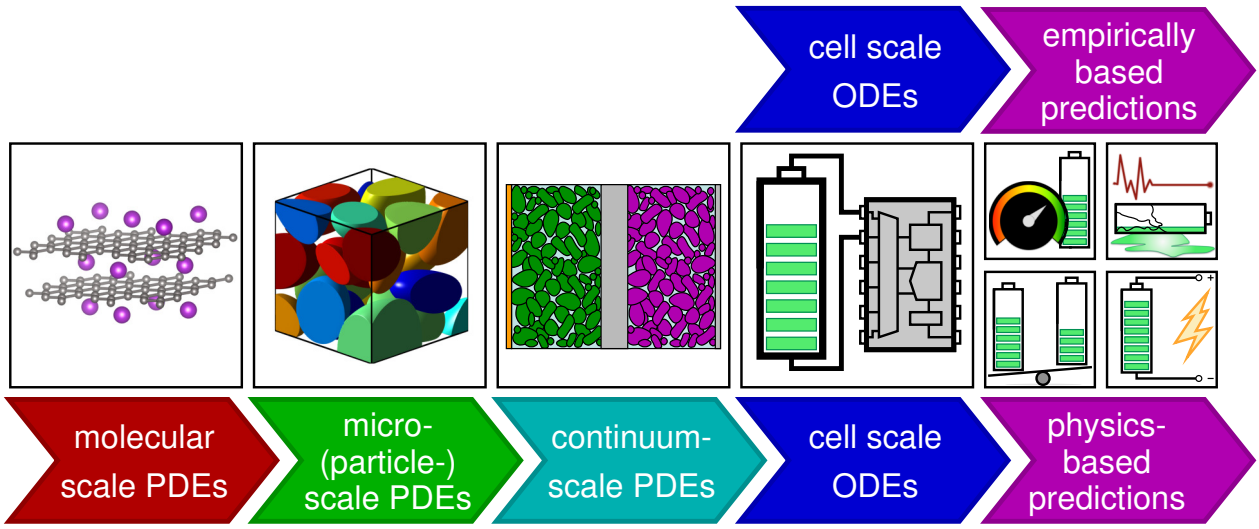
REDUNDANT PARAMETER ELIMINATION

1.1: Introduction to the course

- In ECE5710, you learned how to make sets of equations (models) that described how battery cells work, inside and out.



- We looked first at empirical equivalent-circuit models (ECM), which can describe input/output (current/voltage) behaviors of battery cells.

  Features of equivalent-circuit models (ECMs):

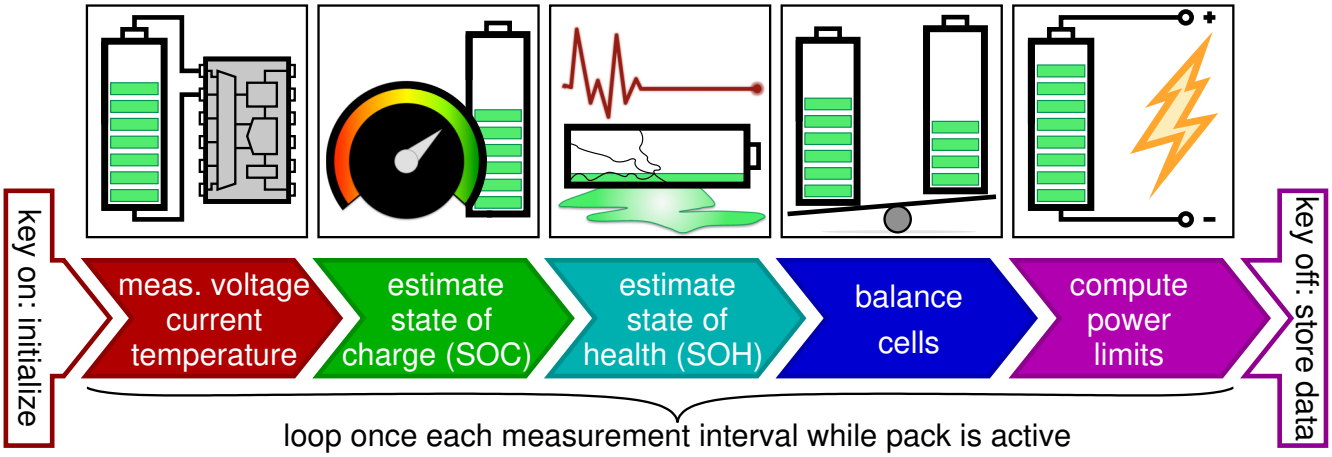
  - Amounts to an empirical curve fit that interpolates between data seen when fitting the model (extrapolation is not reliable).
  - Can predict input/output (current/voltage) behavior only, not internal electrochemical states.
  - *But, yields fast, robust simulations.*

- Then we studied physics-based models (PBM) which can additionally describe the internal electrochemical processes occurring in the cell.

Features of physics-based models (PBMs):

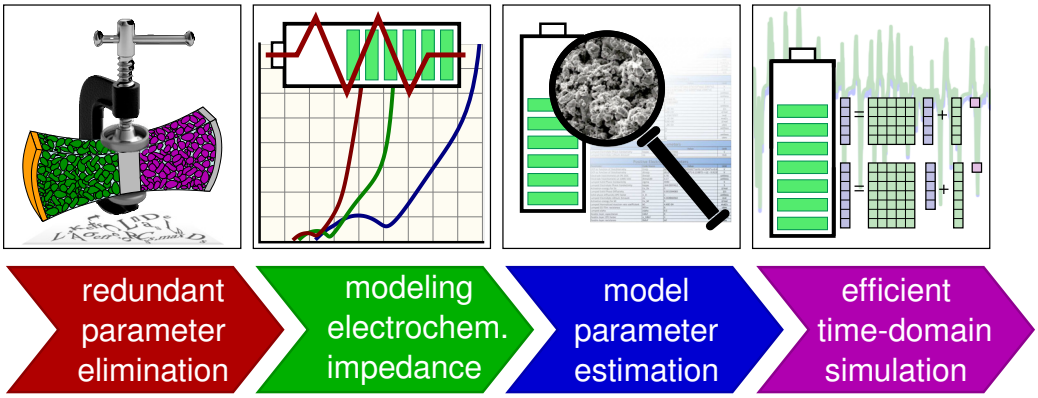
- *Can predict over wide range of operating conditions.*
- *Can predict internal state of cell (useful for aging prediction).*
- But, slow simulations having robustness/convergence issues.

- **We claimed that knowledge of a cell's internal electrochemical state—which requires PBMs—would be necessary if we wish to control a cell to its physical limits (the focus of this course).**
- However, PBMs are also computationally complex, so we relied on reduced-order models (ROMs) to simplify the computations required.
- Either ECMs or PBMs (or ROMs) can be used by algorithms in battery-management systems (BMSs) to regulate battery usage.
- The figure below shows the main algorithm control loop in a BMS: In ECE5720 you learned how to perform all these tasks using ECMs.



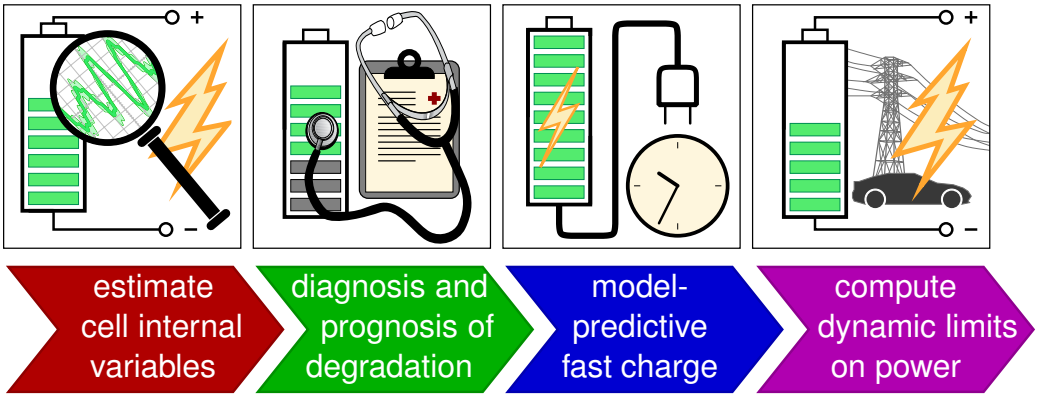
- This course teaches how to perform the same general tasks—plus fast charge—using PBMs instead of ECMs.
  - To do so, we must revisit both the modeling and controls aspects of the first two courses.

- For modeling, you will learn how to:



  - Reformulate the PBM to eliminate redundant parameter values;
  - Use reformulated PBM to model cell electrochemical impedance;
  - Identify parameter values of physics-based full-order model (FOM);
  - Create a physics-based ROM from this FOM for use by a BMS.

- For control, you will learn how to:



  - Estimate the entire cell internal electrochemical state;
  - Use the model to predict how the cell will age over time;
  - Use the PBM ROM to compute optimal fast-charge profiles;
  - Compute power-limits estimates to optimize both life, performance.

- Physics-based battery management is a “cutting edge” topic and there are important and significant pioneering research efforts underway across the world.

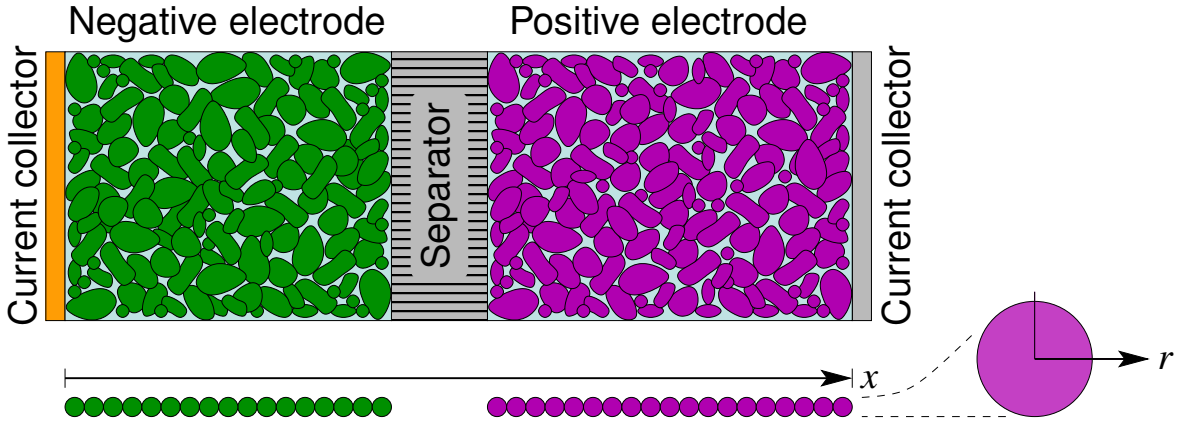
- In this course, I present the fundamental challenges that must be overcome to make physics-based BMS practical, and an approach we have developed at UCCS to address those challenges.
  - All topics I present have been validated at least in simulation; most have undergone early-stage validation in the lab.
  - Yet, there remains work to test and refine all content further.
- While there are other excellent approaches being developed by other research teams, I believe that the background you gain in this course will prepare you to understand those as well.

