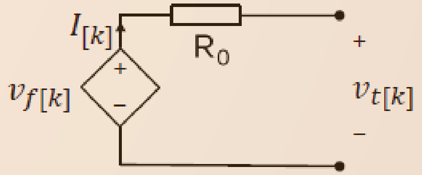
where:

  - U_{cathode} and U_{anode} are the open-circuit potentials (OCPs),
  - η_{cathode} and η_{anode} are the kinetic overpotentials (from Butler–Volmer kinetics),
  - I is the applied current,
  - R_{int} represents internal resistances (e.g., current collector, electrolyte).

It is calculated from surface concentration, not SOC. Sounds familiar?

$$v_{t[k]} = v_{f[k]} - I_{[k]} R_0$$

$$v_{f[k]} = U_{OCV[k-1]} - v_{1[k-1]} - v_{2[k-1]}$$



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Single particle model: Voltage calculation

- **Kinetic Overpotential:** Arises from the activation energy barrier for charge transfer.

$$\eta = (\text{activation overpotential})$$

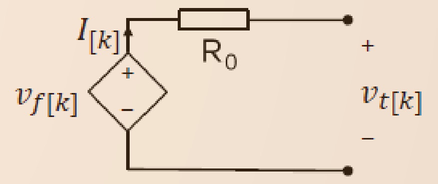
  and is calculated using Butler–Volmer (or its sinh form).
- **Ohmic Overpotential:** Due to resistive losses in the cell,

$$I\,R_{\text{int}},$$

  where R_{int} is the sum of resistances in the electrode, electrolyte, and current collectors.
- Both overpotentials reduce the effective cell voltage compared to the difference in OCPs.

What is the equivalent of overpotential in the ECM model from lecture 6?

$$v_{t[k]} = v_{f[k]} - I_{[k]}R_0$$
$$v_{f[k]} = U_{OCV[k-1]} - v_{1[k-1]} - v_{2[k-1]}$$