Roadmap for this chapter

- This is an advanced course, so I do not spend much time on review.
  - You may wish to consult App. 1.b for a brief refresher.
- However, since the Doyle–Fuller–Newman PBM is core to everything we do in this course, I will review it quickly before continuing.
- Then, I show how to correct a fatal deficiency in the model to enable identifying its parameter values for physical cells, so that ultimately the reformulated model can be used in a BMS.

1.2: The Doyle–Fuller–Newman P2D model

- The continuum models that we developed can be used in 3D, but in ECE5710 we specialized to a 1D description of cell dynamics, with an added "pseudo-dimension" that describes activity inside the solid.



- The diagram shows the geometry of a lithium-ion cell cross section (roughly to typical scale), model x and model r pseudo dimensions.
- The operation of a lithium-ion cell is described using four PDEs (with boundary conditions, initial values) and one algebraic closure term.
- Within the cell, the following state variables are of interest:
  - The concentration of lithium in the solid, $c_{\mathrm{s}}(x,r,t)$, and particularly at the surface of the solid, $c_{\mathrm{s,e}}(x,t)$,
  - The concentration of lithium in the electrolyte, $c_{\mathrm{e}}(x,t)$,
  - The potential in the solid, $\phi_{\mathrm{s}}(x,t)$,
  - The potential in the electrolyte, $\phi_{\mathrm{e}}(x,t)$, and
  - The rate of lithium movement ("flux") between phases, $j(x,t)$.
- We now review the model equations. In the following, note that all variables are functions of x and t; all parameters are functions of the cell region but are assumed to be uniform across that cell region.

- Notation is condensed vis-à-vis ECE5710; cf. appendix for a glossary.

EQUATION I: Charge conservation in the solid (for $\mathrm{r} \in \{\mathrm{n}, \mathrm{p}\}$).[1]

- Partial-differential equation:

$$\frac{\partial}{\partial x}\sigma_{\mathrm{eff}}^{\mathrm{r}}\frac{\partial}{\partial x}\phi_{\mathrm{s}}^{\mathrm{r}} = a_{\mathrm{s}}^{\mathrm{r}} F j^{\mathrm{r}}.$$

- Boundary conditions:

$$\sigma_{\mathrm{eff}}^{\mathrm{r}}\frac{\partial}{\partial x}\phi_{\mathrm{s}}^{\mathrm{r}}\bigg|_{x=0} = \sigma_{\mathrm{eff}}^{\mathrm{r}}\frac{\partial}{\partial x}\phi_{\mathrm{s}}^{\mathrm{r}}\bigg|_{x=L^{\mathrm{tot}}} = \frac{-i_{\mathrm{app}}}{A},$$

$$\frac{\partial}{\partial x}\phi_{\mathrm{s}}^{\mathrm{n}}\bigg|_{x=L^{\mathrm{n}}} = \frac{\partial}{\partial x}\phi_{\mathrm{s}}^{\mathrm{p}}\bigg|_{x=L^{\mathrm{n}}+L^{\mathrm{s}}} = 0.$$

- Initial values:

$$\phi_{\mathrm{s}}^{\mathrm{n}} = 0, \quad \text{and} \quad \phi_{\mathrm{s}}^{\mathrm{p}} = U_{\mathrm{ocp}}^{\mathrm{p}}(\theta_{\mathrm{s},0}^{\mathrm{p}}) - U_{\mathrm{ocp}}^{\mathrm{n}}(\theta_{\mathrm{s},0}^{\mathrm{n}}),$$

where $\theta_{\mathrm{s},0}^{\mathrm{r}} = c_{\mathrm{s},0}^{\mathrm{r}}/c_{\mathrm{s,max}}^{\mathrm{r}}$ are the initial electrode stoichiometries.

EQUATION II: Mass conservation in the solid (for $\mathrm{r} \in \{\mathrm{n}, \mathrm{p}\}$).

- Partial-differential equation:

$$\frac{\partial c_{\mathrm{s}}^{\mathrm{r}}}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(D_{\mathrm{s}}^{\mathrm{r}} r^2 \frac{\partial c_{\mathrm{s}}^{\mathrm{r}}}{\partial r}\right).$$

- Boundary conditions:

$$D_{\mathrm{s}}^{\mathrm{r}}\frac{\partial c_{\mathrm{s}}^{\mathrm{r}}}{\partial r}\bigg|_{r=R_{\mathrm{s}}^{\mathrm{r}}} = -j^{\mathrm{r}}, \qquad D_{\mathrm{s}}^{\mathrm{r}}\frac{\partial c_{\mathrm{s}}^{\mathrm{r}}}{\partial r}\bigg|_{r=0} = 0.$$

- Initial values:

$$c_{\mathrm{s},0}^{\mathrm{r}} = c_{\mathrm{s,max}}^{\mathrm{r}}\left(\theta_0^{\mathrm{r}} + z_0(\theta_{100}^{\mathrm{r}} - \theta_0^{\mathrm{r}})\right),$$

where $0 \le z_0 \le 1$ is initial cell state of charge, θ_0^{r} is the value of $\theta_{\mathrm{s}}^{\mathrm{r}} = c_{\mathrm{s}}^{\mathrm{r}}/c_{\mathrm{s,max}}^{\mathrm{r}}$ when the cell is resting at 0 % SOC, and $\theta_{100}^{\mathrm{r}}$ is the value of $\theta_{\mathrm{s}}^{\mathrm{r}}$ when the cell is resting at 100 % SOC.

[1] Superscript "n" = negative-electrode region, "s" = separator region, "p" = positive-electrode region, "r" = any applicable cell region. $L^{\mathrm{tot}} = L^{\mathrm{n}} + L^{\mathrm{s}} + L^{\mathrm{p}}$.

EQUATION III: Charge conservation in the electrolyte (for $\mathrm{r} \in \{\mathrm{n}, \mathrm{s}, \mathrm{p}\}$).

- Partial-differential equation (where $j^{\mathrm{s}} = 0$):

$$\frac{\partial}{\partial x}\kappa_{\mathrm{eff}}^{\mathrm{r}}\left(\frac{\partial}{\partial x}\phi_{\mathrm{e}}^{\mathrm{r}} + \frac{2RT\left(t_+^0 - 1\right)}{F}\left(1 + \frac{\partial \ln f_\pm}{\partial \ln c_{\mathrm{e}}}\right)\frac{\partial \ln c_{\mathrm{e}}^{\mathrm{r}}}{\partial x}\right) + a_{\mathrm{s}}^{\mathrm{r}} F j^{\mathrm{r}} = 0.$$

- Boundary conditions:

$$-\kappa_{\mathrm{eff}}^{\mathrm{r}}\left[\frac{\partial}{\partial x}\phi_{\mathrm{e}}^{\mathrm{r}} + \frac{2RT\left(t_+^0 - 1\right)}{F}\left(1 + \frac{\partial \ln f_\pm}{\partial \ln c_{\mathrm{e}}}\right)\frac{\partial \ln c_{\mathrm{e}}^{\mathrm{r}}}{\partial x}\right]\Bigg|_{\substack{x = 0,\\ x = L^{\mathrm{tot}}}} = 0$$

$$-\kappa_{\mathrm{eff}}^{\mathrm{r}}\left[\frac{\partial}{\partial x}\phi_{\mathrm{e}}^{\mathrm{r}} + \frac{2RT\left(t_+^0 - 1\right)}{F}\left(1 + \frac{\partial \ln f_\pm}{\partial \ln c_{\mathrm{e}}}\right)\frac{\partial \ln c_{\mathrm{e}}^{\mathrm{r}}}{\partial x}\right]\Bigg|_{\substack{x = L^{\mathrm{n}},\\ x = L^{\mathrm{n}} + L^{\mathrm{s}}}} = \frac{i_{\mathrm{app}}}{A}.$$

- Initial values across the entire cell are:

$$\phi_{\mathrm{e}}^{\mathrm{r}} = -U_{\mathrm{ocp}}^{\mathrm{n}}(\theta_{\mathrm{s},0}^{\mathrm{n}}).$$

EQUATION IV: Mass conservation in the electrolyte (for $\mathrm{r} \in \{\mathrm{n}, \mathrm{s}, \mathrm{p}\}$).

- Partial-differential equation (where $j^{\mathrm{s}} = 0$):

$$\frac{\partial(\varepsilon_{\mathrm{e}}^{\mathrm{r}} c_{\mathrm{e}}^{\mathrm{r}})}{\partial t} = \frac{\partial}{\partial x} D_{\mathrm{e,eff}}^{\mathrm{r}} \frac{\partial}{\partial x} c_{\mathrm{e}}^{\mathrm{r}} + a_{\mathrm{s}}^{\mathrm{r}}(1 - t_+^0)\, j^{\mathrm{r}}.$$

- Boundary conditions:

$$\left.\frac{\partial c_{\mathrm{e}}^{\mathrm{r}}}{\partial x}\right|_{x=0} = \left.\frac{\partial c_{\mathrm{e}}^{\mathrm{r}}}{\partial x}\right|_{x=L^{\mathrm{tot}}} = 0$$

$$\left. D_{\mathrm{e,eff}}^{\mathrm{n}} \frac{\partial c_{\mathrm{e}}^{\mathrm{n}}}{\partial x}\right|_{x=(L^{\mathrm{n}})^-} = \left. D_{\mathrm{e,eff}}^{\mathrm{s}} \frac{\partial c_{\mathrm{e}}^{\mathrm{s}}}{\partial x}\right|_{x=(L^{\mathrm{n}})^+}$$

$$\left. D_{\mathrm{e,eff}}^{\mathrm{s}} \frac{\partial c_{\mathrm{e}}^{\mathrm{s}}}{\partial x}\right|_{x=(L^{\mathrm{n}}+L^{\mathrm{s}})^-} = \left. D_{\mathrm{e,eff}}^{\mathrm{p}} \frac{\partial c_{\mathrm{e}}^{\mathrm{p}}}{\partial x}\right|_{x=(L^{\mathrm{n}}+L^{\mathrm{s}})^+}$$

$$\left. c_{\mathrm{e}}^{\mathrm{n}}\right|_{x=(L^{\mathrm{n}})^-} = \left. c_{\mathrm{e}}^{\mathrm{s}}\right|_{x=(L^{\mathrm{n}})^+}$$

$$\left. c_{\mathrm{e}}^{\mathrm{s}}\right|_{x=(L^{\mathrm{n}}+L^{\mathrm{s}})^-} = \left. c_{\mathrm{e}}^{\mathrm{p}}\right|_{x=(L^{\mathrm{n}}+L^{\mathrm{s}})^+}.$$

- Initial values across the cell are:

$$c_{\mathrm{e}}^{\mathrm{r}} = c_{\mathrm{e},0}.$$

EQUATION V: The standard reaction kinetics (Butler–Volmer equation) we studied in ECE5710 derived (for $\mathrm{r} \in \{\mathrm{n}, \mathrm{p}\}$):

$$j^{\mathrm{r}} = j_0^{\mathrm{r}} \left\{ \exp\left(\frac{(1-\alpha^{\mathrm{r}})F}{RT} \eta^{\mathrm{r}} \right) - \exp\left(\frac{-\alpha^{\mathrm{r}} F}{RT} \eta^{\mathrm{r}} \right) \right\}$$

$$j_0^{\mathrm{r}} = k_{\mathrm{norm},0}^{\mathrm{r}} \left(\frac{c_{\mathrm{e}}^{\mathrm{r}}}{c_{\mathrm{e},0}} \right)^{1-\alpha^{\mathrm{r}}} \left(1 - \frac{c_{\mathrm{s,e}}^{\mathrm{r}}}{c_{\mathrm{s,max}}^{\mathrm{r}}} \right)^{1-\alpha^{\mathrm{r}}} \left(\frac{c_{\mathrm{s,e}}^{\mathrm{r}}}{c_{\mathrm{s,max}}^{\mathrm{r}}} \right)^{\alpha^{\mathrm{r}}}$$

$$\eta^{\mathrm{r}} = \phi_{\mathrm{s}}^{\mathrm{r}} - \phi_{\mathrm{e}}^{\mathrm{r}} - U_{\mathrm{ocp}}^{\mathrm{r}}(c_{\mathrm{s,e}}^{\mathrm{r}}/c_{\mathrm{s,max}}^{\mathrm{r}}) - F R_{\mathrm{f}}^{\mathrm{r}} j^{\mathrm{r}}.$$

- This Butler–Volmer closure term is a good description of reaction kinetics for constant-current events, but misses some critical cell behaviors at high frequencies.
- For example, a double layer of charges can develop at the interface between the solid and electrolyte, which has a capacitive effect.
- You will learn how to refine this kinetics equation in the next chapter.

1.3: Reducing number of model parameters: method

- The DFN equations reviewed in Topic 1.2 contain 36 parameters (plus U_{ocp} relationships) whose values must be determined.
- Some of these are redundant/ unidentifiable, and can be eliminated via a systematic parameter-reduction method.
  - Normalize length scales;
  - Define new scaled variables to replace original variables;
- Outcome is that we find lumped scaling constants that eliminate redundancy from the equations.

Negative electrode	Separator	Positive electrode
$\sigma^{\text{n}}_{\text{eff}}$		$\sigma^{\text{p}}_{\text{eff}}$
a^{n}_{s}		a^{p}_{s}
L^{n}	L^{s}	L^{p}
$\kappa^{\text{n}}_{\text{eff}}$	$\kappa^{\text{s}}_{\text{eff}}$	$\kappa^{\text{p}}_{\text{eff}}$
D^{n}_{s}		D^{p}_{s}
R^{n}_{s}		R^{p}_{s}
$\varepsilon^{\text{n}}_{\text{e}}$	$\varepsilon^{\text{s}}_{\text{e}}$	$\varepsilon^{\text{p}}_{\text{e}}$
$D^{\text{n}}_{\text{e,eff}}$	$D^{\text{s}}_{\text{e,eff}}$	$D^{\text{p}}_{\text{e,eff}}$
$k^{\text{n}}_{\text{norm},0}$		$k^{\text{p}}_{\text{norm},0}$
$c^{\text{n}}_{\text{s,max}}$		$c^{\text{p}}_{\text{s,max}}$
α^{n}		α^{p}
R^{n}_{f}		R^{p}_{f}
θ^{n}_{0}		θ^{p}_{0}
θ^{n}_{100}		θ^{p}_{100}
A, t^0_+, $\partial \ln f_{\pm}/\partial \ln c_{\text{e}}$, $c_{\text{e},0}$ span all		

- All equations are reformulated using the lumped parameters.
  - Minimizes the number of parameter values we must determine from cell tests in order to characterize the dynamics of a cell.

Intensive versus extensive quantities

- A quick example might help illustrate the issue we are trying to solve.
- Newton's 2nd law states: "*force equals mass times acceleratio*n".
- Equivalently, "*force equals density times volume times acceleration*".
  - So, both $F = ma$ and $F = \rho V a$ are true.

- If we measure $F = 1\,\text{N}$ and $a = 1\,\text{m}\,\text{s}^{-2}$, we find $m = F/a = 1\,\text{kg}$.
- But, based only on these measured F and a, we have *no idea* what are the distinct values of ρ and V.
  - We could have $\rho = 1\,\text{kg}\,\text{m}^{-3}$ and $V = 1\,\text{m}^3$;
  - We could have $\rho = 0.5\,\text{kg}\,\text{m}^{-3}$ and $V = 2\,\text{m}^3$;
  - We could have $\rho = 2\,\text{kg}\,\text{m}^{-3}$ and $V = 0.5\,\text{m}^3$ (etc.).
- The issue is that ρ and V are joined together in Newton's model in a way that is *mathematically impossible* to separate using measurements of only $\{F, a\}$. It simply cannot be done.
  - Would need to perform an independent *kind* of experiment (e.g., measure ρ or V directly) to determine both values with certainty.
- Why do we have this problem with our PBMs? Recall from ECE5710 that we say that a property is intensive if it is a normalized quantity.
  - e.g., pressure, temperature, concentration, and density.
  - If everything (dimensions, moles, etc.) in a system is doubled, the value of an intensive property remains unchanged.
- We say that a property is extensive if it is a total quantity.
  - e.g., internal energy, Gibbs free energy, volume, and mass.
  - If everything in a system is doubled, the value of an extensive property also doubles.
- In ECE5710 we preferred to work with intensive properties.
  - This allowed us to derive models that apply directly to any scale, whereby we scale intensive values to fit a particular application.
- But, for the parameter-estimation problem (Ch. 3), we *require* that the model be expressed using extensive properties!

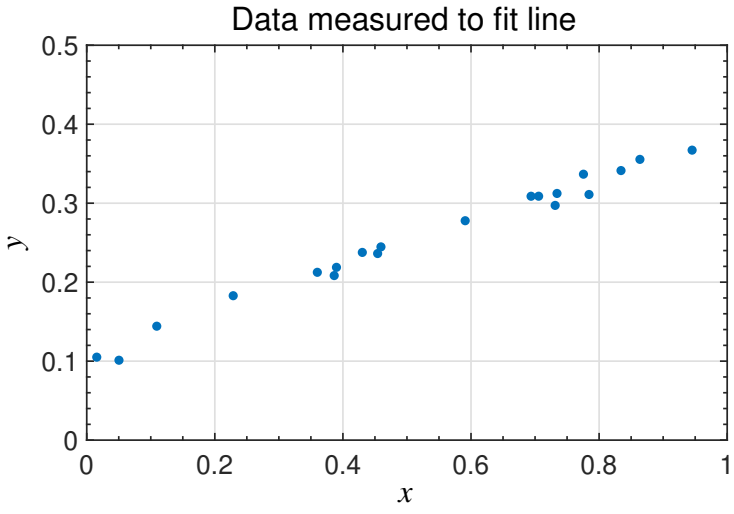
  - In Newton's example, we can identify mass (extensive) but not density (intensive, scaled by volume to compute mass).

- So, we will reformulate the physics-based-model PDEs to lump together groups of parameters that always appear together in equations and *cannot* be identified independently (although many researchers who do not recognize this problem have tried!).
  - This is like lumping ρ and V by defining a new variable $m = \rho V$.
  - The lumped parameters are identifiable from input/output measurements, whereas the original parameters are not.
- In the majority of the cases, the effect of the reformulation is simply to convert intensive properties to extensive properties, but there are a few exceptions, where more parameters combine to form a group.

How are we going to do this?

- We first apply the method we will use to a simple example to illustrate the process, and then to the P2D model.
- Assume that we have measurements (x, y) where $0 \leq x \leq 1$.
- For simplicity, we skip the step of normalizing x since it already has a normalized range.
- Now, suppose we desire to fit these data to some physically derived relationship:

$$My = (A + B)x + C.$$



- We define scaled variables: let $\breve{y} = y/\bar{y}$ and $\breve{x} = x/\bar{x}$.

  - $(\bar{\cdot})$ indicates a constant (not yet determined), usually chosen to normalize the primary variable to make the $(\breve{\cdot})$ variable unitless;
  - $(\breve{\cdot})$ is a temporary notation that indicates a (possibly time-varying) variable that has been normalized and (often) made unitless.

- Substituting, then looking in more detail at the quantities in brackets:

$$M\bar{y}\breve{y} = (A+B)\bar{x}\breve{x} + C$$

$$\breve{y} = \left[\frac{(A+B)\bar{x}}{M\bar{y}}\right]\breve{x} + \left[\frac{C}{M\bar{y}}\right].$$

- Define $\bar{y} = C/M$ and $\bar{x} = C/(A+B)$. Then, $\breve{y} = \breve{x} + 1$.
- This equation itself has no remaining constants that can be identified.
- To implement the physical relationship, we must find:
  - Modified slope (reciprocal) $\bar{x}$ and modified y-intercept $\bar{y}$.
- These (or variations on these) are the only two parameters that can be identified from input/output data.
- It is impossible to find unique values for A, B, C, and M from input/output data to characterize this model.

1.4: Reducing number of model parameters: solid

- We now apply this method to the DFN model, equation by equation.
- I recommend that you first look through the next two topics quickly and then return to study them more carefully to catch the details.
- Start by normalizing the 1D length: Let $\tilde{x} = (x - x_0^{\rm r})/L^{\rm r} + x_1^{\rm r}$ where $x_0^{\rm r}$ is starting location of each region and $x_1^{\rm r}$ is the index of each region.
  - $0 \le \tilde{x} \le 1$ is in the negative electrode;
  - $1 \le \tilde{x} \le 2$ is in the separator;
  - $2 \le \tilde{x} \le 3$ is in the positive electrode.
- Then also, for any generic variable "$(\cdot)$",

$$\frac{\partial(\cdot)}{\partial x} = \frac{1}{L^{\rm r}}\frac{\partial(\cdot)}{\partial \tilde{x}}.$$

EQUATION I: Charge conservation in the solid.

- Let $\breve{\phi}_{\rm s}^{\rm r} = \phi_{\rm s}^{\rm r}/\bar{\phi}_{\rm s}^{\rm r}$ and $\breve{j}^{\rm r} = j^{\rm r}/\bar{j}^{\rm r}$ and note that we can also write:

$$\frac{\partial \phi_{\rm s}^{\rm r}}{\partial(\cdot)} = \bar{\phi}_{\rm s}^{\rm r}\frac{\partial \breve{\phi}_{\rm s}^{\rm r}}{\partial(\cdot)}.$$

- We substitute these definitions into the PDE (assume $\sigma_{\rm eff}^{\rm r}$ uniform):

$$\frac{\partial}{\partial x}\sigma_{\rm eff}^{\rm r}\frac{\partial}{\partial x}\phi_{\rm s}^{\rm r} = a_{\rm s}^{\rm r}F j^{\rm r}$$

$$\frac{\bar{\phi}_{\rm s}^{\rm r}\sigma_{\rm eff}^{\rm r}}{(L^{\rm r})^2}\frac{\partial^2}{\partial \tilde{x}^2}\breve{\phi}_{\rm s}^{\rm r} = a_{\rm s}^{\rm r}F\bar{j}^{\rm r}\breve{j}^{\rm r}$$

$$\frac{\partial^2}{\partial \tilde{x}^2}\breve{\phi}_{\rm s}^{\rm r} = F\left[\frac{a_{\rm s}^{\rm r}(L^{\rm r})^2\bar{j}^{\rm r}}{\bar{\phi}_{\rm s}^{\rm r}\sigma_{\rm eff}^{\rm r}}\right]\breve{j}^{\rm r}.$$

- We will ultimately define $\bar{j}^{\rm r}$ and $\bar{\phi}_{\rm s}^{\rm r}$ to make the bracketed constant in this equation disappear, to help minimize the number of parameter values that must be determined.