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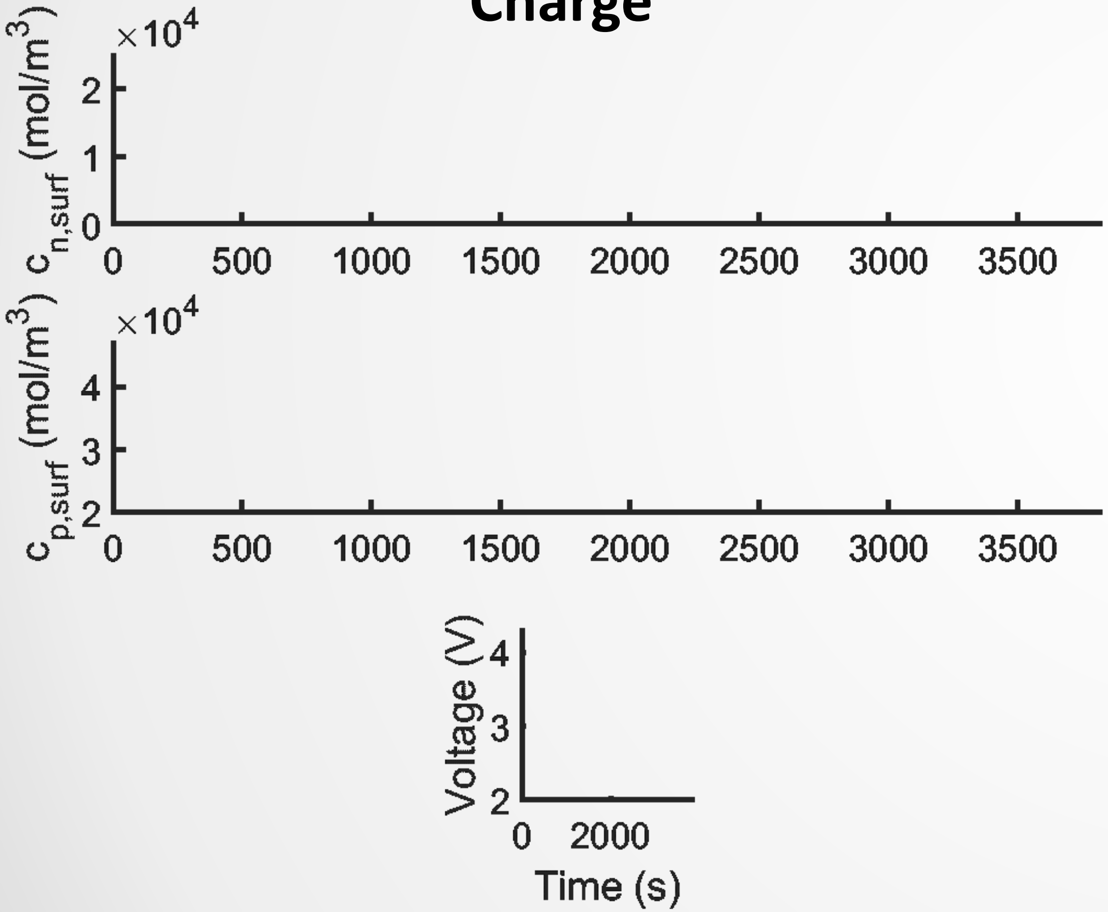
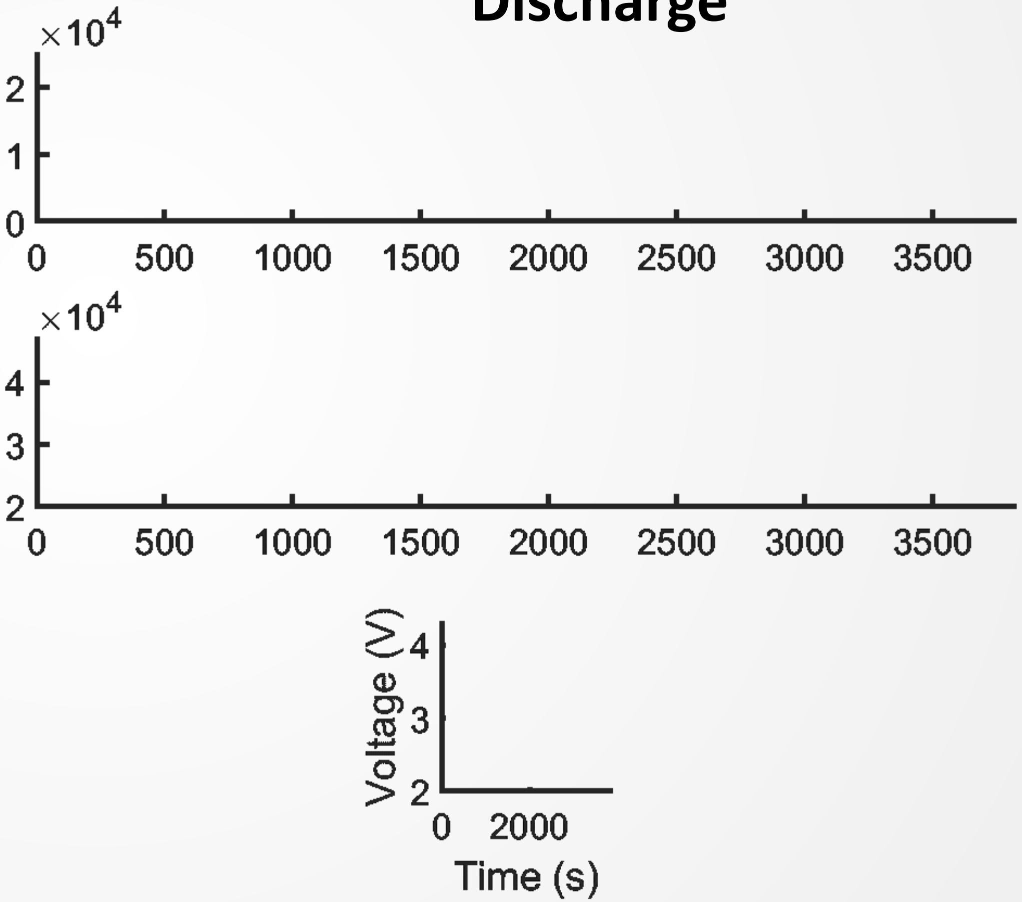
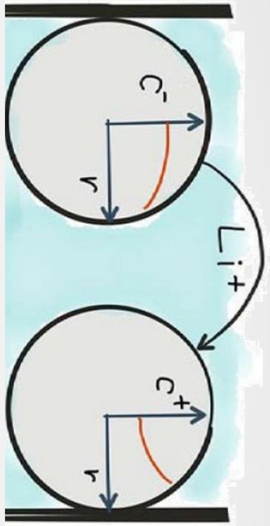
Single particle model: simulation