- Using the same approach, the nonzero boundary conditions are rewritten as:

$$\left.\frac{\sigma^{\rm n}_{\rm eff}\bar{\phi}^{\rm n}_{\rm s}}{L^{\rm n}}\frac{\partial}{\partial\tilde{x}}\breve{\phi}^{\rm n}_{\rm s}\right|_{\tilde{x}=0} = \left.\frac{\sigma^{\rm p}_{\rm eff}\bar{\phi}^{\rm p}_{\rm s}}{L^{\rm p}}\frac{\partial}{\partial\tilde{x}}\breve{\phi}^{\rm p}_{\rm s}\right|_{\tilde{x}=3} = \frac{-i_{\rm app}}{A}$$

$$\left[\frac{A\sigma^{\rm n}_{\rm eff}\bar{\phi}^{\rm n}_{\rm s}}{L^{\rm n}}\right]\left.\frac{\partial}{\partial\tilde{x}}\breve{\phi}^{\rm n}_{\rm s}\right|_{\tilde{x}=0} = \left[\frac{A\sigma^{\rm p}_{\rm eff}\bar{\phi}^{\rm p}_{\rm s}}{L^{\rm p}}\right]\left.\frac{\partial}{\partial\tilde{x}}\breve{\phi}^{\rm p}_{\rm s}\right|_{\tilde{x}=3} = -i_{\rm app}.$$

- Finally, consider the initial values:
  - $\phi^{\rm n}_{\rm s,0} = \breve{\phi}^{\rm n}_{\rm s} = 0$ in the negative electrode.
  - $\phi^{\rm p}_{\rm s,0} = U^{\rm p}_{\rm ocp}(\theta^{\rm p}_{\rm s,0}) - U^{\rm n}_{\rm ocp}(\theta^{\rm n}_{\rm s,0})$ in the positive electrode, so

$$\breve{\phi}^{\rm p}_{\rm s,0} = \left(U^{\rm p}_{\rm ocp}(\theta^{\rm p}_{\rm s,0}) - U^{\rm n}_{\rm ocp}(\theta^{\rm n}_{\rm s,0})\right)/\bar{\phi}^{\rm p}_{\rm s}.$$

- We now make our first assignments.
  - Let $\bar{\phi}^{\rm r}_{\rm s} = \dfrac{L^{\rm r}}{A\sigma^{\rm r}_{\rm eff}}$ and define $\bar{\sigma}^{\rm r} = \dfrac{A\sigma^{\rm r}_{\rm eff}}{L^{\rm r}}$, so $\bar{\phi}^{\rm r}_{\rm s} = 1/\bar{\sigma}^{\rm r}$.
  - Let $\bar{j}^{\rm r} = \dfrac{1}{a^{\rm r}_{\rm s}AL^{\rm r}}$.
- This reduces our PDE to:

Equation: $$\frac{\partial^2\breve{\phi}^{\rm r}_{\rm s}}{\partial\tilde{x}^2} = F\breve{j}^{\rm r}$$

Boundary values: $$\left.\frac{\partial}{\partial\tilde{x}}\breve{\phi}^{\rm n}_{\rm s}\right|_{\tilde{x}=0} = \left.\frac{\partial}{\partial\tilde{x}}\breve{\phi}^{\rm p}_{\rm s}\right|_{\tilde{x}=3} = -i_{\rm app}$$

Initial Conditions: $$\breve{\phi}^{\rm n}_{\rm s,0} = 0 \text{ and } \breve{\phi}^{\rm p}_{\rm s,0} = \left(U^{\rm p}_{\rm ocp}(\theta^{\rm p}_{\rm s,0}) - U^{\rm n}_{\rm ocp}(\theta^{\rm n}_{\rm s,0})\right)/\bar{\phi}^{\rm p}_{\rm s}.$$

- We have completely eliminated all parameters from the PDE's equation and its boundary values but we still must identify $\bar{\phi}^{\rm p}_{\rm s}$ and specify $\theta^{\rm n}_{\rm s,0}$ and $\theta^{\rm p}_{\rm s,0}$ to be able to describe initial values.
- We also must have equations $U^{\rm r}_{\rm ocp}(\theta^{\rm r}_{\rm s})$ for both electrodes.

EQUATION II: Mass conservation in the solid.

- We let $\tilde{r}^{\rm r} = r/R_{\rm s}^{\rm r}$ and $\breve{c}_{\rm s}^{\rm r} = c_{\rm s}^{\rm r}/\bar{c}_{\rm s}^{\rm r}$.
- Then, using EQUATION II from Topic 1.2,

$$\frac{\partial c_{\rm s}^{\rm r}}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(D_{\rm s}^{\rm r} r^2 \frac{\partial c_{\rm s}^{\rm r}}{\partial r}\right)$$

$$\bar{c}_{\rm s}^{\rm r}\frac{\partial \breve{c}_{\rm s}^{\rm r}}{\partial t} = \frac{1}{(R_{\rm s}^{\rm r}\tilde{r})^2}\frac{1}{R_{\rm s}^{\rm r}}\frac{\partial}{\partial \tilde{r}}\left(D_{\rm s}^{\rm r}(R_{\rm s}^{\rm r}\tilde{r})^2 \frac{\bar{c}_{\rm s}^{\rm r}}{R_{\rm s}^{\rm r}}\frac{\partial \breve{c}_{\rm s}^{\rm r}}{\partial \tilde{r}}\right)$$

$$\frac{\partial \breve{c}_{\rm s}^{\rm r}}{\partial t} = \frac{1}{\tilde{r}^2}\frac{\partial}{\partial \tilde{r}}\left(\left[\frac{D_{\rm s}^{\rm r}}{(R_{\rm s}^{\rm r})^2}\right]\tilde{r}^2 \frac{\partial \breve{c}_{\rm s}^{\rm r}}{\partial \tilde{r}}\right).$$

- The nonzero boundary condition is:

$$D_{\rm s}^{\rm r}\left.\frac{\partial c_{\rm s}^{\rm r}}{\partial r}\right|_{r=R_{\rm s}^{\rm r}} = -j^{\rm r}$$

$$\left.\frac{D_{\rm s}^{\rm r}\bar{c}_{\rm s}^{\rm r}}{R_{\rm s}}\frac{\partial \breve{c}_{\rm s}^{\rm r}}{\partial \tilde{r}}\right|_{\tilde{r}=1} = -\bar{j}^{\rm r}\breve{j}^{\rm r}$$

$$\left.\frac{\partial \breve{c}_{\rm s}^{\rm r}}{\partial \tilde{r}}\right|_{\tilde{r}=1} = -\left[\frac{\bar{j}^{\rm r}R_{\rm s}^{\rm r}}{D_{\rm s}^{\rm r}\bar{c}_{\rm s}^{\rm r}}\right]\breve{j}^{\rm r}.$$

- The initial values can be rewritten as:

$$c_{\rm s,0}^{\rm r} = c_{\rm s,max}^{\rm r}\left(\theta_0^{\rm r} + z_0(\theta_{100}^{\rm r} - \theta_0^{\rm r})\right)$$

$$\breve{c}_{\rm s,0}^{\rm r} = \bar{c}_{\rm s,max}^{\rm r}\left(\theta_0^{\rm r} + z_0(\theta_{100}^{\rm r} - \theta_0^{\rm r})\right).$$

- We now make additional assignments, defining:
  - $\bar{D}_{\rm s}^{\rm r} = \dfrac{D_{\rm s}^{\rm r}}{(R_{\rm s}^{\rm r})^2}$,
  - $\bar{c}_{\rm s}^{\rm r} = \dfrac{\bar{j}^{\rm r}R_{\rm s}^{\rm r}}{D_{\rm s}^{\rm r}}$ and $\bar{c}_{\rm s,max}^{\rm r} = \dfrac{c_{\rm s,max}^{\rm r}}{\bar{c}_{\rm s}^{\rm r}} = \dfrac{a_{\rm s}^{\rm r}AL^{\rm r}c_{\rm s,max}^{\rm r}D_{\rm s}^{\rm r}}{R_{\rm s}^{\rm r}}$.

- Note that cell total capacity (in Ah) can be written as:[2]

$$Q = \varepsilon_{\mathrm{s}}^{\mathrm{r}} A L^{\mathrm{r}} F c_{\mathrm{s,max}}^{\mathrm{r}} \left|\theta_{100}^{\mathrm{r}} - \theta_{0}^{\mathrm{r}}\right| /3600.$$

- If we assume spherical particles, then $\varepsilon_{\mathrm{s}}^{\mathrm{r}} = a_{\mathrm{s}}^{\mathrm{r}} R_{\mathrm{s}}^{\mathrm{r}}/3$. So,

$$Q = \frac{a_{\mathrm{s}}^{\mathrm{r}} A L^{\mathrm{r}} F c_{\mathrm{s,max}}^{\mathrm{r}} R_{\mathrm{s}}^{\mathrm{r}}}{10\,800} \left|\theta_{100}^{\mathrm{r}} - \theta_{0}^{\mathrm{r}}\right| = \frac{\bar{c}_{\mathrm{s,max}}^{\mathrm{r}} F (R_{\mathrm{s}}^{\mathrm{r}})^2}{10\,800 D_{\mathrm{s}}^{\mathrm{r}}} \left|\theta_{100}^{\mathrm{r}} - \theta_{0}^{\mathrm{r}}\right|,$$

  or,

$$\bar{c}_{\mathrm{s,max}}^{\mathrm{r}} = \frac{10\,800 \bar{D}_{\mathrm{s}}^{\mathrm{r}} Q}{F \left|\theta_{100}^{\mathrm{r}} - \theta_{0}^{\mathrm{r}}\right|}.$$

- So, we can eliminate $\bar{c}_{\mathrm{s,max}}^{\mathrm{r}}$, reducing our PDE to:

$$\frac{\partial \breve{c}_{\mathrm{s}}^{\mathrm{r}}}{\partial t} = \frac{1}{\tilde{r}^2} \frac{\partial}{\partial \tilde{r}} \left(\bar{D}_{\mathrm{s}}^{\mathrm{r}} \tilde{r}^2 \frac{\partial \breve{c}_{\mathrm{s}}^{\mathrm{r}}}{\partial \tilde{r}} \right)$$

$$\left.\frac{\partial \breve{c}_{\mathrm{s}}^{\mathrm{r}}}{\partial \tilde{r}}\right|_{\tilde{r}=1} = -\breve{j}^{\mathrm{r}}$$

$$\breve{c}_{\mathrm{s},0}^{\mathrm{r}} = \frac{10\,800 \bar{D}_{\mathrm{s}}^{\mathrm{r}} Q}{F \left|\theta_{100}^{\mathrm{r}} - \theta_{0}^{\mathrm{r}}\right|} \left(\theta_{0}^{\mathrm{r}} + z_0(\theta_{100}^{\mathrm{r}} - \theta_{0}^{\mathrm{r}})\right).$$

- At this point, we need to identify Q, $\bar{\sigma}^{\mathrm{p}}$, θ_0^{n}, θ_0^{p}, $\theta_{100}^{\mathrm{n}}$, $\theta_{100}^{\mathrm{p}}$, $\bar{D}_{\mathrm{s}}^{\mathrm{n}}$, and $\bar{D}_{\mathrm{s}}^{\mathrm{p}}$.
- We don't need to find $\bar{\sigma}^{\mathrm{n}}$ (yet) because we don't need to find $\bar{\phi}_{\mathrm{s}}^{\mathrm{n}}$ (yet).