Charge



Discharge





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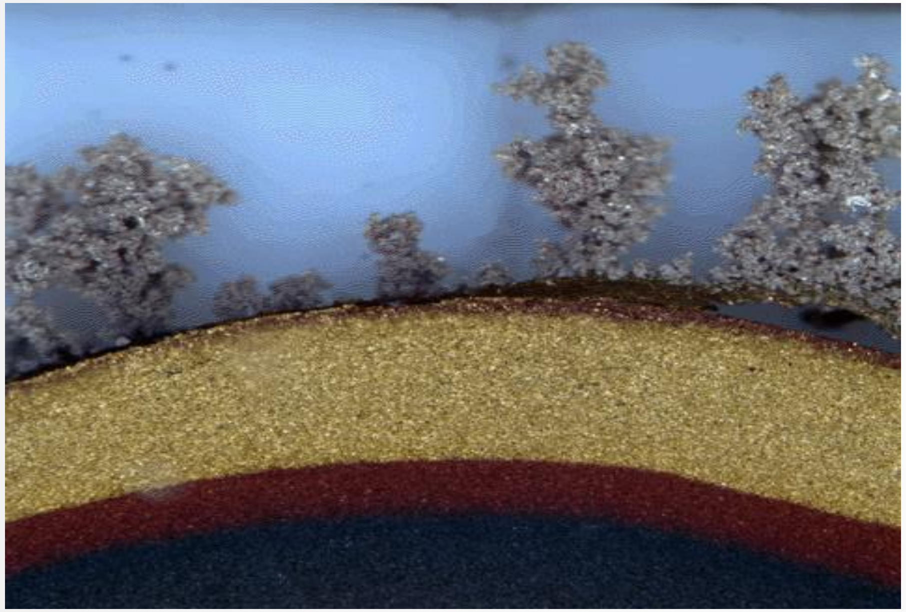
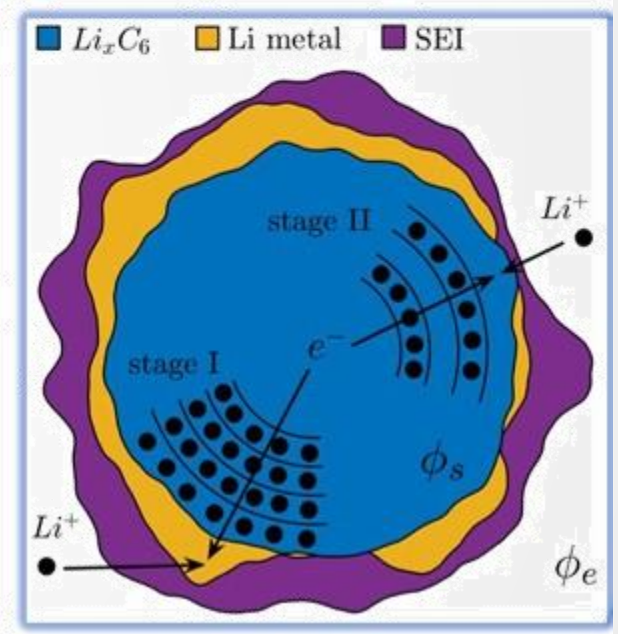
Single particle model: Ageing

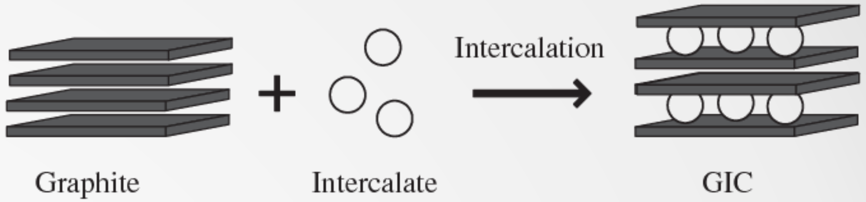
$$j_{\text{tot}} = j_{\text{intercalation}} + j_{\text{SEI}} + j_{\text{plating}} + \dots$$