[2] Note that electrochemists may be more comfortable expressing capacity in mol rather than Ah. However, it "feels" more natural to most engineers to express capacity in Ah and so this will be our convention.

1.5: Reducing number of model parameters: electrolyte, kinetics

EQUATION III: Charge conservation in the electrolyte.

- We let $\breve{\phi}_{\rm e}^{\rm r} = \phi_{\rm e}^{\rm r}/\bar{\phi}_{\rm e}^{\rm r}$ and $\breve{c}_{\rm e}^{\rm r} = c_{\rm e}^{\rm r}/\bar{c}_{\rm e}^{\rm r}$. This changes our electrolyte charge-conservation equation EQUATION III from Topic 1.2 to:

$$\frac{\partial}{\partial x}\kappa_{\rm eff}^{\rm r}\left(\frac{\partial}{\partial x}\phi_{\rm e}^{\rm r} + \frac{2RT\left(t_+^0-1\right)}{F}\left(1+\frac{\partial \ln f_\pm}{\partial \ln c_{\rm e}}\right)\frac{\partial \ln c_{\rm e}^{\rm r}}{\partial x}\right) + a_{\rm s}^{\rm r}Fj^{\rm r} = 0$$

$$\frac{1}{L^{\rm r}}\frac{\partial}{\partial \tilde{x}}\left(\frac{\kappa_{\rm eff}^{\rm r}\bar{\phi}_{\rm e}^{\rm r}}{L^{\rm r}}\frac{\partial}{\partial \tilde{x}}\breve{\phi}_{\rm e}^{\rm r} + \frac{\kappa_{\rm eff}^{\rm r}}{L^{\rm r}}\frac{2RT\left(t_+^0-1\right)}{F}\left(1+\frac{\partial \ln f_\pm}{\partial \ln c_{\rm e}}\right)\frac{\partial \ln \breve{c}_{\rm e}^{\rm r}}{\partial \tilde{x}}\right) + a_{\rm s}^{\rm r}F\bar{j}^{\rm r}\breve{j}^{\rm r} = 0$$

$$\frac{\partial}{\partial \tilde{x}}\left(\left[\frac{\kappa_{\rm eff}^{\rm r}A\bar{\phi}_{\rm e}^{\rm r}}{L^{\rm r}}\right]\frac{\partial}{\partial \tilde{x}}\breve{\phi}_{\rm e}^{\rm r} + T\left[\frac{2R(t_+^0-1)}{F}\left(1+\frac{\partial \ln f_\pm}{\partial \ln c_{\rm e}}\right)\frac{\kappa_{\rm eff}^{\rm r}A}{L^{\rm r}}\right]\frac{\partial \ln \breve{c}_{\rm e}^{\rm r}}{\partial \tilde{x}}\right) + \underbrace{a_{\rm s}^{\rm r}AFL^{\rm r}\bar{j}^{\rm r}}_{F}\breve{j}^{\rm r} = 0.$$

- The nonzero boundary conditions are:

$$-\kappa_{\rm eff}^{\rm r}\left[\frac{\partial}{\partial x}\phi_{\rm e}^{\rm r} + \frac{2RT\left(t_+^0-1\right)}{F}\left(1+\frac{\partial \ln f_\pm}{\partial \ln c_{\rm e}}\right)\frac{\partial \ln c_{\rm e}^{\rm r}}{\partial x}\right|_{\substack{x=L^{\rm n}\\ x=L^{\rm n}+L^{\rm s}}} = \frac{i_{\rm app}}{A}$$

$$-\left[\frac{\kappa_{\rm eff}^{\rm r}A\bar{\phi}_{\rm e}^{\rm r}}{L^{\rm r}}\right]\frac{\partial}{\partial \tilde{x}}\breve{\phi}_{\rm e}^{\rm r} - T\left[\frac{2R(t_+^0-1)}{F}\left(1+\frac{\partial \ln f_\pm}{\partial \ln c_{\rm e}}\right)\frac{\kappa_{\rm eff}^{\rm r}A}{L^{\rm r}}\right]\frac{\partial \ln \breve{c}_{\rm e}^{\rm r}}{\partial \tilde{x}}\Bigg|_{\tilde{x}=1,2} = i_{\rm app}.$$

- The initial values are reformulated as (where $\theta_{\rm s,e}^{\rm r} = c_{\rm s,e}^{\rm r}/c_{\rm s,max}^{\rm r}$):

$$\phi_{\rm e,0}^{\rm r} = -U_{\rm ocp}^{\rm n}(\theta_{\rm s,e}^{\rm n}) \quad \text{and so} \ldots \quad \breve{\phi}_{\rm e,0}^{\rm r} = -U_{\rm ocp}^{\rm n}(\theta_{\rm s,e}^{\rm n})/\bar{\phi}_{\rm e}^{\rm r}.$$

- We define:
  - $\bar{\phi}_{\rm e}^{\rm r} = \dfrac{L^{\rm r}}{\kappa_{\rm eff}^{\rm r}A}$ and $\bar{\kappa}^{\rm r} = \dfrac{A\kappa_{\rm eff}^{\rm r}}{L^{\rm r}}$, so $\bar{\phi}_{\rm e}^{\rm r} = 1/\bar{\kappa}^{\rm r}$.
  - $\bar{\kappa}_D = \dfrac{2R(t_+^0-1)}{F}\left(1+\dfrac{\partial \ln f_\pm}{\partial \ln c_{\rm e}}\right)$.

- This reduces the PDE and its nonzero boundary conditions to:

$$\frac{\partial}{\partial\tilde{x}}\left(\frac{\partial}{\partial\tilde{x}}\breve{\phi}_{\rm e}^{\rm r}+T\left[\bar{\kappa}_D\bar{\kappa}^{\rm r}\right]\frac{\partial\ln\left(\breve{c}_{\rm e}^{\rm r}\right)}{\partial\tilde{x}}\right)+F\,\breve{j}^{\rm r}=0$$

$$-\frac{\partial}{\partial\tilde{x}}\breve{\phi}_{\rm e}^{\rm r}-T\left[\bar{\kappa}_D\bar{\kappa}^{\rm r}\right]\frac{\partial\ln\left(\breve{c}_{\rm e}^{\rm r}\right)}{\partial\tilde{x}}\bigg|_{\tilde{x}=1,2}=i_{\rm app}$$

$$\breve{\phi}_{\rm e,0}^{\rm r}=-U_{\rm ocp}^{\rm n}(\theta_{\rm s,e}^{\rm n})/\bar{\phi}_{\rm e}^{\rm r}.$$

- This PDE adds $\bar{\kappa}^{\rm n}$, $\bar{\kappa}^{\rm s}$, $\bar{\kappa}^{\rm p}$, and $\bar{\kappa}_D$ to the list of values to be identified.

EQUATION IV: Mass conservation in the electrolyte.

- We now look at the mass-conservation EQUATION IV from Topic 1.2.

$$\frac{\partial(\varepsilon_{\rm e}^{\rm r}c_{\rm e}^{\rm r})}{\partial t}=\frac{\partial}{\partial x}D_{\rm e,eff}^{\rm r}\frac{\partial}{\partial x}c_{\rm e}^{\rm r}+a_{\rm s}^{\rm r}(1-t_+^0)\,j^{\rm r}$$

$$\varepsilon_{\rm e}^{\rm r}\bar{c}_{\rm e}^{\rm r}\frac{\partial\breve{c}_{\rm e}^{\rm r}}{\partial t}=\frac{1}{L^{\rm r}}\frac{\partial}{\partial\tilde{x}}\frac{D_{\rm e,eff}^{\rm r}\bar{c}_{\rm e}^{\rm r}}{L^{\rm r}}\frac{\partial}{\partial\tilde{x}}\breve{c}_{\rm e}^{\rm r}+a_{\rm s}^{\rm r}(1-t_+^0)\bar{j}^{\rm r}\breve{j}^{\rm r}$$

$$\left[\frac{\varepsilon_{\rm e}^{\rm r}\bar{c}_{\rm e}^{\rm r}AL^{\rm r}}{1-t_+^0}\right]\frac{\partial\breve{c}_{\rm e}^{\rm r}}{\partial t}=\frac{\partial}{\partial\tilde{x}}\left[\frac{D_{\rm e,eff}^{\rm r}A\bar{c}_{\rm e}^{\rm r}}{L^{\rm r}(1-t_+^0)}\right]\frac{\partial}{\partial\tilde{x}}\breve{c}_{\rm e}^{\rm r}+\breve{j}^{\rm r}.$$

- The nonzero slope boundary condition at the neg/sep interface is:

$$D_{\rm e,eff}^{\rm n}\frac{\partial c_{\rm e}^{\rm n}}{\partial x}\bigg|_{x=(L^{\rm n})^-}=D_{\rm e,eff}^{\rm s}\frac{\partial c_{\rm e}^{\rm s}}{\partial x}\bigg|_{x=(L^{\rm n})^+}$$

$$\left[\frac{D_{\rm e,eff}^{\rm n}A\bar{c}_{\rm e}^{\rm n}}{L^{\rm n}(1-t_+^0)}\right]\frac{\partial\breve{c}_{\rm e}^{\rm n}}{\partial\tilde{x}}\bigg|_{\tilde{x}=1^-}=\left[\frac{D_{\rm e,eff}^{\rm s}A\bar{c}_{\rm e}^{\rm s}}{L^{\rm s}(1-t_+^0)}\right]\frac{\partial\breve{c}_{\rm e}^{\rm s}}{\partial\tilde{x}}\bigg|_{\tilde{x}=1^+}.$$

- The nonzero slope boundary condition at the sep/pos interface is:

$$\left[\frac{D_{\rm e,eff}^{\rm s}A\bar{c}_{\rm e}^{\rm s}}{L^{\rm s}(1-t_+^0)}\right]\frac{\partial\breve{c}_{\rm e}^{\rm s}}{\partial\tilde{x}}\bigg|_{\tilde{x}=2^-}=\left[\frac{D_{\rm e,eff}^{\rm p}A\bar{c}_{\rm e}^{\rm p}}{L^{\rm p}(1-t_+^0)}\right]\frac{\partial\breve{c}_{\rm e}^{\rm p}}{\partial\tilde{x}}\bigg|_{\tilde{x}=2^+}.$$

- The continuity boundary conditions at the electrode/separator boundaries are: $\breve{c}_{\rm e}^{\rm n}\big|_{\tilde{x}=1^-}=\breve{c}_{\rm e}^{\rm s}\big|_{\tilde{x}=1^+}$ and $\breve{c}_{\rm e}^{\rm s}\big|_{\tilde{x}=2^-}=\breve{c}_{\rm e}^{\rm p}\big|_{\tilde{x}=2^+}$.