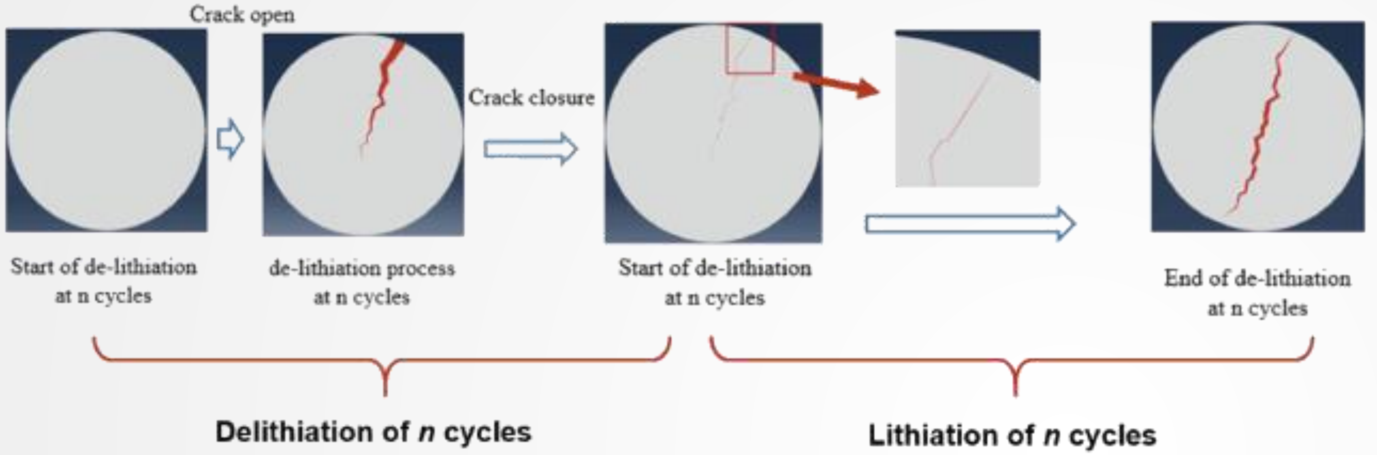


Loss of lithium inventory (LLI)