- The initial values are reformulated as:

$$c_{\mathrm{e}}^{\mathrm{r}}(x,0) = c_{\mathrm{e},0}$$
$$\breve{c}_{\mathrm{e}}^{\mathrm{r}}(\tilde{x},0) = \frac{c_{\mathrm{e},0}}{\bar{c}_{\mathrm{e}}^{\mathrm{r}}}.$$

- We define $\bar{c}_{\mathrm{e}}^{\mathrm{r}} = c_{\mathrm{e},0}$, which makes $\breve{c}_{\mathrm{e},0}^{\mathrm{r}} = 1$; we define $\bar{q}_{\mathrm{e}}^{\mathrm{r}} = \varepsilon_{\mathrm{e}}^{\mathrm{r}}\bar{c}_{\mathrm{e}}^{\mathrm{r}}AL^{\mathrm{r}}F/(3600(1-t_+^0))$, and $\bar{D}_{\mathrm{e}}^{\mathrm{r}} = D_{\mathrm{e,eff}}^{\mathrm{r}}A\bar{c}_{\mathrm{e}}^{\mathrm{r}}/(L^{\mathrm{r}}(1-t_+^0))$. Then,

$$3600\bar{q}_{\mathrm{e}}^{\mathrm{r}}\frac{\partial\breve{c}_{\mathrm{e}}^{\mathrm{r}}}{\partial t} = F\frac{\partial}{\partial\tilde{x}}\bar{D}_{\mathrm{e}}^{\mathrm{r}}\frac{\partial\breve{c}_{\mathrm{e}}^{\mathrm{r}}}{\partial\tilde{x}} + F\breve{j}^{\mathrm{r}}$$
$$\bar{D}_{\mathrm{e}}^{\mathrm{left}}\frac{\partial\breve{c}_{\mathrm{e}}}{\partial\tilde{x}}\bigg|_{\mathrm{left}} = \bar{D}_{\mathrm{e}}^{\mathrm{right}}\frac{\partial\breve{c}_{\mathrm{e}}}{\partial\tilde{x}}\bigg|_{\mathrm{right}}.$$

- It appears that we now need also to find $\bar{q}_{\mathrm{e}}^{\mathrm{n}}$, $\bar{q}_{\mathrm{e}}^{\mathrm{s}}$, $\bar{q}_{\mathrm{e}}^{\mathrm{p}}$, $\bar{D}_{\mathrm{e}}^{\mathrm{n}}$, $\bar{D}_{\mathrm{e}}^{\mathrm{s}}$, and $\bar{D}_{\mathrm{e}}^{\mathrm{p}}$.
- But note there is a relationship between $\bar{D}_{\mathrm{e}}^{\mathrm{r}}$ and $\bar{\kappa}^{\mathrm{r}}$ that we can exploit:

$$\kappa_{\mathrm{eff}}^{\mathrm{n}} = \kappa(\varepsilon_{\mathrm{e}}^{\mathrm{n}})^{\mathrm{brug}}, \qquad D_{\mathrm{e,eff}}^{\mathrm{n}} = D_{\mathrm{e}}(\varepsilon_{\mathrm{e}}^{\mathrm{n}})^{\mathrm{brug}}$$
$$\kappa_{\mathrm{eff}}^{\mathrm{s}} = \kappa(\varepsilon_{\mathrm{e}}^{\mathrm{s}})^{\mathrm{brug}}, \qquad D_{\mathrm{e,eff}}^{\mathrm{s}} = D_{\mathrm{e}}(\varepsilon_{\mathrm{e}}^{\mathrm{s}})^{\mathrm{brug}}$$
$$\kappa_{\mathrm{eff}}^{\mathrm{p}} = \kappa(\varepsilon_{\mathrm{e}}^{\mathrm{p}})^{\mathrm{brug}}, \qquad D_{\mathrm{e,eff}}^{\mathrm{p}} = D_{\mathrm{e}}(\varepsilon_{\mathrm{e}}^{\mathrm{p}})^{\mathrm{brug}}.$$

- Therefore,

$$\frac{D_{\mathrm{e,eff}}^{\mathrm{n}}}{\kappa_{\mathrm{eff}}^{\mathrm{n}}} = \frac{D_{\mathrm{e,eff}}^{\mathrm{s}}}{\kappa_{\mathrm{eff}}^{\mathrm{s}}} = \frac{D_{\mathrm{e,eff}}^{\mathrm{p}}}{\kappa_{\mathrm{eff}}^{\mathrm{p}}} = \frac{D_{\mathrm{e}}}{\kappa}.$$

- Similarly,

$$F\frac{\bar{D}_{\mathrm{e}}^{\mathrm{n}}}{\bar{\kappa}^{\mathrm{n}}} = F\frac{\bar{D}_{\mathrm{e}}^{\mathrm{s}}}{\bar{\kappa}^{\mathrm{s}}} = F\frac{\bar{D}_{\mathrm{e}}^{\mathrm{p}}}{\bar{\kappa}^{\mathrm{p}}} = \bar{\psi},$$

  and if we have already identified the set of $\bar{\kappa}^{\mathrm{r}}$, then can compute the set of $\bar{D}_{\mathrm{e}}^{\mathrm{r}}$ by knowing only $\bar{\psi}$.

- We re-write the PDE, its boundary conditions, and initial condition as:

$$3600\bar{q}_{\mathrm{e}}^{\mathrm{r}}\frac{\partial\breve{c}_{\mathrm{e}}^{\mathrm{r}}}{\partial t} = \bar{\psi}\frac{\partial}{\partial\tilde{x}}\bar{\kappa}^{\mathrm{r}}\frac{\partial\breve{c}_{\mathrm{e}}^{\mathrm{r}}}{\partial\tilde{x}} + F\breve{j}^{\mathrm{r}}$$

$$\bar{\kappa}^{\text{left}} \frac{\partial \breve{c}_\text{e}}{\partial \tilde{x}}\bigg|_{\text{left}} = \bar{\kappa}^{\text{right}} \frac{\partial \breve{c}_\text{e}}{\partial \tilde{x}}\bigg|_{\text{right}}$$

$$\breve{c}_\text{e}|_{\text{left}} = \breve{c}_\text{e}|_{\text{right}}$$

$$\breve{c}^\text{r}_{\text{e},0} = 1.$$

- Therefore, we now need also to find only $\bar{q}^\text{n}_\text{e}$, $\bar{q}^\text{s}_\text{e}$, $\bar{q}^\text{p}_\text{e}$, and $\bar{\psi}$.

EQUATION V: The reaction kinetics.

- Can have many forms, depending on double-layer model used.
- Here, we investigate the default Butler–Volmer EQUATION V.

$$j^\text{r} = j^\text{r}_0 \left\{ \exp\left(\frac{(1-\alpha^\text{r})F}{RT}\eta^\text{r} \right) - \exp\left(\frac{-\alpha^\text{r} F}{RT}\eta^\text{r} \right) \right\}$$

$$j^\text{r}_0 = k^\text{r}_{\text{norm},0} \left(\frac{c^\text{r}_\text{e}}{c_{\text{e},0}} \right)^{1-\alpha^\text{r}} \left(1 - \frac{c^\text{r}_{\text{s,e}}}{c^\text{r}_{\text{s,max}}} \right)^{1-\alpha^\text{r}} \left(\frac{c^\text{r}_{\text{s,e}}}{c^\text{r}_{\text{s,max}}} \right)^{\alpha^\text{r}}.$$

$$\eta^\text{r} = \phi^\text{r}_\text{s} - \phi^\text{r}_\text{e} - U^\text{r}_\text{ocp}(c^\text{r}_{\text{s,e}}/c^\text{r}_{\text{s,max}}) - F R^\text{r}_\text{f} j^\text{r}.$$

- Inserting our prior definitions,

$$\breve{j}^\text{r} = \breve{j}^\text{r}_0 \left\{ \exp\left(\frac{(1-\alpha^\text{r})F}{RT}\eta^\text{r} \right) - \exp\left(\frac{-\alpha^\text{r} F}{RT}\eta^\text{r} \right) \right\}$$

$$\breve{j}^\text{r}_0 = \left[\frac{k^\text{r}_{\text{norm},0}}{\bar{j}^\text{r}} \right] \left(\breve{c}^\text{r}_\text{e} \right)^{1-\alpha^\text{r}} \left(1 - \frac{\breve{c}^\text{r}_{\text{s,e}}}{\bar{c}^\text{r}_{\text{s,max}}} \right)^{1-\alpha^\text{r}} \left(\frac{\breve{c}^\text{r}_{\text{s,e}}}{\bar{c}^\text{r}_{\text{s,max}}} \right)^{\alpha^\text{r}}$$

$$\eta^\text{r} = \bar{\phi}^\text{r}_\text{s}\breve{\phi}^\text{r}_\text{s} - \bar{\phi}^\text{r}_\text{e}\breve{\phi}^\text{r}_\text{e} - U^\text{r}_\text{ocp}(\breve{c}^\text{r}_{\text{s,e}}/\bar{c}^\text{r}_{\text{s,max}}) - F\left[R^\text{r}_\text{f}\bar{j}^\text{r}\right] j^\text{r}.$$

- Let $\bar{k}^\text{r}_0 = k^\text{r}_{\text{norm},0}/\bar{j}^\text{r}$ and $\bar{R}^\text{r}_\text{f} = R^\text{r}_\text{f}\bar{j}^\text{r}$. Then, the additional parameter values that we must identify are $\bar{k}^\text{n}_0$, $\bar{k}^\text{p}_0$, $\bar{R}^\text{n}_\text{f}$, $\bar{R}^\text{p}_\text{f}$, $\bar{\phi}^\text{n}_\text{s}$, α^n and α^p.
  - If we assume that $\alpha = 0.5$, we no longer need to find α^n and α^p.

1.6: Summary of reformulated PDEs

- We have reduced the number of parameters that must be identified from 36 down to 23 (21 if we assume $\alpha^{\mathrm{r}} = 0.5$).
- Thirteen "degrees of freedom" have been removed, making the parameter-estimation task possible with input/output data.
- Any similar formulation with the same number of parameter values will also be minimal.

Negative electrode	Separator	Positive electrode
$\bar{\sigma}^{\mathrm{n}}$		$\bar{\sigma}^{\mathrm{p}}$
$\bar{\kappa}^{\mathrm{n}}$	$\bar{\kappa}^{\mathrm{s}}$	$\bar{\kappa}^{\mathrm{p}}$
$\bar{D}_{\mathrm{s}}^{\mathrm{n}}$		$\bar{D}_{\mathrm{s}}^{\mathrm{p}}$
$\bar{q}_{\mathrm{e}}^{\mathrm{n}}$	$\bar{q}_{\mathrm{e}}^{\mathrm{s}}$	$\bar{q}_{\mathrm{e}}^{\mathrm{p}}$
$\bar{k}_0^{\mathrm{n}}$		$\bar{k}_0^{\mathrm{p}}$
$\bar{R}_{\mathrm{f}}^{\mathrm{n}}$		$\bar{R}_{\mathrm{f}}^{\mathrm{p}}$
α^{n}		α^{p}
θ_0^{n}		θ_0^{p}
$\theta_{100}^{\mathrm{n}}$		$\theta_{100}^{\mathrm{p}}$
Q, $\bar{\kappa}_D$, and $\bar{\psi}$ span all regions		

- So, we slightly modify our notation to be easier to interpret.
- We find that we must know $\bar{\phi}_{\mathrm{s}}^{\mathrm{r}}$ and $\bar{\phi}_{\mathrm{e}}^{\mathrm{r}}$ in all cell regions.
  - Therefore, we may as well write the PDEs in terms of ϕ_{s} and ϕ_{e} but with the new lumped-parameter constants.
- But, after the reformulation, neither $\bar{c}_{\mathrm{s}}^{\mathrm{r}}$, $\bar{c}_{\mathrm{e}}^{\mathrm{r}}$, nor $\bar{j}^{\mathrm{r}}$ "show up" in the final PDEs, so we do not need to (nor can we) identify these values.
  - So, for now, corresponding PDEs remain functions of $\breve{c}_{\mathrm{s}}^{\mathrm{r}}$, $\breve{c}_{\mathrm{e}}^{\mathrm{r}}$, and $\breve{j}^{\mathrm{r}}$.
- Also the "breve" in $\breve{j}^{\mathrm{r}}$ becomes cumbersome, so rename $i_{\mathrm{f}}^{\mathrm{r}} = F\breve{j}^{\mathrm{r}}$, recognizing that $\breve{j}^{\mathrm{r}}$ has units mol s^{-1} and so $i_{\mathrm{f}}^{\mathrm{r}}$ has units A.
  - Subscript "f" stands for "faradaic"... more on this in Ch. 2; note that $i_{\mathrm{f}}^{\mathrm{r}}$ is different from i_{app} and from $i_{\mathrm{s}}^{\mathrm{r}}$ and $i_{\mathrm{e}}^{\mathrm{r}}$.
- Recapping, then, the charge-conservation in the solid equation, where $\phi_{\mathrm{s}}^{\mathrm{r}}$ is measured in volts and $\bar{\sigma}^{\mathrm{r}}$ in siemens is:

Charge conservation in the solid:

- The reformulated PDE is:

$$\bar{\sigma}^{\mathrm{r}} \frac{\partial^2 \phi_{\mathrm{s}}^{\mathrm{r}}}{\partial \tilde{x}^2} = i_{\mathrm{f}}^{\mathrm{r}}.$$

- The nonzero boundary conditions are:

$$\bar{\sigma}^{\mathrm{n}} \frac{\partial}{\partial \tilde{x}} \phi_{\mathrm{s}}^{\mathrm{n}} \bigg|_{\tilde{x}=0} = \bar{\sigma}^{\mathrm{p}} \frac{\partial}{\partial \tilde{x}} \phi_{\mathrm{s}}^{\mathrm{p}} \bigg|_{\tilde{x}=3} = -i_{\mathrm{app}}.$$

- The initial values in the positive electrode are ($\phi_{\mathrm{s},0}^{\mathrm{n}} = 0$)

$$\phi_{\mathrm{s},0}^{\mathrm{p}} = U_{\mathrm{ocp}}^{\mathrm{p}}(\theta_{\mathrm{s},0}^{\mathrm{p}}) - U_{\mathrm{ocp}}^{\mathrm{n}}(\theta_{\mathrm{s},0}^{\mathrm{n}}).$$

- For mass conservation in the solid, $\bar{D}_{\mathrm{s}}^{\mathrm{r}}$ is in s^{-1} (okay), but $\breve{c}_{\mathrm{s}}^{\mathrm{r}}$ is in $\mathrm{mol\,s}^{-1}$, which is an awkward unit for concentration.
- Rewrite PDE in terms of the already-defined unitless concentration $\theta_{\mathrm{s}}^{\mathrm{r}} = \breve{c}_{\mathrm{s}}^{\mathrm{r}} / \bar{c}_{\mathrm{s,max}}^{\mathrm{r}} = c_{\mathrm{s}}^{\mathrm{r}} / c_{\mathrm{s,max}}^{\mathrm{r}}$, which does not require finding any additional parameter values.

Mass conservation in the solid:

- The PDE for $0 \leq \theta_{\mathrm{s}}^{\mathrm{r}} \leq 1$ is:

$$\frac{\partial \theta_{\mathrm{s}}^{\mathrm{r}}}{\partial t} = \frac{1}{\tilde{r}^2} \frac{\partial}{\partial \tilde{r}} \left(\bar{D}_{\mathrm{s}}^{\mathrm{r}} \tilde{r}^2 \frac{\partial \theta_{\mathrm{s}}^{\mathrm{r}}}{\partial \tilde{r}} \right).$$

- The nonzero boundary condition is:

$$\bar{D}_{\mathrm{s}}^{\mathrm{r}} \frac{\partial \theta_{\mathrm{s}}^{\mathrm{r}}}{\partial \tilde{r}} \bigg|_{\tilde{r}=1} = -\frac{\left| \theta_{100}^{\mathrm{r}} - \theta_0^{\mathrm{r}} \right|}{10\,800 Q} i_{\mathrm{f}}^{\mathrm{r}}.$$

- The initial condition is: $\theta_{\mathrm{s},0}^{\mathrm{r}} = \theta_0^{\mathrm{r}} + z_0(\theta_{100}^{\mathrm{r}} - \theta_0^{\mathrm{r}})$.

- For charge conservation in the electrolyte, $\phi_{\mathrm{e}}^{\mathrm{r}}$ is measured in volts, $\bar{\kappa}^{\mathrm{r}}$ in siemens, and t_+^0 is unitless.
- For cleaner notation, define unitless ratio of concentrations $\theta_{\mathrm{e}}^{\mathrm{r}} = \breve{c}_{\mathrm{e}}^{\mathrm{r}}$.

Charge conservation in the electrolyte:

- The PDE is:

$$\frac{\partial}{\partial \tilde{x}}\left(\bar{\kappa}^{\mathrm{r}}\left(\frac{\partial}{\partial \tilde{x}}\phi_{\mathrm{e}}^{\mathrm{r}}+\bar{\kappa}_D T\frac{\partial \ln\left(\theta_{\mathrm{e}}^{\mathrm{r}}\right)}{\partial \tilde{x}}\right)\right)+i_{\mathrm{f}}^{\mathrm{r}}=0.$$

- The nonzero boundary conditions are:

$$-\bar{\kappa}^{\mathrm{r}}\left[\frac{\partial}{\partial \tilde{x}}\phi_{\mathrm{e}}^{\mathrm{r}}+\bar{\kappa}_D T\frac{\partial \ln\left(\theta_{\mathrm{e}}^{\mathrm{r}}\right)}{\partial \tilde{x}}\right]_{\tilde{x}=1,2}=i_{\mathrm{app}}.$$

- The initial condition is: $\phi_{\mathrm{e},0}^{\mathrm{r}}=-U_{\mathrm{ocp}}^{\mathrm{n}}(\theta_{\mathrm{s},0}^{\mathrm{n}})$.

- For mass conservation in the electrolyte, $\bar{q}_{\mathrm{e}}^{\mathrm{r}}$ is in Ah.

Mass conservation in the electrolyte:

- The PDE is:

$$3600\bar{q}_{\mathrm{e}}^{\mathrm{r}}\frac{\partial \theta_{\mathrm{e}}^{\mathrm{r}}}{\partial t}=\bar{\psi}\frac{\partial}{\partial \tilde{x}}\bar{\kappa}^{\mathrm{r}}\frac{\partial}{\partial \tilde{x}}\theta_{\mathrm{e}}^{\mathrm{r}}+i_{\mathrm{f}}^{\mathrm{r}}.$$

- The nonzero boundary conditions at the separator interfaces are:

$$\theta_{\mathrm{e}}|_{\mathrm{left}}=\theta_{\mathrm{e}}|_{\mathrm{right}}\quad\text{and}\quad\bar{\kappa}^{\mathrm{left}}\left.\frac{\partial \theta_{\mathrm{e}}}{\partial \tilde{x}}\right|_{\mathrm{left}}=\bar{\kappa}^{\mathrm{right}}\left.\frac{\partial \theta_{\mathrm{e}}}{\partial \tilde{x}}\right|_{\mathrm{right}}.$$

- The initial condition is: $\theta_{\mathrm{e},0}^{\mathrm{r}}=1$.

- For kinetics equation, $\bar{k}_0^{\mathrm{r}}$ is in amperes, $\bar{R}_{\mathrm{f}}^{\mathrm{r}}$ is in ohms, and η^{r} is in volts.

Kinetics:

$$i_{\mathrm{f}}^{\mathrm{r}}=i_0^{\mathrm{r}}\left\{\exp\left(\frac{(1-\alpha^{\mathrm{r}})F}{RT}\eta^{\mathrm{r}}\right)-\exp\left(\frac{-\alpha^{\mathrm{r}}F}{RT}\eta^{\mathrm{r}}\right)\right\}$$

$$i_0^{\mathrm{r}}=\bar{k}_0^{\mathrm{r}}\left(\theta_{\mathrm{e}}^{\mathrm{r}}\right)^{1-\alpha^{\mathrm{r}}}\left(1-\theta_{\mathrm{s,e}}^{\mathrm{r}}\right)^{1-\alpha^{\mathrm{r}}}\left(\theta_{\mathrm{s,e}}^{\mathrm{r}}\right)^{\alpha^{\mathrm{r}}}$$

$$\eta^{\mathrm{r}}=\phi_{\mathrm{s}}^{\mathrm{r}}-\phi_{\mathrm{e}}^{\mathrm{r}}-U_{\mathrm{ocp}}^{\mathrm{r}}(\theta_{\mathrm{s,e}}^{\mathrm{r}})-\bar{R}_{\mathrm{f}}^{\mathrm{r}}i_{\mathrm{f}}^{\mathrm{r}}.$$