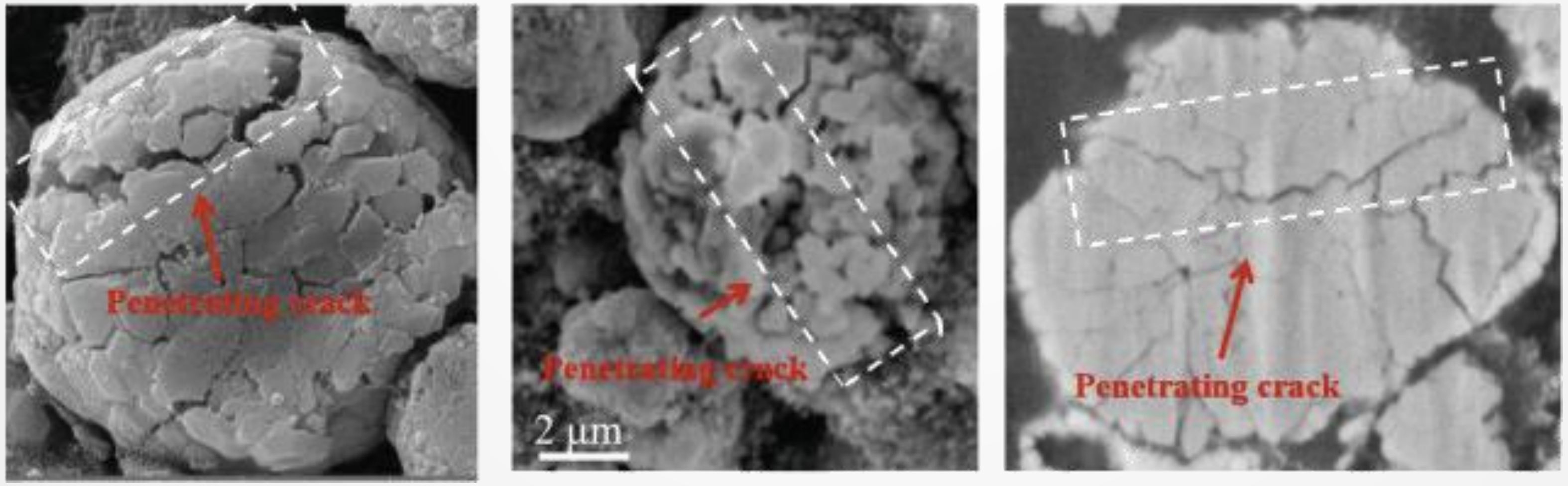
Single particle model: Ageing





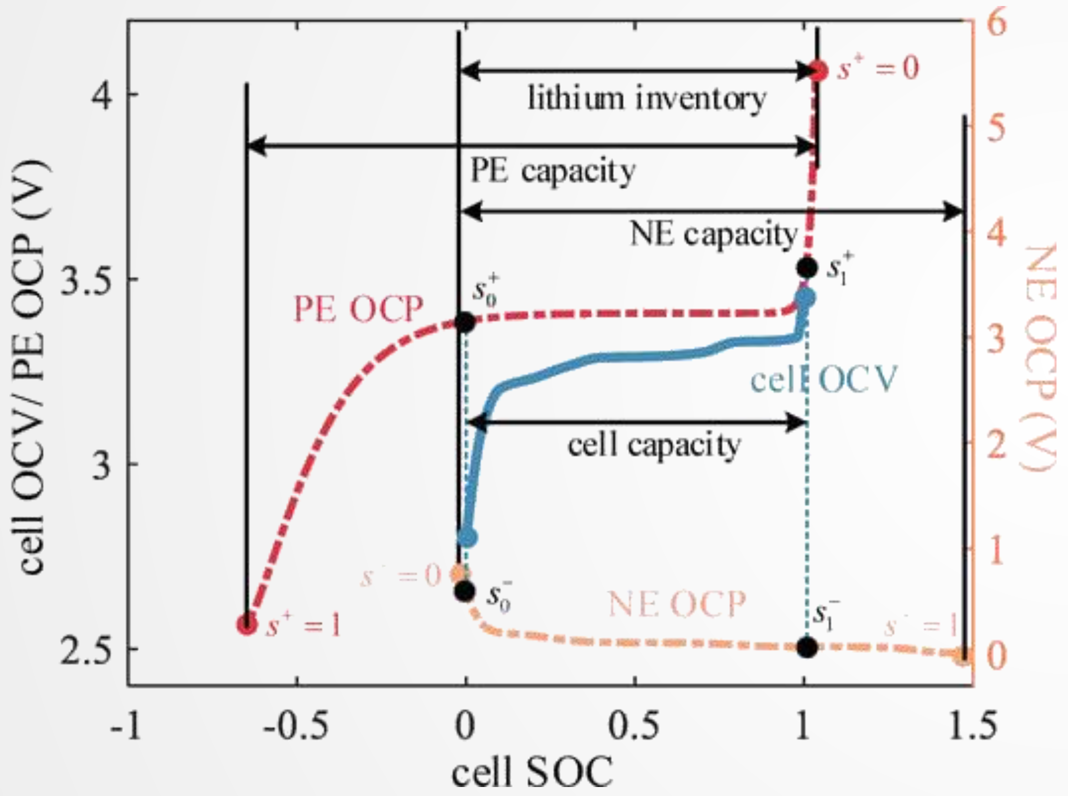
pressure

strain



Loss of active material (LAM)

Single particle model: Ageing



Four important ageing-related parameters:

```
% Max solid-phase concentrations [mol/m^3]
para.cs1_max = 30556;
para.cs3_max = 51555;

% Stoichiometry bounds determined by electrode balancing and ageing
para.soc0_a = 0.0068; % anode stoichiometry at 0% SOC
para.soc1_a = 0.7560; % anode stoichiometry at 100% SOC
para.soc0_c = 0.8933; % cathode stoichiometry at 0% SOC
para.soc1_c = 0.4650; % cathode stoichiometry at 100% SOC
```