1.7: Recovering the original electrochemical variables

- The reformulated PDEs allow us to simulate $\phi_{\mathrm{s}}^{\mathrm{r}}$, $\phi_{\mathrm{e}}^{\mathrm{r}}$, $\theta_{\mathrm{s}}^{\mathrm{r}}$, $\theta_{\mathrm{e}}^{\mathrm{r}}$, and $i_{\mathrm{f}}^{\mathrm{r}}$, which is sufficient to be able to compute cell voltage.
  - This is why we can identify the required parameter values from current/voltage input/output data.
- However, what if we desire the ability also to simulate $c_{\mathrm{s}}^{\mathrm{r}}$, $c_{\mathrm{e}}^{\mathrm{r}}$, and j^{r}?
  - This will turn out not to be as necessary as it might seem.
  - For example, performance limits $0 \leq c_{\mathrm{s}}^{\mathrm{r}} \leq c_{\mathrm{s,max}}^{\mathrm{r}}$ automatically translate to $0 \leq \theta_{\mathrm{s}}^{\mathrm{r}} \leq 1$ without needing to simulate $c_{\mathrm{s}}^{\mathrm{r}}$ directly or to identify any new parameter values.
- To recover all original electrochemical variables from the modified set, we would need to be able to identify ten additional values:[3]
  - A, L^{n}, L^{s}, L^{p}, $a_{\mathrm{s}}^{\mathrm{n}}$, $a_{\mathrm{s}}^{\mathrm{p}}$, $R_{\mathrm{s}}^{\mathrm{n}}$, $R_{\mathrm{s}}^{\mathrm{p}}$, t_{+}^{0}, $c_{\mathrm{e},0}$.
  - Most of these are dimensional and relatively easy to measure via cell teardown if needed.
  - No fancy electrochemical techniques are needed.
- Finding the electrochemical variables:

$$c_{\mathrm{s}}^{\mathrm{r}} = c_{\mathrm{s,max}}^{\mathrm{r}} \theta_{\mathrm{s}}^{\mathrm{r}}$$

$$c_{\mathrm{e}}^{\mathrm{r}} = c_{\mathrm{e},0} \theta_{\mathrm{e}}^{\mathrm{r}}$$

$$j^{\mathrm{r}} = \frac{1}{a_{\mathrm{s}}^{\mathrm{r}} A L^{\mathrm{r}} F} i_{\mathrm{f}}^{\mathrm{r}}.$$

[3] This is an interesting result. We removed 13 degrees of freedom but require finding only 10 parameters to find the complete set. Where did the other three go? One was gained by replacing two $c_{\mathrm{s,max}}$ parameters with a single Q parameter; the other two were by replacing three D_{e} parameters with a single relationship in $\bar{\psi}$.

Where to from here?

- We now have a reformulated physics-based PDE model of a lithium-ion cell that has a minimal number of unknown parameter values.
- For BMS purposes such as SOx estimation, we need to convert this to a reduced-order state-space model.
- We follow the same general procedure we did in ECE5710, with some enhancements:
  - We first find transfer functions for each electrochemical variable.
  - Then, we estimate parameter values corresponding to a real cell from laboratory tests (“system ID”).
  - We then use a subspace realization algorithm to convert the transfer functions into reduced-order models (ROMs).
- When we have done so, we will be able to simulate cells and packs.
- Further, we can use the ROMs for BMS tasks such as SOC estimation, SOH estimation, power-limits estimation, and so forth.
- We look at these topics in that order.

Appendix 1.a: Summary of variables

Notation conventions for variables and parameters

- Variables are always denoted using the form: $\mathrm{name}_{\mathrm{phase}}^{\mathrm{modifier,region}}$ or $\mathrm{name}_{\mathrm{phase}}^{\mathrm{region}}$:
  - "name" is the variable identifier, such as ϕ for potential, θ for normalized concentration, and so forth.
  - "modifier" is a temporary descriptive tag sometimes added during a derivation, but is not permanent (i.e., the modifier is eventually removed from the name).
  - "region" is the cell domain to which this variable applies: either n, s, or p, for the negative electrode, separator, and positive electrode, respectively.
    - Sometimes this is left blank when an equation applies to multiple regions.
    - Sometimes the identifier "r" is given, showing more explicitly that the equation applies to multiple regions.
  - "phase" is the material to which this variable applies, such as "s" for solid, "e" for electrolyte, "f" for film, and so forth.
- Constant parameters are always of the form: $\overline{\mathrm{name}}_{\mathrm{phase}}^{\mathrm{modifier,region}}$ or $\mathrm{name}_{\mathrm{phase}}^{\mathrm{modifier,region}}$:
  - The presence of an overbar denotes a lumped parameter.
  - "name" is the parameter identifier, such as κ for electrolyte conductivity.
  - "region" and "phase" have the same interpretation as for variables.
  - "modifier" is again a temporary descriptive tag sometimes added during a derivation, but is not permanent.

Variables and parameters used only in derivations but not thereafter

Roman

- $\bar{c}_{\mathrm{e}} = c_{\mathrm{e},0}$ [mol m^{-3}].
- $\breve{c}_{\mathrm{e}} = c_{\mathrm{e}}/\bar{c}_{\mathrm{e}} = \theta_{\mathrm{e}}$ [u/l].
- $\bar{c}_{\mathrm{s}} = \dfrac{\bar{j} R_{\mathrm{s}}}{D_{\mathrm{s}}} = \dfrac{R_{\mathrm{s}}}{a_{\mathrm{s}} A L D_{\mathrm{s}}}$ [s m^{-3}].
- $\bar{c}_{\mathrm{s,max}} = c_{\mathrm{s,max}}/\bar{c}_{\mathrm{s}} = a_{\mathrm{s}} A L D_{\mathrm{s}} c_{\mathrm{s,max}}/R_{\mathrm{s}}$ [mol s^{-1}].
- $\breve{c}_{\mathrm{s}} = c_{\mathrm{s}}/\bar{c}_{\mathrm{s}} = a_{\mathrm{s}} A L D_{\mathrm{s}} c_{\mathrm{s}}/R_{\mathrm{s}}$ [mol s^{-1}].

- $\bar{D}_\mathrm{e} = \dfrac{D_{\mathrm{e,eff}} A c_{\mathrm{e},0}}{L(1-t_+^0)}$ [mol s^{-1}].
- $\bar{j} = \dfrac{1}{a_\mathrm{s} A L}$ [m^{-2}].
- $\breve{j} = j/\bar{j} = i_\mathrm{f}/F = a_\mathrm{s} A L j$ [mol s^{-1}].

Greek

- $\bar{\phi}_\mathrm{s} = 1/\bar{\sigma}$ [Ω].
- $\bar{\phi}_\mathrm{e} = 1/\bar{\kappa}$ [Ω].

Variables and parameters used continually after this point

Roman

- $\bar{D}_\mathrm{s} = D_\mathrm{s}/R_\mathrm{s}^2$ [s^{-1}].
- $\bar{k}_0 = F k_{\mathrm{norm},0}/\bar{j} = a_\mathrm{s} A L F k_{\mathrm{norm},0}$ [A], where $k_{\mathrm{norm},0} = k_0 (c_{\mathrm{e},0})^{1-\alpha} c_{\mathrm{s,max}}$ [mol m^{-2} s^{-1}].
- $i_\mathrm{f} = F\breve{j} = Fj/\bar{j} = a_\mathrm{s} A L F j$ [A].
- $\bar{q}_\mathrm{e} = \dfrac{\varepsilon_\mathrm{e} c_{\mathrm{e},0} A L F}{3600(1-t_+^0)}$ [Ah].
- Q [Ah] is cell total capacity.
- $\bar{R}_\mathrm{f} = R_\mathrm{f}\bar{j} = \dfrac{R_\mathrm{f}}{a_\mathrm{s} A L}$ [Ω].

Greek

- α [u/l] is charge-transfer coefficient.
- ϕ_e [V], potential in the electrolyte (unchanged from standard definition).
- ϕ_s [V], potential in the solid (unchanged from standard definition).
- $\bar{\kappa} = \kappa_\mathrm{eff} A/L$ [S], where $\bar{\kappa}$ is treated as a constant.
- $\bar{\kappa}_D = \dfrac{2R(t_+^0-1)}{F}\left(1 + \dfrac{\partial \ln f_\pm}{\partial \ln c_\mathrm{e}}\right)$ [V K^{-1}], where $\dfrac{\partial \ln f_\pm}{\partial \ln c_\mathrm{e}}$ is treated as a constant.
- $\bar{\psi} = F\bar{D}_\mathrm{e}^\mathrm{n}/\bar{\kappa}^\mathrm{n} = F\bar{D}_\mathrm{e}^\mathrm{s}/\bar{\kappa}^\mathrm{s} = F\bar{D}_\mathrm{e}^\mathrm{p}/\bar{\kappa}^\mathrm{p}$ [V].
- $\bar{\sigma} = \sigma_\mathrm{eff} A/L$ [S].
- $\theta_\mathrm{e} = \breve{c}_\mathrm{e} = c_\mathrm{e}/c_{\mathrm{e},0}$ [u/l]; note that $\theta_{\mathrm{e},0} = 1$ always.
- $\theta_\mathrm{s} = \breve{c}_\mathrm{s}/\bar{c}_{\mathrm{s,max}} = c_\mathrm{s}/c_{\mathrm{s,max}}$ [u/l]; note that $\theta_{\mathrm{s},0} = \theta_0 + z(\theta_{100} - \theta_0)$.

Appendix 1.b: Review of BMS terminology and tasks

- State of charge (SOC) z of a battery cell is a value between 0 and 1 (often reported in percent between 0 % and 100 %):
  - When the cell is fully charged, $z = 100\,\%$;
  - When the cell is fully discharged, $z = 0\,\%$.
- We define the total capacity Q of a cell to be the total amount of charge removed when discharging it from $z = 100\,\%$ to $z = 0\,\%$.
  - Q is usually measured in Ah or mAh.
- The resting (equilibrium) voltage of a cell is called its open-circuit voltage (OCV), and is a function of SOC and temperature.
- Cell voltage under load is a function of OCV plus ohmic resistance plus dynamic polarization that is dominated by diffusion effects.
- The total energy that can be extracted from a cell before reaching a minimum SOC can be computed from its OCV relationship

$$E(t) = Q \int_{z_{\text{min}}}^{z(t)} \text{OCV}(\xi)\, \text{d}\xi \approx Q V_{\text{nom}} \Delta z.$$

  - We can compute energy if we have estimates of SOC and Q.
  - Be careful with units: If Q is in Ah then E is in Wh.
  - Note: Total energy is different from discharge energy.
- If a cell is required to operate within a specific voltage window, the power it can deliver is limited by its resistance.
  - So, we can compute power if able to estimate SOC and resistance.
- Battery packs often built by connecting cells first in parallel and then in series, where every parallel-cell module may have a different SOC.

  - Therefore, it does not make sense to talk about a battery-pack SOC, although many people try to come up with definitions for one.

- A BMS is an embedded system (purpose-built electronics plus processing to enable a specific application).
  - Protects the safety of the battery operated device's operator. Detects unsafe operating conditions and responds.
  - Protects cells of battery pack from damage in abuse/failure cases.
  - Prolongs life of battery pack (normal operating cases).
  - Maintains battery pack in a state in which it can fulfill its functional design requirements.
  - Informs the application controller how to make the best use of the battery pack **right now** (*e.g.*, power limits), control charger, etc.
- BMS provides estimates of available energy and power to the load.
- As a cell ages, its total capacity tends to decrease and its resistance tends to increase.
  - The first effect is called capacity fade; the second is power fade.
- Therefore, the computations of total capacity and resistance must be ongoing. This task is referred to as state-of-health (SOH) estimation.
  - In this course, you will learn methods of deeper diagnostics.